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Historical Records of Australian Science

Supplementary Material

Severyn Marcel (Sever, Sev) Sternhell 1930–2022

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CURRICULUM VITAE:

PROFESSOR SEVER STERNHELL, FAA, FRACI

Personal

Surname:	Sternhell
Christian Name:	Sever
Place and date of birth:	Lwow, Poland, 30 May 1930
Nationality:	British by naturalisation, May 1952
Marital status:	Married, three children
Home Address:	33 Grafton Avenue Naremburn, NSW 2065 Tel: +612 9439 1463
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Academic Record

Leaving Certificate:	November 1947, from Newington College, Stanmore, NSW.
B.Sc. First Class Honours	Department of Organic Chemistry, University of Sydney, Thesis submitted November 1951. Supervisor: Dr Francis Lions.
M.Sc.	University of Sydney. Thesis submitted in March 1953. Supervisors: Professor A.J. Birch and Dr F. Lions.
Ph.D. and D.I.C.	University of London, Imperial College. Thesis submitted in October 1960. Supervisor: Professor D.H.R. Barton, F.R.S., Nobel Laureate.
D.Sc.	University of London, 1966.

Professional Record

<u>Research Chemist</u>	Research and Development Department of Beetle-Elliot (Plastics) Ltd., now Monsanto, April 1953 - September 1955.
<u>Research Officer</u>	Division of Coal Research, C.S.I.R.O., (then Senior Research Officer Principal Research Officer), September 1955 - April 1964.
<u>Senior Lecturer</u>	Department of Organic Chemistry, The University of Sydney, appointed April 1964.

Reader in Organic Chemistry	University of Sydney, July 1967.
Professor of Organic Chemistry	University of Sydney, December 1977-July 1998
Emeritus Professor	University of Sydney, from July 1998

- Head of School of Chemistry, University of Sydney, 1977-1978, 1986.
- Head, Department of Organic Chemistry, University of Sydney, 1977-1998.
- Fellow of the Australian Academy of Science since 1992.
- Fellow of the Royal Australian Chemical Institute.
- Visiting Professor at the University of Tennessee, January-July, 1969.
- Visiting Professor at the Eidg. Technische Hochschule, Zurich, May-August, 1972.
- Visiting Professor at the University of Arizona, October-December, 1974.
- Visiting Professor at Oxford University, April-July, 1979.
- Member of the National Committee for Chemistry of the Australian Academy of Science.
- Member of the editorial board of Nuclear Magnetic Resonance Abstracts, 1964-1976.
- Member of editorial board of "Magnetic Resonance in Chemistry" (Wiley)
- Member of International Advisory Board for "Methods in Stereochemical analysis" (Verlag Chemie).
- Member of editorial board of "Magnetic Resonance Analysis".
- Member of the Ph.D. Award Committee, University of Sydney, 1976-1984. Chairman, 1978-1984.
- Founding Chairman, University of Sydney Committee for Graduate Studies, 1984-1987.
- Member, Management Committee, National Nuclear Magnetic Resonance Centre, 1972-1978.
- Consultant to RIKER International Pharmaceutical Company, 1967-1970.
- Member of the Chemistry Panel of the Australian Research Council 1988-1992. Chairman 1991-1992.
- Member of the Materials Science Priority Panel of the Australian Research Council 1989-1992.
- Chairman of the Interdisciplinary Panel of the Australian Research Council 1992.
- Chairman of Sectional Committee 5 (Applied Physical Sciences) of the Australian Academy of Science

Research Publications: 196 research publications including 3 books, multiple book chapters and major reviews.

List of Publications

S. Sternhell

Refereed publications, books and book chapters

1. A.J. Birch, P. Hextall, and S. Sternhell, "Reduction by dissolving metals. X. Aromatic compounds containing electron sinks". *Aust. J. Chem.,* **7**, 256-260 (1954).

2. J.D. Brooks and S. Sternhell, "Chemistry of brown coals. I. Oxygen-containing functional groups in Victorian brown coals". *Aust. J. Appl. Sci.,* **8**, 206-221 (1957).

3. J.D. Brooks, R.A. Durie, and S. Sternhell, "Chemistry of brown coals. II. Infrared spectroscopic studies". *Aust. J. Appl. Sci.,* **9**, 63-80 (1958).

4. J.D. Brooks, R.A. Durie, and S. Sternhell, "Chemistry of brown coals. III. Pyrolytic reactions". *Aust. J. Appl. Sci.,* **9**, 303-320 (1958).

5. R.A. Durie and S. Sternhell, "Chemistry of brown coals. IV. Action of oxygen in presence of alkali". *Aust. J. Appl. Sci.,* **9**, 360-369 (1958).

6. R.A. Durie and S. Sternhell, "Chemistry of brown coals. V. Victorian brown coals and their alkali-soluble and alkali-insoluble fractions". *Aust. J. Appl. Sci.,* **9**, 370-374 (1958).

7. S. Sternhell, "Chemistry of brown coals. VI. Further aspects of the chemistry of hydroxyl groups in Victorian brown coals". *Aust. J. Appl. Sci.,* **9**, 375-379 (1958).

8. J.D. Brooks and S. Sternhell, "The action of alkalis on low-rank coals". *Fuel, London,* **37**, 124-125 (1958).

9. R.A. Durie and S. Sternhell, "Some quantitative infrared absorption studies of coals, pyrolysed coals, and their acetyl derivatives". *Aust. J. Chem.,* **12**, 205-217 (1959).

10. R.A. Durie and S. Sternhell, "Comparative infrared absorption studies of brown coals and lignin". Proceedings of Symposium on the nature of coal. *C.F.R. Inst. (India),* p.157-163 (1959).

11. B.M. Lynch, J.D. Brooks, R.A. Durie, and S. Sternhell, "Chemistry of humic acids formed by alkali treatment of brown coals". *Proc. R. Dublin Soc., Ser. A.*, **1**, 123-131 (1960).

12. J.D. Brooks, R.A. Durie, B.M. Lynch, and S. Sternhell, "Infrared spectral changes accompanying methylation of brown coals". *Aust. J. Chem.,* **13**, 179-183 (1960).

13. R.A. Durie, B.M. Lynch, and S. Sternhell, "Comparative studies of brown coals and lignin. I. Infrared spectra". *Aust. J. Chem.,* **13**, 156-168 (1960).

14. D. Arigoni, D.H.R. Barton, E.J. Corey, O. Jeger, L. Caglioti, Sukh Dev, P.G. Ferrini, E.R. Glazier, A. Melera, S.K. Pradhan, K. Schaffner, S. Sternhell, J.F. Templeton, and S. Tobinga, "The constitution of Limonin". *Experientia*, **16**, 41-49 (1960).

15. D.H.R. Barton, S.K. Pradhan, S. Sternhell, and J.F. Templeton, "Triterpenoids. XXV. The constitution of Limonin and related bitter principles". *J. Chem. Soc.,* 255-275 (1961).

16. R. Jones and S. Sternhell, "Chemistry of brown coals. VII. Estimation of active hydrogen". *Fuel, London,* **41**, 457-469 (1962).

17. D.E. Bland and S. Sternhell, "High resolution NMR spectra of methanol lignin" *Nature, London,* **196**, 985-986 (1962). .

18. D.H.R. Barton, R. O'Brien, and S. Sternhell, "A new reaction of hydrazones". *J. Chem. Soc.,* 470-476 (1962)

19. R.B. Conrow, R.A. Durie, J.S. Shannon, and S. Sternhell, "Studies in aerial oxidation. I. Oxidation of vitrain from a bituminous coal". *Fuel, London,* **42**, 275-290 (1963).

20. C.W. Shoppee, R.E. Lack, and S. Sternhell, "Steroids. XIX. The structure of digifolein and digifologenin". *J. Chem. Soc.,* 3281-3286 (1963).

21. H. Rottendorf and S. Sternhell, "Hydrogenolysis of aryl p-toluene sulphonates with hydrazine in present of palladium". *Aust. J. Chem.,* **16**, 647-657 (1963).

22. D.J. Collins, J.J. Hobbs, and S. Sternhell, "The stereochemistry of rings A and B in 6-substituted-Δ^4-3-ketosteroids. A study of ^{1}H allylic spin-spin coupling in rigid systems". *Tetrahedron letters,* 197-203 (1963).

23. D.J. Collins, J.J. Hobbs, and S. Sternhell, "The stereochemistry of rings A and B in 6-substituted-Δ^4-3-ketosteroids. A study of ^{1}H allylic spin-spin coupling in systems with defined geometry". *Aust. J. Chem.,* **16**, 1030-1041 (1963).

24. J.T. Pinhey and S. Sternhell, "^{1}H spin-spin coupling across one double and four single bonds". *Tetrahedron letters,* 275-280 (1963).

25. H. Rottendorf and S. Sternhell, "Spin-spin coupling between benzylic and ring proton". *Tetrahedron letters,* 1289-1295 (1963).

26. D.J. Collins, J.J. Hobbs, and S. Sternhell, "An NMR study of the stereochemistry of some steroidal 4,5-epoxy derivatives". *Tetrahedron letters,* 623-628, (1963).

27. R. Jones, A.J. Ryan, S. Sternhell, and S.E. Wright, "The structures of some 5-pyrazolones and derived 2-arylazo-5-pyrazolones". *Tetrahedron,* **19**, 1497-1507 (1963).

28. C.G. Macdonald, J.S. Shannon, and S. Sternhell, "Geminal H-D spin-spin coupling and isotope effects in partially deuterated methylaromatic compounds". *Aust. J. Chem.,* **17**, 38-46 (1964).

29. S. Sternhell, "Long-range H^1-H^1 spin-spin coupling in NMR spectroscopy". *Revs. Pure Appl. Chem.,* **14**, 15-46 (1964). (Review); see also “Citation Classic” **28**, 262 (1980).

30. S. Sternhell, "High resolution NMR spectroscopy". *Coal Res. in CSIRO*, No.21, p. 7-18 (1963). (Review)

31. H. Rottendorf and S. Sternhell, "Spin-spin coupling between side-chain and ring protons and the effect of electron delocalization on allylic coupling." *Aust. J. Chem.,* **17**, 1315-1328 (1964).

32. S. Sternhell, "Experiments in artificial coalification". *Aust. J. Chem.,* **17**, 1236 (1964).

33. R.N. Mirrington, E. Ritchie, C.W. Shoppee, W.C. Taylor, and S. Sternhell, "The constitution of Radicicol". *Tetrahedron letters,* 365-370 (1964).

34. J.S. Shannon, H. Silberman, and S. Sternhell, "Incorporation of a C_2 fragment in the course of photolysis of some aromatic Schiff's bases in ethanol". *Tetrahedron letters,* 659-661 (1964).

35. C.W. Shoppee, F.P. Johnson, R.E. Lack, and S. Sternhell, "Long-range spin-spin coupling involving the angular methyl groups in steroids". *Tetrahedron letters,* 2319-2322 (1964).

36. C.J. Moye and S. Sternhell, "The degradation of aromatic rings: the action of alkaline hypochlorite on phenol". *Tetrahedron letters,* 2411-2417 (1964).

37. J.T. Pinhey and S. Sternhell, "Structure of α-hydroxysantonin and some aspects of the stereochemistry of artemesin, β-santonin and 1-D-desmotropo-α-santonin". *Aust. J. Chem.,* **18**, 543-557 (1965)

38. J.W. Milne, J.S. Shannon, and S. Sternhell, "Studies in aerial oxidation. II Salts of methylbenzoic acids". *Aust. J. Chem.,* **18**, 139-149 (1965).

39. D.E. Bland and S. Sternhell, "Estimation of condensed units in methanol lignins from *Pinus radiata* and *Eucalyptus regnans* from PMR spectra". *Aust. J. Chem.,* **18**, 401-410 (1965).

40. C.W. Shoppee, F.P. Johnson, R.E. Lack, R.J. Rawson, and S. Sternhell, "Steroids. Part XXIV. The preparation and NMR spectra of some 6-substituted-4-methylcholest- 4-enes". *J. Chem. Soc.,* 2476-2482 (1965).

41. C.W. Shoppee, T.E. Bellas, R.E. Lack, and S. Sternhell, "Steroids. Part XXV. The stereochemistry of ring A and the NMR spectra of some α-halogeno steroidal ketones". *J. Chem. Soc.,* 2483-2489 (1965).

42. D. Brookes, S. Sternhell, B.K. Tidd, and W.B. Turner, "Long-range coupling in avenaciolide and related compounds". *Aust. J. Chem.,* **18**, 373-377 (1965).

43. R.F.C. Brown, S. Sternhell, and R.N. Warrener, "The direction of platinumcatalysed hydrogenation of an unsymmetrical anhydride in the norbornane series". *Aust. J. Chem.,* **18**, 731-9 (1965).

44. R.F.C. Brown, I.D. Rae, and S. Sternhell, "Synthetic studies in the 1,2-dithiole series. II". *Aust. J. Chem.,* **18**, 61-69 (1965).

45. G.P. Newsoroff and S. Sternhell, "Spin-spin coupling between protons on sp^2 hybridized benzylic carbon atoms and ring protons". *Tetrahedron letters,* 3499-3505 (1964).

46. H. Rottendorf, S. Sternhell, and J.R. Wilmshurst, "PMR spectra of some β-methylstyrenes, ββ-dimethylstyrenes and α-methylstilbenes and a discussion of long-range shielding and coupling effects in these and related systems". *Aust. J. Chem.,* **18**, 1759-1773 (1965).

47. R.F.C. Brown, I.D. Rae and S. Sternhell, "PMR spectra of some 1,2-dithiole-3-ones and 1,2-dithiole-3-thiones". *Aust. J. Chem.,* **18**, 1211-1219 (1965).

48. C.W. Shoppee, F.P. Johnson, R.E. Lack, and S. Sternhell, "Steroids. Part XXVI. Virtual allylic coupling in the 60 Mc NMR spectrum of 4,4-ethylene-dithiocholest-4-en-3-one". *J. Chem. Soc.,* 2489-2492 (1965).

49. M. Martin-Smith, S.T. Reid and S. Sternhell, "Spin-spin coupling between H-2 and H-6 in benzothiophenes and indoles". *Tetrahedron letters*, 2393-2398 (1965).

50. P.J. Collin, J.S. Shannon, H. Silberman, S. Sternhell and G. Sugowdz, "Incorporation of one or two R-C-C fragments in the course of photolysis of some Schiff's bases in primary alcohols $R-CH_2-CH_2-OH$". *Tetrahedron letters,* 2063-2065 (1965).

51. S. Sternhell, "Applications of NMR spectroscopy to industrial problems". *Australian Chemical Processing and Engineering,* **18**, No.5, 17-22 (1965). (Review)

52. P.J. Collin and S. Sternhell, "NMR spectra of crotonic, citraconic, and ββ-dimethylacrylic acids, their methyl esters and potassium salts". *Aust. J. Chem.,* **19**, 317-320 (1966).

53. C.W. Shoppee, F.P. Johnson, R.E. Lack, and S. Sternhell, "Line width of NMR signals due to tertiary methyl groups". *Chem. Comm.,* 347 (1965).

54. R.K. Norris and S. Sternhell, "Isomerization of 5,6-dihalogenocyclohex- 2-ene-1,4-diones to 2,3-dihalogeno-1,4-hydroquinones". *Chem. Comm.,* 608 (1965).

55. K. Nilsson and S. Sternhell, "NMR spectra of atropic acids". *Acta Chem. Scand.,* **19**, 2441-2442 (1965).

56. R.K. Norris and S. Sternhell, "Long-range spin-spin coupling in 1,4-benzoquinones and some related compounds". *Aust. J. Chem.,* **19**, 617-627 (1966).

57. R.K. Norris and S. Sternhell, "NMR spectra of '*p* -nitrosophenol' and its methyl derivatives". *Aust. J. Chem.,* **19**, 841-860 (1966).

58. R.F.C. Brown, I.D. Rae, J.S. Shannon, S. Sternhell, and J.M. Swan, "Synthetic studies in 1,2-dithiole series. IV. Methylation of 4-benzamido-1,2-dithiole-3-thione". *Aust. J. Chem.,* **19**, 503-511 (1966).

59. R.N. Mirrington, E. Ritchie, C.W. Shoppee, S. Sternhell, and W.C. Taylor, "Some metabolites of *Nectria radicicola* Gerlach and Nilsson. The structure of radicicol (monorden) ". *Aust. J. Chem.,* **19**, 1265-1284 (1966).

60. R.A. Durie, Y. Shewchyk, and S. Sternhell, "Spectroscopic studies of the hydrogen distribution in the vitrains and their solvent extracts from some Australian Bituminous Coals". *Fuel, London,* **45**, 99 (1966).

61. F.P. Johnson, A. Melera, and S. Sternhell, "Interproton spin-spin coupling across four single bonds in 'non-W' configuration". *Aust. J. Chem.,* **19**, 1523-1526 (1966),

62. C.G. Macdonald, J.S. Shannon, and S. Sternhell, "Geminal interproton coupling constants in 2,2,3,3-tetramethylbutane and tetramethylsilane". *Aust. J. Chem.,* **19**, 1527-1528 (1966).

63. G.P. Newsoroff and S. Sternhell, "Nuclear magnetic resonance spectra of α,β,β-trimethylstyrenes". *Aust. J. Chem.,* **19**, 1667-1675 (1966).

64. C.J. Moye and S. Sternhell, "The degradation of aromatic rings: the action of hypochlorite on phenols". *Aust. J. Chem.,* **19**, 2107-2118 (1966).

65. C.W. Shoppee, F.P. Johnson, R.E. Lack, and S. Sternhell, "Line widths of nuclear magnetic resonance signals of tertiary methyl groups". *Tetrahedron, supplement 8, Part II*, 421-442 (1966).

66. R.K. Norris and S. Sternhell, "Tautomerism and *syn-anti* isomerism in the *p*-nitrosophenol-*p*-benzoquinone monoxime system". *Tetrahedron letters,* 97-101 (1967).

67. G.P. Newsoroff and S. Sternhell, "High barrier to rotation about an sp^2-sp^3 carbon-carbon bond". *Tetrahedron letters,* 2539-2542 (1967).

68. G.C. Brophy, Olga N. Laing, and S. Sternhell. "Removal of oxygen from NMR samples". *Chemistry and Industry,* 22 (1968).

69. G.P. Newsoroff and S. Sternhell, "Spin-spin coupling between protons bonded to sp^2 and sp^3 hybridized benzylic carbon atoms and ring protons". *Aust. J. Chem.,* **21**, 747-760 (1968).

70. R.F.C. Brown, L. Radom, S. Sternhell, and I.D. Rae, "Proton magnetic resonance spectra of some aromatic amines and derived amides". *Canad. J. Chem.,* **46**, 2577-2587 (1968).

71. P.J. Collin, J.S. Shannon, H. Silberman, S. Sternhell, and G. Sugowdz, "Photochemistry of some aromatic Schiff's bases and NMR spectra of some benzo[f]quinolines". *Tetrahedron,* **24**, 3069-3083 (1968).

72. B. Caddy, M. Martin-Smith, R.K. Norris, S.T. Reid, and S. Sternhell, "Proton magnetic resonance spectra some benzo[b]thiophens. An investigation of substituent effects in a heteroaromatic system". *Aust. J. Chem.,* **21**, 1853-1866 (1968).

73. A.G. Moritz, J.D. Saxby, and S. Sternhell, "Long-range ^{31}p- ^{1}H spin-spin coupling in *ortho*-styryldiphenylphosphine". *Aust. J. Chem.,* **21**, 2565-2567 (1968).

74. D.E. Bland, A. Logan, M. Menshun, and S. Sternhell, "The lignin of sphagnum". *Phytochemistry,* **7**, 1373-1377 (1968).

75. R.K. Norris and S. Sternhell, "The equilibrium between *syn* and *anti* 2-substituted 1,4-benzoquinone-4-oxime acetates". *Tetrahedron letters,* 5511-5514 (1968).

76. G.P. Newsoroff and S. Sternhell, "A re-evaluation of the steric dependence of allylic coupling constants". *Tetrahedron letters*, 6117-6122 (1968).

77. U.E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, "Estimation of chemical shifts of olefinic protons using additive increments. Part II: the compilation of additive increments for 43 functional groups". *Tetrahedron,* **25**, 691-697 (1969).

78. L.M. Jackman and S. Sternhell, *Applications of nuclear magnetic resonance spectroscopy in organic chemistry,* Pergamon Press, London, pp. 1-456 (1969).

79. U.E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, "Estimation of the chemical shifts of olefinic protons using additive increments. Part III: examples of utility in NMR studies and the identification of some structural features responsible for deviations from additivity". *Tetrahedron,* **25**, 2023-2034 (1969).

80. R.K. Norris and S. Sternhell, "2-Substituted and 2,6-disubstituted 1,4-benzoquinone 4-oximes ("*p*-nitrosophenols")". *Aust. J. Chem.,* **22**, 935-970 (1969).

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82. S. Sternhell, "Correlation of interproton spin-spin coupling constants with structure". *Quarterly Reviews*, **23**, 236-270 (1969). (Review); see also “Citation Classic” **7**, 14 (1988).

83. K.J. Armstrong, M. Martin-Smith, N.M.D. Brown, G.C. Brophy, and S. Sternhell, "Benzo[b]thiophen derivatives. Part IX. Nitration of benzo b thiophen and the isomeric nitrobenzo[b]thiophens". *J. Chem. Soc. (C)*, 1766-1775, (1969).

84. I. Brown, S.T. Reid, N.M.D. Brown, K.J. Armstrong, M. Martin-Smith, W.E. Sneader, G.C. Brophy, and S. Sternhell, "Benzo[b]thiophen derivatives. Part X.

Nitration of benzo[b]thiophen-3-carboxylic acid". *J. Chem. Soc. (C)*, 2755-2758 (1969).

85. G.C. Brophy, J. Mohandas, M. Slaytor, S. Sternhell, T.R. Watson, and L.A. Wilson, "Novel lignans from a *Cinnamomum* Sp. from Bougainville". *Tetrahedron letters,* 5159-5162 (1969).

86. A. Pross and S. Sternhell, "Oxidation of hydrazones with iodine in the presence of base". *Aust. J. Chem.,* **23**, 989-1003 (1970).

87. P.J. Beeby and S. Sternhell, "The preparation of isomeric 1-substituted 4-*t*-butyl-1-methylcyclohexanes". *Aust. J. Chem.,* **23**, 1005-1014 (1970)

88. M.J. Lacey, C.G. Macdonald, A. Pross, J.S. Shannon, and S. Sternhell, "Geminal interproton coupling constants in some methyl derivatives". *Aust. J. Chem.,* **23**, 1421-1429 (1970).

89. G.C. Brophy, S. Sternhell, N.M.D. Brown, I. Brown, K.J. Armstrong, and M. Martin-Smith, "Benzo[b]thiophen derivatives. Part XI. Nitration of 3-acetyl- and 3-formyl-benzo[b]thiophens". *J. Chem. Soc. (C)*, 933-937 (1970).

90. G.C. Brophy, D.J. Collins, J.J. Hobbs, and S. Sternhell, "Dimers of α,β-substituted styrenes: tetralin derivatives from reaction of 1-(*p*-chlorophenyl)-2,2-dimethylpropan-1-ol with sulphuric acid". *Aust. J. Chem.,* **23**, 1587-1603 (1970).

91. G.C. Brophy and S. Sternhell, "A simple vacuum technique for removal of dissolved oxygen from NMR samples". *Chem. and Ind.,* 1109 (1970).

92. W.A. Bubb and S. Sternhell, "The Wessely Acetoxylation". *Tetrahedron letters,* 4499-4502 (1970)

93. P.J. Beeby and S. Sternhell, "Nucleophilic substitution reactions of 4-*t* -butyl-1-methylcyclohexanols". *Aust. J. Chem.,* **24**, 809-821 (1971)

94. R.K. Norris and S. Sternhell, "2-Substituted and 2,6-disubstituted 1,4-benzoquinone 4-oximeacetates". *Aust. J. Chem.,* **24**, 1449-1465 (1971).

95. J.R. Campbell, A. Pross, and S. Sternhell, "Preparation and chemistry of some 1-iodo-1-phenylpropenes". *Aust. J. Chem.,* **24**, 1425-1436 (1971).

96. A. Pross and S. Sternhell, "The reaction of hydrazones with chlorine and bromine". *Aust. J. Chem.,* **24**, 1437-1447 (1971).

97. T.J. Gerteisen, D.C. Kleinfelter, G.C. Brophy, and S. Sternhell, "Properties of 2-arylnorbornene oxides and of the dimer formed by dehydration of 2-*p*-anisylnorbornane-2,3-*cis-exo*-diol". *Tetrahedron,* **27**, 3013-3023 (1971).

98. L. Bauer, C.L. Bell, G.C. Brophy, W.A. Bubb, E.B. Sheinin, S. Sternhell, and G.E. Wright, "Nuclear Magnetic Resonance Spectra of 1,4-ethenoisoquinolin-3(2H)-ones". *Aust. J. Chem.,* **24**, 2319-2323 (1971).

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103. G.P. Newsoroff, R.J. Spear, and S. Sternhell, "The N.M.R. spectrum of 2-methylenecyclobutanone". *Aust. J. Chem.,* **25**, 1325-1328 (1972).

104. G.P. Newsoroff and S. Sternhell, "Interproton allylic spin-spin coupling involving exocyclic groups". *Aust. J. Chem.,* **25**, 1669-1693 (1972).

105. R.K. Norris and S. Sternhell, "2-Substituted and 2,6-disubstituted 1,4-benzoquinone 4-oxime methyl ethers". *Aust. J. Chem.,* **25**, 1907-1919 (1972).

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107. W.H. Cherry, J.T. Craig, Q.N. Porter, H.G. Upstill and S. Sternhell, "Anomalous Diels-Alder Reactions of 2-methyl-3-vinylbenzo[b]thiophens". *Tetrahedron letters,* 4727 (1972).

108. R.K. Norris and S. Sternhell, "3-Substituted 1,4-benzoquinone 4-oximes". *Aust. J. Chem.,* **25**, 2621-2629 (1972).

109. J.R. Kalman, J.T. Pinhey, and S. Sternhell, "Reactions of lead tetrakistrifluoroacetate with aromatic and metalloaromatic compounds. A new route to phenols". *Tetrahedron letters,* 5369-5372 (1972).

110. R.K. Norris and S. Sternhell, "The reactions of some 5,6-dihalogenocyclohexen-2-ene-1,4-diones (1,4-benzoquinone dihalides) in boron trifluoride diethyletherate". *Aust. J. Chem.,* **26**, 333-343 (1973).

111. Jane Beeby, T. Hoffmann-Ostenhof, E. Pretsch, W. Simon and S. Sternhell, "Estimation of the chemical shifts of aromatic protons using additive increments". *Analytical Chemistry*, **45,** 1571-1573 (1973).

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A STUDY OF
THE MANNICH REACTION AND MISCELLANEOUS SYNTHESES
IN HETEROCYCLIC CHEMISTRY

B.Sc. HONOURS THESIS

SUBMITTED AT THE UNIVERSITY OF SYDNEY

1951

S. STERNHELL

CONTENTS

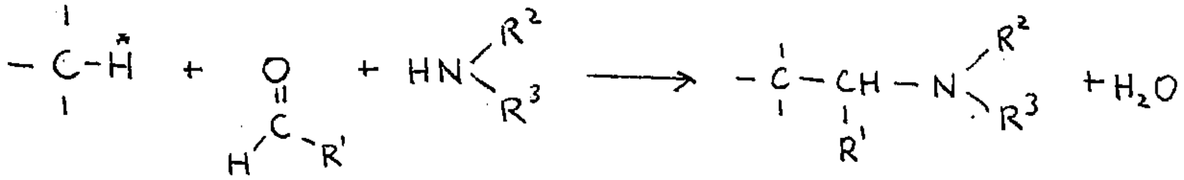
SECTION 1

A STUDY OF THE MANNICH REACTION IN HETEROCYCLIC CHEMISTRY

INTRODUCTION TO SECTION 1 : THE MANNICH REACTION.

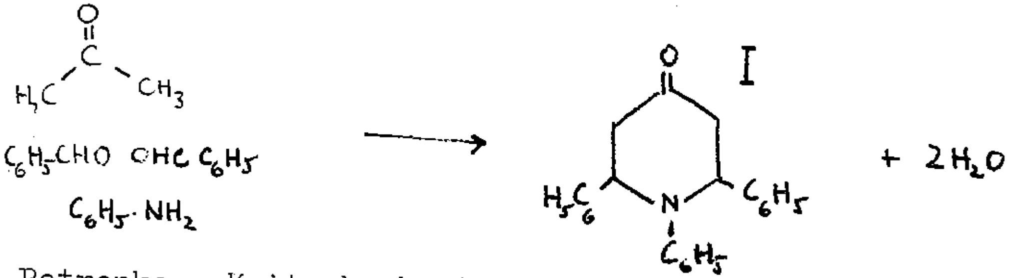
The Mannich reaction is essentially a condensation involving a hydrogen supplied by an ammonium salt (or a primary or secondary amine) an aldehyde and an active hydrogen.

The active hydrogen is thus replaced replaced by an aminoethyl or a substituted aminoethyl group and the general reaction may be represented by the following equation:



Where R = alkyl, aryl or hydrogen and $\overset{*}{H}$ is a reactive hydrogen. Usually the salt of the amine is used.

The above definition embraced some reactions not usually classified as "Mannich reactions" eg the condensation between acetone, benzaldehyde and aniline to give a piperidone derivative (I) (1)


I

and other Petrenko - Kritschenko type reactions.

The first reactions of the Mannich type were carried out by Tollens in 1903 (2) (3) who isolated the tertiary amine (II) produced by the action of formaldehyde on ammonium chloride and acetophenone. Petrenko-Kritschenko and associates carried out similar reactions shortly afterwards. (4)(5)(6)(7). The first detailed study of the reaction was made by Mannich who studied the condensation of antipyrine, formaldehyde and ammonium chloride.

$$NH_4Cl + 3CH_2O + 3C_6H_5\text{-}CO\text{-}CH_3 \longrightarrow N(CH_2CH_2\text{-}CO\text{-}C_6H_5) + 3H_2O$$

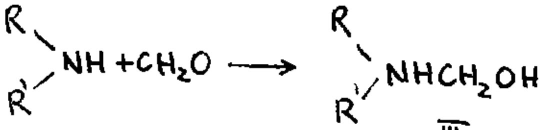
II

The classical example of the Mannich reaction is the reaction of aceton with formaldehyde and a secondary amine: (8)(9).

$$CH_3-CO-CH_3 + CH_2O + HN(CH_3)_2 \longrightarrow CH_3-CO-CH_2CH_2-N(CH_3)_2 + H_2O$$

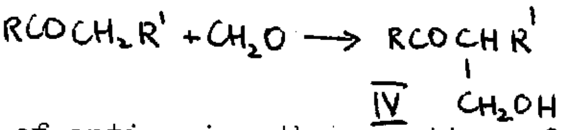
It is interesting to note that if it is possible to attach a second amin methyl group to the molecule it will attach itself to the same carbon ~~ax~~ atom. If ammonia(or a primary amine) is used the primary (or secondary) amine formed often reacts with a further molecule of the active hydrogen donor to give secondary (or tertiary) amines.

The mechanism of the Mannich reaction has not yet been estabilished; two intermediate steps are possible either an aminomethanol (III) or a keto-alcohol (IV) (if the hydrogen is activated by a carbonyl group) being formed



$$RR'NH + CH_2O \longrightarrow RR'NHCH_2OH$$

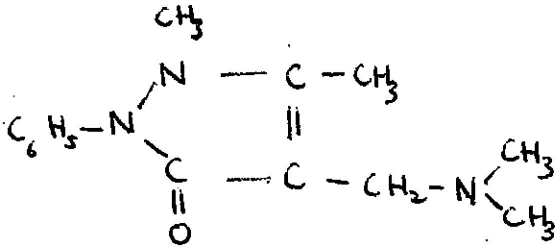
III



$$RCOCH_2R' + CH_2O \longrightarrow RCOCHR'(CH_2OH)$$

IV

But it has been found that in the case of antipyrine the reaction of dimethylaminoalcohol gives a poorer yield of the condensation product (V



V

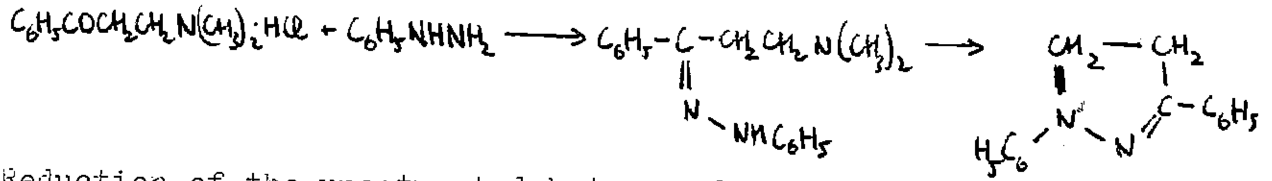
than the reaction of formaldehyde and dimethylamine or formaldehyde and dimethylamine hydrochloride , while the methylol from antipyrine does not react with dimethylamine at all. (10).Thus neither of these represents a true primary step in the Mannich reaction.

The importance of the Mannich reaction in synthesis is due to the variet of products obtainable from the Mannich bases.

On heating or distillation most Mannich bases decompose to yield an amine and an unsaturated compound eg (11):

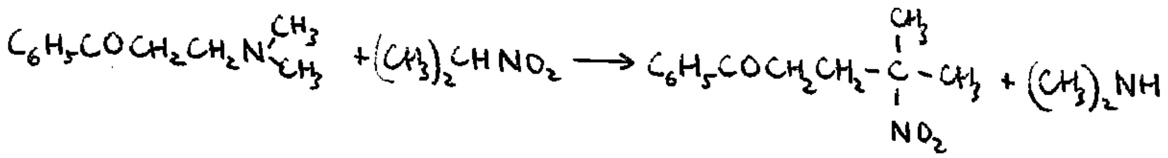
$$C_6H_5-CO-CH_2-CH_2-N(CH_3)_2 \xrightarrow{\Delta} C_6H_5-CO-CH=CH_2 + N(CH_3)_2 \cdot HCl$$

Pyrazolines may be prepared directly from Mannich bases by treatment with phenyl hydrazine. Eg 1:3diphenylpyrazoline may be prepared in the following way. (12)(13).

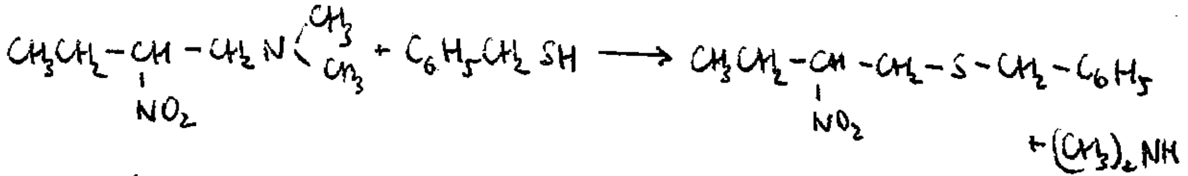


Reduction of the unsaturated ketones obtained from decomposition of some Mannich bases affords a convenient method of preparation of highe homologues of the original ketones. (14)

Decomposition of Mannich bases in presence of certain reagents yields condensation products (15) analogous to those obtainable by a Michael reaction between those reagents and the unsaturated compounds produced from the Mannich bases.

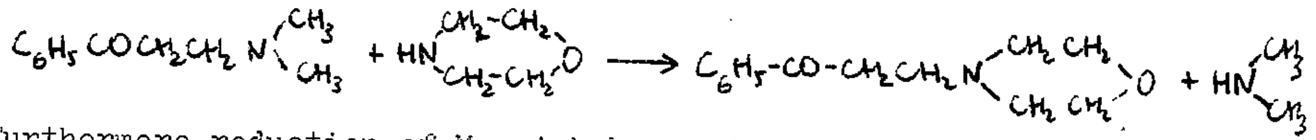


$$C_6H_5COCH_2CH_2N(CH_3)_2 + (CH_3)_2CHNO_2 \longrightarrow C_6H_5COCH_2CH_2-\overset{CH_3}{\underset{NO_2}{C}}-CH_3 + (CH_3)_2NH$$



$$CH_3CH_2-\underset{NO_2}{CH}-CH_2N(CH_3)_2 + C_6H_5CH_2SH \longrightarrow CH_3CH_2-\underset{NO_2}{CH}-CH_2-S-CH_2-C_6H_5 + (CH_3)_2NH$$

Also base exchange may take place, which is particularly useful if the use of primary amines in the original reaction is to be avoided.



Furthermore reduction of Mannich bases from ketones is a convenient source of b-aminoalcohols. (16)(17)

The above is only a brief survey of the Mannich reaction and some of its aplications in synthesis. In the first section of this work an attempt has been made to apply the Mannich reaction to some problems in heterocyclic synthesis.

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(2) van Marle and Tollens , B. 36 1351

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(4) Petrenko-Kritschenko , B. 39 1358

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(10) Bochendorf and Koralewski , Arch.Pharm. 271 101

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(13) Jacob and Madinaveitia , Soc. 1929 (1937)

(14) Mannich and Lammering , B. 55 3510

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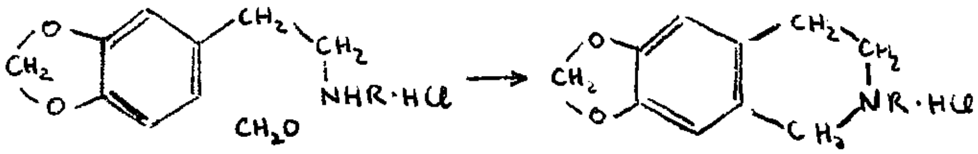
SECTION 1A: ATTEMPTED SYNTHESIS OF DIHYDROISOINDOLES

The fact that the active hydrogen in the Mannich reaction may be supplied by the aromatic nucleus has been utilised in some syntheses based on internal condensation. Becker and Decker (1)(2)(3) and Pictet and Spengler(4) succeded in preparing some tetrahydroisoquinoline derivatives by heating substituted homo benzylamine hydrochlorides with formaldehyde in sealed tubes.



It was therefore expected that a similar condensation using substituted benzylamine hydrochlorides would yield dihydroisoindoles. The main difficulty lied in overcoming the strong deactivating, or meta directing, properties of the group $-CH_2N^+$ eg

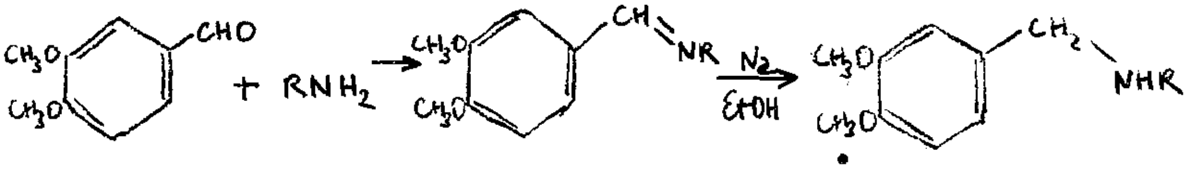
$-CH_2-NH_3^+$ is 49% meta directing

$-CH_2-N(CH_3)_3^+$ is 88% meta directing

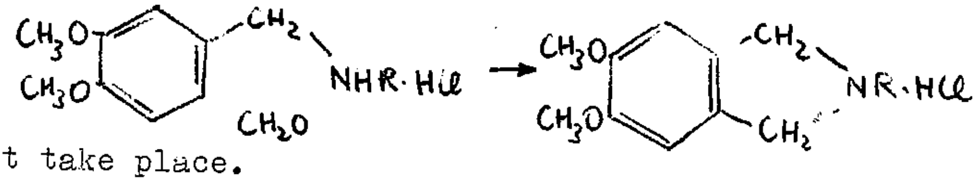
while $-CH_2-CH_2-N(CH_3)_3^+$ is only 19% meta directing

as shown by the work of Holleman, Ingold and Reese (5)(6)(7) Therefore 3:4 dimethoxybenzyl alkylamines were chosen as the strong ortho-para directing properties of the methoxy groups were expected to overcome the inhibiting influence of the $-CH_2^+$ group. These secondary amines were prepared by reduction of the corrseponding Schiffs bases with sodium and alcohol (8) The Schiffs bases were prepared by condensation of ethylamine and n-butylamine with veratric aldehyde(9).

The starting material, veratric aldehyde, was prepared by meth lation of vanilin with dimethyl sulphate according to two ~~meth~~ methods (10) and (11) the respective yields being 72.5% and 78.1% of theory.



Condensation with formaldehyde was then attempted under a variety of conditions both acid (1) (12)and neutral but the desired product could not be isolated . It was concluded that the expected reaction



did not take place.

The two Schiffs bases (3:4dimethoxybenzylideneethylamine and 3:4dimethoxybenzylidene n-butylamine) and the two secondar amines (3:4dimethoxybenzylethylamine and 3:4dimethoxybenzyl n-butylamine) have not been described in the literature . The Schiffs bases were not submited to analysis ,their constitution being proved by analysis of their reduction products.

EXPERIMENTAL

1.Preparation of 3:4dimethoxybenzylideneethylamine

A solution of veratric aldehyde (21.1g) in absolute alcohol(50 ml) was cooled on an ice bath and treated with ethylamine (8ml in presence of conc hydrochloric acid (1 drop).The mixture was allowed to stand at room temperature for one hour with occasio stirring .At the end of this period the alcohol was boiled off on the water bath and the residue was vacuum distilled. Yield:21.4g ie 89%.Bp: 126-7°C/1.2mmHg. Mp:43°C.

2.Preparation of 3:4dimethoxybenzylethylamine

3:4dimethoxybenzylideneethylamine (19g) and absolute alcohol (100ml) were refluxed on the water bath while clean sodium (11g was introduced through the condenser over a period of two hours After the sodium has dissolved, water (300ml) and conc. hydrochloric acid (150 ml) were added and the mixture was boiled on the water bath to decompose any unreduced Schiffs base.The mixture was cooled and ether extracted then made alkaline and further ether extracted the second extract being then dried over anhydrous magnesium sulphate. The ether was boiled off on the water bath and the residue was vacuum distilled.

~~Yield:~~

Yield:9.8g ie 59.4% Bp:113.5-114°C/0.5mmHg.

3:4dimethoxybenzylethylamine may also be prepared without isolating the intermediate Schiffs base.The overall yield of the purified product is then 64.4%.

Nitrogen calculated for $C_{11}H_{17}O_2N$ ~~is~~ 7.22% Found:7.17%

3.Preparation of 3:4dimethoxybenzylidenen-butylamine

Using conditions analogous to those in exp.1 a 90.0% yield of a colourless oil Bp: 134-5°C/0.55mmHg was obtained

4.Preparation of 3:4dimethoxybenzyl n-butylamine

Using conditions analogous to those in exp.2 a 69.0% yield of the amine was obtained.Bp:133-5°C/0.6mmHg

3:4dimethoxybenzyl n-butylamine was also prepared without isolating the intermediate Schiffs base.The overall yield of the purified product was 75.8%.

Nitrogen calculated for $C_{13}H_{21}O_2N$ ~~is~~ 6.28% Found:6.40%

A picrate,probably $C_{13}H_{21}O_2N.C_6H_3O_7N_3$, was also prepared. Mp:160.
-161.5°C

5.Attempted closure of dihydroisoindole rings ~~using~~ under acid conditions using hydrochloric acid.(1)

3:4dimethoxybenzylethylamine (9.5g) conc. hydrochloric acid (5ml) and formaldehyde (35 ml of 40% aqueous solution) were sealed into glass tubes and heated in a Carius oven for four hours at 130°C. A clear brown liquid was obtained. This was made strongly alkaline with caustic soda and ether extracted.The ether extract was dried, the ether boiled off and the residue vacuum distilled.

About 2 ml of oily liquid Bp:113.5°C/0.6 mmHg were obtained which gave tests for secondary amines ie the starting material.

In the aqueous layer a brown oil seperated out which was ether insoluble.It was extracted with chloroform but resisted attempts of vacuum distillation. It was possibly a 3:4dimethoxybenzylethylamine formaldehyde polymer .

Similar reaction was attempted using 3:4dimethoxybenzyl n-butylamine but the only product obtained was the starting material which was identified by the melting point of its picrate.

6.Attempted closure of dihydroisoindole rings under acid conditions using sulphuric acid.

3:4dimethoxbenzyl n-butylamine (12g) was dissolved in 70% sulphuric acid (23.4g) and formaldehyde (5ml of 40% aqueous solution) was added with vigorous stirring . The mixture was stirred for 2 hours at room temperature and was made alkaline with concentrated sodium hydroxide solution and extracted with chloroform. The combined ~~x~~ extracts were dried , the solvent distilled off, and the residue was vacuum distilled. Bp:130-35°C/0.5 mmHg. Picrate: Mp:159-60°C, ie the substance is the starting material. A certain amount of tarry material could not be distilled and all efforts to recrystalise it from alcohol and chloroform failed.

Similar attempts were made using further portions of 3:4dimethoxybenzyl n-butylamine and 3:4dimethoxybenzylethylamine at slightly elevated temperature and at 100°C. ~~The~~ An attempt was also made to isolate a tertiary amine by the Hinsberg method (13) (14) but no tertiary amine was found.

7.Attempted closure of dihydroisoindole rings under neutral conditions

Using conditions similar to those in Exp.6 but without the presence of acid both 3:4dimethoxybenzylethylamine and 3:4dimethoxybenzyl n-butylamine failed to yield N-alkyl 3:4dimethoxydihydroisoindoles. The reaction was carried out both at room temperature and on the water bath.

Isolation of the products was attempted both by vacuum distillation and by preparing a nitrosamine derivative of the secondary amine (15 by treating ~~with~~ an acid solution of the product with a nitrite solution. No tertiary amine was found.

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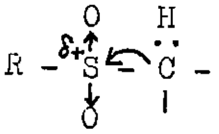
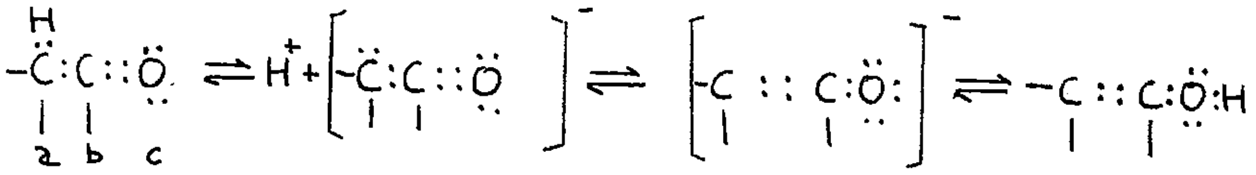
(3) Decker , D.R.P. 257138
(4) Pictet and Spengler, B. 44 2030 (1911)
(5) Holleman , Chem.Rev. 1 189 (1924)
(6) Ingold , Ann.Repts.Chem.Soc. 23 129 (1926)
(7) Reese , Chem.Rev. 14 55 (1937)
(8) O.Fischer , A. 241 330 (1887)
(9) H.Zaunschirm,A. 245 279
(10) Blatt,"Organic Syntheses" Vol.2 p.619
(11) Vogel,"Textbook of practical organic chemistry" p.762
(12) G.M.Robinson,Soc. 1915 p.267
(13) Hinsberg , B. 23 2963
(14) Hinsberg and Kessler, B. 38 906 (1905)
(15) O.Fischer and Diepolder , A. 286 163

SECTION 1B: REACTIONS OF METHYLENE GROUPS ADJACENT TO THE SULPHONE GROUP.

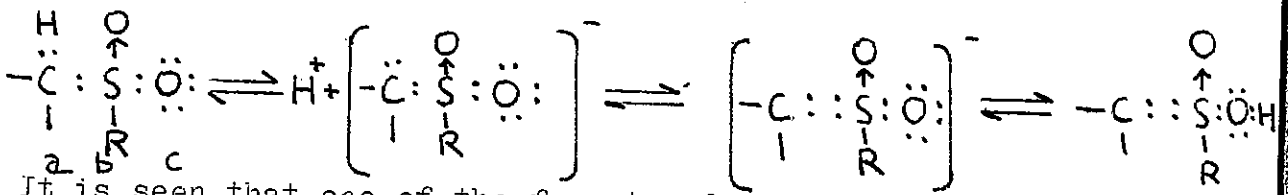
The sulphone group involves tetravalent sulphur - in accordance with parachor values obtained by Freimann and Sudgen (1). As the two sulphur-oxygen bonds are semipolar double bonds , electrons are drawn away from adjacent methylene groups thus facilitating removal of protons from adjacent carbon atoms by an inductive mechanism:



However an effective group for prototropic change must not only have a strong electron attraction but also must provide a suitable seat for the charge on the anion (2). The enolisation of carbonyl compounds is an example of prototropy in a system fulfilling both of these requirements:



Now the corresponding b- and c- atoms in sulphones are conacted by a single pair of electrons , and the anions are therefore different from those pictured above;



It is seen that one of the formulae for the anion has an unshared pair of electrons on carbon and the other requires that sulphur expand its valence shell to ten electrons. However experimental evidence has shown that anions derived from sulphones may be formed although neither of the alternative formulae is universally accepted.(3)(4)(5). In general it is agreed that the sulphone group is electron attracting , but with less tendency to undergo polarisation than groups like cyano , nitro and carbonyl.

Thus we would expect sulphones with adjacent methylene groups to undergo reactions similar to the corresponding carbonyl compounds but to a lesser degree. This is justified by experimental evidence as the following brief summary shows:

Sulphones react with Grignard reagents forming halomagnesium derivatives of the sulphone and liberating the hydrocarbon (6)(7) eg:

$$p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2\text{-}CH_3 + RMgX \longrightarrow p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2\text{-}CH_2\text{-}MgX + RH$$

Sodium salts are not easily formed but phenylbenzylsulphone is slightly soluble in sodium hydroxide (8). Benzylmethylsulphone is stable to hot permanganate and nitric acid (9) and also does not react with selenium dioxide.

Methyl p-tolyl sulphone reacts with benzaldehyde to give a benzylidene derivative (10) in low yield:

$$p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2\text{-}CH_3 + C_6H_5CHO \xrightarrow{NaOEt} p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2\text{-}CH{=}CH\text{-}C_6H_5$$

Benzyl p-tolylsulphone also undergoes the Michael condensation (11

It may be noted that o- and p- nitrobenzyl p-tolylsulphones give coloured salts with sodium ethoxide which may then be condensed with alkyl halides (12).

In agreement with expectation the sulphone group is predominately metadirecting in the aromatic nucleus.

The methylene group in 1:3disulphones is considerably more reactive than the adjacent methylene group in simple sulphones. Bis (ethyl sulphonyl)methane may be alkylated (13):

$$(C_2H_5\text{-}SO_2)_2CH_2 + 2CH_3I + 2KOH \longrightarrow$$
$$(C_2H_5\text{-}SO_2)_2C(CH_3)_2 + 2KI + 2H_2O$$

It does not however react with nitrous acid or couple with benzene diazonium chloride. 1:3disulphones are soluble in alkali and may be easily halogenated. (14)(15).

The aim of the present work ~~is~~ was to investigate the reactions of methylene groups situated between a sulphone group and another electron attracting group eg carbethoxy and carbonyl groups , aspecially with regard to the Petrenko-Kritschenko reaction.

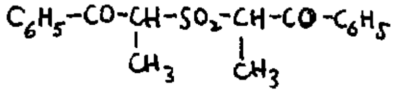
Two compounds were chosen: Diphenacylsulphone I and diethylsulphonyl diacetate II:

$$C_6H_5-CO-CH_2-SO_2CH_2-CO-C_6H_5 \qquad C_2H_5OOC-CH_2-SO_2-CH_2-COOC_2H_5$$

I II

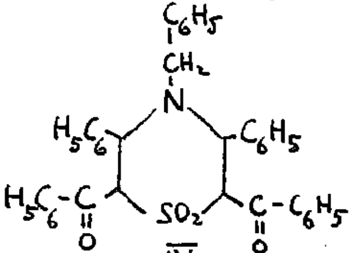
Diphenacylsulphone was prepared by condensing bromacetophenone with alcoholic sodium sulphide to give diphenacylsulphide in 75% yield and oxidising the product with cold , slightly acid , permanganate (5%) to give diphenacylsulphone in av. 33% yield.(16). Sulphonyldiacetic ester was prepared by oxidation of thiodiglycolic acid with cold ,alkaline 5% permanganate in 76% yield and esterification of the product with absolute alcohol in presence of sulphuric acid in av. 66% yield. The ester is an oil Bp:154-160°C at 3mmHg. (17)

Diphenacylsulphone was found to condense with methyl iodide in presence of alkali to give a dimethiodide derivative III and to undergo the Petrenko-Kritschenko reaction with benzaldehyde and benzylamine in cold to give 2:6diphenoxy3:5diphenyl4benzyltetrahydrothiazine dioxide IV.

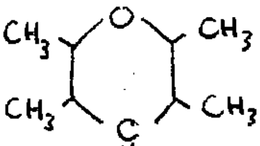


$$C_6H_5-CO-\underset{CH_3}{\underset{|}{CH}}-SO_2-\underset{CH_3}{\underset{|}{CH}}-CO-C_6H_5$$

III



IV



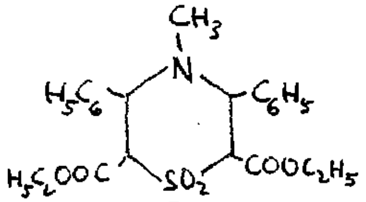
V

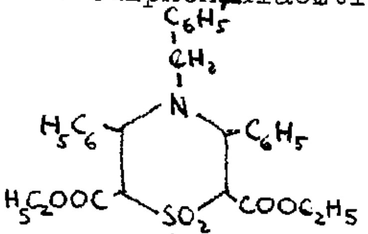
It may be noted that diacetylacetone also forms a dimethidide derivative which then cyclises to tetramethyl γ-pyrone(by the action of acids)V. (18)

Sulphonyldiacetic ester is known to undergo condensation with alkyl iodides (17) .

It was found to undergo the Petrenko-Kritschenko reaction with benzaldehyde and methylamine and benzaldehyde and benzylamine in cold, to give 2:6dicarbethoxy3:5diphenyl4methyltetrahydrothiazine dioxide VI and 2:6dicarbethoxy3:5diphenyl4benzyltetrahydrothiazine dioxide VII.

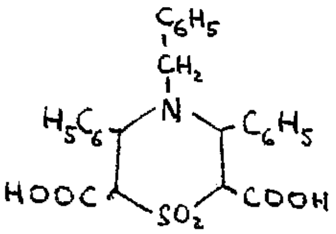
It may be noted that when excess methylamine is used the main product is dimethylamide of sulphonyldiacetic acid VIII.

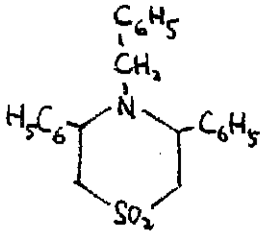

VI


VII

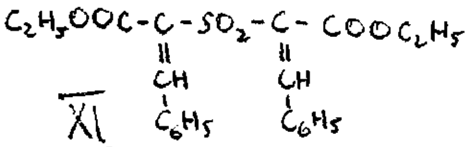
$CH_3NHCO-CH_2-SO_2-CH_2-CONHCH_3$
VIII

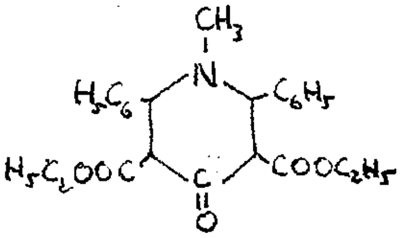
VI was hydrolysed (with 5N hydrochloric acid) and decarboxylated (with 5N sodium hydroxide) to give 2:6dicarboxylicacid3:5diphenyl 4benzyltetrahydrothiazinedioxide IX and 3:5diphenyltetrahydrothiazinedioxide X respectively.

IX


X


Sulphonyldiacetic ester was also found to form a dibenzylidine derivative XI when treated with benzaldehyde in presence of some piperidine.


$$C_2H_5OOC-\underset{\underset{C_6H_5}{|}}{\underset{CH}{\overset{\|}{C}}}-SO_2-\underset{\underset{C_6H_5}{|}}{\underset{CH}{\overset{\|}{C}}}-COOC_2H_5$$
XI

XII


It may be noted that acetonedicarboxylic ester also undergoes the Petrenko-Kritschenko reaction with benzaldehyde and methylamine to give 2:6dicarbethoxy3:5diphenyl4methyltetrahydropyridone XII.(19)(20). The ease of formation of thiazine derivatives may be taken as possible additional evidence of the tetrahedral configuration of the valence bonds in the sulphone group. Physical evidence in favour of tetrahedral (or easily deformable planar) configuration includes measurments of dipole moments of several sulphones (21 to 23 inclusive) and electron diffraction patterns (24). Sulphones also exist as parts of sixmembered oxygen containing rings (25)

EXPERIMENTAL

1. Condensation of diphenacylsulphone with methyl iodide

Diphenacylsulphone (1.35 g), sodium hydroxide (1g) and methyl iodide (2ml) were refluxed in 90% alcohol (22 ml) for 15 minutes. The mixture was then boiled for a further 5 minutes to allow the excess methyl iodide to evaporate. Water (25 ml) and concentrated hydrochloric acid (5 ml) were then added and the product collected and recrystallised from alcohol. White needles Mp: 181-2°C were obtained. The product was soluble in alkali showing the presence of active hydrogen.

Calculated: C 65.46% H 5.46% (for dimethiodide derivative)
Found: C 65.3 % H 5.6 % $C_{18}H_{18}O_4S$

2. Preparation of 2:6diphenoxy3:5diphenyl4benzyltetrahydrothiazine dioxide.

Diphenacyl sulphone (2.7 g) and benzaldehyde (2 ml) were dissolved in warm (30 -40°C) benzene (20ml) and benzylamine (1.2 ml) was slowly added. The mixture was allowed to stand for several days, then alcohol (20 ml) was added and the precipitate collected, washed with a large volume of hot alcohol and recrystallised from a mixture of acetone and water. White prisms Mp: 209°C were obtained.

Calculated: C 75.90% H 5.30% N 2.39% for $C_{37}H_{31}O_4NS$
Found: C 76.2% H 5.3%

3. Preparation of 2:6dicarbethoxy3:5diphenyl4methyltetrahydrothiazinedioxide.

Methylamine, generated from methylamine hydrochloride (1g), was slowly passed into a mixture of diethylsulphonyldiacetate (2.06g) freshly distilled benzaldehyde (2 ml) and absolute alcohol (6 ml) cooled in an ice bath. There was a marked colour change and the mixture was allowed to stand for 24 hours. A white precipitate appeared which was recrystallised from absolute alcohol to constant melting point. White needles Mp: 205°C were obtained.

Calculated: C 62.02% H 6.07% N 3.15% for $C_{23}H_{27}O_6NS$
Found: C 61.8 % H 6.3 % N 3.2 %

4.Preparation of 2:6dicarbethoxy3:5diphenyl4benzyltetrahydro - thiazinedioxide

Benzylamine (1 ml) was slowly added to an ice cooled mixture of diethylsulphonyldiacetate (2.06g) , freshly distilled benzaldehyde (2 ml) and absolute alcohol (6 ml). The mixture was allowed to ~~sta~~ stand for several days. On addition of alcohol (20 ml) and water (a few drops) a white precipitate appeared which was recrystallised from alcohol to constant melting point. Fine , white , needles Mp:158.5-160.5°C were obtained. Yield (in another run) 45%.

Calculated: C 66.80% H 5.95% N 2.69% for $C_{29}H_{31}O_6NS$
Found: C 67.0 % H 6.2 % N 2.9 %

5.Preparation of dimethylamide of sulphonyldiacetic acid.

Large excess (1 mole) of methylamine gas was bubbled through a mixture of diethylsulphonyldiacetate (2.06 g) , benzaldehyde (2ml) and absolute alcohol (6 ml). A white precipitate appeared immediatelly and was collected and recrystallised from alcohol to a constant melting point. Small white cubes Mp:187-8°C were obtained.

Calculated: C 34.61% H 5.77% N 13.46% for $C_6H_{12}O_4N_2S$
Found: C 35.4 % H 6.2 % N 13.3 %

6.Preparation of 2:6dicarboxylic acid3:5diphenyl4benzyltetrahydrothiazinedioxide.

2:6dicarbethoxy3:5diphenyl4benzyltetrahydrothiazinedioxide (2.6g) was refluxed with 5N hydrochloric acid (50 ml) for four hours. At no stage did the mixture become homogenous . The product was collected , washed with water and recrystallised from a mixture of acetone and water to a constant melting point. Fine needles Mp:164°C were obtained.

Calculated: C 64.52% H 4.95% N 3.01% for $C_{25}H_{23}O_6NS$
Found: C 66.5 % H 6.0 % N 3.0 %

7.Preparation of 3:5diphenyl4benzyltetrahydrothiazinedioxide.

2:6dicarbethoxy3:5diphenyl4benzyltetrahydrothiazinedioxide (2.6g) was refluxed with 5N sodium hydroxide (100 ml) for three hours.

The product was collected , washed with cold water and recrystallised to constant melting point from absolute alcohol. White needles Mp: 185-6°C were obtained.

Calculated: C 73.21% H 6.10% N 3.71% for $C_{23}H_{23}O_2NS$
Found: C 72.1 % H 6.4 % N 3.8 %

8.Preparation of a-àdibenzylidine derivative of diethylsulphonyl-diacetate.

One drop of piperidine was added to a mixture ~~x~~ of diethylsulphonyl diacetate (2.06 gm) , benzaldehyde (2 ml) and absolute alcohol (6 ml).The mixture was allowed to stand for several days. Absolute alcohol (20 ml) was added an a precipitate appeared and was collected and recrystallised to constant melting point from absolute alcohol. Stubby , white, needles Mp:144.5°C were obtained.

Calculated: C 63.77% H 5.31% for $C_{22}H_{22}O_6S$
Found: C 64.2 % H 5.9 %

REFERENCES used in section 1B

(1) Freimann and Sudgen , Soc. 263 (1928)

(2) Gilman , "Organic Chemistry" p879

(3) Shriner , Struck and Jorison J.Am.Chem.Soc. 52 2060

(4) Gibson , Chem.Rev. 14 431

(5) Arndt and Martius , A. 499 228

(6) Kohler and Potter , J.Am.Chem.Soc. 58 2166

(7) Ziegler and Connar , J.Am.Chem.Soc. 60 33

(9) Fromm and Gaupp , B. 41 3419

(10) Kohler and Potter , J.Am.Chem.Soc. 57 1316

(11) Connor , Fleming and Clayton , J.Am.Chem.Soc. 58 1386

(12) Shriner and Greenlee , J.Org.Chem. 4 242

(13) Fromm , A. 253 141

(14) Baumann , B. 19 2811

(15) Stuffer , B. 3226 (1890)

(16) Fromm and Flaschen , A. 394 310

(17) Löven , B. 17 2818

(18) Collie and Steele , Soc. 77 961

(19) Mannich and Mohs , B. 63 608

(20) Petrenko-Kritschenko , B. 42 3683

(21) Sutton , New and Bentley , Soc. 652 (1933)

(22) Coop and Sutton , Trans.Faraday Soc. 35 505

(23) Bergmann and Tschidenowski , B. 65b 457

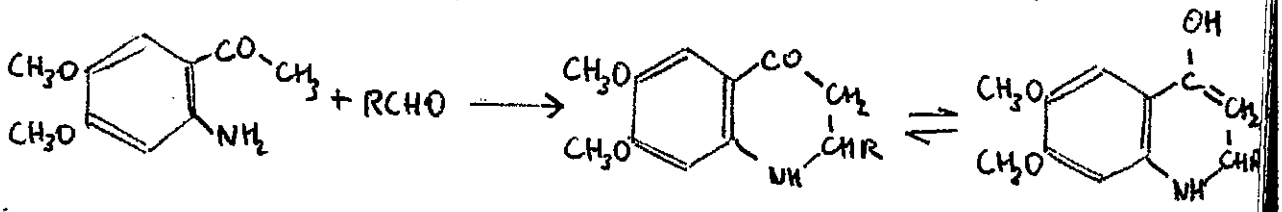
(24) Hompson and Sutton , Proc.Roy. Soc. 143a 147

(25) M^{c}Clent and Sniles , Soc. 1016 (1937)

SECTION 1C: ATTEMPTED SYNTHESIS OF 4 HYDROXYDIHYDROQUINOLINES

Internal condensation of o-aminoacetoveratrone with aldehydes would be expected to yield derivatives of 6:7dimethoxy4hydroxyquinoline. This could be accomplished in three ways:

1) Direct condensation of o-aminoacetoveratrone (or its hydrochloride) with an aldehyde.



However , primary aromatic amines do not usually take part in a Mannich reaction in a simple manner, (1) and hence other - less direct - methods were also attempted.

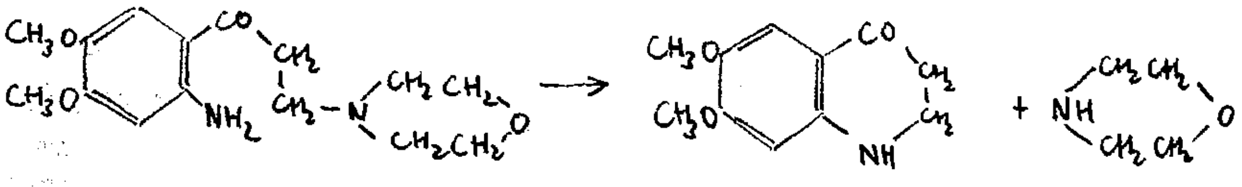
Acetoveratrone was prepared in 76% yield from veratrole and acetyl chloride in presence of anhydrous alluminium chloride (2).

6-Nitroacetoveratrone was prepared in 62% yield by nitration of acetoveratrone using cold concentrated nitric acid (3).

6-Aminoacetoveratrone hydrochloride ~~was~~ (not previously described) was prepared in 80.5% yield by catalytic reduction of 6-nitroacetoveratrone.

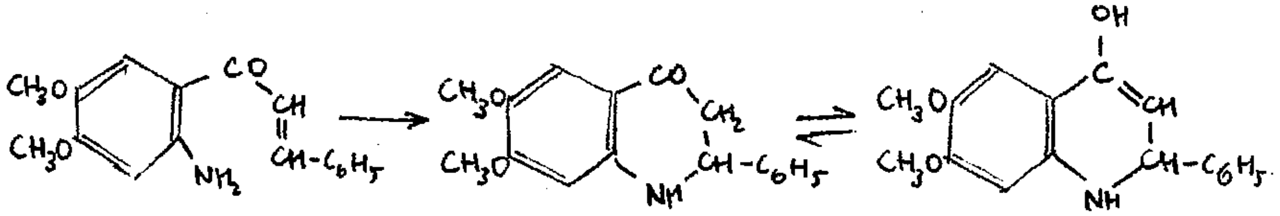
An attempt was made to condense 6-aminoacetoveratrone with paraformaldehyde but no crystalline products were obtained. Using benzaldehyde a picrate Mp: 215.5°C . Analysis results pending.

2) Base exchange method, (5) utilising o-amino b-morphilinoethyl-3:4dimethoxyphenyl ketone.



However , the starting material could not be prepared. The Mannich base from acetoveratrone and morphiline was prepared in 38% yield (4) , but its nitration product gave incorrect analysis figures.

3) Internal condensation of benzylidene derivatives of o-amino acetoveratrone.



This type of reaction (an apparent addition of an amine across a double bond) is a feature of the Skraup reaction (5)(6) and as such not impossible to expect.

The benzylidene derivative of o-nitroacetoveratrone was prepared in 62% yield but attempts to reduce it with acid metal mixtures proved unsuccesful.

EXPERIMENTAL

1.Catalytic reduction of 6-nitroacetoveratrone

The nitro compound (22.5g) was dissolved in hot absolute alcohol (350 ml) and reduced with hydrogen over Raney nickel at pressure of a few inches of water. The reduction was completed in 1½ hours. The catalyst was filtered off and the product collected as hydrochloride by blowing dry hydrogen chloride through the alcoholic solution of the amine.

Yield: 18.6g ie 80.5%. Decomposes slowly at about 300°C.

Calculated for ~~x~~ $C_{10}H_{13}O_3N.HCl$ N: 6.0%

Found N: 6.4%

The amine behaves like a typical aromatic amine ie it may be diazotized etc. On making the solution of diazocompound alkaline ~~the~~ an intense red dye is produced possibly by auto-coupling.

2.Attempted condensations of 6-aminoacetoveratrone with aldehydes

A mixture of 6-aminoacetoveratrone ~~12x~~ hydrochloride (2.3g) paraformaldehyde (0.4 g) and absolute alcohol (30 ml) was refluxed on the water bath for 1 hour. Dilute hydrochloric acid (1 ml) was added and refluxing continued for a further 10 minutes to depolymerise any unused paraformaldehyde. The mixture was then cooled and made alkaline with ammonia. An oily layer appeared but no crystalline products could be obtained.

Using benzaldehyde under similar conditions and extracting the product with ether some product was isolated in the form of the picrate Mp: 215.5°C

Calculated for $C_{23}H_{20}O_{10}N_4$ · C 54.1% H 3.9% N 10.6%
Found: C % H % N %
Calculated for picrate of 6-aminoacetoveratrone:
For $C_{16}H_{16}O_{10}N_4$ C 45.5% H 3.8% N 12.8%

3.Nitration of 6-amino b-morpholi~~xx~~noethyl 3:4dimethoxyphenyl ketone.

The free base (1 g) was dissolved in concentrated nitric acid (10 ml) and allowed to stand at room temperature for 30 minutes. The mixture was then neutralised by addition of concentrated ammonium hydroxide and the ppte formed was collected and recrystallised twice from absolute alcohol. Yellow rhombic crystals Mp:183°C were obtained.

Calculated for $C_{15}H_{20}O_6N_2$ C 55.6% H 6.2% N 8.6%
Found C 45.8% H 5.4% N 10.6%

Apparently some polynitro compound was formed and the mixture was not sufficiently purified by recrystallistion.

4.Preparation of 3:4dimethoxy6nitrochalcone .

6-nitroacetoveratrone (11.25 g) was dissolved in alcoholic alkali (250 ml) and benzaldehyde (50 ml) was added .The mixture was ~~xxx~~ allowed to stand for 6 hours and on cooling and adding a drop of water the product seperated out and was recrystallised from aqueous alcohol. Mp:158.5°C. Yield: 15.65g ie 61.2%

Calculated for $C_{17}H_{15}O_5N$: N 4.5%
Found: N 4.8%

REFERENCES used in section 1C

(1) "Organic reactions" , 1 312

(2) Mannich , Arch.Pharm. 248 137

(3) R.Robinson , Soc. 125 653

(4) F. Lions , Private communication 1951

(5) Harradence and Lions , J.Proc.Roy.Soc. N.S.Wales 72 233

(6) Blaise and Maire , Bull.soc.chim. 3 662

(7) Morton , "The Chemistry of Heterocyclic Compounds" p.263

SECTION 2

MISCELLANEOUS HETEROCYCLIC SYNTHESES

SECTION 2A: SYNTHESIS OF 4:5:6:7TETRAHYDROBENZTHIAZOLES

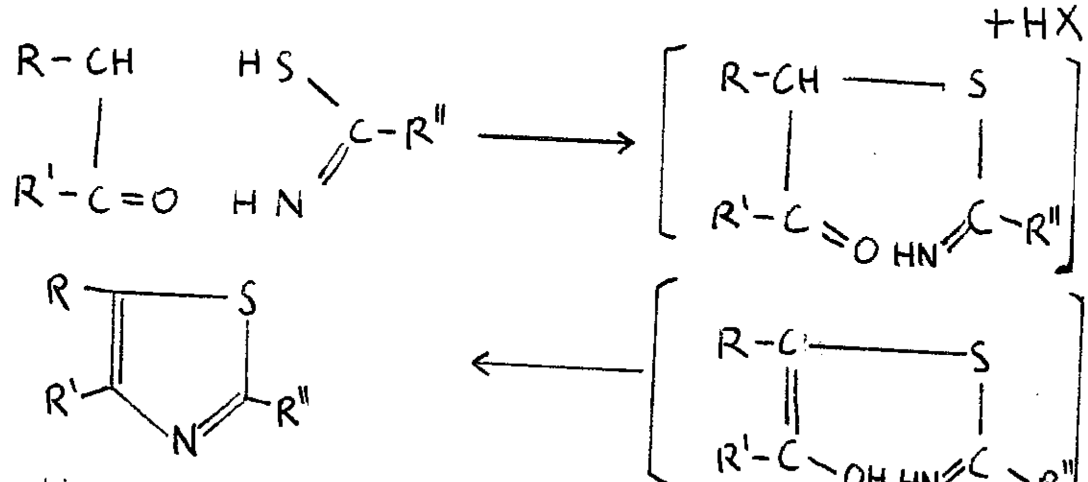
The main methods of synthesis of thiazoles are:

1) Reaction of thioamides and a-halo carbonyl compounds (1)
2) Reaction of ammonium dithiocarbamate and a-halo carbonyl compounds (to give mercapto thiazoles in which the -SH group may then be eliminated by oxidation or reduction)(2)
3) The reaction of a-acylamine carbonyl compounds with phosphorous pentasulphide .(3)
4) Rearrangement of a-thiocyanoketones. (4)

(References are to the first examples of the reaction in literature.)

Of the above methods the first is by far the most important and most widely used. Its mechanism is postulated (5) as involving:

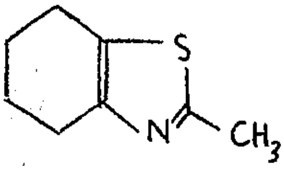
a) Formation of a carbon sulphur bond by elimination of HX
b) Ring closure with the enolic form of the ketone , with elimination of water.



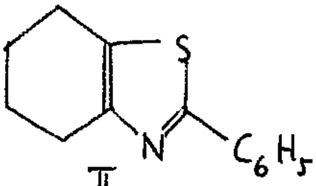
The reaction os exothermic and there is no real evidence for a stepwise process, but the identity of the products obtained precludes the possibility of an alternate mechanism ie the elimination of hydrogen halide between the halogen and the NH- group. Among the a-halo carbonyl compounds employed , no mention is made in the literature of a-halo cyclohexanone and tetrahydro benzthiazoles are unknown.

An attempt has here been made to synthesise some of these compounds by reacting a-chlorocyclohexanone with some thioamides in alcoholic solution. a-chlorocyclohexanone was prepared by passing chlorine through a cold suspension of calcium carbonate in cyclohexanone in 75% yield. (6). Thiobenzamide was prepared by heating benzonitrile with alcoholic hydrogen sulphide in presence of ammonia in an aoutoclave (7) in 53% yield. Thioacetamide was prepared by treating acetamide with phosphorous pentasulphide in a benzene suspension (8) in 29% yield.

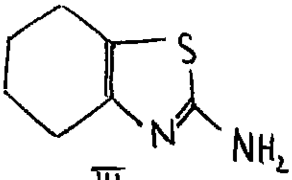
The following substances were prepared: 2-methyltetrahydrobenzthiazole (I) , 2-phenyltetrahydrobenzthiazole (II) and 2-aminotetrahydrobenzthiazole (III).



I



II

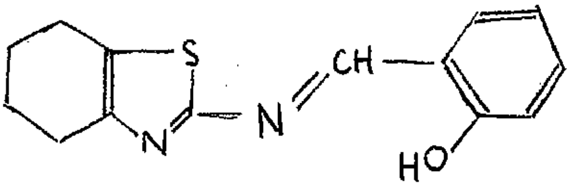


III

I and II are oily liquids which may be distilled under reduced pressure. They were characterised by their picrates. A hygroscopic methiodide of I was also prepared , it decomposed easily on heating evolving a mercaptan. 2-aminotetrahydrobenzthiazole (prepared from a-chlorocyclohexanone and thiourea) behaves like a normal aromatic amine; it gives a fairly stable diazocompound which may be coupled with b-naphtol to give an intense red dye.

A yiellow salicylidene derivative of III was prepared IV , which gives a coordination complex with copper.

IV



All tetrahydrobenzthiazoles are bases , easily soluble in dilute hydrochloric acid.

EXPERIMENTAL

1.Preparation of 2-methyltetrahydrobenzthiazole

a-chlorocyclohexanone (12 ml) , thioacetamide (7.5 g) and absolute alcohol (50 ml) were refluxed together for 1½ hours. Concentrated hydrochloric acid (20 ml) was then added and the mixture ether extracted (2 portions of 50 ml). The aqueous layer was then made alkaline with with sodium hydroxide (20 g) and ether extracetd (2 portions of 100 ml). This ether extract was dried over anhydrous sodium sulphate , the ether evaporated off and the residue distilled under reduced pressure. An oil Bp: 118°C/1.2 mmHg was obtained. Yield: 7.3g ie 41.7%

Calculated: C 62.75% H 7.19% N 9.15% for $C_8H_{11}NS$

Found: C % H % N 9.6 %

A picrate was prepared Mp:125-6°C.

Calculated: N 14.66% for $C_8H_{11}NS.C_6H_3N_3O_7$

Found: N %

2.Preparation of 2-phenyltetrahydrobenzthiazole

a-chlorocyclohexanone (6.65 g) , thiobenzamide (6.75g) and absolute alcohol (15 ml) were refluxed together for 2 hours. Concentrated hydrochloric acid (15 ml) and water (80 ml) were then added and the mixture was ether extracted (2 portions of 50 ml).The aqueous layer was then made alkaline with sodium hydroxide (10g) and ether extracted (2 portions of 100 ml). The ether extract was dried over anhydrous sodium sulphate , the ether evaporated off and the residue distilled under reduced pressure. A colourless oil Bp:150°C/1.5 mmHg was obtained. Yield: 54.1%

Calculated: N 6.51% for $C_{13}H_{13}NS$

Found: N 6.7 %

A picrate was prepared Mp:150.5°C

Calculated: N 12.61% for $C_{19}H_{16}O_7N_4S$

Found: N 13.1%

3. Preparation of 2-aminoterahydrobenzthiazole

a-chlorocyclohexanone (6.65 g) , thiourea (3.8 g) and absolute alcohol (15 ml) were refluxed together for 2 hours. Concentrated hydrochloric acid (15 ml) and water (80 ml)were then added and the mixture was ether extracted (2 portions of 80 ml). The aqueous layer was made alkaline with sodium hydroxide (20 g) and ether extracted (2 portions of 120 ml). This ether extract was dried over anhydrous sodium sulphate ~~and~~, the ether evaporated off and the residue distilled under reduced pressure. A colourless oil Bp:150-154°C/2 mmHg was obtained which solidified to a white solid Mp:87-8°C, which was recrystallised from alcohol to yield white needles. Yield:7.7g ie 65%

Calculated: N 18.18% for $C_7H_{10}N_2S$

Found: N %

A salicylidene derivative was prepared by dissolving the amine (1g) in absolute alcohol (40 ml) and adding salicylaldehyde (1.5 ml). On coolingthe mixture ~~a~~ yellow plates were deposited. The product was recrystallised from alcohol to constant melting point (116°C).

Calculated: N 10.85% for $C_{14}H_{14}N_2SO$

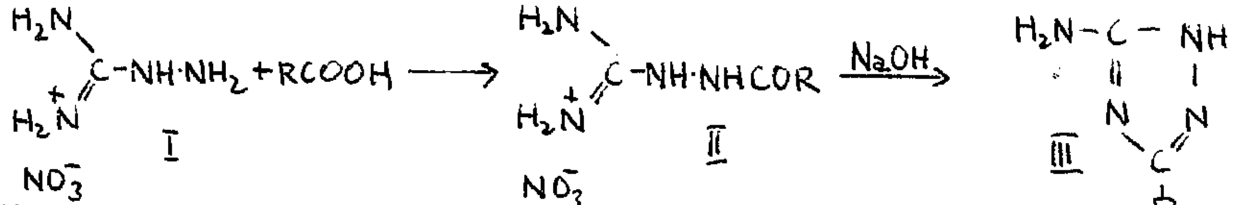
Found: N 11.0 %

REFERENCES used in section 2A

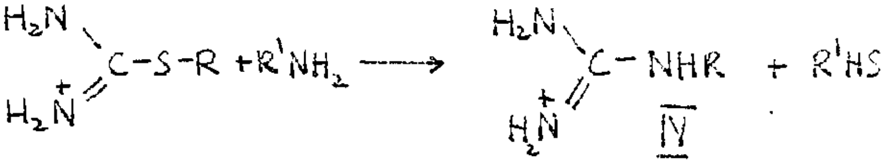
(1) Wilstätter and Wirth , B. 42 1908
(2) Midzatti , Gaz. Chim. Ital. 231 578
(3) Gabriel , B. 43 1283
(4) Aropides , A. 249 7
(5) Organic Reactions VI p.373
(6) Refi and Kötz , J.Pr.Chem. 80 487
(7) Gabriel and Heymann , B. 23 157
(8) Hantzsch , A. 250 264

SECTION 2B: ATTEMPTED SYNTHESIS OF 5-AMINO 3-PHENYL 1:2:4:TRIAZOLE

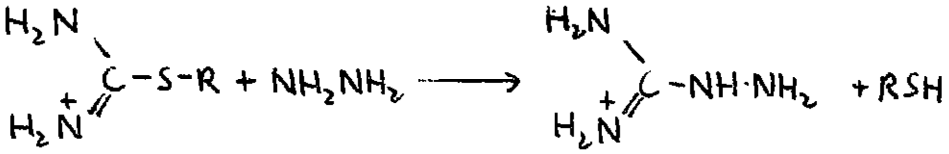
Aminoguanidine nitrate I may be acylated by treatment with carboxylic acids to amidoguanidines II which cyclise on warming with alkalies to yield 5-amino 3-alkyl 1:2:4-triazoles III (1) (2).(10)



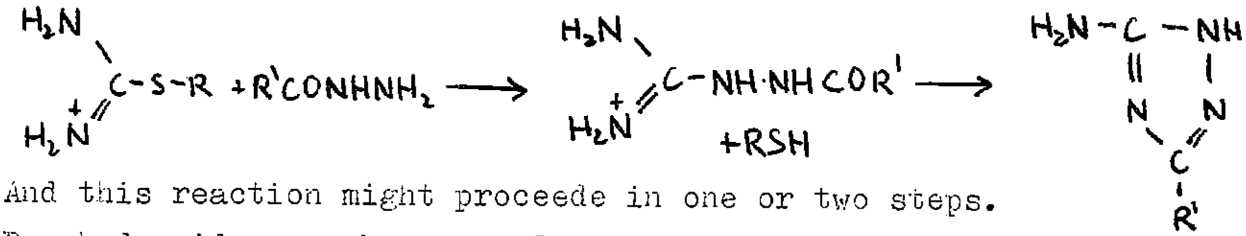
Now, it is well known (3) that S-alkylisothiouronum salts condense with amines to give alkyl guanidines IV with evolution of mercaptan.



Also, aminoguanidine itself , is prepared by condensation of S-alkyl isothiouronium salts with hydrazine(4):



It was thought , therefore , that S-alkylisothiouronium salts may react with acyl hydrazides to give amidoguanidines with evolution of mercaptans which would in turn cyclise to yield 5-amino 3-alkyl 1:2:4 triazoles.



And this reaction might proceede in one or two steps. Benzhydrazide was chosen as 3-phenyl 5-amino 1:2:4triazole is known (5). It was prepared in 60% yield by refluxing ethyl benzoate with hydrazine in absolute alcohol (6).

Several S-alkylisothiouronium salts were used. These were easily prepared by heating thiourea with the appropriate alkyl halide (or sulphate) in nearly theoretical yields. (7)(8)(9).
The starting materials were then brought together both by direct fusion and by refluxing in absolute alcohol. The temperature of the reaction was also varied. In eache case a vigorous evolution of mercaptan occured but the desired product could not be isolated from the reaction mixtures. It was concluded that decomposition occured yielding a mixture of low melting materials.

EXPERIMENTAL

1.Reaction of S-benzylisothiouronium chloride with benzhydrazide

Equimolecular proportions of S-benzylisothiouronium chloride and benzhydrazine were fused together over boiling bromobenzene (Bp:155-158°C) for one hour. The mercaptan evolved was steam distilled from the acid solution of the fusion mixture, the residue charcoaled filtered , made alkaline with sodium hydroxide and the volume reduced by evaporation under reduced pressure. A white amorphous material (Mp: about 100°C) seperated out but could not be obtained in a crystalline form.

2.Reaction of S-methylisothiouronium sulphate with benzhydrazide

Equimolecular proportions of S-methylisothiouronium sulphate and benzhydrazide were fused together over boiling ethyl benzoate (Bp: 214°C) for three hours. A vigorous evolution of methyl mercaptan took place. The mixture was made alkaline with sodium hydroxide and an amorphous precipitate appeared which defied all attempts to recrystallise it.

3.Reaction of S-methylisothiouronium iodide with benzhydrazide

Equimolecular proportions of the reagents were reacted a)by fusion over bromobenzene b)by fusion over methylsalicylate c) by refluxing in absolute alcohol. In each case vigorous evolution of mercaptan occured but no crystalline product could be obtained either from the acid or from the alkaline reaction mixtures.

REFERENCES used in section 2B

(1) Thiele and Heidenreich , B. 26 2599

(2) Thiele and Manchot , A. 303 33

(3) Arndt , B. 54 2236

(4) Kirster and Smith , J.Am.Chem.Soc. 58 800

(5) Benack , Dissert. (München 1896) S.20

(6) Curtius and Sruve , J.Prac.Chem. 50 295

(7) Renshaw and Searle , J.Am.Chem.Soc. 59 2057

(8) Urquhart , Gates and Connor , Org.Syntheses 21 36

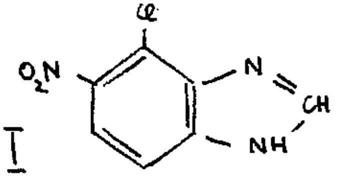
(9) Arndt , Milde and Eckert , B. 54 2236

(10) Franklin and Bergstrom , Chem.Rev. 16 305

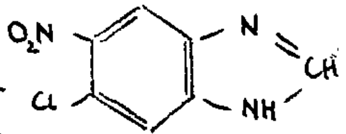
SECTION 2C : SUBSTITUTION IN THE BENZIMIDAZOLE SYSTEM

It has been shown (1) that the -Cl group in the o-chloro nitro benzimidazole I is activated by the nitro group while that in its isomer II is not.

I

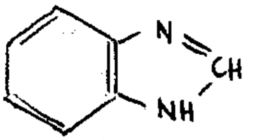


II

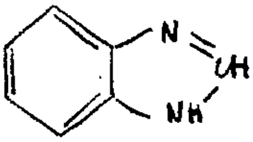


This was taken as some evidence in favour of the theory that the structure III contributes more to the resonance energy of the benzimidazole hybrid than the structure IV.

III



IV



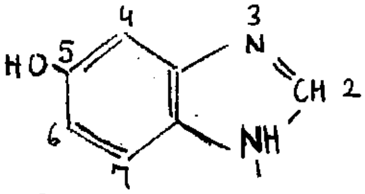
On the other hand it has been noted that both the **4** and 6 positions in 5 hydroxybenzimidazole V are activated by the -OH group, which seems to indicate that the structures III and IV contribute equally to the resonance hybrid. (2)

It must be noted that for the sake of this argument the mobility of the hydrogen attached to the nitrogen (the imino group) is immaterial. Actually 5hydroxybenzimidazole is **5**(**6**)hydroxybenzimidazole.

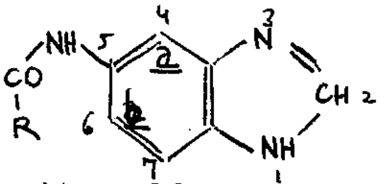
In line with the latter argument is also the fact that dihydroimidazole is a stable compound (3) ,unlike dihydrobenzene (4) (XXXXXZ) , and hence structure IV would not involve any considerable loss of resonance energy.

The position of further substitution (eg nitration) in 5(6)acylamino benzimidazole VI would possibly throw some further light on the question.

V



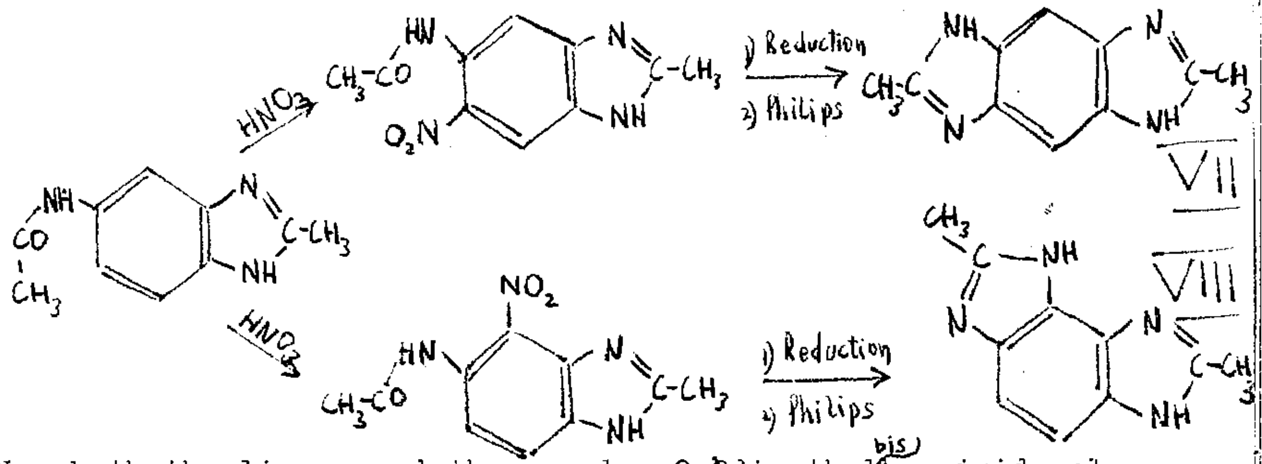
VI



ie if the substitution occured in position a it would indicate that the structure III is of predominating importance ,while if it occured in position b ,or a mixture of isomers was obtained, it would indicate that the structures III and IV were of equal importance.

This would obviously not furnish any conclusive evidence as no indication would be obtained of the effect of possible steric hindrance in position a and of directional influence of the imidazole system which would activate position b. (5)

The position of nitration was to be tested by performing the following series of reactions:

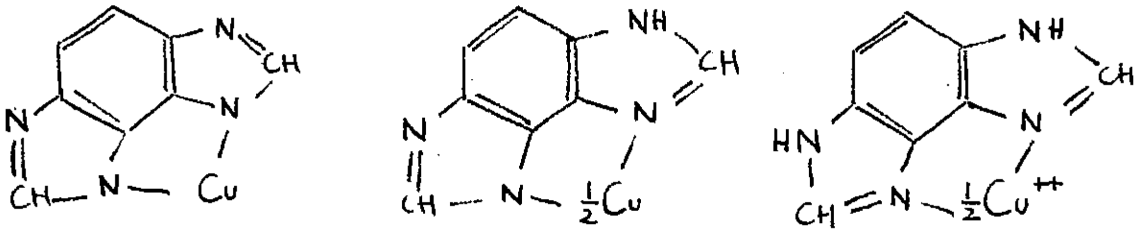


VII

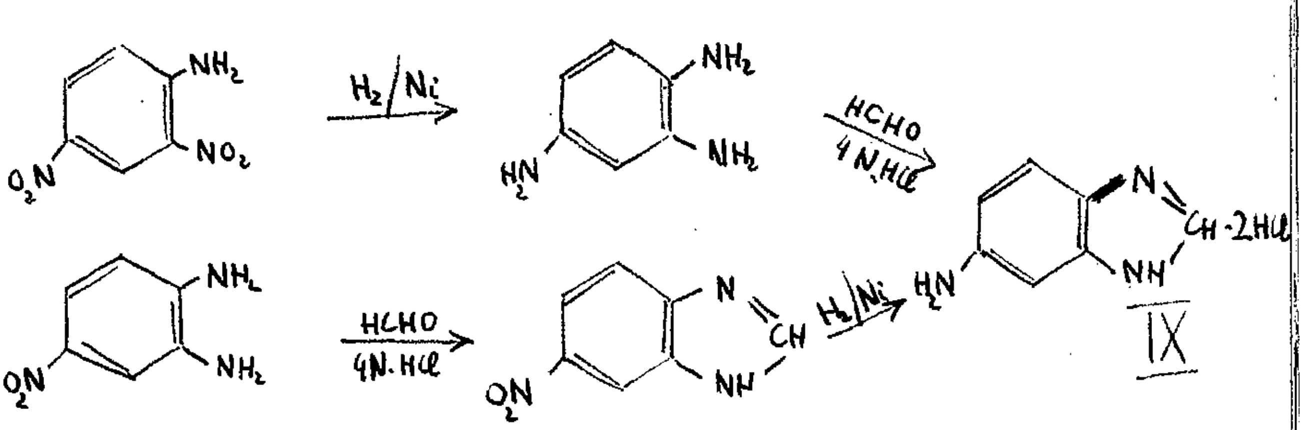
VIII

Now both the linear and the angular 2:2'dimethylbisbenzimidazoles VII and VIII are known (5)(6) and thus by identification of the final product the position of nitration in 5(6)acylaminobenzimidazole would be found.

The angular bisbenzimidazole would be expected to show some chelating properties.Eg with copper one of the following complexes would be expected to form:



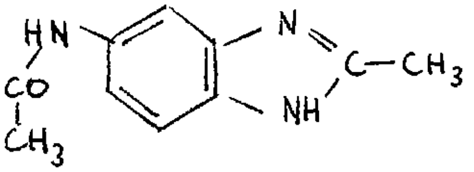
5(6)aminobenzimidazolehydrochloride was prepared both from 2:4dinitroaniline and from p-nitrophenylenediamine.



IX

But the acylation and nitration product of IX did not analyse correctly.

2methyl5(6)acetaminobenzimidazole was also prepared X



X

But the nitration of X gave an unstable tarry product. At this stage work on this project was abandoned.

EXPERIMENTAL

1.Preparation of 1:2:4triaminobenzene from 2:4dinitroaniline

2:4dinitroaniline (18g) was reduced with hydrogen over Raney nickel at room temperature and low pressure (8).After absorbtion of hydrogen ceased the catalyst was filtered offand the alcoholic solution of the amine was saturated with hydrogen chloride.The hydrochloride was collected and dried.It decomposes at about 300°C.
Yield:16.5g ie 83.7% .Further amounts were prepared by the same method the respective percentage yields being 81.0% and 82.1%.

2.Preparation of 5(6)aminobenzimidazole from 1:2:4triaminobenzene

1:2:4triaminobenzenehydrochloride(3.92g),4N hydrochloric acid (20 ml) and 90% formic acid (5 ml) were refluxed together for one hour (9).The mixture was then evaporated to dryness under reduced pressure and the residue recrystallised from 5N hydrochloric acid and alcohol. Yield:2.1g ie 51.2%. Decomposes without melting.
A portion was purified by repeated recrystallisation from 5N hydrochloric acid and methylated spirits.
N calculated: for B.HCl 24.85% for B.2HCl:20.49%. N found:20.67%

3.Preparation of 5(6)nitrobenzimidazole from p-nitro o-phenylenediamine sulphate .

p-nitrophenylenediamine sulphate (50.5 g) , 4N hydrochloric acid (250 ml) and 90% formic acid were refluxed together for 1 hour.(9) The mixture was neutralised with concentrated ammonia, the precipitate collected and recrystallised from water (4 litres).
Mp:193°C . Theoretical Mp:203°C (10). Yield:34.0g ie 83.5%
In another run :34.5g ie 84.5%

4.Preparation of 5(6)aminobenzimidazole from 5(6)nitrobenzimidazole

This was attempted using tin and hydrochloric acid and also using stannous chloride and hydrochloric acid with subsequent precipitation of tin as the sulphide but the desired product could not be isolated.

A succesfull reduction with nickel and hydrogen was accomplished in about 80% yield.

5.Attempted acetylation and nitration of 5(6)amino benzimidazole

5(6)aminobenzimidazolehydrochloride (6.15g) was dissolved in water (17 ml). Sodium acetate (6g) was added and the solution was shaken with acetic anhydride (10 ml) for 15 minutes and then boiled for 3 minutes to decompose excess acetic anhydride. The mixture was cooled , conc. ammonia was added and the precipitate collected and recrystallised from water . Yield: 3g ie 57.1%. Mp:226°C.

The product was nitrated by dissolving in cold nitric acid , precipitating by dilution and neutralisation and recrystallised from water to constant melting point. (252°C).

Nitrogen calculated for mononitro derivative of 5(6)acetamino benzimidazole: 25.45% Nitrogen found : 17.66%

6.Preparation of 2-methyl 5(6)acetaminobenzimidazole.

1:2:4triaminobenzenehydrochloride (13.6g) , glacial acetic acid (25 ml) and 4N hydrochloric acid (80 ml) were refluxed together for one hour, charcoaled, filtered and evaporated to dryness under reduced pressure.

The crude product (5-amino 2-methyl benzimidazole)was dissolved in water (20 ml) and shaken with sodium acetate (12g) and acetic anhydride (20ml) for 20 minutes , then boiled for 3 minutes. The mixture was made alkaline with ammonia and the product collected and recrystallised from water. Mp:244-6°C. Overall yield: 9.0g ie 67.0%.

Nitrogen calculated: 22.23% Nitrogen found:22.50%
for $C_{10}H_{11}N_3O$

7. Attempted nitration of 2methyl5(6)acetaminobenzimidazole.

This was attempted using: a)Cold concentrated nitric acid. b) A mixture of 9 parts of concentrated nitric acid and 1 part of fuming nitric acid at about 40°C. c) Fuming nitric acid at about 60°C. In each case the unchanged 2methyl5(6)acetamino benzimidazole was recovered.

On using a mixture of equal volumes of concentrated nitric acid and concentrated sulphuric acid at room temperature a sudden reaction occured but only amorphous products could be recovered from the reaction mixture.

8. Attempted Skrauping of 5(6)aminobenzimidazole

5(6)aminobenzimidazolehydrochloride (6.15g) , arsenic oxide (5.3g) glycerol (30 g) and concentrated sulphuric acid (10 ml) were heated at 140-60°C for 6½ hours with mechanical stirring. (11).

Only amorphous basic materials could be isolated from the reaction mixture.

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ACKNOWLEDGEMENTS

I wish to thank Professor R.J.W. Le Fevre for permission to spend the honours year in the departament, Dr F. Lions for continuous help and guidance and Mrs E. Bielski for the analyses recorded in this thesis.

1951

I. Stenbell

SOME REDUCTIONS WITH SODIUM AND ETHANOL IN LIQUID AMMONIA, SYNTHESIS AND REACTIONS OF 5-METHYLPYRAZOLE-3-ALDEHYDE AND ADDITION OF THIOLS TO SOME REACTIVE DOUBLE BONDS.

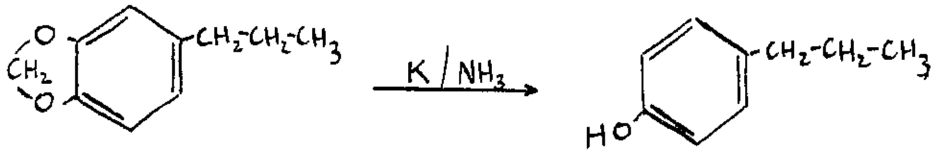
A THESIS FOR THE DEGREE OF MASTER OF SCIENCE
SUBMITTED
BY S. STERNHELL B.Sc.HONS. AT THE UNIVERSITY OF SYDNEY
FEBRUARY 1953

CONTENTS

SECTION 1

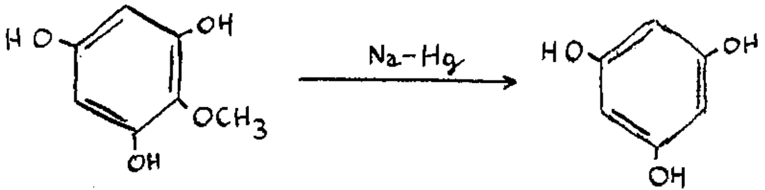
SOME REDUCTIONS WITH SODIUM AND ETHANOL IN LIQUID AMMONIA

The reduction of benzene rings carrying ether groups by sodium-ammonia solutions usually proceeds by the addition of two hydrogen atoms to the ring . Eg anisole and alkyl anisoles may be reduced to the corresponding dihydro compounds /11/. In some cases fission of the C-O bond occurs preferentially , especially in the case of methylenedioxy benzenes . Eg para-n-propylmethylenedioxybenzene may be converted to para-n-propylphenol by potassium amide /12/:

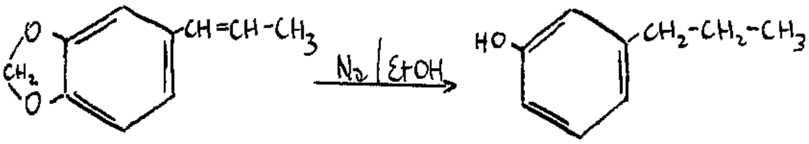


Such fissions are known to occur even with sodium and alcohol and are more marked :

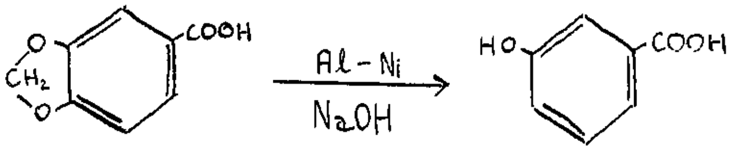
a/With more than one alkoxy group - in meta or ortho - position - in the ring. Eg methoxyphloroglucinol may be converted to phloroglucinol by the action of sodium amamlgam /13/:



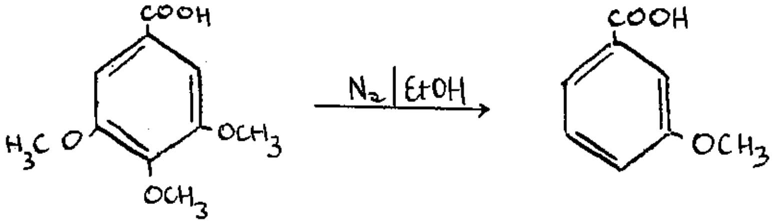
b/With a double bond conjugated with the ring. Eg 1-p-methylenedioxyphenylpropylene is reduced to m-n-propylphenol by the action of sodium and alcohol , the fission probably preceeding the reductuin of the double bond. /14/:



c/When electron attracting groups , such as the carboxyl group - are present. Eg piperonic acid may be reduced to m-hydroxy benzoic acid by alluminium-nickel alloy in sodium hydroxide/15/.



and trimethyl gallic acid may be reduced to m-methoxybenzoic acid by the action of sodium and ethanol/16/.



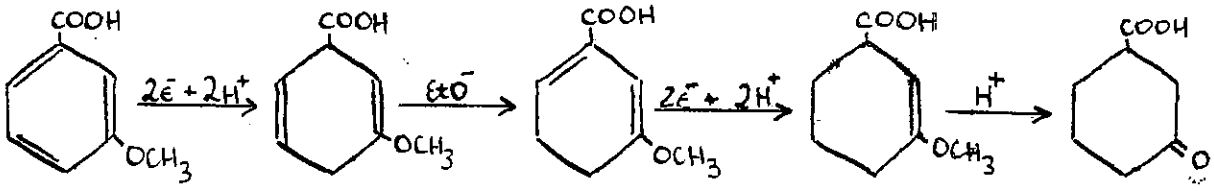
This is in accord with the view taken of the mechanism , namely that the first step consists of addition of two electrons with formation of ions /17/

Thus any group capable of lowering the energy of formation required by stabilising the negative charge on the benzene ring will tend to make the fission of the etheral bond easier.

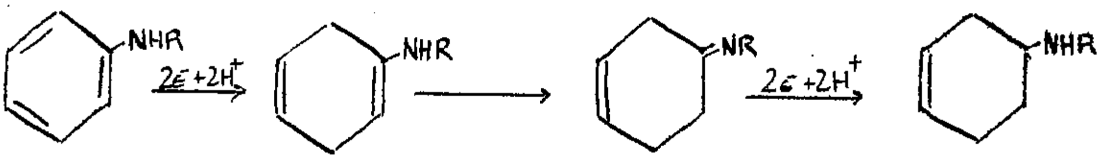
Little work has so far been done on the reduction of benzene rings containing electron stabilising groups and ether groups , partly because the only group which appears to be unaffected by sodium-ammonia solutions is the carboxyl group.

Reduction of o- and p-methoxybenzoic acids results in almost complete removal of the ether group. /18/. Action of sodium and alcohol produces cyclohexanone carboxylic acid / 19, 20/. Ie here the carboxyl group has the maximum activating effect.

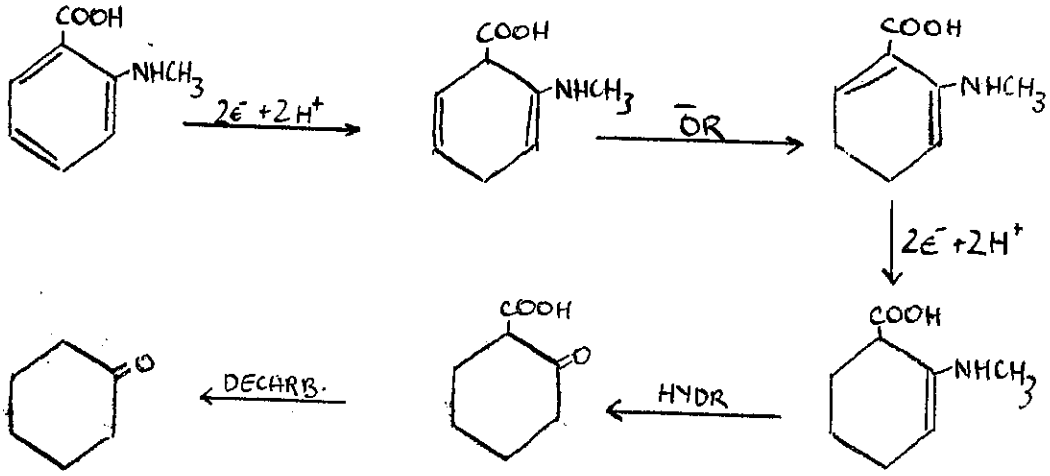
In the case of m-methoxybenzoic acid the ether might be expected to remain. This has been comfirmed , the reduction of m-methoxybenzoic acid with sodium and alcohol in liquid ammonia followed by acid hydrolysis yielding cyclohexanone -3-carboxylic acid. The carboxyl group also activates prototropic rearrangement and the alkaline conditions are responsible for the formation of conjugated intermediates. Thus the course of the reaction could be visualised as:



In order to use the reaction for preparative purposes, where ortho and para compounds are concerned , it would be necessary to render fission more difficult. This could be done by substituting dialkylamino groups for the ether groups as R_2N^- is more difficult to produce than RO^- since HNR_2 is less "acidic" than HOR. Both hydrogens in the amino group would have to be substituted by alkyl groups to prevent reduction through imino form /21/:



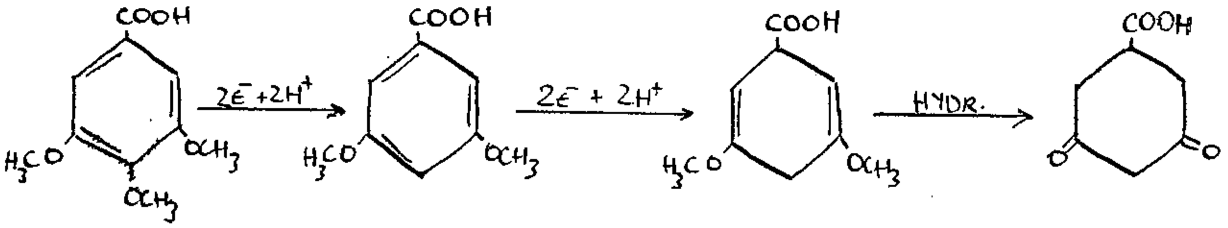
It was found that the main product of reduction of N-methyl anthranilic acid with sodium and alcohol in liquid ammonia is cyclohexanone presumably obtained by the following series of reactions:



It is possible that some aminoacid was also formed by isomerisation to the imino form followed by further reduction.

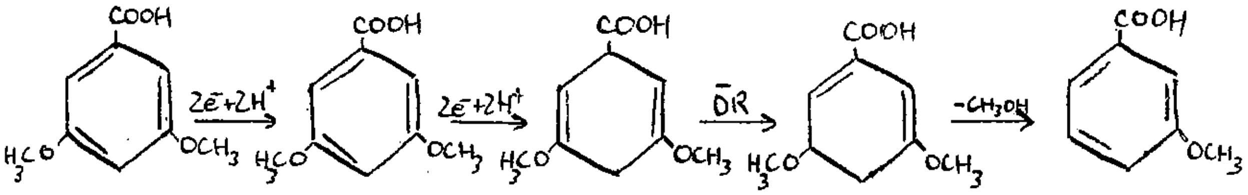
Compounds containing more than one methoxy groups and a carboxyl group behave as expected , the para methoxyl being removed. Thus veratric acid yields cyclohexanone -3-carboxylic acid on treatment with sodium and alcohol in liquid ammonia followed by acid hydrolysis while trimethylgallic acid yields dihydroresorcylic acid under the same conditions.

In case of trimethylgallic acid it is interesting to note that the reduction does not proceed past the dihydro stage /like in m-methoxy benzoic acid/. This is to be expected as the methoxy groups render the formation of the anion more difficult and due to the partial conjugation of the double bonds with the lone electrons on the oxygen which renders the conjugation with the carboxyl group more difficult. Thus the reduction of trimethylgallic acid with sodium and alcohol in liquid ammonia followed by acid hydrolysis may be visualised as the following series of reactions



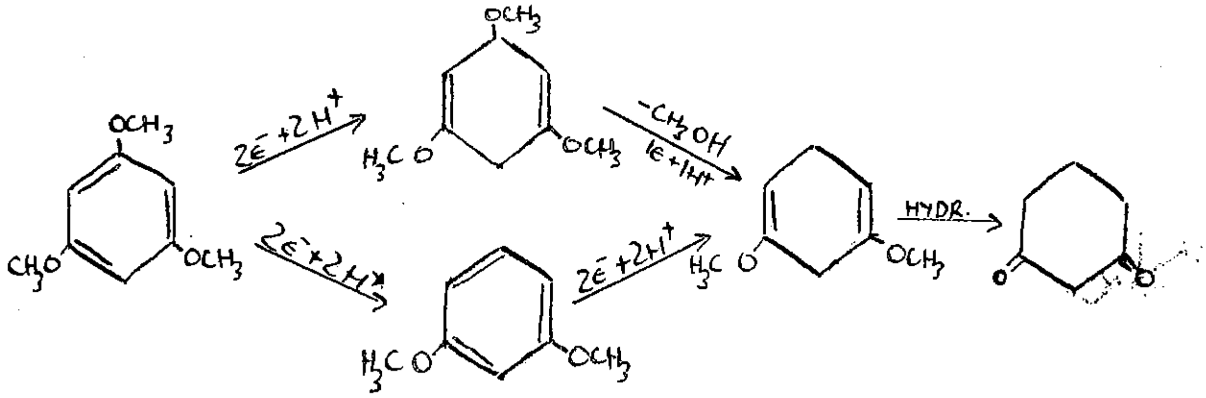
However when the reaction is carried out under strongly alkaline conditions - such as sodium and ethanol /16/-

isomerisation followed by spliting off of methanol with subsequent formation of m-methoxybenzoic acid occurs:



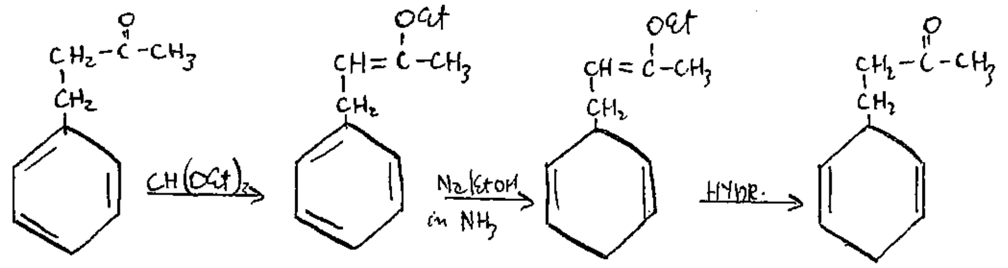
This has been comfirmed by boiling the product obtained by reduction of trimethylgallic acid with sodium and alcohol in liquid ammonia / 3-5-dimethoxy-1-4-dihydrobenzoic acid/ with t-butoxide. A good yield of m-methoxy benzoic acid was obtained.

Trimethylphloroglucinol yielded 1-3-cyclohexandione when treated with sodium and ethanol in liquid ammonia and than hydrolysed with dilute acid. This reduction could have proceeded by two different courses the first step consisting either of ether fission or of nuclear reduction.



However as the trimethoxydihydrobenzene would split off methanol /22/ the final product would be the same.

Some preliminary attempts were made in this work to find methods of protecting electron attracting groups from reduction. Formation of acetals is the obvious method of protection of carbonyl groups because these are saturated and hence non-reducible. However aromatic aldehydes and ketones often tend to form enol ethers which would themselves tend to be reduced if oonjugated. However this method was proved succesful in case of 2-phenylethyl-methyl ketone /23/.



The reduction of anisacetal with sodium and ethanol in liquid ammonia yielded the expected product namely the dihydro compound. Hydrolysis then produced the extremely unstable keto-aldehyde.

Unprotected carbonyl groups are reduced partially to the carbinol and partially to the hydrocarbon. Thus p-methoxy acetophenone yielded a mixture of 4-methoxydihydrophenyl-methyl carbinol and 4-ethyldihydroanisole. The fact that the removal of oxygen is not complete is probably due to the stabilising influence of p-methoxy group /24/.

EXPERIMENTAL

Reduction of m-methoxybenzoic acid

m-Methoxybenzoic acid / 5 g / was dissolved in ethanol / 15 ml / and liquid ammonia / 150 ml / and clean sodium / 3 g / was added slowly with stirring. After the reaction was completed a solution of ammonium chloride / 25 g / in water / 60 ml / was added and the mixture was warmed on the water bath untill most of the ammonia evaporated off. The mixture was then acidified with concentrated hydrochloric acid , boiled for one minute , cooled and ether extracted. The extract was dried over anhydrous sodium sulphate and the solvent was evaporated off. The residue consisted of a colourless oil Bp: 142-5°C / 2.5-4.0 mmHg which was recrystallised from a mixture of benzene and petroleum ether to give colourless needles Mp: 76°C. Yield: 3.3g ie 71%. It gave a semicarbazone derivative Mp: 183-4°C from ethanol. The ultraviolet absorption spectrum of the product in ethanol shows a maximum at 278 milimicrons thus corresponding to an unconjugated carbonyl group /1/. The melting point of cyclohexanone-3-carboxylic acid is 76°C. /2/, and its semicarbazone melts at 184°C.

A 2-4-dinitrophenylhydrazone was also prepared Mp:230°C.

Reduction of veratric acid

Veratric acid was prepared from veratric aldehyde by the method of Perkin /3/ in about 30% yield.

Veratric acid / 5 g / was dissolved in ethanol / 20 ml / and liquid ammonia / 300 ml / and treated with sodium / 3 g /. After the reaction was compleated , ammonium chloride / 20g/ was added and ammonia was evaporated off. The residue was made 2N with respect to hydrochloric acid , boiled for one minute and ether extracted. The extract was dried over anhydrous sodium sulphate and the solvent was distilled off. The residue - a colourless oil - was recrystallised from a mixture of ether and petroleum ether Mp: 76°C undepressed by cyclohexanone-3-carboxylic acid. Semicarbazone: Mp:183°C.

Reduction of trimethyl gallic acid

Trimethyl gallic acid was prepared by the method of Organic Syntheses[/4/] in about 50% yield from gallic acid.

Trimethylgallic acid / 10.6 g / was dissolved in ethanol / 75 ml / and liquid ammonia / 500 ml / and reduced with sodium / 6 g /. After the reaction was completed , the mixture was treated with ammonium chloride / 25 g / and ammonia was evaporated off on the water bath. The mixture was made acid with 2N hydrochloric acid / 100 ml / and boiled for a short time and ether extracted. The extract was dried over anhydrous sodium sulphate and the solvent distilled off. The residue was recrystallised from ethyl acetate giving colourless needles Mp:180°C. Yield: 5 g.

Calculated for $C_7H_8O_4$: C 53.87% H 5.13%
Found: C 54.1% H 5.36%

Dihydroresorcilic acid is soluble in ethanol and acetone, somewhat soluble in glacial acetic acid and ethyl acetate and insoluble in benzene and non-polar solvents.

It gives a red colouration with ferric chloride solution, decolourises bromine water in cold and gives a precipitate with dinitrophenylhydrazine reagent.

It condenses with formaldehyde to give a product Mp:270°C from aqueous alcohol, probably a dimer.

Reduction and alkaline isomerisation of trimethylgallic acid

Trimethylgallic acid / 10.6 g / was dissolved in ethanol / 20 ml / and liquid ammonia / 500 ml / and treated with sodium / 6 g / . After the reaction was compleated , a solution of sodium / 10 g / in butanol / 100 ml / was added and the solution was refluxed in such a way as to allow ammonia to escape. After two hours the solution was cooled , ether / 200 ml / was added and the mixture was extracted with water. The aqueous solution was acidified with sulphuric acid , warmed and ether extracted. The extract was dried over anhydrous sodium sulphate , the solvent was distilled off and the residue was recrystallised from water. Mp: 105°C undepressed by m-methoxybenzoic acid. Yield /of pure product/ 5.3g ie 70%.

Reduction of trimethylphloroglucinol

Trimethylphloroglucinol was prepared from phloroglucinol by the method of Mannich /5/.

Trimethylphloroglucinol / 4.2 g / was dissolved in ethanol / 20 ml / and liquid ammonia / 150 ml / and treated with sodium / 2 g /. After the reaction was compleated , a solution of ammonium chloride / 10 g / in water / 50 ml / was added and the mixture was ether extracted , the extract dried over anhydrous sodium sulphate and the solvent evaporated off. The residue was hydrolysed with a very small amount of 5N hydrochloric acid and purified by recrystallisation from glacial acetic acid. Mp: 105°C

The product yielded an oxime Mp:155°C from water and a bis compound with formaldehyde Mp:133°C from aqueous alcohol. The melting points of cyclohexane-1-3-dione and its corresponding derivatives are 105-6°C, 154-7°C and 132-3°C respectively /6/.

Reduction of N-methylanthranilic acid

N-methylanthranilic acid was prepared from anthranilic acid by the method of Wilstatter /7/ in 65% yield.

N-methylanthranilic acid / 15.1 g / was dissolved in a mixture of ethanol / 50 ml / , ether / 100 ml / and liquid ammonia / 300 ml / and treated with sodium / 10 g /.

After the reaction was compleated a saturated solution of ammonium chloride / 80 ml / was added and most of the ammonia was evaporated off on the water bath. The mixture was then strongly acidified with concentrated hydrochloric acid and refluxed for half an hour.

A dinitrophenylhydrazone obtained from the mixture melted at 156°C , undepressed by the dinitrophenylhydrazone of cyclohexanone. Ultraviolet absorption spectrum of the dinitrophenylhydrazone in alcohol showed a maximum at 263 milimicrons , corresponding to cyclohexanone /1/.

Yield of cyclohexanone - obtained by estimating the carbonyl compound in the mixture - was 25%.

No attempt was made to isolate or estimate any other products.

Reduction of p-methoxyacetophenone

p-Methoxyacetophenone was prepared from anisole by the method of Strauss /8/ in 92% yield.

p-Methoxyacetophenone / 15 g / was dissolved in ethanol / 80 ml / and liquid ammonia / 400 ml / and treated with sodium / 20 g /. After the reaction was compleated , a solution of ammonium chloride / 60 g / in water / 150 ml / was added and the mixture was ether extracted. The extract was dried over anhydrous sodium sulphate, the solvent distilled off and the residue fractionated.

Low boiling fraction /6.1 g / Bp: 60-65°C/0.5 mm Hg

2-4-dinitrophenylhydrazone Mp:138°C from ethanol.

Calculated for $C_{14}H_{16}N_4O_4$: C 55.26% H 5.26% N 18.42%

Found: C % H % N %

Semicarbazone Mp:167°C from ethanol.

Calculated for $C_9H_{15}ON_3$: C 59.67% H 8.29% N 23.20%

Found: C % H % N %

High boiling fraction /6.3g/ Bp:120-125°C / 0.5 mm Hg

Dinitrophenyhydrazone Mp: 164°C from ethanol. Mp.of the dinitrophenylhydrazone derivative of 4-ethylidenecyclohex-2-enone is 164°C /9/.

Reduction of anisacetal

Anisacetal was prepared from anisaldehyde by the method of Claisen /10/ in quantitative yield.

Anisacetal / 21g / was dissolved in ethanol / 100 ml / and liquid ammonia / 400 ml / and treated with sodium / 20 g /. After the reaction was compleated , a solution of ammonium chloride / 60 g / in water / 180 ml / was added and the mixture was ether extracted. The extract was dried over anhydrous sodium sulphate the solvent was distilled off and the residue was vacuum distilled. It formed a colourless oil Bp:100-104°C / 0.7 mm Hg . Yield: 10.0 g ie. 50%.

Calculated for $C_{12}H_{20}O_3$:	C	67.92%	H	9.43%
Found:	C	%	H	%

The product immediatelly decomposes in presence of dilute acid.

It yields a dinitrophenylhydrazone derivative Mp: about 270°C with decomposition which is highly insoluble in all solvents.

Dioxime Mp:

Calculated for $C_7H_{10}O_2N_2$:	C	54.54%	H	6.49%	N	18.18%
Found:	C	%	H	%	N	%

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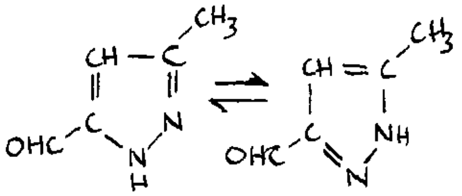
SECTION 2

SYNTHESIS AND REACTIONS OF 5-METHYLPYRAZOLE-3-ALDEHYDE.

The interest in 5-methylpyrazole-3-aldehyde centres on the fact that the molecule contains an aldehyde group adjacent to a nitrogen atom which may be either basic or acidic depending on the position of the labile hydrogen atom /I/.



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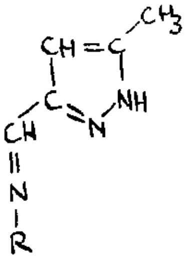

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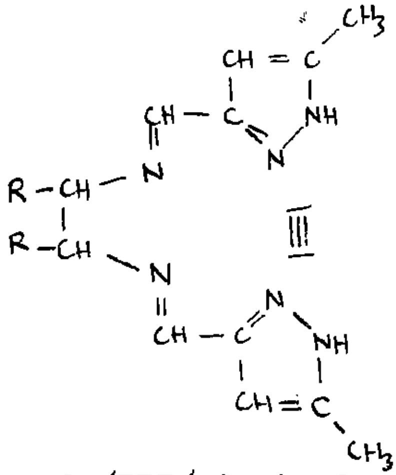
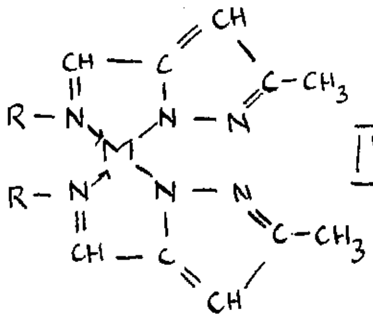


III

Thus Schiff's bases of the type /II/ and /III/ derived from the aldehyde may be expected to exhibit interesting chelating properties. Under neutral conditions a metal having a coordination number of four would be expected to form internal complexes of the type /IV/ and /V/



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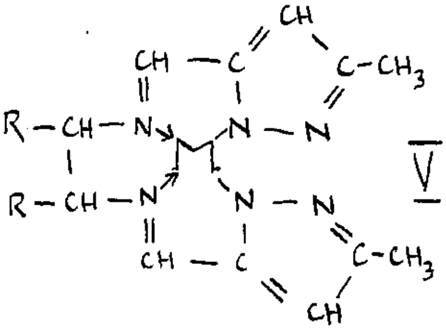
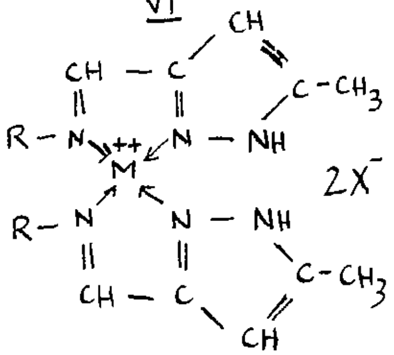


V

while under slightly more acid conditions , ionic complexes of the type /VI/ and /VII/ would probably form.

VI



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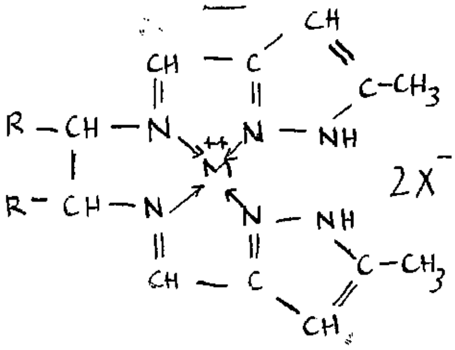
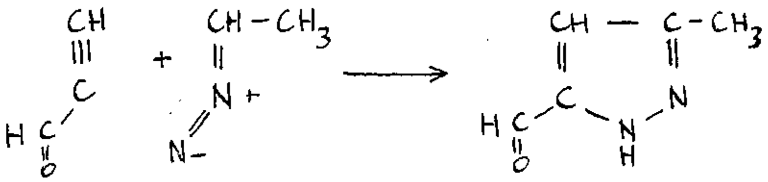
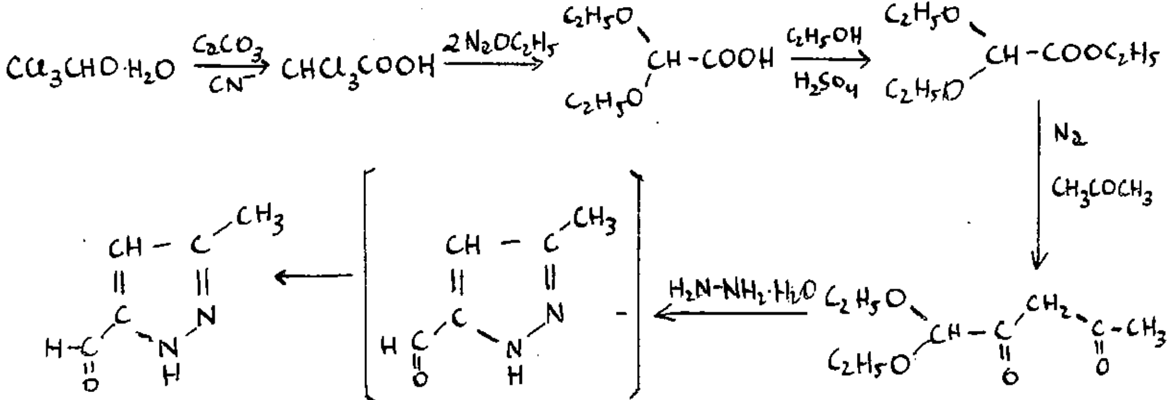


The aim of this project was to evolve a method of synthesis of 5-methylpyrazole-3-aldehyde and its Schiff's bases. The aldehyde has been synthesised by Hüttel /1/ from propynal and diazoethane in ether , according to the reaction:



This method is not very satisfactory due to poor yield and difficulty in obtaining propynal. A different method was therefore evolved utilising the following series of reactions:



The advantages of this method are the availability of the starting materials and a fair overall yield.

Dichloroacetic acid was prepared fro chloral hydrate by the method described in Organic Syntheses /2/in average yield of 90%.

The product was then converted to ethyldiethoxyacetate by the method of Blaise and Picard /3/ in average yield of 50% for the two steps.

Ethyldiethoxyacetate was then condensed with acetone by a method analogous to that of Helferich and Russe /4/ , the reaction proceeding in average yield of 62%.

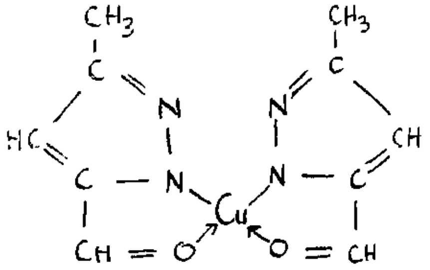
Diethoxyacetylacetone thus obtained was condensed with hydrazine hydrate. Water split off in the reaction , and that present in the hydrate , was sufficient to hydrolyse the acetal formed and a nearly quantitative yield of 5-methylpyrazole-3-aldehyde was thus obtained.

The aldehyde may be obtained as white needles , Mp. 192°C from water or glacial acetic acid. The product obtained by Hüttel and purified by sublimation melted at 190°C.

It reduces Fehling's and Tollens reagents only on prolonged boiling. It yields a dinitrophenylhydrazone derivative Mp.278°C from glacial acetic acid.

In presence of piperidine the aldehyde condenses with piperonal -probably on the methyl group - to give a colourless product Mp.211°C from alcohol.

The aldehyde yields a copper complex /VIII/ soluble in chloroform and insoluble in polar solvents.Mp. 250°C d.



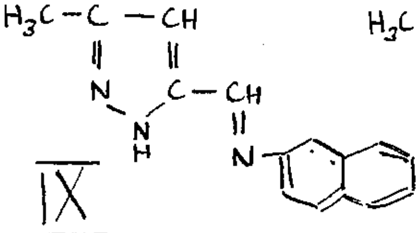
VIII

5-methylpyrazole-3-aldehyde does noth condense with primary amines even on prolonged refluxing in alcohol or heating without solvent. Presence of small quantities of mineral acids did not catalyse the reaction.

However nearly quantitative yields of Schiff´s bases were obtained on warming the calculated quantities of the aldehyde and primary amines in glacial acetic acid for a short time.

The Schiff´s bases derived from 5-methylpyrazole-3-aldehyde are extremely unstable in presence of dilute acids , soluble in alcohol , acetone and ethyl acetate and insoluble in water , benzene and nonpolar solvents.

Schiff´s bases derived from β-naphtol /IX/ ~~x~~ Mp.2o7°C and from o-phenylene diamine /X/ Mp.2728 were obtained.



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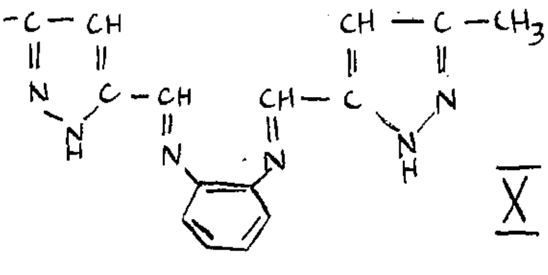

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5-methylpyrazole-3-aldehyde also condensed with aniline ethylenediamine and cyclohexylamine but the products obtained were difficult to purify.

In methanolic solutions all of the above Schiff's bases gave precipitates with methanolic cupric acetate.

EXPERIMENTAL

Preparation of diethoxyacetylacetone

Sodium / 3.8 g / was granulated under dry xylene /5/ and washed by decantation with dry ether. The granules were covered with dry ether , dry alcohol / 8 g / was added and the mixture was refluxed for five hours with stirring and exclusion of moisture. Ether was distilled off and ethyldiethoxyacetate / 29.3 g / was added with cooling to the residue of sodium ethoxide. The mixture was shaken untill homogenous and acetone / 10 g / was added. The mixture was shaken for 20 minutes when it set to a yellow mass. Ice water / 50 ml / was carefully added and the solution was ether extracted the extracts being discarded. The aqueous layer was acidified with concentrated hydrochloric acid and ether extracted. The extract was washed with sodium bicarbonate solution , dried over anhydrous sodium sulphate and fractionated. Fraction collected boiled at 87-8°C / 1.2-1.4 mm Hg. Yield : 19.5 g ie 62.2%.

On addition to methanolic cupric acetate the diketone yielded a copper derivative Mp.126°C from alcohol.

Condensation of diethoxyacetylacetone with hydrazine hydrate

Diethoxyacetylacetone / 37.6 g / was dissolve in alcohol

/ 30 ml /and hydrazine hydrate / 10 g / was slowly added. A considerable amount of heat was evolved and on standing a white precipitate appeared. Yield: 20.6 g ie 94% . The product was purified by recrystallisation from water and glacial acetic acid. Mp: 192°C.

Calculated for $C_5H_6N_2O$:	C 54.77%	H 5.59%	N 25.60%
Found:	C 54.55%	H 5.48%	N 25.45%

Preparation of copper derivative of 5-methylpyrazole-3-aldehyde

5-methylpyrazole-3-aldehyde / 0.55 g / and neutral cupric acetate / 1.0 g / were refluxed together in methyl alcohol / 80 ml / for five minutes. The solution was evaporated to dryness and the product purified by recrystallisation from chloroform and ethanol. Mp:250°C d.

Calculated for $C_{10}H_{10}O_2N_4Cu$:	CuO 28.27%
Found :	CuO 28.40%

Preparation of Schiff's base from 5-methylpyrazole-3-aldehyde and β-naphtol

5-methylpyrazole-3-aldehyde / 1.1 g/ and β-naphtol / 1.43g/ were warmed together in glacial acetic acid / 10 ml/ for five minutes on the water bath. The reaction mixture was rapidly poured into 10N ammonium hydroxide and the precipitate formed was collected and dried. Yield: 2.5 g ie quantitative. The product was obtained as an amorphous powder and purified by reprecipitation from alcohol with water. Mp: 207°C

Calculated for $C_{15}H_{13}N_3$: C 76.60% H 5.53% N 17.87%

Found: C % H % N %

Preparation of Schiff's base from 5-methylpyrazole-3-aldehyde and o-phenylenediamine

5-methylpyrazole-3-aldehyde / 1.1 g / and o-phenylenediamine / 0.55 g / were warmed together in glacial acetic acid / 10 ml/ for five minutes on the water bath. The reaction mixture was rapidly poured into 10N ammonium hydroxide / 35 ml / and the precipitate formed was collected and dried. Yield: 1.5 g ie quantitative.

The product was purified by recrystallisation from aqueous alcohol as white needles Mp: 272°C

Calculated for $C_{16}H_{16}N_6$: C 65.75% H 5.48% N 28.77%

Found: C % H % N %

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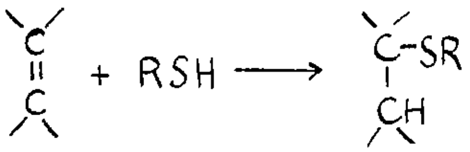
SECTION 3

ADDITION OF THIOLS TO SOME REACTIVE UNSATURATED COMPOUNDS.

Thiols are known to react with unsaturated compounds according to the general reaction



The addition usually proceedes contrary to Markownikow's rule due to traces of peroxides in reagents used. / 1 , 2 , 3, 4/. The mechanism of the reaction apparently involves an attack by the $-S\bar{R}$ ion on the polarised double bond /5/ ie it is formally similar to the Michael reaction. Compounds containing activated double bonds undergo the reaction more readily - eg α-β unsaturated carbonyl compounds /6/. Often traces of sodium ethoxide or piperidine are necessary for the reaction to proceede.

The aim of this project was to correlate the biological activity of certain unsaturated compounds with thiol abroption.

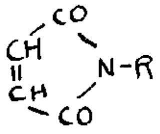
In general the compounds studied or their analogues show inhibiting activity towards the mytosis of cells or certain enzymatic processes.

Now , thiol groups are often associated with cell division and hence absorption of thiols may afford a possible explanation of the inhibiting activity of the unsaturated compounds .

An attempt at such correlation was made by D.H. Marrion / 7 , 8 / who found that N-alkyl maleimides - which show pronounced biological activity of the inhibiting type - react readily with thiols and even with incipient thiol groups such as existing in S-alkylisothioureas.

It is also known that quinones react with thiols and also that some quinones have marked biological effects of the inhibiting type. /9/. In this work analogues of the above compounds were reacted with thiols - mainly benzyl mercaptan and thiophenol - under neutral and alkaline conditions.

The analogues of N-alkyl maleimides /I/ chosen were: N-anilino maleimide prepared by the method of Duden /10/ , maleic hydrazide /III/ prepared by the method of Foesterling /11/ and fumaramide /IV/ prepared from fumaryl chloride and ammonia /12,13/.



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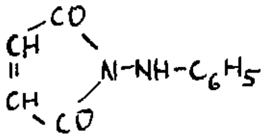

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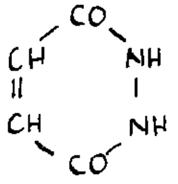

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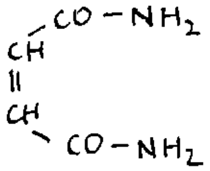
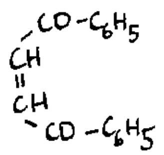


IV

It is interesting to note that maleic hydrazide has been widely studied /14,15,16,17,18/ as a temporary growth inhibiting agent in plants.

A close analogue of p-benzoquinone namely dibenzoyl ethylene /V/, prepared by the method of Bogoslawskij /19/ was also used. Dibenzoyl ethylene is known to have an inhibiting effect on carboxylase /20/ and antibacterial effect /21,22/.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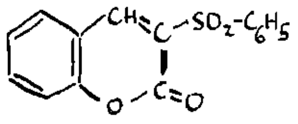
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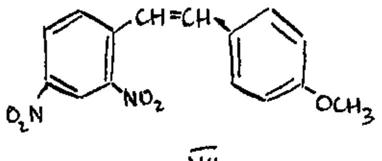
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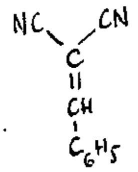
VIII

Three other substances containing electron attracting groups in the alpha position to the double bond were also investigated: 3-phenylsulphonecoumarin /VI/ prepared by the method of Tragner and Lux /23/ , 2-4-dinitro-4'-methoxystilbene /VII/ prepared by the method of Nisbet /24/, and 1-1-dinitrile-2-phenylethylene. /VIII/

However , under the experimental conditions employed , no addition of thiols to the compounds tested was observed.

EXPERIMENTAL

Reaction of N-anilinomaleimide and benzyl mercaptan

N-anilino maleimide /0.94g/ was refluxed with benzyl mercaptan / 1.0 ml/ in ethanol / 40 ml / for four hours. On cooling a white crystalline precipitate appeared, which was collected and purified by recrystallisation from ethanol. Mp:255°C. Yield: 0.8 g.

Lassigne´s test showed no presence of sulphur. The product did not depress the melting point of N-anilinomaleimide.

The same reaction was carried out in presence of trace of sodium hydroxide but again the starting material only was recovered from the reaction mixture.

Reaction of maleic hydrazide with thiols

Maleic hydrazide /0.5 g / was treated with a slight excess of a/ Benzyl mercaptan

b/ n-Amyl mercaptan

in alcohol / 10 ml / and the mixture refluxed for a short time. In each case the product obtained on cooling was identified as maleic hydrazide by mixed melting points.

Reaction of fumaramide with benzyl mercaptan

Fumaramide / 1.14 g / and benzyl mercaptan / 1.24 g / were refluxed in water / 60 ml / for seven hours. On cooling a white solid appeared . It was collected , washed with alcohol and recrystallised from water. Mp: 265-70°C undepressed by fumaramide. Lassigne's test showed absence of sulphur.

Reaction of thiols with dibenzoyl ethylene

Dibenzoyl ethylene was refluxed with a slight excessx of

a/Benzyl mercaptan

b/Thiophenol

c/p-cresol

in alcohol for a short time. In each case the starting material crystallised out on cooling and was identified by its mixed melting point with dibenzoyl ethylene.

Reaction of thiols with 3-phenylsulphonecoumarin

3-phenylsulphonecoumarin was reacted with thiophenol in a/ Alcohol b/Dioxane in and without the presehce of a trace of alkali.

The experiments were repeated usingbenzyl mercaptan. In each case the product melted at about 215-18°C , undepressed by 3-phenylsulphonecoumarin.

Reaction of 2-4-dinitro-4'-methoxystilbene with thiophenol

2-4-dinitro-4'-methoxystilbene / 1.5 g / and thiophenol / 1 ml / were boiled in alcohol / 200 ml / for five minutes. On cooling a crystalline precipitate appeared, Mp:162°C , which was identified as 2-4-dinitro-4'-methoxystilbene by mixed melting point.

The same reaction was carried out in presence of a trace of sodium hydroxide but only the starting material was recovered.

Reaction of 1-1-dinitrile-2-phenylethylene with thiophenol

The unsaturated compound and thiophenol were refluxed in ethanol for 30 minutes. The reaction mixture was evaporated to dryness and the residue recrystallised from benzene. Mp:84°C not depressed by addition of 1-1-dinitrile-2-phenylethylene.

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Analyses recorded in this work are by Mrs E. Bielski of the Chemistry Department .

February 1953

STUDIES IN THE CHEMISTRY OF LIMONIN

A thesis submitted by
Sever Sternhell

in partial fulfilment of the requirements
for the admittance to the degree of

Doctor of Philosophy
in the University of London

Imperial College
London

September
1960

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CONTENTS

Page

Page

SUMMARY

The following original contributions were made to the chemistry of limonin:

1. The reactions of hexahydrolimoninic acid with acids were elucidated (see section 6[@])

2. The isomerization of tetrahydrolimonin was examined (see section 2).

3. The reaction of tetrahydrodesoxylimonin with acetic anhydride and hydroiodic acid was explained (see section 7).

4. Tetrahydrodesoxylimonin was degraded, giving the substitution pattern at C_8 and C_9 (see section 5).

5. Limonilic acid was degraded (see section 11).

6. The structure of citrolin was determined (see section 12).

The following original contributions were made to the chemistry of obacunone and nomilin (see section 15) :

1. The degree of unsaturation of

[@] This , and all subsequent internal references, refer to subsections of the main discussion section.

obacunoic acid was determined.

2. Some derivatives were prepared by degradation of lactone D of obacunoic acid, showing close analogy to limonin.

3. iso-Obacunoic acid was prepared.

4. The positive iodoform test given by obacunoic acid was verified and interpreted by means of model experiments.

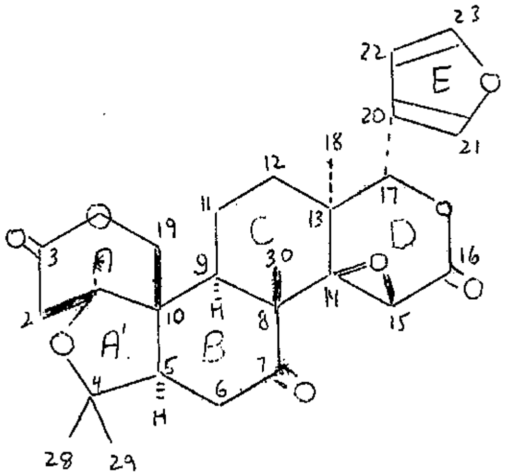
5. A plausible structure for obacunoic acid was postulated.

In addition , a number of model investigations was carried out concerned with new methods of decarboxylation (see sections 16 and 17).

The above results and all chemical reactions of limonin , are discussed and interpreted in terms of the structure which was proposed on the basis of chemical evidence and fully confirmed by X-ray crystallographic analysis. A plausible biogenetic scheme for limonin, obacunone and nomilin is proposed on the basis of accepted biogenetic schemes for triterpenes.

INTRODUCTION

Limonin, $C_{26}H_{30}O_8$, the chief bitter principle of citrus fruit, was first isolated by Bernay[1] in 1841 and has since been studied by American, Australian, British, German, Indian, Italian, Japanese and Swiss workers who have described their findings in over thirty publications. In addition , the chemistry of limonin has been investigated by three teams working in collaboration and headed respectively by Prof. D .H.R. Barton (Imperial College , London), Prof. E.J. Corey (University of Illinois) and Prof. O. Jeger (E.T.H. , Zurich). The findings of the combined groups resulted in publication[2] of the full structure of limonin (I), which was confirmed by the results of X-ray crystallographic analysis[3] carried out by Prof. J.M. Robertson, in collaboration with the team at Imperial college. The latter work also elucidated the stereochemistry of the molecule. The full experimental details of the chemical work - including the contribution of the present author - are awaiting publication.



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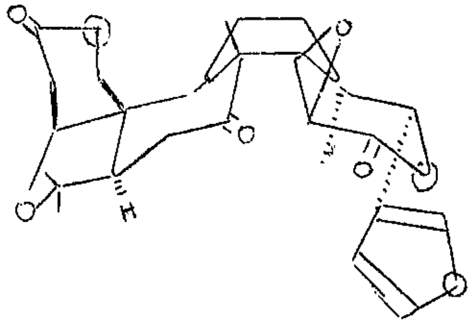


In the present work an attempt has been made to discuss all known chemical reactions of limonin in terms of structure (I) , rather than to deduce (I) rigidly on the basis of the chemical evidence alone. It is hoped that the work has gained in clarity and brevity what it might have lost in subtlety.

Accordingly, following a brief summary of the published work, the main discussion section is devoted to the interpretation of the chemistry of limonin. The order of presentation was chosen to minimise the number of crossreferences to work yet not discussed. After the various aspects of the chemistry of limonin are described in the first thirteen subsections, the chemical evidence is summarised in section 13B and the biogenetic implications of the work are discussed in section 14.

Work dealing with the chemistry of the two minor bitter principles of citrus fruit, obacunone and nomilin , is discussed in section 15 which also contains a full description of published work on this topic.

A number of model experiments is described in the following two sections , and the thesis closes with the account of the experimental work carried out by the author.

SUMMARY OF PUBLISHED WORK

The original discoverer of limonin, Bernay, classified the material as an alkaloid[1] on the basis of a spurious test for nitrogen. This error was rectified by Schmidt[4] who also noted that while limonin was resistant to oxidation , it was degraded to low molecular weight products once oxidation started.

As early as 1879 , Paterno and Oglioloro[5] interpreted their analytical results in terms of the correct formula $C_{26}H_{30}O_8$, but it did not gain universal acceptance until much later. Hoffman[6] isolated limonin among a number of plant products, but did not investigate its constitution. He considered that it was probably a glycoside. Another preliminary investigation was described by Peters and Frierichs[7] who carried out unsuccesful attempts to methylate, oxidise and estimate the methoxyl groups in limonin.

A great deal of confusion arose from the fact that limonin isolated by numerous workers from several sources was often described as a separate bitter principle due to the poor characterisation of the material. Thus Fujita and Wada[8] isolated "obaculactone" , Chen and Chen[9] "evodin" and Feist and Schulte[10] "citrolimonin" , all of which were eventually proved to be identical with limonin largely due to the efforts of Schechter and Haller[11] who in another contribution[12] also investigated the toxicity of limonin-containing extracts to insects. The question was further complicated by the isolation of similar , but genuinely different bitter principles obacunone and nomilin from citrus fruit, which have since been investigated by Emerson[13,14] and Dean and Geissman[15].

Limonin was also isolated by Mookerjee[16], Nolte and Loesecke[17] and Higby[18], but these authors did not make any major contributions to the chemical investigations.

Serious attempts to discover the structure of limonin date from the work of Koller and Czerny[19,20]. In spite of working with the wrong molecular formula, $C_{23}H_{28}O_7$, these workers made important contributions to limonin chemistry. By hydrogenating over palladium-carbon they obtained tetrahydrolimonin and hexahydrolimoninic acid to which they assigned wrong formulae, although they observed the correct hydrogen uptake. They also obtained 1:2:5 trimethyl naphthalene and isophthalic acid by alkali fusion and benzene pentacarboxylic acid by oxidation with manganese dioxide and sulphuric acid.

In 1946 , Geissman and Tulagin[21] summarised all the previous work and prepared the novel derivatives limonilic acid (by the action of alkaline manganate) and citrolin (by the action of hydroiodic acid). From the latter reaction they also isolated a small yield of another important derivative, desoxylimonin. They also showed that acetone was formed as a result of alkali fusion of limonin and that neither of the two lactones present can be opened by methylation.

The optical, crystallographic and X-ray properties of limonin were studied by Jones and Palmer[22]. The X-ray data suggested that the molecule was rather flat and the comparison of the calculated and determined densities of limonin and its acetic acid solvate gave an accurate check of its molecular weight.

The hydrogenation of limonin was re-investigated by Rosenfeld and Hofman[23], who confirmed the earlier results of Koller and Czerny[20] and also found that the acidic product , hexahydrolimoninic acid, could be decarboxylated by heating at 240°C under nitrogen.

Brachvogel[24] also obtained tetrahydrolimonin by hydrogenation over palladium catalysts and further obtained a compound $C_{26}H_{30}O_8$, which contained one active hydrogen atom but was not acidic, by hydrogenation over platinum oxide. The latter was most likely tetrahydrolimonol. She also produced an independent proof of the degree of unsaturation of limonin by measuring the uptake of bromine. Brachvogel further found 1:2:5 trimethyl naphthalene among the products of zinc distillation and acetone and ortho-cresol among the products of alkaline fusion of limonin. The latter reaction also gave rise to an unidentified "lactone" $C_{13}H_{14}O_2$.

Chandler and Kefford[25,26,27,28] proved that limonin had a ketonic function by preparing a 2:4 dinitrophenylhydrazone as well as an oxime , reducing the ketone to an alcohol (limonol) with aluminium isopropoxide and assigning the carbonyl frequencies in the infrared spectrum. They also isolated another natural product , a bitter principle obtainable from limonin by permanganate oxidation , and named it limonexic acid.

In 1952, Emerson[29] prepared and thoroughly characterised tetrahydrolimonin, hexahydrolimoninic acid, tetrahydrolimonin oxime, limonilic acid, methyl limonilate oxime, tetrahydrolimonilic acid, a di-acid with both limonilic and limoninic functions, citrolin and variuos derivatives of the above acids. He interpreted correctly that hydrogenolysis opened one lactone ring and limonilic acid change the other one and investigated the chemistry of citrolin by hydrogenation and alkaline decomposition.

Fujita and Hirose[30] produced "dihydrolimonin" (probably limonol) by reducing limonin with sodium amalgam and "dehydrolimonin" (probably desoxylimonin) by action of iodine in acetic acid. They also showed that limonin oxime could be converted back to limonin , i.e. that it was a simple ketonic derivative, and prepared etiolimonic acid[31] by ozonolysis.

Evidence for the presence of a β-substituted , isolated, furan nucleus was produced by

Fujita and Akatsuka[32] and Kubota and Kotoroyama[33] and finally confirmed by NMR measurments carried out by Corey[34]. This gave a rational explanation for the hydrogenation and hydrogenolysis behaviour of limonin and explained the nature of limonexic and etiolimonic acids.

In 1957 , Jeger and his co-workers[35] , re-investigated all the reduction and hydrogenation products of limonin and carried out and interpreted the complex reaction which limonol undergoes with alkali. They also described an investigation into the alkaline degradation of limonin which has since yielded a number of interesting results.

However, even in this work, only the relation between the furan and the lactone ring D could be deduced with any degree of certainty.

DISCUSSION

Note on spectroscopic results

As in the case of most complex molecules, the infrared spectra of limonin and its derivatives proved to be far too complicated for the interpretation of the majority of the bands. A further complication arose from the comparatively large number of carbonyl groups present which made the interpretation of the frequencies occuring in the carbonyl stretch region more difficult than usual. Some spectra could not be fully resolved and in others it appeared possible that some displacement of peak frequencies occured due apparently to purely "algebraic" ineraction. Nevertheless, valuable information was obtained from the study of carbonyl frequencies because of often remarkable consistency in certain series of reactions (e.g. acid isomerisation of hexahydrolimoninic acid, hydroiodic acid degradation of limonin, limonilic acid and its derivatives).

A further limitation on any generalisations which could be derived from the infrared spectra of limonin and its derivatives is due to the fact that most of the spectra were obtained by using Nujol mulls. However, in all cases where spectra were also obtained in solution (limonin, desoxylimonin, octahydroacetate of limonin, cisoid diene acid, methyl limonilyl ketone) the differences from mull spectra were negligible. This may be due to the fact that intermolecular interactions in large and complex molecules may be less important than it is generally realised.

Unless otherwise stated, all interpretations of infrared spectra are based on the work of Bellamy[36] and of ultraviolet spectra on Gillam and Stern[37] or Fieser and Fieser[38].

Nuclear magnetic resonance spectra , were kindly determined by Dr L.M. Jackman and his collaborators.

1. THE FURAN AND LACTONE FUNCTIONS OF LIMONIN

a. Reactions of the furan nucleus

The considerable evidence for the presence of a β-substituted furan ring in limonin has already been reviewed in the literature[35,34] and only a brief summary is presented here. The furan ring is the only unsaturated structure in limonin; no evidence of other unsaturation has ever been obtained.

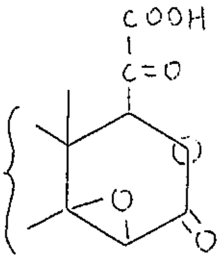
The ultraviolet absorption spectrum of limonin shows a flat peak at about 208mμ (ε:7,000) which is characteristic of a furan. Phillips[39] identified a number of bands in the infrared spectrum of limonin as due to the characteristic vibrations of the furan group. The peaks at 1505-1502 cm^{-1}(m) and at 875 cm^{-1}(s) have proved to be of diagnostic value. Corey[34] interpreted the proton magnetic resonance spectrum of limonin as showing the presence of a β-substituted furan nucleus.

Hydrogenation of limonin over rhodium-carbon[40] gives almost exclusively a neutral tetrahydro derivative (tetrahydrolimonin, $C_{26}H_{34}O_8$) whose infrared spectrum shows the absence of the characteristic furan bands and which has no strong absorption in the ultraviolet. Formation of tetrahydrolimonin can thus be interpreted as a straightforward hydrogenation of the furan ring.

When limonin is hydrogenated over palladium-carbon , it yields some tetrahydrolimonin, but the main product[20,29] is an acidic hexahydro derivative ,whose chemistry is discussed in sections 1b and 2c.

Hydrogenation in the presence of platinum oxide[30] may cause the reduction of the ketone (section3) to the alcohol, as well as the saturation of the furan ring, but may also result in the uptake of four moles of hydrogen to give a neutral , dihydroxylic compound named hexahydrolimondiol[35]. As this compound undergoes the merolimonol change (see section 8) to give a product identical with that obtained from limonol, it is likely that the second hydroxyl group is generated by a hydrogenolytic cleavage of the tetrahydrofuran ring - possibly while the furan is partially hydrogenated to the unstable dihydro derivative. Hexahydrolimondiol was also obtained in the course of the present work when limonin was hydrogenated over a rhodium-carbon catalyst at about 125 atmospheres.

The furan ring of limonin undergoes a number of oxidation reactions. Ozonolysis[32,35] yields two products ; aetiolimonic acid (I) and trisnor acid (II) , both are the expected products from a β-substituted furan nucleus.



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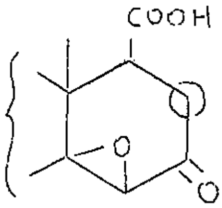

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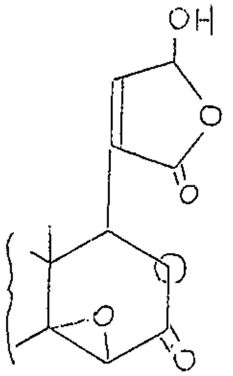
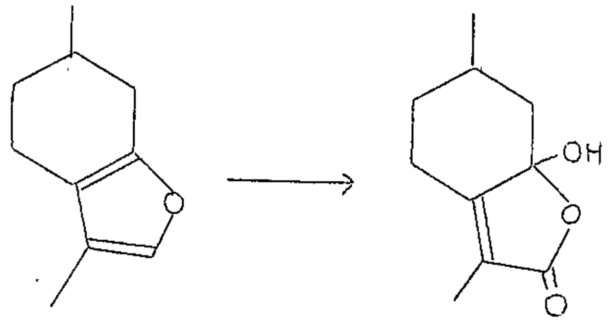
Oxidation of limonin with gaseous oxygen in presence of ultraviolet light and eosin[35], or alternatively oxidation with either performic acid or permanganate[26,28] gives limonexic acid (III).



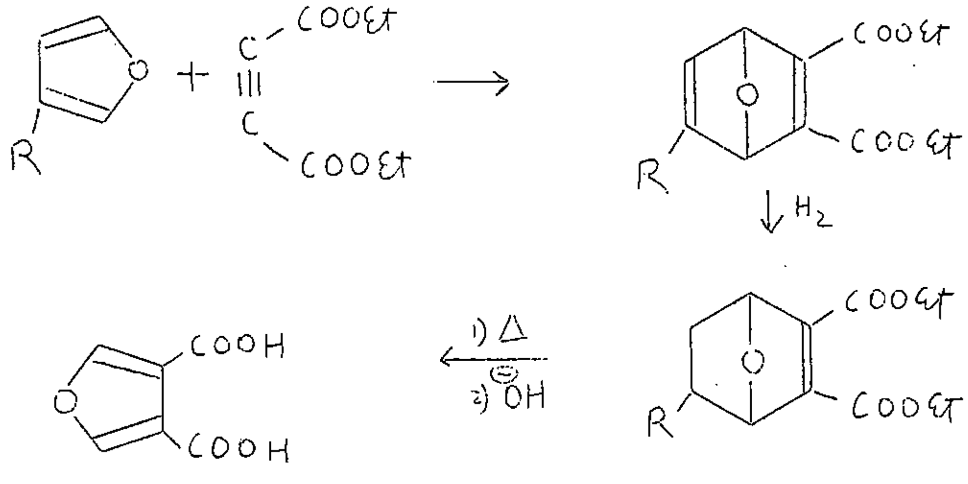
(III)



(IV) (V)

In accordance with the above structure, the ultraviolet absorption spectrum of limonexic acid shows a maximum at 209 mμ (ε:11,800). The infrared spectrum shows bands at 3255 cm^{-1} (hydroxyl) and 1803 cm^{-1} (α-β unsaturated γ-lactone) , but none of the bands assigned to furan. An analogous oxidation of menthofuran (IV) to the lactone (V) by hydrogen peroxide in acetic acid, chromic acid, or oxygen in the presence of ultraviolet light has been described by Woodward and Eastman[41].

Kubota and Tokoroyama[33] carried out the following series of reactions on a pentoal derived from limonin by lithium aluminium hydride reduction, thus providing further evidence for the presence of a furan ring unsubstituted in either of the α positions in limonin.

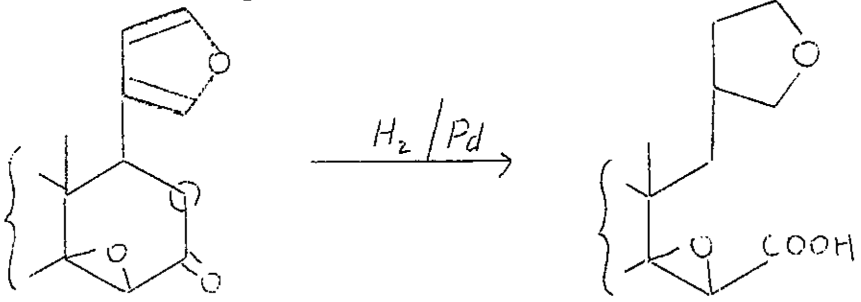


b. The lactone rings

The fact that limonin contained two lactone rings was established very early[7]. These appear to be δ constituted from infrared data (bands near 1755 cm^{-1} in limonin itself and varying from 1760 to 1740 cm^{-1} in various derivatives retaining unaltered lactone functions).

Hydrogenolysis of limonin (VI) to a hexahydro acid , hexahydrolimoninic acid $C_{26}H_{36}O_8$ (see section 1a), suggests that the alcoholic oxygen of one of the lactone rings is situated allylically with respect to the furan ring. The fact that tetrahydrolimonin cannot be further hydrogenolysed confirms this. As hexahydrolimoninic acid is abnormally strong (pK:3.2) an oxygen function has to be placed α to the carbonyl group. Further work described in sections 3, 6 and 8 gave good evidence that hexahydrolimoninic acid possesses the part structure (VII). An exactly analogous situation has been described in the chemistry of columbin[42]. Other reactions of the lactone groups in limonin are given under separate headings.

(VI)



(VII)

2. REACTIONS OF THE EPOXIDE

a. Reduction

Corey[40] obtained desoxylimonin , $C_{26}H_{30}O_7$, by reduction of limonin ,$C_{26}H_{30}O_8$, with chromous chloride. This result was comfirmed in the course of the present work. Desoxylimonin had been previously obtained[21,29] as a byproduct of citrolin (section 12) by the action of hydroiodic acid on limonin. Modification of the latter procedure by Pradhan[43], gave desoxylimonin in good yield.

Desoxylimonin is a neutral dilactone retaining the ketone function (oxime[39,43]) and the furan ring (bands at 1503 and 875 cm^{-1} in the infrared spectrum). The ultraviolet spectrum of desoxylimonin shows a maximum at 213 mμ (ε:15,800) ; after subtracting the spectrum of limonin a maximum remains at 218 mμ (ε:10,500), characteristic of an α-β unsaturated lactone or ester. The infrared spectrum of desoxylimonin gives further evidence for the presence of such grouping; the carbonyl bands being situated at 1746 cm^{-1} (δ lactone) and at 1715 cm^{-1} (α-β unsaturated δ lactone and ketone), the second band being much stronger than the first. In contrast , the infrared spectrum of limonin itself shows the major band near 1755 cm^{-1} (two δ lactones) and the minor band at 1709 cm^{-1} (ketone).

As a confirmation, the tetrahydro derivative of desoxylimonin was prepared[43], both by the action of hydroiodic acid on tetrahydrolimonin and by hydrogenation of desoxylimonin (see also section 7). As expected, the ultraviolet spectrum of tetrahydrodesoxylimonin, $C_{26}H_{34}O_7$, shows a maximum at 218.5 mμ (ε:10,600) and the infrared spectrum shows carbonyl bands at 1752 cm^{-1} (δ lactone) and at 1720-1707 cm^{-1} (α-β unsaturated lactone and ketone), but no bands characteristic of the furan.

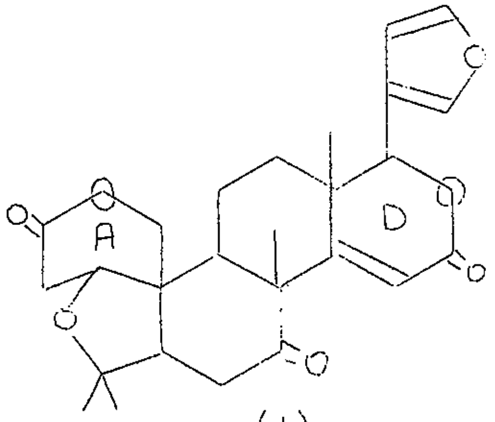
Tetrahydrodesoxylimonin was also prepared by Corey[40], by the action of chromous chloride on tetrahydrolimonin, who also converted it to a dihydro derivative by hydrogenating over a rhodium catalyst and oxidising the dihydro-tetrahydrodesoxylimonol formed with chromic acid in pyridine.

The following evidence can be advanced to show that it is the lactone ring D which is involved in the reduction of limonin to desoxylimonin, rather than the lactone ring A:

(i) The low pK value of hexahydrolimoninic acid[29] (section 1b) requires the presence of an α-negative substituent in the lactone D . It is the reduction of such a group which could be expected to give rise to an α-βunsaturated lactone function , in particular if the α-oxygen was a part of an epoxide ring (see below).

(ii)Emerson[29] has shown that a dicarboxylic acid could be formed either by hydrogenolysis of limonilic acid (where lactone A is involved, see section 11) or by iodine/alkali oxidation of hexahydrolimoninic acid thus proving that different lactones were involved in hydrogenolysis and in limonilic acid formation. As lactone D has the α-oxygen function,it is unlikely that lactone A is involved in the formation of desoxylimonin.

(iii) A desoxylimonin analogue of limonilic acid was prepared by Pradhan[43] and showed the same spectroscopic properties as desoxylimonin itself. That is it is an α-β unsaturated lactone, λ_{max}:213-4 mμ (ε:15,400). This



(I)

also indicated that the carboxylic group of lactone A , which had been opened by the limonilic acid reaction , was not involved in the formation of desoxylimonin.

(iv) The fact that desoxylimonin does not give any acidic product when hydrogenated over palladium carbon (see preparation of tetrahydrodesoxylimonin) , also indicates that lactone D was altered in some way in the transformation of limonin to desoxylimonin.

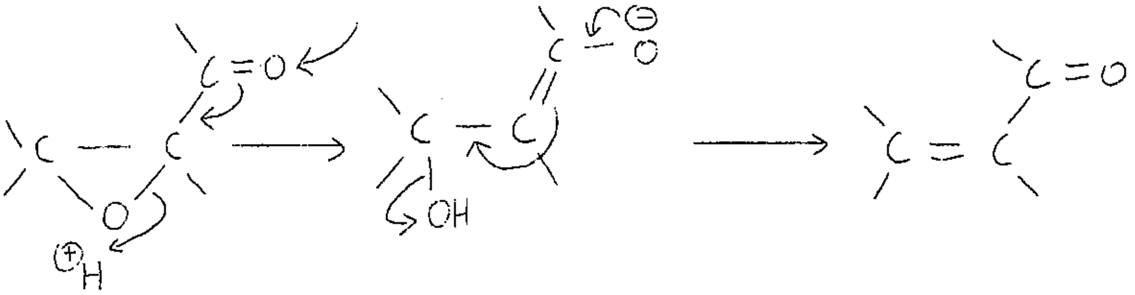
The degree of substitution at the double bond of the α-βunsaturated lactone in desoxylimonin is indicated by the nature of the transformation products of tetrahydrolimonin with acid (see section 2b) and the nature of decarboxyhexahydrolimoninic acid (see section 2c). The position of the maximum in the ultraviolet spectrum of tetrahydrodesoxylimonin (page 20) is also consistent with the presence of a trisubstituted double bond.

On the basis of the above evidence , structure (I) was assigned to desoxylimonin.

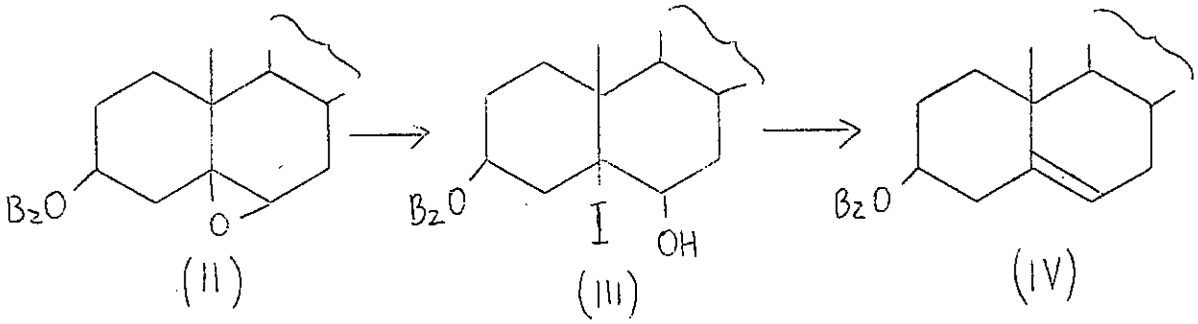
Besides evidence discussed in sections 2b and 2c, the following evidence can be advanced to show that the unsaturated lactone in desoxylimonin has been derived from a reduction of an epoxide α-β to the carbonyl group of lactone D in limonin:

(i) The occurence and course of the merolimonol reaction (see section 8) requires that an epoxide of the postulated degree of substitution be present in the lactone D of limonin.

(ii) Chromous chloride is a specific reducing agent for epoxides α-β to a carbonyl group[44], the following mechanism being postulated for the reaction:



(iii) Epoxides are also known to be reduced by hydroiodic acid[45]. E.g. it was shown that cholesteryl benzoate β-oxide (II) may be converted to the iodohydrin (III) and thence to cholesteryl benzoate (IV) by treatment with hydroiodic acid in chloroform.



From the structure (I), it would appear possible to epoxidise desoxylimonin (or its tetrahydro derivative) back to limonin (or tetrahydrolimonin) respectively. Numerous attempts to react tetrahydrodesoxylimonin with either perbenzoic or peracetic acids were made both by Pradhan[43] and in the course of the present work, but in all cases the starting material was recovered unchanged.

b. Isomerisation of tetrahydrolimonin with acid

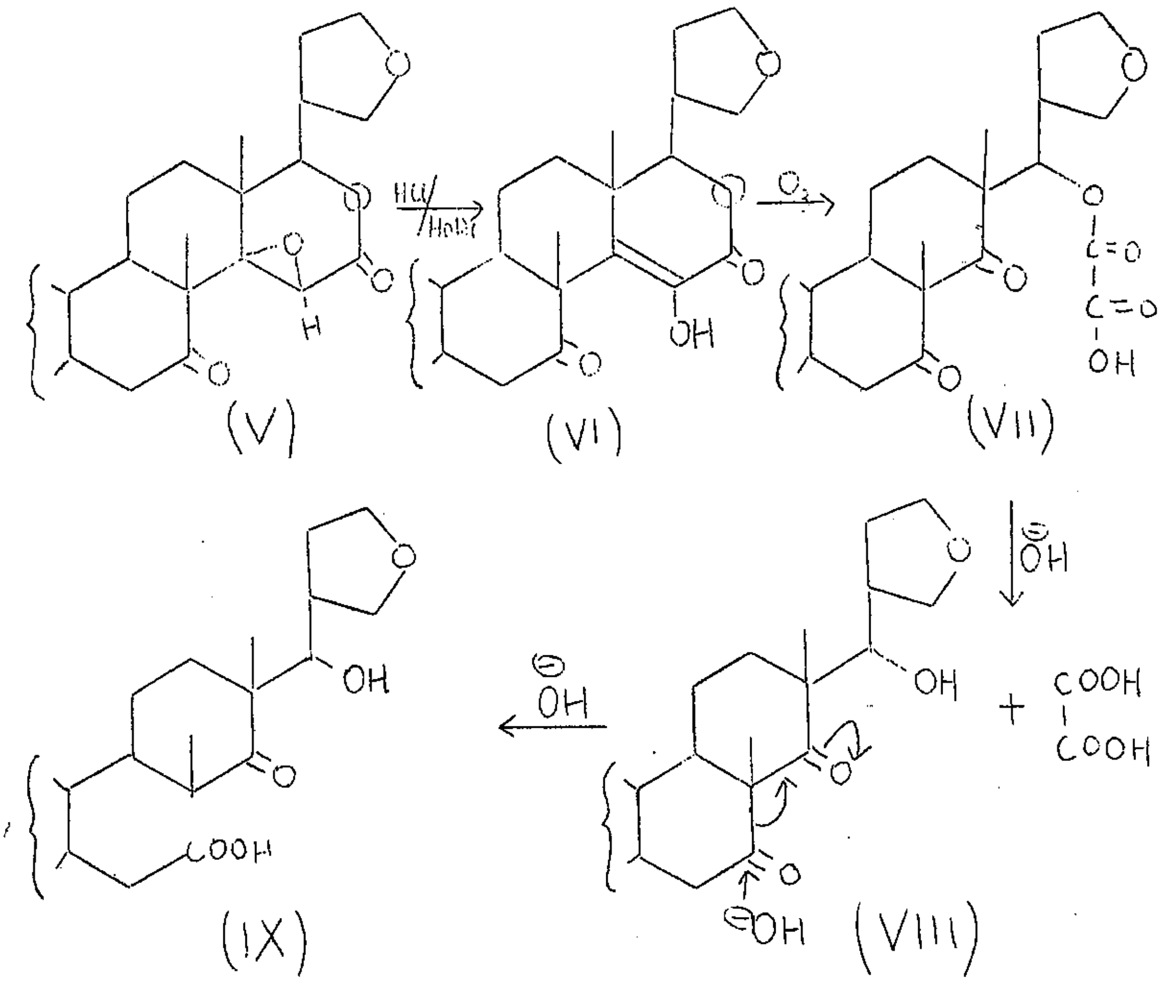
Treatment of tetrahydrolimonin (V), $C_{26}H_{34}O_8$ with a mixture of concentrated hydrochloric acid and acetic acid, yielded[43] an isomeric substance, which will be referred to as _iso_-tetrahydrolimonin. The ultraviolet spectrum of _iso_-tetrahydrolimonin showed a maximum at 257 mμ (ε:5,500) which shifted to 290 mμ (ε:4,200) in the presence of alkali. The neutral monoacetate showed a maximum at 218 mμ (ε:11,000). _iso_-Tetrahydrolimonin is an enolic substance, i.e. it is soluble in dilute alkali but not in sodium carbonate solutions and gives a positive ferric chloride test. The infrared spectrum of _iso_-tetrahydrolimonin shows a band at 3250 cm^{-1} (enolic hydroxyl).

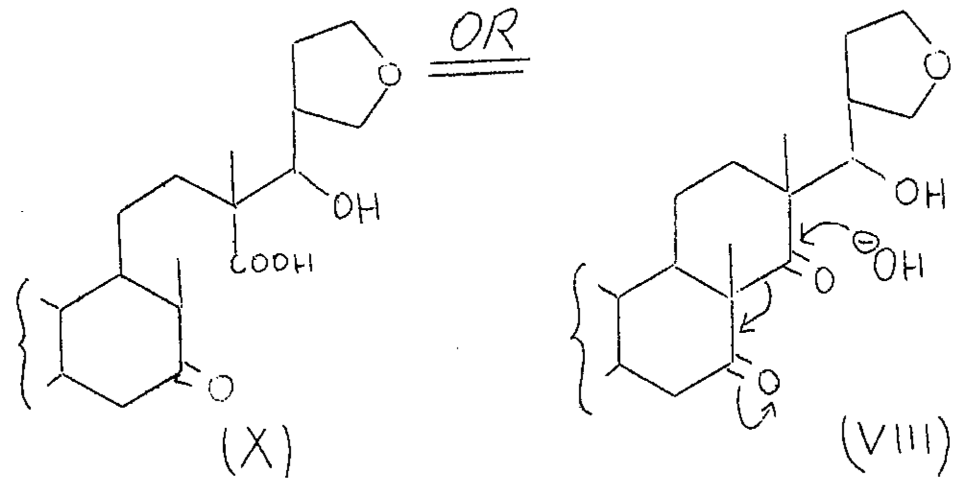
In the course of the present work, iso-tetrahydrolimonin was ozonised and treated with alkali to give oxalic acid and an amorphous acidic material containing two carboxylic (and/or lactonic) groups.

Pradhan[43] demonstrated that the reaction leading to iso-tetrahydrolimonin involves the epoxide because desoxytetrahydrolimonin (where the epoxide had been reduced to a double bond, see section 2a) can be recovered unchanged from a mixture of concentrated hydrochloric and acetic acids.

On the basis of the above data, iso-tetrahydrolimonin was assigned the structure (VI). The amorphous acidic product of ozonolysis and hydrolysis of (VI) is probably a mixture of (IX) and (X) which are likely hydrolysis products of an intermediate β-diketone (VIII), the expected major hydrolysis product of the primary ozonolysis product (VII).

The acid isomerisation of tetrahydrolimonin provided evidence for the presence of an epoxide α-β to the carbonyl of lactone D and for the presence of a hydrogen at C_{15} (see section 2a).


(V)
HCl/HOAc
(VI)
O3
(VII)
OH⊖
(VIII)
⊖OH
+ COOH COOH
OH⊖
(IX)

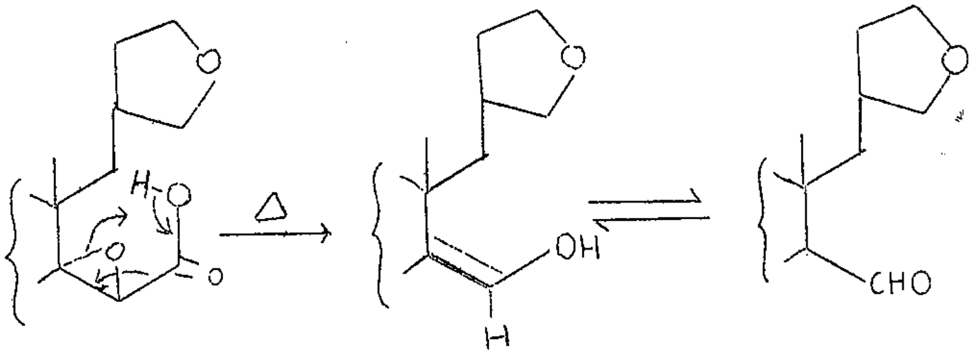

OR
(X)
⊖OH
(VIII)

Earlier work[39] indicated that limonin itself undergoes an analogous reaction in the presence of concentrated hydrochloric acid and acetic acid. An amorphous product was isolated whose ultraviolet spectrum showed a maximum near 212 mμ (ε: 7,000 , furan) and at 258 mμ (ε:9,700). The latter maximum shifted to 291 mμ (ε:8,000) in presence of alkali. The infrared spectrum showed bands at 3400cm^{-1} (hydroxyl), 1743 cm^{-1} (δ lactone) , 1712 cm^{-1} (α-β unsaturated lactone and ketone) , 1607 cm^{-1} (conjugated system) and furan bands. Unfortunately no crystalline derivatives could be obtained.

c. Decarboxylation of hexahydrolimoninic acid

Hexahydrolimoninic acid (XI) , $C_{26}H_{36}O_8$ (see section 1b) loses carbon dioxide on heating to about 240°C to give a neutral compound[23]. Bis-oxime and bis-dinitrophenylhydrazone derivatives[40,46] of this compound have been prepared, showing that a new carbonyl group has been generated.

The pyrolytic decomposition of an α-oxy acid to give a new carbonyl function has been interpreted as evidence for the presence of an α-glycidic system [47] in lactone D of limonin. The course of the reaction is envisaged as follows:



(XI) (XII)

The only evidence for the presence of an aldehydic function in the decarboxylated hexahydrolimoninic acid (XII) was obtained from its NMR spectrum[46] but this result has been disputed[40]. It is possible , however that group migration may have taken place to give a ketonic rather than an aldehydic carbonyl function[47].

3. THE REACTIONS OF THE CARBONYL GROUP

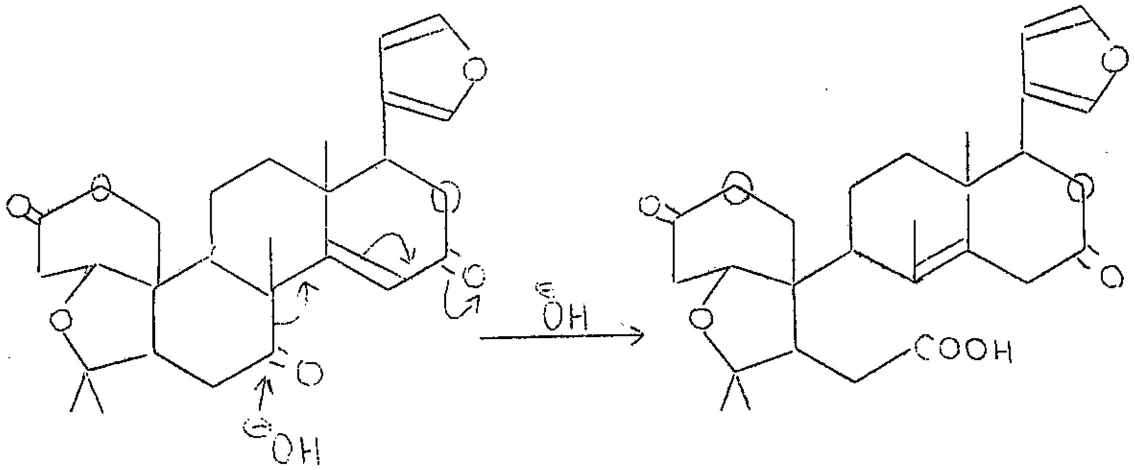
The presence of a ketonic carbonyl in limonin is indicated by the band at 1709cm^{-1} in the infrared and a maximum at 285mμ (ε:33) in the ultraviolet spectrum. These suggest that the ketone is present in a six membered (or larger) ring.

Although the typical derivatives of the ketonic carbonyl group proved difficult to crystallize, the dinitrophenylhydrazone[26] and the oxime[26,29] were eventually prepared. The carbonyl group can also be reduced with aluminium iso-propoxide[26] or with either sodium borohydride[35] or sodium amalgam[30] to give two isomeric alcohols limonol and epi-limonol , thus comfirming that the ketone group of limonin was present in a ring. The ease of acetylation of epi-limonol and the choice of the reagents used for its preparation indicate that epi-limonol is the equatorial and limonol the axial derivative. Both can be oxidised back to limonin with chromic oxide in pyridine[35].

4. DESOXYLIMONIC ACID

The reaction of desoxylimonin with alkali described below, gave an indication of the relative position of the ketonic carbonyl group with respect to the lactone D . This was also independently comfirmed by the merolimonol reaction (see section 8).

Treatment of desoxylimonin (I), $C_{26}H_{30}O_7$, (see section 2a) with aqueous alkali, gave a dilactone carboxylic acid[43] (II), $C_{26}H_{32}O_9$ which no longer possesed a ketonic function. The ultraviolet spectrum of this product, which was named desoxylimonic acid, showed no maximum near 214 mμ but had instead a strong end absorption indicating the presence of an isolated double bond. The course of the reaction may be envisaged as follows:



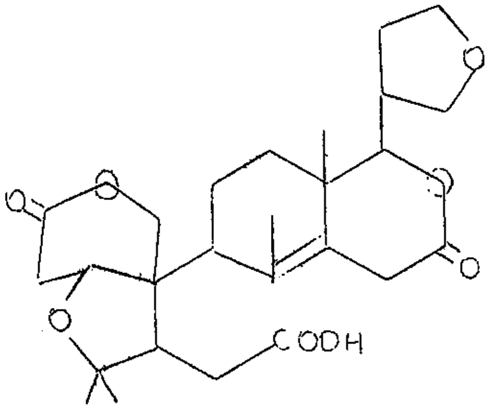
(I) (II)

It can be seen that the reaction is in fact an "acid" hydrolysis of a vinylogue of a β-keto ester. The mechanism , which requires both the presence of a carbonyl and an α-β unsatureated lactone, is confirmed in that neither limonin nor desoxylimonin oxime undergo the above reaction in the presence of alkali[43].

It is well known that the occurence of an "acid" hydrolysis of a β-keto ester is governed by the relative ease of attack of the hydroxyl ions on the carbon carrying the ketonic function and the hydrolysis of the ester group. In the case of the desoxy derivative of limonilic acid (see section 11), the carbon carrying the ketonic function appears to be sterically hindered by the presence of the α-oxygen, and thus desoxylimonilic acid was recovered unchanged[43] from treatment with alkali.

In the course of the present work, the tetrahydro analogue of desoxylimonic acid was prepared by the action of alkali on tetrahydrodesoxylimonin, by hydrogenation of desoxylimonic acid and by the action of alkali on tetrahydrodesoxyiodoacetate (see section 7). The properties of this compound were in full agreement with the structure expected (III), i.e.

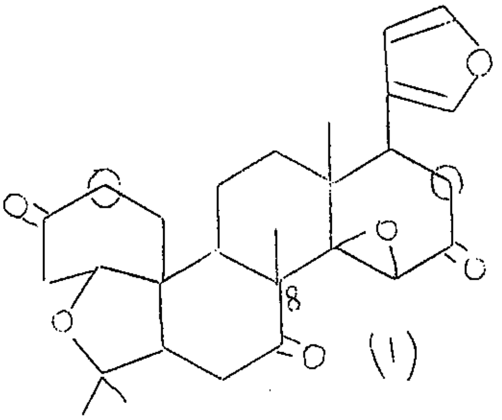
it was a dilactone carboxylic acid and its ultraviolet spectrum showed no maximum but a strong end-absorption (ε:10,000 - 11,000) at 202mμ. The infrared spectrum showed diffuse bands in the 3500-3000 cm^{-1} region (carboxylic hydroxyl), 1755cm^{-1} (δ lactone A), 1725 cm^{-1}-1715 cm^{-1} (δ lactone D and carboxylic acid) and no furan bands,.



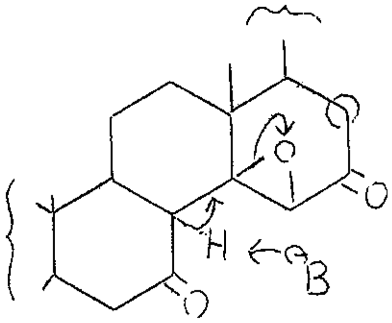
(III)

5. DEGRADATION OF TETRAHYDRODESOXYLIMONIC ACID

Pradhan[43] proposed that the position C_8 in the structure of limonin (I) could not have a hydrogen substituent, as such a molecule would be expected to undergo β-elimination in the manner indicated below on treatment with alkali to give a γ-hydroxy-α-β unsaturated ketone, while limonin was known to be stable to refluxing 6% methanolic potassium hydroxide.[43]



(I)



In the course of the present work, it was shown by degradation of tetrahydrodesoxylimonic acid (see section 4) that C_8, in fact, bears a methyl substituent.

a. Ozonolysis

Ozonolysis of tetrahydrodesoxylimonic acid (II), $C_{26}H_{36}O_8$, yielded an amorphous product whose

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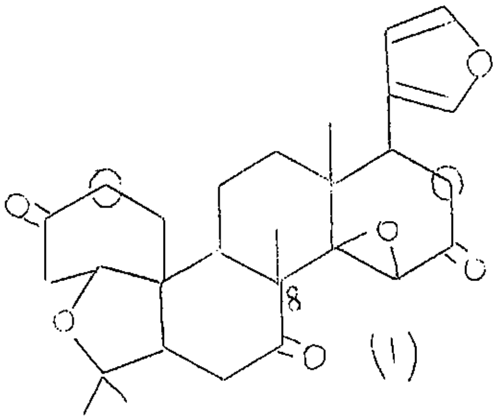
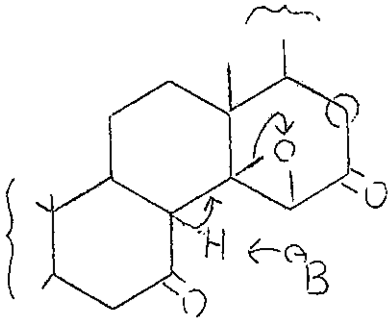


(I)



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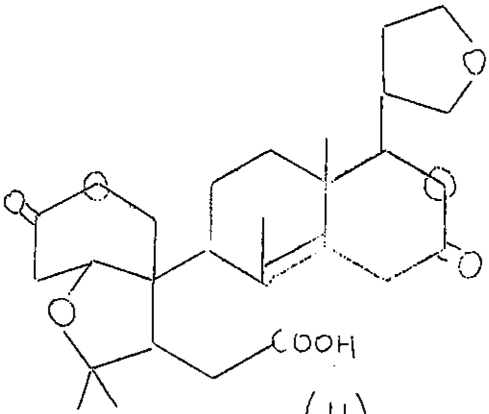
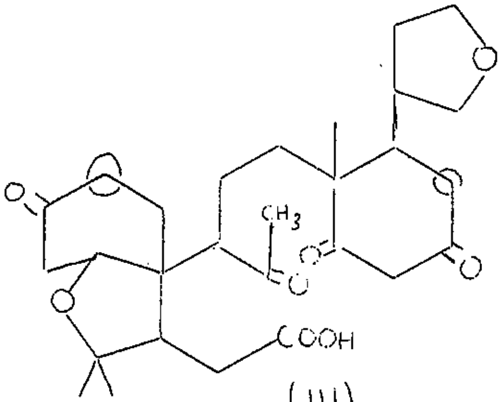
a. Ozonolysis

Ozonolysis of tetrahydrodesoxylimonic acid (II), $C_{26}H_{36}O_8$, yielded an amorphous product whose ultraviolet spectrum showed a maximum at 273mμ in the presence of alkali (ε:5,500) and which gave an immediate iodoform test. These properties are entirely consistent with structure (III):



(II)

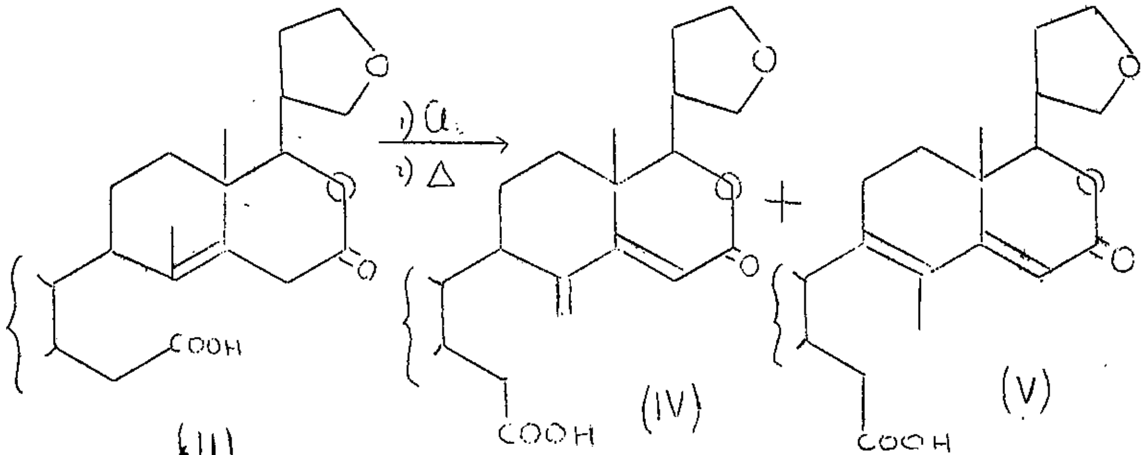


(III)

b. Chlorination and dehydrochlorination

Although tetrahydrodesoxylimonic acid can be recovered unchanged from solutions of bromine in either carbon tetrachloride or acetic acid , chlorination by a solution of chlorine in acetic acid followed by heating under moderate vacuum at 100°C, yielded two isomeric products , the cisoid (IV) and transoid (V) diene acids , $C_{26}H_{34}O_8$.

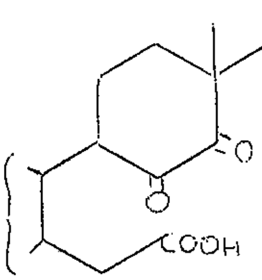
No chlorine containing material could be isolated in pure state , but a study of the ultraviolet spectra of the material during the course of thermal dehydrochlorination indicated that the double bond conjugated with the carbonyl group of lactone D was formed first. The ultraviolet spectrum of the <u>cisoid</u> diene acid showed a broad maximum at 255 mμ (ε:7,800) while that of the <u>transoid</u> diene acid had a maximum at 284 mμ (ε:16,400) and a subsidiary maximum at 230 mμ (ε:6,300). The infrared spectrum of the <u>cisoid</u> isomer showed two bands at 1620 and 1603 cm^{-1}, that of the <u>transoid</u> isomer had a single band at 1594 cm^{-1}.



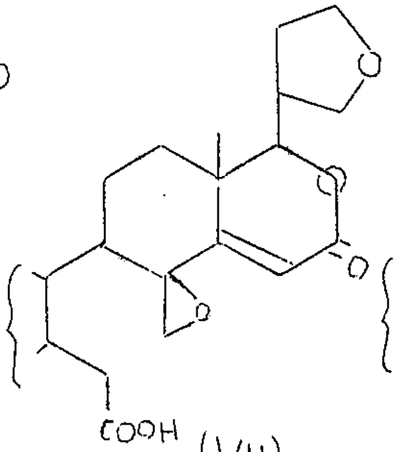
The ultraviolet spectra of the methyl esters of both isomers were nearly identical with those of the parent acids. The relative intensities and positions of all the relevant spectroscopic features agree well with the structures (IV) and (V).

Ozonolysis of (IV) yielded significant

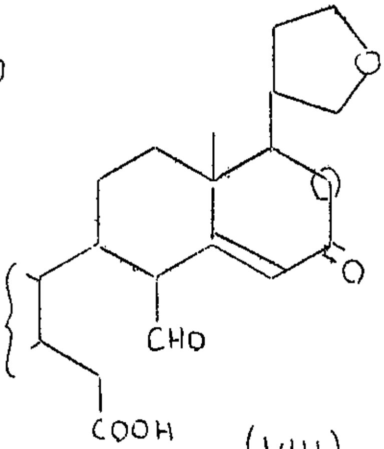
quantities of formaldehyde in confirmation of the presence of an exocyclic double bond. The method of estimation of formaldehyde was checked by using blanks and pyrethrosin[48]. The main ozonolysis product could not be obtained in a crystalline form, but its ultraviolet spectrum in the presence of alkali (λ_{max}:384 mμ , ε:2000) indicated that the expected enolisable product (VI) could be responsible, although the position of the maximum was at a somewhat high wave length.



(VI)



(VII)



(VIII)

Treatment of the *cisoid* diene acid (IV) with peracetic acid, gave an oxide , $C_{26}H_{34}O_9$, whose ultraviolet spectrum had a maximum at 217-8 mμ (ε:9,000) showing that an α-β unsaturated lactone system was present, i.e. that the epoxide formed on the exocyclic double bond in accordance with the structure (VII). On treatment with boron trifluoride, (VII) yielded an amorphous material whose ultraviolet spectrum showed a maximum at 390 mμ (ε:2000) in presence of alkali. This material could be an enolisable aldehyde of structure (VIII).

Chlorination of the cisoid diene acid (IV) resulted in the uptake of one mole of chlorine to give an amorphous product containing an α-β unsaturated lactone grouping.

Further evidence for the presence of a methyl group at C_8 was obtained from proton magnetic resonance spectra. It was found that while tetrahydrodesoxylimonic acid (II) had no peaks in the region associated with vinylic hydrogen , the cisoid diene acid (IV) had three such peaks (tau :4.60,4.38,3.97 ppm) in this region.

The above evidence leaves little doubt about the presence of a methyl at C_8 and of at least one hydrogen atom at C_9.

The predominant formation of the energetically unfavourable cisoid structure can be readily explained by postulating that the intermediate chloro-compound is either wholly or partially in a configuration where the chlorine at C_8 and the hydrogen at C_9 are in relative positions unfavourable to dehydrohalogenation.

Tetrahydrodesoxylimonic acid remained unaffectd by selenium dioxide,perphthalic acid . peracetic acid and strong mineral acid. Some of this indicates a high degree of hindrance in the region of the tetra-substituted double bond, which is quite apparent on construction of a model.

6. SOME TRANSFORMATIONS OF HEXAHYDROLIMONINIC ACID

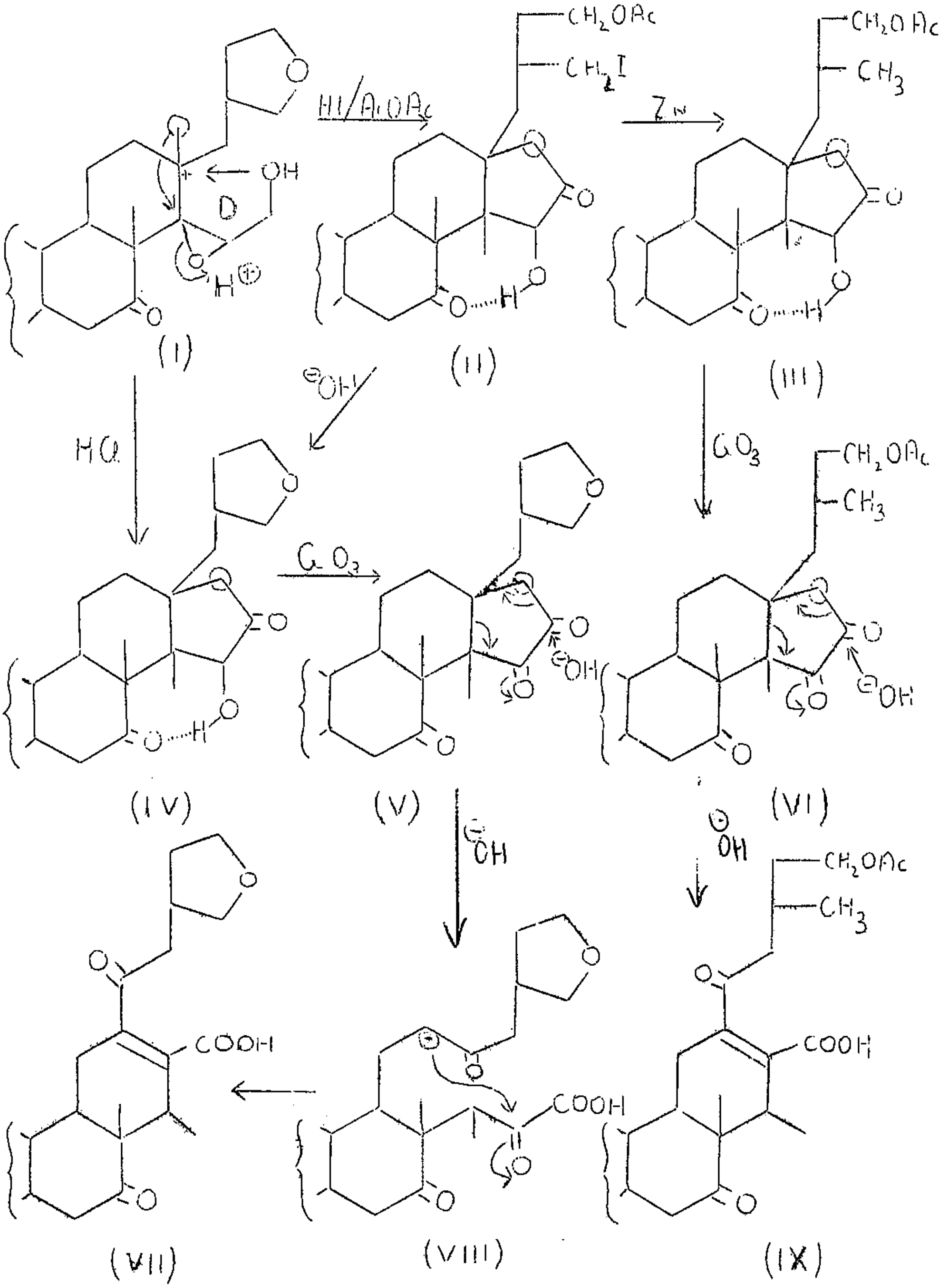
The reaction of hexahydrolimoninic acid with hydroiodic acid and acetic anhydride in acetic acid and also with hydrochloric acid in dioxane was first described by Pradhan[43] and was repeated and extended in the course of the present investigation.

Hexahydrolimoninic acid (I) , $C_{26}H_{36}O_8$, yields a neutral iodo-monoacetate (II) , $C_{28}H_{39}O_9I$, by the action of hydroiodic acid and acetic anhydride in acetic acid. The infrared spectrum of this compound indicated that it contained a γ lactone and a hydroxyl group , as well as a displaced ketonic carbonyl (bands at 1789,1755,3300 and 1677 cm^{-1}). The ultraviolet spectrum showed a peak at 290 $m\mu$ (ε:26) , showing that the ketonic function was retained and that no α-β unsaturated carbonyl group had been introduced. On treatment with zinc , the iodo-monoacetate (II) gave a desiodo compound (III) , $C_{28}H_{40}O_9$, whose infrared spectrum was very similar to that of (II). By the action of alkali , (II) lost iodine and acetyl to give a neutral isomer of hexahydrolimoninic acid (IV) whose infrared spectrum retained bands at 1789,3300 and 1686 cm^{-1}.

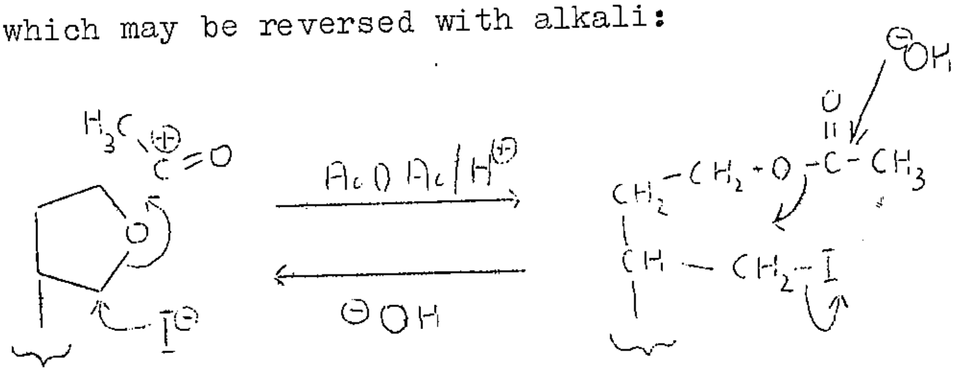
The action of concentrated hydrochloric acid in dioxane on (I) gave (IV) directly. The presence of free hydroxyl groups in (III) and (IV) was confirmed by active hydrogen determinations and by oxidation with chromic acid and pyridine , when analogous α-keto γ-lactones (V), $C_{26}H_{34}O_8$, and (VI), $C_{28}H_{38}O_9$, were obtained. The infrared spectra of (V) and (VI) no longer showed any bands in the O-H stretching region , but had bands near 1790 cm^{-1}(γ lactone), 1775 cm^{-1} (non enolised cyclopentanone α-to lactone carbonyl) and 1720cm^{-1} (non hydrogen-bonded ketone).

The lack of evidence for an enolic grouping in (V) and (VI) requires C_{14} to be tertiary in these compounds , and by implication also in (II), (III) and (IV), as α-keto-γ-lactones with a hydrogen in the β position are fully enolised[49,50].

The fact that limonin does not undergo an analogous reaction with acids indicated that the hydrogenolysed ring D lactone and/or the tetrahydro furan ring were participating.


HI/AcOAc
Zn
HCl
⊖OH
CrO3
⊖OH
⊖OH
CH2OAc
CH2I
CH3
COOH
OH
D
H⊕
(I)
(II)
(III)
(IV)
(V)
(VI)
(VII)
(VIII)
(IX)

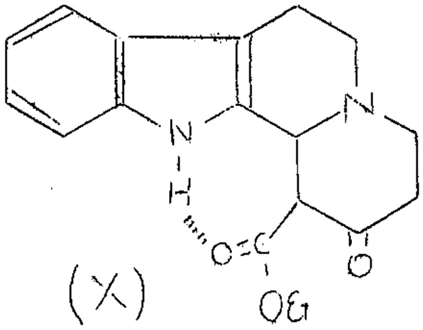
The introduction of iodine and acetate is considered to be an opening of the tetrahydrofuran ring, which may be reversed with alkali:



An analogous reaction takes place with tetrahydrodesoxylimonin (see section 7). The relative positions of the acetate and iodine in (II) were not investigated and the order shown in (II),(III),(VI) and (IX) is arbitrary.

The principal reaction (I) to (IV) was postulated to involve an opening of the epoxide by protonation , followed by methyl migration from C_{13} to C_{14} and the closing of a γ lactone on the C_{13} carbonium ion. No exact analogy could be found in the literature.

The abnormally low carbonyl frequencies in (II),(III) and (IV) are probably due to intramolecular hydrogen bonding with the hydroxyl group at C_{15}. Although a seven membered ring is involved, this hypothesis receives strong support from the observation that the abnormally low carbonyl band does not appear in the spectra of (V) and (VI) where the hydroxyl group is oxidised to a ketone, or in the spectrum of an acetate of (IV) which was also prepared. The bands near 1680 cm^{-1} cannot be due to an α-β unsaturated carbonyl function as neither (III) nor (IV) show any strong absorption in the ultraviolet. Intermolecular hydrogen bonding is unlikely , as the infrared spectrum of (IV) was the same in chloroform solution as in Nujol mull. An analogy for a strong hydrogen bonding effect involving a 7 membered ring can be found in the infrared spectrum of (X)[51], which shows bands at 1709cm^{-1} (ketone) and 1695 cm^{-1} (hydrogen bonded ester). The abnormally low ester band cannot be due to an enolic structure, as a crystalline enolic form of (X) was isolated independently.



(X)

The α-keto-γ-lactones (V) and (VI) react with alkali to give amorphous acidic products with very similar ultraviolet spectra. The acid derived from (V) shows a maximum at 244 mμ (ε: 3,800) in the ultraviolet and bands near 1755 (δ lactone), 1715 (carboxylic acid) and 1670 cm^{-1} (α-β unsaturated ketone) in the infrared. The nature of the products could not be established as no crystalline derivative was obtained, but the structure (VII) derived from (V) via the intermediate (VIII) offers an interesting hypothesis ,apparently in full agreement with the facts available and involving a plausible mechanism. Some support for the structure (VII) can be derived from the fact that the intensity of the band near 250 mμ can be considerably reduced by boiling with zinc in acetic acid, while the ultraviolet spectrum was unaffected by the action of alkaline hydrogen peroxide , indicating the absence of an α-keto carboxylic acid.

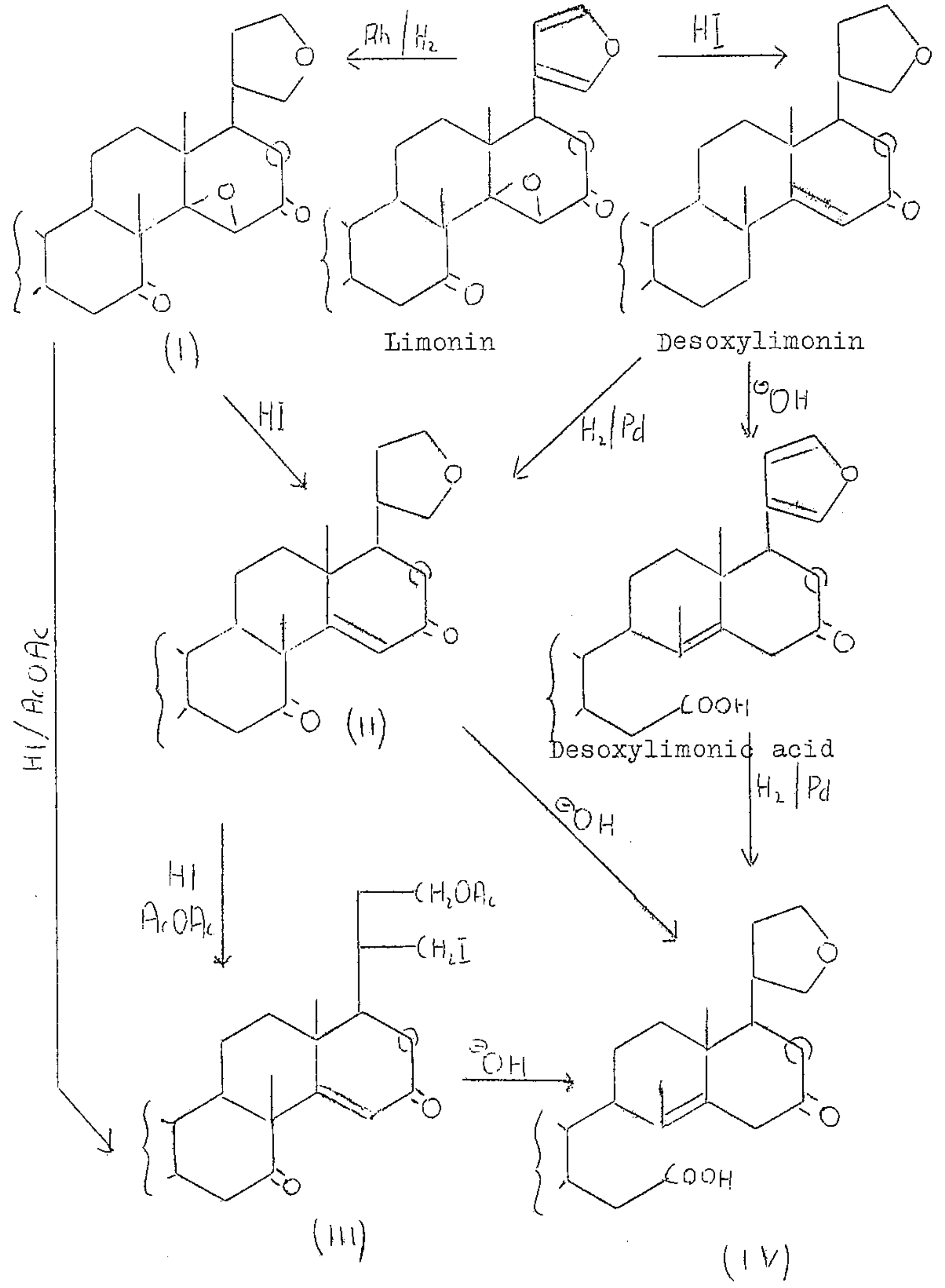
Structure (IX) represents the analogous product obtained by treatment of (VI) with alkali.

7. IODOACETYLATION OF TETRAHYDROLIMONIN

Pradhan[43] obtained a neutral iodoacetate by the action of hydroiodic acid and acetic anhydride in acetic acid on either tetrahydrolimonin (I) or tetrahydrodesoxylimonin (II) (see section 2a).

In the course of the present work it was established that this iodomonoacetate (III), $C_{28}H_{37}O_8I$, could be converted to a dilactone carboxylic acid, tetrahydrodesoxylimonic acid (IV)(see section 4). The ultraviolet absorption spectrum of (III) shows a maximum at 219 mμ (ε:12,700), which , together with the fact that it was also obtained from tetrahydrodesoxylimonin (II), indicates that it contains an α-β unsaturated lactone system in the ring D.

The structure of the acid (IV), was established independently (see section 4) and thus it becomes apparent that (III) differs from (II) only by the opening of an oxide ring to give an iodoacetate, the oxide being regenerated by the action of alkali. By analogy with the reactions described in section 6, the tetrahydrofuran is probably involved. Again , the relative positions of iodine and acetyl are arbitrary.


Rh / H₂
HI
Limonin
Desoxylimonin
(I)
HI
H₂ / Pd
⊖OH
(II)
COOH
Desoxylimonic acid
H₂ / Pd
⊖OH
HI / AcOAc
HI
AcOAc
CH₂OAc
CH₂I
⊖OH
COOH
(III)
(IV)

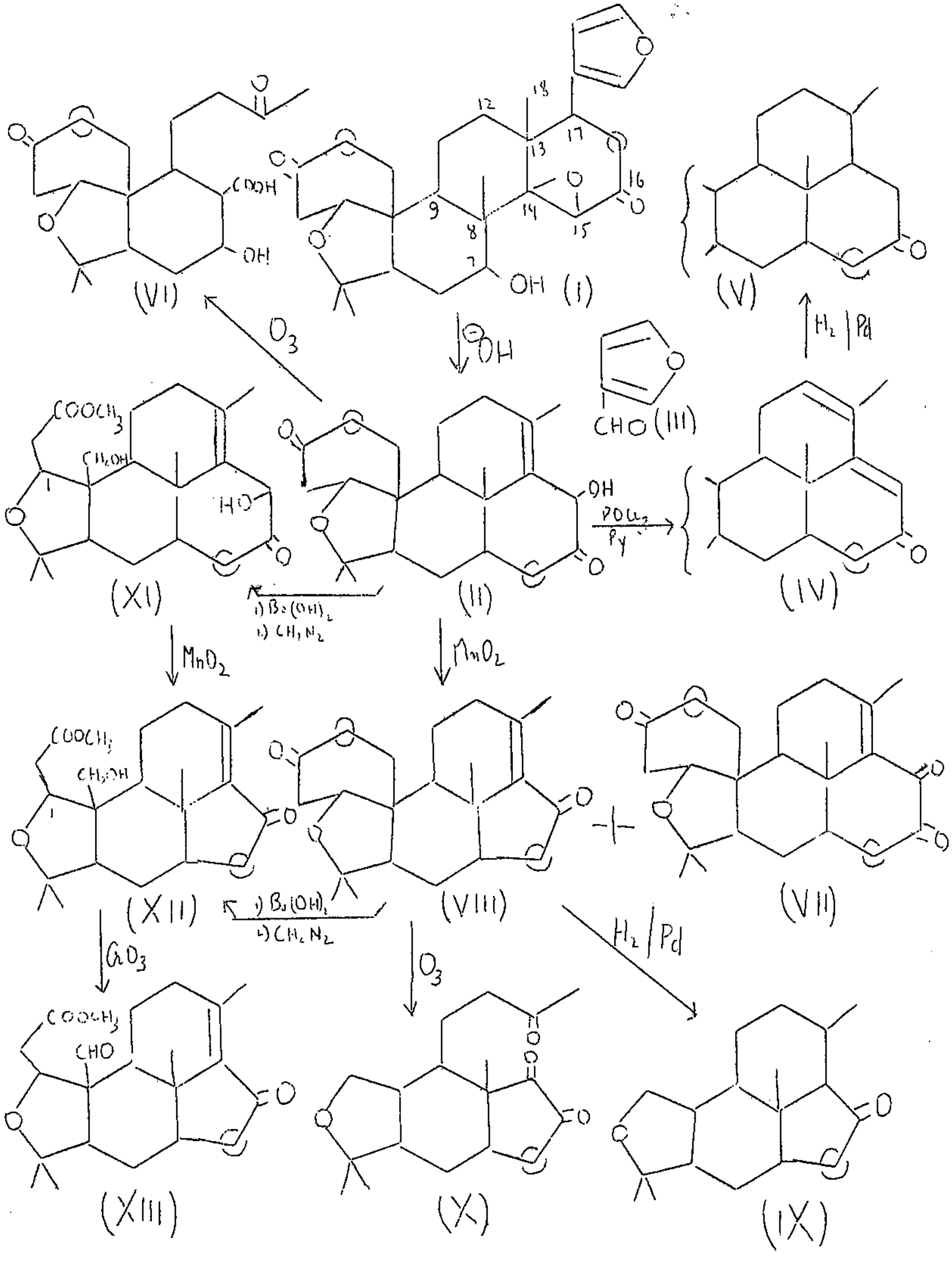
8. MEROLIMONOL AND ITS DERIVATIVES

The work summarized in this and the following section was performed almost entirely by the Zurich group[46], although contributions to the chemistry of merolimonol were also made by Corey[40]. Some of the earlier results in this series have already been published[35].

Limonol(I) (see section 3), but not the epimeric epi-limonol, reacts with alkali to give merolimonol (II) and a smaller fragment identified as furan-3-aldehyde (III). Merolimonol, which was further characterised by its monoacetate, can be easily dehydrated to a doubly unsaturated conjugated lactone (IV) which may be converted to a tetrahydro derivative (V). Merolimonol is cleaved by ozonolysis to give the keto-acid (VI), characterised by its methyl ester, methyl ester acetate and methyl ester oxime. (VI) Gives a positive iodoform test, thus proving the presence of a methyl substituent at C_{13}. Oxidation of merolimonol with manganese dioxide in benzene solution gives the expected ketone (VII) and a decarboxylated derivative (VIII), whose infrared and ultraviolet spectra show the presence of a δ lactone and of an α-β unsaturated γ lactone. Hydrogenation of (VIII) gives the saturated γ lactone (IX) which could also be obtained by hydrogenating merolimonol to dihydromerolimonol and oxidising with pyridine/chromic oxide. Ozonolysis, or alternatively hydroxylation followed by leadtetraacetate cleavage, of (VIII) affords the α-keto-γ-lactone (X) which is a methyl ketone, thus confirming the presence of a methyl group at C_{13}. Furthermore, (X) is a non-enolisable α-keto-γ-lactone[49,50], thus showing that C_8 cannot have a hydrogen substituent (see sections 5 and 6).

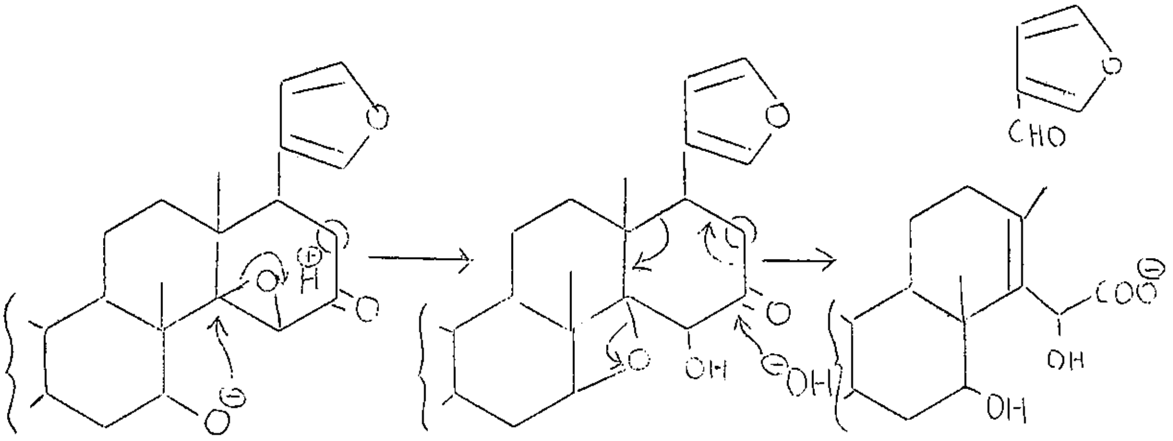
The above series of reactions provide independent evidence (see also section 4) for the relation between C_{14}, C_{15} and C_{16} with C_7 and C_8, and also for the relation of C_{12} and C_{13} with C_{14} etc.

When merolimonol is treated with barium hydroxide under the conditions of formation of limoclastic acid (section 9), it yields an amorphous acid which has been characterised by its crystalline methyl ester (XI). This acid cannot be lactonised, in contrast with the behaviour of limonin. This phenomenon


(I)
18
12
13
17
16
9
8
14
15
7
OH
(VI)
COOH
OH
O3
⊖OH
(III)
CHO
(V)
H2 | Pd
(II)
OH
POCl3 / Py
(IV)
(XI)
COOCH3
CH2OH
HO
1) Ba(OH)2
2) CH2N2
MnO2
MnO2
(XII)
COOCH3
CH2OH
(VIII)
(VII)
1) Ba(OH)2
2) CH2N2
H2 | Pd
CrO3
O3
(XIII)
COOCH3
CHO
(X)
(IX)

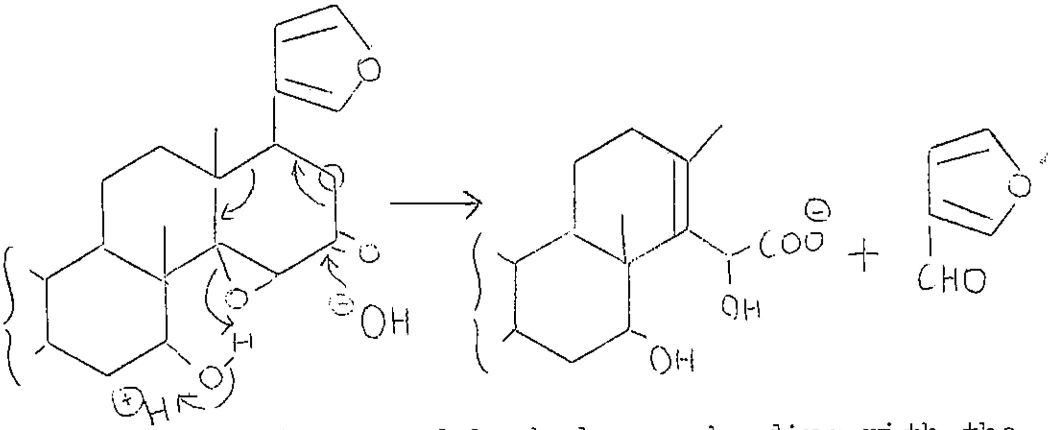
can be explained by postulating that an inversion can occur at C_1 in the course of a reversible β-elimination and addition of the ethereal oxygen of ring A'.(see section 9). Oxidation of (XI) with manganese dioxide gives a γ-lactone (XII) which may also be obtained by baryta cleavage of (VIII) followed by esterification with diazomethane. The hydroxyl function of (XII) can be converted to an aldehyde (XIII) thus showing the position of the terminus of lactone A (see also sections 9,10 and 11).

Two mechanisms have been suggested to explain the formation of merolimonol from limonol. In mechanism (i) below:



the epoxide is opened by a displacement effected by the oxygen of limonol.

In the alternative mechanism (ii):



the epoxide is opened by hydrogen bonding with the hydroxyl of limonol. In both cases alkaline cleavage results in the loss of a five carbon fragment and the production of a hydroxy acid which lactonises on acidification to give merolimonol.

Of the two mechanisms , (i) appears preferable , as a study of a model reveals that an axial hydroxyl group at C_7 is well positioned for this type of displacement , while the formation of a strong hydrogen bond between the epoxide and the axial C_7 hydroxyl appears unlikely.

9. ALKALINE DEGRADATION OF LIMONIN - THE LIMOCLASTIC ACID SERIES

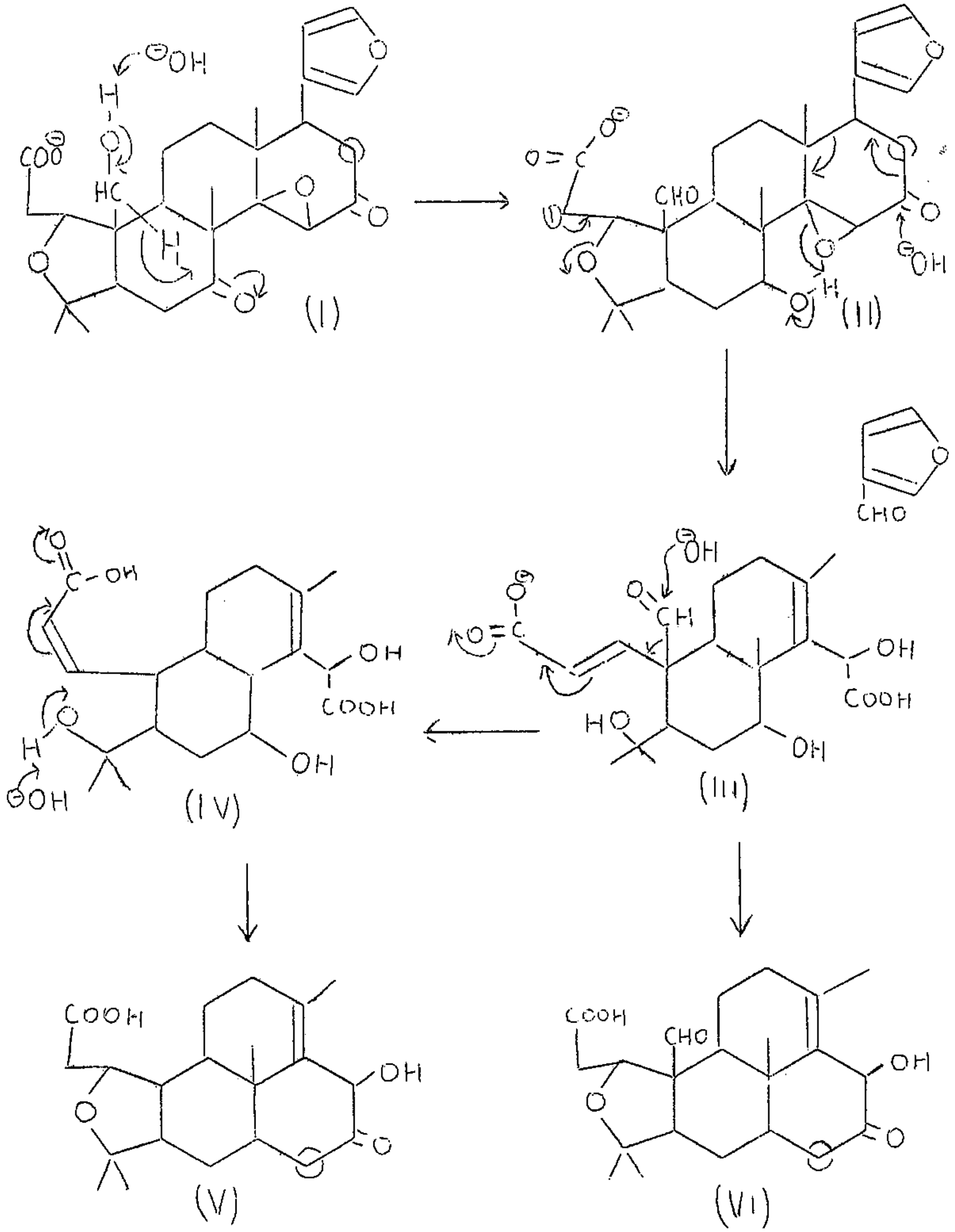
When limonin is treated with barium hydroxide solution under relatively vigorous conditions, an acidic substance is formed of the molecular formula $C_{20}H_{28}O_6$, which was designated as limoclastic acid.

As limoclastic acid appeared to undergo all the reactions characteristic of merolimonol and its derivatives (see below and see section 8), a change analogous to the merolimonol transformation was considered as having taken place during the formation of limoclastic acid. The stoichiometry of the reaction then requires that formic acid must be lost as a minor fragment besides furan-3-aldehyde.

As a reduction of the ketone group of limonin (I) to an alcohol is necessary before a merolimonol type of change could occur, and as the carboxylic acid group of limoclastic acid was considered to be derived from lactone A, it was reasonable to suppose that an intramolecular hydride transfer[52] between the alcoholic group of lactone A and the ketone has taken place, aided no doubt, by favourable stereochemical configuration. This gives a limonol-type compound (II), in which the ether ring A' could be reversibly opened to provide an electron sink for a conventional deformylation in the form of an α-β unsaturated acid (III). Such a compound could also undergo the merolimonol change to give (IV) and finally, a re-closure of ring A' was postulated (see sections 11e and 15b) to give limoclastic acid formulated as (V). Support for the above scheme was obtained when an aldehyde corresponding in all its properties to (VI) was also isolated as a minor product of the reaction.

Limoclastic acid undergoes the following series of reactions which confirm structure (V) assigned to it and are closely analogous to the reactions of merolimonol (see section 8).

The methyl ester of limoclastic acid (V) may be dehydrated to an anhydro-derivative (VII), which on hydrogenation followed by hydrolysis furnishes the tetrahydro acid (VIII). The monoacetate of methyl limoclastate also furnishes an analogous dihydro derivative.

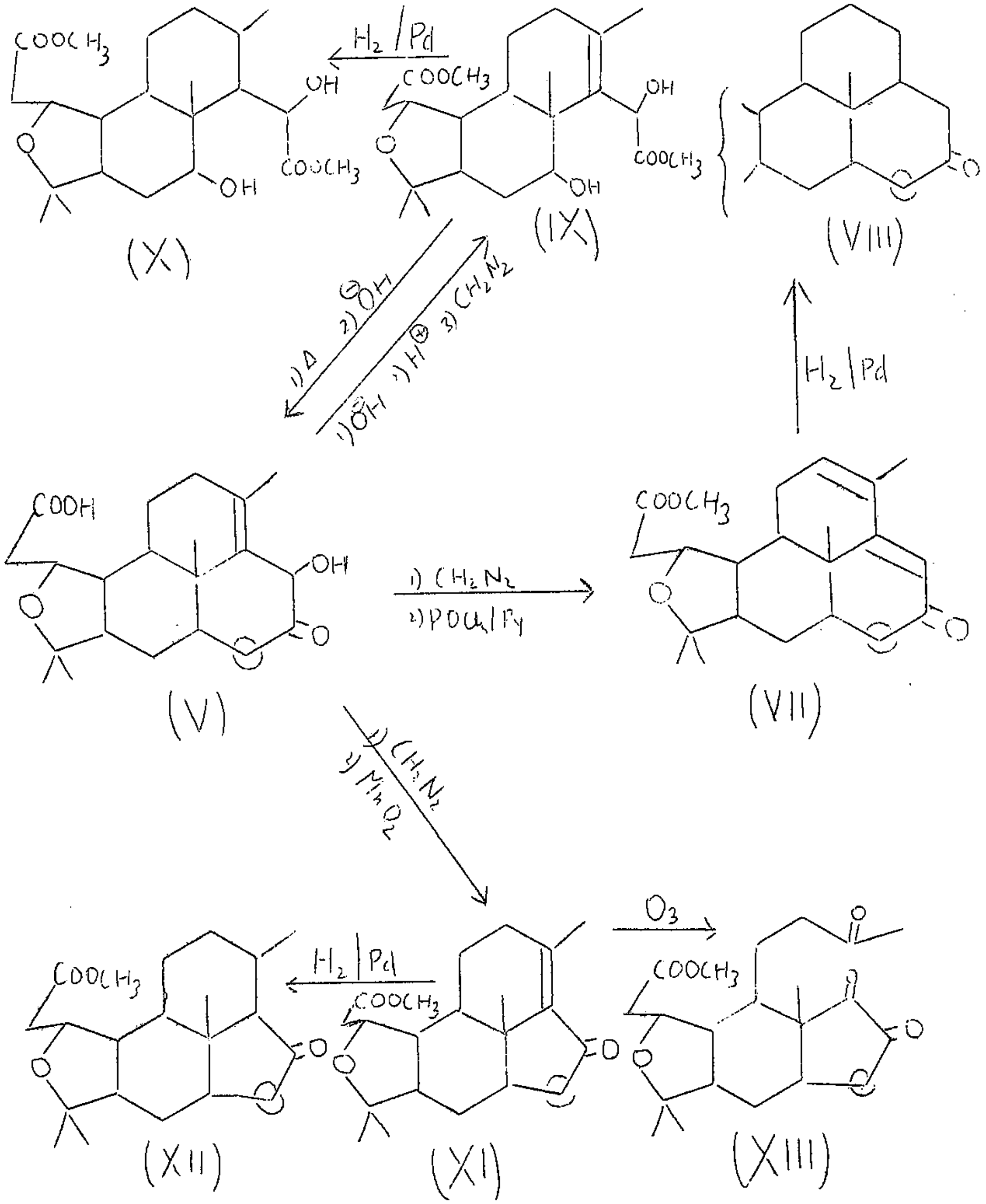


⊖OH
COO⊖
HC
H
(I)
O=C-O⊖
CHO
⊖OH
(II)
CHO
⊖OH
O=C-O⊖
CH
OH
COOH
HO
OH
(III)
C-OH
OH
COOH
OH
⊖OH
(IV)
COOH
OH
O
(V)
COOH
CHO
OH
O
(VI)

Alkaline hydrolysis of limoclastic acid and esterification prior to lactonisation gives a diester (IX) , characterised as a mono-acetate, and capable of being converted to methyl limoclastate on gentle pyrolysis. Hydrogenation of (IX) yields a saturated dihydro derivative (X), characterised as a diacetate.

Oxidation of methyl limoclastate with manganese dioxide gives the nor compound (XI), which can be converted to the saturated γ-lactone (XII) by hydrogenation. Ozonolysis of (XI) gives an α-keto-γ-lactone (XIII) which gives a positive iodoform test , but does not enolise.

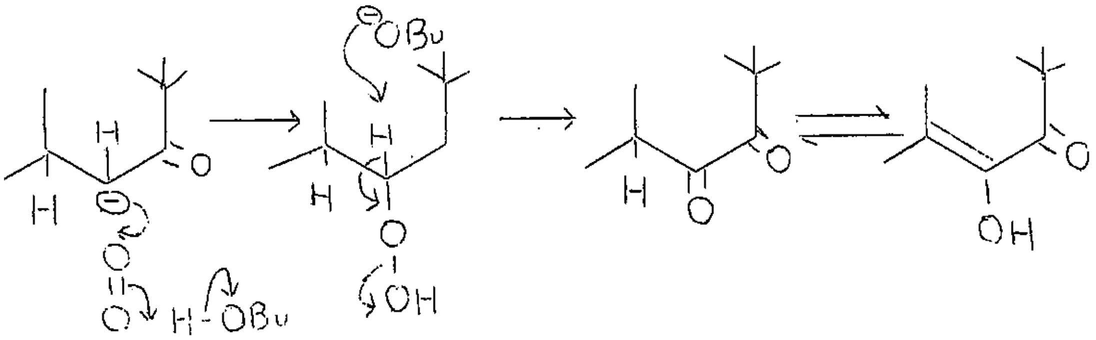
The chemistry of limoclastic acid confirms all the conclusions reached on the basis of the chemistry of merolimonol and in addition provides independent evidence for the nature of the alcoholic group of lactone A (primary) and - if the genesis of limoclastic acid is considered as proceeding by the mechanism outlined above - also gives a unique relationship between C_1,C_2,C_3 and C_{10} and the ether group of ring A'.


COOCH3
OH
OH
COOCH3
(X)
H2 / Pd
COOCH3
OH
COOCH3
OH
(IX)
(VIII)
1) Δ 2) ⊖OH
1) ⊖OH 2) H⊕ 3) CH2N2
H2 | Pd
COOH
OH
(V)
1) CH2N2
2) POCl3 / Py
COOCH3
(VII)
1) CH2N2
2) MnO2
O3
COOCH3
H2 | Pd
COOCH3
COOCH3
(XII)
(XI)
(XIII)

10. THE METHYLENE GROUP ADJACENT TO THE KETONE CARBONYL - THE DIOSPHENOLS AND THEIR DEGRADATION

Limonin, tetrahydrolimonin and desoxylimonin have been shown[53] to undergo analogous reactions with oxygen in the presence of potassium tertiary butoxide , resulting in the uptake of one atom of oxygen and the loss of two atoms of hydrogen. The ultraviolet spectra of the products are characteristic[54] of diosphenols , e.g. limonin diosphenol has λ_{max} at 282 mμ (ε:10,400) , which changes to λ_{max}: 335 mμ (ε:5,000) in the presence of alkali. The infrared spectrum , which shows bands at 3480 cm^{-1} (hydroxyl) 1748 cm^{-1} and 1736 cm^{-1} (δ lactones) and at 1689 cm^{-1} and 1661 cm^{-1} (the system -CO-C(-OH)=C), also agree with the presence of such a feature. The diosphenols derived from limonin dissolve in sodium hydroxide solutions but not in sodium bicarbonate solutions and give positive colour tests with ferric chloride. Neutral monoacetates of the diosphenols were prepared in the usual manner and showed no hydroxyl bands in their infrared spectra. The ultraviolet spectrum of the acetate of the diosphenol derived from limonin itself showed a maximum at 244 mμ (ε: 11,200).

The following mechanism has been postulated for the formation of diosphenols under the conditions described above:



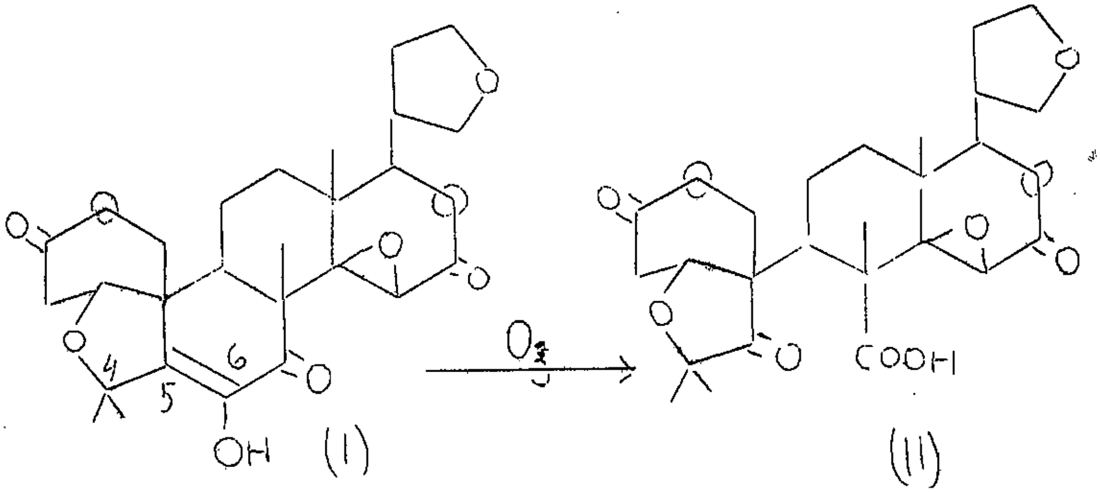
This novel reactions has since been extended to other systems[53] containing a methylene group adjacent to a ketonic carbonyl.

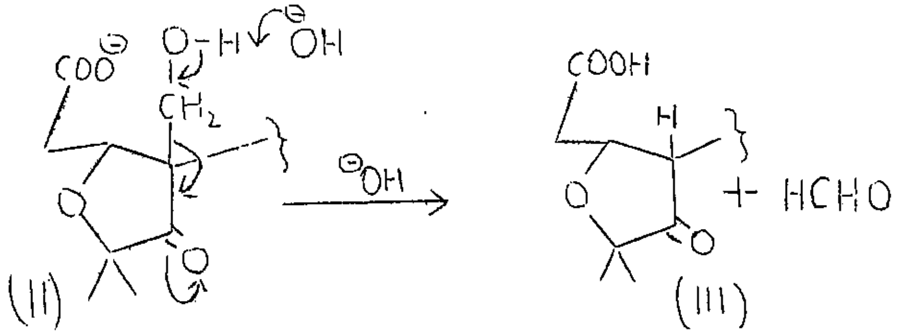
The occurence of this reaction provided evidence for the presence of a methylene group at C_6 , α- to the ketone in limonin, and of at least one (from the position of the maximum in the ultraviolet , of only one) hydrogen in the β- position at C_5. Thus on the basis of the above evidence, and considering the nature of desoxylimonic acid (see sections 4 and 5) , limonin should have two hydrogen atoms activated by the presence of the ketonic carbonyl , which is in agreement with early deuturation studies[39,40].

The diosphenol derived from tetrahydrolimonin , which on the basis of the above was assigned the structure (I), yields a keto-acid on ozonolysis, which analyses well for (II) and is accordingly a dilactone monocarboxylic acid. The infrared spectrum (bands at 1760,1735,1725(sh)cm^{-1}) and the ultraviolet spectrum (λ_{max}:296mμ , ε:35) of this substance also agree with the structure assigned. The infrared spectrum of the tri-sodium salt of (II) shows a single band at 1748 cm^{-1} as compared with a band at 1690 cm^{-1} for the di-sodium salt of limonin. This can be interpreted as indicating the presence of a ketone group in a five membered ring with a negative (oxygen) substituent in the α position.

As expected, (II) reacts with zinc and acetic acid , but no crystalline derivative could be isolated.

On action of mild alkali, (II) undergoes a retro-aldol reaction [55] by the mechanism shown below, to give significant quantities of formaldehyde and an amorphous acid, presumably (III).





The de-formylation reaction of (II) provided evidence for the nature (primary hydroxyl) and mode of attachment of the alcoholic oxygen of lactone A (see also sections 9 ,11 and 12), although it did not exclude C_4 as a possible position for attachment of the $-CH_2OH$ group.

11. LIMONILIC ACID AND ITS DERIVATIVES

a. The structure of limonilic acid

Oxidation of limonin with potassium manganate[21] or with iodine and alkali[29], yields limonilic acid, $C_{26}H_{30}O_9$, which is a monolactone monocarboxylic acid and retains the ketonic function of limonin[21]. A tetrahydro analogue has also been prepared, either by hydrogenation of limonilic acid or by the action of iodine and alkali on tetrahydrolimonin[21,29,40,43].

No hydroxyl groups, additional unsaturation or new carbonyl groups have been generated by the transformation of limonin into limonilic acid, as shown by the following evidence:

(i). The infrared spectrum of methyl limonilate shows no bands attributable to hydroxyl groups[43].

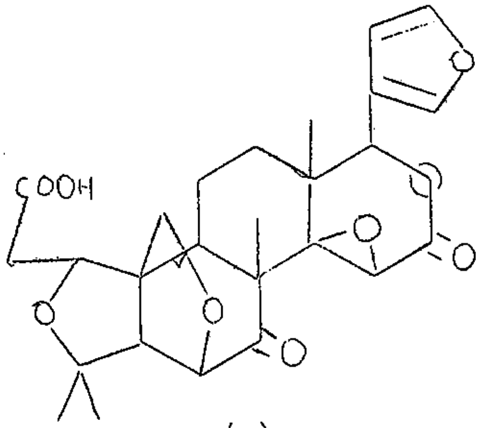
(ii). There is no evidence for the presence of double bonds in tetrahydrolimonilic acid, i.e. it does not take up hydrogen in the presence of palladium-carbon and its ultraviolet spectrum shows only very small end absorption, while its infrared spectrum shows no bands between 1690 and 1500 cm^{-1} [43].

(iii). The ultraviolet spectrum of methyl limonilate oxime shows no carbonyl band[43] and the NMR spectrum of methyl limonil~~l~~ate[46] shows no aldehyde protons.

The behaviour of methyl limonil~~l~~ate[29] on hydrogenation was analogous to that of limonin (see section 1) , a neutral tetrahydro and an acidic hexahydro derivative being formed, showing that the furan ring was not involved in the limonilic acid transformation and that the carboxylic acid group of limonilic acid was derived from lactone A rather than from lactone D. This was confirmed by Emerson[29], who showed that hexahydrolimoninic acid reacted with iodine and alkali to give a diacid identical with the acidic product of hydrogenation of methyl limonilate followed by hydrolysis. The formation of a desoxy compound from limonilic acid[43] (see section 2a) provides further evidence that lactone D was not involved in the formation of limonilic acid.

The ketonic group of limonilic acid is

of a different type than that present in limonin: The ultraviolet spectrum of limonilic acid[43] showed a maximum at 309 mμ (ε:37) as compared with limonin (λ_{max}:285 mμ , ε:33). In the present work, the comparison of the infrared spectra of limonilic acid, tetrahydrolimonilic acid, limonilyl chloride and methyl limonilyl ketone (see below) with those of limonin and its simple derivatives tetrahydrolimonin and hexahydrolimoninic acid, indicated that the carbonyl absorption band due to the ketone carbonyl in limonilic acid and its simple derivatives occurs near 1722 cm^{-1} as compared with 1709 cm^{-1} for limonin and its simple derivatives. The nature and magnitude of these spectral changes is in accord with the presence of an α-negative (i.e. oxygen) substituent in limonilic acid ketone. The sodium salts of limonin and limonilic acid , where only the ketonic absorption remains in the carbonyl region, also showed marked



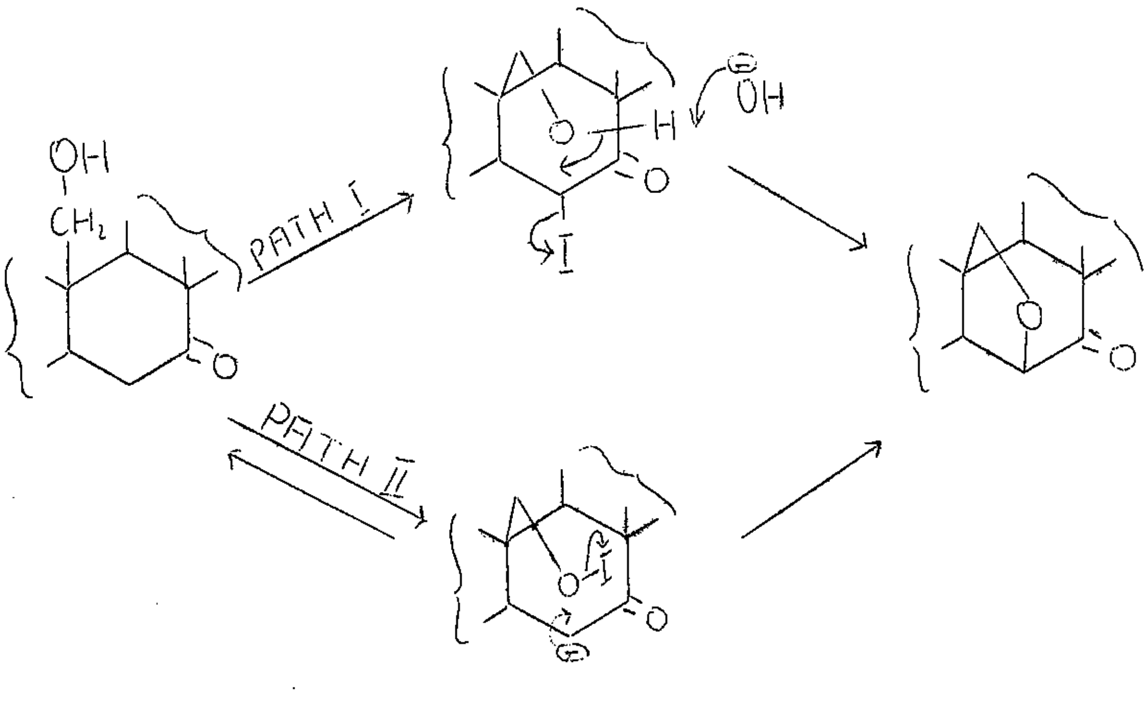
(1)

differences in the frequency of the carbonyl band , which occured at 1690cm^{-1} and 1717cm^{-1} respectively. Failure of desoxylimonilic acid to undergo the desoxylimonic acid change (see section 4) also indicates that the environment of the ketone was altered by the limonilic acid transformation , while the failure of desoxylimonic acid and of epi-limonol to react with iodine and alkali indicates that the presence of the ketonic carbonyl group is essential for the reaction[43]. Furthermore, it was shown[43] that the oxime of limonilic acid was much more difficult to prepare than that of limonin and that limonilic acid does not not undergo the diosphenol reaction (see section 10).

The above evidence indicates that the limonilic acid transformation involves the condensation of the hydroxyl group derived from hydrolysis of lactone A with a carbon α to the ketone group, to form a new ether ring. In view of the structure of limonin , limonilic acid may thus be represented by structure (I). Strong confirmation of this was obtained , when it was found that limonilic acid could be reduced back to limonin by the action of aluminium amalgam[46] or lithium amalgam[53].

This formulation of the limonilic acid transformation placed obvious steric restrictions on the structure of limonin, thus excluding many possible structures.

The limonilic acid change appears to be a novel reaction without precedent in the literature, probably made possible only by the unusual steric arrangement present in limonin. The reaction mechanism may involve either an initial iodination of the ketone (path I) or a carbanion displacement at the "alkyl hypoiodide" (path II). The latter mechanism is supported by the extreme rapidity of the reaction.



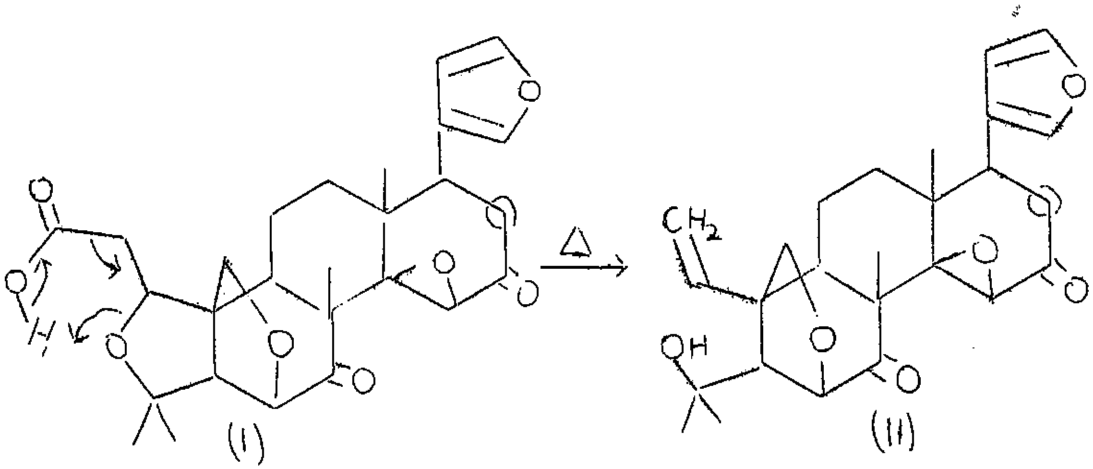
b. Rate of hydrolysis of methyl limonilate

The rate of alkaline hydrolysis of methyl limonilate relative to those of the methyl esters of some model primary, secondary and secondary α-oxygen substituted acids was measured by Templeton[53], sufficient precautions for complete hydrolysis of lactone D being taken. The hydrolysis rate of methyl limonilate was found to be close to those of secondary and secondary α-oxygenated esters but considerably slower than that of a primary ester. This misleading result may be due to steric hindrance by more removed groups in limonin.

c. Decarboxylation of limonilic acid

Emerson[29] observed that limonilic acid lost carbon dioxide at its melting point. Templeton[53] isolated two crystalline compounds from the action of heat alone or boiling quinoline on limonilic acid. One of these has been characterised as $C_{25}H_{30}O_7$, a neutral monolactone retaining the ketone and furan functions and in addition containing a hydroxyl group. (Bands in infrared at 3340,1742,1715,1500 and 875cm^{-1}, λ_{max}:306-12 , ε:43 and λ_{max}:208 , ε: 7,000).

The unsaturated alcohol (II) was postulated as the structure of this compound , which could be derived from limonilic acid (I) in the following manner (see also section 16):



Although no direct evidence of unsaturation could be obtained (negative TNM test, lack of absorption larger than that due to furan in the ultraviolet) , the compound gave a dihydro derivative on hydrogenating over palladium carbon , which retained the furan function. The hydroxyl group of (II) proved unreactive to acetylation and oxidation with chromic oxide in pyridine.

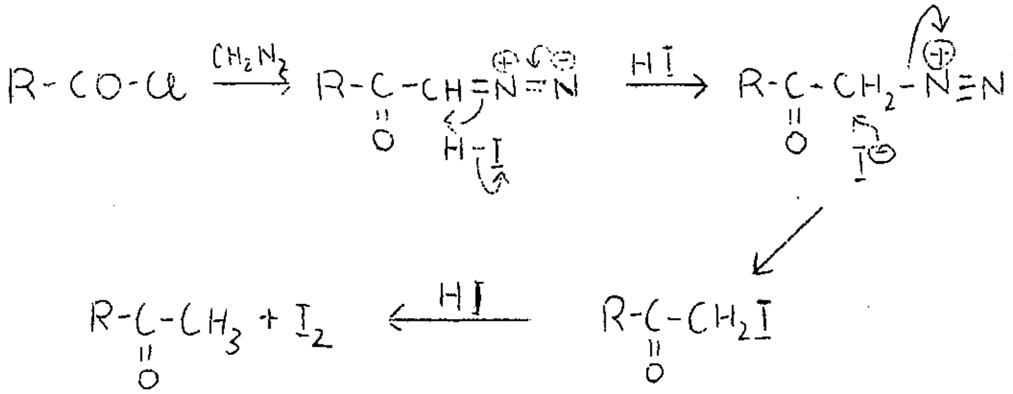
d. Preparation and properties of methyl-limonilyl ketone

A Bayer-Villager degradation of limonilic acid via methyl-limonilyl ketone (see below) was envisaged in the course of the present work, but the difficulty of obtaining the tetrahydro analogue of methyl-limonilyl ketone caused the project to be abandoned.

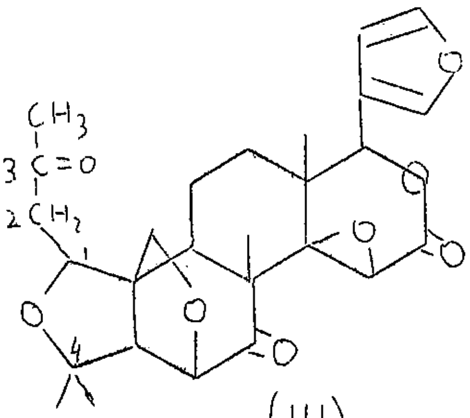
Methyl-limonilyl ketone itself was prepared successfully and its properties can be shown to fit in with the accepted structure of limonin and limonilic acid.

The acid chloride of limonilic acid (limonilyl chloride) was prepared in the usual manner and its infrared spectrum showing bands at 1791 cm^{-1} (acid chloride), 1740 cm^{-1} (δ lactone) and 1722 cm^{-1} (ketone bearing an α-oxygen substituent), as well as its reaction with methanol to give methyl limonilate were accepted as proof of its structure.

Limonilyl chloride was then converted to methyl-limonilyl ketone by the following series of reactions[56,57]:



The properties of methyl-limonilyl ketone, $C_{27}H_{32}O_8$, agree with structure (III). Thus its ultraviolet spectrum shows an extended low intensity (ε: approx.50) peak between 288 and 310 mμ and a high intensity peak at 207 mμ (ε:7,000 , furan). Its infrared spectrum shows discrete bands at 1735 cm^{-1}(δ lactone), 1722 cm^{-1}(ketone with an α-negative substituent) and 1712 cm^{-1} (methyl ketone). The position of the new maximum in the ultraviolet and the new carbonyl band in the infrared (1712 cm^{-1} both in Nujol and in chloroform) agree with the absence of an α- oxygen substituent at C_2 (see derivation of structure, section 13b).



(III)

Methyl-limonilyl ketone gives an instantaneous iodoform test ; the main acidic product could not be crystallized but its infrared spectrum is very similar to that of the expected limonilic acid. As expected, methyl-limonilyl ketone failed to react with zinc and acetic acid in accordance with the absence of a new, α oxygen substituted ketone (see above). However, this piece of negative evidence is of very doubtful value , as limonilic acid itself also failed to react with zinc and acetic acid[43].

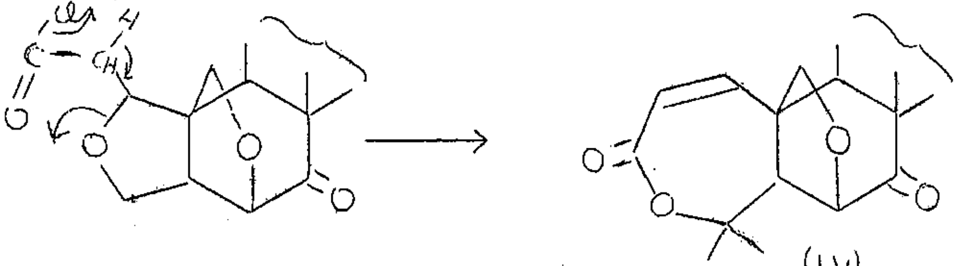
Although (III) would be expected to undergo β-elimination with alkali , methyl-limonilyl ketone was recovered unchanged from 1N aqueous sodium hydroxide solution after several hours heating. This can be easily explained , when the position of equilibrium between obacunoic and iso-obacunoic acids is considered (see section 15.b.iv).

The formation of a monobenzylidine derivative was indicated by the development of absorption at 293 mμ (ε:3,000) in an alkaline solution of methyl-limonilyl ketone and benzaldehyde.

An alternative method of preparation of methyl-limonilyl ketone via a malonic ester synthesis was also investigated with partial success (see relevant experimental section).

e. Pyrolysis of limonilyl chloride

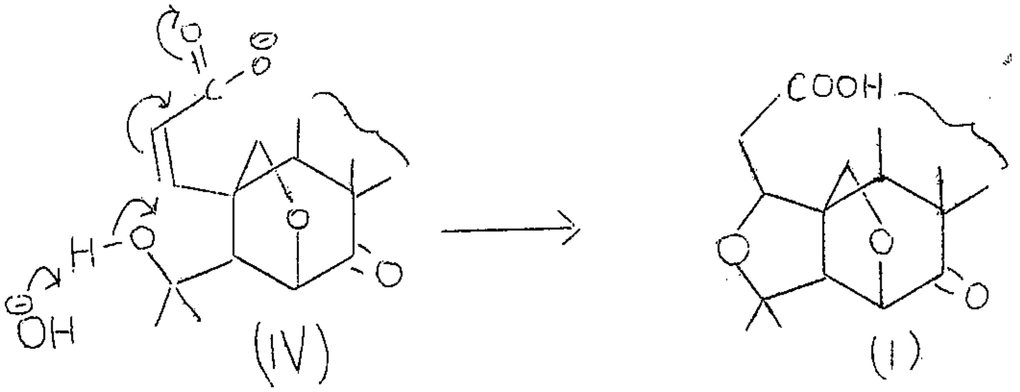
In the course of the present work, it was found that limonilyl chloride (see above) lost hydrogen chloride on heating to about 230°C , giving rise to a neutral , amorphous dilactone which could be converted to an amorphous acid by mild alkali. On more prolonged treatment with alkali , limonilic acid was obtained. The ultraviolet spectrum of the crude lactone showed a peak at 207 - 10 mμ (ε:13,000) and on subtraction of the spectrum of methyl-limonilyl ketone a peak remained at 210-15 mμ (ε:6,500). The infrared spectrum of the crude lactone showed bands at 1750, 1715,1505 and 875 cm^{-1} thus possibly indicating the presence of a δ lactone, an unsaturated lactone and ketone and of the furan ring. No hydroxyl bands were present.



(IV)

Although the failure to obtain crystalline products makes accurate interpretation of the results impossible, the formation of a seven membered, α-β unsaturated lactone (IV) by the mechanism illustrated above agrees with the experimental results available.

The lactone (IV) could then be converted to limonilic acid under the influence of alkali in the following manner:



The close analogy of this reaction to the mechanism proposed for the formation of limoclastic acid (see section 9) and iso-obacunoic acid (see section 15) , makes this mechanism very attractive.

12. THE STRUCTURE OF CITROLIN

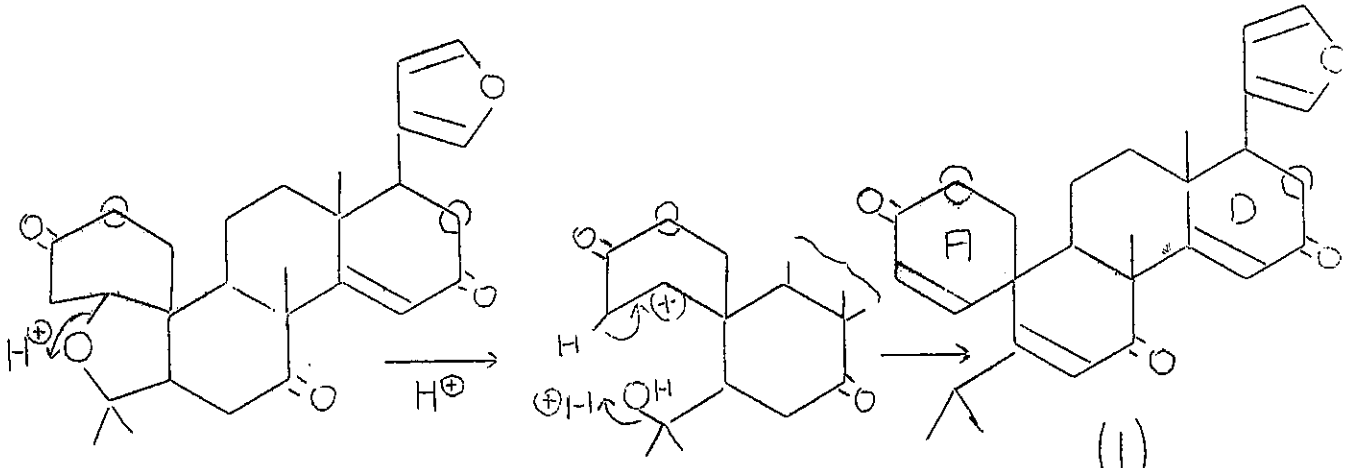
Citrolin has been obtained by the action of hydroiodic acid on limonin[21,29,39,40] and by the action of hydroiodic acid on desoxylimonin[39]. In the course of the present work, it was shown that citrolin may also be obtained by the action of hydrobromic acid on desoxylimonin.

Although the analytical data published are conflicting, the best results [29,39] indicate that citrolin has the formula $C_{26}H_{28}O_6$, i.e. that it is formed by the loss of a molecule of water from desoxylimonin $C_{26}H_{30}O_7$. The validity of the above formula received further support when citrolin was prepared by the action of hydrobromic rather than hydroiodic acid i.e. under conditions which would not normally lead to a reduction of the type which is involved in the formation of desoxylimonin from limonin (see section 2a).

Citrolin is a neutral dilactone retaining the furan and ketone functions[21,29,39]. Emerson[29] showed that citrolin contains at least four double bonds on the basis of hydrogenation experiments , but no crystalline derivatives could be isolated. Citrolin has been shown to contain all the four methyl groups present in limonin[40] as determined by NMR measurments (present work).

The ultraviolet spectrum of citrolin shows a maximum at 213.5 mμ (ε:25,200) and a shoulder near 240 mμ (ε:18,500). When the spectrum of desoxylimonin is subtracted from the spectrum of citrolin, two maxima appear at 213.5 mμ (ε:9,500) and at 241mμ (ε:13,700). The infrared spectrum of citrolin shows a large band at 1724-16 cm^{-1} and a smaller band at 1670 cm^{-1} as compared with bands at 1746 cm^{-1} and 1715 cm^{-1} for desoxylimonin.

The above data indicate that citrolin has two α-β unsaturated lactones and an α-β unsaturated ketone. Having regard for the structure of desoxylimonin (section 2a), structure (I) was proposed for citrolin , which may be formed from desoxylimonin by the following mechanism:



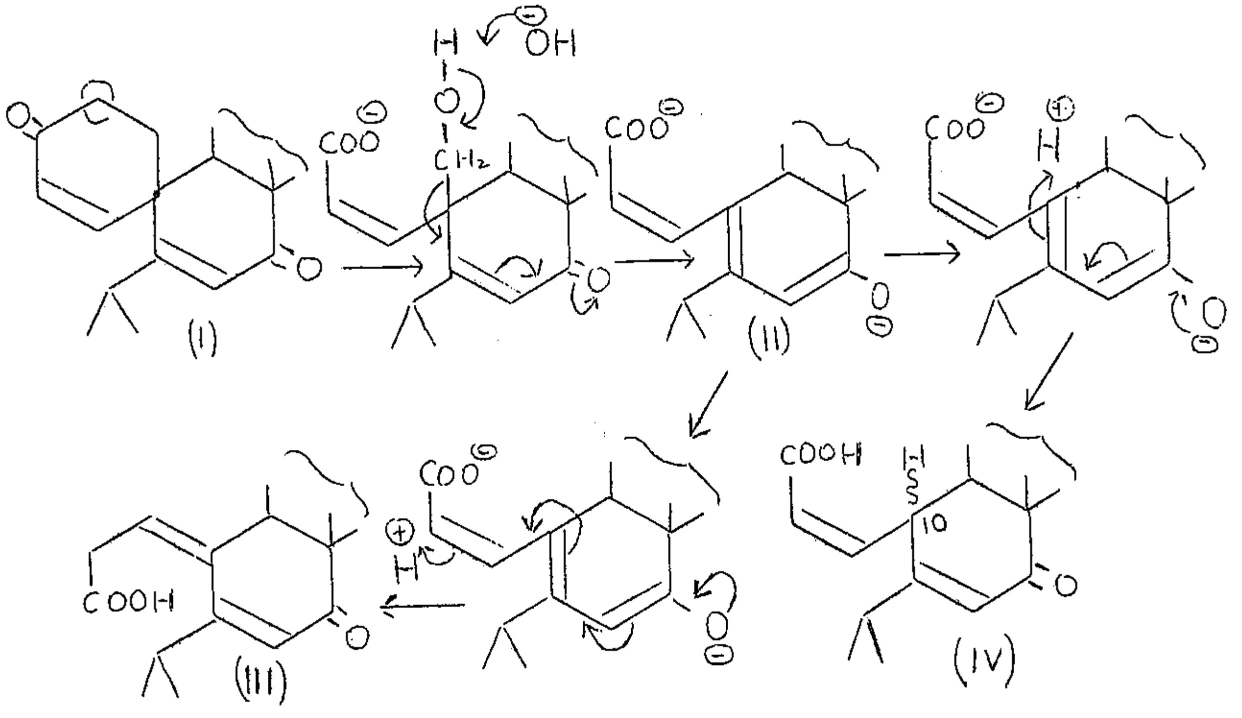
(I)

Hydrogenation experiments carried out in the course of the present work further confirm structure (I). A neutral dihydro derivative , $C_{26}H_{30}O_6$ was isolated following hydrogenation of citrolin over palladium-carbon. The ultraviolet spectrum of this substance (λ_{max}:216 mμ, ε:17,200 and shoulder near 231-43 mμ , ε:14,700) together with the presence of BANDS at 1757,1713 and 1668 cm^{-1} in the infrared and the furan bands, indicate that one of the two α-β unsaturated lactones has been hydrogenated. In confirmation , when the ultraviolet spectrum of desoxylimonin was subtracted from that of dihydrocitrolin, only a single peak remained at 248 mμ (ε:10,600).

The α-β unsaturated lactone of desoxylimonin was not hydrogenated under similar conditions (see preparation of tetrahydrodesoxylimonin) and the ultraviolet spectrum of dihydrocitrolin remained unaltered in the 280 mμ region on heating with 2N alkali (see below) , indicating that it was the lactone A which was hydrogenated.

A further neutral crystalline substance was isolated as a minor product of hydrogenation of citrolin . The infrared spectrum of this material was similar in the carbonyl region (bands at 1753, 1698 and 1663 cm^{-1}) to that of dihydrocitrolin, but the furan bands were no longer present. The ultraviolet spectrum showed a maximum at 238 mμ (ε:13,700) and a shoulder between 222 and 230 mμ (ε:13,000). These features indicate that this product differs from dihydrocitrolin only in the saturation of the furan ring , i.e. that it is hexahydrocitrolin. Unfortunately insufficient sample was available for elementary analysis.

Citrolin is unstable to alkali[29] yielding formaldehyde[53] and acidic products[40] which retain the ultraviolet spectrum of citrolin and analyse for "deformylated" materials $C_{25}H_{28}O_6$. Two such acids were obtained by Corey[40]. Under more severe conditions (heating with 2N alkali), citrolin gave rise to an acidic compound whose ultraviolet spectrum showed a maximum at 286-8 mμ[53] but which could not be obtained in a crystalline form. Phillips[39] isolated an acid of this kind, which showed two maxima in the ultraviolet spectrum (at 214 mμ, ε:14,000 and at 280 mμ , ε:5,000) and had bands in the infra-red spectrum near 1720,1687,1630 and 1608 cm^{-1}. The formation of all these products can be adequately explained by the scheme shown below:

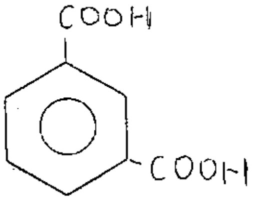


Thus , depending on the position of protonation of the transition state (II) one can obtain either a dienone (III) or an α-β unsaturated ketone not conjugated with an α-β unsaturated acid (IV). The structure (IV) which should correspond to the acids isolated by Corey[40] would be expected to show isomerism depending on the configuration at C_{10}.

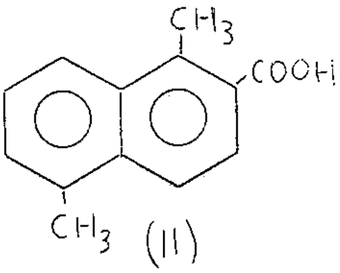
13A. MISCELLANEOUS REACTIONS OF LIMONIN AND ITS DERIVATIVES

a. Potassium hydroxide fusion

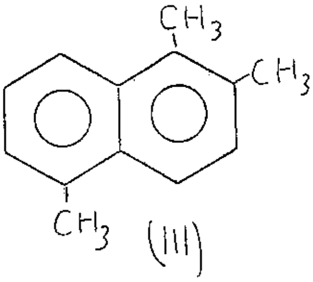
Potassium hydroxide fusion of limonin[20,24] yielded *iso*-phthalic acid (I) and a "lactone"[24] of composition $C_{13}H_{14}O_2$ or $C_{13}H_{12}O_2$ which is probably identical with 1:5dimethyl-2-naphthoic acid (II), also obtained from potash fusion of columbin[42]. Acetone, in yields of up to 0.7 mole , was also identified as one of the products of potassium hydroxide fusion of limonin[20,24,21,29] and also of limonilic and hexahydrolimoninic acids[29]. The formation of (I) cannot be easily explained in terms of the accepted structure of limonin , but (II) could be easily derived from rings B and C while the high yield of acetone provided some evidence for the substitution at C_4.



(I)



(II)



(III)

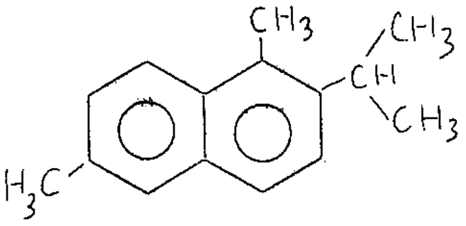
b. Selenium dehydrogenation

Selenium dehydrogenation of the non-volatile residue of potassium hydroxide fusion [20] or of zinc distillation residue[24] of limonin, gave 1:2:5:trimethyl naphthalene (III), probably derived from rings B and C of limonin.

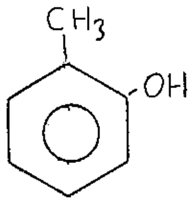
Selenium dehydrogenation of merolimonol or limoclastic acid[35,46] gave a naphthalene $C_{15}H_{18}$ which has been tentatively identified as 1:6:dimethyl-2-*iso*propyl naphthalene (IV). The identification of this compound provided direct evidence for the presence of the *iso*propyl group in limonin.

c. Zinc dust distillation

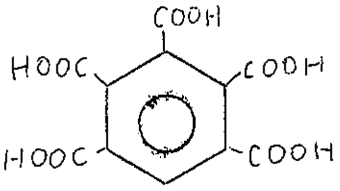
The only identifiable product of zinc dust distillation[24] of limonin , was *o*-cresol (V), probably derived from ring B of limonin.



(IV)



(V)



(VI)

d. Oxidation with manganese dioxide and sulphuric acid

Koller and Czerny[20] isolated benzenepentacarboxylic acid (VI) by oxidation of limonin with manganese dioxide and sulphuric acid. To obtain this product from limonin, methyl migrations must be postulated. There is some precedent[58] for the appearance of too highly substituted benzene carboxylic acids by oxidation under strongly acidic conditions.

e. Lithium aluminium hydride reduction

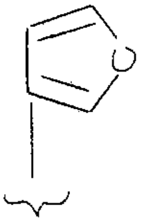
Jeger and his co-workers[35,46] isolated a product which still contained the furan function, from lithium aluminium hydride reduction of limonin and which appeared to be a heptol on the basis of the number of active hydrogens remaining in the tetra- and penta-acetates derived from it. This indicated that both the ether functions could be reductively cleaved and in view of the established structure of limonin , the cleavage of the ring A' ether can only be explained as due to the assistance of the β-carbonyl function of lactone A. The mechanism of such an assistance cannot be easily visualised.

There is no Page 82 in the thesis.

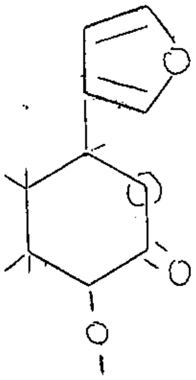
13B. SUMMARY OF CHEMICAL EVIDENCE FOR THE STRUCTURE OF LIMONIN

As already indicated in the introduction, a rigid derivation of the structure of limonin from chemical evidence alone was not attempted in the present work. In this section a brief summary will be presented of the way in which the accepted structure of limonin was in fact postulated on the basis of chemical evidence, prior to the results of the X-ray crystallographic analysis becoming known.

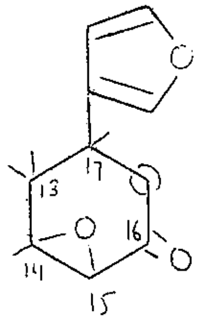
Spectroscopic and other evidence (section 1a) enables us to assign the β-mono substituted furan ring (I) as a part structure of limonin. The results of the hydrogenolysis experiments and the nature of hexahydrolimoninic acid (section 1b) makes it possible to expand this to structure (II):



(I)

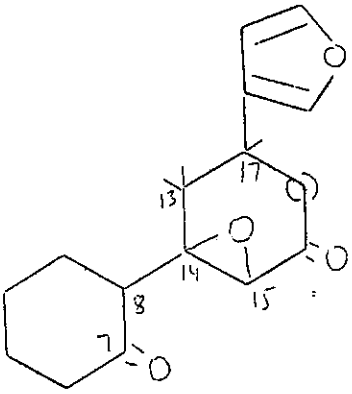


(II)

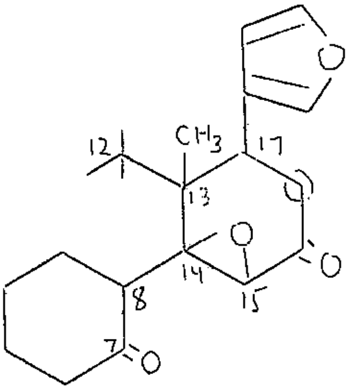


(III)

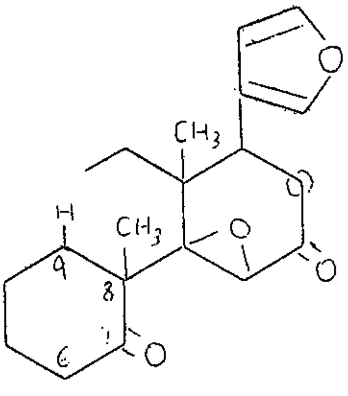
The nature of the negative substituent at C_{15} and the degree of substitution at C_{14} and C_{15} is revealed by experiments described in section 2, thus enabling us to write (III) as a partial structure of limonin. This can be further expanded to (IV) on the basis of interpretation of the formation of desoxylimonic acid (section 4). The nature of substitution at C_{15},C_{14} and possibly C_{13} is also confirmed by the transformations of hexahydrolimoninic acid with acid (section 6). The formation of merolimonol (section 8) and the properties of its degradation products gave a further independent proof of the relation between the lactone ring D and the ketone at C_7 and furthermore revealed the nature of substitution at C_{13} and C_{17} and the presence of carbon at C_{12}, thus yielding the expanded partial structure (V).



(IV)



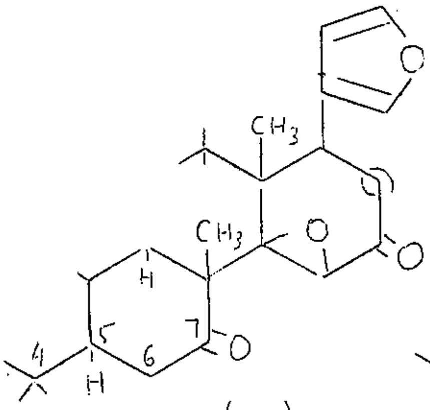
(V)



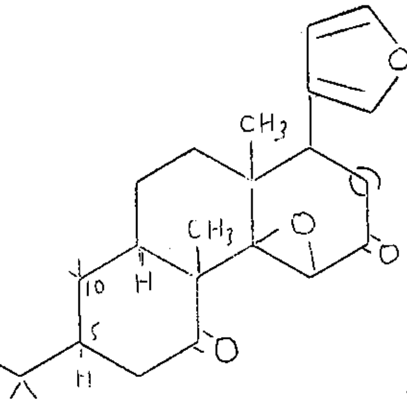
(VI)

This may be further expanded to (VI) from the consideration of the nature of degradation products of tetrahydrodesoxylimonic acid (section 5).

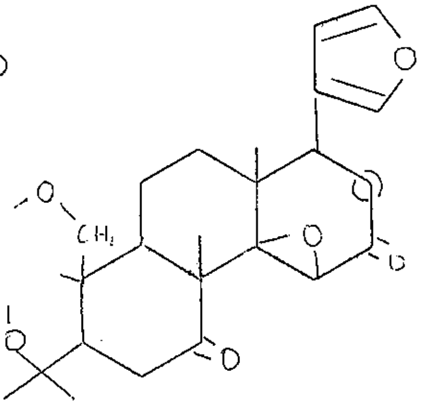
The nature of substitution at C_6 and the presence of hydrogen at C_5 and carbon at C_4 was revealed by the formation of limonin diosphenols (section 10) thus giving the partial structure (VII). The bicarbocyclic nature of limonin and the presence of several naphthalene derivatives among the drastic degradation products of limonin (section 13A) allows us to expand (VII) into (VIII).



(VII)



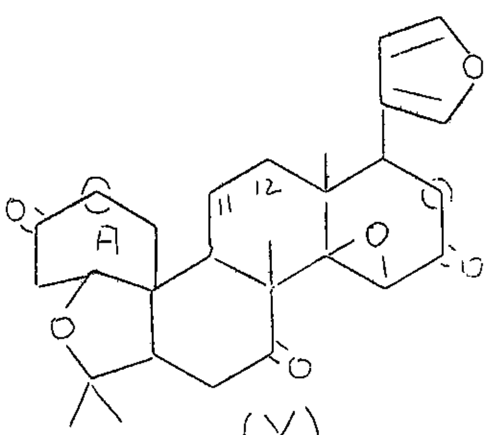
(VIII)



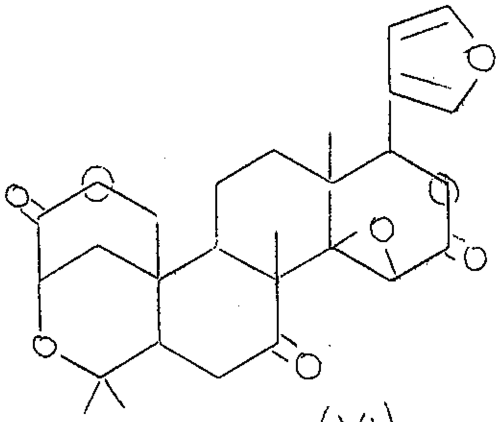
(IX)

The alkaline degradation of the ozonolysis products of tetrahydrolimonindiosphenol (section 10), the formation of limonilic acid (section 11) and the alkaline degradation of citrolin (section 12) indicate that the group $-CH_2OH$, the terminus of lactone A, is placed either at C_{10} or at C_4. This, together with the formation of <u>iso</u>propyldimethyl naphthalene and of acetone , by drastic degradation of limonin made structure (IX) extremely attractive.

Given the fact that lactone A is a δ lactone and considering the formation of citrolin (section 12), (IX) was expanded into either (X) or (XI):



(X)



(XI)

Of these two structures (X) was favoured as it provided a plausible mechanistic basis for the formation of limoclastic acid (section 9) and also was more in accord with the nature of some degradation products of limonilic acid (section 11), and the limonin diosphenols (section 10). The main reasons why (X) could not be considered rigidly derived were: a)lack of evidence for the primary nature of limonilic acid, b) lack of knowledge about substitution at C_{11} and C_{12}.

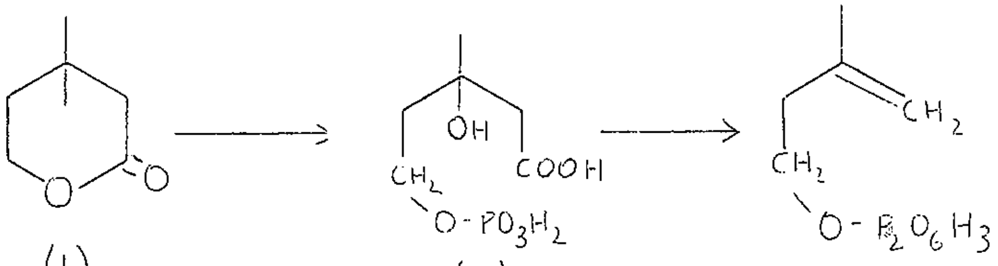
14. BIOGENESIS OF LIMONIN

a. Biogenesis of triterpenes

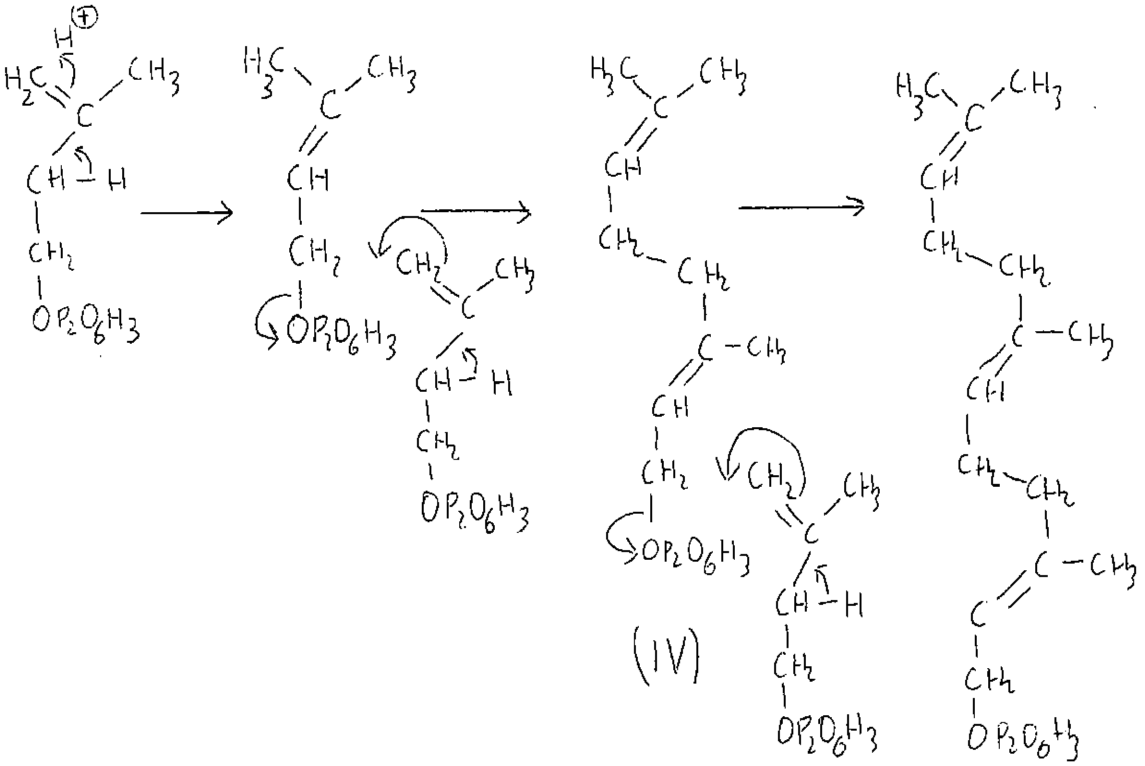
Regularities of structure among the terpenes were noted in the last century and , in fact, the simple "isoprene rule" holds for a considerable proportion of terpenes known[59].

Serious attempts to elucidate the biosynthesis of natural products in the living organisms date from the introduction of tracer analysis. The mechanism of biosynthesis has attracted considerable attention, has been reviewed recently[60,61] and has also been the subject of an international symposium[62].

Briefly, present knwoledge indicates that the precursor of the five carbon ("isoprene") fragment is mevalonic lactone (I) which is in turn derived from acetate units by a process whose details are unknown[63,64,65]. Mevalonic lactone is then converted by phosphorylation to (II) and then by decarboxylation and further phosphorylation to iso-pentenyl pyrophosphate (III) from which geranyl pyrophsophate (IV) and farnesyl pyrophsophate (V) may be derived as shown.[66]



(I) (II) (III)



(IV) (V)

Further condensations could lead to geranyl-geraniol and squalene and hence by cyclisation[60] to mono-, sesqui-, di-, and triterpenes as well as steroids[62]. It should be noted that the SN2 reactions indicated may in fact proceed by a different mechanism.

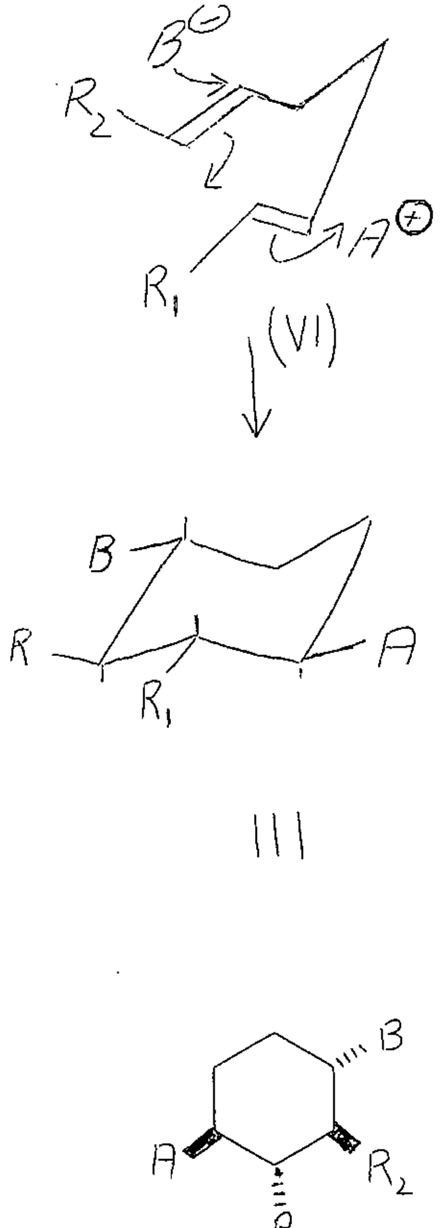
The experimental evidence for this scheme consists of isolation of readioactive terpenes and steroids , as well as of the abovementioned intermediates, from biological systems into which labelled acetate or mevalonic lactone were introduced. Degradation of the various products obtained showed that the labelled carbon atoms were introduced in the positions predicted by the theory[61,67,68,69,70,71,72,73,74].

While geraniol, farnesol, geranylgeraniol and squalene are found in nature , there is no positive evidence suggesting that they are the immediate precursors of all mono-, sesqui-, di-, and triterpenes. However, schemes for the biogenesis of these classes of compounds based on the above acyclic precursors have been so fruitful[60] that it seems probable that these compounds or their "biological equivalents" are actually involved.

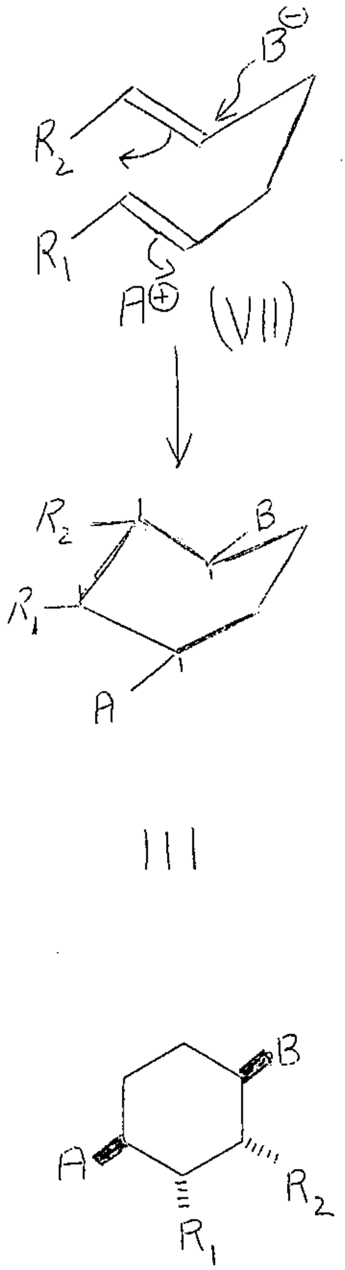
In particular , all known cyclic triterpenes including lanosterol - and hence steroids - may be derived from squalene by means of acid catalysed cyclisations and rearrangement of carbonium ions[75]. As limonin has been postulated (see below) to be derived from a normal triterpene, it is pertinent to summarize the arguments of Ruzicka et. al.[75]

Assuming trans addition to double bonds, two products could be expected from an acid (A^+) initiated cyclisation of a cyclohexadiene, depending on whether the acyclic precursor was in a "chair favouring" conformation (VI) or in a "boat favouring" conformation (VII) , viz. the "anti" and "syn" conformations shown. B^- denotes the "base" which neutralises the carbonium ion formed.

A further assumption made, concerned the trans nature of acid catalysed 1-2 rearrangements, which, like additions to double bonds are postulated to proceed via non-classical carbonium ions. As a consequence , the migrating group - usually methyl or proton - never crosses from the α to the β side.



"ANTI"

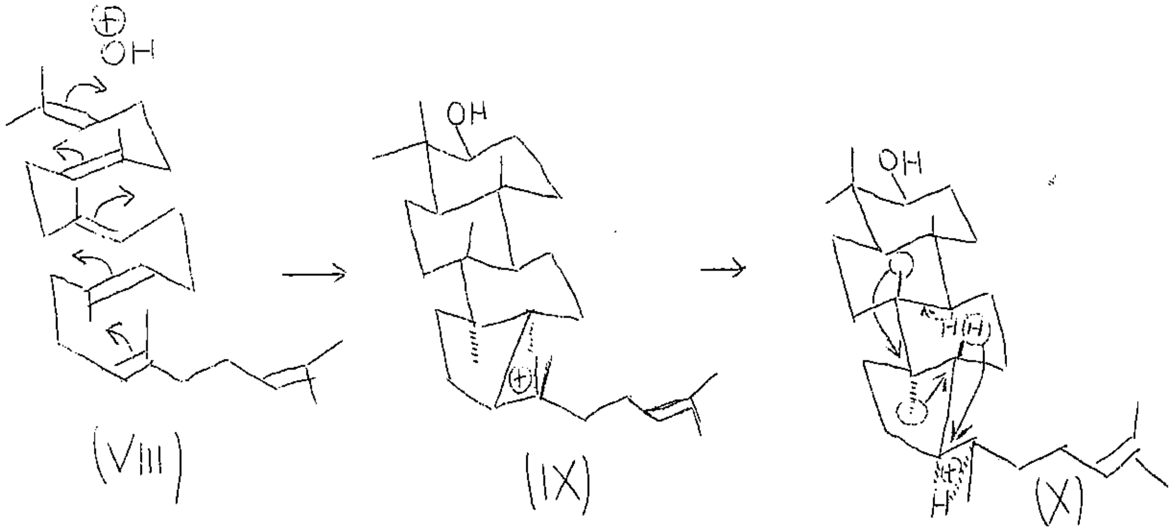


"SYN"

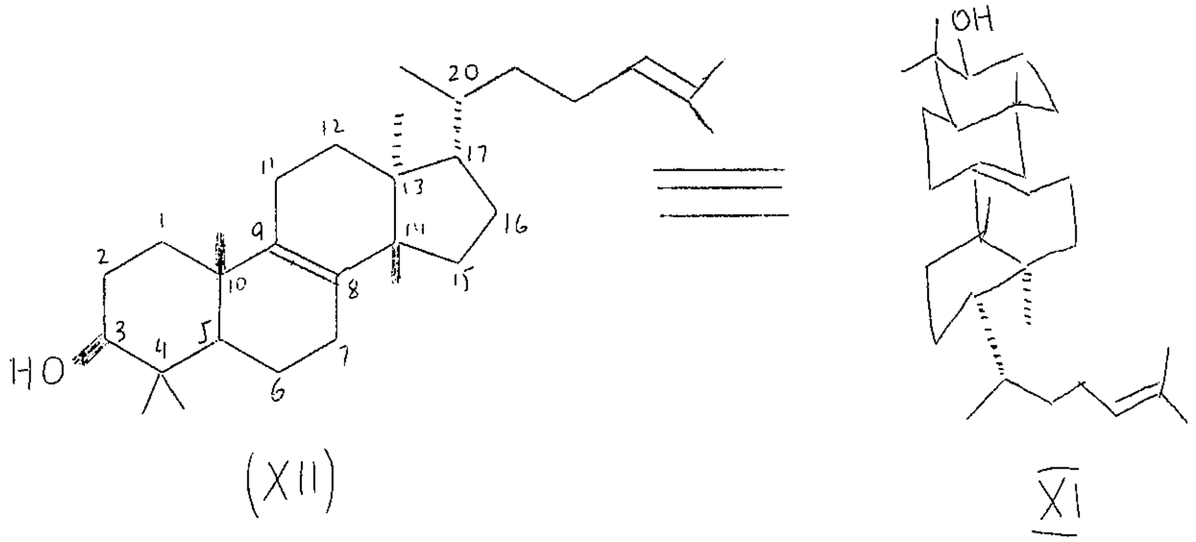
It was also necessary to assume that squalene - or its biological equivalent - was in an all trans configuration , an assumption for which there is some experimental basis[76].

As no stable intermediates, formed by neutralisation of the positive charge (by hydration or proton splitting) at some intermediate stage of cyclisation have been isolated, the authors have postulated that the formation of the naturally occuring triterpenes is a "non-stop" process, presumably due to the rigid adhesion of the reacting molecule on the enzyme surface.

Utilising these simple assumptions, the Swiss workers were able to account for the structures and stereochemistry of all the known types of triterpenes by starting from different arrangements of "chair favouring" and "boat favouring" portions of the squalene chain. For example , the "chair-chair-chair-boat-straight chain" conformation of squalene (VIII), may give rise to the tetracyclic triterpene euphol (see section 14b) by the following mechanism:



(VIII) (IX) (X)



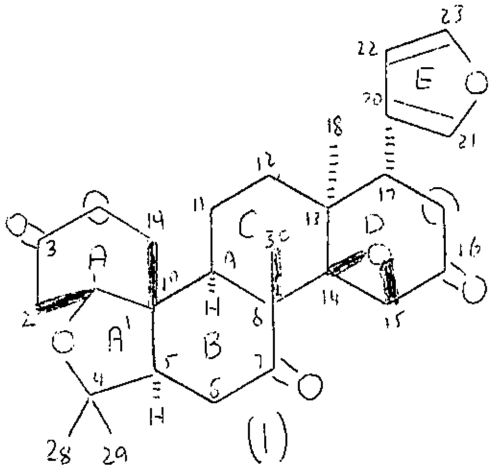
(XII) XI

Cyclisation is accompanied by the rearrangement of the non-classical carbonium ion (IX) to (X) and by a concerted transfer of proton from C_{13} to C_{17} (on β side), transfer of methyl from C_{14} to C_{13} (α side), transfer of methyl from C_8 to C_{14} (β side) and elimination of proton from C_9 (from α side), to give (XI), which can be conventionally represented as euphol (XII).

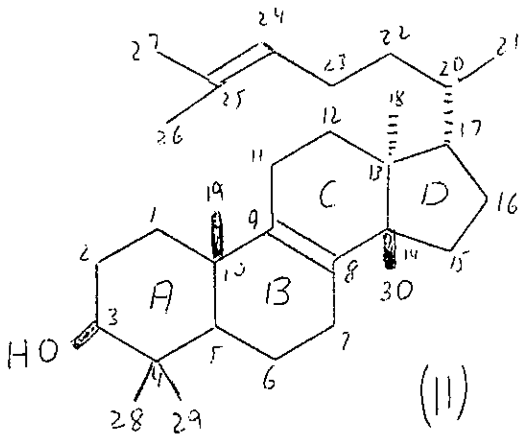
Conversion of (X) to (XI) is here indicated as a series of 1-2 shifts, but the Swiss workers also considered the possibility of 1-3 shifts in some cases. In the case of cyclisation of squalene to lanosterol[61,77], it has been shown that 1-2 shifts actually occur.

b. BIOGENESIS OF LIMONIN

Limonin (I) appears to be closely related to the tetracyclic triterpene euphol[78,79] (II). Three series of steps must be postulated for a biogenesis of limonin from a euphol type compound:

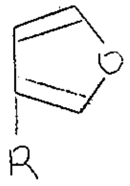


(I)

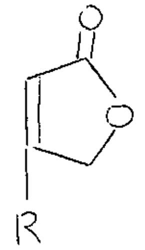


(II)

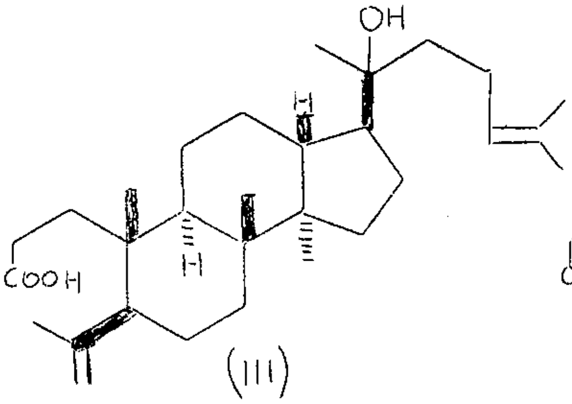
(i) Four carbon atoms are removed from the end of the side chain and carbons C_{20} to C_{23} are converted to a furan ring. A similar process appears to be involved in the formation of cardiac glycosides



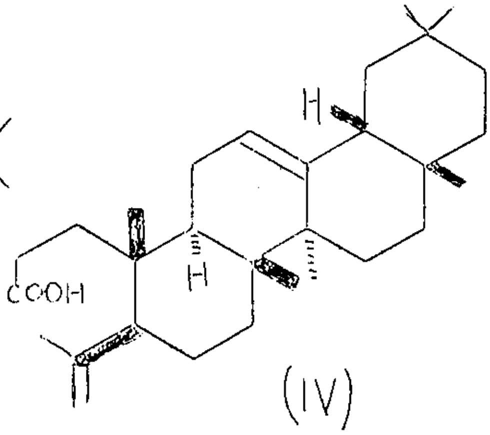
being equivalent to



(ii) The ring A of the triterpenoid skeleton is cleaved oxidatively between C_3 and C_4 and the C_3 carbonyl thus formed is oxidatively cyclised onto C_{19}. The recently described structures of dammarenolic[80] (III) and nycanthic[81] (IV) acids afford a precedent for a C_3 - C_4 biogenetic cleavage of the triterpenoid skeleton.



(III)

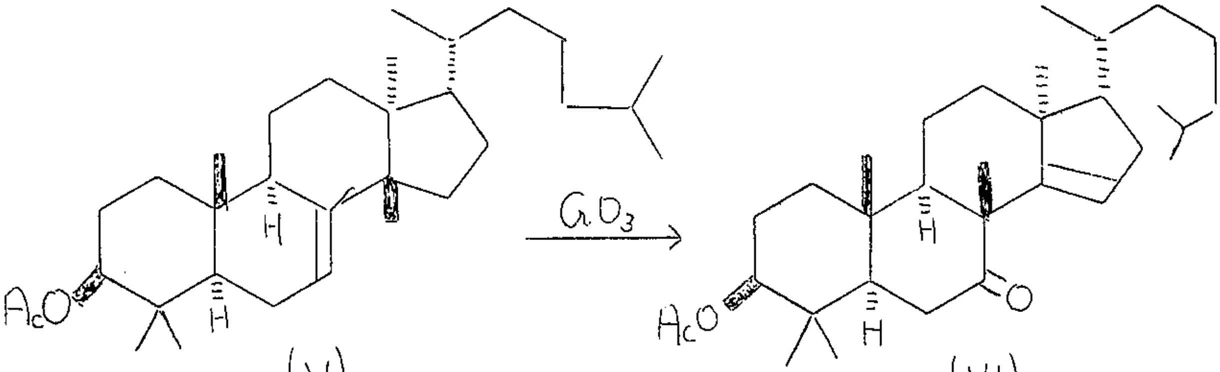


(IV)

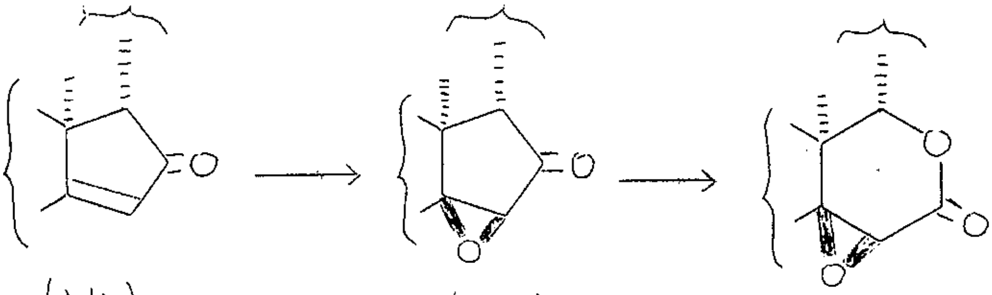
No analogy for an oxidative closure on a methyl group is known, but recent work[82] indicates that similar reactions may occur under the influence of ultraviolet light.

(iii). The ring D of a euphol type terpene is oxidised to a lactone by a Beyer Villager type of reaction and a methyl migration from C_{14} to C_8 must be postulated.

A possible analogy may be found in the chromic acid oxidation of dihydrobutyrospermol acetate[83] (V) to give the 7-ketone (VI). This type of compound could be oxidised further to a 16 ketone (VII) , epoxidised to an oxido-ketone (VIII) and then give a limonin type structure (IX) by a Beyer Villager oxidation.



(V) (VI)



(VII) (VIII) (IX)

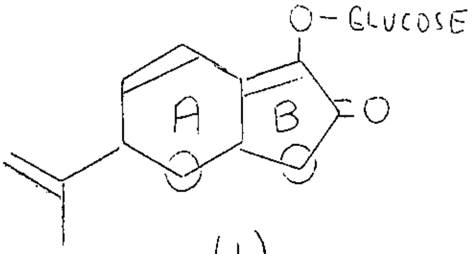
The numbering of the carbon atoms in the structure of limonin follows from the above ideas of its biogenesis.

On the basis of the above, the absolute configuration of limonin would be expected to be the same as that of the ketone (VI). The rotary dispersion curve[84] of tetrahydrolimonin shows a strong, negative Cotton effect and corresponds to the type shown by saturated steroidal 7-ketones , thus providing support for the above hypothesis.

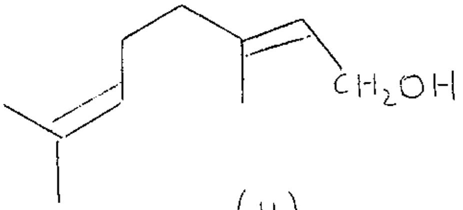
c. The biogenesis of some lactonic bitter principles

Lactonic bitter principles form a chemically ill-defined group , being best classified as non-alkaloidal , bitter plant products containing lactone groups. A review of the chemistry of bitter principles has appeared recently[85]. The majority of the known bitter principles are terpenoid , and although they are often of considerable chemical complexity, their biogenesis is relatively straightforward. In the present section some of the more chemically interesting bitter principles are presented from the point of view of their biogenesis.

Gentiopikrin (I)[86], the bitter principle of gentiana lutea has the geraniol (II) skeleton. If the monoterpene character of gentiopikrin is in fact correct, then the cyclisation of lactone B provides an example of oxidative cyclisation on a methyl group (see section 14 b).

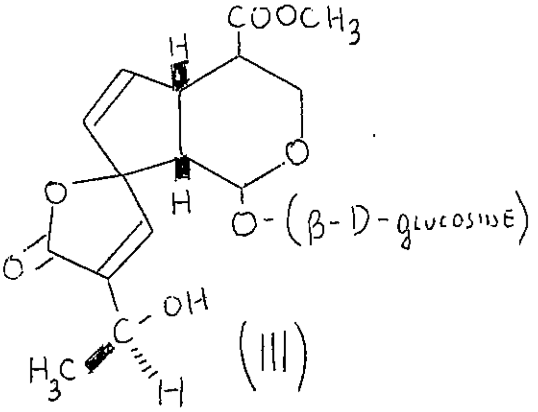


(I)

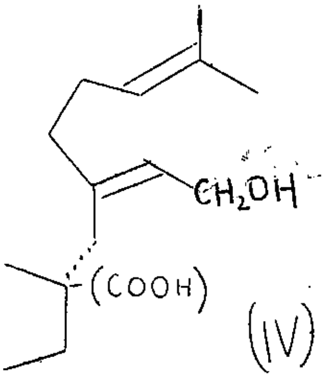


(II)

Plumerid[87] (III) was postulated to be derived from geraniol and an "acetoacetate unit"(IV):

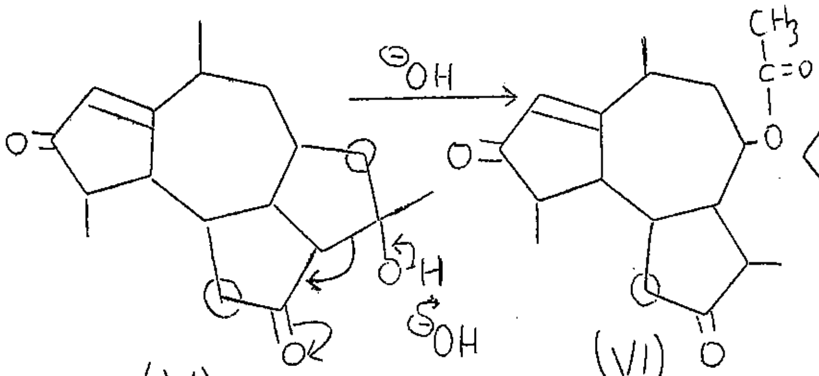


(III)

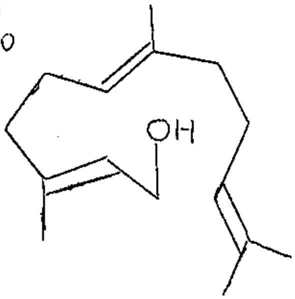


(IV)

Tenulin (V) , a sesquiterpenoid bitter principle[88] of <u>helenium tenuifolium</u> and the isomeric <u>iso</u>-tenulin (VI) both contain the unrearranged farnesol skeleton (VII):

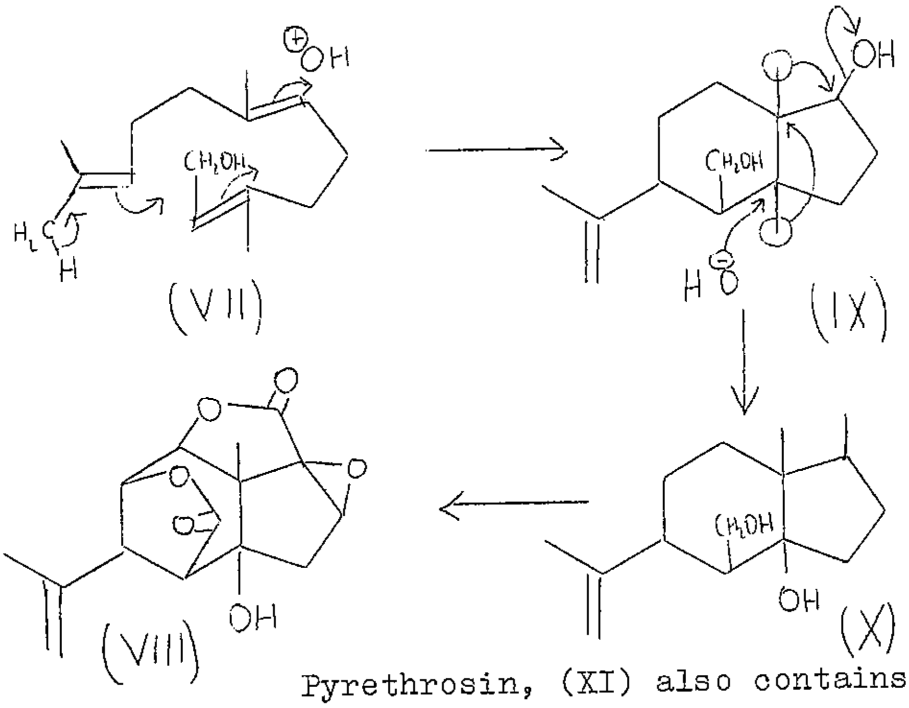


(V) (VI)

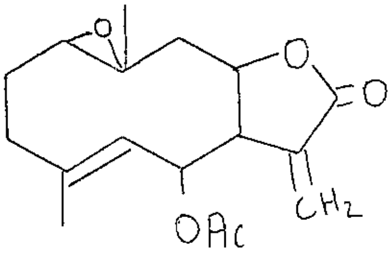


(VII)

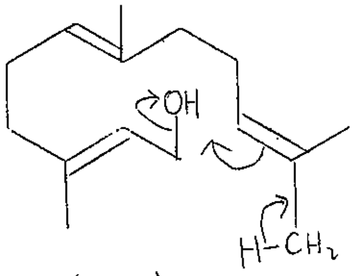
Picrotoxinin (VIII)[89], the bitter principle from <u>anamirta cocculus</u> can also be derived from farnesol (VII) via the intermediates (IX) and (X):



Pyrethrosin, (XI) also contains the unrearranged farnesol chain (XII), and is of special interest[48] as the first ten membered sesquiterpene isolated.



(XI)

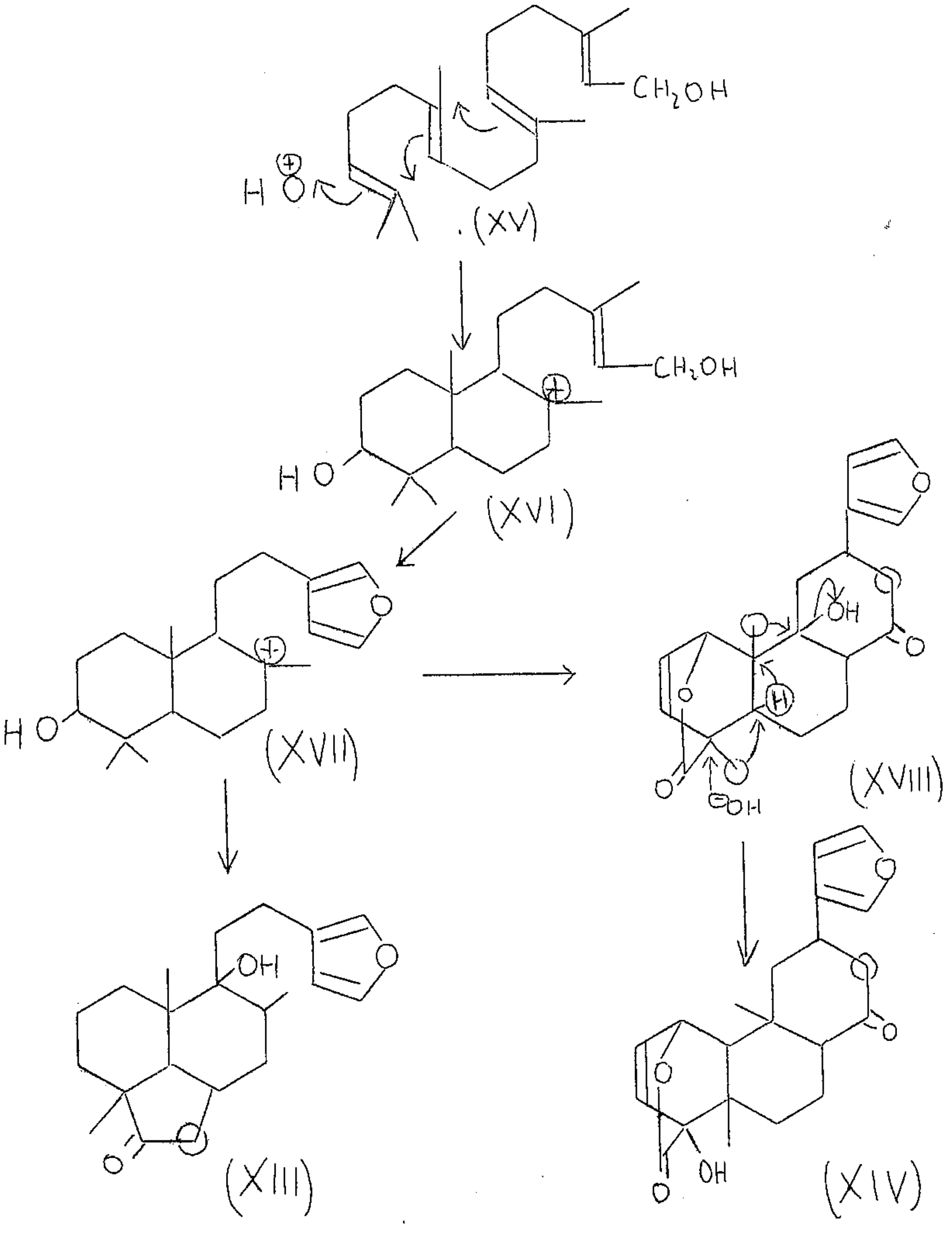


(XII)

It must be noted, that the biogenetic reactions of the sesquiterpenes shown here are purely schematic. The actual intermediates postulated[91,90] in the formation of sesquiterpenes are ten and eleven membered cyclic cations resulting from rearrangements of non-classical carbonium ions formed from either <u>cis</u> or <u>trans</u> farnesol. The "large ring hypothesis" was introduced to account for various stereochemical features found in naturally occuring sesquiterpenes.

Both marrubiin (XIII)[92], the bitter principle of <u>marrubicum vulgare</u> and columbin (XIV)[42], a bitter principle of colombo root, are diterpenes, but while marrubiin retains the skeleton of geranylgeraniol (XV) and of the intermediates (XVI) and (XVII), in the case of columbin a rearrangement of (XVIII) has been postulated to account for the abnormal diterpene skeleton.

So far, limonin,nomilin and obacunone are the only well established triterpenoid bitter principles.


CH₂OH
HO
(XV)
CH₂OH
HO
(XVI)
HO
(XVII)
OH
(XVIII)
⊖OH
OH
(XIII)
OH
(XIV)

15. THE CHEMISTRY OF OBACUNONE AND NOMILIN

a. Summary of previous work

i. Isolation of obacunone and nomilin

Obacunone was isolated by Kaku and Ri[93] from the bark of phellodendron amurense and is identical [94] with cassimirolid , which was isolated earlier from cassimiroa edulis , another member of the rutacea family , by Power and Callan[95].

Obacunone, together with the entirely new bitter principle nomilin , was later isolated by Emerson[13,14] from immature navel oranges and from citrus seed oil. Later work[15,40] showed that both nomilin and obacunone occur in grapefruit seed oil and in the course of the present work , it was shown that either or both of the bitter principles may be obtained from grapefruit seeds in approximately 0.03% yield. Some evidence[53] exists that the bitter principle involved is in fact nomilin.

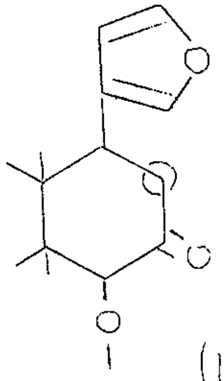
ii. Relation of obacunone to nomilin

Reliable characterisation of obacunone and nomilin is due to Emerson[13,14] who also elucidated the relationship between them. Both bitter principles were shown to be dilactone ketones by equivalent determinations and preparation of oximes and furthermore nomilin, $C_{28}H_{34}O_9$, was shown to contain one acetoxy group which was lacking in obacunone, $C_{26}H_{30}O_7$. On mild alkaline hydrolysis both materials yielded obacunoic acid, $C_{26}H_{32}O_8$, thus showing that nomilin was acetoxy obacunone and that the acetoxy group was capable of being eliminated under alkaline conditions. In confirmation it was also found possible to convert nomilin to obacunone by heating in the presence of pyridine.

iii. The functional groups of obacunone and nomilin

Besides the work of Emerson[13,14], only one other investigation has been described into the chemistry of nomilin and obacunone[15], from which all the information in this subsection has been abstracted.

(1): Degree of unsaturation: On the basis of hydrogenation experiments, Dean and Geissman[15] assigned four double bonds to obacunone and obacunoic acid and three double bonds to nomilin. The amounts of hydrogen uptake by obacunoic acid and methyl obacunoate , quoted by the above authors, were found incorrect in the course of the present work (see below) and it can be stated with reasonable certainty that obacunoic acid has only three double bonds.



(I)

Hydrogenation over palladium-carbon also caused hydrogenolysis with formation of an abnormally strong carboxylic acid - a situation completely analogous to the hydrogenolysis of limonin and columbin (see section 1). The infrared spectra of obacunone and nomilin show the characteristic furan frequencies ,identical with those detected in limonin (especially bands at 1505 and 875 cm^{-1}) and their NMR (see below) and ultraviolet spectra are also in accord with the presence of a β-substituted furan nucleus. On the basis of the above, (I) becomes an attractive partial structure for obacunone and nomilin. The presence of a β-substituted furan in obacunone was also indicated by experiments[33] analogous to those described on page 17. In the course of the present work further evidence has been obtained in support of (I). (see below).

(2) The nature of the lactone groups: On the basis of infrared and ultraviolet spectra both lactones in obacunone were assigned the δ configuration, one of them being α-β unsaturated. It is the unsaturated lactone which is hydrolysed in the formation of obacunoic acid , which is of normal acid strength.

(3) The nature of the ketonic carbonyl: Two isomeric obacunols can be obtained by reduction of the ketonic carbonyl in a manner analogous with limonin (see section 3). This , and the infrared frequency of the ketonic carbonyl absorption suggests that the ketonic function of obacunone is present in a ring, probably six membered or larger. The assignement of all the carbonyl frequencies was further supported by careful quantitative studies of the infrared spectra of a number of derivatives and model compounds.

(4) Obacunoic acid: As expected, obacunoic acid is a mono lactone mono carboxylic acid[13,14] and the infrared spectrum of methyl obacunoate shows the

presence of a hydroxyl group. Emerson[14] ,Kaku and Ri[93] and Callan and Power[95] were able to prepare an acetyl derivative of obacunoic acid by heating with acetic anhydride and sodium acetate, but this experiment could not be repeated by Dean and Geissman[15], suggesting that the hydroxyl group in obacunoic acid is difficult to acetylate. There is no evidence for the presence of any hydroxyl groups in either obacunone or nomilin.

(5) Miscellaneous : Unlike limonin, nomilin appears to give no acetone on fusion with alkali. Also unlike limonin, obacunone gives a positive iodoform test.

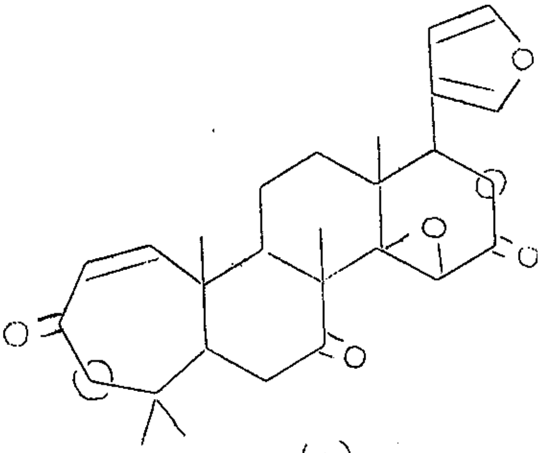
Obacunone gives a hydrochloride, which can be re-converted to the starting material by warming with pyridine. Spectroscopic evidence suggests that the double bond involved is conjugated with a lactone carbonyl. The same double bond appears to be capable of being selectively hydrogenated to give dihydro obacunone.

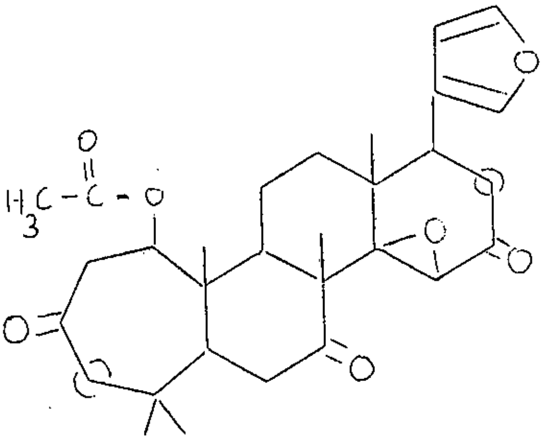
α-Obacunol appears to undergo a complex change with alkali to give an amorphous product.This suggests an analogy with the merolimonol change (see section 8).

b. The present work

i. Biogenetically attractive structures of obacunone and nomilin

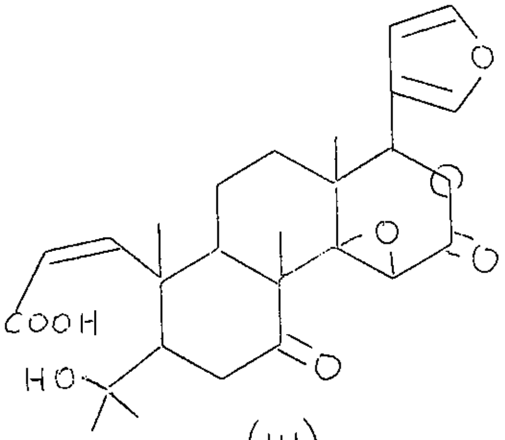
On the basis of published work (see section 15a) and the known structure of limonin, Barton[2] proposed structure (I) for obacunone and (II) for nomilin. It follows, that the common derivative of obacunone and nomilin , obacunoic acid, should have structure (III).


(I)



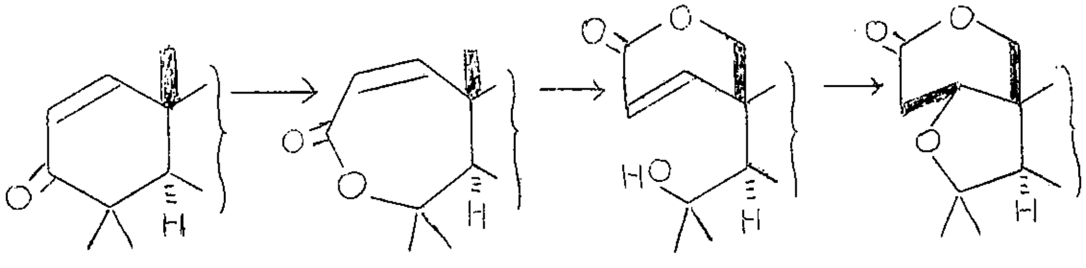
(II)

It can be seen that the part structure proposed for obacunone (V) is , in fact, an intermediate in the postulated transformation of the normal terpene structure (IV) to limonin (VI). (see section 14b). Nomilin, may then be derived by acetoxylation of (V).



(III)

Besides being attractive biogenetically, structures (I),(II) and (III) , agree with all the known properties of obacunone, nomilin and obacunoic acid (see section 15a) except:



(IV) (V) (VI)

(a) Experiments of Dean and Geissman[15] suggested that obacunone and nomilin had one more double bond each than shown in structures (I) and (II).

(b) Obacunoic acid was reported[15] to give a positive iodoform test.

In the course of the present work, it was shown that obacunoic acid contains only three double bonds and that structures similar to that postulated for obacunoic acid (III) can give rise to iodoform.

Other evidence was also introduced in favour of structures (I),(II) and (III). All the work described in the remainder of this section was performed by the present author with the exception of oxidation of obacunoic acid with oxygen in the presence of potassium tertiary butoxide[53].

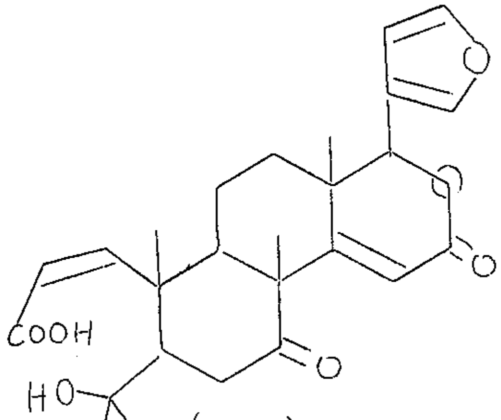
ii. Hydrogenation of obacunoic acid and methyl obacunoate

When hydrogenated over palladium-carbon, obacunoic acid was found to take up 3.74 moles of hydrogen to give an amorphous acid. As hydrogenation over palladium always leads to hydrogenolysis of lactone D in limonin , this result indicated that only three moles of hydrogen were taken up by unsaturated structures in obacunoic acid.

More important, it was found that hydrogenation of methyl obacunoate over palladium-carbon also resulted in the uptake of 3.75 moles of hydrogen to give methyl-hydrogenoctahydroobacunoninate identical in its properties with the material described by Dean and Geissman[15], who however recorded a higher hydrogen uptake in an identical experiment. On the basis of structure (III) for obacunoic acid, methyl-hydrogenoctahydroobacunoninate should be (VII) (see below).

ii. Reactions of obacunoic acid analogous to limonin

(1) Desoxyobacunoic acid: Treatment of obacunoic acid, $C_{26}H_{32}O_8$ with chromous chloride[44,96] resulted in the formation of a desoxy acid $C_{26}H_{32}O_7$ whose ultraviolet spectrum showed a peak at 206-208 mμ (ε: 22,000) which is in agreement with structure (VIII), the expected product of a reaction analogous to the formation of desoxylimonin from limonin.

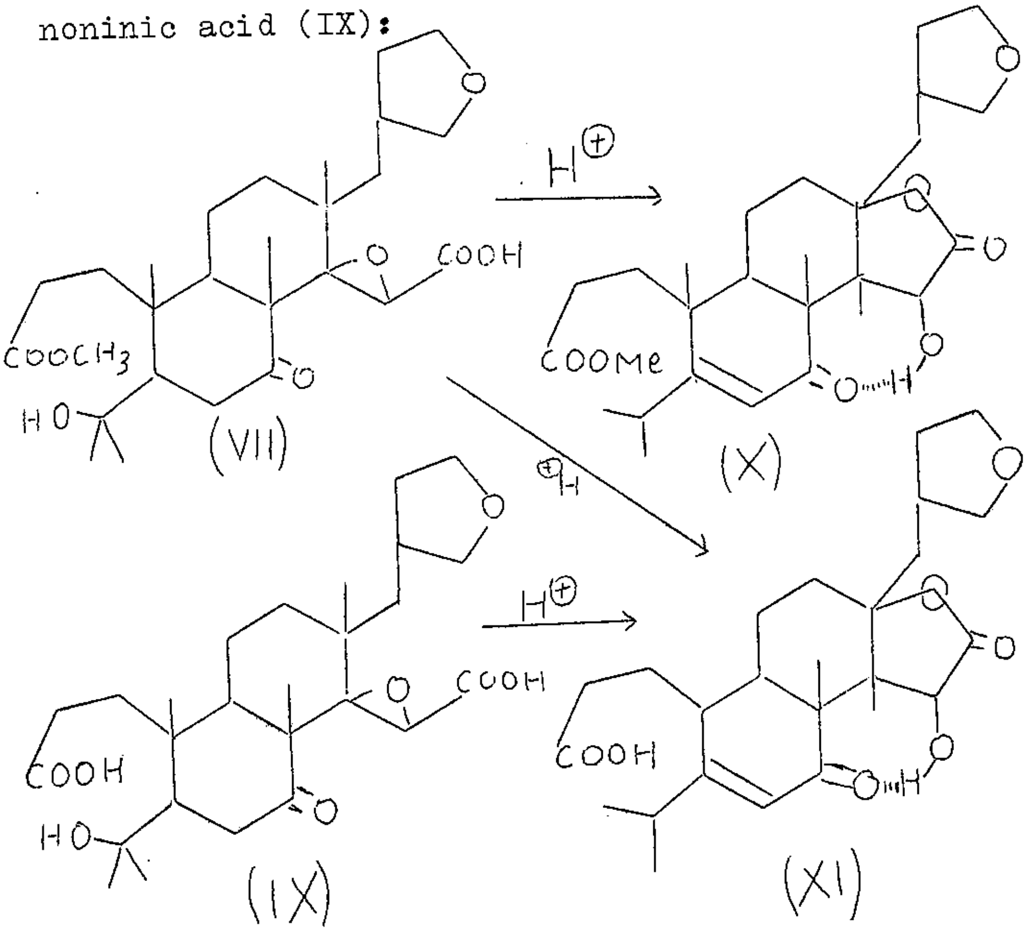


(VIII)

The infrared spectrum of desoxyobacunoic acid, had no bands above 1715 cm^{-1} in the carbonyl region , in accordance with the presence of an α-β unsaturated lactone, an α-β unsaturated acid and a cyclohexanone. Treatment of (VIII) with alkali followed by acidification resulted in the formation of an acidic material which exhibited no maximum in the ultraviolet but retained strong end absorption , a reaction analogous to the formation of desoxylimonic acid from desoxylimonin (see section 4) , as expected from structure (VIII).

(2). Action of strong acids on methyl-hydrogenoctohydroobacunoninate and octohydroobacunoninic acid

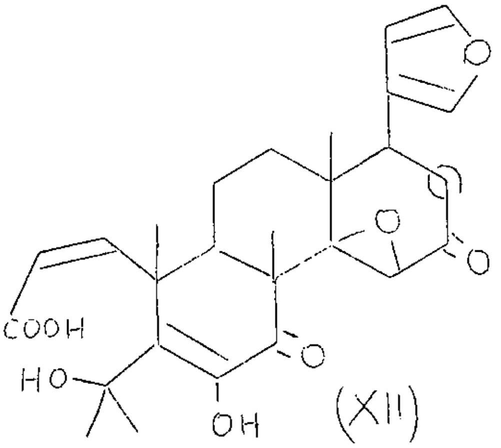
Treatment of methyl-hydrogenoctohydroobacunoninate with strong acid under conditions analogous to those described in section 6, gave an amorphous, neutral material (X) whose infrared spectrum showed bands at 3200 cm^{-1}(hydroxyl), 1787 cm^{-1} (γ lactone), 1732 cm^{-1} (methyl ester) and 1631 cm^{-1} (very strong)(hydrogen bonded, α-β unsaturated ketone). The presence of the α-β unsaturated ketone was confirmed by the ultraviolet spectrum which showed a maximum at 247 mμ (ε:8,000). An acidic product (XI), was also isolated, whose infrared spectrum showed bands near 3400-3000 cm^{-1} (hydroxyl), 1785 cm^{-1} (γ lactone) , 1720 cm^{-1} (saturated carboxylic acid) and 1631 (v.s.)cm^{-1} (hydrogen bonded, α-β unsaturated ketone). The ultraviolet spectrum of the acidic product was very similar to that of the neutral material. An amorphous acidic material identical in its spectroscopic properties with the acidic material (XI) was also obtained by the action of strong acid on the amorphous hydrogenation product of obacunoic acid itself, probably octohydroobacunoninic acid (IX):



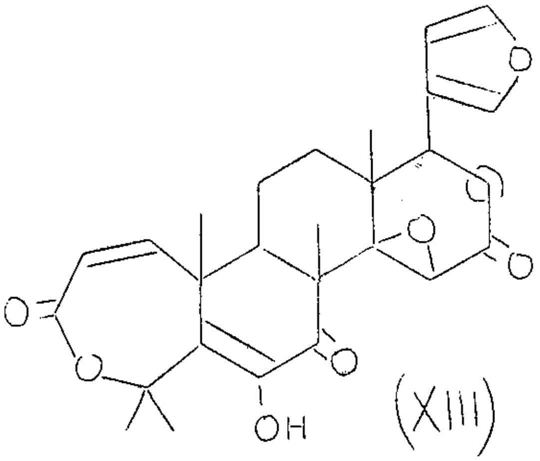
The above reactions fit well with the structure (VII) for methyl-hydrogenoctohydroobacunoninate , the products being analogous to those obtained from hexahydrolimoninic acid (see section 6), but accompanied by the elimination of hydroxyl from C_4 and conjugation of the resulting double bond with the ketone at C_7. In particular the frequency of the very strong absorption at 1631 cm^{-1} is very strongly indicative of a hydrogen bonded , α-β unsaturated ketone.

(3).Oxidation of obacunoic acid with oxygen in the presence of potassium tertiary butoxide: Using conditions identical to those employed for the oxidation of limonin (see section 10), Templeton[53] oxidised obacunoic acid to a material which showed the diosphenol chromophore , nearly identical with that shown by limonin diosphenol, in the ultraviolet and infrared. However,instead of the composition $C_{26}H_{30}O_9$ expected for the predicted acid (XII), the product analysed for $C_{26}H_{28}O_8$, was insoluble in sodium bicarbonate solutions and was shown to be a dilactone. A plausible structure for this material is the lactone (XIII), which may be formed from the initial product

(XII) by an indirect mechanism:



(XII)

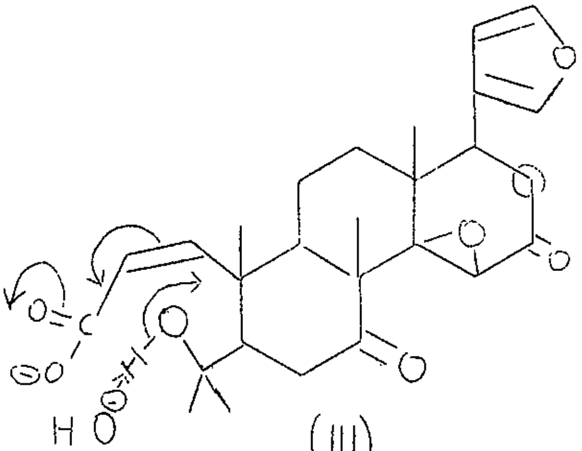


(XIII)

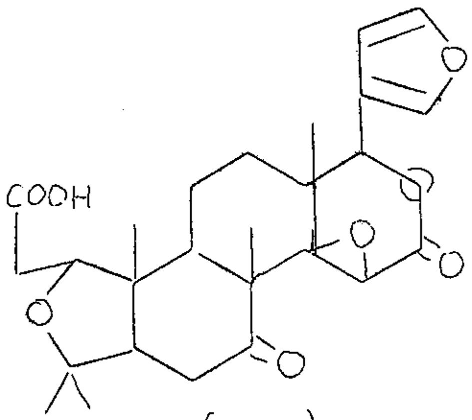
iv. Formation of iso-obacunoic acid

Treatment of methyl obacunoate or obacunoic acid with methanolic sodium methoxide gave an isomeric acid, iso-obacunoic acid (XIV). In accordance with structure (XIV), this material had a considerably lower absorption in the ultraviolet (λ_{max}:208 mμ, ε:5,200) than obacunoic acid, and lacked the band at 1630 cm^{-1} in the infrared which was assigned to the double bond conjugated with the carboxylic acid carbonyl in the spectrum of obacunoic acid. Bands at 3500-3000 cm^{-1}(carboxylic hydroxyl),1741 cm^{-1} (lactone D), 1716 cm^{-1} (ketone and carboxylic acid), as well as furan bands in the infrared spectrum of iso-obacunoic acid support structure (XIV).

The mechanism proposed for the formation of iso-obacunoic acid from obacunoic acid is shown below. It can be seen that it is analogous to that which may be involved in the regeneration of limonilic acid from pyrolysed limonilyl chloride (section 11e) and to that proposed for the formation of limoclastic acid (section 9):



(III)



(XIV)

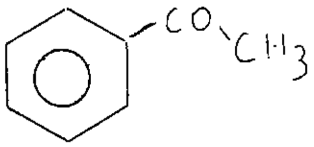
v. Inerpretation of the positive iodoform test given by obacunoic acid

Dean and Geissman[15] reported that obacunone gave a positive iodoform test. This finding was confirmed in the course of the present work, when it was found that a highly purified sample of obacunoic acid also gave a positive iodoform test, while iso-obacunoic acid failed to react with iodine and alkali and was recovered unchanged from the reaction mixture.

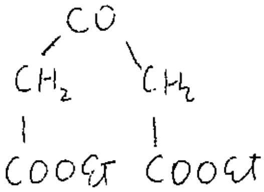
Iodoform tests were then carried out on a number of medel compounds using a standard procedure[97]:

STRUCTURE	SUBSTANCE	% YIELD IODOFORM
XV	Acetophenone	30
XVI	Acetonedicarboxylic ester	16,21
III	Obacunoic acid	15
XIV	*iso*-Obacunoic acid	nil
	Limonin	nil
XVII	Cinnamic acid	nil
XVIII	Crotonic acid	nil
XIX	Dihydrocarvone[98]	nil
XX	Dihydrocarvone hydrate[99]	4
XXI	Carvone	nil
XXII	Carvonehydrate[100]	6
XXIII	α-Terpineol	nil
XXIV	Dihydro-*iso*-photosantonic lactone[101]	4

From the consideration of the structures below, it can be seen that a positive iodoform test can be obtained not only with methyl ketones (XV), or with substances which hydrolyse to methyl ketones (XVI);

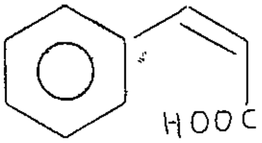


(XV)

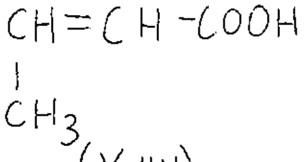


$$\begin{array}{ccc} & CO & \\ CH_2 & & CH_2 \\ | & & | \\ COOEt & & COOEt \end{array}$$

(XVI)

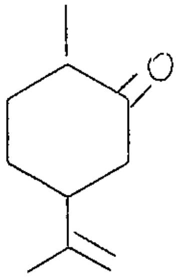


(XVII)

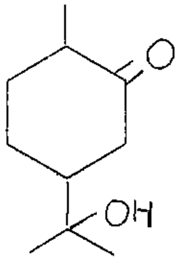


$$\begin{array}{l} CH=CH-COOH \\ | \\ CH_3 \end{array}$$

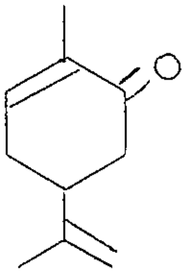
(XVIII)



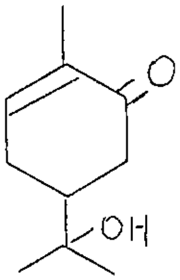
(XIX)



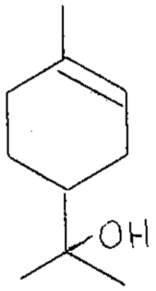
(XX)



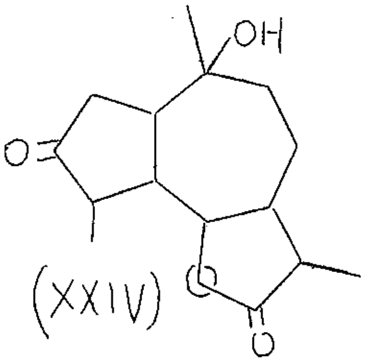
(XXI)



(XXII)

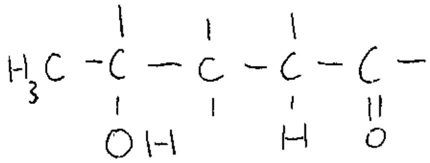


(XXIII)



(XXIV)

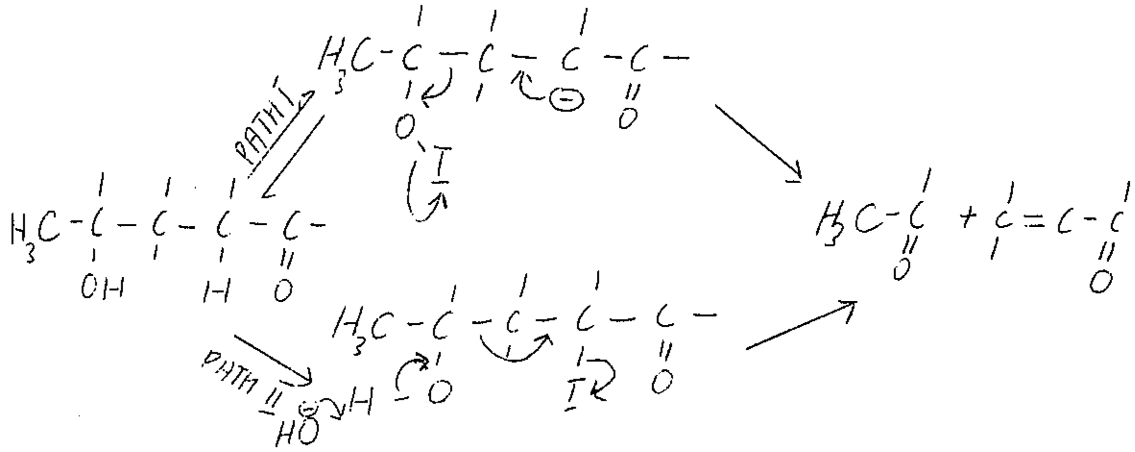
but also with substances (XX),(XXII),(XXIV) containing the grouping



$$\mathrm{H_3C}-\underset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-$$

and as such a grouping has been postulated for obacunoic acid (III) but not for <u>iso</u>-obacunoic acid (XIV), the positive iodoform test obtained with the former and the negative result with the latter provides some evidence for the correctness of the structure assigned to obacunoic acid and hence to obacunone.

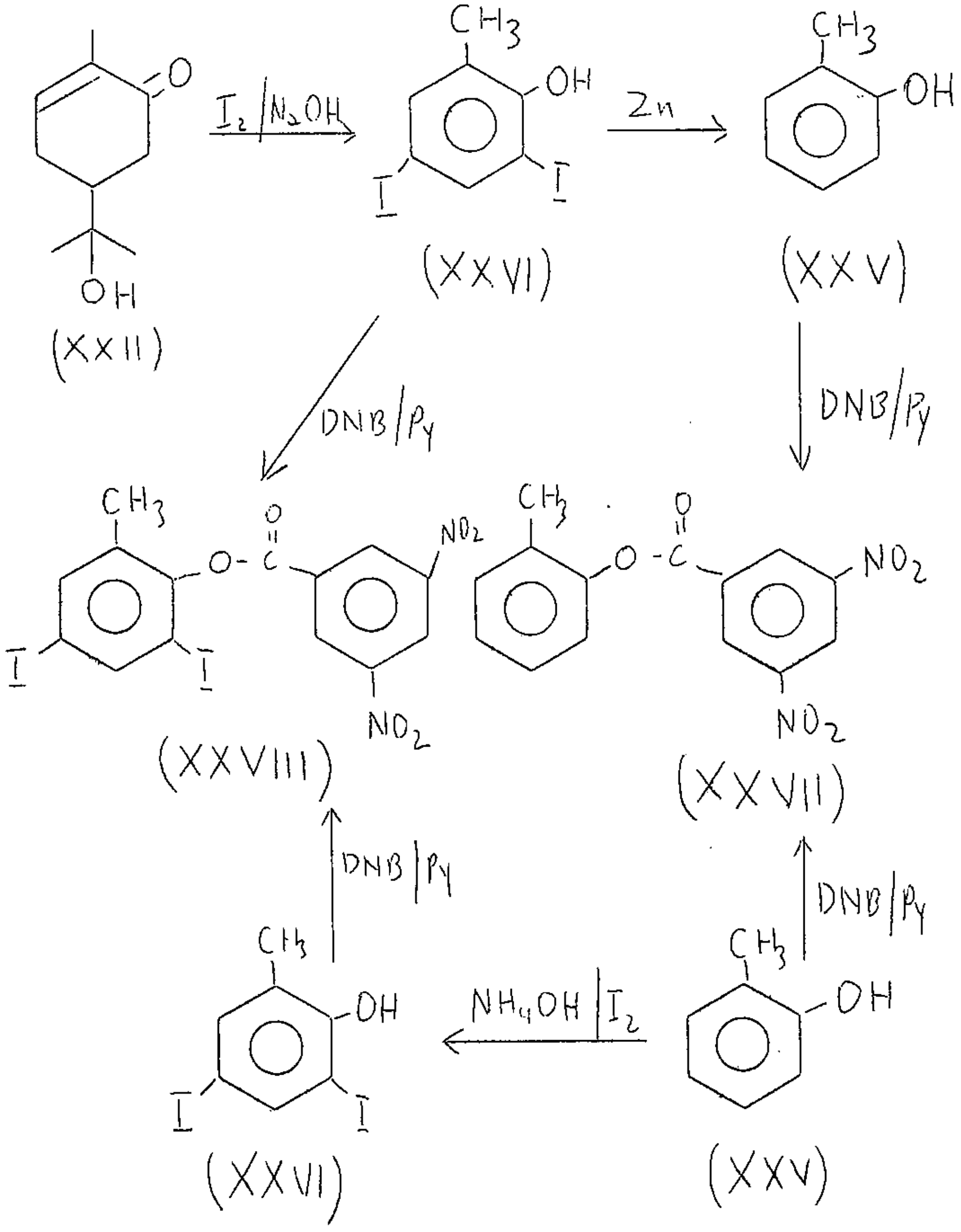
Two mechanisms may be postulated for the reaction:



Path I involves a preliminary equilibrium with the hapohalide while path II involves a preliminary α iodination of the ketone, (see section 11), and the methyl ketone formed then gives iodoform in the usual manner.

The major product of such a reaction should be an α-β unsaturated ketone. No chromophore assignable to such a structure could be found in the crude reaction product of obacunoic acid with iodine and alkali, but as the reaction, which gives rise to iodoform takes place only to a small extent, it is possible that the α-β unsaturated ketone was further oxidised, or that it is undetectable in small concentration.

In the case of carvone hydrate, the expected product, *ortho*cresol (XXV) , was isolated in a small yield following treatment with iodine and alkali and de-iodination of the phenolic fraction of the product. When the de-iodination step was omitted, di-iodo-*o*-cresol (XXVI) (probably the 2:4 diiodo isomer)[102] was isolated. The cresols were identified by the comparison of their 3:5:dinitrobenzoates, (XXVII) and (XXVIII), with those prepared from authentic specimens. (Note: DNB stands for 3:5 dinitrobenzoyl chloride).


(XXII)
I_2/NaOH
(XXVI)
Zn
(XXV)
DNB/Py
DNB/Py
(XXVIII)
(XXVII)
DNB/Py
DNB/Py
NH_4OH/I_2
(XXVI)
(XXV)

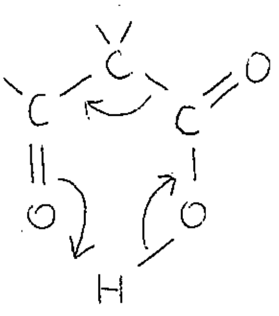
(vi) The NMR spectrum of methyl obacunoate

The table below lists some of the features of a high resolution proton magnetic resonance spectrum of methyl obacunoate , together with the assignements made. In particular , the AB quartet (J: 12 c.p.s.) is almost identical with that shown by the spectrum of *cis* methyl crotonate[103] and five distinct methyl peaks may be seen as compared with four in the spectrum of limonin and citrolin. In general, this evidence lends strong support for the assignement of structure (III) to obacunoic acid.

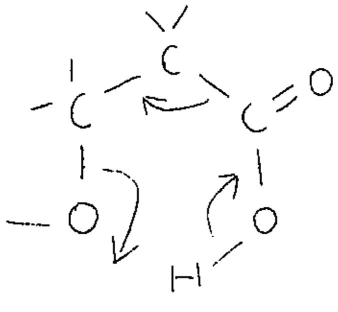
Tau (p.p.m.)		Assignement
9.043	9.008	Four angular methyl groups at C_{19}, C_{28} , C_{29} and C_{30}
8.97	8.88	
8.618		Methyl group adjacent to furan (C_{13})
6.33		Methyl ester group
4.63		Proton at C_{17}
4.490	4.24	αH A-B quartet at C_1-C_2
4.08	3.798	β H
3.668		β hydrogen of furan ring
2.506		α hydrogens of furan ring

16. ATTEMPTED THERMAL DECARBOXYLATION OF SOME DERIVATIVES OF CARBOXYLIC ACIDS

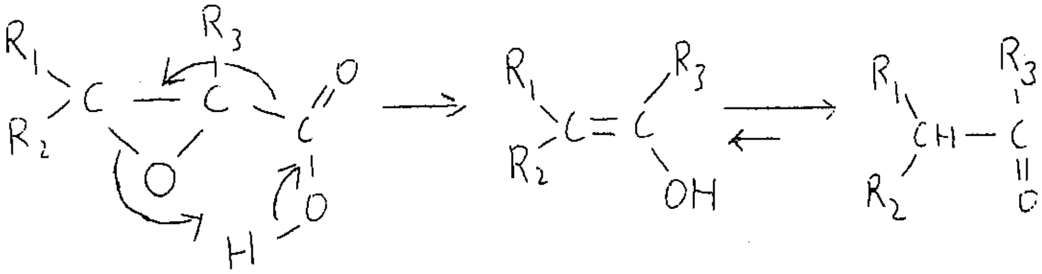
In general, uncatalysed thermal decarboxylation of carboxylic acids can be accomplished under relatively mild conditions, only if the environment of the carboxylic carbonyl group is favourable[104]. Thus β-keto acids[105](I) and β-oxy acids (II) are believed to decarboxylate by cyclic mechanisms shown below. An interesting example of the latter , is the decarboxylation of glycidic acids[106] (III), which is the final step in Darzen's glycidic ester synthesis[47].



(I)

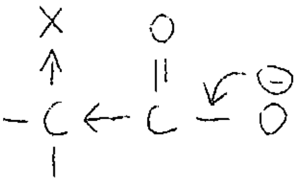


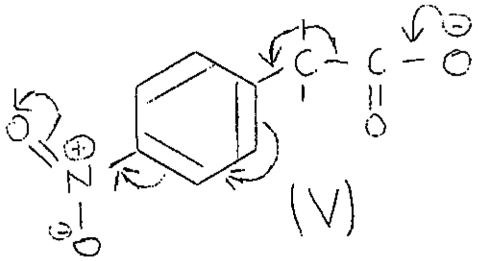
(II)



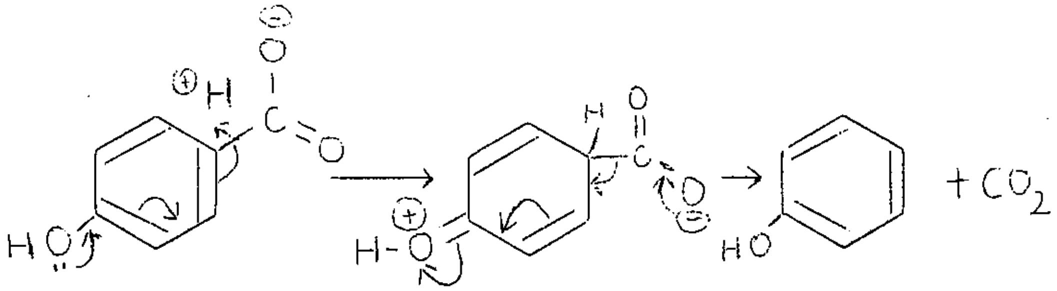
(III)

The presence of a negative substituent in the α position to the carboxylic carbonyl can also facilitate thermal decarboxylation - which often proceeds via the carboxylate ion - either by an inductive effect (IV) or by electron shift (V):

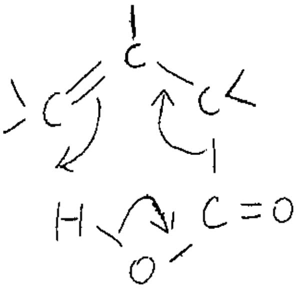

(IV)


(V)

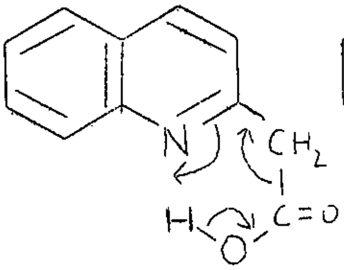
The decarboxylation of hydroxy benzoic acids has been formulated[107] as proceeding via an electrophilic substitution by a proton - which is still available in the mildly alkaline solution used - followed by decarboxylation proper according to the scheme set out below:



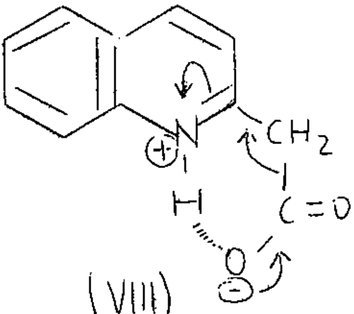
A cyclic intermediate was also postulated for the thermal decarboxylation[108] of β-γ unsaturated carboxylic acids (VI) , and it was also suggested that α-β unsaturated carboxylic acids are decarboxylated after a prior isomerisation of the double bond to the β-γ position[109].



(VI)



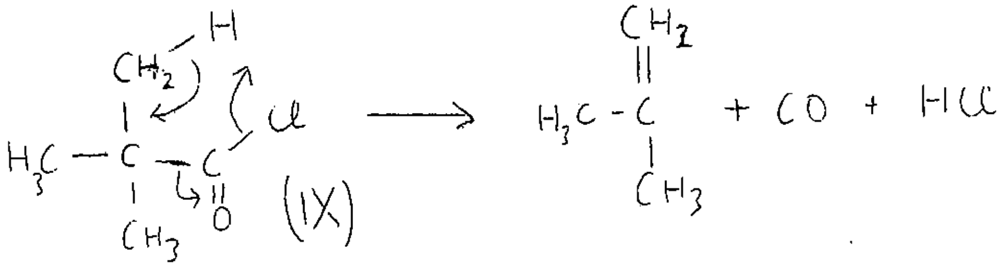
(VII)



(VIII)

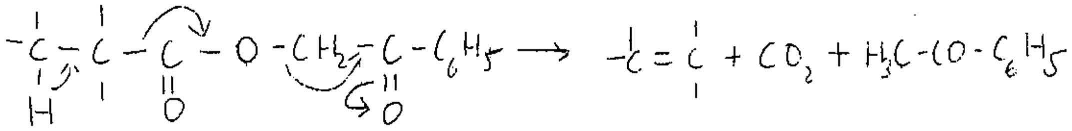
It is also known[108] that some heterocyclic acids (e.g. 2-quinolyl acetic acid) decarboxylate readily. Again , attractive cyclic transition states involving either the acid itself (VII) or its zwitterion (VIII) can be postulated.

An interesting example of decarboxylation is the decarbonylation of pivalic acid chloride (IX)[110], possibly involving the following mechanism, although catalysis by al~~l~~uminium chloride suggests that carbonium ions are involved:

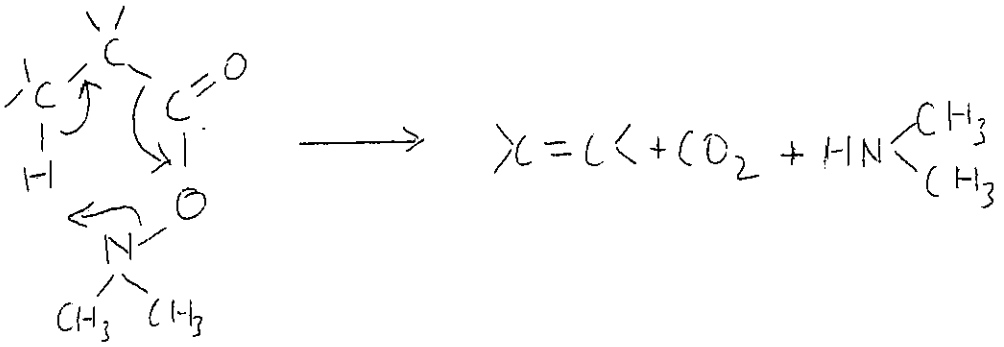


In the course of the present work, an attempt was made to produce structures electronically favourable for decarboxylation by a suitable choice of R' in ester-type structures R-CO-O-R'.

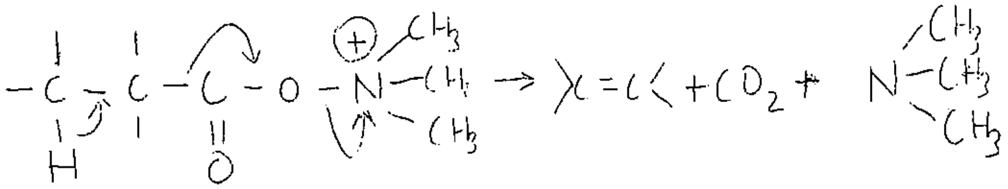
It appeared possible that phenacyl esters of carboxylic acids which had a hydrogen in the β position to the carboxylic carbonyl may decompose thermally in the following manner to give unsaturated compounds:



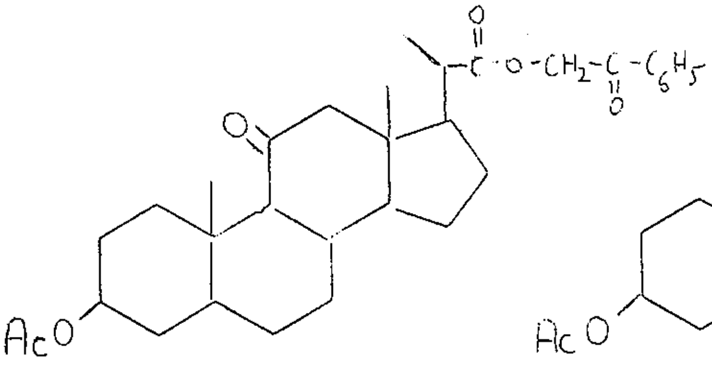
Another route to decarboxylation appeared in a thermal decomposition of O-acyl-NN-dimethyl hydroxylamines[111,112,113], possibly involving a cyclic transition state:



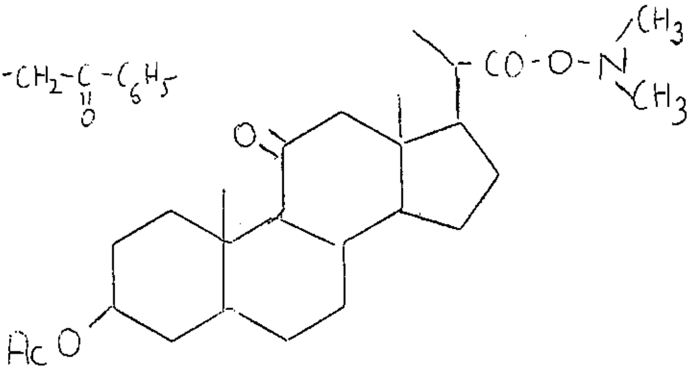
An even more favourable case would be presented by the thermal decomposition of quarternised O-acyl-NN-dimethyl hydroxylamines:



The desired intermediates (X) and (XI) derived from the model 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid[114] were prepared , but all efforts to decarboxylate them thermally were unsuccessful. Quarternisation of (XI) followed by pyrolysis also did not yield any decarboxylated material.



(X)



(XI)

17. IRRADIATION OF ACYL CHLORIDES WITH ULTRAVIOLET LIGHT

The irradiation of acyl chlorides in solution was studied as a possible general method for decarboxylation of carboxylic acids.

A literature search revealed that no such studies have been described, although the photolysis of a simple acyl bromide in the gas phase has been described[115]. From the consideration of the nature of the products obtained, which included carbon monoxide, dialkyl, diacyl, paraffin and alkyl halide species, the primary process was postulated as:

$$\text{R-CO-Br} \xrightarrow{h\nu} \text{R-CO}\cdot + \text{Br}\cdot \qquad \text{......(i)}$$

The acyl radicle could then dissociate into an alkyl radicle and carbon monoxide:

$$\text{R-CO}\cdot \longrightarrow \text{R}\cdot + \text{CO} \qquad \text{.....(ii)}$$

and reactions of the various radicles formed can account for all the products observed.

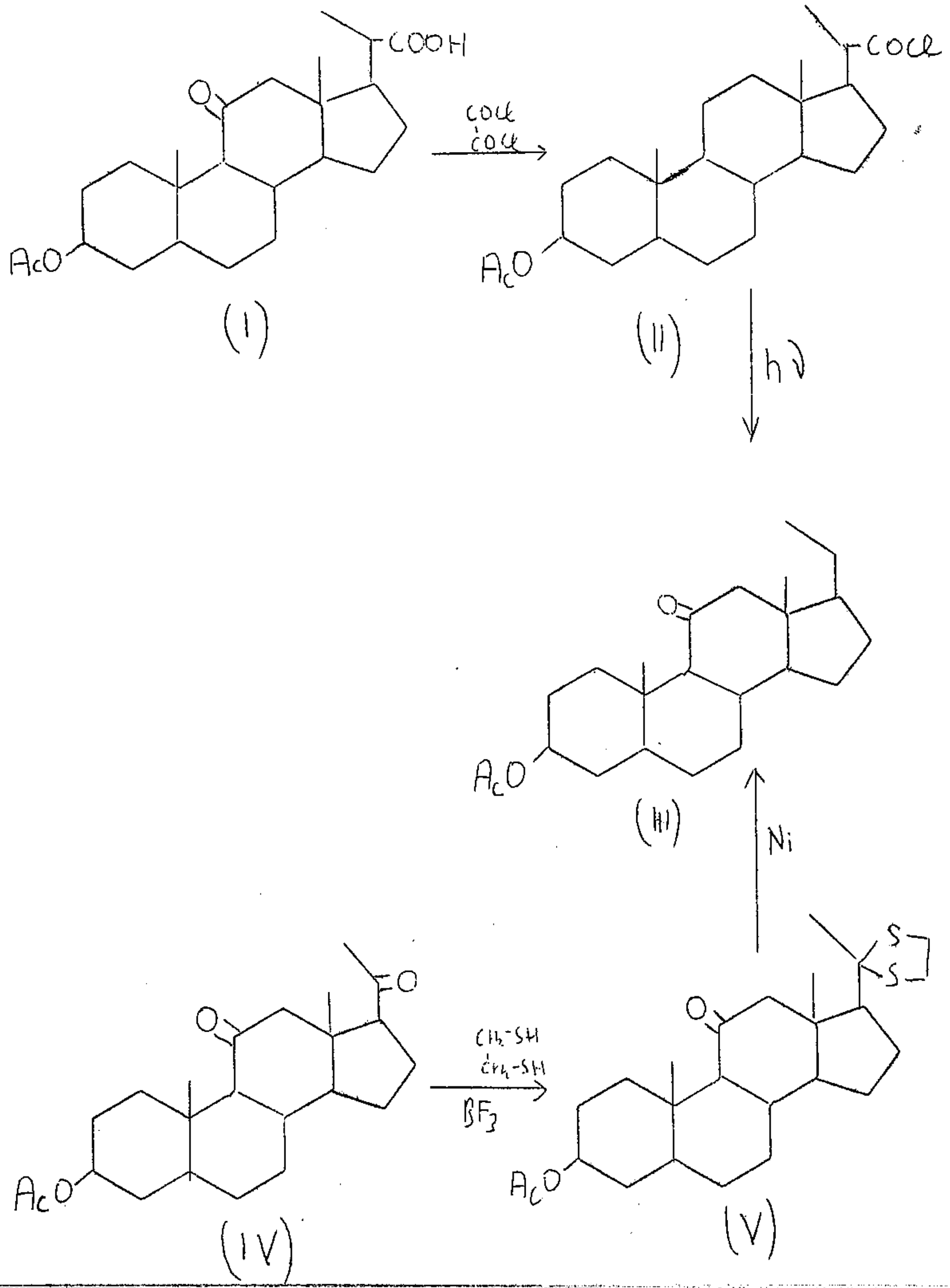
In the present investigation, 3-β-acetoxy-11-keto-bisnor-<u>allo</u>-cholanic acid chloride (II), derived from the known acid[114] (I) was found to yield a neutral product of composition corresponding to (III) on irradiation in dioxane solution. The structure of (III) was independently proved by synthesis from the known[116,117] 3-β-acetoxy-11:20-diketo-*allo*-pregnane (IV) via the 20-dithioketal[118]. The formation of the 20 rather than of the 11 derivative was assumed on grounds of better steric accessibility of the 20 position. A Huang-Minlon reduction of (IV) resulted in the formation of the known[119,120] 3-β-hydroxy-*allo*-pregnane.

To account for the formation of the saturated decarboxylated derivative (III), one must postulate an exchange reaction of the type:

$$R. + R'H \longrightarrow RH + R'. \qquad ....(iii)$$

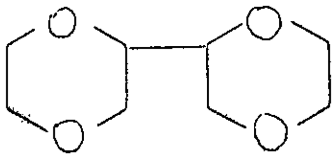
which is a common process in photochemical and free radicle reactions[121]. In the present case , R'H could be a solvent molecule or another molecule of the photolysed species.

The irradiation of another model compound, 3-β-11-α-diacetoxy-bisnor-*allo*-cholanic acid chloride, and of limonilyl chloride resulted only in the formation of amorphous neutral materials whose infrared spectra showed that decarboxylation has taken place.


COOH
AcO
(I)
COCl
COCl
COCl
AcO
(II)
hν
AcO
(III)
Ni
AcO
(IV)
CH₂-SH
CH₂-SH
BF₃
S
S
AcO
(V)

Thus it appears that although acid chlorides can be generally decarboxylated by irradiation in dioxane , the method suffers from practical difficulties , possibly due to the large number of side reactions possible.

It was also observed , that irradiation of dioxane itself resulted in the formation of a product whose elementary composition and molecular weight corresponded to $C_8H_{14}O_2$ and whose infra-red spectrum had no bands in either the O-H stretching, the carbonyl or the double bond regions. The NMR spectrum showed only a single broad band in the same position as that shown by the spectrum of dioxane. On the basis of the above, structure (VI) was assigned to this material.



(VI)

The reaction leading to di-dioxane (VI), was not investigated in detail, but preliminary results indicate that traces of oxygen in the nitrogen which was passed through all the irradiated mixtures , might be responsible.

EXPERIMENTAL

General

a) Unless otherwise stated all ultraviolet spectra were determined in ethanol on a Unicam model 500 spectrophotometer.

b) Unless otherwise stated all infrared spectra were determined in a Nujol mull on a Perkin-Elmer model 21 spectrophotometer.

c) The phrase "working up" indicates that the reaction mixture was poured into chloroform , washed with water and extracted with a solution of sodium bicarbonate. The chloroform extract was evaporated to dryness to yield the crude neutral fraction. The bicarbonate solution was acidified , extracted with chloroform and the extract was evaporated to dryness to yield the crude acidic fraction. In the case of reactions where hydroiodic acid was used the original chloroform extract was washed with saturated sodium sulphite solution . Where pyridine was used , the chloroform extract was washed with dilute hydrochloric acid.

d) All melting points were determined on a Koffler block.

Extraction of limonin from grapefruit seeds

Freshly ground grapefruit seeds (2.5 kg) were soaked in acetone (12 l) for 8 days with occasional stirring. The extract was filtered and the crushed seeds were washed with a further portion of acetone (3 l). The combined extracts were distilled under atmospheric pressure until the temperature of the liquid reached 110°C. The syrupy residue was poured into petroleum ether (Bp. 60-80°C, 2.5 l) and cooled for two days at 0°C. The precipitate was collected, washed with methanol (2 x 100 ml) and crystallized from methylene dichloride/ iso-propanol to give limonin (21.4 g).

Mp.: 290-2°C

$(\alpha)_D$: - 124° (c:1.3, acetone)

U.V.: λ_{max}: 207-10 mμ , ε:6,800

I.R.:1761,1709,1504,876 cm^{-1}

I.R. in chloroform: 1755,1715,1505,875 cm^{-1}

I.R. of disodium salt : 1690 cm^{-1}

Hydrogenation of limonin

a)Over rhodium-carbon at atmospheric pressure

Limonin (10 g) was dissolved in glacial

acetic acid (500 ml) and hydrogenated at atmospheric pressure over 5% rhodium-carbon (10 g) for 8 hours when uptake of hydrogen ceased. The reaction mixture was filtered , the solvent was distilled under vacuum and the product was worked up as usual. On recrystallization from methylene-dichloride/methanol the neutral fraction gave tetrahydrolimonin (6.1 g), Mp.: 280-93°C.

Acidification of the bicarbonate extract followed by prolonged cooling yielded crystalline hexahydrolimoninic acid (1.34 g),Mp.:165-8°C , not depressed by mixing with an authentic specimen.

b)Over palladium-carbon at atmospheric pressure

Limonin (7.0 g) in glacial acetic acid (500 ml) was hydrogenated over 10% palladium-carbon (7.0 g) for 3 hours when uptake of hydrogen ceased. The reaction mixture was filtered , the solvent was distilled under vacuum and the residue was worked up as usual except that a saturated solution of sodium carbonate was used to extract the acidic component . Acidification of the carbonate extract followed by prolonged cooling gave crystalline hexahydrolimoninic acid (5.4 g) ,Mp.: 163-71°C . I.R.: broad band near 3400,1750,1710-1700 cm^{-1}

Crystallization of the neutral fraction from methylene dichloride/methanol yielded tetrahydrolimonin (0.6 g), Mp.:285°C.

c)Over rhodium-carbon at high pressure

Limonin (10 g) in glacial acetic acid (500 ml) was hydrogenated over 5% rhodium-carbon (10 g) for 12 hours at 125 atmospheres with stirring.The reaction mixture was filtered, the solvent was distilled under vacuum and the product worked up as usual. On crystallization from methylene dichloride/methanol, the neutral fraction yielded hexahydrolimondiol (4.46 g) , Mp.:299-302°C $(\alpha)_D$: -50° (c: 1.0 , pyridine).

Acidification of the bicarbonate extract followed by prolonged cooling gave hexahydrolimoninic acid (0.7 g) , Mp.: 161-6°C not depressed by mixing with an authentic specimen.

Desoxylimonin

a) By action of hydroiodic acid on limonin

Limonin (10 g) in a mixture of glacial

acetic acid (80 ml) and hydroiodic acid (S.g. 1.7, 40 ml) was warmed at 50-60°C for 3½ hours. Working up as usual gave neutral fraction (6.9 g) which on crystallization from methylene dichloride/methanol yielded desoxylimonin (5.23 g).

Mp.: 325-33°C

U.V.: λ_{max}:213.5 mμ , ε:15,800

I.R.: 1746,1715,1695(sh),1503,875 cm^{-1}

I.R.:in chloroform: 1755,1715 cm^{-1}

b) By action of chromous chloride on limonin

Limonin (530 mg) in glacial acetic acid (25 ml) and acetone (25 ml) was treated with a solution of chromous chloride (1M , 14 ml) under nitrogen. The mixture was allowed to stand at room temperature for 44 hours, acetone was distilled under vacuum and the residue was poured into a large volume of water. The crystalline precipitate which appeared on cooling was collected and recrystallized from methylene dichloride/methanol to give desoxylimonin (444 mg) , Mp.:327-35°C identified by its infrered spectrum.

Tetrahydrodesoxylimonin

Desoxylimonin (514 mg) in glacial acetic acid (50 ml) was hydrogenated over 10% palladium - carbon (500 mg) until hydrogen uptake ceased (66ml at 20°C). Working up as usual gave neutral material (517 mg) which was crystallized from methylene dichloride/ethanol to give tetrahydrodesoxylimonin. The analytical sample was dried under vacuum at 145°C for 40 hours.

Calculated for $C_{26}H_{34}O_7$:	C:68.10%	H:7.47%
Found:	C:68.16%	H:7.46%

Mp.: 292-300°C

$(\alpha)_D$: -81° (c : 1.2 , chloroform)

U.V.: λ_{max}:218.5 mµ ε:10,600

I.R.: 1752,1720,1707 cm^{-1}

Isotetrahydrolimonin

Tetrahydrolimonin (2.08 g) in glacial acetic acid (30 ml) and concentrated hydrochloric acid (20 ml) was warmed on the steam bath for 90 minutes. Working up as usual gave neutral (1.38 g) and acidic (593 mg) fractions . The neutral fraction was found to be partially soluble in cold dilute sodium hydroxide solution. The remaining neutral material (225 mg) was identified by its melting point and infrared spectrum as unreacted tetrahydrolimonin. The alkali soluble material was worked up as usual to give neutral (844 mg) and acidic (118 mg) fractions. The neutral fraction was crystallized from methylene dichloride/ethanol to yield isotetrahydrolimonin.

Mp.: 260°C

U.V.: λ_{max} :257 mμ ε:5,460

U.V. in presence of alkali: λ_{max}:290 mμ ε:4,200

I.R. a weak broad band near 3300,1751,1723 cm^{-1}

The two acidic fractions could not be crystallized. They had very similar infrared spectra and no maxima in the ultraviolet spectra. The second acidic fraction was found to have an equivalent weight of 221.

Ozonolysis of isotetrahydrolimonin

Isotetrahydrolimonin (249 mg) was dissolved in chloroform (50 ml),cooled to the temperature of a carbon tetrachloride/dry ice mixture and ozonised oxygen was passed through the solution. After 25 minutes the absorption maximum at 257 mu fell to a negligible value, water (15 ml) was added, chloroform was boiled off and the clear aqueous solution was warmed on the steam bath for 30 minutes. The solution was evaporated to dryness and the total residue was found to be soluble in sodium bicarbonate solution. It could not be crystallized.

The crude product was found to have an equivalent weight of 138 and addition of a solution of calcium nitrate to the solution of the hydrolysed material obtained from the determination of equivalent weight caused the immediate precipitation of calcium oxalate which was identified by its infrared spectrum. The major hydrolysis product was acidic and could not be crystallized.

Desoxylimonic acid

Desoxylimonin (2.0 g) was dissolved in 2N sodium hydroxide solution (50 ml) and heated on the steam bath for 100 minutes. The mixture was acidified with concentrated hydrochloric acid and worked up as usual to give acidic product (1.76 g) which on crystallization from methylene dichloride / iso-propanol yielded desoxylimonic acid.

Mp.: 250-2^{o}C

$(\alpha)_D$: -139^{o} (c:1.0 , acetone)

I.R.: diffuse band near 3200,1750(sh),1734,1719, 1503,874 cm^{-1}.

Desoxylimonic acid was converted to its methyl ester by treatment with excess ethereal diazomethane in a dioxane solution. Mp.:161-6^{o}C not depressed by admixture with an authentic specimen.

Tetrahydrodesoxylimonic acid

a) From tetrahydrodesoxyiodoacetate

Tetrahydrodesoxyiodoacetate (272 mg) was shaken with a solution of potassium hydroxide (3 g) in water (20 ml) until a homogenous solution was obtained. The mixture was allowed to stand at room temperature for 19 hours . Acidification with dilute sulphuric acid caused precipitation of crystalline tetrahydrodesoxylimonic acid (184 mg) which was recrystallized from aqueous acetone.The analytical sample was dried under vacuum at 105^{o}C for 18 hours.

Calculated for $C_{26}H_{36}O_8$: C:65.53% H:7.61%

Found: C:65.49% H:7.78%

Mp.: 276-84°C

$(\alpha)_D$: -89° (c: 1.1 , pyridine)

Equivalent weight: 168

U.V.: end absorption at 202 mμ ε: 11,000

I.R.: diffuse 3200,1758,1730,1716 cm^{-1}

b)From tetrahydrodesoxylimonin

Tetrahydrodesoxylimonin (150 mg) was warmed on the steam bath with 2N sodium hydroxide solution (30 ml) for two hours. The solution was cooled and acidified with dilute hydrochloric acid. The crystalline precipitate was collected and re - crystallized from aqueous acetone to give tetrahydrodesoxylimonic acid ,Mp.: 275-80°C whose infrared spectrum was identical with spectrum of the material prepared by the method a).

c)From desoxylimonic acid

Desoxylimonic acid (572 mg) in glacial acetic acid (75 ml) was hydrogenated over 10% palladium-carbon (1.0 g) which was previously pre-hydrogenated. The material took up 51 ml of hydrogen and working up as usual gave acidic material

(620 mg) which on crystallization from aqueous acetone yielded tetrahydrodesoxylimonic acid Mp.: 266-72°C whose infrared spectrum was identical with that of a specimen prepared by method a).

Ozonolysis of tetrahydrodesoxylimonic acid

In a typical experiment , tetrahydrodesoxylimonic acid (130 mg) was ozonised in a mixture of glacial acetic acid (30 ml) and chloroform (45 ml) at -13°C. Aliquots were removed at intervals and worked up by addition of water and distillation of solvents under vacuum. The ultraviolet spectra of materials thus obtained showed no maxima in ethanol solution but on addition of alkali a peak appeared at 273 mμ which disappeared on re-acidification. The intensity was found to vary with the time of ozonolysis reaching a maximum of ε:5,500 after 10-15 minutes and decreasing sharply after longer periods. The materials thus obtained could not be crystallized although a variety of ozonolysis procedures was used including reactions with calculated quantities of ozone as estimated by an iodometric method.

The crude ozonolysis products gave immediate positive iodoform tests. A model substance , diethylacetonedicarboxylic ester, also gave a positive iodoform test but not immediately.

Attempted bromination of tetrahydrodesoxylimonic acid

Tetrahydrodesoxylimonic acid (44 mg) in glacial acetic acid (4 ml) was treated with excess bromine in glacial acetic acid. The mixture was allowed to stand at room temperature for two hours, was warmed briefly on the steam bath and the solvent was distilled under vacuum. The crude residue (50 mg) crystallized on addition of a drop of acetone to give unchanged starting material identified by its melting point (275-80°C), mixed melting point and infrared spectrum.

Treatment of tetrahydrodesoxylimonic acid with acid

Tetrahydrodesoxylimonic acid (51 mg) was warmed on the steam bath with a mixture of concentrated hydrochloric acid (3 ml) and dioxan (3 ml) for 18 hours. Working up as usual gave crude acidic product (45 mg) which had infrared and ultraviolet spectra similar to those of the starting material but which could not be crystallized.

Chlorination and dehydrochlorination of tetrahydrodesoxylimonic acid

In a typical experiment, tetrahydrodesoxylimonic acid (720 mg) was dissolved in glacial acetic acid (100 ml) and a solution of chlorine (0.20 milimole) in carbon tetrachloride (28 ml) was added. The mixture was allowed to stand in the dark at room temperature for 16 hours , the solvents were distilled under vacuum and the solid residue was heated under vacuum for 3 hours at 110°C.Crystallization from acetone/ether gave cisoid diene acid (390 mg).

Calculated for $C_{26}H_{34}O_8$:	C:65.80%	H:7.22%
Found:	C:65.70%	H:7.40%

Mp.: 259-69°C

$(\alpha)_D$: +231° (c:0.8 , chloroform)

U.V.: λ_{max}:255 mμ ε:7,750 (a broad band)

I.R.:1760,1714,1703,1619,1600 cm^{-1}

I.R. in chloroform : almost identical

Cisoid diene acid was converted to its methyl ester by treatment with excess ethereal diazomethane at room temperature for 45 minutes ,working up as usual and crystallization from acetone/ether.

Calculated for $C_{27}H_{36}O_8$: C:66.37% H:7.43%

Found: C:66.21% H:7.34%

Mp.:200-204°C

$(\alpha)_D$: +226 (c: 1.3 , chloroform)

U.V.: λ_{max}: 255 mμ ε:7,700 (a broad band)

Further slow crystallization of the residue from the preparation of the cisoid diene acid from acetone/ether gave transoid diene acid (80 mg).

Calculated for $C_{26}H_{34}O_8 \cdot \frac{1}{2}H_2O$: C:64.60% H:7.30%

Found: C:64.76% H:7.02%

M.p.:260-71°C

$(\alpha)_D$: +260 (c:1.2 methylene dichloride)

U.V.:λ_{max}:230 mμ ε:6,300 and λ_{max}:284mμ ε:16,400

I.R.:1752,1731,1704,1594 cm^{-1}

The transoid diene acid was converted to itsmethyl ester by treatment with excess ethereal diazomethane at room temperature for 45 minutes, working up as usual and crystallization from acetone/ether.

Calculated for $C_{27}H_{36}O_8 \cdot \frac{1}{2}H_2O$: C:65.68% H:7.50%

Found: C:65.09% H:7.19%

Mp.:207-12°C

$(\alpha)_D$: +234° (c: 1.8 , chloroform)

U.V.: λ_{max}:229mμ ε:5,400 and λ_{max}:283 mμ ε:18,650

<u>Note:</u> The crude material obtained after chlorination but before heating had the following ultraviolet spectrum: λ_{max}:230 mμ ε:6000 and a shoulder approximately at 250 mμ ε:4000. All attempts of crystallization resulted only in the cisoid diene acid being isolated. On heating the spectrum of the material changed slowly to the one expected from a mixture of cisoid and transoid diene acids. Alcoholic potassium hydroxide or collidine had an effect similar to heating but the products were darker and difficult to crystallize. Although only small amounts of the transoid diene acid were actually isolated , the ultraviolet spectra of the mother liquors indicated that the actual proportions of the cisoid/transoid isomers formed were between 2/1 and 4/1.

Ozonolysis of cisoid diene acid

Cisoid diene acid (133 mg) was dissolved in chloroform (20 ml) and ozonised at -20°C for 15 minutes. Zinc dust (0.5 g) and water (8 ml) were added and the mixture was distilled. The aqueous layer of the distillate was separated, treated with excess aqueous dimedone reagent ,allowed to stand for 20 hours and the dimedone-formaldehyde adduct (identified by its melting point and mixed melting point) was collected , dried and weighed. Yield: 18.5 mg (13.2% of theory).

Under identical conditions , pyrethrosin ($C_{17}H_{22}O_5$, 110 mg) gave 14.8 mg of the dimedone-formaldehyde adduct (13.4% of theory). Blanks using tetrahydrolimonin (100 mg) gave less than 2 mg of precipitate with the dimedone reagent.

The main ozonolysis product could not be crystallized. The ultraviolet spectrum of the crude material showed a small (ε: 2,000) peak at 384 mμ in presence of alkali which disappeared on re-acidification.

Cisoid diene acid oxide

Cisoid diene acid (74 mg) was dissolved in peracetic acid (80% , 2 ml) previously saturated with sodium acetate. The mixture was allowed to stand for 16 hours at 0°C and the excess peracetic acid was destroyed with sodium sulphite. Working up as usual and crystallization from acetone/ether gave cisoid diene acid oxide (35 mg). The analytical sample was dried under vacuum for 28 hours at 110°C.

Calculated for $C_{26}H_{34}O_9$:	C:63.66%	H:6.99%
Found:	C:63.87%	H:7.13%

Mp.: 243-9°C

$(\alpha)_D$: +88° (c: 0.4 , chloroform)

U.V.: λ_{max}: 217-8 mμ   ε:9,100

I.R.: 1767,1718,1708 cm^{-1}

Treatment of cisoid diene acid oxide with boron trifluoride

Cisoid diene acid oxide (3.8 mg) was dissolved in boron trifluoride-ether (45%,0.5 ml) and the mixture was allowed to stand at room temperature for 15 hours. The mixture was poured into water and worked up as usual to give an amorphous material whose ultraviolet spectrum showed no maxima in ethanol but a maximum appeared at 390 mμ (ε:2000) following the addition of a drop of alkali and disappeared on re-acidification.

Chlorination of cisoid diene acid

Cisoid diene acid (28.5 mg) was dissolved in glacial acetic acid (20 ml) and a solution of chlorine in carbon tetrachloride (3 ml, approx. 0.0 5 milimole of chlorine) was added. The mixture was allowed to stand in the dark at room temperature for 16 hours. Blank determinations and the determination of excess chlorine in the reaction mixture showed that 1.2 moles of chlorine were taken up. Working up as usual gave an acidic product which could not be crystallized. U.V.: λ_{max}:225 mμ ε: 7,000.

Attempted isomerisation of cisoid diene acid

Samples of cisoid diene acid were heated on the steam bath in 6N hydrochloric acid perchloric acid/acetic acid, hydrochloric acid/dioxane, and hydrochloric acid/acetic acid. In no case a shift in the maximum in the ultraviolet spectrum larger than 7 mμ could be detected.

Treatment with sulphuric acid/acetic acid caused the maximum to shift to 284 mμ but the intensity remained unchanged and no material could be recovered from the solution.

Isomer of hexahydrolimoninic acid

a)By action of hydrochloric acid in dioxane on hexahydrolimoninic acid

Hexahydrolimoninic acid (616 mg) was heated on the steam bath with a mixture of dioxan (10 ml) and concentrated hydrochloric acid (10 ml) for 17 hours. Working up as usual yielded neutral material (524 mg) which on crystallization from methylene dichloride/ethanol gave the isomer of hexahydrolimoninic acid.

Calculated for $C_{26}H_{36}O_8$: Active hydrogen:0.212%
Found: Active hydrogen:0.223%
Mp.: above 350°C
I.R.:3280,1787,1754,1684 cm^{-1}

b)By action of hydrochloric acid in methanol on hexahydrolimoninic acid

Hexahydrolimoninic acid (395 mg) was refluxed on the steam bath in a mixture of methanol (10 ml) and concentrated hydrochloric acid (10 ml). Aliquots were withdrawn at intervals and the specific rotation was determined. After 5½ hours the specific rotation was -74.5° as compared with the initial value of -28.4°. The mixture was worked up as usual to give neutral material (227 mg) which on crystallization from methylene dichloride/ethanol yielded the isomer of hexahydrolimoninic acid Mp.: above 345°C , identified by its infrared spectrum.

Acetylation of the isomer of hexahydrolimoninic acid

The isomer of hexahydrolimoninic acid (90 mg) was dissolved in a mixture of acetic anhydride (5 ml) and pyridine (5 ml) and allowed to stand at room temperature for 17 hours. The mixture was poured into water and worked up in the usual manner to give neutral material (70 mg) which on crystallization from ethanol yielded the acetate of the isomer of hexahydrolimoninic acid.

Mp.:187-92°C

I.R.: 1788,1755,1710,1235 cm^{-1}.

Action of hydroiodic acid and acetic anhydride on limonin

Limonin (517 mg) was dissolved in a mixture of acetic anhydride (5 ml) , glacial acetic acid (20 ml) and hydroiodic acid (S.g. 1.94 , 12 ml) and allowed to stand at room temperature for 40 hours. Working up as usual gave neutral product (280 mg) which on crystallization from chloroform/ ethanol yielded desoxylimonin , Mp.:312-28°C identified by its infrared spectrum.

Heptahydroiodoacetate

Hexahydrolimoninic acid (640 mg) was dissolved in a mixture of acetic acid (16 ml) and acetic anhydride (4 ml) and hydroiodic acid (S.g. 1.94 , 6 ml) was added with cooling. The mixture was allowed to stand at room temperature for 24 hours. Working up as usual yielded neutral product (751 mg) which on crystallization from ethanol gave heptahydroiodoacetate.The analytical sample was dried under vacuum for 48 hours at 80°C.

Calculated for $C_{28}H_{39}O_9I$: C:52.17% H:6.04% OAc:6.66%

Found: C:52.48% H:5.93% OAc:6.77%

Mp.:218-21°C

I.R.:3260,1790,1755,1730,1677,1240 cm^{-1}

Octahydroacetate

Heptahydroiodoacetate (500 mg) was dissolved in glacial acetic acid (50 ml) and heated on the steam bath with zinc powder (3 g) for 10 minutes with constant shaking. Working up as usual and crystallization from methylene dichloride/ethanol gave octahydroacetate. The analytical sample was dried under vacuum at 120°C for 15 hours.

Calculated for $C_{28}H_{40}O_9$: OAc:8.25% Active H:0.194%

Found: OAc:8.50% Active H:0.183%

Mp.:246-56°C

I.R.:3280,1790,1751,1730,1683,1240 cm^{-1}.

α-keto-γ-lactone

Isomer of hexahydrolimoninic acid (226 mg) was allowed to stand at room temperature with a well ground mixture of chromic oxide (700 mg) and pyridine (6 ml) for 22 hours. Water was added and sulphur dioxide was passed into the reaction mixture until it turned green. Working up as usual gave neutral product (181 mg) which on crystallization from acetone/ethanol yielded α-keto-γ-lactone. The analytical sample was dried under vacuum for 7 days at 50°C.

Calculated for $C_{26}H_{34}O_8$: C:65.80% H:7.22%

Found: C:66.04% H:7.26%

Mp.:246-53°C

$(\alpha)_D$: -43° (c: 1.5 ,chloroform)

U.V.:no strong absorption. On addition of alkali a peak appeared slowly at 252 mμ (ε:5,700), not reversible on re-acidification.

I.R.:1790,1775,1755,1720 cm^{-1}.

α-keto-γ-lactone acetate

Octahydroacetate (290 mg) in pyridine (5.5 ml) was slowly added to a well ground suspension of chromic oxide (364 mg) in pyridine (3 ml). The mixture was allowed to stand at room temperature overnight , water was added and sulphur dioxide was passed in until a green colour was obtained. Working up as usual gave neutral material (284 mg) which on crystallization from acetone/ethanol gave α-keto-γ-lactone acetate. The analytical sample was dried under vacuum for 50 hours at 120°C.

Calculated for $C_{28}H_{38}O_9$: C:64.85% H:7.39% OAc:8.29%

Found: C:64.69% H:7.55% OAc:8.10%

Mp.:235-9°C

$(\alpha)_D$: -45° (c: 1.6 ,acetone)

U.V.:no strong absorption . On addition of alkali a peak appeared slowly at 250mμ (ε:4,500) which could not be reversed with acid.

I.R.:1792,1775,1750,1730(sh),1717(sh),1235 cm^{-1}

Action of alkali on α-keto-γ-lactone

α-keto-γ-lactone (69 mg) was dissolved in a mixture of ethanol (35 ml) and 0.4N sodium hydroxide (2.00 ml) and allowed to stand for 20 minutes at 40°C. Backtitration with standard acid compared with a blank showed that the equivalent weight of the original substance was 246. Working up as usual gave an acidic product (32 mg) which could not be crystallized.

U.V.: λ_{max}:244 mμ ε:3,800

I.R.: 1755,1715,1670 cm^{-1}.

The crude product (16 mg) was refluxed

in glacial acetic acid (3 ml) with zinc dust (100 mg) for 7 hours. Working up as usual gave an acidic product (13 mg) which could not be crystallized.

U.V.: λ_{max}:250 mμ ε:2,200 .

Action of alkaline hydrogen peroxide on α-keto-γ-lactone

α-keto-γ-lactone (28 mg) was allowed to stand in 0.4 N sodium hydroxide solution (2.5 ml) for 25 minutes at room temperature. Hydrogen peroxide (100 volume, 0.5 ml) was added and the mixture was allowed to stand at room temperature for a further 15 minutes. Working up as usual gave an acidic product (10 mg) which could not be crystallized.

U.V.: λ_{max}:244 mμ ε:4,300

Tetrahydrodesoxyiodoacetate

Tetrahydrolimonin (367 mg) in a mixture of glacial acetic acid (15 ml) and hydroiodic acid (S.g. 1.94 , 10 ml) was warmed at 55-58°C for 3½ hours. Working up as usual gave neutral product (438 mg) which on crystallization from ethanol yielded tetrahydrodesoxyiodoacetate . The analytical sample was dried under vacuum for 48 hours at 90°C.

Calculated for $C_{28}H_{37}O_8I$: C:53.50% H:5.89% OAc:6.86%
Found: C:53.81% H:5.99% OAc:6.89%
Mp.:238-9°C
$(\alpha)_D$: -105° (c: 0.9 , chloroform)
U.V.: λ_{max}:219 mμ ε:12,700
I.R.: 1748,1726,1715,1238 cm^{-1}

Limonilic acid

Limonin (10.0 g) was dissolved in 4N sodium hydroxide solution (250 ml) and a solution of iodine (6 g) and potassium iodide (6 g) in water (100 ml) was added at room temperature. The mixture was allowed to stand for 25 minutes, some solid sodium sulphite was added and the mixture was acidified with concentrated hydrochloric acid and allowed to cool for 2 hours. The resulting precipitate was collected, washed with water and re-crystallized from aqueous acetone to give limonilic acid (9.9 g).

Mp.: 282-7°C
I.R.:diffuse 3,200, 1741,1721,1702(sh),1502,874 cm^{-1}.
I.R. of disodium salt: 1717 cm^{-1}.

Tetrahydrolimonilic acid

Tetrahydrolimonin (1.36 g) was dissolved in 4N sodium hydroxide solution (50 ml) and a solution of iodine (1 g) and potassium iodide (1 g) in water (20 ml) was added at room temperature. The mixture was allowed to stand for 20 minutes, some solid sodium sulphite was added and the mixture was acidified with concentrated hydrochloric acid and allowed to cool for 2 hours. The resulting precipitate was collected, washed with water and recrystallized from aqueous acetone to give tetrahydrolimonilic acid (750 mg).

Mp: 267-73°C (sinters at 180°C)

I.R.: 1742,1725,1695 cm^{-1}

Limonilyl chloride

Limonilic acid (1.93 g) in tetrahydrofuran (30 ml) was refluxed on the steam bath with oxalyl chloride (5 ml) for 1 hour. The mixture was evaporated to a syrupy consistency under vacuum and crystallized from benzene/petroleum ether to give limonilyl chloride (2.26 g). Beilstein test: +ve.

Mp.: 220-4°C

$(\alpha)_D$: +84° (c: 1.3 , chloroform)
I.R.:1791,1740,1722,1500,872 cm^{-1}
No reliable analytical figures could be obtained as the material was prone to hydrolysis.

Methyl limonilate from limonilyl chloride

Limonilic acid (234 mg) in tetrahydrofuran (6 ml) was refluxed on the water bath with oxalyl chloride (1 ml) for one hour. Methanol (10 ml) was added and reflux continued for 10 minutes. The solvents were eveporated under vacuum and the mixture was worked up as usual to give neutral material (214 mg) which on crystallization from methanol yielded methyl limonilate , Mp.:229-33°C not depressed by admixture of an authentic specimen prepared by the action of ethereal diazomethane on limonilic acid. The two samples had identical infrared spectra.

Limonilyl malonic ester

Limonilic acid (680 mg) was refluxed in tetrahydrofuran (15 ml) with oxalyl chloride (3 ml) on the steam bath for 1 hour. The solvents were distilled under vacuum until the mixture reached a syrupy consistency.

Sodium (300 mg) was dissolved in diethyl malonate (6 ml) in tetrahydrofuran (10 ml) by refluxing on the steam bath and the solution was added to the syrupy limonilyl chloride and reflux continued for one hour. Working up as usual gave a neutral material (704 mg) which could not be crystallized.

U.V.: λ_{max}:209 mμ ε:6,800 and λ_{max}:263mμ ε:5,600
U.V. in presence of alkali: λ_{max}:272 mμ ε:11,200

Methyl-limonilyl ketone

Limonilic acid (2.06 g) in tetrahydrofuran (30 ml) was refluxed on the steam bath with oxalyl chloride (5 ml) for 1 hour. The solvents were distilled under vacuum until the material reached a syrupy consistency and the crude limonilyl chloride was crystallized from benzene/petroleum ether and dried under vacuum at 50°C. The crystalline material was dissolved in tetrahydrofuran (30 ml) and poured slowly into ethereal diazomethane (prepared from 25 g of nitroso-N-methyl urea) with cooling in an ice bath.The mixture was allowed to stand at room temperature for 1 hour and ether was distilled under vacuum at room temperature. The residue was dissolved in chloroform , shaken with hydroiodic acid (S.g. 1.7 , 6 ml) for 5 minutes and worked up as usual. The neutral material was dissolved in ethanol (30 ml) and boiled with 0.4N sodium hydroxide solution (30 ml) on the steam bath for 30 minutes the ethanol being allowed to distill . The solution was cooled, extracted with chloroform, the extract was discarded and the alkaline solution was worked up as usual to give neutral material (1.58 g). This was dissolved in benzene (50 ml) , filtered and chromatographed on alumina (grade I, 6 g). The material washed through with benzene (100 ml) and with 7% acetone/benzene (200 ml) was combined and crystallized from benzene petroleum ether to give methyllimonilyl ketone (782 g).

Calculated for $C_{27}H_{32}O_8 \cdot 2C_6H_6$: C:73.10% H:6.92%

Found: C:73.26% H:6.88%

Mp: Benzene solvate:110-112°C.Amprphous material precipitated from acetone with petroleum ether:145°C.

$(\alpha)_D$: +85° (c:1.1 , acetone)

U.V. of benzene solvate: fine structure with principal maximum at 255 mμ (ε:357). Also λ_{max}:288mμ (ε:54) and an inflexion near 310 mμ (ε: 40).

U.V. of material freed from benzene: λ_{max}:207mμ ε:7,000.

Equivalent weight of benzene solvate: 600

I.R. of benzene solvate: 1735,1722,1712,1500,876,691cm^{-1}.
(1735, 1722, 1713, 1500, 875 in CHLOROFORM)

Action of zinc and acetic acid on methyl-limonilyl ketone

Methyl-limonilyl ketone (60 mg) was refluxed in glacial acetic acid (10 ml) with powdered zinc (1 g, previously activated by shaking with dilute aqueous copper sulphate, washing and drying) for 17 hours. The mixture was filtered, the solution was evaporated to dryness under vacuum and the residue was worked up as usual to give neutral material (54 mg) which yielded crystalline methyl-limonilyl ketone on addition of a drop of benzene, Mp.: 110°C, identified by its infrared spectrum.

Action of alkali on methyl-limonilyl ketone

Methyl limonilyl ketone (71 mg) was

warmed on the water bath with 1N sodium hydroxide solution (6 ml) for 1 hour. Working up as usual gave neutral material (64 mg) which crystallized on addition of a drop of benzene and had melting point and rotation identical with that of the starting material.

In another experiment , methyl-limonilyl ketone (0.630 mg) was heated on the steam bath in 1N sodium hydroxide solution (5 ml) and the ultraviolet spectrum was examined at intervals. No change was observed during 2 hours.

Reaction of methyl-limonilyl ketone with benzaldehyde in the presence of alkali

Methyl-limonilyl ketone (100 mg) in ethanol (10 ml) and 4N sodium hydroxide (3 ml) was allowed to stand at room temperature with benzaldehyde (1 ml) for 17 hours. Working up as usual gave neutral material (88 mg) which could not be crystallized. U.V.: end absorption at 208 mμ: ε:16,000 and λ_{max}: 293 mμ ε:3,100.

Oxidation of methyl-limonilyl ketone with iodine and potassium hydroxide

Methyl-limonilyl ketone (41 mg) was dissolved in 1N sodium hydroxide (10 ml), excess iodine in potassium iodide solution was added and the mixture was allowed to stand at room temperature for 20 minutes. A copious precipitate of iodoform appeared as soon as the reagents were mixed. This was collected and crystallized from ethanol, Mp.: 121-3°C not depressed by mixing with an authentic specimen. The alkaline solution was worked up as usual to give an acidic product (25 mg) which could not be crystallized. The infrared spectrum of this material was very similar to that of limonilic acid. $(\alpha)_D$: +86° (c:0.9 , acetone)

Pyrolysis of limonilyl chloride

In a typical experiment , limonilyl chloride (33 mg) was heated under a stream of nitrogen at 234°C and the gas was passed into water and titrated with sodium hydroxide solution. In 8 minutes hydrochloric acid equivalent to 3.5 ml of 0.1 N alkali was evolved (63% of theory). Only neutral material could be isolated from the residue on working up as usual.

Larger batches of limonilyl chloride were pyrolysed at 234°C under vacuum (0.5 mm Hg). The pyrolysis was virtually complete after 6 minutes and only neutral material could be isolated from the reaction mixture by working up in the usual manner. The material could not be crystallized. Equivalent weight: 226, 233. After working up, the alkali treated material was acidic.

U.V.: λ_{max}: 207-10 mμ ε: 13,000. When the spectrum of methyl-limonilyl ketone was subtracted a maximum near 210-15 mμ remained (ε:6,500).

I.R.: 1750,1715,1502,875 cm^{-1}.

Treatment of pyrolysed limonilyl chloride with alkali

The crude neutral product of pyrolysis of limonilyl chloride (313 mg) was heated on the steam bath in acetone (10 ml) and 2N sodium hydroxide (5 ml) for 30 minutes. Working up as usual gave an acidic product (174 mg) which on crystallization from aqueous acetone yielded limonilic acid (50 mg) identified by its melting point and infrared spectrum.

Citrolin from desoxylimonin

Desoxylimonin (716 mg) was refluxed with hydrogen bromide in glacial acetic acid (50% weight/volume , 10 ml) for 40 minutes. The mixture was cooled, poured into water and worked up as usual to give only neutral material. Crystallization from tetrahydrofuran/iso-propanol yielded citrolin (392 mg).

Mp.: 294-8°C

U.V.: λ_{max}:213.5 mμ ε:25,200 and shoulder near 240 mμ ε:18,500. When the spectrum of desoxylimonin was subtracted from that of citrolin two maxima appeared: 206-15mμ (ε:9,500) and 244 mμ (ε:13,700)

I.R.: 1724-1716,1670,1504,875 cm^{-1}.

Hydrogenation of citrolin over palladium-carbon

In a typical experiment , citrolin (71.4 mg) in dioxan (10 ml) was hydrogenated over previously pre-hydrogenated palladium-carbon (10%, 114 mg) until 4.2 ml of hydrogen (approximately 1.05 mole) was absorbed. The mixture was filtered, the solution was evaporated to dryness under vacuum and the residue was worked up as usual to give only neutral material. Crystallization from acetone/ ethanol yielded dihydrocitrolin (50 mg). The analytical sample was dried under vacuum for 14 hours at 100°C.

Calculated for $C_{26}H_{30}O_6$: C:71.21% H:6.90%

Found: C:71.41% H:7.13%

Mp.:282-6°C

$(\alpha)_D$: -106° (c:1.0 , chloroform)

U.V.: λ_{max}:216 mμ ε:17,200 and shoulder near 231-243 mμ (ε:14,700). When the spectrum of desoxylimonin was subtracted from that of dihydrocitrolin a maximum remained at 248 mμ ε:10,550

I.R.:1756,1712,1667,1500,874 cm^{-1}.

In other experiments, when larger volumes of hydrogen were absorbed under similar conditions, a second crystalline neutral product , hexahydrocitrolin, could be isolated in a small yield besides dihydrocitrolin. Insufficient sample was available for analysis but material crystallised from ethanol/ acetone had the following properties:

Mp.: 290°C

U.V.: λ_{max}:238 mμ ε:13,700 and shoulder near 225mμ
(ε: 13,000)

I.R.: 1753,1698,1663 cm^{-1} (no furan bands).

Treatment of dihydrocitrolin with alkali

Dihydrocitrolin (3.00 mg) in ethanol (5.0 ml) and 2N sodium hydroxide (25 ml) was heated on the steam bath under nitrogen. Ultraviolet spectra of the reaction mixture were determined at intervals both in alkaline and acidified solution. No significant changes could be observed in the region between 245 and 300 mμ in a period up to 2 hours.

Obacunoic acid

Crushed grapefruit seeds (5 kg) were extracted for limonin in the usual way. The mother liquors remaining after crystallization of limonin (35.2 g) were evaporated to dryness and worked up to give a crude neutral residue (24 g) which was boiled with acetone (100 ml) and 1N sodium hydroxide solution (200 ml) for 1 hour , acetone being allowed to evaporate. Working up as usual gave an acidic material (12 g) which on crystallization from acetone/ether yielded obacunoic acid (1.8 g). The analytical sample was dried under vacuum for 74 hours at 93°C.

Calculated for $C_{26}H_{32}O_8$: C:66.08% H:6.83% activeH(2):4.24%
Found: C:65.82% H:6.86% activeH: 4.26%

Mp.: 205-8°C

$(\alpha)_D$: -103° (c:1.2,tetrahydrofuran)

U.V.: λ_{max}:204-5mμ (ε:18,000). At 210mμ,ε:14,000

I.R.:3220,diffuse absorption between 3400-2800,1745, 1710,1621,1503,874 cm^{-1}.

Methyl obacunoate

(i)By action of ethereal diazomethane on obacunoic acid

Obacunoic acid (460 mg) in tetrahydrofuran

(25 ml) was treated with excess ethereal diazomethane at room temperature for 1 minute. The mixture was evaporated to dryness under vacuum at room temperature and the residue was crystallized from ether to give methyl obacunoate (400 mg). Part of the sample was purified and dried under vacuum for 41 hours at 95°C.

Mp.:173-6°C

$(\alpha)_D$: -94° (c:1.2, methylene dichloride)

U.V.:λ_{max}: 203 mμ (ε:7,100), at 210 mμ, ε:6,700

I.R.:3540,1738,1716,1623,1503,1204,875 cm^{-1}.

(ii) By action of methyl iodide on obacunoic acid

Obacunoic acid (98 mg) in acetone (30 ml) was treated with 0.10 N sodium hydroxide solution (5.50 ml) and methyl iodide (5 ml). The mixture was allowed to stand at room temperature for 17 hours. Working up as usual and crystallization from ether gave methyl obacunoate (66 mg), Mp.:168-73°C, whose infrared spectrum was identical with that of a sample prepared by the action of diazomethane on obacunoic acid.

Hydrogenation of obacunoic acid

Obacunoic acid (105 mg) was hydrogenated over previously prehydrogenated palladium-carbon (10%, 150 mg) in glacial acetic acid (10 ml). Uptake of hydrogen ceased when 20.25 ml (3.74 moles) were absorbed at 24°C. Working up as usual gave an acidic material (109 mg) ,which could not be crystallized.

Methyl-hydrogen octahydroobacunoninate

Methyl obacunoate (328 mg) in acetic acid (25 ml) was hydrogenated over previously prehydrogenated palladium-carbon (10%, 690 mg) , suspended in acetic acid (10 ml). The uptake of hydrogen ceased when 63.5 ml were absorbed at 22°C (3.86 moles). Working up as usual gave acidic material (220 mg) which was crystallized from aqueous methanol to yield methyl-hydrogen octahydroobacunoninate (150 mg).

M.p.:173-5°C

$(\alpha)_D$: +120° (c:1.1 , methanol)

I.R.:3470,3230,1741,1720,1705 cm^{-1}.

In another experiment , methyl obacunoate (19.4 mg) was found to absorb accurately determined 3.75 moles of hydrogen under the same conditions. Working up as usual and crystallization from aqueous methanol gave methyl-hydrogen octahydroobacunoninate which was identified by its mixed melting point and infrared spectrum.

Desoxyobacunoic acid

Obacunoic acid (136 mg) was dissolved in a mixture of acetone (16 ml) and acetic acid (6 ml) and a solution of chromous chloride (1N, 5.0 ml) was added under nitrogen. The mixture was shaken under nitrogen for 43 hours at room temperature, acetone was evaporated under vacuum and water (100 ml) was added. Working up as usual and crystallization from methylene dichloride/benzene gave desoxyobacunoic acid (107 mg). The analytical sample was dried under vacuum for 54 hours at 95°C.

Calculated for $C_{26}H_{32}O_7$: C:68.40% H:7.07%
Found: C:68.33% H:7.17%
Mp.: 158-79°C
$(\alpha)_D$: - 101° (c:1.0 , methylene dichloride)
U.V.: λ_{max}:206-8mμ (ε:22,600), at 210mμ ε:21,800
I.R.: 3360,1715,1695,1636,1502,875 cm^{-1}.

Treatment of desoxyobacunoic acid with alkali

Desoxyobacunoic acid (3.8 mg) was refluxed on the steam bath in a mixture of methanol (2 ml) and 2N sodium hydroxide solution (2 ml) for 90 minutes. Working up as usual gave an acidic material (1.2 mg), which could not be crystallized.

U.V.: at 206mμ; ε:10,000 , at 210 mμ ; ε:7,700

Treatment of methyl-hydrogen octahydroobacunoninate with strong acid.

(i) Action of concentrated hydrochloric acid in dioxan

Methyl-hydrogen octahydroobacunoninate (83 mg) was heated on the steam bath with a mixture of concentrated hydrochloric acid (2 ml) and dioxane (2 ml) for 16 hours. Working up as usual gave a neutral fraction (30 mg) and an acidic fraction (49mg) neither of which could be crystallized. The crude materials had the following spectroscopic properties:

Neutral: I.R.: 3200, 1732, 1631, 1787 cm^{-1}
U.V.: λ_{max}: 247 mμ (ε: 8,000)
Acid: I.R.: 3200, diffuse bands between 3400-3000, 1785, 1720, 1631 cm^{-1}.
U.V.: λ_{max}: 250.5 mμ (ε: 9,200)

(ii) Action of concentraded hydrochloric acid in methanol

Methyl-hydrogen octahydroobacunoninate (2.57 mg) was refluxed on the steam bath with a mixture of concentrated hydrochloric acid (12.5 ml) and methanol (12.5 ml). Aliquots were withdrawn at intervals and their ultraviolet spectra were determined. A peak appeared at 250 mμ after 40 minutes of refluxing (ε:4,400) , increased to ε:12,000 after approximately 12 hours and remained unaltered after a total reflux time of 25 hours.

The experiment was repeated with 71 mg of the starting material but both the neutral (52 mg) and the acidic (20 mg) fractions which were obtained could not be crystallized.

Treatment of hydrogenated obacunoic acid with strong acid.

The crude acidic material obtained by hydrogenation of obacunoic acid over palladium-carbon (91 mg) was heated on the steam bath with a mixture of concentrated hydrochloric acid (2 ml) and dioxane (2 ml) for 17 hours. Working up as usual gave an acidic material (62 mg) which could not be crystallized.

I.R.: Diffuse bands in the 3500-3000 region, 1785, 1720, 1630 cm^{-1}.

U.V.: λ_{max}: 250 mμ, ε: 10300

The ultraviolet spectrum of a sample of the crude product heated in 2N sodium hydroxide solution for 100 minutes on the steam bath and worked up as usual, remained unaltered in the region between 230 and 320 mμ.

iso-Obacunoic acid

Methyl obacunoate (122 mg) in dry methanol (8 ml) was added under nitrogen to a solution of sodium (0.5 g) in dry methanol (5 ml). The mixture was refluxed under nitrogen for 1 hour, water (10 ml) was added and reflux was continued for a further 30 minutes. Acidification and working up as usual, gave only acidic material (prolonged shaking with bicarbonate solution was necessary to effect extraction), which on crystallization from methylene dichloride/benzene yielded iso-obacunoic acid (70 mg). The analytical sample was dried under vacuum for 45 hours at 95°C.

Calculated for $C_{26}H_{32}O_8$: C: 66.08% H: 6.83%

Found: C: 65.95% H: 6.93%

Mp.: 155-61°C

$(\alpha)_D$: -41° (c:1.2 in methylene dichloride)

U.V.: λ_{max}:208 mμ (ε:5,200)

I.R.: Diffuse bands between 3500 and 3000 ,1741,1716
1704,1505,876 cm^{-1}.

When obacunoic acid was treated with a solution of sodium methoxide under identical conditions, iso-obacunoic acid was also obtained but large losses were incurred during crystallization. The purified product was identified by its melting point, mixed melting point and infrared spectrum.

Hydrogenation of iso-obacunoic acid

iso-Obacunoic acid (19.5 mg) in glacial acetic acid (10 ml) was hydrogenated over previously prehydrogenated palladium-carbon (10% , 65 mg), until hydrogen uptake ceased. The volume of hydrogen taken up at 20°C was 2.96 ml (2.94 moles). Working up as usual gave an acidic product which could not be crystallized.

Treatment of obacunoic acid with iodine and alkali

Obacunoic acid (analytical purity,55 mg) was dissolved in 2N sodium hydroxide solution (3 ml) and was treated with excess aqueous iodine and potassium iodide. A precipitate appeared , was collected, purified by sublimation at 100°C and identified as iodoform by its melting point and mixed melting point with an authentic sample. The weight of the crude dried precipitate was 7 mg (approximately 15% of theory). The filtrate was worked up as usual to give an acidic product (46 mg) which could not be crystallized.

I.R.: Diffuse bands between 3500 and 3000,1745-1705, 1630,1500,875 cm^{-1}.

U.V.: End absorption at 208 mμ , ε: 12,000

Treatment of iso-obacunoic acid with iodine and alkali

iso-Obacunoic acid (44 mg) was dissolved in sodium hydroxide solution (2N, 2.5 ml) and treated with excess aqueous iodine and potassium iodide. No precipitate appeared on standing at room temperature for 30 minutes. Working up as usual and crystallization from benzene gave iso-obacunoic acid (30 mg), Mp.: 150-155°C , whose infrared spectrum was identical with that of an authentic sample.

Dihydrocarvone

Carvone (50 ml) in ethanol (300 ml) was added to a suspension of zinc dust (100 g) in water (300 ml) and sodium hydroxide (50 g). The mixture was refluxed for 16 hours , ethanol was allowed to distill and the residue was filtered and extracted with ether. The extract was dried, ether was evaporated off and the residue was distilled under reduced pressure. The fraction boiling between 134-144°C at 60 mm Hg was collected (26 g) and identified as dihydrocarvone.

$n_d^{23°C}$: 1.4718

I.R.: 1705,1640,895 cm^{-1} (c.f. carvone:1680,1640,895cm^{-1})

U.V.: No strong absorption between 210-300 mμ

Dihydrocarvonehydrate

Dihydrocarvone (14 g) was mixed with cooling with dilute sulphuric acid (40% w/w , 120g) and the mixture was shaken at room temperature for 24 hours. Sodium hydroxide solution (4N,200 ml) was added with cooling and the mixture was extracted with ether. The extract was dried, ether was distilled off and the residue was distilled under reduced pressure.

The fraction boiling between 136-41°C at 10 mm Hg (7.2 g) was collected and redistilled to give pure dihydrocarvonehydrate.

$n_d^{21°C}$: 1.4773

I.R.: 3400,1705 cm^{-1}

A GLC run showed that the sample was at least 98% pure.

Carvonehydrate

Carvone (100 ml) was added to a solution of sodium metabisulphite (anhydrous, 90 g) in water (200 ml). The mixture was boiled until homogenous (45 minutes) and cooled to 0°C. A mixture of sulphuric acid (80 g) and water (80 ml) was added with cooling and the pale, homogenous solution was allowed to stand at room temperature for 6 days. Sodium hydroxide solution (6N, 300 ml) was added with cooling and the mixture was extracted with ether. The extract was dried, ether was evaporated off and the residue was distilled under reduced pressure. The fraction boiling between 152-4°C at 10mm Hg (64 g) was collected and redistilled to give carvonehydrate (39 g).

I.R.: 3400,1680 cm^{-1}

Ferric chloride test: negative.

Treatment of carvonehydrate with iodine and alkali

Carvonehydrate (4.95 g) in dioxane (50 ml) was treated with sodium hydroxide solution (4N, 100 ml) and a solution of iodine (30 g) and potassium iodide (40 g) in water (100 ml). A dense precipitate of iodoform formed and was removed by filtration. The filtrate was acidified and worked up as usual. The neutral fraction was divided into material insoluble in dilute sodium hydroxide solution and enolic material (1.68 g), which was a dark oil with a strong phenolic odour and gave a green colouration with ferric chloride. The crude phenolic material was warmed on the steam bath with 3:5:dinitrobenzoyl chloride (2 g) and pyridine (20 ml) for 30 minutes. Working up as usual and chromatography on alumina (grade III) gave diiodo-o-cresyl-3:5:dinitrobenzoate (900 mg i.e. 5.6% of theory) which did not depress the melting point of a specimen prepared from authentic diiodo-*o*-cresol. The two samples had identical infrared spectra.

Calculated for $C_{14}H_8O_6N_2I_2$: C:30.35%, H:1.45%, N:5.07%, I:45.8%

Found: C:31.16% H:1.55% N:5.17% I:45.6%

Mp.: 206-13°C, from ethanol.

In another experiment, the phenolic fraction (1.69 g), which was obtained in the manner described above from carvonehydrate (5.48 g) , was dissolved in 2N sodium hydroxide solution (30 ml) and refluxed under nitrogen with zinc dust (10 g) and powdered iron (2 g) for 2 hours. Working up as usual gave an oil (770 mg) which had a strong phenolic odour and gave a negative Beilsten test.

A portion of the material (460 mg) in benzene (20 ml) was refluxed with 3:5dinitrobenzoyl chloride (2.2 g) and pyridine (2 ml) for 20 minutes. Working up as usual and crystallization from ethanol gave o-cresyl-3:5dinitrobenzoate (207 mg i.e. 3.5% of theory) , Mp.:135-8°C, not depressed by admixture of authentic material. The two samples had identical infrared spectra.

Diiodo-o-cresol

o-Cresol (5 g) in aqueous ammonia (20N, 80 ml) was treated with a solution of iodine (20 g) and potassium iodide (25 g) in water (40 ml) at room temperature. A precipitate was formed immediatelly, which on crystallization from glacial acetic acid gave diiodo-o-cresol (4.5g), Mp.:65-9°C, I.R.:3,400,860,855 cm^{-1}.

3-β-Acetoxy-11-keto-bisnor-allo-cholanic acid

The crude mixture of 3-β-acetoxy- and 3-β-hydroxy-11-keto-bisnor-*allo*-cholanic acids (3.97 g) was dissolved in pyridine (10 ml) and acetic anhydride (10 ml) and the mixture was allowed to stand at room temperature for 20 hours. The reaction mixture was poured into water and the precipitate was collected and crystallized from aqueous acetone to give 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid (3.39 g).

Mp.: 189-98°C

I.R.: 1727,1709,1683,1250 cm^{-1}.

3-β-Hydroxy-11-keto-bisnor-allo-cholanic acid

The crude mixture of 3-β-acetoxy-and 3-β-hydroxy-11-keto-bisnor-*allo*-cholanic acids (5.78 g) was heated on the steam bath with ethanol (25 ml) and 2N sodium hydroxide (25 ml) for 1 hour. The mixture was acidified and the precipitate was collected and crystallized from aqueous methanol to give 3-β-hydroxy-11-keto-bisnor-allo-cholanic acid (4.68 g). Mp; 252-60°C. $(\alpha)_D$:+27°(c:4.8,chloroform). I.R.:3350,1702,1680 cm^{-1}.

Phenacyl ester of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid

The crude mixture of 3-β-acetoxy and 3-β-hydroxy 11-keto-bisnor-allo-cholanic acids (3.06 g) was dissolved in a solution of sodium carbonate (670 mg) in water (15 ml). Phenacyl bromide (2.4 g) in ethanol (35 ml) was added and the mixture was heated on the water bath for 2 hours. Working up as usual gave only neutral material , which was heated with a mixture of acetic anhydride (10 ml) and pyridine (10 ml) on the steam bath for 1 hour.The reaction mixture was poured into water and worked up as usual . Crystallization from aqueous methanol gave the phenacyl ester of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid (2.88 g). The analytical sample was dried under vacuum for 15 hours at 85°C.

Calculated for $C_{32}H_{42}O_6$:	C:73.53%	H:8.10%	OAc:8.24%
Found:	C:73.47%	H:8.35%	OAc:8.18%

Mp.:159-60°C

$(\alpha)_D$: +16.7° (c:3.4 , chloroform)

U.V.: λ_{max}:242mμ ε:12,700

I.R.:1744,1724,1710,1694,1599 cm^{-1}

Heating of phenacyl ester of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid with collidine

The ester (246 mg) was refluxed with collidine (10 ml) for 2 hours. Working up as usual and crystallization from aqueous methanol gave the starting material (185 mg) , Mp.:159-60°C whose infrared spectrum was identical with that of an authentic sample.

In other experiments , the phenacyl ester was heated with collidine in a sealed tube for 12 hours at 250°C and with specially dried collidine for 15 hours at 260°C. In both cases the starting material was recovered in the form of the 3-β-hydroxy-11-keto-bisnor-allo-cholanic acid , following hydrolysis with dilute alkali.

Dimethyl cyclohexylamine oxide

Dimethyl cyclohexylamine (63 g) was dissolved in a mixture of acetone (50 ml) and hydrogen peroxide (100 volume , 67 ml). The mixture warmed up spontaneously. After the initial reaction subsided , the mixture was refluxed on the steam bath for 5½ hour and excess reagents and solvents were distilled at 100°C under approximately 30 mm Hg. The remaining material solidified on cooling and was crystallised from benzene to give *dimethyl cyclohexylamine oxide* Sublimation point:100-110°C.

N-N-Dimethyl hydroxylamine

Dimethyl *cyclo*hexylamine oxide (50 g) was pyrolysed at 150-200°C and the fraction of distillate boiling between 94 and 97°C was collected and re-distilled to give *N-N-dimethyl hydroxylamine* (16.3 g) characterised by its hydrochloride Mp.:99-105°C.

3-β-Acetoxy-11-keto-bisnor-allo-cholanic acid chloride

3-β-Acetoxy-11-keto-bisnor-*allo*-cholanic acid (1.78 g) was refluxed in tetrahydrofuran (8 ml) with oxalyl chloride (3 ml) for 1 hour.The mixture was evaporated under vacuum to a syrupy consistency and crystallized from petroleum ether to give *3-β-acetoxy-11-keto-bisnor-allo-cholanic acid chloride* (1.26 g).

Calculated for $C_{24}H_{35}O_4Cl$:C:68.14% H:8.34% Cl:8.38% OAc:10.1
Found: C:66.73% H:7.95% Cl:7.98% OAc:11.3
Mp.:161-4°C $(\alpha)_D$: +17.6° (c:3.1,chloroform)
I.R.:1780,1730,1706,1248 cm^{-1}.

O-Dimethyl hydroxylamine ester of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid

3-β-Acetoxy-11-keto-bisnor-allo-cholanic acid chloride (480 mg) was dissolved in tetrahydrofuran (2.5 ml) and N-N-dimethyl hydroxylamine (0.2 ml) was added. The mixture was allowed to stand at room temperature for 80 minutes. Working up as usual and crystallization from aqueous methanol gave O-dimethyl hydroxylamine ester of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid (500 mg). The analytical sample was dried under vacuum for 12 hours at 90°C.

Calculated for $C_{26}H_{41}O_5N$: C:69.76% H:9.23% N:3.13% OAc:9.60%
Found: C:70.04% H:9.34% N:3.06% OAc:9.43%
Mp.:148-52°C
$(\alpha)_D$: +26° (c: 1.1 , chloroform)
I.R.: 1756,1731,1704,1247 cm^{-1}.

Attempted decarboxylation of O-dimethylhydroxylamine ester of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid

a) By pyrolysis

The ester was pyrolysed (i)at 200°C and (ii) at 238°C , under a stream of nitrogen and the gas was passed through a solution of barium hydroxide. No precipitate of barium carbonate appeared in 30 minutes and the residual material gave , after hydrolysis with dilute alkali and working up as usual,high yields of 3-β-hydroxy-11-keto-bisnor-allo-cholanic acid ,which was identified by its melting point and infrared spectrum.

b) By quaternization followed by pyrolysis

The ester (112 mg) was dissolved in dry methyl iodide (2.5 ml), the mixture was refluxed for several hours with exclusion of moisture, evaporated to dryness and heated at 100°C for several minutes. Hydrolysis with dilute alkali and working up as usual gave 3-β-hydroxy-11-keto-bisnor-allo-cholanic acid (91 mg) , Mp.:256-9°C,whose infrared spectrum was identical with that of an authentic sample.

The above experiment was repeated with the following modifications:

(i) The ester was heated with dry methyl iodide in a sealed tube at 147°C for 1½ hours.

(ii) The ester was refluxed with dry methyl iodide, the mixture was evaporated to dryness and the residue was refluxed in dry collidine for 1½ hours.

(iii) The ester was heated with dry methyl iodide in a sealed tube at 170°C for 4 hours.

In all cases the 3-β-hydroxy-11-keto-bisnor-allo-cholanic acid was isolated from the reaction mixtures following hydrolysis with dilute alkali and working up as usual. Substitution of benzyl bromide for methyl iodide in an experiment in which the ester was heated in a sealed tube at 150°C resulted in an intractable tar.

O-Benzyl-N-oxy-piperidine

Benzoyl peroxide (7.5 g) was dissolved in ether (300 ml) and shaken at room temperature with piperidine (6 ml) for 12 hours. An oily layer separated out and was discarded. The ethereal layer was saturated with hydrogen chloride and the precipitate which formed was collected after cooling. The crude hydrochloride was decomposed with water, extracted with ether,washed with bicarbonate solution and evaporated to dryness. Crystallization from petroleum ether gave O-benzyl-N-oxy piperidine (1.92 g) Mp.:59-62°C.

Treatment of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid chloride with triethylamine in the presence of air.

3-β-Acetoxy-11-keto-bisnor-allo-cholanic acid (1.22 g) was refluxed in tetrahydrofuran (10 ml) with oxalyl chloride (0.60 ml) for 1 hour. The mixture was cooled to room temperature , dry air was passed through it and triethylamine (2.50 ml) in tetrahydrofuran (20 ml) was added. Air was passed through the mixture for 22 hours, water was added and the mixture was worked up as usual to give a neutral material (630 mg) which on crystallization from methylene dichloride/petroleum ether yielded 3-β-acetoxy-11-keto-bisnor-allo-cholanic anhydride. The analytical sample was dried under vacuum for 45 hours at 85°C.

Calculated for $C_{48}H_{70}O_9$: C:72.88% H:8.92% OAc:10.87%

Found: C:73.12% H:9.19% OAc:11.07%

Mp.:237-44°C

$(\alpha)_D$: +35° (c:1.5 , chloroform)

I.R.: 1813,1744,1731,1704,1242 cm^{-1}.

Irradiation of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid chloride.

The acid chloride (951 mg) in dioxane (60 ml) was irradiated@ for 3 hours. Aliquots were withdrawn at intervals, poured into water and titrated with 0.1 N sodium hydroxide solution. At the end of the irradiation period the titre fell to 20% of the original value and was decreasing only very slowly. Working up as usual gave the crude neutral product (897 mg) which was dissolved in a mixture of petroleum ether (40 ml) and benzene (20 ml) and filtered through a column of alumina (grade III, 8 g). The material washed through and that elluted by a further portion of the same solvent mixture (60 ml) was combined (460 mg) and crystallized from aqueous methanol to give 3-β-acetoxy-11-keto-allo-pregnane which was identical in all respects with a sample prepared from 3-β-acetoxy-11-20-diketo-allo-pregnane.

Calculated for $C_{23}H_{36}O_3$: C:76.62% H:10.07% OAc:11.93%

Found: C:76.60% H:10.28% OAc:11.87%

Mp.: 159-62°C

$(\alpha)_D$: +38° (c: 1.3 , chloroform)

I.R.: 1731,1705,1250 cm^{-1}

U.V.: end absorption at 208 mμ ,ε: 500

@Standard irradiation conditions: The solution was placed in a quartz flask fitted with a reflux condenser and irradiated with a mercury lamp (150 w) placed as closely as possible to the flask. Dry, oxygen free nitrogen was passed through the solution throughout the irradiation period.

<u>Treatment of 3-β-acetoxy-11-20-diketo-allo-pregnane with ethane dithiol</u>.

3-β-Acetoxy-11-20-diketo-*allo*-pregnane (465 mg) was treated with ethane dithiol (10 drops) and boron trifluoride (45% in ether, 15 drops) at room temperature. The mixture , which formed a homogenous solution , set to a solid after one minute, was allowed to stand at room temperature for five minutes and was poured into methanol. Some sodium bicarbonate was added and the mixture was worked up as usual . Crystallization from methylene dichloride/ ethanol gave <u>3-β-acetoxy-11-keto-20-dithioketal-allo-pregnane</u> (300 mg).

Calculated for $C_{25}H_{38}O_3S_2$: C:66.64% H:8.50% S:14.2%

Found: C:66.03% H:8.49% S:14.1%

Mp.: 234-7°C

$(\alpha)_D$: + 21.5° (c: 1,5 in chloroform)

I.R.: 1725,1695,1249 cm^{-1}.

3-β-Acetoxy-11-keto-allo-pregnane

3-β-Acetoxy-11-keto-20-dithioketal-allo-pregnane (237 mg) in absolute ethanol (50 ml) was refluxed with Raney nickel (activity W1, 2g) for 16 hours. The mixture was filtered,evaporated to dryness and worked up as usual to give give 3-β-acetoxy-11-keto-allo-pregnane, Mp. 160-3°C (from aqueous methanol) not depressed by admixture of material prepared by irradiation of 3-β-acetoxy-11-keto-bisnor-allo-cholanic acid chloride. The two samples had identical infrared spectra.

$(\alpha)_D$: +40° (c: 1.9 , chloroform).

Huang-Minlon reduction of 3-β-acetoxy-11-20-diketo-allo-pregnane.

The ketone (683 mg) in diethylene glycol (20 ml) was refluxed with hydrazine (aqueous,64% w/w, 2.0 ml) and potassium hydroxide (3 g) for 90 minutes under nitrogen. Water was allowed to distill until the temperature of the liquid rose from an initial 140°C to 200°C. Reflux was then continued for a further 4 hours and the mixture was cooled and worked up as usual to give a neutral material (580 mg) which crystallized on addition of methanol to yield 3-β-hydroxy-allo-pregnane. The analytical sample was dried under vacuum for 45 hours at 80°C.

Calculated for $C_{21}H_{36}O$: C:82.83% H:11.92%

Found: C:82.77% H:12.19%

Mp.: 139-40°C

$(\alpha)_D$: +21° (c:1.3 , chloroform)

IR: 3200 cm^{-1} , no bands in 1800-1500 cm^{-1} region.

Another crystalline reduction product (Mp.:168-72°C) was isolated from the mother liquors in small yield. The infrared spectrum of this material was very similar to that of the major product.

3-β-11-α-Dihydroxy-bisnor-allo-cholanic acid

The crude mixture of 3-β-acetoxy and 3-β-hydroxy 11-keto-bisnor-allo-cholanic acids (12 g) was dissolved in ethanol (350 ml), and sodium (35 g) was added slowly to the mixture while it was refluxed on the steam bath. A thick paste was formed as all the sodium dissolved. Water (125 ml) was added and the homogenous mixture was refluxed on the steam bath for 30 minutes, cooled and acidified with hydrochloric acid . The precipitate was collected and crystallized from aqueous methanol to give 3-β-11-α-dihydroxy-bisnor-allo-cholanic acid (9.1g). The analytical sample was dried under vacuum for 51 hours at 100°C.

Calculated for $C_{22}H_{36}O_4$: C:72.49% H:9.96%
Found: C:72.28% H:9.86%
Mp.:277-81°C
$(\alpha)_D$: -36° (c: 0.8 , chloroform)
I.R.: 3400,3220,2600,1667 cm^{-1}

3-β-11-α-Diacetoxy-bisnor-allo-cholanic acid

3-β-11-α-dihydroxy-bisnor-allo-cholanic acid (9.0 g) was allowed to stand at room temperature for 21 hours with a mixture of pyridine (22 ml) and acetic anhydride (22 ml). Working up as usual and crystallization from acetone/petroleum ether gave 3-β-11-α-diacetoxy-bisnor-allo-cholanic acid (8.38g). The analytical sample was dried under vacuum for

27 hours at 100°C.

Calculated for $C_{26}H_{40}O_6$: C:69.61% H:8.99% OAc:19.2%

Found: C:69.35% H:9.21% OAc:19.6%

Mp.: 206-8°C

(α)$_D$: -40° (c:1.7 , chloroform)

I.R.: 3000 (diffuse),1735,1705,1251 cm^{-1}.

<u>3-β-Hydroxy-11-α-acetoxy-bisnor-allo-cholanic acid</u>

3-β-11-α-diacetoxy-bisnor-<u>allo</u>-cholanic acid (320 mg) was heated on the steam bath in a mixture of tetrahydrofuran (30 ml) and 1N sodium hydroxide solution (10 ml) for 1 hour. Working up as usual and crystallization from methanol gave <u>3-β-hydroxy-11-α-acetoxy-bisnor-allo-cholanic acid</u> (303 mg).

Calculated for $C_{24}H_{38}O_5$: C:70.90% H:9.42% OAc:10.6%

Found: C:71.20% H:9.72% OAc:10.6%

Mp.: 308-14°C

(α)$_D$ - 47° (c: 0.9 , pyridine)

I.R.: 3340,1723,1698,1286 cm^{-1}.

<u>3-β-11-α-Diacetoxy-bisnor-allo-cholanic acid chloride</u>

3-β-11-α-diacetoxy-bisnor-<u>allo</u>-cholanic acid (675 mg) was refluxed with oxalyl chloride (1 ml) in tetrahydrofuran (10 ml) for 1 hour. The solution was evaporated to dryness under vacuum and the residue was crystallized from benzene/petroleum ether to yield 3-β-11-α-diacetoxy-bisnor-allo-cholanic acid chloride (321 mg).

Mp.: 147-55°C

I.R.: 1785,1731,1250 cm^{-1}.

Irradiation of 3-β--11-α-diacetoxy-bisnor-allo-cholanic acid chloride

The acid chloride (300 mg) , in dry dioxane (15 ml) was irradiated for 4 hours. Aliquots were withdrawn at intervals, poured into water and titrated with 0.1 N sodium hydroxide solution. At the end of the irradiation period the titre fell to 30% of the original value and was decreasing only very slowly. Water (5 ml) was added to the reaction mixture which was then heated on the steam bath for 20 minutes . Working up as usual gave a neutral product (186 mg) which could not be crystallized. The crude neutral material was heated on the steam bath with 4N sodium hydroxide solution (5 ml) and ethanol (10 ml) for 1 hour and worked up as usual to give a neutral material whose infrared spectrum had very strong bands in the O-H strtch region and no bands between 1800 and 1500 cm^{-1}.

Irradiation of limonilyl chloride

Limonilyl chloride (1.31 g) in dioxane (18 ml) was irradiated for 60 minutes, when the infrared spectrum of an aliquot ceased to show a separate band near 1790 cm^{-1}. Water (5 ml) was added and the solution was allowed to stand at room temperature for 2½ hours. Working up as usual gave acidic material (450 mg),which crystallized from aqueous acetone to yield limonilic acid identified by its infrared spectrum and mixed melting point, and neutral material (450 mg), which could not be crystallized even after chromatography on alumina. The crude neutral material elluted from alumina with benzene/acetone had the following infrared spectrum: no bands in the O-H stretch region,1745, 1726,1503 and 875 cm^{-1}.

Di-dioxan

Dioxan (50 ml) was irradiated for 3 hours, the solvent was evaporated to dryness and the solid residue (33 mg) was sublimed to give di-dioxane.

Calculated for $C_8H_{14}O_4$: C:55.16% H:8.10% Mol.wt. 174

Found: C:55.05% H:8.08% Mol.wt. 172

N.M.R.:Single broad band (tau: 6.33-6.50) (c.f. dioxane at 6.43)

I.R.:2924,2850,1360,1340 (hexachlorobutadiene mull)
1300,1280,1234,1125,1066,956,924,900,879,688 cm^{-1}
(nujol mull)

Sublimation point: 110°C.

In other experiments the following yields of di-dioxane were obtained under the following conditions:

(i).Dioxane (50 ml) was distilled without prior irradiation. No solid material was obtained.

(ii).Dioxane (50 ml) was irradiated under nitrogen for 18 hours. Yield of di-dioxane:33 mg.

(iii). Dioxane (50 ml) wqs irradiated without nitrogen flushing, for 20 hours. Yield of di-dioxane: 58 mg.

(iv).Dioxane (25 ml) was irradiated under a stream of dry air for 22 hours. The yiellow solution contained undistillable residue (2.5 g),which could not be crystallized.

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OUR MOB

A FAMILY CHRONICLE

by

Sever and Alice Sternhell

First Edition 2002

Front Cover:
Sternhell family photo taken in Ottynia in 1913 (Appendix 7). Left to right: Sev's father, Samson Sternhell (1900-1959) in the Austro-Hungarian Hapsburg Empire school uniform at the age of 13. Two unrelated young men. Sev's grandmother, Caroline Sternhell nee Gottlieb (1881-1944*). Sev's grandfather, "Dziadzio Altur" (1876-1933). Miss Fischer, tutor to the Sternhell children.Tauba Silberhertz nee Sternhell. With her is her young daughter Genia* (sister of Kuba Silberhertz* but missing from Appendix 7). Sev's great-grandfather Mishulen Holder-Sternhell (1848-1919), patriarch of the family and mayor of Ottynia. He is holding his granddaughter, Genia Sternhell (1906-1943*) who later married Emil (Milek) Mannheim (1899-1959).

Back Cover:
Alice's parents, Alfred Zalcberg (1892-1942*) and Eugenia Zalcberg nee Scheinwechsler (1902-1942*) in Czestochowa in 1930's, Appendix 1, 2 and 4.

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TO THOSE WHO PERISHED

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INDEX

PREFACE : A LETTER TO MY SONS

Dear Peter, James and Roger,

This book is a family history, undoubtedly patchy and incomplete but enough to let our descendants know where they hail from, who their ancestors were and how they lived. In particular, I wish to record for them the events of the Holocaust as they affected myself, your mother, our parents and the more distant family.

At the heart of this book, although attached as **appendices**, are your family trees which should enable you to trace your ancestors, work out relationships with family you have met and possibly to make contact with your more distant relatives. I have done this from first principles: you three are at the centre of the scheme and clearly you have 4 grandparents and 8 great-grand parents, all of whom were known either to me or your mum (2 of your grandparents and 5 great-grand parents perished in the Holocaust). Thus you have your immediate family tree entitled "Direct Ancestry" and 8 satellite family trees for your more distant ancestors, in one case going back to the beginning of the XVIth century. One of the 8 trees is missing, because we lack information about your maternal grandfather Alfred's mother. There are also additional charts for some sub-sets of relatives, as well as the beginning of the "new" family tree of your wives and children.

This book has a form of a rough autobiography, but this is only a narrative convenience: I am not trying to tell you about myself but about your roots. I find it easiest to write as if I was talking to you, so in a way the whole book and not just the preface, is "a letter to my sons". There is a further problem: your mother and I have considered writing this book as a team but decided against it because it appeared too difficult. I have dealt with your mother's family trees to the best of my ability and with her help, but she has written her own story, particularly of the war and the Holocaust, which forms a large chapter of this book **("Your Mother's Story")**.

On rereading the manuscript, I am struck by the prominence I had given to the "Jew" issue, in contrast to the fact that Jews, antisemitism, etc., were hardly ever mentioned in our household as you were growing up. This is clearly due to the fact that being Jewish was the defining factor in the life of our ancestors, including the recent ones in pre-war Poland, and that during World War II, being Jewish in Europe was a matter not so much of life-or-death, but of a nearly certain death. However, in kindly and decent Australia, being Jewish is of very little importance - may this state of affairs long last.

CHAPTER 1: OLD TALES

Your tribe is called Ashkenazi Jews. After the destruction of Jerusalem in AD73 and the expulsion of Jews from ancient Israel, they settled all over Europe, the Middle East, North Africa and, eventually in Northern Europe, particularly in what was to become Germany. The Southern Jews are known as the Sephardis and the northern ones, particularly the ones who moved East to escape persecution in the Ghettos of mediaeval Germany, became the Ashkenazis. It is also believed by some, that the original Ashkenazis intermarried with the now vanished tribe of Khazars who once inhabited the steppes North of the Black and Caspian seas. It is a historical fact that in the 9th century, the Khazars (a warlike nation of nomadic horsemen) were under pressure from Christian Byzantium pressing North along the shores of the Black sea and from the Islamic Caliphate pressing North across the Caucasus, both of whom regarded the Khazars as Godless barbarians. The Khan (Chief) of the Khazars decided to take up Judaism as a defensive compromise, which did not do much good in the end, as the Khazars appear to have vanished from history. What is merely a speculation is that the Ashkenazi Jews moving East encountered their co-religionist Khazars and, racism not having yet been invented, considered them kin and hence intermarried with them. This would explain the blue eyes and blond hair common among the Ashkenazi Jews much better than a long succession of rapes and unlikely Slavonic milkmen. I must admit that I rather like the idea of a partly Khazar ancestry: it is the nearest thing to being descended from Genghis Khan!

Sev Sternhell at the grave of Judah ben Bezalel (Rabbi Loeb 1512-1609) in the old Jewish cemetery of Prague. Photo taken in 1993.

Whatever is the case, you belong to a remarkable tribe and can claim as your own, not only the Bible, Moses, Jesus Christ and more than 3,500 years of recorded Jewish history, but the fact that for good or evil, Marx, Einstein and Freud, among many other recent movers and shakers, were Ashkenazi Jews.

Your most famous ancestor was Judah ben Bezalel (Rabbi Loew or Loeb, 1512-1609) the Rabbi of Prague, which was then the foremost centre of Judaism in Europe. He is most widely known as the creator of the mythical Golem (clearly fiction), but he was an important historical figure and an adviser to the Holy Roman Emperor, Rudolph II. Rabbi Loeb had two daughters, Minnie and Ruchale (Rachel) who married two wealthy young merchants from Eastern Galicia named Allerhand and Katz. Ruchale Katz and her husband set up a court in Kolomyja and their daughter, also called Ruchale, married (ca. 1640) the son of a rabbinical family Sternhell. My great-grandmother Eugenia Sternhell (1855-1912), a direct descendant of Ruchale Katz married my great-grandfather Mishulen Holder (1848-1919, the mayor and the most prominent citizen of Ottynia), who took his wife's name because a cousin of his married an Austrian Colonel and thus disgraced the family name by marrying a gentile! To add to the disgrace, one of their children became a priest!

A direct descendant of Minnie Allerhand, Professor Allerhand, a contemporary of my father's, knew our family well in pre-war Lwow and he and my father cross-checked their ancestries. In every Sternhell generation there was a girl called Rachel (Ruchale), the last Ruchale being my father's youngest sister Rela Sternhell-Zimring (1918-1943*). At present, Jimmy's and Beverley's daughter Leanne Rachel carries on the name. A photograph of me standing at the grave of Rabbi Loeb in Prague in 1993 is reproduced in this book.

Eugenia Sternhell's sister married Herman Arnold and they had twin girls Ala (Aliza) and Lonka whom I remember as identical high-school girls before the war. Lonka perished in the Holocaust and Ala married Menahem Begin, once a terrorist (Chief of Irgun Zvai Leumi) during the British Mandate of Palestine, later the Prime Minister of Israel (1977-1982) and a Nobel Laureate (Peace Prize in 1978, jointly with Anwar Sadat). I remember clandestinely meeting Ala when my father and I resided in Palestine in 1945/6 and when Begin was on the run from the British authorities. We met in the Tel Aviv Zoo and Ala had with her their little son, Zeev Binyamin (Benny) Begin, born in 1943 who would become a Professor of Geology and later an Israeli politician of some note. The second time I met the Begins, was while I attended a conference in Jerusalem in 1981 and I visited them in the Prime Ministerial mansion, the Nobel Prize prominently on the wall of the modest lounge room where we were having tea. Itzhak Shamir, then the foreign minister, once a terrorist and a future Prime Minister of Israel joined us. A photograph from this occasion survives.

On your mother's side, the most prominent ancestor was Nathan Altman (1865-1922) who lived in Berlin and was an important figure in modernistic painting – a few years ago some of his paintings were on a traveling exhibition at the NSW Gallery. Your mother and I visited the exhibition and were not necessarily overwhelmed by the pictures, but Altman was undoubtedly a major figure. He was a brother of Emilia Altman-Scheinwechsler who was your grandmother Eugenia Scheinwechsler-Zalcberg's mother and hence your great-grandmother.

There is also a nebulous story circulating among your mother's family: when one of the mediaeval Polish kings died without leaving an obvious heir, the assembled magnates decided to appoint a temporary king ("a king for a day") while they deliberated upon a permanent successor. To make sure that the temporary monarch did not claim the throne, they chose a Jew, who could not possibly become a king of Poland and that Jew is claimed to have been a distant ancestor of your mother's. The succession was reported to have worked smoothly, but the "king for a day" managed to grant his Jewish compatriots important privileges during his short reign. The problem is that the incident does not appear in standard historical works, but it is a nice story just the same.

If you look carefully through the appended family trees, you will find echoes of other interesting characters, but I have insufficient information to elaborate on them and the people I have relied on to produce the family trees are either dead or very old.

CHAPTER 2: A VANISHED WORLD

The world into which your mother and I were born has vanished without a trace. You might think that this is not at all extraordinary, that 70 years in an era of rapid change would alter any social arrangements, but our world vanished far more comprehensibly than, say, the Australian world of the early Depression era in the thirties as viewed from the perspective of the new millenium. Our world *literally* vanished: most of our families, school friends and casual acquaintances were murdered in the Holocaust. The pre-war Polish republic disintegrated under the Nazi onslaught, the end of the war brought 45 years of Communist rule to Poland and all this happened during an era when social and technological change was rapid in any case. When I try to recapture our pre-war Polish/Jewish *milieu*, it seems stranger to me than the descriptions of Tudor England or contemporary Nepal. However, that was the world that formed your mother and me and therefore, indirectly you as well.

Our social position in pre-war Poland was dominated by us being Jewish, although both mine and your mother's families were, in fact highly assimilated, i.e., very much Polish culturally. Thus unlike the masses of poor Jews - the majority of the 3,500,000 Polish Jews - we spoke only Polish at home and I knew no other language. My parents also spoke fluent German having been born in the Austro-Hungarian province of Galicia before World War I, which became a part of Poland after 1918. They used German as a "secret" language when they wished to keep things from me, in much the same way as a generation on, your mother and I used Polish to keep things from you. The result was that I acquired a smattering of German very early on. My parents also spoke French and could communicate in Ukrainian, the language of the villagers in Eastern Galicia. The language of the Jewish masses was Yiddish, a dialect composed principally of mediaeval German and Hebrew and a few generations back our ancestors undoubtedly spoke mainly this, now dead, language. However, in my time in pre-war Poland (1930-1939) even my grandparents spoke only Polish at home, although they also spoke German and Yiddish.

It was this language divide which was the most obvious mark of the assimilated Jews, although with it went a secular attitude which distinguished them from the intensely religious majority of Jews. There were further subtleties: the effectively assimilated Jews divided between the genuinely assimilated, i.e., those who thought of themselves as Poles of Jewish background and the nationalistic Jews (Zionists) who professed, often more in word than deed, an attachment to the tiny Jewish settlement in the pre-war

British mandate of Palestine which was to evolve into the state of Israel. While the dividing line between these two effectively assimilated groups was blurred, my parents were more of the Zionist persuasion and your mother's parents were more genuinely assimilated.

While many individual Poles were personal friends of assimilated Jews, the population was overwhelmingly deeply antisemitic and this persists to this day even though the Holocaust left a negligible Jewish population in present day Poland: they have achieved antisemitism without Jews! The popular antisemitism was reflected in Government policies, such as restrictions on the number of Jews admitted to universities. The Jews who were admitted to universities, were forced to sit on segregated "Ghetto benches". There were also beatings of Jewish students at both universities and high schools and while real Pogroms did not occur in inter-war Poland, the atmosphere was ugly.

However, life went on normally because Jews were historically used to being a persecuted minority and families such as those of your grandparents led comfortable middle-class lives. We lived in well-appointed rented flats (as most Europeans still do), ate and dressed well and led sophisticated intellectual lives. We also lived in a world where middle-class families invariably had personal servants, typically just one live-in maid/cook.

MY WORLD

I was born on May 30, 1930 at No 8 Bema St., Lwow. The house still stood in 1993 when your mum and I visited Lwow, now Lwiw the principal city in Western Ukraine. The street looked much as it did 60 years ago, although no longer named after General Bem, an early XIXth century Polish freedom fighter (who happened to have been Jewish!), but after an obscure Ukrainian, Yaroslav Mudryi (Yaroslav the Wise). In fact, the XIXth century "Habsburg" character of Lwow, similar to Krakow, Prague and Vienna has been uncannily preserved. However, architecture is all that remains: whereas the prewar population of Lwow (360,000) was about one-third Jewish and two-thirds Polish, only Ukrainians inhabit it now. The Jews were almost entirely exterminated by the Germans between 1941 and 1944 and the Poles moved West after Lwow and the entire Eastern region of Poland were attached to the Soviet Union in 1945.

My father Samson (1900-1959) was a lawyer (Polish jurisdiction did not distinguish between solicitors and barristers), who after a short period of practicing in a provincial town after his marriage in 1924, moved to Lwow, where he became a junior partner to Dr Sommerstein, a prominent Jewish lawyer who was a member of the Polish Parliament (Sejm) - a most unusual distinction for a Jew. My father who survived the war and died of natural causes in 1959 in Sydney, was unusually able intellectually and was offered an academic position if he would only convert to Catholicism. He refused, out of pride rather than religiosity as he was for all practical purposes an atheist.

My parents were members of the Polish-Jewish “intelligentsia”, a well known classification in Europe for which there is no exact equivalent in English. Members of the intelligentsia were educated, middle-class, not rich and shared “progressive” attitudes as well as intellectual interests, or at least, intellectual pretensions. Equality of sexes was taken for granted and in this respect that *milieu* was miles ahead of even contemporary Australia. The men in my parents’ circle were overwhelmingly members of professions (doctors, lawyers, engineers, dentists, architects, academics, pharmacists, vets, newspaper editors, etc.,) and while their wives typically had some tertiary qualifications (my mother started a law degree, but discontinued due to the ugly antisemitic atmosphere at the University of Lwow) they were, in fact, rather leisurely housewives – remember that all the cleaning and practically all the cooking was done by servants. From my childish perspective, my mother’s life revolved around cafes, dress-makers and entertainment and no one would have predicted that such an apparent air-head would prove tough enough to survive the Holocaust and to carve out a new life in Australia.

One very important way in which the pre-war Polish (and Polish/ Jewish) society differed from the Australian society in the year 2000, was the central importance of the extended family. You boys have seen a faint echo of this in our life in Sydney before the death of my mother in 1991 in the form of family gatherings, but the pre-war situation was very different. First of all, the extended family was very much larger (few survived the Holocaust), but it was also much more strongly knit. In our particular case, the dominant Sternhell/Gottlieb clan was further strengthened by having a clear physical focus in my paternal grand-parents’ country estate. This was a large property by Polish standards (Australian stations can be unimaginably larger, of course) and was mainly leased from a member of the Polish aristocracy although some of it was owned outright. The lives of this branch of the family were similar to those of the country gentry in a XIXth century Russian novel and were quite unusual for Jews who were traditionally traders or artisans. The estate, at first based on the village of Stropkov and later on the village of Hostov, was the rallying place for the long summer holidays where most of the clan gathered - 30 people staying at the property for two months was not at all unusual. Even when not gathered at the estate, most of the clan lived either in Lwow, the smaller provincial centre of Stanislavov (now Ivano Frankivsk after a Ukrainian poet) or in the small towns of Ottynia, Zydaczow, Kolomyja and Grodek Jagielonski. All these localities were within about 100 kilometers and there was always a lot of reciprocal visiting between the various branches.

In fact, this is how my parents met. When my father was studying law at the Lwow University, he boarded with the parents of my mother, the two families being related by marriage as my maternal uncle Efroim Weiler was married to my paternal aunt Chaja Gottlieb (see family tree). This couple helped my paternal grandparents to manage the estate and lived there the year around. They were childless and perished in the Holocaust.

My father was 20 when he met my mother who was then 16, nature took its course and they were married after a 4 year long engagement and after my father graduated. I was born 6 years later in 1930 while my parents were sharing an apartment on Bema St No.8 with my maternal grandparents Julius and Rose Wachs, both of whom perished in Belzec under particularly heart-wrenching circumstances in August 1942.

I do not remember our initial sojourn at Bema 8, for my parents and I (I was destined to remain an only child) moved to a flat at Sixtuska 65 in a very nice area close to a lovely midtown park named Ogrod Jezuicki - The Jesuits' Garden. This park was still lovely when your mother and I visited it in 1993 and, untypically of childhood memories, remained as large as my memory of it. My father's office was adjacent to the flat and I have vivid memories from Sixtuska even though we left it when I was about 4 years old to move back to sharing the flat at Bema 8 with my maternal grandparents. Presumably this was done to save money as the family, while not at all hard-up, was certainly not wealthy.

My maternal grandfather Julius Wachs was a cloth merchant and later a small-scale manufacturer of stationery. He was a ramrod straight, lean and powerful man who had served in the Austro-Hungarian army in World War I. My mother told me decades later that he was something of a womaniser. My maternal grandmother Rose (nee Weiler) was a small dark-haired woman who doted on me and who was my favourite relative – I have as many early memories of her as I have of my own mother. She was hit by a runaway car in about 1937 and was partially crippled for the rest of her life and also suffered from leukemia. Nevertheless, till her death in Lwow in the great Action of August 1942, she helped to look after me as she lived just around the corner from us in the Ghetto and I saw her very often till the end.

At the age of six, I went to a primary school at Zygmuntowska St. The building still stood in 1993 and was still a school, although of a Ukrainian kind. My school was an oddity: it was established to cater for the children of the Zionist Jewish intelligentsia. Thus, unlike a typical Polish/Jewish school, it was entirely secular, but devoted to the Zionist ideals of the formation of a Jewish nation “like all the others” in Palestine, the biblical home of the Jews. The school took this seriously and subjects like arithmetic were taught in Hebrew, which gave rise to the joke that our school was populated by Jewish children who spoke only Polish but were taught in Hebrew. The principal advantage of this school was that we were not subject of antisemitic violence from our gentile fellow scholars. Instead, boys from gentile schools had to ambush us on the way home from school and engage us in battles confined to fists and stones - we gave as much as we took. My parents, typical of their race and class, were education-centred. Any mark below “excellent” returned at the six-monthly report was considered a disgrace and I vividly remember the trauma of bringing home a report with 4 merely “good” marks among the remaining “excellents”. A suitable young woman was hired to take me in hand and I soon reverted to an unblemished record and my “rightful” third or fourth position in the class. I was not a swot, but rather something of a *baciarz* (a street fighter), as the late Manny Mansberg, the sole school friend who made it through the war and to Australia, vividly recalled.

We moved flats twice before the war and finally settled in a modern apartment block at Mohnackiego 56, across the road from the villa of the counts Lubomirski, one of the most famous of Polish aristocratic families. They hardly ever occupied this “town-house”, which still stood in 1993, presumably spending their time on their estates or in the south of France. Mohnackiego street also boasted a few other aristocratic villas and the back of our block of flats was adjacent to the Citadel, an early XIXth century red brick fortress, which served as one of the garrisons of Lwow. This presented an irresistible temptation for the housemaids and I remember acting as a courier between them and the soldiers, presumably arranging assignations.

My father’s life revolved around his law office and my mother’s around the home, dressmakers etc., but that left plenty of time for social activities. These involved not only “going out” as we understand it now, i.e., visiting, eating in restaurants, going to the cinema or theatre (Lwow boasts an imposing theatre modeled after the Paris Opera house), but also endless sessions in cafes - continental habitats resembling non-alcoholic pubs. Every member of the intelligentsia had his or hers café, where they met their friends. My father also regularly played bridge at his Club. The rest of my parents’ lives were filled with the extended family and my childhood memories are full of indulgent aunts and uncles and some cousins to play and fight with. Some of them, like my maternal grandparents, lived in Lwow, but I also remember numerous train journeys all over Eastern Galicia to visit family in various small towns.

My summers were largely spent at the country estate of my paternal grandmother Caroline (1881-1944*). As my paternal grandfather Gershon, nicknamed Altur, (1876-1933) died relatively young and I can only just remember him, I always thought of the estate as belonging to my grandmother Caroline, a short fat woman of iron will who ran the very large estate and controlled hundreds of very rough, indeed murderous, Ukrainian peasants. As I was an only child, my closest young relative was my cousin Tania (1927-1943*), also an only child, the daughter of my father's sister Genia Mannheim (1906-1943*). We invariably spent the summer holidays together and were very close, although we fought like cats and dogs. Besides us two, during the summers there was a large and variable number of assorted relatives at the estate, particularly in its earlier version at Strupkow which was based on a very attractive chateau with a huge ballroom which served as dormitory for us young ones. Some of my earliest memories relate to Strupkow and I remember my grandfather Altur building sand-castles for me when I could not have been older than 3.

The second estate, Hostow was acquired in about 1935 and was based on a more modest house, although the estate itself was larger in terms of land, cattle and staff. It had a huge yard surrounded by barns and workshops (it boasted the very epitome of modernity: a tractor!) and I spent many hours watching our carpenters and blacksmiths at work. Also, as Tania and I got a bit older, we were permitted to ride horses and this became the main attraction.

As we got older, we also tended to spend only a part of the long (July and August) summer holidays at the estate. I remember a month spent in the Carpathian resort of Jaremcze with our families and friends and two occasions when just Tania and I were sent off to children's holiday homes, also in the Carpathian mountains. We had a whale of a time! In 1937 I went with my parents for a month to the Romanian resort on the Black Sea called Carmen Sylva and loved it. A photograph survives.

With the coming of the war and the Soviets, the estate was confiscated and grandmother Caroline moved to Nadworna in the foothills of the Carpathians where she lived with Genia, Tania and Tania's father Emil (Milek) Mannheim (1898-1959). My uncle Emil was a chemical engineer who managed the oil refinery in Nadworna, owned by believe it, or not, *Italian* interests! Emil survived the war and died in Sydney in 1959, his second wife Anda, who became somewhat estranged from the rest of the family in her dotage, died only recently. In Sydney, Emil worked together with Hugo Hayman, Sylvia's second husband and father of Michael and Lynnie, in a pharmaceutical manufacturing enterprise called Andrews Laboratories owned by Andrew Ungar, a family friend. This firm was later taken over by the giant multinational Johnson & Johnson and Hugo worked for them till his retirement. The other relatives who helped Caroline to run the estate, my uncle Efroim (Froim) Weiler (?-1942*) and his wife Chaia (ne' Gottlieb ?-1942*), moved to Zydaczow where they lived with the rest of the Gottlieb family. They all perished in the Holocaust (this is what the asterisk at the date of death signifies) and so did Caroline herself after hiding for 2 years on aryan papers in a district where she was well known. Eventually she was denounced and killed and I have heard that she died by an SS-man's bullet with dignity, unlike practically all the rest of us, who died miserably.

YOUR MOTHER'S WORLD

Your mother, Alicja (pronounced Alicya and anglicised to Alice) Zalcberg, was born on December 4, 1932 in Czestochowa in Western Poland. Her father Alfred (1892-1942*) who was trained as a textile engineer at the Liege University in Belgium, was the Chief Engineer in a paper mill "Warta" in Czestochowa, a large enterprise and the biggest exporter of paper in pre-war Poland. Her mother Eugenia (1902-1942*) was a dentist although she did not practice her profession before the war. The Zalcbergs also had an older daughter Wanda (1923-1942*).

As you can see from the family trees, we have a lot of information about your maternal grandmother's family (the Scheinwechslers and the Altmans) but much less on your maternal grandfather (the Zalcbergs). As you can see from the Scheinwechsler part of the family tree, the people you know/knew well (George Bochenek and Charles Groden) are first cousins of your mother's, although much older than her. You have also met another cousin, Richard Groden who lives in America.

Czestochowa was a smallish town (population ca. 100,000) at that time, but very famous for its monastery at Jasna Gora ("Bright Mountain") which is the holiest place for Polish Catholics. This is mainly due to the cult of the "Black Madonna" an icon dating from early mediaeval era housed in the monastery to this day. The monastery was besieged by Swedes during the 30 Years War in the XVIIth century (Poland's history has been, to put it mildly, turbulent) and a fictional description of this siege by Henry Sienkiewicz, a XIXth century novelist who also wrote "Quo Vadis", was well known to every Polish child and added much to the mystique of Jasna Gora. Swedish cannon balls can be seen embedded in the walls of the monastery to this day.

The Zalcberg household was very much like mine: a live-in servant, a personal coach complete with a coachman for the Chief Engineer, the expectation of the daughters of the house completing not only high school, but a serious University course. I sense that the Zalcberg family was less dominated by clannishness, i.e., that the extended family was probably less close than mine, but the relationships with even the more remote relatives and in-laws were much closer than what is common in contemporary Australia. The Zalcbergs also appeared to be less conscious of, or less concerned about the endemic Polish antisemitism, but this may simply mean that little Alice was sheltered from such problems. I was after all, two and a half years older than her and therefore much more exposed to the world around me.

Alice was too young to go to school in pre-war Poland and her first school year would have started in September 1939, which was of course, the start of World War II.

Lea Weiler, mother of 14, died in 1908 (Appendix 1 and 6), Sev's maternal greatgrandmother. Note coral brooch, which was passed down generations and is now in our possession.

Simon Weiler (1850-1922) (Appendix 1 and 6), Sev's maternal great-grandfather.

Julius Wachs (1877-1942*) and Rose Wachs nee Weiler (1883-1942*), Sev's maternal grandparents (Appendix 1, 5 and 6). Street photograph in Lwow in early 1930s).

Rose Wachs nee Weiler (1883-1942*) with her son Zygmunt (Mundek) Wachs-Walker (1906-1982), who is in the uniform of a schoolboy in the Habsburg (Austrohungarian) empire (Appendix 5). Photo taken in Vienna between 1915 and 1918, where Rose with her children Mundek and Maria (Sev's mother) took refuge during WWI, while their father, Julius Wachs was in the Austrian army.

Maria Sternhell nee Wachs
(Sev's mother) at 14 in 1918
(Appendix 1 and 5).

Herman Weiler* (Appendix 6) in Austrian officer's uniform during WWI.

Sternhell family photo taken in Ottynia in 1913 (Appendix 7). Left to right: Sev's father, Samson Sternhell (1900-1959) in the Austro-Hungarian Hapsburg Empire school uniform at the age of 13. Two unrelated young men. Sev's grandmother, Caroline Sternhell nee Gottlieb (1881-1944*). Sev's grandfather, "Dziadzio Altur" (1876-1933). Miss Fischer, tutor to the Sternhell children.Tauba Silberhertz nee Sternhell. With her is her young daughter Genia* (sister of Kuba Silberhertz* but missing from Appendix 7). Sev's great-grandfather Mishulen Holder-Sternhell (1848-1919), patriarch of the family and mayor of Ottynia. He is holding his granddaughter, Genia Sternhell (1906-1943*) who later married Emil (Milek) Mannheim (1899-1959).

Caroline Sternhell nee Gottlieb with her 3 younger children, Arthur (1913-2000), Genia (1906-1943*) and Rela (Ruchale, 1918-1943*). Photo taken in approximately 1928.

Genia Mannheim nee Sternhell (1906-1943*), photo taken approximately 1926, Appendix 7.

Gershon Sternhell (1876-1933), Appendix 7. Photo taken in 1913.

The house at Bema No. 8 in Lwow where Sev was born in 1930. Photo taken in 1993.

Sternhell family photo taken in 1933, shortly before Gershon Sternhell's death (Appendix 6 and 7). Standing, left to right: Christina Rossler (Sev's German nanny Tincia, shortly to return to Nazi Germany). Maria Sternhell nee Wachs. Caroline Sternhell* nee Gottlieb. Gershon Sternhell. Efraim Weiler (d.1942*). Sitting, left to right: Lola Weiler* (daughter of Jacob*) Sev Sternhell at the age of 3. Samson Sternhell. Rela Sternhell*.

Emil (Milek) Mannhein (1899-1959) (Appendix 7), with his daughter Tania (1927-1943*) in Nadworna ca. 1932.

Sternhell family photo taken in 1938 in Jaremcze in the Carpathians. Back row: Samson, Rela and Maria. Front row: Tania Mannheim and Sev Sternhell.

Skiing behind a horse-drawn sled in Nadworna, ca. 1938: Tania Mannheim, Sev Sternhell and Samson Sternhell

CHAPTER 3: WAR

World War II started on September 1, 1939 with the attack by Nazi Germany on Poland, which was followed two days later by a declaration of war on Germany by Britain and France. This momentous turn of history had complex origins and was certainly not unexpected, as Europe had been unstable since the beginning of World War I in 1914. This is not the place to discuss history or politics, so I will confine myself to describing the impact of the war on our lives.

As international tension mounted, my mother and I returned from summer holidays at my grandmother Caroline's estate in mid August, which was earlier than usual for the start of the school year on September 1. Zig-zag trenches less than a meter wide and two meters deep were being dug in gardens and parks to offer protection against bombs. In the event, no one used them, as people preferred to huddle in cellars instead. Strips of paper were being glued on window panes to prevent them from being blown out by explosions and injuring people below. The use of war gases was anticipated and gas masks were distributed and practiced with. There was palpable tension and it was obvious even to a nine-year old that something awful was about to happen.

When the war came however, the beginning was abrupt. I was visiting my young married aunts, Sylvia whom you knew and Rela (1918-1943* the last Ruchele named after the original Ruchele Loeb) who lived with their young husbands in adjacent flats in a modern apartment block surrounded by a large garden about 2 km from our flat in Lwow. Of these 4 then young, vigorous and promising people only Sylvia survived the Holocaust.

It was September 1 and as the start of the school year was postponed indefinitely I was playing in the garden with some other children, when my aunt Rela rushed out yelling "come inside – I have just heard on the radio that the Germans are bombing Krakow!" Seconds later, there was a drone of aeroplanes and the soon-to-become familiar womp-womp of aerial bombardment – the Germans were bombing Lwow!

By the standards of the mass bombings in the course of WWII, this was a relatively light air-raid, but much damage was done including the main railway station since rebuilt in the same style. About 700 people were killed and Sylvia's husband, a doctor, Henryk (Henio) Sigal, later killed by the Nazis under particularly horrific circumstances, came home late that night after operating on wounded non-stop for 16 hours, with dreadful tales to tell.

For some reason I was staying with Sylvia and Rela for the next few days and I remember jubilant crowds surging through the streets singing the Marseillaise (presumably they were unfamiliar with God Save the King) when Britain and France declared war on Germany. Meanwhile, the German Wehrmacht was slicing through Poland at a devastating speed, aided by the relentless Luftwaffe - the whole campaign took only three weeks.

General mobilisation was declared on September 1 and my father was drafted and put into uniform. My mother and I visited him at the barracks and I remember being most impressed with his rifle, which I later realised was a WWI Lee Enfield, the trusty “303” of the Australian Army in WWI and WWII. He was a private and did not see much fighting, but was defending the outskirts of Lwow when the Red Army (in collusion with the Germans following the Ribentrop-Molotov pact) poured in from the East ending this phase of the war. My father rushed into his office, changed into civilian clothing and that was the end of my family’s armed resistance.

A few days after the outbreak of the war, my mother and I went by train to Zydaczow, presumably to escape bombing to stay with Sylvia and Siamo’s (Siamo “Smex”, known to you as Sasha) parents, my aunt Adele (ne’ Silberherz 1882-1942*) and uncle Froim (Efraim Gottlieb, 1878-1942*, brother of my grandmother Caroline). Zydaczow was untouched by war, never saw any German troops and was overrun by the Soviet Red Army pouring in from the East about September 20th, 1939. The Soviet soldiers were well behaved and did not bother the civilian population at all. They announced that they “liberated” us from the Polish fascist regime. In fact, what we witnessed was another partition of Poland, this time between Nazi Germany and Soviet Russia. Lwow was incorporated into the Soviet Ukrainian Republic, the regions further North into Soviet Belorussia and Vilno into Soviet Lithuania.

In October, my mother and I returned to Lwow, rejoined my father, went back to our flat and resumed a sort-of normal life. Food was scarce during the cold winter of 1939/1940 but more serious were the deportations (about 1,800,000 in all) of suspect classes, such as families of army officers, politically active persons, clergy and, ridiculous as it was, refugees from Western Poland who escaped the German army. Among the latter group were many Jews and some of them were deported to Siberia or Khazakhstan. We saw this as a great tragedy, but it was this group of people that formed the bulk of Holocaust survivors: even though they endured great privations and many died, they escaped the worst. Anna Haber, Richard Haber’s first wife and the mother of Paul, Mark and Ivonne, was one of them and her mother died in Khazakhstan.

However, by the standards of what was about to happen, a certain normality prevailed: while our standard of living certainly went down, we were not seriously hungry, my father got a job working for the electrification commission and I went to school. Schooling was chaotic at first, but eventually I settled into a school (the building still stands and is still a school) where Polish was the main language of instruction, with Ukrainian as the language of the Ukrainian Republic and Russian as the *lingua franca* of the Soviet Union. On top of this there was German as a foreign language, together with quite rigorous arithmetic, general science, geography and hopelessly biased history. Quite a lot to expect from a 10-to-11 year olds! Kids my age, were expected to join the Pioneers (a sort of communist boy-and-girl scouts) and we were indoctrinated quite a lot, but we shrugged it all off: in one ear and out the other! I cannot say that we lived a life of continuous fear (except for the prospect of deportations) or hardship and I had innumerable friends with whom I got into all sorts of mischief.

By the end of the 1940/41 School year in June 1941, life was so normal that I went to spend the long summer holidays in Nadworna with my aunt Genia (my father's sister Eugenia, 1906-1943*) her husband Emil (Milek) Mannheim (1899-1959) and their daughter, my cousin Tania (1927-1943*). My younger paternal aunt Rela (1918-1943*) also joined us. Her husband Celek Zimring, a veterinarian and a student friend of Arthur's, remained in Lwow due to work commitments. He was drafted into the Red Army in June 1941 when the Germans attacked and retreated with it, never to be heard of again. My grandmother Caroline (1881-1944*) lived with the Mannheims permanently after the Soviets confiscated her estate in Hostow. My uncle Milek, a chemical engineer, retained his job as the Chief Engineer of the oil refinery, the principal industry of Nadworna. I fully expected to spend the summer lazing on the banks of the swift-flowing local river Bystrzyca and playing with Tania and her friends, but history of the worst sort intervened. On June 22, 1941 Hitler's armies attacked the Soviet Union and swiftly occupied its western part. Nadworna fell without a fight 4 or 5 days after the start of the German/Soviet war and the Russians did not even manage to put the refinery to the torch in an efficient way. They did however make last minute efforts at morale-lifting propaganda. I remember leaflets with the message in Ukrainian: "Zgladimy z lica zemli fascistic psiw!", which translates: "We shall wipe the fascist dogs from the face of the earth!" - and so they did, after rivers of blood had been shed and mountains of misery endured.

The real nightmare was about to start.

Amendment to 2nd Edition

THE NADWORNA MASSACRE

Since the appearance of the first edition of this memoir, I have come across two documents highly relevant to the events that took place in Nadworna on October 6, 1941 and came to be called *The Nadworna Massacre*. They are the monograph *The Origins of the Final Solution* by the noted Holocaust scholar, Christopher R. Browning, 615pp (University of Nebraska Press, Lincoln and Yad Vashem, Jerusalem, 2004) and a SHOAH Resource Center document by Dieter Pohl dated 1998 and entitled *Hans Kruger and the Murder of the Jews in the Stanislawow Region (Galicia).*

Briefly, the SS-Uniformed thugs I escaped by the skin of my teeth on that date were not members of the Sonderkommando 6 of the Einsatzgruppe C commanded by SS-Standartenfuhrer Erhardt Kroeger, but the Reserve Police Battalion 133 commanded by SS-Hauptsturmfuhrer Hans Kruger, a much bigger and nastier beast. My confusion arose from the similarity of their surnames: I knew that the chief murderer of the Jews of Eastern Galicia was headquartered in Stanislawow and called “Kruger” and when I read about the activities of Einsatzgruppe C (which actually did most of their “work” further East) and the fact that the commander of one of its Sonderkommandos was called Erhardt Kroeger, I put 2 and 2 together and got it wrong. This does not affect my actual memory of that day, which was of special historical importance as some historians of the Holocaust (Pohl, p.12 *loc.citt.*) believe that the Nadworna Massacre marked the actual beginning of the “Final Solution”.

Hans Kruger (born in 1909), whom I still vividly remember in his SS uniform with the “Totenkopf” (skull-and-bones) emblem and boots, was a real horror who reportedly enjoyed his “work”. At the end of the war he was captured in Holland but as his activities in Poland were unknown, he was released in 1948. He lived and prospered in West Germany and became so confident that he started to participate in right-wing German politics. However, his past caught up with him in 1959 and eventually he was sentenced to life imprisonment by a German court in 1968 after a trial lasting for 2 years during which he indulged in numerous antisemitic outbursts. He was released in 1986 and died in 1988.

Sev Sternhell
September 2005

CHAPTER 4: THE HOLOCAUST

Nadworna was not situated on a major strategic route and the German mechanised units just passed through, shortly after the long columns of the retreating horse-drawn vehicles of the Red Army left. Before retreating, the NKVD, the precursor of the KGB and the main instrument of internal terror, killed all the political prisoners in their hands. Even in little Nadworna (population about 6,000), there was an NKVD prison and they killed about 80 prisoners and buried them in a shallow grave in an area known as Bukovinka (beech forest) on the outskirts of Nadworna. When the local Ukrainians discovered this grave a few weeks later, they rounded up a couple of hundreds of Nadworna's Jews, including my uncle Milek, and forced them with great brutality to disinter the bodies and clean them up. A Pogrom resulted with several deaths, as the Ukrainians chose to blame the Jews for Soviet atrocities. Interestingly, my uncle Milek observed that several of the victims of the NKVD were in fact Jews: they were circumcised.

After a short period of chaotic rule by armed Ukrainian gangs, the Hungarian army allied with Germany occupied this area, which was quite close to the Hungarian border. The Hungarians were civilised, did not bother Jews or anybody else, but unfortunately departed after a few weeks. While they were in occupation, the Hungarian regime deported (essentially chucked over the Carpathian mountains) some thousands of Hungarian Jews whom they considered not to be Hungarian citizens, i.e., they were people of Polish-Jewish parentage. About 2,000 of these poor people burdened with only what they could carry, turned up in Nadworna, swelling its Jewish population to 4,500. The local Jews billeted these refugees in their homes and fed them: in our place landed an upper middle class family who spoke excellent German, as well as, of course Hungarian, but not Polish. They were a middle aged married couple with three handsome strapping sons aged between 18 and 29.

After the Hungarians departed, the Germans set up a civil administration headed by a "Landesrat" sometimes also called "Landeskommissar", a sort of a chief public servant. This middle-aged and somewhat bewildered German recruited a few Jews as his advisers and helpers (after all, the Jews were educated and spoke German!) with the principal adviser being a physician, Dr Schall, an in-law of Milek's and a very close friend of our family. This was to save my life.

A BRUSH WITH THE EINSATZGRUPPE C (See however p.22)

We continued living fearfully, but not dramatically till October 6, 1941.

The day dawned like any other, except that I noted some Ukrainian youths being led down the street by a few armed and helmeted SS-men: the first SS I had ever seen. They were obviously from out of town and were, as I much later discovered, members of the Einsatzgrouppe C commanded by SS Brigade Fuhrer Dr Otto Rasch. The young Ukrainians were loudly repeating in Ukrainian that “We have nothing to fear, we have done nothing!”, but the SS paid no attention. We had no idea what this was all about, but they were in fact loaded into a truck and taken to Bukovinka to dig mass graves for us, after which they were simply let go. At exactly 11 am, all hell broke lose: numerous trucks disgorged what appeared to be hundreds of helmeted SS-men carrying their “ein-und-dreitzigs”, the 31-shot machine pistols around their necks. Guided by uniformed Ukrainian militiamen they brought along, they went from house to house and herded all Jews out. They must have been helped by local Ukrainians, who were the only ones who knew where the Jews lived, but I don’t recall this. We were totally bewildered and shocked as our family of six (Milek, Genia, Tania, Grandmother Caroline, Rela and myself) was marched down the main street to the soccer field in front of the main church of Nadworna. The very large soccer field appeared from a distance to be covered with bundles of clothing: in fact they were the Jews of Nadworna, made to kneel and get up, kneel and get up over and over again - there must have been at least 1000 people on this field by the time we arrived. The SS surrounded the field and some Ukrainian militiamen kept belting people on the edges of the crowd with long sticks rather like the “laths” carried by the police in India and Nepal. To one side stood their commanding officer (SS-Standartenfuehrer Erhardt Kroeger - according to my research on the Internet 60 years later, who was the commandant of Sonderkommando 6, under Rasch) with an alsatian dog who was attacking (not very severely) the Jews nearest to Kroeger. We joined the crowd and were made to kneel and get up repeatedly (God only knows why), while more and more Jews were herded on to the soccer field. After a while, trucks began to load groups of Jews of about 50 at a time and drove off - they were loaded from the front of the field while we were close to the back. Suddenly, we heard a loud yell of “Schall! Schall” and “Micka! Micka!” the latter being the diminutive name of Mrs Schall, who was Milek’s sister. Seconds later, one of the Ukrainians next to Kroeger yelled out “Mannheim! Mannheim!” and the six of us ran towards Kroeger. Next to him stood Dr Schall, white as chalk and the German Landesrat, only slightly less bewildered and terrified. It transpired later that the Landesrat wished to save Schall, who in turn tried to save his immediate family and us. When Micka and their little daughter failed to appear after a few minutes, Kroeger turned to us and harangued us to help the Landesrat who could only interject numerous “Jawohls!!” (Yes indeed!!). A couple of armed SS-men escorted us back to our house and told us to stay put, which we certainly did. I emphasize that we had absolutely no idea what was really going on. We scrapped together a meal and tried to sleep. Next morning, Miedzic a Ukrainian foreman in the oil refinery, a decent man and a long-time loyal subordinate of Milek's turned up to see if we were still here and told us what happened: the trucks took their loads to Bukovinka, where the Jews were made to strip naked and were machine gunned into the freshly dug mass graves. Earlier that morning, Miedzic had walked to those graves, which were yet to be covered and identified people we knew in the top layer of corpses. The trucks kept going back and forth between the soccer field and Bukovinka till the last load went to their deaths at 11 pm, at which time the "aktion" (a dreaded word we later got to know well) ceased abruptly. The last 200-300 people still on the soccer field were simply left behind unharmed. Murder by the clock! 11am to 11pm! How German!

Of the 4,500 Jews in Nadworna about 2,500 died on that day. Micka Schall and her little daughter were never dragged out of the crowd: either they got there after we left, or they were too fearful to heed the life-saving call. Of the family of 5 Hungarian Jewish refugees in our house (they were caught apart from us) only the mother survived: she lost her husband and three sons on that one day and, I am absolutely sure, did not survive for long herself.

The story of the Einsatzgruppen (imaginatively named A, B, C and D) is not as well known as the story of the Extermination Camps (Auschwitz, Treblinka, Belzec, Sobibor, Chelmno and Majdanek), but in 1941-1942 they followed the advancing German army in the East and by "actions" similar to what I witnessed in Nadworna, killed an estimated 1,500,000 Jews. The notorious massacre in Babi Yar (Old Woman's Ravine) near Kiew in which 30,000 Jews were killed over one week-end and 90,000 in total, is the best known of these "actions". As the Germans retreated in 1943-1944, they dug up most of the mass graves and burned the decomposing bodies using Jewish slave workers who were subsequently killed. However, they missed a few smaller graves and as with all massacres, enough of us survived to bear witness. I have found on the Internet a number of memoirs by survivors from Nadworna, which feature that day, October 6, 1941, very prominently. A copy of a particularly dreadful memoir is appended to this book. Otto Rasch was tried in 1948 but died of natural causes before being sentenced. Erhardt Kroeger was tried in 1967 - I could not discover the result. Other commanders of the Einsatzgruppen were tried and hanged or sentenced to long prison terms.

THE LWOW GHETTO

Back in Nadworna, the family decided that I must be returned to Lwow and rejoin my parents. A brave Polish lass, about 19 years old, took me to Lwow by train as her little brother and we made this perilous journey without incident. Lwow's Jews comprising about 140,000 (the numbers swollen by people from some neighbouring small towns), had not yet been subjected to serious mass murder: the worst that had happened was a Pogrom causing the deaths of about 3,000, when hundreds of bodies left in the NKVD prison were discovered by the advancing Germans and their Ukrainian followers. I brought the first news of the operation of the Einsatzgruppen, but even though many similar reports followed, we still did not realize that we were dealing with a program of extermination.

The Germans herded Lwow's Jews into a Ghetto, but the district was not walled in at this stage: it was a so-called open Ghetto. You could walk out of the Ghetto, but if you wore the identifying white armband with a blue star you could well finish up in the dreaded Janowska labour-cum-transit camp where many thousands perished. If you took the armband off and were discovered, you also finished up in Janowska or were shot on the spot. We shared a small flat with a family called Blind, a one-time business partner of my maternal grandfather's. The Blinds had three children then aged 14 to 17, one girl and two boys to whom I grew quite close. The Blind family was eventually totally exterminated. The Germans also organized a Jewish self-government under what we would now call a committee of 12 prominent Jews, the so-called Judenrat. The membership of the Judenrat had a high turn-over as the SS when seriously displeased occasionally executed (by public hanging) some, or all of the members of the Judenrat. The Judenrat ran the Judische Gemeinde, a bureaucracy about 4,000 strong, which looked after the usual municipal matters within the Ghetto, such as food rationing, hospitals, garbage removal, etc., etc., including an (unarmed) Jewish Police force of a few hundreds which kept order and criminals at bay. My father was the Personnel Chief of the Jewish Gemeinde and thus formally the immediate boss of these 4,000 people. His "Ausweiss" (identity card) stating this, complete with his photograph is in my possession: an undoubtedly unique document.

Winter of 1941/42 went by without any massacres in Lwow, but hunger was beginning to be felt. As my father's salary was a mere formality and as the food rations were very small, we and everyone else, lived by selling our belongings to peasants in exchange for food. While the Ghetto was open, this worked without interference from the Germans. Psychologically, this was a disastrous time, for what with German victories in the East and South and with Japan's own blitzkrieg in the Far East, it looked as if the war was being lost.

At 11 years of age, I was healthy and irrepressible and somehow never doubted our survival. My maternal grandparents Julius and Rose Wachs lived just around the corner from us and I had many friends from my Soviet School very near. Three of us (me and one boy and one girl, both exactly my age) were organized by our parents to be tutored by a tragic widowed and pregnant school teacher (her husband was killed in the Pogrom in Lwow in the first days of German advance), who valiantly tried to teach us arithmetic, Latin and Polish literature. This “School” lasted till the first great action at Easter 1942 when over 30,000 Jews (including our teacher and her new baby) were taken to the just-established local Death Camp of Belzec. Even though Belzec, where at least 700,000 Jews were eventually killed according to a study I found on the Internet, had only two survivors, we soon got wind of what was going on through Polish, Ukrainian and even some German sources. This action worked by selection of “non-working” people (the old, the young, the sick, etc.) and even then we still had not cottoned on to the fact that eventually *absolutely all of us* were earmarked for death.

In July 1942, a ferocious one-day Action claimed about 8,000 victims and started with a close shave for me. I was visiting a friend’s place about half a kilometer from our flat along the main street of the Ghetto, Sloneczna St., when trucks carrying helmeted SS appeared all over and the SS started to grab people off the street. I took off in the direction of our flat followed by a yell of “Halt!” and a stream of bullets whistling past my ears. I think that I did a credible Olympic time for 400 meters. For some reason, presumably on information he got from reliable sources, this was the moment when my father and many others realized that we were all to be exterminated. Indeed, shortly afterwards (August 10-August 23, 1942) the Germans carried out the biggest action in Lwow and the second biggest (after an action in Warsaw at about the same time) single mass murder of Polish Jews during the Holocaust. It started with a request for all identity cards to be stamped by the SS-und-Polizeifuhrer Galizien office, to determine if the holders held jobs useful to the Germans. Any people without a stamped identity card were subject to deportation to the Death Camps of Belzec or Sobibor, but the system worked erratically and many people whose identity cards had been stamped were also taken away. By then I had learned to recognize the really dangerous Sonderdienst (special service) or Sicherheitsdienst (security service) units, by the yellow-edged diamond with SD on their sleeves. Truck-loads of such troops would arrive in the morning and the helmeted and armed thugs would go through the streets house-by-house selecting people and taking them away. They stopped in the evening, leaving the Ghetto surrounded by armed SS and came back the next day. Anyone who ran or tried to hide was shot on the spot. People who had lost their children, parents or spouses occasionally committed suicide by jumping from upper story balconies. On Sloneczna St, between our house and the notorious “most” or bridge (really a railway viaduct which is still there) corpses littered the roadway. It was hell on earth and it lasted for two weeks. When it ended, the Jews of Lwow were a mere remnant. The Judische Gemeinde estimated that 55,000 people had been killed. I lost any number of relatives and friends. My maternal grandparents were taken away and a friend later told me that my poor crippled grandmother Rose was cruelly beaten by an SS-man, because she could not walk fast enough to the truck on her crutches. My mother went to her grave in peaceful Australia in 1991 without ever having been told about that. The Germans never admitted what was happening: the lie, which no one any longer believed, was that the people taken away were "resettled in the East". When my father asked one German Army (Wehrmacht) officer, whom he knew through the municipality, what on earth would happen in a "resettlement camp" with old people who could not work, particularly with my poor, crippled grandmother, he was told: "Aber kartoffeln schalen kann sie doch?" ("But can she peel potatoes?"). To this day, whenever I peel potatoes, this phrase comes back to haunt me.

I am appending an extract from the *"Encyclopedia of the Holocaust"* (Macmillan, New York 1990) dealing with the history of the Lwow Ghetto. It tallies pretty well with my memories, although some numbers of victims (though not the dates of the Actions) are significantly different. If you add their numbers, the total number of Jews exterminated in, or from Lwow was 110,000 while my father's and my recollections added up to 124,000. A chilling memorial tablet on the site of the Ghetto erected by the Ukrainian authorities (photo taken by me in 1993 is appended) states 136,800. Whatever is the case, it was a horrendous number. My father would have been in an almost unique position to write an authoritative history of the Lwow Ghetto, but he never did. A pity.

ARYAN PAPERS

The ordinary story of Jews in German-occupied Europe during World War II was simple (death), but the stories of survival are all extraordinary, full of coincidences and unlikely happenings. I think that my survival story was unlikely even by these standards. It was just one bloody unlikely and/or lucky thing after another. It was like tossing up a coin and getting "Heads" every time. Given that out of the 3,500,000 Jews in pre-war Poland at most 5-10% survived and that most of them survived because the Russians deported them to Siberia or Khazakhstan between 1939 and 1941, it really did take extraordinary luck to survive like I and your mum did. For my father, my mother and me to survive partly on independent trajectories (at one stage the three of us were in three different countries!) was totally improbable. If I were a believer, direct divine intervention via archangel Gabriel would offer the most obvious explanation.

The first key accident was my aunt (really a cousin of my father's Sylvia, whom you all knew well before her death in 1979), running into one of her Polish friends on the street. There was Sylvia, having just been through the great August 1942 action and having lost her husband under horrific circumstances (Henio was a gynecologist and was recruited from his hospital to perform a late abortion on an SS-officer's girlfriend. The woman died and Henio was tortured to death at the Gestapo prison on Lackiego 29 - the building still stands) walking on the street when she was hailed by Ula whom she knew from art school during the Soviet era. Ula, then about 32 years old and a very attractive and impetuous woman, instantly told Sylvia that she was going to "save you and your family!", totally ignoring the fact that the penalty for any such action was death. Ula was brought to our place to meet my parents and me and was instantly taken by me, or perhaps by my "aryan" looks - I certainly was very blond, blue eyed and straight-nosed. She kept repeating that, no matter what, I was not going to die. We already had some Aryan papers in the form of forged birth certificates, some of which are still in my possession. My father became Kazimierz Korytowski and had an authentic birth certificate, which had belonged to a deceased Pole of that name. My mother had a forged birth certificate and a forged marriage certificate and I became a totally fictitious Severyn Korytowski, there being no need to change my given name, which was not at all Jewish.

It would take a very long book to describe our Odyssey on Aryan papers. At first my mother and myself travelled to Krakow by train (train journeys were specially dangerous as the SS haunted trains inspecting papers - and penises) with Kazik (Kazimierz) Schultz, the boyfriend of Ula's sister and the man who really saved my life, as Ula decamped the scene after making the initial contact. In late 1942 Krakow was horrifically dangerous but I survived and already showed signs of cheek and courage which was to serve me well: thus I always traveled in the "Nur fur Deutche" (Germans only) tram carriages on the theory that document checks would be less likely. It worked, helped no doubt by my positively Nordic appearance.

My mother got a job as a housemaid with a German family and eventually changed jobs to serve a family of an SS-officer who was transferred to Vienna. She was treated abominably as a sub-human Pole, but survived the war and finished up testifying in a British court in Vienna in 1945 when her ex-employer was charged and jailed for something a lot more horrendous than belting a Polish maid! Sylvia went off on Aryan papers to Warsaw, where she survived the great Polish uprising in 1944 and was reunited with my mother when the latter returned to Poland from Vienna. My father stayed on in the Ghetto and survived two more actions before going on Aryan papers in Krakow. As his only significant asset, he was carrying with him my mother's engagement ring concealed in a bar of soap. It stayed there throughout the rest of the war and was duly returned to my mother in Paris in 1946. *Your* mother now wears it. After a succession of close shaves in Krakow he walked over the Carpathians to Hungary, still on false papers. As I remained in German occupied Poland, we were during all of 1943 and a bit of 1944 in three different countries - something of a survival record, I am sure. Normal postal service existed in German-occupied Europe and we remained in touch by means of guardedly written letters.

My position in Krakow was clearly not tenable and I returned with Kazik Schultz to Lwow, where I stayed in his flat till Easter 1944. Let me diverge for a moment to describe the almost comic circumstances of my return journey to Lwow and the family relations of Ula, her sisters and Schultz.

First the train journey, which took only about 8 hours although it seemed a lot longer. Kazik Schultz was a Volksdeutche (ethnic German) although he spoke no German at all and was a fierce Polish patriot. However, declaring yourself a Volksdeutche brought better food rations and some safety from being caught for forced labour in Germany - a fate that befell perhaps 2,000,000 Poles. Volksdeutches could also travel in Germans-only train carriages. On the principle that such carriages were less likely to be inspected by the SS, we traveled in one from Krakow to Lwow. Unfortunately, the remaining occupants were soldiers on their way to the Eastern front and opposite me sat a middle-aged Feldvebel (sergeant), Iron Cross and all, who took an instant liking to the blond youth across the aisle - perhaps I reminded him of his son or nephew. The trouble was that while I might have *looked* German, my command of the German language was rather limited. I was thus on my very best behaviour and kept saying “Ja, Herr Feldvebel” and “Nein, Herr Feldvebel” while fed chocolate and patted on the head. Kazik Schultz, whose German was precisely nil, just sat there and prayed. However, we eventually got to Lwow unharmed and the kindly Feldvebel went on his way to the Eastern front and most probably death.

In Lwow, I joined Kazik's household, which was somewhat complicated. Ula (Eleonora Bereznicka) had two sisters, both older than her. The oldest was a divorced woman, Mrs Leszczynski who had a grown up son Roman, then 22 and an aspiring poet - bits of his efforts remain embedded in my memory. The middle sister, named Kazika (by a long arm of coincidence there was Kazik and Kazika while my father's Aryan name was also Kazik!) was a very sexy woman then about 36, married to an extremely nice railway employee Kazik (again!) Zurek, but living with Kazik Schultz. The Schultz household consisted of Kazik, Roman, Mrs Leszczynski, the very elderly father of the three sisters who acted as cook, and me who was a ticking bomb - the Germans would have killed all of them, together with me, for (unknowingly, except for Kazik and Kazika) harboring a Jew on Aryan papers. Kazika lived with us most of the time and Ula, as well as Kazik's 19-year old daughter (he was divorced) made occasional appearances, while the whole family (including Kazika's husband) and some close friends gathered in Kazik's flat for Xmas and Easter. A novel waiting to be written, but I will only relate some highlights of my life there between November 1942 and March 1944. Kazik was a great bloke, even though he looked like a thug (he had been a heavyweight amateur wrestler in pre-war Poland) and I really liked him as well as being grateful. He also saved our family photographs and memorabilia, some of which are reproduced in this book. Being caught in possession of these might have meant death, but what the hell: he was harboring a Jewish boy! Photographs of Kazik and Kazika are in my possession and one is also reproduced in this book. My parents helped them financially, but they showed no desire to emigrate to Australia, we lost touch after my father died and they must both be dead by now of old age. Ula, was brought over to Australia in 1948 and immediately became the object of my mother's and Sylvia's plots to marry her off. In the event, all by herself she met an American major in the Marines who was in Sydney on a good-will visit and he married her and carried her off to California! Unfortunately, it was not a happy ending: Ula remained in touch with us for some years, but then the major informed us that she died suddenly, presumably of some sort of heart problem. She could not have been more than 45 years old and if there is a Catholic heaven after all, I am sure she has a place there.

I rarely left the flat, the biggest danger being recognition by my numerous Polish and Ukrainian contemporaries from my Soviet school days, who would have very likely denounced me just for the hell of it. It is quite true that many of the Holocaust survivors, including of course myself, owe their lives to courageous Poles and that the number of Poles who deliberately denounced Jews was small. However, the great bulk of the population was not just (understandably, in view of the consequences) unwilling to help, but quite *happy* about what was happening to us. They did not just sit on their hands - they *applauded*, and I have lost count of the number of times I heard Kazik's acquaintances say that "the one good thing that Hitler has done, is to rid us of our Jews!". Others who survived on Aryan papers tell the same story. In fact, the only person who both did not know that I was a Jew and who was genuinely outraged by what the Germans did to us, was Kazika's husband Kazik Zurek - a really decent man.

Kazik was not only in touch by mail with both my father and mother but also directly with Milek who was on Aryan papers in Lwow. Unusually he, a circumcised man, survived while the women of the family, Genia, Rela and Tania were caught on their way to Germany as (Aryan) slave-labourers, after being denounced by one of Tania's school friends at the railway station in Stanislawow.

The hunt for Jews hiding out on Aryan papers went on relentlessly: one day early in 1943 I was startled to hear machine pistol fire just outside. Peaking through a chink in the curtains I saw a number of corpses in the gutter just across the road from us, a veritable river of blood flowing down the gutter and SS-men milling about. It transpired, that the family in the ground-floor flat across the road, no more than 50 meters from us, was discovered hiding Jews and all of them were executed. The total killed was 9 and the corpses were left lying in the gutter all day, presumably as an example. For some reason, I was more scared then, than ever before or after and my knees were actually knocking.

In June 1943, the Germans finally "liquidated", i.e., finished off, the Lwow Ghetto. From a rise behind our block of flats I saw a column of smoke as the very last of the Jews put up a fight and the Germans were burning them out.

As a Volksdeutche, Kazik had a right to own a radio and Roman and I listened to the Polish language BBC broadcasts and Moscow long-wave radio, becoming quite expert at picking up the broadcasts through the German interference. Naturally, there was a death-sentence for listening to this, but it never worried us. The tide of war was turning dramatically after the Stalingrad debacle at Xmas 1942. The 9 am BBC broadcast, always starting with the Morse-code "V" for victory (dot-dot-dot-dash), announced dramatically practically every morning that "last night, the planes of the RAF Bomber Command were over Germany". By 11am we learned if it had been Hamburg, Cologne, Berlin, Munich, Essen or Bochum and we gloated. By daytime, the Flying Fortresses of the 8th US Air Force took over. At midnight, radio Moscow brought the canons firing victory salvos on the Red Square in Moscow, followed by enumeration of villages and towns liberated and Germans killed or taken prisoner. We followed the North African campaign blow by blow, from the moving barrage from a thousand guns at El Alamein to the surrender of Von Armin's army in Tunisia and eventually to the invasion of Italy and Badoglio's change of sides. Only the Pacific war was awaiting a turning point, but even there the Japanese advance stalled completely. We knew that it was only a matter of time before we won - the problem was to survive till then.

Late in 1943, I formed a scheme of doing something toward the victory myself. The insane plan, formed entirely in my adolescent head, was to derail a German arms or troop train and to join the partizans (guerillas) in the woods. One morning, I wrote an appropriate letter to Kazik, apologising for any inconvenience and thanking him for all he had done, stole some tools and went off. Finding (without a map) an appropriate railway line took some time and when I started to undo the nuts holding the rails, it was quite dark. Unfortunately, it is a lot harder to undo rails than one might think, although at least I was on target: trains loaded with tanks, trucks and artillery going East were passing every 20 minutes or so. I gave up on the mechanical approach and started to dig out the ballast from under the rails. After about an hour, my fingers were bleeding but I was making no progress and decided to give up and let others win the war. I started walking back towards Lwow along the train line. Suddenly, walking in the opposite direction and just visible in the pre-dawn gloom, was a German soldier, rifle and all. Oddly enough, I was not afraid and reasoned quickly that if I dived from the railway line, he would hunt me down and kill me, so I continued walking. *He* walked off the line and I passed without incident, not even panicked, presumably with archangel Gabriel in close attendance. Eventually, I got back home where Kazik and Kazika were awaiting the arrival of the SS having reasoned that I would have taken identification with me and been inevitably caught. I forgot to write that I carried no papers whatsoever and relied on a kitchen knife with which I planned to kill myself (by cutting my wrist - it was all thought out) if captured. There have always been some doubts about my sanity!

HUNGARY AND BERGEN-BELSEN

In February 1944, my father wrote to us in the usual oblique way, that he had arranged a guide to take me over the Carpathians to Hungary. It was no simple matter to get to the frontier and it was decided that Roman should come with me as well. We boarded a train for Stanislawow, changed to a train going to Worochta (passing Nadworna of the Einsatzgruppe C memory) and met the guide without any incident. The last bit of the journey to the frontier was a bit trickier, as only local residents could go to the last little station (Woronienka) and it was decided that the guide with two Jewish girls on Aryan papers, would take the front compartment and try to detain the German policeman (local Schupo, not SS) whom he knew, to prevent him from getting to the rear compartment occupied by Roman and me. If that did not work, given that we had no convincing (or even unconvincing) excuse for being on the train, Roman was to grab the Schupo in a bear hug, while I stuck a knife (the same as used for the railway expedition) in his back and we were to toss the body out of the window into the snow. I am confident that we would have carried this out, but fortunately female company and a bottle of vodka kept the Schupo busy till Woronienka and we reached the guide's house without incident. After a 24 hour rest and accompanied by the guide, the two girls and another Jew we set out in pitch darkness and in knee-deep snow over the Carpathians for Hungary. The trip took about 12 hours and toward the end I was hallucinating from exhaustion, but the highlight happened quite early: we were crossing a culvert under a railway line, the thin ice crackling loudly under our boots, when suddenly the guide motioned us to stop. There were two German soldiers right above us, chatting and smoking. We froze still and had they had a dog, it would have been curtains, but they tired of the spot and walked off while we walked on, archangel Gabriel in attendance.

There was a nasty surprise when we finally staggered to a small railway station on the Hungarian side: the roads were jammed with German trucks, artillery and tanks, this (Easter, March 18, 1944) being the day when Hitler decided that Hungary was an unreliable ally and had to be occupied. There were no immediate consequences for us as the German army was frying bigger fish, but eventually this meant that the last sanctuary for Jews in Europe was gone and the Hungarian Jews largely disappeared in an orgy of murder in Auschwitz. Roman and I got to Budapest without incident and met my father. Roman joined a displaced persons camp south of Budapest and survived the war unscathed, to return to Poland after the war and die of natural causes in his early fifties.

My father placed me with a peasant family in a village Tarnok Ligelt, about 20 km South of Budapest. Mr and Mrs Kovacs (smith) were lovely people (with a lovely 20 year old daughter, Lilly, my first real sex interest). Other than her, the entertainment was watching the USAF bomb Budapest in daytime, the RAF taking over at night. Even though some planes came down in the vicinity and we inspected the wreckage and the mutilated bodies of our airmen, there was no question that we were winning the war in a big way and this was confirmed on June 6, 1944: D-day!

Meanwhile, I lived a normal boyish life, learned Hungarian at an amazing speed, made friends and helped in the fields by digging potatoes. However, my position was highly precarious: I had no real papers and was obviously not a Hungarian. My lovely hosts, who knew me to be Polish, but of course not Jewish, got the idea of presenting me as a German. One day, a real German woman (there were German settlers all over Eastern Europe) searched me (a countryman!) out and embraced me in the middle of the village street, babbling in German. Even my very brief answers showed my poor command of German and she said suspiciously “Du bist doch nicht Deutche!” (you are not German). Quick as a flash I answered “Volksdeutche!”, which fobbed her off, another close shave notched up.

Toward the end of June, my father visited and told me about a scheme, which later became known as the Rozse Kasztner project, for the Germans to exchange a transport of Hungarian Jews for (variously reported), wounded German prisoners, trucks or money, and my father’s Zionist connections got us two places on the initial (and, as it turned out only) transport. I vividly remember my father saying to me: “There is a 50:50 chance that we will go straight to Auschwitz and be killed, but it might work. Shall we go?” I also remember replying: “50:50 !! Great, let us go!”, the odds being much better than our chances of survival even at this late stage. I bid tearful farewell to the Kovacses and my lovely Lilly, and off I went.

We boarded the transport together with 1,680 Hungarian Jews from a Budapest transit camp on Columbus Street and set off, the standard 70 persons to a cattle truck, hoping to finish up in Tangiers. The trucks were open and we knew where we were. As we passed Bratislava there were a very tense couple of hours: North at that stage meant Auschwitz, and my father and I were going to jump. However, the train turned West, past Vienna (my father identified St Stephen’s Kirche and we knew my mother was somewhere there) to a brief stop at Linz, where we learned that Lwow had been liberated by the Red Army. The train then turned inexplicably North and eventually went past Hannover and Celle to what we later learned was the concentration camp of Bergen-Belsen, generally abbreviated to “Belsen”.

It has been estimated that some 50,000 people perished in Belsen and when British and Canadian troops liberated the camp in April 1945, they saw Dantean scenes of mounds of emaciated corpses and clusters of equally emaciated survivors. All this, particularly bulldozers shoving piles of corpses into mass graves, was faithfully recorded on film and turns up every now and again on TV documentaries, thus giving the impression that Belsen was hell on earth. However, by comparison with the extermination camps in Poland, where *millions* died, and even with many other Konzentration Lagern, such as Matthausen, Buchenwald and Dachau, Belsen was a mere first circle of hell, though hardly a holiday camp.

Firstly, while the food (half a litre of soup and 600 g of heavy bread daily, being the principal diet) was reliably delivered to us, it literally amounted to starvation rations: we arrived at the end of June 1944 and by the time we left over 5 months later we were reduced to walking skeletons. Secondly, there really was no escape: the camp was divided into various sub-camps by barbed wire fences and we were in the Barracke 11 and in half of the Barracke 10 and were known as the “Hungarian Camp”. Much more serious obstacles surrounded the camp as a whole. Our sub-camp was on the edge and part of our border was in fact the camp’s outer perimeter consisting of a single barbed wire fence, a carefully brushed sand strip on which any footstep would show, a triple barbed wire fence with coiled and overhanging sections and an electrified fence. Every hundred meters or so, stood a well-constructed watch tower, much more elaborate than the ones I saw in Auschwitz on a visit in 1993, with an SS-man, a searchlight and a machine gun. Just to make sure, SS with dogs patrolled the woods outside the camp perimeter. There was no doubt about it: they had us, but the psychological effect was oddly calming. There was no need to worry about being caught - one already was and all we had to do was to try and not starve or otherwise die. We were essentially kept on ice and not subject to any serious brutality, beyond kicks and blows at the daily “appel”, the counting ritual unfailingly performed by a bored and infuriated SS-man or woman, one of whom was the notorious Irma Grese later convicted by the British for multiple murders and hanged. We were made to stand in rows five deep in front of our barracke - my father and I, together with 120 others were in room 10C, which was approximately twice the size of our present lounge room. It rained a lot and the strain of standing for usually an hour or so was too much for an increasing number who were counted separately in the barracke. The SS were continually losing count and their tempers and obviously did not see anything odd about counting prisoners who could not possibly escape. The “appel” ritual was maintained in all camps, labour, concentration and even extermination where the population was rapidly disappearing. Just another part of the German obsession with order!

The guards were a mixed lot, ranging from sadistic psychopaths to criminal elements glad not to be at the front. I particularly remember a relatively harmless elderly SS-man nicknamed by us Popeye the Sailor for his remarkable similarity to the cartoon character. One day, one of our young men on the soup-detail, i.e., the group bringing in the 50 litre soup containers from the camp’s kitchens into our compound, yielded to temptation and picked up a raw potato from the floor of the kitchen. He was caught and not shot, presumably only because the camp Kommandant was responsible for keeping *all* of us on ice. Instead, the lad was sentenced to two weeks in solitary confinement in a freezing cell of about 2 meters square. Popeye was detailed to escort him to the lock-up and told him: “Don’t worry lad, I served 14 years for murder and it did me no harm!”

Other groups in Belsen fared much worse. The remaining part of Barracke 10 was occupied by 300 “Poles”, who were Polish Jews with various South American papers, with whom we could communicate by walking in pairs a couple of meters from the dividing fence and talking loudly apparently within our respective camps. It transpired that there were originally

2000 such “Poles” occupying the rest of the Barracke 10 and Barracke 11, but shortly before our arrival their papers were re-examined and the 1,700 whose identity papers were more dodgy, were transported to Auschwitz and killed. My father knew some of the people in the remnant “Polish” camp and many more people in the vanished group, which included the Lisowoder family from Lwow with their two boys the older one, Roman, being my best friend back in the pre Holocaust world! On a more cheerful note, many of the remaining 300 “Poles” lived through Belsen and I met a young man slightly older then me in Palestine in 1946 who told me how their group survived. In March 1945, the Camp Commandant (the notorious Joseph Kramer, later executed by the British), decided that this group of 300 should be killed and as the “facilities” of Auschwitz were no longer available (they fell to the Red Army in January 1945) and as he apparently did not want to murder them inside his camp, they were put on a train with the idea of executing them somewhere in the countryside. Fortunately an American armored column intercepted the train and upon learning what was going on, promptly executed the would-be executioners!

Besides the “Poles” we had two other neighboring sub-camps. One of them housed some hundreds of Soviet prisoners, who had been political commissars. There were such “Politruks” attached to all units of the Red Army and normally, they were executed by the Germans as soon as they fell into their hands. Our neighbors somehow escaped this fate and were used to do all sorts of heavy labour inside the camp. They were horribly treated and I personally saw on two occasions an SS man beating a prisoner to death with an iron bar. I doubt if many of them survived.

Our other neighbors were 4,000 Dutch Jews and their families, who were kept on ice just like us, but for a different and bizarre reason: they were diamond cutters and the Germans must have concluded that after they conquer the world and all the diamond mines, they would need such people, who are very difficult to train! I don’t know about their fate and I suspect that the father of Anne Frank who survived Belsen might have been one of them as there were no other “Dutch” sub-camps.

We had no contact with the external world, but a torn piece of a German newspaper blew in with the story of the “Attentat” - the attempt on Hitler’s life in July 1944. There was little doubt that we were going to win the war shortly and, in particular, as Belsen was on the direct line from Southern England to Berlin, we could observe on many occasions armadas of American bombers flying serenely in their hundreds above our heads, the sun reflecting from their polished aluminum wings and fuselages.

In August 1944, the SS officer whom we knew to be responsible for the

Kasztner project, Obersturmbanfuhrer (colonel) Hermann Krumey (later tried and convicted as one of Eichmann's closest accomplices by a German court in 1969) turned up and selected about 300 of us as a trial batch to be sent to Switzerland. In the months after their departure, we had no idea what was going on and simply got thinner and weaker waiting for something to happen. Indeed, on December 6, 1944 Krumey turned up again and we were informed that we were indeed "exchanged" for something unspecified (it turned out to be simply cash supplied by American Jews and going into Krumey's pocket!) and were going to Switzerland. We were cautiously jubilant but my father and I, who have had much more gruesome experiences with the Germans than our Hungarian fellow prisoners, still thought in terms of rescue *or* Auschwitz. We were marched 5 kilometers to the station (a great effort in our emaciated condition) guarded by the usual machine-pistol toting SS and their guard dogs and put on a normal passenger train. A good sign!

The distance between Belsen and the Swiss frontier is only about 600 km, but the train took three days to cover it, most of the time being spent hiding in tunnels to escape American fighter-bombers - Hitler's "Festung Europa" (fortress Europe) had no roof. We repeatedly passed through burning cities, like scenes from some Wagnerian Gotterdammerung, confirming that no matter what happened to us, Germany was definitely going Kaput. Meanwhile, having eaten all the food we kept for emergencies (after all, it would not be needed whether we were going to Switzerland *or* to Auschwitz!) we developed diarrhea and spent a lot of our time queueing up at the toilets. Eventually, as dusk fell on December 9, 1944 the terrain became hilly and forested and we hoped that we were somewhere near Switzerland - in fact we were very close to Constantz on the Bodensee. At this stage the train stopped for several hours and nothing happened. We were later told that Krumey demanded a large additional sum of money, threatening to divert us to Auschwitz. This might have been a bluff, given that Auschwitz was about to fall to the Red Army, but the Swiss advanced the sum required (they were later repaid by American Jews) and we were saved. Meanwhile, we had no idea of the drama and when the train finally crept forward, well after midnight, we were literally and figuratively in the dark. I was sitting next to the window and I saw in the faint light that the gray helmet of a soldier being passed by the train appeared to be of a subtly different shape. It was indeed - he was Swiss! Minutes later, the lights in the carriage went on and a Swiss officer entered saying: "We gehts, mine Damen und Herren?" (How are you ladies and gentlemen?). It is impossible to describe the feeling of elation and relief. We survived. The nightmare was over.

The house at Sloneczna 47 in the Lwow Ghetto, where Sev and his parents lived between November 1941 and October 1942. Photo taken in 1993.

The notorious “most”, i.e., “bridge”, really a railway viaduct, which crossed Sloneczna St, about a 100 meters from No. 47, where the Sternhells lived. It was the scene of unbelievable violence in 1941-1943. The photo, taken in 1993, shows Alice in front of a part of the memorial erected to commemorate the massacres in the Lwow Ghetto.

Memorial plaque erected by the Ukranian Government near the “most”, which reads: ***In this “ road of death” in the years 1941-1943, the German-Fascist occupiers murdered 136,800 Jews in the Lwiw Ghetto.*** **Photo taken in 1993.**

The Sternhell family (Samson, Maria and Sev) in the Lwow Ghetto in 1942. These photos were taken to be used in false documents. The strain is showing, but don’t I look Aryan!

Kazik and Kazika Schultz in Krakow in 1958. He saved Sev's life at the risk of his own.

Survival! Sev and his father Samson in Switzerland, just before we left for Palestine late in 1945. We are almost back to normal weight.

Sev and his friend (Ricsi Heffner) in Switzerland.

CHAPTER 5: ODYSSEY

The Swiss have come in for much criticism for their handling of the bank accounts of Jews who perished in the Holocaust and for refusing entry to some of the refugees who turned up at their frontiers during World War II. Whatever might be true of Swiss bankers, the Swiss Government was acutely aware of being an island in a Nazi/Fascist sea during the war and it tried not to provoke the Germans too much. Of course, by the time we arrived in December 1944, their fear of German invasion lessened as Nazi Germany was coming close to collapse. Even though Switzerland was neutral, there was no question whom they considered their enemy and they were an armed camp with fields of barbed wire on Alpine slopes, tunnels bulging with arms hacked into mountains and anti-tank traps ready to block the roads. Food was rationed but they fed us generously and looked after us very, very well. My late father and I have had nothing but warm feelings for Switzerland and the Swiss.

We were initially taken to StGallen and housed in a school where we were given the first of numerous medical examinations. I was as tall as I was ever going to be and my father was of the same height: he weighed in at 30 kg and I at 27, the doctor clicking his tongue in disbelief. We were literally walking skeletons, but otherwise apparently in good shape. Swiss newspapers were full of reports about us, as we were the first large group of witnesses from Nazi occupied Europe. The Swiss medical personnel who were looking after us, had the good sense not to overfeed us, but even the carefully chosen light diet was enough to give us spectacular diarrhea. As soon as one left a lavatory, it was advisable to join a lavatory queue again! However, this did not last long and *nothing* could spoil the feeling of survival for us. We were born again.

After a couple of days, we were loaded on a train to be taken to a more permanent location. Well, not quite *all* of us: among us was a “saint” in the person of the Szatmary Rebbe, Rabbi Yoel Teitelbaum. He was an otherworldly figure who managed to look quite saintly even in Belsen (he was in Barracke 10E, two doors down from us) and he, his wife and his children survived together with the rest of us. As we were about to entrain in StGallen, a group of Swiss Hasidim rushed the crowd and “kidnapped” the Rabbi and his family in spite of the fact that we were formally internees and under the guard of armed Swiss soldiers. The Swiss ignored the incident and indeed let us come and go as we pleased throughout our stay in their country. The train proceeded through stunning Swiss scenery finishing up in Caux-sur-Montreux above the lake of Geneva, where we were put up in a huge and very elegant hotel built in a strange Moorish style. The feeling of safety, the plentiful food, the amazing scenery and the kindness of our hosts provided an unbelievable contrast with our experiences under the Nazis. One minute you were about to be exterminated and the next you were in a holiday resort in Switzerland! The building still stands at Caux and in 1994 served as a conference centre.

After a few weeks, the Swiss separated youngsters between the ages of 10 and 18 from the main group and put us initially in a hotel at Weggis on the Lake of the Four Cantons (more amazing scenery) and later in Bex in the Rhone Valley (still more amazing scenery!). Those of us who had families in the main camp could travel to visit and family could visit us. The main purpose of setting up the youth camp was to provide us with some structured education and to feed us up in a serious way. Thus for breakfast there was an infinite supply of cocoa and I remember having regularly 17 cups at a sitting together with copious food! Nothing like a Konzentration Camp to whet the appetite of a 15-year old! However, many months later my nickname was still "Ghandi" on account of my ribs showing so prominently. Hard to believe this, given my present shape, but true.

Life in the youth camp was great: not only were we all happy to be alive, but we were a mixed mob and sex replaced survival as the main preoccupation. The personnel at the camp were young Swiss and French Zionists who made valiant efforts to teach us Hebrew and learn to work on the land at the extensive gardens we had in Bex. I quite liked this, but I had no intention of becoming a Kibbutznik. Meanwhile the Nazi Reich was collapsing. I well remember a headline in the *Neue Zuricher Zeitung* in about March 1945: "Das Drittes Reiches letzte Wochen!" (The last weeks of the Third Reich) and indeed, the war in Europe ended triumphantly on May 8, 1945 about a week after Hitler committed suicide like a cornered rat in crumbling Berlin. This did not bring back the millions who perished, but it certainly was a happy ending of a sort.

It took my father quite a long time to contact Arthur in Australia, the communication systems being busy with the war, but eventually we got through. The first message we got back contained the news of Vivianne's birth. Sort of symbolic. We had no idea who (if anybody) of our family and friends survived the Nazis, but we were reasonably optimistic about my mother because when we last heard from her early in 1944, she was miserable, but relatively safe, as a Polish slave woman in Vienna.

Following personal intervention by Winston Churchill, our whole group was permitted to enter British-mandated Palestine and my father and I joined the transport which was organized in August 1945 even though we considered Australia to be our final destination. We went by train to Bari and then embarked on a troopship for Haifa. Days after our arrival, we learned that my mother and Sylvia were alive and well in Warsaw. They shortly relocated to Berlin where Siamo Gottlieb (Smex or Sasha to you) was a medical capitan with the British Army of Occupation - talk about a reversal of fortunes! However, it soon transpired that out of our vast extended family in Poland practically no-one was left: Siamo, Gencia and Milek and that was that.

My father and I stayed in Palestine, first in Haifa and then in Tel-Aviv till May 1946 while our landing permits for Australia and transport got organized. I learned English and swam a great deal. We eventually embarked for Marseilles and Paris where we arrived in June 1946, shortly being joined by my mother and Sylvia. We stayed in Paris till November 1946 when we secured a passage on MS Monkay, a 16,000 tonne cargo-mixed of Messagerie Maritime bound for Sydney from Marseilles, thus becoming the boat people of 1947. Except that the ship was requisitioned for 4 weeks by the French army as soon as we docked in Saigon to carry troops and supplies to Hanoi to fight the Viet Minh (the precursors of Viet Cong), the journey was only moderately uncomfortable. There is nothing like World War II to give you a sense of proportion and although my mother and Sylvia found the mouse-sized flying cockroaches and saucer-sized spiders a bit of a trial, I found Saigon fun and interesting. However, it was with relief that on February 11, 1947 we docked at Brown’s No9 wharf in Woolloomooloo to start our new life.

Siamo Gottlieb (Sasha, Smex) reunited with sister Sylvia in Berlin 1946 (Appendix 8)

**Reunited in Paris in 1946.
Left to right: Sev, Samson Sternhell, Sylvia and Maria Sternhell nee Wachs (Appendix 9)**

On the way to Australia: Sylvia, Samson Sternhell and Maria Sternhell on board of MS *Monkay* in December 1946

CHAPTER 6: A GOOD LIFE

Even before the War my parents were contemplating emigration, as Europe was threatened by war and antisemitism. After the Holocaust, emigration was the most obvious choice. Australia turned out to be the destination for the remnant of our family, because Arthur (1913-1999) emigrated to Australia early during the war (in 1940 via the Panama Canal) following Mundek (1906-1982), who emigrated in 1939. Mundek, in turn chose Australia, because it was the only one of the likely destinations, which recognized his Italian medical degree. You are Australians because of a quirk of medical regulations in the state of Victoria!

Mundek and Arthur were young, able and energetic professionals, who fitted in and established themselves in Australia very rapidly. Mundek married Ruth Hirsch in May 1938 (in a double wedding with Rela and Celek Zimring, which I attended in Lwow) and the young couple initially settled in Mitiamo in rural Victoria, where Mundek started off as a general practitioner. The locals, who took to the pleasant and handsome young couple, had no trouble with the name “Ruth”, but found the pronunciation of Zygmunt Wachs beyond them. They persuaded Mundek to change his name to “Walker” and suggested “Charles” as the first name “because you are a good Charlie”. Ruth soon gave birth to their son, my cousin Irwin Walker (now a successful Canadian medical academic), but died soon afterwards. Mundek moved to Melbourne, married your auntie Gertel who made a wonderful mother to young Irwin and after serving as a medical major in the Australian Army in New Guinea, returned to Melbourne where he developed a thriving practice in dermatology and an interest in sports medicine. Because of the latter, he became prominent in the Melbourne Polish community, which was then as now, mad about soccer (Mundek was an international soccer and ice-hockey player in his youth).

Arthur, a veterinary surgeon, converted his Polish degree in England in 1938-40 and in the last minute before the outbreak of the war brought out Anita Schwartz (1917-1980) to London where they were married. This undoubtedly saved her life, as her parents, Dr and Mrs Schwartz (Dr Schwartz was a well known skin and STD specialist in pre-war Lwow) and younger sister Resia (Teresa) all perished. I remember visiting the Schwartzes with my parents just before they were captured and killed in the August 1942 action. In Sydney, Arthur became well-connected, partly through the mentorship of Sir Ian Clunies-Ross, then a Professor of Veterinary Science at the University of Sydney and later the Chairman of CSIRO. Arthur specialised in treating race-horses and, Australia being what it is, he became very well known. For decades, whenever I was introduced as a Sternhell, people would ask: “Are you related to Arthur Sternhell, the Vet?” Arthur and Anita’s only child, my cousin Vivian (1945-) and her husband Greg Zeltzer have two children Katrina (b.1971 now married to Chad Jankelowitz and mother to Romy b. 2001 and Coby b. 2003) and Ralph (b. 1975 and now married to Michelle Shvartsberg and father to Jessica Anita b. 2003).

Sylvia (1914-1979) arrived in Australia together with us and, in time married her second husband Hugo Heyman. They had two children Lynnie and Michael, who now live with their families in the USA. They were followed by Siamo Gottlieb and his wife Gencia. Siamo (1911-1997) worked as an accountant and Gencia (1922-) is now the last person alive in our family to experience the Holocaust as an adult. Milek (1899-1959) and his second wife Anda, also a Holocaust survivor, came shortly after and Milek together with Hugo Heyman, was employed by a local pharmaceutical company, Andrews Laboratories owned by a family friend Dr Andrew Ungar.

My parents enjoyed and appreciated Australia, but at 47 years of age, my father considered himself too old to convert his degree. He engaged in a succession of very modest and not very successful businesses instead. My mother did better: after working as a sales lady for a number of dress shops, she opened one of her own, the tiny “Sondra Salon” in Hall St., Bondi which she ran till she was 74 years old! It was not exactly a gold mine, but it brought steady income and kept her in comfort, together with a pension she received from the German Government. We helped her by providing her with a flat, which we still own. My father died at 59 of a brain tumor and my mother was a widow for 32 years, but coped well.

Sylvia’s brother Siamo Gottlieb (1912-1999), generally known as Sasha or by his childhood nickname “Smex”, came to Australia after being discharged from the British Army and married Eva Fraenkel who had been as a child rescued in one of the “Kindertransporten” from Nazi Germany to England in the late 1930s. They settled originally in Brisbane, Sasha became a psychiatrist and eventually they moved to Sydney. They have 3 children (all doctors married to other doctors!) and nine grandchildren.

Siamo Gottlieb, Siamo (Sasha-Smex) Gottlieb and my late father Samson were the “three Sams” of the family in Australia.

On arrival in Australia in February 1947, I was packed off to board at Newington College, Stanmore where Arthur (who could be very persuasive!), persuaded the Headmaster to accept me into the final year in spite of the fact that I have never attended High School, or even completed Primary School. It worked and I completed my Leaving Certificate in November 1947 and off I went to Sydney University in February 1948 without losing any time through World War II! In case you are interested in my professional career, I have appended a section from the November 1999 issue of the *Aus-*

tralian Journal of Chemistry dedicated to me among other “Golden Oldies”.

Your mother arrived in 1948 on a notoriously mismanaged migrant ship “Derna”, whose epic voyage has been described in a book by Diane Armstrong (*“The Voyage of Their Lives”*) published recently. Having lost her parents in the Holocaust, she became the adopted daughter of her cousin Jerzyk (George) Bochenek and his wife Henryka (Rysia). Too poor to study her first choice, Dentistry, the profession of her late mother Eugenia (1902-1942*), she settled on Pharmacy and I demonstrated to her when she was a first year student while I was an Honors (Fourth Year) student. In any case, our families knew each other and we were doomed to meet. In time (1953) we married and the rest you know. Our lives since have been normal “good lives” by Australian standards, but quite wonderful by comparison with what we had been through.

In retrospect, even the Holocaust has been of some value, as it has given us a sense of proportion: we don’t get hysterical about the normal problems and disappointments of life. Whenever someone carried on about some ordinary setback, my late mother would say “So, has Hitler come back?” There is also another, grimmer, lesson from the Holocaust: an unimaginably horrible catastrophe *can* happen in the midst of apparent normality. In fact, several have already occurred since World War II.

Australia is a great country and has allowed us to have the three of you and to enjoy life in peace and security. Above all, it is a democracy by the most important of definitions: when you hear a noise outside your door in the wee hours of the morning, it is the garbos (not the Gestapo or the NKVD).

All three of you are now married, established and parents to a total of 7 of our grandchildren. Adolf Hitler is undoubtedly revolving in his grave.

Arthur and Anita Sternhell (nee Schwartz), shortly after their arrival in Sydney in 1940 (Appendix 7).

Mundek Wachs (later Charles Walker, Appendix 5), In an Australian Major's uniform in WWII.

Wedding photo of Mundek Wachs and Ruth Hirsh in Lwow, 1938.

Photo taken at the old Chequers nightclub in Sydney in 1948.
From left to right: Samson Sternhell, Gertel Walker (nee Teichert), Maria Sternhell, Sev Sternhell, Charles Walker (Zygmunt Wachs), Anita Sternhell and Arthur Sternhell (Appendix 5 and 7)

YOUR MOTHER'S STORY

THE FIRST GIFT – 1932

They say that you are given the gift of life but once, yet your father claims that I was given this gift three times.

The first time was when my mother, Eugenia Zalcberg nee Scheinwechsler (1902-1942*) gave birth to me on a cold winter's day, December 4, 1932, somewhere in Czestochowa. I surmise it was cold, being early winter in Poland. I do not know what sort of birth it was. Was I born at home or in a hospital? Was it an easy or a difficult confinement? What sort of pregnancy did my mother have? Was I planned or was I an accident? There is no one to ask. I envy my friends with elderly, sometimes demented and very difficult mothers; they are demanding and infuriating, but they are there and can be asked questions.

My maternal grandfather, Wolf Scheinwechsler (1859-1934) was a journalist in Chestochowa. I don't remember him, as he died when I was two. My maternal grandmother Emilia Scheinwechsler nee Altman (1863-1942*), moved to Warsaw after his death to live with her daughter Edzia Bochenek (1889-1942*) and Edzia's son Jerzyk (George Bochenek 1907-1989, whom you knew). There were four sisters and a brother. My mother was the youngest. Besides aunt Edzia, there were aunts Sabina (1889-1942*) who lived in Lodz and Tasia (1893-1942*) who lived in Czestochowa. They were all widows by the time I was born. My mother's brother, Tadek (1890-1937) was a widower with a son, Henio, he had by his first wife. They also lived in Warsaw. Henio (1911-1955) was a lawyer married to Lydia. Tadek had a new wife, Franka, who was later the first surviving relative to contact me after the Holocaust, and a baby son Wojtek (1935-1942*). Sabina Plocki had a son, Stefan (1912-1942* or 1943*), who was an engineer. He married Lucyna in 1938. Lucyna disappeared in the Holocaust, as did Stefan. Tasia Grodzinski lived in Czestochowa with her two sons Kazik (Charles Groden b.1911, who now lives in Lindfield and who completed his degree in Zurich) and Rysio (Richard b.1916, who now lives in Florida). These two boys were out of the country most of the time, studying in universities all over Europe and that is how they saved their lives.

Jerzyk Bochenek was a chemical engineer and an importer. He had a younger sister Janina, who, before my time, was killed in a freak accident at the age of 16 in 1928. An aeroplane made a landing in a park where she was on a holiday and she was killed by the propeller. Because of this, Jerzyk never flew in an aeroplane. Jerzyk was married to your Auntie Rysia (b. 1918). They saved themselves by leaving Poland at the beginning of the war (see *Letters to Jane*).

I had a sister Wanda (1923-1942*) who was nine years older than I, so that you can see that Wojtek and I were the babies of the family, the other four cousins being adults by the time we were born.

My father came from a small family, his only sibling was his sister Hanka, who married a Polish Catholic and had a daughter Irena. Hanka's husband left her sometime before the war and she lived with my grandparents. The husband was a nasty piece of goods and during the war when Hanka was on Aryan papers together with grandma Zalcberg (grandpa Zalcberg died before the war) and Irena, he blackmailed her.

Alice's parents, Alfred Zalcberg (1892-1942*) and Eugenia Zalcberg nee Scheinwechsler (1902-1942*) in Czestochowa in 1930's, Appendix 1, 2 and 4.

The house at No. 25, Kosciuszko St., in Czestochowa where Alice lived before the war. Photo taken in 1993.

Alice's maternal grandparents, Wolf Scheinwechsler (1859-1934) and Emilia Scheinwechsler nee Altman (1863-1942*), Appendix 1, 3 and 4.

Alice with her mother Eugenia (1902-1942*) and Aunt Tasia (1893-1942*) - Appendix 4.

Alice with her sister Wanda (1923-1942*) and aunt Natalia (Tasia) Grodzinski, nee Scheinwechsler (1893-1942*) - Appendix 2 and 4.

Alice with her father Alfred (1892-1942*) and Aunt Tasia (1893-1942*) - Appendix 2 and 4.

Alice with Mrs Karolina Tomaszkiewicz in Krakow in 1946.

Henryk (Henio) Scheinwechsler (1911-1955) with his second wife Lucyna Berland and daughter Joanna—Appendix 4. Photo taken in 1952.

My father studied textile engineering in Liege (Belgium) so he spoke French fluently and could translate “on the run” as he read Jules Verne stories aloud to me. After the First World War, my father couldn’t get a job in textiles so he finished up in Czestochowa in an enterprise called “Warta”, where he eventually became the technical director. Warta was the biggest paper mill in Poland and actually exported paper. This was unusual, as Poland did not export many manufactured goods then.

My mother was a dentist, but gave up work when she married dad and I only knew her as a lady of leisure. A hairdresser, a manicurist, a dressmaker and a corset maker used to come to the flat. She went to Warsaw to have shoes made. A broken nail was a catastrophe. In the morning while my mother was still in bed, my father having left for work and my sister for school, the cook would come in and ask what the “wielmozna pani” (roughly, highborn lady) wished prepared for lunch. Lunch was the biggest meal of the day – soup, meat and two vegs and pudding, which was, usually stewed fruit or “compot”. Lunch was served at exactly 1pm and if it was 5 minutes late, my father would throw a wobbly. After lunch, my father always took a nap. His coach and driver would pick him up at the mill to arrive home at exactly 1pm and take him back at exactly 3pm.

After such a pampered existence, my mother picked up the reins during the war and ran a dental practice, the family’s finances and the household extremely well.

My sister Wanda was 9 years older than I and was just about to start “lyceum”, the last 2 years of high school before the Matriculation, which was the entrance exam to the University. She had a lot of friends, both male and female and entertained them in her large bedroom, which doubled as the family’s “salon”. Middle class teenagers in those days were not wild, or sex-obsessed and certainly did not segregate at parties like here: men at one end and women at the other.

My mother furnished the “salon” with wonderful antiques, for which she was always travelling to Warsaw. Her last purchase that I remember was an antique sewing table full of little drawers for different coloured cottons. It was used to support the gramophone, which was essential to Wanda’s dance parties and which I was occasionally permitted to wind up.

I don’t remember my Zalcberg grandparents well. I recall one Xmas going to their flat (they lived quite close to us) and either my sister’s or my cousin Irene’s plait catching fire from the lit candles on the Xmas tree. I also remember that when my grandfather visited us, he used to bring me “landrynki” – boiled lollies shaped like half-moons.

THE WAR – 1939

My cousin Jerzyk owned a villa in Milanowek, outside Warsaw and in the summer of 1939 my parents took advantage of his generosity and took my sister and myself on holidays there. We collected our summer clothes, tennis rackets, my sister's governess and got a train there. Milanowek was a holiday resort of sorts and was one of the few, if not the only place in Poland to grow mulberry trees and hence it had a silk-producing industry. The villa was situated at the end of a long drive lined with peonies and roses. On the left-hand side was a grove of large pine trees under which we gathered mushrooms and on the right-hand side was a forest of young beeches, where mushrooms and blueberries were found.

My father, like most of his generation, was extremely interested in politics and for a long time was predicting the war, but just as we left Czestochowa he bet a packet of expensive cigarettes that Hitler would not start anything before 1st of September. My parents wondered for a long time as to who won the bet, as the war started on that very day. War brings about shortages and my mother busily shopped for flour, sugar, etc. However, one thing she did not stock up on, were cigarettes for my father, as she strongly disapproved of his smoking. My poor father was going out of his brain and I remember collecting rose petals and various leaves for him to roll and light up. Later in the war some cheap Polish tobacco appeared and I used to roll his cigarettes on a special little gadget which pushed tobacco into paper tubes.

There were a lot of discussions by the grown-ups, some of them held frustratingly in German or French, or when I was asleep and they decided that we would not go back to Czestochowa. I think that there was mail from family and friends from home and Warsaw and Milanowek sounded safer. I overheard a lot of discussions for plans to go "East", but my mother would always come up with "not with the child" and "we only have these summer clothes and not even an overcoat between us", so we stayed put. The governess was sent home and my mother decreed that we were to pretend to be Christians and not wear the armbands, as ordered on the pain of death by the Germans.

I was supposed to start school on the 1st of September, but as this was out of the question, my father drew up a huge multiplication table and hung it on the toilet door and that is how I learned to multiply. I also became an avid reader of matrimonial ads in the newspaper. Don't ask me why, I thought of them as something racy and forbidden.

We were looking after Jerzyk's dog, Puk, a cocker spaniel who was the stupidest dog that I have ever met. My father had to hold him at night instead of just letting him go into the garden to have a pee, as he was petrified of the neighing of horses from nearby houses!

As the war progressed, my mother bought 2 chickens so we would have fresh eggs. One was snow-white “Aryjka” (Aryan) and one was grey “Zydowka” (Jewess). Eventually we let the Aryjka brood and we had a batch of chicks. One of those chicks, which we thought was male, was very unfortunate. It was the runt of the litter and the other chicks wouldn’t let him near any food, so we removed him and my sister Wanda nursed him into health after a plank fell on him. He was named Abram, apparently reminding our parents of some person. When we finally moved from Milanowek, my mother took all the chickens to family and friends in Warsaw, but could not part with Abram and have him made into chicken soup. We took him with us to Czestochowa where we gave him to a Polish woman, a friend’s housekeeper who promised to look after him as well as her numerous cats. Some time later, the woman visited us in the Czestochowa Ghetto and the first egg that “Abram” laid was given to me to eat – a great honour. We did not have the heart to change “her” name to something more feminine.

Mail was obviously coming through, as my parents were getting news from my aunts in Warsaw and aunt Tasia in Czestochowa. At one stage my grandmother Emilia visited us in Milanowek and much to my mother’s disgust, proceeded to use up the last of some semolina that we were saving as invalid food, in case someone had stomach trouble. Grandma cooked up the semolina and gave it to the dog, who, of course wouldn’t touch it.

Early in September 1939 Jerzyk and Rysia dropped in on us in Milanowek – all I remember about this visit was that Rysia thought that I was about 4 years old: I was very small.

Aunt Tasia went for a short time to Warsaw with a girlfriend and stayed with Jerzyk and Rysia. The Bochenek’s flat was then requisitioned by the Germans, Tasia moved back to Czestochowa and Jerzyk and Rysia joined the gathering at Jerzyk’s mother’s flat. At one stage that flat contained my aunt Edzia, my grandmother Emilia, Jerzyk, Rysia, my aunt Sabina and a young husband-and-wife, who came from Lodz with Sabina. One day the Germans came to the door and took away the young husband, who was never seen again. Luckily, Jerzyk was out at the time or they would have taken him also. After that, Jerzyk and Rysia managed to escape from Poland (see Rysia’s book *“Letters to Jane”*).

The news from Warsaw must have been pretty bad, for as my parents pored over the mail, they looked very uneasy. We also learned from Tasia in Czestochowa, that our flat had been ransacked by our Polish neighbours. Tasia described how she saw the locals wearing our clothes and carting around our possessions. Here we were freezing in summer gear, but our tennis racquets were safe with us!

After many months, sometime in March 1941, we took the very dangerous step of catching a train to Czestochowa. We arrived to find our flat gone: the Germans had requisitioned it two days earlier. We moved in with aunt Tasia. All I remember of her flat were the numerous and very beautiful miniature "salons" she had handcrafted and her endless piano playing. We weren't there very long when the Germans announced the creation of the Ghetto. Tasia had to move and so did we. My mother arranged to borrow a lot of ancient dental equipment from her colleague, Dr. Dziubinski. Because she needed a surgery, we were allotted 2 rooms and a kitchen in the Ghetto – a real luxury. One room was my sister's room and the waiting room, the other the surgery, my parents' and my bedroom. My bed had a curtain across it so that the patients had some privacy. The equipment my mother managed to scrounge was pretty ancient. The drill was foot-operated and I was sometimes allowed to power it. The surgery kept us fed – people would pay mum with an egg or a piece of fruit, but the main income was from the ration of medicinal alcohol my mother received, presumably for sterilising instruments. Vodka was in high demand.

I was flabbergasted: our home had no bathroom! There was an outside dunny, an open pit which my mother declared to be totally unsanitary. In this connection, there was a lot of discussion regarding the curfew. One was not allowed outside after a certain hour in the evening and we were not sure if our yard was "outside" with the consequence of the risk of getting shot if one went out for a pee. My father concocted some sort of a "toilet" in the space under the roof – I presume that it was a bucket with a comfy seat, which dad emptied when we were not looking. All our household goods and furniture was given to us by good Polish friends.

My mother was very proud of her cooking and of being able to improvise new tasty dishes out of ingredients that she would not have dreamt of eating or serving before the war. She discovered pumpkins and turnips and made wonderful soups – also jams from unlikely fruit and vegetables. One day, my mother was picked up and arrested for forgetting to wear her armband, but managed to buy herself out with a bribe.

In Tasia's building in the Ghetto, there was a case of typhus, so they shaved her head. My mother was very upset for her, as the hair grew back gray.

There was a prevailing sense of dread and threatened violence, which I sensed from the very beginning of the war and which intensified now.

I was still a bad eater and sickly to boot. I was not allowed to go out on the street. I read as many books as dad could provide. Dad taught me long division and gave me children's "science" books. He also translated "Don Quixote" from Russian and Jules Verne's books from French for me. He had a wonderful knack of reading aloud in Polish from a foreign text without faltering. For a very short time (2 or 3 days) my parents sent me to a "school" where children of different ages gathered in someone's garden, carefully walking to and from homes at different times, as school of any sort was forbidden on the pain of death. On my first day I discovered that we were writing a book: each child would submit a chapter and the best one would be used. This captured my imagination and I sat down at home and wrote my version, which was about the adventures of some children travelling with a bear. I signed myself with a pseudonym "Azalea" and when my entry was deemed the best, I nearly burst with pride, but could not admit that it was mine. There were a lot of guesses about the authorship and a much older girl was thought to have used "Azalea", as her name also began with an "A". However, after this promising start, my parents must have decided that it was too dangerous to continue and I went back to being bored at home. The only other thing I remember about the "school" is the packed lunch I took with me. My mother made me a tomato, radish and chives sandwich and my sister peeled an apple all in one long peel and then wrapped the peel back around the apple. Also I remember driving everybody mad begging them to draw an aeroplane for me – I needed it as an illustration for my chapter (to this day I cannot draw) and to spell the German for "Halt, who goes there?".

There were other children in our yard – several buildings surrounded the open space on three sides. My father dug up the earth in the middle and planted some vegetables of which he was inordinately proud. I found the other children very coarse: the boys tried to pee on me and they all made fun of me as I was very slow and when we played hide-and-seek I could never get to the wall we were supposed to touch in time. I cut one of my knees deeply in one of those games and my mother was very worried and put some very strong peroxide on it, as well as iodine. I see now that she was worried about tetanus.

It was an "open ghetto", where Aryans could come and visit. My father's sister Hanka, who was living on Aryan papers with her daughter Irena and grandmother Zalcberg, visited us. My mother was worried that Hanka wanted to bring grandma to live with us, crowded as we were. Grandma had obviously a better chance of survival on Aryan papers. Hanka slept in my bed and I shared my father's bed. For dinner my mother made potatoes, well greased with pork fat, which must have disagreed with me. I woke up in the middle of the night feeling sick, but I did not want to wake up dad, till it was too late and I sicked up all over him.

I also remember our cousin Jozef Szarf (his mother was a sister of my grandfather Wolf Scheinwechsler) and his brother Izio visiting us in the Ghetto, where they also lived. For my ninth birthday, I wanted a pair of skates, God knows where I was supposed to use them. I was told that they were too expensive. Our cousin overheard me and brought me a pair of skates, which were never used by me, of course. I got my second choice – a green comb. Wanda had a green plastic comb and I wanted one like hers, but my mother bought me a fancy, pale green, translucent one and I was very disappointed. Later, when I was on my own, I wished that I had that comb with me. Izio survived the war in a labour camp in Czestochowa and now lives with his wife Jadzia in Tel Aviv. They have a son, named Ami and 2 grandchildren. His brother, Jozef, who was in the same camp, did not survive; they had periodic line-ups where the guards would shoot every tenth person.

We also had a visit from a relative (a Sudowicz), who lived on Aryan papers and was an agriculturalist. My mother was very impressed by him, he was very dashing, handsome and brave. I think that he is the person (misspelled as Sodowicz) mentioned in the book *“Escape from Treblinka”* by Samuel Willenberg. He was the leader of the group, which attacked the SS arsenal during the revolt of 1943 in the Treblinka death camp. Presumably, he perished sometime during this uprising, or later when hunted down by the Germans in the woods. I was to meet his brother, Edward, in London many years later. These brothers were related by marriage to my mother.

I was forever sick and as tonsillectomy in the Ghetto was out of the question, I was mollycoddled as always. I developed diarrhoea and a doctor put me on a diet of home-made bread and cottage cheese made at home from skim milk – I was beginning to like this sort of food. The doctor also diagnosed “murmurs” in my heart.

In our building there was another family with 3 sons. They were religious Jews and my mother did not think that they were “our sort of people”, but felt very sorry for the mother who was badly undernourished and probably had TB. My mother decided that she was going to save her with lard, which was the only fat available, as butter was very hard to come by. Mum spent days chopping and melting down pig fat and told the woman’s eldest son, Moishe to feed it to her. Wanda (then 19) and Moishe became very friendly and wanted to go steady. The name “Moishe” would have been enough to set my mother’s teeth on edge and as far as the lack of education! Wanda was still having private lessons in English in the Ghetto and preparing to go to the University after the war. Anyway, there were rows.

NIGHTMARE – 1942

Early in September 1942 rumours started circulating that the Germans were planning a big action. In fact as you can see from the appended extract from the *“The Encyclopedia of the Holocaust”* they sent 39,000 Jews from Czestochowa to the extermination camp in Treblinka between September 22 and October 8, 1942. The evening before the action started, a day before the Day of Atonement, the holiest of Jewish holidays, I was lying in bed as usual, when Mrs Dziubinski the wife of my mother’s colleague, called on us. She declared that she would take me out of the Ghetto. Needless to say, I did not want to go. I refused to take anything with me, not even the comb that was my birthday present a year earlier, or any of my wonderful books. I did not want to go and I howled and screamed. I somehow knew that I would never see my family again. I was right. I lost my family for ever and I never got over this. I mourn the loss to this day. I lost my whole world, my home and my childhood. I no longer belonged anywhere.

Mrs Dziubinski and I left the Ghetto about 8 or 10 pm – it was twilight and we just walked out – no one stopped us. The action started at 4 am and our street was first, i.e., I escaped death by a few hours. Before I left, there was talk about Wanda joining me next morning, but of course it never happened. In any case, as my sister was older she would need a “Kenkarte” rather than an easy-to-forge birth certificate. My birth certificate came from a girl called Eulalia Waleria Zwolska, who had died. This meant that my Aryan name was now “Lala” and as my parents always called me “Ala”, this was quite close.

We walked to the Dziubinski’s flat, which was not very far away. Mrs Dziubinski put me to bed and I cried myself to sleep. Next morning I woke up and before opening my eyes I thought “What a horrible dream – thank God it was only a nightmare”. I opened my eyes and saw a beautiful wardrobe with a mirror across from my bed and then I knew that it was not a dream. I cried solidly for days. I had to be hidden in that bed all the time, during which Mrs Dziubinski taught me my prayers.

After a few days Mrs Dziubinski took me by train to the countryside to stay with a relative of hers, a school teacher. I started to run around with peasant children, ate apples off the trees and all my ills seemed to leave me.

After a few weeks, Mrs Dziubinski came and took me by train to Krakow. We arrived at the main station after the curfew hour, but we had been told that people coming off the train were allowed to walk home. With me clutching her hand, we started walking to her parents’ place. We were soon stopped by a man (Gestapo?) who declared that Mrs Dziubinski looked Jewish and he was taking us to the Police station. Mrs Dziubinski had dark thoughtful eyes and, especially with a scarf around her head, she did indeed look Jewish. She wanted to show him her documents on the street, but he insisted we come with him. In the entrance to the Police station, he took her papers, which were of course perfectly OK, shone his torch in my face and said: “The child looks Jewish too”. I thought fast: now a Polish child told that she looked Jewish would laugh, so I smiled and looked amused. He than told me to say my prayers. I recited “Our Father….” And started on “Hail Mary…” when he stopped me, and let us go. Had he asked to see my birth certificate, it would have been curtains, as he naturally assumed that we were mother and daughter. My “story” was extremely flimsy “I lost my parents”, which I imagined as meaning that I was walking with my parents somewhere and I got lost.

Mrs Dziubinski’s parents, Mr and Mrs Pompow lived with their maiden daughter in a large flat. I was not allowed to walk around the flat, in case neighbours heard a child’s footsteps or leave my hair ribbons in the bathroom. I wonder what they did with my washing. A maid used to clean the flat, except for one room – the study. They taught me how to darn socks and I spent all day behind the desk and a potted palm in this study under the window, hidden from view. One morning the maid came in to stoke the fire as usual. The draft from the window (it was mid-winter by then) made me sneeze. I nearly died of fear, but Mrs Pompow heard me and rushed into the room, sneezing her head off and muttering “I must be catching a chill”.

The Pompows were, quite rightly, petrified. They confided in a good friend of theirs, an ex priest, now a Methodist minister, Jan Tomaszkiewicz who arranged for his widowed sister-in-law to take me in. Mrs Dziubinski paid some money for my maintenance. The sister-in-law, Mrs Mendrys, lived in a one-room flat with her twentyish daughter, Kristina, in Podgorze, a suburb of Krakow. I slept in a bed in the kitchen while she and her daughter shared the room. There were awful bedbugs in my bed and every night I used to go over the mattress and remove them all into a bowl of water. To solve this problem, the two ladies put the bed in the attic so that the bedbugs would freeze to death. I had my doubts, thinking that the eggs would survive. It was worse than that – they did not die, just dehydrated and in the middle of the night I woke up covered in very hungry “pluskwy”. As luck would have it, there was a black-out and in pitch black I found candles, boiled some water and started removing the tiny pale, starving bugs into the boiling water while trying not to wake up my hostesses.

I was let lose. The widow was a heavy smoker and did not like walking or shopping, so I was sent out to buy her cigarettes and to bargain for food. I became and expert shopper and spent most of the day on the street. I also went to church, which was next door, especially during May when I took part in May processions carrying reliquaries on a cushion.

Children started yelling “Jewess” after me on the street. I suppose I was new in the district and they got suspicious. I did not tell my guardian, as I did not want to be thrown out. Then, rather suddenly Mrs Mendrys died of a heart attack. I remained with Kristina, who was working while I did my best to keep house. From time to time some young man would come calling, trying to pick up and seduce Kristina. One day, a man brought a bottle of homemade cherry brandy and as Kristina refused to have any, I showed off and when given a large glassful drank the lot in one go – boy, did I get drunk and, later, sick! I thought I was dying. The young people laughed and laughed.

Kristina obviously could not cope with me any more, which was just as well as I was being followed home. I was getting very scared and took circuitous routes home. Mr Tomaszkiewicz persuaded his wife Karolina to take me in. It was a horrifying welcome for me at their place. Mrs Tomaszkiewicz, whom I was to call “aunt”, was cooking in a filthy kitchen, throwing off-cuts of cabbage on the floor. She then made some ravioli with meat and accused me of stealing some of the prepared meat, smacked my face and yelled. Not only I would not steal food (I was still a fussy eater), but I hated that sort of boiled and minced meat and I kept saying “but I don’t even like it!”. I realised later that she kept her husband on very short rations and he must have helped himself.

They had a dog, named Aza who had puppies, which we managed to give away. Never mind bedbugs – the fleas were worse. Every night I picked the black rows from the quilt seams and drowned them and every day more would come. The place was filthy. Auntie was a well-known opera singer when she met Mr Tomaszkiewicz, who fell in love with her, left the Church, became a Methodist minister and promised to take her to America. The war, of course, intervened and Mr Tomaszkiewicz had no money either, just a good education. Consequently Mrs Tomaszkiewicz had it in for education and kept ranting about “useless scholars”. I was not allowed to go near a book. I did all the cleaning, cooking preparation, stoking the fires and shopping. She would send me out to buy a hundred grams of ham, fifty grams of butter and a white bread roll for herself and gave the left-overs to the dog, while she kept her husband and me starving. The larder was under lock and key. I was continually shouted at, smacked on the face and worst of all, when she really got highly strung, she yelled “Jewess” at the top of her very powerful lungs. I was petrified that someone would overhear her. She was however very cunning, passed me off as her husband’s niece from Tarnow and kept saying to the neighbours, that, “all his family looked Jewish”. Everything I did was criticised as being “Jewish” in origin – say the way I chopped an onion. Funnily enough, after the war, I was accused of doing everything like a “Christian”, whatever that meant. My taste was “Jewish” in Poland and “Goyish” in England. Mrs Dziubinski continued to pay for me.

One day I was walking along a main street when I saw a man look at me – there was a look in his eye, perhaps of recognition. I took no chances and in a split second jumped on a moving tram, out the other side and disappeared. I did not tell anybody, of course.

One day in the mid-winter of 1943/1944 I went to buy some cottage cheese from a woman in a block of flats. I wore long woolly underpants in which the elastic had gone and which were fastened with a safety pin. As I started up the stairs, a German soldier in uniform caught up with me, put his hand up my skirt and tried to pull my pants down asking for my name in broken Polish. I said “Lala” and he said “what a pretty name”. I rushed off up the stairs and disappeared. After getting the cheese, I was too scared to come out of that building for a long time. Again, I did not tell anyone. At nine I was a bit too young for my mother to tell me “the facts of life” and I never did find out how babies get into mummy’s tummy, or what men and women do together. I thought it had something to do with breasts, as that is what grown women had, and covered up when sunbathing. Bottoms were obviously covered because they were disgusting and used for defecating. After this encounter I decided that the bottom had something to do with sex.

The worst part of living with strangers was not being able to talk to, confide in, or trust anybody. I even contemplated going to confession to unburden myself, but thought better of it.

THE SECOND GIFT – SALVATION 1945

Early in January 1945 rumours started about the Russians coming – they were rapidly approaching Krakow. Our house was very close to the Debnicki Bridge over the Vistula and as the Russians came nearer, the Germans commandeered parts of our building, set up guns to protect the crossing and mined the bridge. The commanding officer took a great fancy to a young woman in the house. The girl hid in a coal cellar, and the officer started running up and down stairs, looking for her, firing his pistol. He went quite berserk, but as he was the highest-ranking officer present no one could restrain him until they brought someone higher in rank to subdue him and have him carted away. I think that his mind snapped out of the fear of the Russians. There was a lot of shooting and noise on top of the crazed German shooting on the staircase and Mrs Tomaszkiewicz became quite hysterical and shouted at me that “it was all my fault because I was Jewish and brought this upon her”. I was pretty shaken up already and got very upset, burst into tears and rushed out of the room to the little hall on the way to the kitchen. At this moment, the Germans decided to blow up the bridge and as they detonated the charges, all the windows in the house shattered. The hat-and-coat stand fell on me cushioning me in coats, while Mrs Tomaszkiewicz got covered in broken glass, some which made her varicose veins bleed. Mr Tomaszkiewicz was fine.

We moved to a basement room, which had small windows, for shelter. The room had belonged to the caretaker and his wife, who had been arrested by the Germans shortly before for being communist. As I remember it, the room was a large one with a stove and a very large bed.

I looked out of the window and saw a rosy-cheeked (it was very cold) Russian woman wearing a furry hat with the red star riding on a horse. Others followed. Talk about Knights in Shining Armour! They looked wonderful and I knew I would be safe now. This was the Second Gift: Red Army soldiers on horses and the realisation that I had survived.

The Russians set up their Katiushas (rocket launchers) nearby, which made a fearful racket. I started shaking uncontrollably and hid deeply into the cellar near a chimney, known to be the safest place during bombing raids. I was panic stricken. I knew that the rockets were not aimed at us, but I must have suffered shock or perhaps it was a reaction to the relief of having survived. I returned to our new abode after the firing stopped. The Germans wasted their dynamite and our bridge, as the Russian tanks crossed the Vistula on the ice. The river was frozen solid for the first time in many years, as it was one of the coldest winters on record. A few days later I saw my first dead body: the German soldier who had detonated the charges on the bridge hid in an entrance of a building across the road from us and a brick fell down on his head. As far as I know, he was the only casualty of the explosion. The dead German’s feet in his army boots looked enormous.

Somebody started a fire in the stove and it became quite cosy in the basement. Some Russian officers asked to join us, they brought a bottle of vodka with them, which they shared with Mr Tomaszkiewicz. They had not slept for weeks and wanted to get some rest. Mr Tomaszkiewicz remembered the stories of the Red Army’s rapes and covered me up with bedding on the huge bed. The officers took turns to have short naps on a smaller bed in the same room. Mr Tomaszkiewicz had some lively intellectual and political conversations in Russian with them. The poor men, who had not slept in ages, kept waking each other up to take their turns. I will always remember the moaning of one freshly aroused officer: “tovarish, nie mogu, nie mogu!”, “comrade, I can’t, I can’t”. The Russians left next day, but not without leaving me a present: I was covered in body lice! That meant boiling all my clothes, which did not improve the few woollen rags I owned.

Real hardships started. As soon as the Russians arrived, they changed the currency and we had nothing. Also, I think that Mrs Dziubinski stopped paying for me. The only food we had were the few potatoes in the cellar and I spent hours grating them and making latkes out of them. It was a real art to grate the last bit of potato with minimum blood loss and then to fry them on virtually no fat. We had a bit of coal to start the fire in the centrally positioned iron stove for cooking, which also kept us warm. What we did not have was running water, as the pipes had burst during the explosion. That meant a trip to the well with a bucket, which was truly miserable. My gloves had holes in them and the metal pump handle was giving me blisters and frost-bite. There were long queues at the pump. The spilled water around the well froze and it was extremely slippery. The buckets were very heavy.

Mrs Tomaszkiewicz declared herself an invalid and stayed in bed all day, giving me orders and yelling at me. Mr Tomaszkiewicz went out to find a job and a flat. He found a beautiful modern flat about 4km away across the river. It was on the third floor and had three large rooms, two balconies, kitchen, bathroom and toilet. Fleas disappeared and there were no bedbugs either. It used to belong to a German officer and even had a grand piano in it. It had a gas stove, though we never used it as gas was too expensive and I continued to cook on coal. Now it was a matter of moving. I would load two bags with our kitchen utensils, clothes etc., take one in each hand and walk over the frozen river slipping and sliding to the new flat and up the stairs several times a day. Mrs Tomaszkiewicz remained lying down, Mr Tomaszkiewicz continued looking for a job.

Food was a problem. We heard that in a school cellar the Germans left a mountain of potatoes. By this time it was early spring and things were thawing out. There was what appeared to be several meters of potatoes there, unfortunately, they had frozen during that cold winter and as they were thawing out, they rotted. I could feel an occasional good one among the rotten ones with my bare fingers. I spent hours elbow-deep in rotten spuds looking for some good ones, then back home to grate and fry them.

Mr Tomaszkiewicz got a job in an office, which distributed discount coupons to theatres and movies for workers and students. He would bring some coupons home and I would queue up to buy tickets at the highly discounted price and then sell them outside the theatres - I became a scalper. It is a wonder that none of the older spivs beat me up. This became our chief source of income. I never took one zloty for myself, or bought myself any food; I was very thoroughly intimidated and scared. One day I had a ticket left for a famous Polish play “Grazyna” which I did not manage to sell, but I did not stay to see the play and rushed home. Mrs Tomaszkiewicz said that *for that* I should have stayed. I made a lot of money for her at the Russian circus where the tickets were very scarce.

The year 1945 just sort of disappeared. Whenever Mrs Tomaszkiewicz was out and I had finished polishing the floors (I was very proud of the lovely parquet floor and the clean new flat) I would read some of the books Mr Tomaszkiewicz kept in a glass-fronted book case. If she caught me reading, she ranted at me about the uselessness of being “learned”.

In 1946, Mr Tomaszkiewicz found a three months course for adults, who had not finished their primary school and enrolled me in it. I was the youngest pupil there. I started a few days late and at my first arithmetic lesson I was totally lost. They were doing fractions, which I had never seen before. The teacher asked me something, the answer to which was to be “numerators multiplied by numerators and denominators multiplied by denominators”. I misunderstood his question and I answered “subtract” instead of “multiply”. Now the word for “subtract” in Polish sounds like a peasant would pronounce “multiply”, ie., (for Polish speakers “bez” instead of “przez”). The teacher made fun of my pronunciation and said that I was in the city now. Another teacher hearing my name, Eulalia, said that he had never heard of anybody with such a name. All I could say was “me neither”, which was absolutely true – it was a very rare and weird name. My blood ran cold – somebody might have realised that I have false papers and therefore was Jewish. I certainly did not tell anyone of my roots. Even after the liberation, I still would not admit to anyone that I was Jewish. After a few weeks, I was top of the class in everything and I was coaching a young woman in maths. There was a young man there, probably three years older then me with whom I competed – at the final exams we were the only ones with perfect scores. After passing this catch-up course I was accepted at the age of 13 into second year of high school.

Walking home one day I thought I saw my aunt Hanka on the street, but was too scared to approach her and I have regretted my cowardice to this day. During the war it could have been death for both of us if we were seen together. Another time, I thought that I saw a friend of Wanda’s on the “Planty” (the ring of greenery around the old town of Krakow) and again I avoided her eyes. It is hard for me to comprehend now just how cowed I was then. When living on false papers and essentially “on the run” one begins to feel that one is a criminal. When one is being hunted down as an “untermensch” under a death sentence, one starts believing in one’s inferiority. It took me some time to get over this feeling of being inferior to everyone else.

Mrs Dziubinski had plucked me out of the Ghetto because she was a true Christian. She went to confession and communion every morning and had a saintly, sad look in her dark eyes. She never thought of the danger; she even wanted to take Gershon, Moishe's younger brother, and other small boys from our courtyard. My parents did not have any money or possessions to give her. Before the war my mother was a spendthrift, she did not accumulate jewellery and gold like some Jews did, which could be sold in times of crisis. She thought of herself as assimilated and not a foreigner in a strange country, who should be ready to flee at any time. My parents spent their money on their standard of living – servants, lovely furniture, best clothes, cafes, best schools and tutors for Wanda etc. As we abandoned the flat and all its contents when we went on holidays to Milanowek, all the household possessions disappeared and thus could not be sold off slowly for food in the Ghetto. My mother's profession saved us – my father's engineering was of not much use and he could not get any employment.

When the war finished, Mrs Dziubinski, quite rightly, stopped paying for me. I was given the choice by the Tomaszkiewiczes of going back to Mrs Dziubinski who would put me into a convent, or so they said, or stay with them. I chose the devil I knew, as I did not want to enter a convent. At that stage I was sort-of Methodist, although I do not remember ever going to their chapel except once to pick up two pairs of second-hand shoes for myself out of a huge pile, which was sent from the American Methodist church as relief. The shoes I chose felt a bit tight, so I dampened them a little and slept with them on – it worked beautifully and they became very comfortable.

At one stage we had a Russian lady officer billeted with us. She had a lovely voice and auntie was teaching her singing. One day she gave me a large piece of black bread; as I was about to put it away in the kitchen, after thanking her profusely, she told me "niet" it was for *me* to eat. She left shortly for Berlin - I think she was with the NKVD. Later she dropped in on us with her chest covered in medals.

I started high school in September 1946. There was great merriment, when I had to state loudly in every class during enrolment, my previous school: "National Course for Adults for Completion of Elementary School". Much later when I was in boarding school in England, I met a girl who had been in my class in this high school in Krakow. She told me that she immediately worked out that I was Jewish because of that funny adult course, especially as I stated my religion as Protestant and did not go to the Catholic scriptures – apparently a dead give-away. I loved high school – I attended it for about two weeks and had two lessons in Latin. I remember declining the word "to wash": *lavo, lavas, lavat, lavamos, lavabis, lavant.?*

At this stage I was not the sole provider (via the theatre coupons) as Mrs

Tomaszkiewich was giving singing lessons and sublet one room to her niece Kristina, who later had a baby.

I was not quite aware of what was going on around me. I had no access to newspapers or radio. Mrs Tomaszkiewicz’s world revolved around singing and yelling at me and her husband. I was busy with housework, (cooking, cleaning, washing and ironing) buying and selling theatre tickets and doing my homework. I was petrified that “auntie” would stop me going to my class or doing my homework, but getting some money for coaching mollified her a little.

This is the way we washed our clothes. We would take the dirty linen into a room in the loft, start a fire with coal, which we brought up from the cellar, fill a big copper with water, put it on the stove with clothes and boil the dirty linen, while stirring with a big wooden paddle. We would wind the clothes around the stick and bit by bit, transfer them into a large wooden tub, adding cold water to cool clothes sufficiently to scrub them with sparingly used cakes of soap on a corrugated-iron washboard. We would finally rinse, blue and starch them, wring them out and hang them out to dry. Things dried well under the roof, even in very cold weather. They froze stiff, but still dried. Then the ironing. I don’t know how I coped with all this at my age, especially as I was very small. Before the war, my mother employed a special woman to do the washing once a month. She was a very hefty lady with huge arms and a prodigious appetite. Then there was a lady coming in to iron. Occasionally a “chemiczka” (lady chemist) would come to do the dry-cleaning.

I used to walk Aza early in the morning in a little park nearby, while memorising the Polish epic *Konrad Walenrod*. It was a lovely park with large oak trees and lilacs, which flowered spectacularly in spring. When we visited Krakow in 1993, we found this park concreted over for cars to park on. One day, Aza started digging under a large tree. I bent over to see what she was doing and found that she had dug up white “mushrooms” with a lovely smell. I took them home and auntie said that they were valuable truffles. I started getting up earlier and earlier to beat others to my find.

Unbeknownst to me, there were frantic searches going on in Poland to find missing relatives among what remained of the Jewish population. My uncle Tadek’s wife, Franka, survived on Aryan papers and got in touch with my cousin Jerzyk (George Bochenek), who was at this stage in London after demobilisation from the Polish Army of General Anders. Franka, who was widowed, as my uncle Tadek died just before the war, had lived with her son Wojtek in the Warsaw Ghetto. One day, when she was at work the Germans came to her place, picked up Wojtek by the legs and smashed his head against the wall, killing him instantly. After that, Franka obtained Aryan papers, left the Ghetto and survived under the name Obranska. She continued living in Poland under this assumed name until her death in the 1980's.

Presumably through Mrs Dziubinski, Jerzyk and Franka got to know about my whereabouts and Mr Tomaszkiewich got to know Jerzyk's address. Mr Tomaszkiewich wrote a long detailed letter to Jerzyk with a bill for thousands of dollars for saving my life. Needless to say, he did not get them, the Bocheneks being quite penniless, but he did receive some money from Joint, a Jewish organization. Now I know why the Tomaszkiewiczes dissuaded me from going back to Czestochowa with Mrs Dziubinski. The letter from Mr Tomaszkiewicz to Jerzyk, dated 30/8/1946 is now in my memorabilia.

ODYSSEY – 1946

One day, aunt Franka came to pick me up. She brought some clothes with her and insisted that I take nothing with me – how I missed my lovely American shoes for years!

Franka took me to Warsaw. On the way, we stopped in Czestochowa where Franka took me to see her stepson, Henio Scheinwechsler. Henio survived on Aryan papers in Bucharest, where he had a narrow escape in the earthquake of 1940. A large roof girder fell on his bed, missing his head by inches. He divorced Lydia and married Lucyna Berland with whom he had a daughter Joanna in 1953. Henio was a lawyer and he remained in Poland to practice his profession. He died of a heart attack in 1955, while Joanna was still a toddler. His wife moved in with her mother. The widow became very ill with cancer and died quite young. Joanna stayed with her grandmother and was brought up without realising that she was Jewish. Jerzyk and Rysia were in touch with her and occasionally helped her financially. We met Joanna in 1979 in Lyon (France) where she was studying. There is a photo taken in front of the Lyon Cathedral, where we met, in album No.11. She appeared to us as a somewhat highly-strung, neurotic girl. She hinted at a boyfriend, but seemed to be very ashamed of him.

On that visit to Czestochowa, I somehow learnt (probably from Mrs Dziubinski) that my father, who was in a labour camp nearby, sent a Polish policeman to ask Mrs Dziubinski for a pair of socks, as his feet were very cold. She duly gave some to that cop and that was the last anyone ever heard about my father. There was a crashing silence about my mother and Wanda and I presume that they were taken straight to Treblinka and their immediate deaths.

I had not been to Warsaw before, but if I had, I would not have recognised it anyway. Streets of rubble and skeletons of buildings with an occasional blanket hanging in the ruins, signifying that someone, somehow, resided there. This notwithstanding, Warsaw was still the capital of Poland and there was an enormous pressure on such accommodation as there was. Aunt Franka had a one (tiny) room flat with the use of a kitchen. Under the narrow bed, which we shared, she had jars of clarified lard, which I discovered when cleaning the place. Franka wanted to throw the stash out – she never learned how to cook! I was horrified at the very thought, I remembered how I had been frying potato pancakes on a smear of fat and how hard that was. I cut up apples into slices, made batter and fried up apple fritters. Franka was delighted, she thought they were wonderful and as her boyfriend was visiting next day, she served them cold for afternoon tea. After a few days in her flat, Franka arranged a place in a Jewish orphanage and I went by train to Zabrze. I was in the orphanage during October-November 1946, while waiting for passage to England to be arranged.

I was back to being Alicja Zalcberg at last. There were about 3 dozen children of all ages there. The younger ones did not remember their real parents, the older remembered only too well. The food, I thought was wonderful – there was as much bread and cocoa as you wanted and I remember regularly gorging myself on 17 pieces of bread washed down with 17 mugs of cocoa. Heaven. There must be something magical about 17 cups of cocoa, because your father remembers drinking the same number in Switzerland after Belsen. Perhaps this represents the capacity of a starving child’s stomach!

There were bad bedbugs and we older girls (oddly, I don’t remember any older boys only tiny tots) would set up pillows and blankets on top of the dining table at night to escape the bloodsuckers, leaving the littlies to their fate. There were rumours of pogroms (the notorious pogrom in Kielce took place at about that time) and we were quite paranoid about the whole town knowing that a lot of Jews were living in that house. One night, we heard a strange noise, like a baby crying and we got very scared. Some bright spark worked out, that somebody dropped a baby on our doorstep and that the Poles would come in and murder us all for kidnapping a baby to kill and make matzos out of its blood, a well-known calumny. I was sceptical about this, but my companions were shaking with fear. We went to wake up Mr Hubel, who was in charge of us and as we neared his door, we realised that the noise was coming from his room! The poor man was one of the most peculiar and noisiest snorers.

We had somebody come to teach us Hebrew – I did not pay much attention, and later English, which I had no aptitude for either. Many years later I found that my best friend Riky Thieben’s mother was a housekeeper in this orphanage and that Riky herself lived there for a while. By a further coincidence, your uncle, Siamo Gottlieb was a director of this orphanage at one stage. It is a small world, what?

In November 1946 a group of us organized by a Rabbi Scheinberg, who got several such groups out of Poland, travelled by train to Gdansk and then on to Sopoty. Jerzyk arranged from London for me to be included.This was the first time that I saw the sea. The Baltic was grey and cold and I was not frightfully impressed. What did impress me no end, was the beautiful hotel they put us in. The bath was huge and filled with hot water very quickly, it was the fastest-running tap I have ever seen before or since. After a couple of days, we boarded a train, which was loaded onto a Swedish boat. The boat was staffed by tall Swedish Red Cross workers, who spoke English as did the stewards. I could not speak a word, although we had a few lessons in Zabrze. At breakfast we were served cornflakes – it was the nicest thing that I ever tasted, or so I thought at the time and I managed to say "more please" the first time I uttered a word in English. We drove through Sweden in great comfort on the train, which was then loaded onto a ship again. This time we had to cross the North Sea. There was a ferocious storm and I was told later that the lifeboats were ready to be launched and the crew were wearing life jackets. I knew nothing of this. All I knew was that my time had come and I was dying. I was sick the entire trip – I swear I was bringing up the lining of my stomach. I begged a steward for some food and finally someone gave me a banana. It was lovely to sick up something solid for a change. When we docked in Tilbury on the 25th of November I could barely stand up. The earth was swaying for several days after we landed and I had to hold on to railings to walk up any steps.

Jerzyk and another cousin, Edzio (Edward or Ed) Sudowicz, were waiting for me at the wharf. Ed had been in the Polish Armoured Division under the command of General Maczek, which was part of Montgomery's British forces in the invasion of Normandy in 1944. It was this division which closed the Falaise pocket and contributed mightily to this famous German rout. A little later, he took part in the liberation of Breda, which opened up the port of Antwerp to the Allies. He certainly got some of our own back! After the War, he established an engineering firm and became a major supplier to NATO. Roger met Ed in the UK.

Jerzyk had been demobilised from the Polish allied army under General Anders. As he had a university degree, he was commissioned as an officer. He had been stationed in Palestine (Rysia had a civilian job in Jerusalem with the Polish Government in exile) and was instructing big, burly Polish soldiers in the use of arms. Jerzyk was a slight, short-sighted, courteous, cultured continental gentleman and all of us who knew him, find the thought of him with a gun in his hands rather incongruous, to say the least. As well as being a weapons' instructor, he was an English/Polish interpreter, a job he took over from Menahem Begin when the latter deserted the Polish army to become a full-time terrorist with the Jewish underground. Begin's wife, Aliza was a relative of your dad's. How is that for the Six Degrees of Separation?

From that moment on the Tilbury wharf, Jerzyk, soon to be joined by Rysia, became my second family and brought me up as their daughter. As you know, they were/are the nearest to your maternal grandparents and wonderful people. To save Rysia's modesty, I will not enlarge.

They took me to Jerzyk's digs in Gunterstone Rd, Baron's Court. I knew that London was the second biggest city in the world at that time and I expected sky scrapers *a la* Manhattan. Alas! Small cottages, nature strips outside – I said "Even in Czestochowa our footpaths were fully paved!" Next morning I went to the bathroom and washed my teeth before breakfast. As Jerzyk was preparing some food, I said to him "and I don't like the taste of English tooth paste either." It turned out that I used his shaving cream!

Jerzyk would take me to the Polish club in South Kensington and leave me there reading in the Polish library while he went to work on his PhD in Chemistry at Imperial College, for which he had an ex-serviceman's scholarship. After a few days of travelling with him on busses, he put me on a bus and told the driver where to drop me off so that I could go home. I got very nervous and could neither remember, nor pronounce "Gunterstone Road". I went to what I thought was the right street to find that all the houses looked much the same and I could not remember the number. I walked around and around quite desperate, till I found myself in front of a block of flats, where I had been before, visiting a friend of Jerzyk's. I found the friend and she took me home.

My 14th birthday came up on December the 4th. I had not celebrated one for the last five years, but I thought that Jerzyk would get me something. I was very disappointed when he presented me with a bunch of violets at breakfast. In the evening he had to go somewhere on business and he took me with him. He surprised me by taking me to the opera. We saw Rigoletto.

Jerzyk started taking me to English lessons after giving up in frustration teaching me himself – I sure don't have a knack for languages! He took me to Bishop's Mansion in Fulham to two lovely, patrician, English ladies, Misses Bracken who were very patient with me but I still did not learn much. The lessons were given to me, free of charge, by these two delightful, upper-middle class spinsters, who epitomised English decency. They once took me to see the Wizard of Oz at the movies, which I did not really follow.

Early in 1947, Rysia arrived from Palestine and Jerzyk rented a lovely,

George (Jerzyk) Bochenek (1907-1989) in the uniform of a lieutenant in the Polish allied army of General Anders in Palestine in 1943-46, Appendix 4.

George Bochenek and Edward Sudowicz in officer's uniforms of the Polish allied army of General Anders in London in 1946.

Kazik Groden (1911 -) with his wife Netka (nee Kleiner), in Tel-Aviv, 1947.

Alice as a teenager in Sydney.

Alice (front row) on board the MS *Derna* on the way to Australia in 1948. The shirtless youth on her left is Abie Goldberg, then Alice's boyfriend, later the fourth richest man in Australia and later still, a fugitive from Australia when his business empire collapsed.

Alice’s and Sev’s wedding photo, March 23, 1953.

Alice as a graduated, but not yet registered pharmacist at the age of 22 in 1954.

centrally heated flat in Notting Hill Gate. It was horribly expensive and they could not afford it for very long. I remember the toilet – it had a beautiful big wooden seat and it was warm. Rysia kept leaving the central heating on when we went out and left the windows open to air. I wanted to turn it off (my war-time years of stoking stoves and scarce fuel made me frugal) “but it is included in the rent” she said. Hah! When we left Jerzyk was presented with a separate bill for the central heating, which was metered.

We moved to Lily Rd, Fulham. The first time I was put on a bus to go home, I asked the conductor for a ticket to Lily Road. “But, where in Lily Road?” asked the conductor, as the bus went along the very long Lily Road. I answered “Lily Road, please”. This exchange was repeated several times. Finally he gave up, gave me the dearest ticket and I got off when I recognised the house. I always knew where to get off, because there was a big sign saying “PIES” nearby and I often wondered how big a dog must have lived there, as “pies” means “a dog” in Polish.

I still did not speak or understand much English. They enrolled me in a secondary modern school for girls in Fulham. It was an awful school. The girls were really rough and made me repeat all sorts of words and then laughed like hyenas. There was one class that fascinated me. I could catch the word “fiance” so I worked out that it must be some sort of a sex education class and I listened very intently, but nothing made much sense. It took me a long time to work out that it was “finance” and I was attending some sort of a commerce class. My English was still very bad.

In desperation the Bocheneks arranged for me to go to a boarding school in the hope of teaching me English by osmosis. Meanwhile, Rysia got a job in Holborn in a JNF (Jewish National Fund) office and I helped her there a couple of times during school holidays. The school was somewhere in Kent near Sevenoaks. The food was abominable and even with my wartime memories, I realised that it was gross. Some days at breakfast time, there was sugar and some days there was none and I learned to drink tea unsweetened. There were mutton stews with hunks of mutton fat and gristle, boiled with onions and potatoes - revolting. The Yorkshire pudding and the dessert puddings were good. This was the beginning of my life-long problem with rapid weight gain. The school building was beautiful – an old mansion with stables, a gatehouse (the music room) and beautifully kept gardens. I decided to go on a health kick. I cut down on the stodge and started walking early in the morning in the gardens.

The school was a pretty awful one – I don’t think it was very expensive. All sorts of misfits of all ages were there – one was a girl of about 17 or more, who was a bit simple and we had terrible trouble trying to teach her to wash herself, as she used to smell, particularly when she menstruated. She used to forego our once-a-week bath. Another girl seemed quite bright, but could not keep still. I think she was somewhat autistic. The headmistress had a harsh, wheezy voice and I never understood a single word she said. She taught us geography.

There were about 4 or 5 of us Polish girls there trying to learn English but instead we stuck together, conversed in Polish and read Polish books. I attended lessons, but I did not understand anything much, except maths and geometry. Oddly enough, history and English were not too bad as we had a very good teacher.

The headmistress was an awful, money-grasping person and she gave a glowing report on my progress at the end of my first two terms. When she learned that I was leaving early in 1948, she made me sit for exams. I got zero in geography, but much to her fury, did quite well in maths, geometry and even in English. She gave me a dreadful report.

I was enrolled into the 3rd year of a Grammar School. Fulham High was considered a good school and that is where I met Rosella Galant who has been a close friend ever since. We were a pair of outstanding athletes: our personal best, was to “swim” in waist-deep water, holding each other under the chin! I took German, English (Julius Caesar), modern history, music, maths, chemistry and physics. I arrived half way through the year and found that all we did in physics was to copy someone else’s prac book from the previous year during class and for homework. As I had no idea what I was copying, could not decipher the handwriting and could not copy the drawings (I still can’t draw) I was always in hot water with the teacher and utterly confused. At the end of the year we were given an exam. Panic! The teacher told us which subject was going to be examined – the electric bell. I read the notes carefully, understood them and got an excellent mark in the nineties! I also did well in the other subjects, except for music. I have no idea what they did in the first two terms, but in that last term, when I was there, all we did was sing “Nymphs and Shepherds come away” and “Under the Linden tree”. At least they sang, I mouthed (I can’t sing either). At the end of the year, you guessed it – exams. I got 1/100 for knowing that Grieg was Norwegian. I was very embarrassed.

Rysia got me to join Habonim, a Zionist youth organisation, and I started going to camps on weekends. I liked the dancing around the camp fires, but did not really have much in common with the English Jews, who were planning on establishing a Jewish state in Palestine. The Blitz was the harshest experience they have ever had.

The Bocheneks decided to migrate to Australia, because Rysia’s cousin

Roma and her husband Richard Krygier had migrated there earlier via Japan. A passage was arranged for me to Australia from Marseilles in mid-August 1948. Prior to leaving London we ran around visiting all the tourist spots, such as the Tower of London, museums and parks which we never got around to seeing when living nearby. Rysia bought me some new shoes and clothes for the trip.

I arrived in France on the 23rd of August and took a train to a Jewish orphanage in an outer suburb of Paris. The orphanage was populated by teenagers, all Holocaust survivors, mainly from Czechoslovakia, but they all appeared to speak Hungarian. My English was not much use and I was not communicating till I discovered that they were not Hungarians but Czechs and therefore understood Polish. There was an older girl in my room, Rutka, who spoke Polish and took me under her wing. I think all of us were waiting for a boat to take us to Australia. On my first evening there, I went for a walk with a boy in the surrounding woods and he kissed me. I had never been kissed before. It was wonderful. My tummy was turning inside out, my mouth was burning and I was in seventh heaven except that I wanted to wash my mouth out with antiseptic (germs!). Rutka tried to calm me down. His name was Otto Schwartz. He spoke about two words of French to my zero, but we managed to catch the Metro to the Eifel tower and sightsee. He bought me a little model of the tower and I bought him a yellow (his choice) tie. That one kiss went to my head and gave me a feeling of power. I decided that I could do better than Otto and ditched him.

I also visited a cousin, Jerzy Imich, his wife Tosia and small son (about nine years old) somewhere in the country where they were vacationing. I stayed overnight and then my cousin took me to Paris, bought me a handbag, gave me 10 American dollars and took me back to the orphanage. The Imichs survived the war on French Aryan papers, were still pretending to be French even after the war and made sure that I spoke to them only in English, not in Polish. Much later, the son was accidentally pushed under a train on the overcrowded Paris Metro and was killed. After that, Jerzyk and Tosia migrated to Canada.

After about a week, we caught a train to Marseilles. It was a long overnight trip. The train was very crowded, uncomfortable and hot. We kept opening the window, but it kept sliding shut. I managed to fall asleep for a while, when a conductor came to our compartment to check our tickets; I passed mine up, fell asleep and never saw that ticket again, much to Mrs Frant’s, who was in charge of us, consternation. I was in trouble. However, we got to Marseilles and embarked on the Derna.

I did not mind the food on the Derna, only the unrelenting heat. I will not describe the details of that trip, Diane Armstrong did this much better in her book. Every afternoon I reserved my spot on the deck, no way would I stay in the hold for more than a few minutes. I felt very free – no housework, no supervision, no school work! I picked up a new boyfriend – Abie Goldberg. At this stage I was quite a snob: I was going to Australia to finish school and go to University to study dentistry and when Abie said that he was going to Melbourne to work in his uncle's factory, I decided to drop him. I was not going to associate with a factory hand. What would my mother think! Forty years later I met Abie again at a reunion of the "Boat People of 1948" at the Maccabean Hall in Sydney. He became a little roly-poly man. He was there with his wife, who said "Ah, you must be Aliska" (Aliska was what they called me on the Derna) so he must have mentioned me to her. I asked him what he did for a living and he said that he was in business. "What business?" "Szmaty business." "Very nice" I said. Some days later, I found an article on Abie Goldberg in *The Bulletin* , I recognized him from the photo, because I had just seen him. It turned out, that he was the 4th richest man in Australia. I must have been the only person at that reunion who did not know who he was! He must have thought that I was taking the mickey or was daft. He is now bankrupt and on the run in Poland. The last I heard, he was making jeans in Katowice.

It was a strange thing, that on the Derna nobody talked about their wartime experiences. I did not have any hang ups about it, it just never occurred to me to discuss these things and others apparently felt the same.

Derna was a ship from hell. Our journey is described by Diane Armstrong, who was a passenger on the Derna as a small child with her parents, in her book *"The Voyage of Their Lives"*. Diane also touched on some of the passengers' wartime experiences, after interviewing them here and in New Zealand.

NEW LIFE – 1948

We arrived in Melbourne on November 5th, 1948 and our guardians, Mr and Mrs Frant arranged for the Sydney passengers to fly on. It was my first flight and I was quite excited. The plane must have been pressurised, but not enough for my tender ears. I had quite a cold and that probably did not help. By the time we landed in Sydney I was in agony and my earache lasted for days. At the airport I was met by Richard Krygier, who was one of the few emigres to own a car, and my cousin Kazik Groden. Kazik put me up in his tiny flat in Coogee, which he shared with his wife Netka and son Ilan, who was about 8 years old then. I shared a bunk with Ilan for one or two nights.

The Jewish Welfare arranged for me to stay with a Mr and Mrs E. and their 12-year old daughter in a lovely house in Bellevue Hill. On the weekend, they took me on a motor cruiser on the harbour. I kept boasting how I never felt seasick on the Derna, only to become very sick on this little boat. The E's were well-established Australian Jews, who kept up traditions by holding a full-blown Sabbath dinner on Friday nights. They thought that, as I came from "the Old Country", I would be *au fait* with all the religious stuff, give them tips on how to pray and have a Jewish influence on their young daughter. They were relatively simple people, who could not understand why at the age of nearly 16, I would want to go to school, instead of going to work and being a companion for their daughter. I was a big disappointment.

I got new patrons. Mr and Mrs N. owned a large photographic studio and worked very hard. They had a slightly retarded 10-year old daughter, who went to boarding school and a housekeeper to do the cooking etc. During the school vacations, the daughter was home and they needed somebody to walk her to the beach and entertain her. The house was in Dover Heights with a sheer drop down the cliff at the end of the backyard. As you neared the tall wire-mesh fence, the wind would hit you and take your breath away. We would walk to Bondi beach every day and I started acquiring my first Australian tan.

The NSW Education Department decreed that I could start in a Domestic Science school in 4th year, or I could go to Sydney High in 2nd year, as I could not catch up on four years of French, which was then compulsory in high schools. I enrolled in Dover Heights Domestic Science, much to the disgust of my patrons who wanted me to work for them in the studio and look after their daughter on weekends. The Domestic Science School was a bit of a disappointment. My favourite subjects were maths, physics and chemistry, the last two interesting me the most, although I had done only one term of them in London. Here I had to do history, geography, general maths, English and domestic science. In Dover Heights I met Anna Turek, later Anna Haber, who became my close friend. We walked home from school every day and I learned a bit of her life in Poland and Russia during the war. Her mother died in Khazakhstan and Anna looked after her baby brother, Joey. After the war she was reunited with her father and was now living with him, his second wife Christina and Joey in Dover Heights. We were in the same class and were equally talented athletes. Every gym session, we were supposed to jump over a wooden horse; we would take a run and chicken out in the last second. The teacher yelled at us, but to no avail: we were utterly useless.

Jerzyk and Rysia arrived in Sydney on the MS Eridan in February 1949 and eventually found a house to rent at 23 Morrice St, Lane Cove, which was then considered "the sticks". After 2 weeks of Dover Heights Domestic Science school, I reunited with them and transferred to Willoughby Domestic Science school. Shortly after starting there, I was asked to contribute to the school magazine. I wrote a potted biography, a copy of which is included here, spelling mistakes and all. It gives some insight on how I felt then. I went to a lot of trouble to avoid place names. It was just an adolescent literary conceit, but at the time I thought it was sophisticated!

In my class was an English girl, Ann Torrie, who had as much love for sports and gym as I did. As we were the only two girls to take both maths and domestic science (cooking), we concocted a terrific ploy: if we never turned up to gym, the gym teacher would never know that we existed. If anybody would question us, we would say that we thought it was our library period. We got away with it! In two years of school, the gym teacher never discovered us. I must have felt insecure and unsure of myself. I was getting very good marks in all subjects, but I was convinced that the teachers felt sorry for me and made big allowances for my poor English and that I would never pass the Leaving Certificate exam, which was totally external.

I joined a Jewish Zionist and Socialist organisation, Poale Zion, went to meetings on Sundays and camps during summer. This was not for any ideology, just for social contact.

Some time around January 1949, I must have met your father at a picnic at Waterfall, the occasion being memorable because a girl twisted her ankle and the boys, including your father, had to carry her out. Neither of us remembered seeing each other there, but later, we worked it out. We would run into each other at Poale Zion camps, where the Polish-speakers would tend to stick together. There was a bit of necking. Dad, Manny Mansberg and I became firm friends. Manny and Dad, believe it or not, went to the same school before the war to be reunited in Sydney after all those years.

I did not make friends at Willoughby. I was the first girl there with a foreign name and a foreign accent. I felt a little like an outsider. When I wanted to whinge about school, home, and later about work, I would ring Sever who provided a good substitute for a girlfriend. We would go to pictures together each paying our own way. What I resented, though, was walking a long distance (say from Wynyard to Central) to save a few pennies on tram fares. Dad did not wear high heels like I did! Dad taught me to swim at Redleaf pool. I could only swim about 3 meters when we started.

Later, when I went to the Uni, Dad used to demonstrate to me in First Year practical Chemistry, as he was then in his Honours year. I spent some of my lunch-time watching him play bridge with Henry Bauer, Frank Eastwood, Alex Diamantis and company. One lunch hour I visited him in the lab. He was then in the habit of using his ethanol wash-bottle to bring a flame from his bunsen burner on the wooden floor where he could surround himself with a half metre wall of flame as he was sitting on his lab stool. I was sitting on his lap while this was going on and who should walk in but his MSc supervisor, Prof. Arthur J.Birch, FRS. Birch did not know where to look, looked embarrassed and next day asked Sev's lab mate, Frank Donovan: "Is Sternhell married?" "No" "Then who was that woman on his lap?" When I topped the year in the half-yearly physical chemistry exam, Sev was very proud of his "girlfriend".

When Jerzyk and Rysia used to go away to the Blue Mountains for the weekend, I would throw parties, including one memorable drunken New Year's Eve occasion. In October 1951, I went to the Blue Mountains with Jerzyk and Rysia and Sever was there with his parents. We all stayed at Lilianfels, which was then very cheap and run by a Polish woman who served Polish food. After breakfast, Sever took me for a long walk to Mt Solitary. He was very worried because he could not find any water there and we did not carry any, but we managed to complete the walk without any trouble and Sever was very proud of me. We were still "good kissing friends", but not dedicated to each other. Some time later, when the Bocheneks were away, I gave another party and after a few drinks Sev started kissing me and could not stop, declaring that something had happened to him and that he wished to spend the rest of his life with me. Thus I became his exclusive girlfriend – it was still all perfectly chaste, as was usual in those days. We took it for granted, that one day after I passed the final and got my registration, we would marry. The Bocheneks and the Sternhells knew each other quite well, but Sever's parents were unaware of our deep involvement, Sever's policy being, like the CIA's , that you tell people on the "need to know basis" only.

I obtained my Leaving Certificate (later the HSC) at the end of 1950. Jewish Welfare were unwilling to lend me money for university fees to study Dentistry, which was a 4 year course and quite expensive. Pharmacy was only 3 years: 3 years apprenticeship, of which only 2 years were at the University of Sydney part-time. The apprenticeship wages were a pittance, out of which I not only had to provide fares and uniforms, but the university fees. Otherwise, Jerzyk and Rysia supported me fully.

Sometime late in October 1951, Peter Ryba arrived from the UK. His relatives in Sydney, the Fersters, were close friends and employers of Rysia and Rysia kept telling me "Ryba plywa" (fish is swimming) while he was on his way. I introduced him to my mob and Manny became his close friend. Manny, in turn, introduced him to his future wife Edith and was their best man at their eventual wedding. These people, together with Richard Haber, Anna Turek (later Mrs Haber), Walter Langsam, his future wife Clara, Elizabeth Hertzig (later Mrs Symmonds), Janeczka Schneider (later Manny's

**The three (dis)graces.
From top down: Alice, Anna Turek (later Haber) and Elzunia (Elizabeth Hertzig, later Mrs Symonds) on a bushwalk in 1950.**

Alice on board P & O *Strathaird* anchored at Gibraltar on the way to UK on October 1958. She is pregnant with Peter, but unaware of this.

The "Polish Mob" celebrating the Habers' 10th wedding anniversary at La Taverne in Sydney, December 1965. From right to left: Peter Ryba, Edith Ryba, Walter Langsam, Clara Langsam, Janeczka Mansberg, Manny Mansberg, Alice Sternhell, Sev Sternhell and half of Anna Haber's cousin Rachel. The guests of honour (the Habers) are cut off!

**Richard and Anna Haber
ca. 1978.**

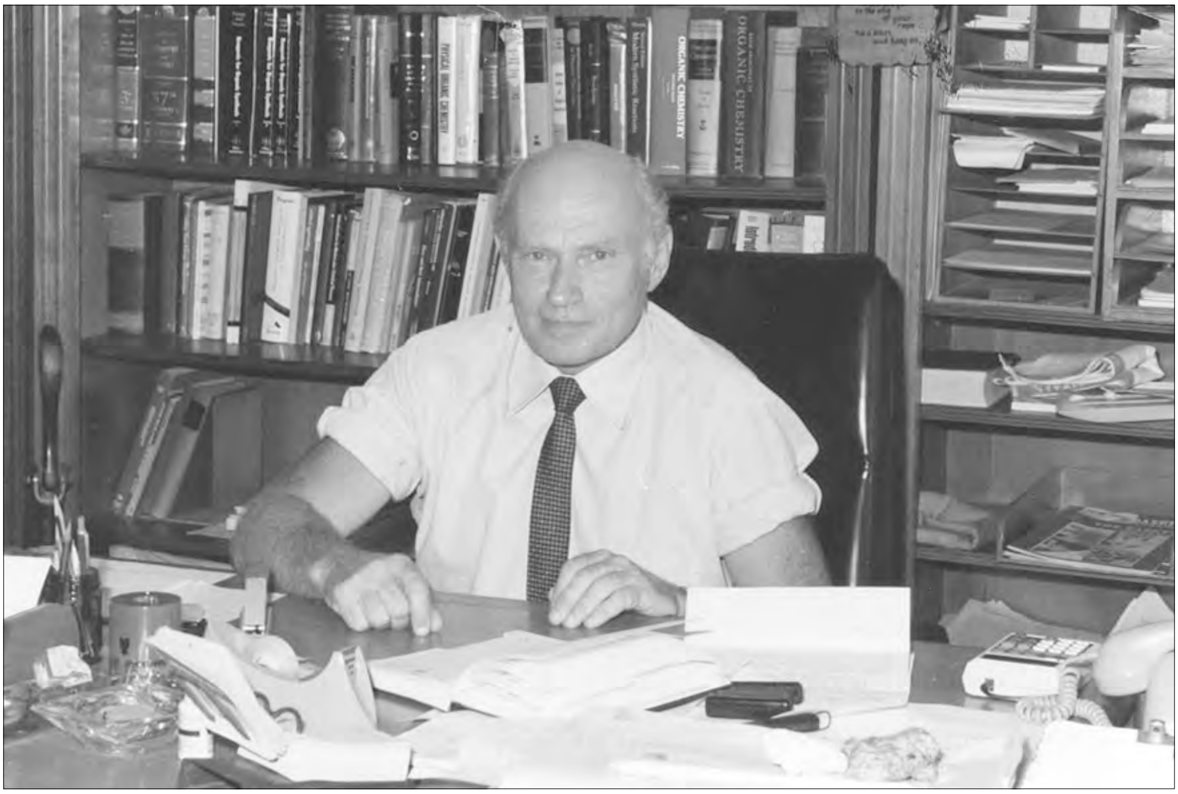
Cheryl, Sev and Alice with James, Roger and Peter in front of the house at No. 41 Findlay Ave., Roseville where they lived from 1964 to 1986. They are on their way to the wedding of Vivian Sternhell and Greg Zeltzer in 1968.

Heide Vossmerbaumer, the children’s early nanny, with Roger in 1965.

Maria Sternhell with Peter, James and Roger in the flat at 10 Beaverbrook Flats, 29 Nelson St., Woollahra where she lived from 1948 till 1973. Photo taken in 1972.

Rosella Rosenberg nee Galant, Alice's oldest friend since 1946. Photo taken in London in 1979.

Henryka Bochenek nee Rones, "Auntie Rysia", in the volunteers' uniform at the Olympic Games in 2000 (Appemdix 10).



Sev Sternhell, BSc(Hons), MSc (Syd.), PhD, DIC, DSc (London), FRACI, FAA in the office he occupied from 1977 to 1998, as Professor of Organic Chemistry and Head of Department of Organic Chemistry, University of Sydney. Photo taken in 1981.

Sev Sternhell, on top of Kala Patar (18,600ft) above the Everest base camp with Everest and Nuptse in the background. Photo taken in January 1983 during the first of his 13 treks in the Himalayas.

wife) and Louie Ferster, formed the nucleus of the “Polish crowd” when we were all young and we saw a lot of them.

One Saturday night in February 1953, we were invited to a party at Richard Haber’s place. His parents lived in Chatswood. Sever by that time owned a beat-up 1946 MAC 350cc Velocette, the first of a long line of motorbikes, so he was going to pick me up in Lave Cove to take me to the party. I had a new black faille, tight-fitting dress and I did not want to sit down so as not to crease it before Sev saw it. I waited and waited. Eventually he rang me up “Mopy, I am in hospital under observation”. What happened was that he was in the middle of overtaking a car on the Pacific Highway, when it swung out and pushed him onto a silent cop. He executed a spectacular somersault, bike and all, over the double yellow line. Dad was fine – no concussion, lack of a helmet notwithstanding (helmets were not compulsory in those days). The motorbike was in pieces and we could not go anywhere on the following Sunday, so I went for lunch at his place in Woollahra. After lunch, we went for a walk in Centennial Park and Sev turned to me and said: “Why do we have to wait for you to graduate before getting married? Why can’t we do it now?” We mulled over our finances for a week or so and decided that, if we got a really cheap room close to where I was apprenticed in Arncliffe (no fares), we could make it on his $24 per week scholarship and my $6 per week wage (it went up from $3 in first year!). Now, how to tell our families without anyone being offended that they were not told first? We decided that as soon as I got home, I was to ring him and tell him that I was ready to spill the beans to my cousins. When I got home from work, Rysia asked me “What is wrong? Sever keeps ringing up to see if you arrived home yet”. I shrugged, rang Sever who told me crossly “Hurry up, we are going out to dinner and I can’t keep stalling”. I said “OK” and hung up, turned to Rysia and announced “We are engaged and the wedding is next month.” I had a pretty mean “master” and I did not trust him to give me any extra holidays so we decided that the only slot for our wedding was at Easter. We gave the family only a month to prepare. My cousins were delighted, but horrified at the “next month”. Your grandmother was delighted and flooded the restaurant, that they went to that night, with tears of happiness. Your grandfather was also delighted. There was one thing about our intended union we did not like: everyone approved.

Before arranging the marriage, I had to get permission from the Child Welfare Department, as I was an orphan and only 20 years old. The age of consent was then 21. We wanted a simple wedding in a registry Office, but Sev’s father reminded us that it was illegal for Jews and Quakers to marry outside their church. This was a privilege granted by, I think, Henry the VIIIth and it was never repealed in Australia. So a Rabbi it was. “If you have a Rabbi, you may as well have it in a synagogue" "OK". Sever's mother went with me to buy a dress for the occasion. There was a nice ballerina length dress in blue "you may as well have it in white" "OK" "If we have a white dress, you may as well have a white veil" "OK". We borrowed a veil from Anulka Muscat who had been married the previous year.

We got married on the 23d of March, 1953 on a very hot and humid day. Jerzyk drove me to a synagogue in Bondi Junction, which is no more, in his Austin A40 with the windows closed, so my veil would not fly everywhere. I thought I would die of overheating and suffocation. As Jerzyk walked me down the aisle, I saw Manny Mansberg, who was our best man in a black borrowed hat, which was much too big and rested on his ears. My mouth started curling and as I was about to burst out laughing, I bit my lip, and looked down at my feet in case I caught someone's eye. I was told later that I looked very demure walking down the aisle.

To this day, your father claims, that one minute he saw a double yellow line upside down as he somersaulted over it and the next thing, he found himself in front of a bearded gentleman speaking Hebrew at him and Alice, who was wearing funny clothes.

We went on our honeymoon to Forster for 6 days. With the cash given to us among our wedding presents, dad bought a new motorbike, a Matchless 500cc single. We had about $80 between us in the bank. We managed to get a room in Arncliffe with an outside dunny without a light and inhabited by red-back spiders. At night we would light some newspapers and burn the creatures off the seat. Eventually dad installed an electric light in the dunny. The rent was $2.40 per week and the landlady, a Mrs Bridges, was a very nice old duck. The mattress was a dreadful, sagging old thing and dad, being bigger, used to roll over on my side and I would finish on the floor; when I eventually told Mrs Bridges, she said "why didn't you tell me earlier?" and bought us a new one. We lived in Arncliffe for about 4 years.

The best wedding present was my Commonwealth Scholarship, which came through for my last year at the Uni. Up till then, I had to pay my own fees out of my $3 a week salary in the second year of apprenticeship and first year Uni. The Jewish Welfare lent me the money and I had to pay it off monthly. One had to be in Australia for 5 years before being eligible for a scholarship. Those were the days before the pill and before every exam, I had the double worry – I will fail the exam and I am pregnant. The more nervous I got, the later my periods were. I sailed through the Uni without much trouble. The Pharmacy Board exams were a different story. They were held every 6 months and to keep the numbers down, they slaughtered us. I finally got through on my third try in February 1955.

I graduated on February 23, 1955 a day before I became naturalised. I had not bothered getting naturalised earlier, as it was quite expensive, but now as an Australian Citizen’s wife, it only cost me $10. It was a very simple ceremony in the Rockdale Town Hall, presided over by the mayor. It was a very happy time for us because we were also elated at my passing the Pharmacy Board finals. I was presented with a bible, which is on our book shelf. Your father’s earlier naturalization was more dramatic: in 1951 he was in his Honours year at the Sydney University when he was awarded an ICI (Imperial Chemical Industries, then a huge multinational) scholarship, which would take him to postgraduate studies. It was at a generous $24 per week, but to the consternation of ICI, it transpired that Australian Citizenship was a condition of the award! The Chairman of ICI (Sir David Rivett, once the Chairman of CSIRO and a big fish all around) interviewed your dad in person, red tape was cut to shreds and he was presented with his naturalisation certificate, signed by Harold Holt, then the minister for Immigration in the Menzies government, later a drowned Prime Minister of Australia.

Once my apprenticeship ended, I was free to work as an unregistered pharmacist anywhere I pleased. I had several jobs – one with Dick Diamond in Liverpool Street. When my “Rego” came through, I had several locum jobs all over Sydney, until I settled down on $40 a week at Glacerium Pharmacy in Railway Square, where I remained for about two and a half years. Believe it or not, we were always saving money by going without. We borrowed a few hundred dollars from my old boss in Arncliffe (which we paid off very quickly) and that was enough for a deposit on a house at 2 Dorritt St, Lane Cove. Bank loans were just about impossible to get and we obtained a private loan through a solicitor at an “outrageous” 4% interest.

Shortly after our marriage dad took a job in a plastics factory Beetle-Elliott (later Monsanto) and after more than two years and shortly before we moved to Lane Cove, he switched to CSIRO. In 1958 he won a CSIRO overseas scholarship to do a PhD at London’s Imperial College.

I did not know it at the time, but I was about 2 weeks pregnant with Peter when we boarded the P&O Strathaird in August 1958. I was morning sick very soon after the boat sailed, but on our arrival in London an English doctor insisted that I was not pregnant, merely sea-sick and I missed my periods because I changed hemispheres! Peter was born in Honeypot Lane Maternity Hospital, which later became a psychiatric establishment – very fitting. I had a very good job in a Bayswater pharmacy, where I worked till a week before Peter’s birth. One year later, I gave birth to James in University College Hospital, St Pancreas, well within the sound of Bow Bells, which makes James a cockney according to that definition. James was planned to arrive on Peter’s birthday and was only six days late!

We shared a very large flat at 4 Douglas Mansions, Quex Rd., West Hampstead with Norma and Alex Diamantis and their baby son Marko. The flat was furnished and Sir Derek Barton FRS, Sev's supervisor, lent a baby cot for Peter. This was the cot in which Sir Derek had slept in HIMSELF – did anything rub off? Where is your Nobel Prize, Peter? The flat became a rallying spot for our fellow Australian ex-pats at various universities in UK and for new arrivals, like Rosie (later to become Noel McAskill's wife). Christmas dinner 1958 was a memorable occasion of that sort, but much marred for us by the news that Sev's father was diagnosed with a brain tumour. Your grandfather died on March 22, 1959 shortly before his first grandson was born. There are some wonderful letters from your grandfather in our memorabilia. Your grandmother claimed that he never knew about the seriousness of his condition, as he was never told the truth at her request. However, dad and I think that he knew all the time and pretended ignorance for hers, and our benefit. His later letters were typed on his typewriter by his ex-secretary, who did a wonderful job of including his own favourite misspellings and had us wondering as to how he was managing to type in his condition. I was extremely fond of my father in law and at the risk of sounding conceited, I think that the feeling was mutual. I missed him for a very long time. Personally I disagree with the idea of withholding information from a patient, especially a very highly intelligent one. Your grandmother's life during those few months revolved around keeping the secret and keeping visitors away from him, so they would not see how "poorly" he looked. It gave her a purpose. When grandpa died, some people were quite shocked, as they never realised how grievously ill he was.

We returned to Australia in December 1960 on the P&O liner "Himalaya" with Peter at 18 months and James at 6 months and the A35 Austin van in the hold. In Australia we had windows cut in it, so that it became a station wagon, it was the only car we ever bought new.

Now that you are all fathers, you will appreciate the following. Disposable nappies were just coming in, but were still prohibitively expensive. In London we had a nappy service and we owned a large number of best quality terry-towelling nappies with identification labels sewn into each one. We found out that they had a daily nappy service on board the Himalaya, so we ordered it. We had an unlimited supply of freshly squeezed oranges and Peter could not get enough of them. He also enjoyed all the food supplied. As he was a very prodigious eater at that stage, he developed spectacular diarrhoea. We just kept putting the dirty nappies into the bucket provided. In the morning, we left the bucket outside the cabin for collection. No collection over the weekend! By the time it was Monday on the notorious Bay of Biscay and I was feeling a bit queasy, it turned out that the nappies had to be first rinsed by us. I took one look at the contents of the buckets and said : “Throw this lot out and let us get the disposables from the ship’s store”. Dad was made of sterner stuff! He went to the gents and one by one, rinsed each shitty nappy. He received some very funny looks from other men using the loo. The man is a saint!

We moved into our house in Lane Cove, which had been leased in our absence to an Indian diplomat. It was a tiny bungalow of less than 8 squares and we were squashed in it. Dad went back to work in CSIRO Coal Research in Delhi Rd. The working bug bit him (he had been inspired by Sir Derek Barton at Imperial College) and he worked till late at night and on weekends. As I could not drive and had no car anyway, I stayed home. Dad did the heavy shopping. Later, when Peter became potty-trained and started kindergarten in 1962, I pushed James in a very beaten-up second-hand stroller and walked to the kindy in Burns Bay Rd. Most of the time, Peter demanded the stroller and I would carry James while pushing Peter in the collapsing stroller (Peter was not the lightest of toddlers). Kindergarten was for those over 3 years old, who were well potty-trained and started at one day a week, progressing in 2 years to 3 days of 5 to 6 hours.

Some time in 1962 I got a learner’s permit. By and by, I received my driving licence. I was by then working odd half-days doing locums all over Sydney while the baby sitter, Carol, looked after the two of you. I drove dad to work at 8.30 am first, then went to work keeping the car. I used to pick dad up at CSIRO, take him home for dinner and then he would drive himself back to work, where he stayed till all hours of the night. Your baby sitter was then Carol de Chatebourg, a very glamorous looking blonde with a gorgeous sports car. I started sending her in her sexy car to pick up dad at Coal Research to be ogled by his fellow scientists. Dad would introduce Carol as his second wife. Small pleasures……

We did not have a washing machine, I washed everything by hand and dried the washing on a Hills hoist. Early in 1964, uncle Arthur picked up an old washing machine which used to belong to a famous artist, Judy Cassab, at an auction. We installed it in the outside laundry, next to the copper. The damn thing used to “walk” when turned on. I remember dad sitting on it during the spin cycle to steady it and soapy foam squeezing between his legs.

Eventually we tied it down with Army belts from a disposal store.

Left to right: Sally Wolf nee Weiler (?-1966), Alice, Alex Modlinger, Stella Modlinger nee Wolf and Jackie Modlinger (Appendix 6). Photo taken in London in 1958.

1968 wedding photo of Vivian Sternhell and Greg Zeltzer (Appendix 7).

Left to right:
Hannie Groden,
Richard Groden,
and Alice,
Cape Kennedy,
Florida 1969
(Appendix 4).

Left to right: David Groden, Virginia Groden and Iris Groden, Cape Kennedy, Florida 1969 (Appendix 4).

Left to right: Ami Scharf, Jadzia Scharf and Izio Scharf in Tel Aviv in 1969. Izio Scharf is related to Alice via Wolf Scheinwechsler (Appendix 4 and Chapter "Your Mother's Story").

Rysia Bochenek, George Bochenek and Jane Bochenek in 1969 (Appendix 4).

Irwin and Susan Walker with their sons Matthew and Timothy at West Head, on a visit to Sydney in 1981 (Appendix 5).

Left to right: Gencia Gottlieb, Siamo Gottlieb and Maria Sternhell nee Wachs, at Maria's 79th birthday party, Sydney 1983. (Appendix 7 and 8).

Katrina Jankelowitz nee Zelter and Chad Jankelowitz in 1999 (Appendix 7).

Siamo (Sasha, Smex) Gottlieb and Eva Gottlieb nee Fraenkel in 1997 at Roger's and Lindy's wedding

Left to right: George Celler, Cassie Celler, Lynnie Celler nee Heyman and Mark Celler in 1999 (Appendix 9).

In 1964 your dad applied for, and obtained, a Senior Lectureship in Organic Chemistry at Sydney University. At that time, the birth of what turned out to be Roger, was planned for mid-September and by taking judicious doses of the pill, he was indeed born on September 16, 1964 at the Mater Miseracordia Hospital. While I was pregnant, we bought a 5 bedroom house at 41 Findlay Av. Roseville, where we lived for the next 22 years. I realized quickly that I would go mad staying at home for 24 hours a day, 7 days a week. We also needed more income to pay off the mortgage on the house. When Roger was 3 months old, I employed a live-in nanny (Heide Vossmerbaumer) and went to work full time at Sheldon's Pharmacy at Crow's Nest – I worked there till we went to America in 1968. I also moonlighted, some evenings and weekends at Spicer's Pharmacy at Lane Cove. Pharmacists were well paid in those days and my salary paid for the nanny and the house repayments.

After Heide got married and left to have kids of her own, we employed Cheryl, a very loving orphaned 17 year old. She stayed with us until she married Bob Stewart and started her own family. After Cheryl left and dad and I went on his first Sabbatical to USA in 1968, Heide, her husband, Peter Vucelic, and baby son Kirk, moved into our place to look after the three of you. After coming back from the USA, I worked only part-time and after hours, when you kids were at school. At the risk of being maudlin, I will say that you three boys made my life worth while. At last I had something to be truly proud of and also to cherish. At the same time, I suddenly had so much more to lose. The fear that something terrible could happen to any of you sends icicles through my soul. All in all, looking at other peoples' children, you lot were very easy to bring up and great successes, each in your own way. I am very proud of you and of all that you have achieved.

I know it is not the done thing to talk about one's health, but this is where the third gift comes in.

THE THIRD GIFT – 1977

In February 1977, just after the 5 of us came back from a holiday at Nambucca Heads with Manny and Janka Mansberg and their boys Robert and Victor, I found a lump in my groin, showed it to dad, who said "show it to Dick". I did. Richard ordered the lump removed and a biopsy showed "Diffuse, well-differentiated lymphocytic lymphoma", or, in short, a non-Hodgkin's lymphoma. I put in the exact medical description in case any of your descendants become haematologists. Dad hot-footed to the Fisher library, the Internet not having been invented yet and worked out that I had about a 5% chance of survival for 5 years. The lymphatic system, with its hundreds of glands is scattered throughout the body, mostly well buried in the body and by the time a lump shows, the body is riddled with cancer. My lymphoma appeared to be localised in the one gland. A few months after a course of radiation I was declared to be completely free of disease. So I had another brush with death and was given a third gift of life.

This event shook both of us out of our complacency. We had become relaxed about life, our main concern was about you boys not coming to any harm. My focus changed and I became a little more selfish and self-centred. I joined a gym and would not go to the library to return a book, or pay some bill, at the cost of missing a gym class. A brush with cancer is a unique experience and very sobering.

The next 25 years passed extremely happily and serenely. Dad still worked very hard, but took time off for a lot of trips. We went to England, Western Europe, Scandinavia, Portugal, Spain, Greece, Eastern Europe, Turkey, China, Central & Northern Australia, Corsica, Sicily and the Greek Islands. One by one, you all graduated. Slowly I realised that I was no longer responsible for you. That lifting of responsibility off one's shoulders is a wonderful experience – you have something to look forward to, albeit it will be a long time in the future. I still worry about the three of you, but I am no longer responsible for your actions and everything is not my fault, though according to tradition, a Jewish mother is guilty of everything (see Philip Roths' *"Portnoy's Complaint"*).

It is interesting how one can come across lost relatives: in 1989, I had a letter from Izio Scharf, which contained a big surprise. There was an addition to it by another cousin, Dadek Scheinwechsler, who had changed his name to Zev Skorkowski. His son's-in-law brother with his wife visited us in Sydney and Peter and James met them at our place – Roger was away at the time. See fifth-last page of photo album No.20. Dadek's great-great-grandfather was one of the 22 Scheinwechsler siblings of my great-great-grandfather Wolf (Wilhelm) Scheinwechsler. Dadek saved himself during the war on Aryan papers and was active in the Polish underground; after the war he migrated to Israel and, later, to Brasil where he died in October 1992. A cousin found, a cousin lost!

We achieved relative financial security. I worked gradually shorter and shorter hours, which have lately degenerated into about 6 hours a week. We no longer have to save for a rainy day or for later – **it is later**. Eventually all three of you got married and started families of your own. What a wonderful and "normal" life! Just like everybody else in a "normal" world! Children, mothers, fathers, grandparents and cousins, totally at home in this wonderful country. I have a wonderful husband, who is my father, mother, brother, sister, best friend and father confessor, who understands me completely and only too well. How many wives can say that about their husbands? We still laugh at each other's jokes and witticisms, which I think is a perfectly valid criterion for a happy marriage. Some of you probably wish that we did not encourage each other in these endeavours. Life is good. I am very grateful for my **three gifts**, and my three sons, who after all are gifts too, as are my 7 grandchildren. I just wish I could slow down the passage of time, which seems to be passing at a breakneck speed. Slow down time please – I like it **now**. Don't move so fast!

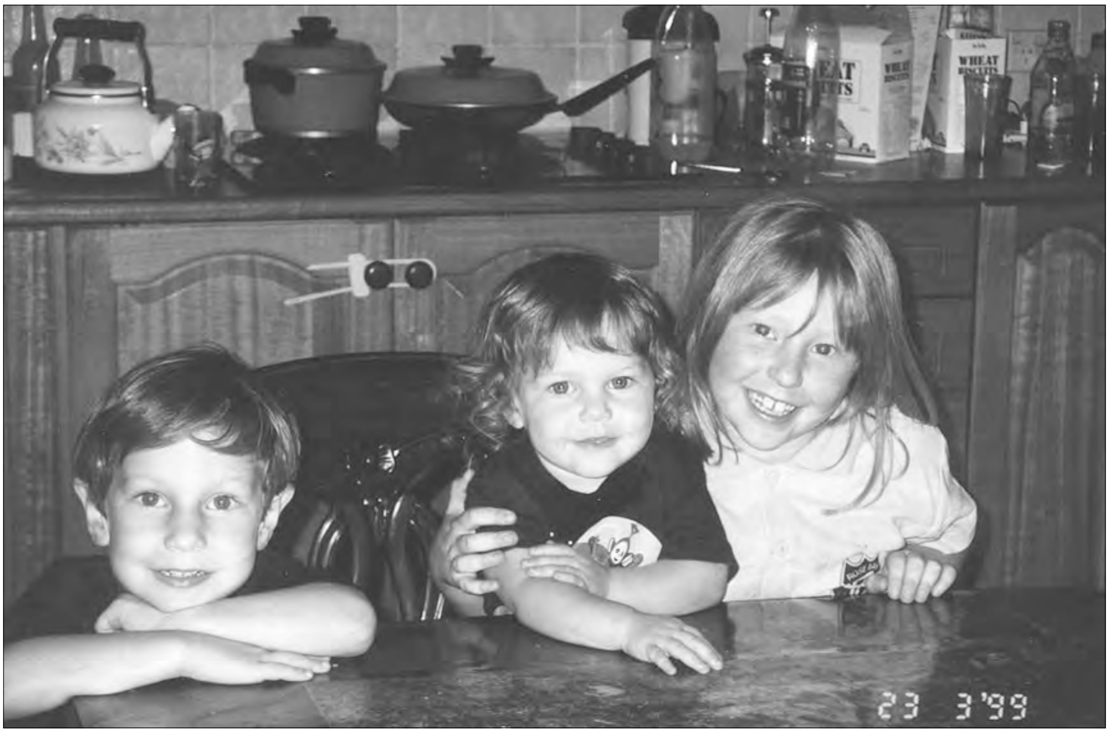
The University of Sydney family.
Left to right: James (BDS, 1985), Roger (BAgrEC Hons, 1988), Peter (MB.BS Hons, 1982), Alice (PhC, 1954) and Sever (BSc.Hons, 1952, MSc, 1953) at Roger's graduation in 1988. Sever is wearing a Sydney DSc parrot suit, which is near enough to the London DSc parrot suit he should be wearing.

Left to right: The Sternhell men, Sever, Roger, James and Peter at James' wedding in 1989 (Appendix 11).

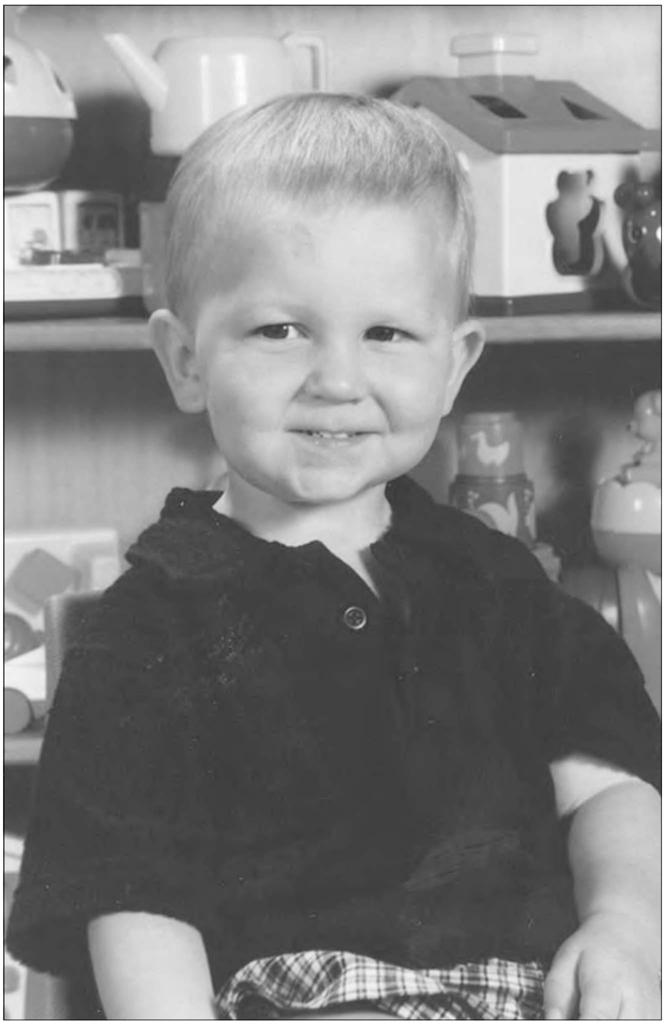
James Frank Sternhell marries Beverley Jane Joffe on 30/4/1989 (Appendix 11).

Roger Mark Sternhell marries Lindy Johnson on 27/12/1997 (Appendix 11).

Peter Samson Sternhell marries Jennie Kathryn Pry on 23/9/1990 (Appendix 11).



Jimmy's and Beverley's children. Left to right: Robert Samuel (b.12/1/1995), Leanne Rachel (b.23/7/1997) and Elizabeth Maria (b.30/8/1991) (Appendix 11).



Samson Andrew Sternhell, b.15/4/1998 (Appendix 11).

Lucy Georgia Sternhell, b.1/7/1998 (Appendix 11).

Molly Rose Sternhell, b.15/5/2000 (Appendix 11).

Leo Andrew Sternhell, half an hour after his birth on 6/12/2001 (Appendix 11).

MISCELLANEOUS DOCUMENTS

Зауваження до заповнення картки

1. Картку заповнює класний керівник.
2. Наприкінці кожної чверті класний керівник видає картку успішності учневі, учень повертає її класному керівникові з підписом батьків у перший день наступної чверті навчального року. Картка зберігається в школі.
3. Успішність відмічається відмітками: відмінно, добре, посередньо, погано, дуже погано.
4. В кінці навчального року картка з відповідним записом та за підписом директора школи видається учневі.

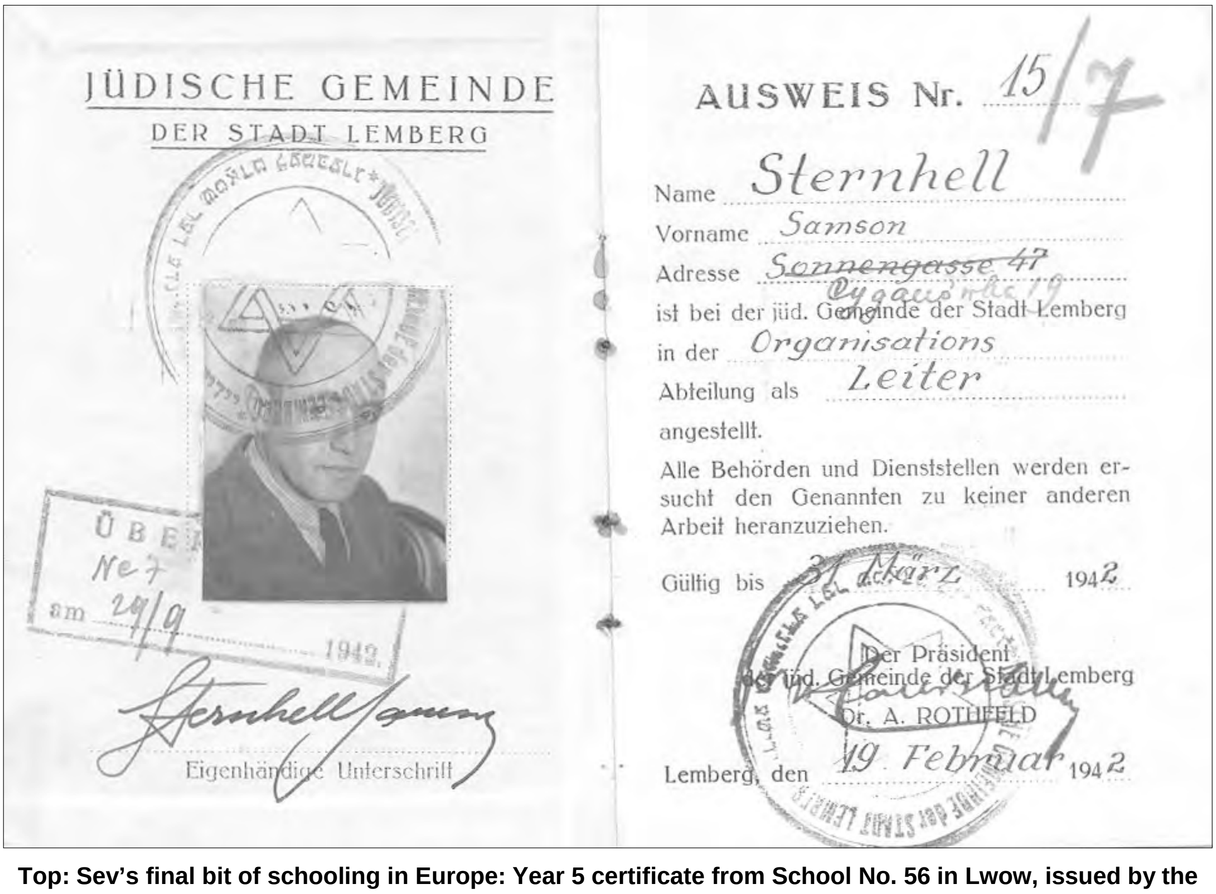
БМ 16445. Друк. в-ва „Пр. Пр.", зам. № 2119 - 4 млн.

Народний Комісаріат Освіти УРСР

КАРТКА
про успішність, поведінку
та відвідування

учня piąta c класу за 1940—41 навч. рік
учениці Sternhell
(Прізвище учня)
Seweryn Samsonowicz
(Ім'я та по батькові)
Niepełna Średnia школи
(Початкова, неповна середня, середня)
№ 56
місто, село Lwów
район Czerwonoarmiejski
область Lwowska

Учень повертає картку у перший день наступної чверті навчального року



JÜDISCHE GEMEINDE
DER STADT LEMBERG

ÜBE
Nr 7
am 29/9 1942.

Sternhell Samson
Eigenhändige Unterschrift

AUSWEIS Nr. 15/7

Name Sternhell
Vorname Samson
Adresse ~~Sonnengasse 47~~
Cygańska 19
ist bei der jüd. Gemeinde der Stadt Lemberg
in der Organisations
Abteilung als Leiter
angestellt.

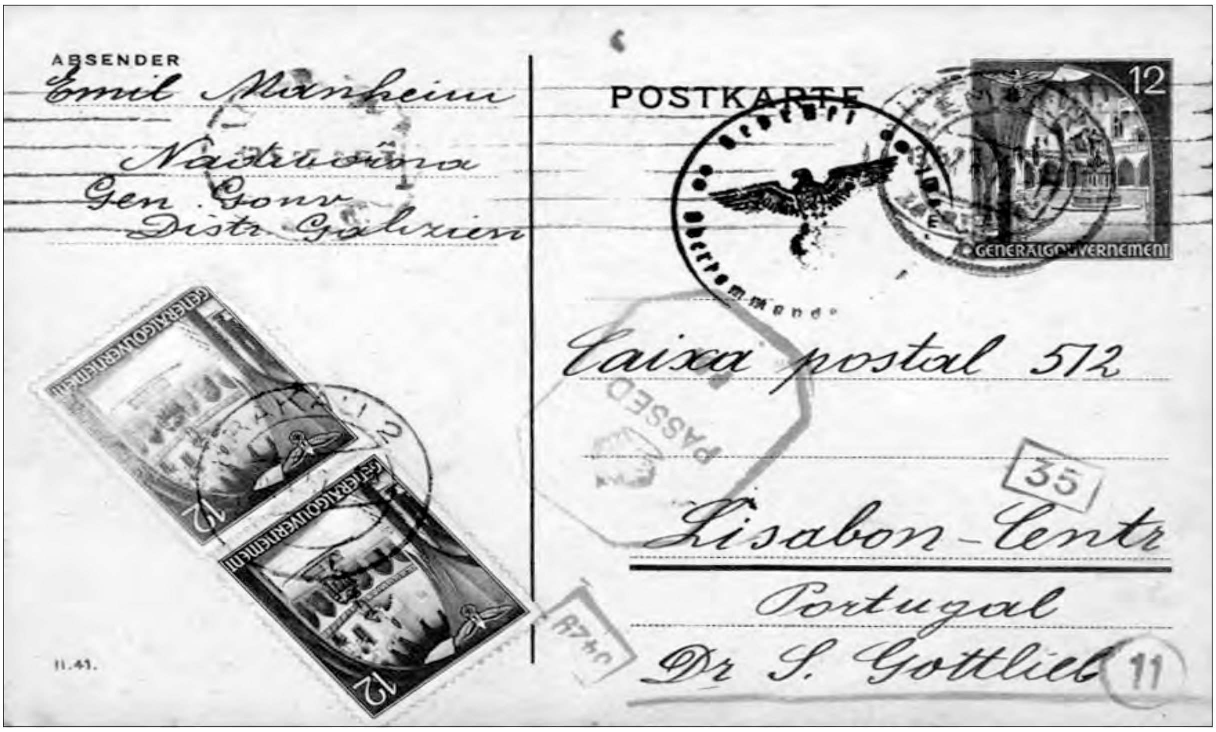
Alle Behörden und Dienststellen werden ersucht den Genannten zu keiner anderen Arbeit heranzuziehen.

Gültig bis 31 März 1942

Der Präsident
der jüd. Gemeinde der Stadt Lemberg
Dr. A. ROTHFELD

Lemberg, den 19 Februar 1942

Top: Sev's final bit of schooling in Europe: Year 5 certificate from School No. 56 in Lwow, issued by the National Komisariat of Education of the Ukranian Soviet Socialist Republic.
Bottom: Samson Sternhell's identity card in the Lwow Ghetto.

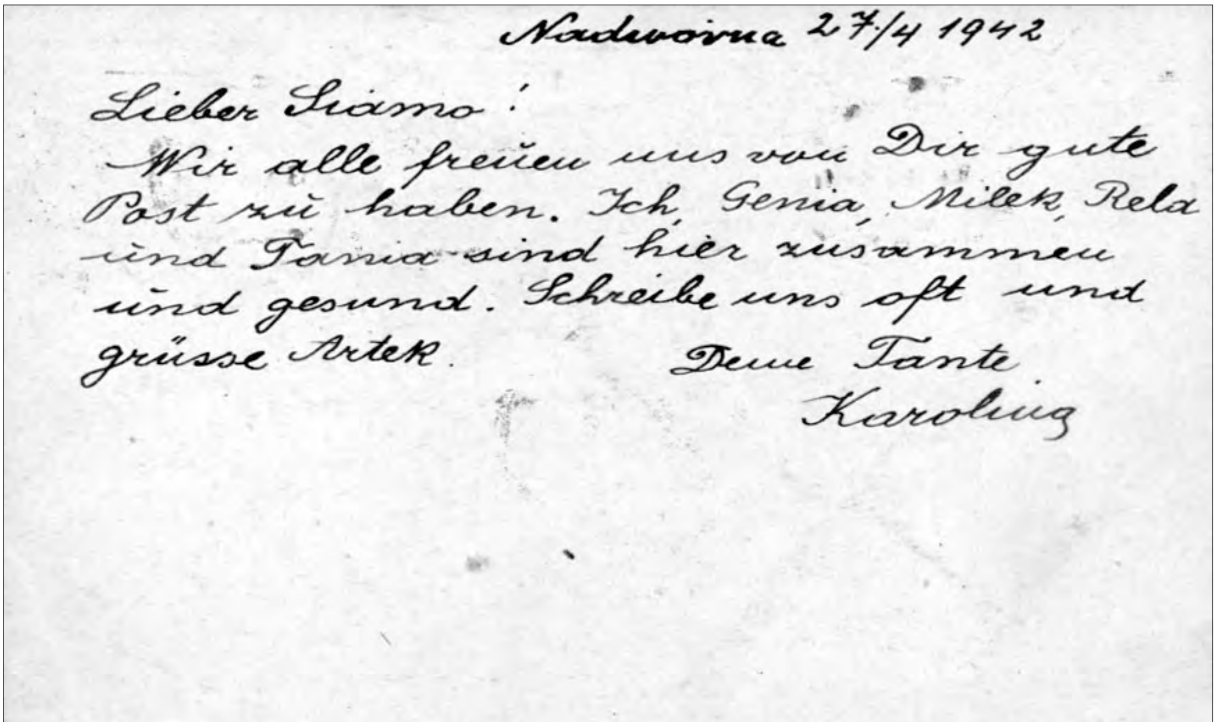


ABSENDER
Emil Manheim
Nadworna
Gen. Gouv.
Distr. Galizien

POSTKARTE

Caixa postal 572

Lisabon-Centr
Portugal
Dr S. Gottlieb



Nadworna 27/4 1942

Lieber Siamo!
Wir alle freuen uns von Dir gute Post zu haben. Ich, Genia, Milek, Rela und Fania sind hier zusammen und gesund. Schreibe uns oft und grüsse Artek.

Deine Tante
Karolina

Postcard from Hell

The late Sasha Gottlieb (Smex, Appendix 8 and 9) gave this postcard to Roger who passed it on to me. Even though the address is in Portugal, Sasha never resided there. He was then serving as a medical Captain in the British Army in WWII and the Lisbon address in neutral Portugal was a Red Cross postal contact. He must have got this contact address to the family in Nadworna and also to his immediate family in Zydaczow, as another postcard of this sort reached him from his parents (also later killed) from Zydaczow.

The postage stamps on this postcard are from Generalgovernement, i.e., the region covering most of the Nazi-occupied Poland. The bulk of Poland's 3,500,000 Jews lived and perished there. In 1939-45 it was a region of Hell ruled from Krakow by the Governor, Dr. Hans Frank. The stamps depict a courtyard in Wavel, the medieval palace of the Polish Kings in Krakow - a nice irony. Frank, a major Nazi war criminal, was tried in Nuremberg in 1946 and was hanged. The Nazi eagle on the round rubber stamp is perched on the nearly obscured swastika. One can just make out the words "Obercommando" meaning "High Command". A more complete version of the Nazi eagle, which we contemptuously called "the goose", can be seen on the postage stamps.

By April 27, 1942 (the date on the postcard) the approximately 6,000 Jews of Nadworna had already been through the Action of October 6, 1941 ("The Nadworna Massacre") in which 2,500 perished and which I survived together with the rest of the family listed in this postcard. In April 1942, the remaining Jews of Nadworna were in a Ghetto from which this postcard originates. By about October 1942 the last of Nadworna's Jews were exterminated. Of the 5 people listed in this postcard (Caroline, Milek, Genia, Rela and Tania) only Milek survived (see Appendix 7 and pp.23-25 and first paragraph on p.32). As this postcard had to pass through German censors, it is bland and partially misleading (e.g., the reference to Sasha's "good position"). It reads in German:

> *"Dear Siamo,*
> *We are all happy that you have obtained a good position. I, Genia, Milek, Rela and Tania are here together and healthy. Write to us and give regards to Arthur.*
> *Your aunt*
> *Karolina* "

The sender is given as Emil Mannheim (Milek), but the postcard is clearly written by a single hand, viz., that of my grandmother Karolina (Caroline Sternhell, nee Gottlieb, Appendix 7,8 and 9). She was the last of this group to be killed (see top of p.13).

Sev Sternhell
September, 2005

Told by Schaje Schmerler

http://www.jewishgen.org/yizkor/Nadvornaya/nad016

A HAND WHICH STUCK OUT OF THE MASS GRAVE

I do not know the reason why the German Commissar (Landeskommissar) decided to send some Jews from the ghetto into the Bukowinka, armed with shovels, so they could "improve" the earth cover over the mass grave of the slaughtered Jews.

This Commissar in civilian clothes who had come to us in Rabbi Mordychaly's Nadwerny from the land of the murderers in order to "take care" of our needs and well-being — this Commissar probably feared an epidemic which was likely to be caused by the thousands of corpses heaped in a barely covered ditch.

This ditch was filled with half of the Jewish population of Nadworna as well as with several hundred Hungarian Jews who, under the"protection" of this Commissar in civilian clothes, had been cruelly murdered on October 6, 1941, and who were now, after the long winter, already decomposing. This Commissar who was so very much "concerned", with the health of the population, figured that he would prevent an epidemic by piling on a heavy layer of earth.

We, my son Dolphi and myself, were among the people sent there to take care of this work.

We, as well as the others who went there with us, took along, besides the shovels, a few candles to light at the place of those dearest and most beloved to us.

When we arrived at that vale of tears we faced a horrible and unforgettable sight. There were enough traces left to see of the awful tragedy that had taken place there about eight months ago.

Strewn all over were many torn shirts, underwear, shredded left-overs of dresses, "Laabzydeklych keys, documents, photos, wigs (Scheitel). Also torn prayer books were lying around; some in Hungarian translation; most likely the Hungarian Jews (there were several hundreds of them) who had lost their lives there, had brought these prayer books from Hungary.

We were gripped by terror and horror when we saw a chewed-off hand, pointing towards heaven, stick out of the middle of the mass grave.

That hand, reaching towards heaven from the grave, was raised like a signal of accusation against God and men for the gigantic crime committed here by bestial men — themselves created by God who cruelly murdered here thousands of innocent people, hundreds of children among them, for no other reason than that they were Jews.

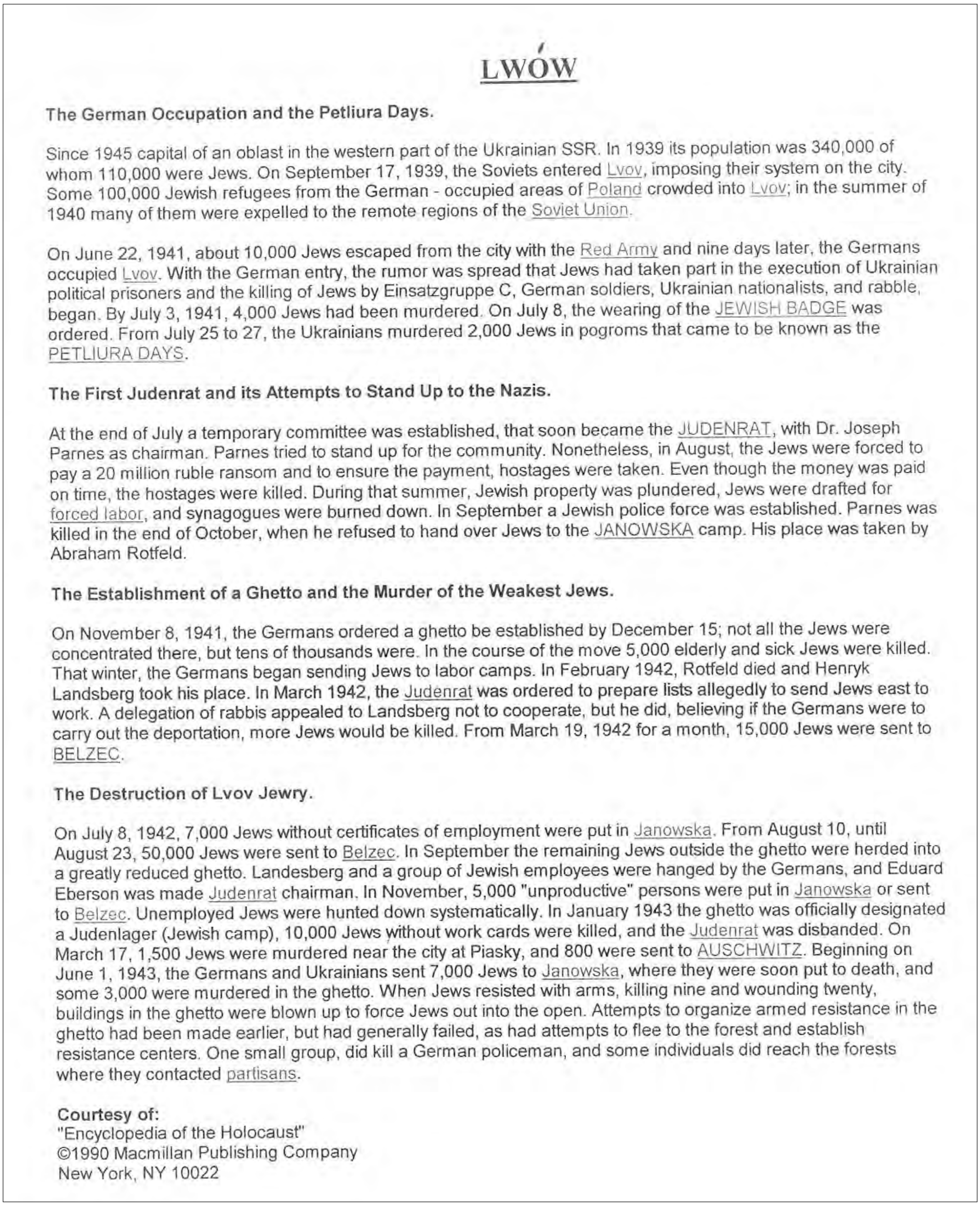
I cannot free myself from the feeling of guilt I felt at the sight of that outstretched accusing hand.

A feeling of guilt which probably bothers everyone of us: why did we not have the courage and the "Gewure" to do what one of our people, Simson has proven himself able to do in the olden times, long past.

This was when Simson — blind, chained, and helpless in the midst of his numerous enemies was forced to be present at a funny show: the killing of a Jew. The Jew Simson, however, preserved his human dignity despite his helplessness, and did not sell his life cheap. With a scream he tore down the pillars on which the temple rested, and the temple where thousands of his enemies had come together in order to make fun of the helpless Jew Simson, collapsed and under its ruins buried many thousands of his enemies, and Simson along with them. And this is how the Jew Simson died.

We covered the grave with earth, after we had put to rest there the scattered wigs, prayer books, "Taleskutens", and more.

We could not stay there long because from the woods some Ukrainian fellows were approaching. Hurriedly we lit the candles we had brought, said the "Kadysh" and left the place of the martyrs which we would, unfortunately, never be able to visit again.



LWÓW

The German Occupation and the Petliura Days.

Since 1945 capital of an oblast in the western part of the Ukrainian SSR. In 1939 its population was 340,000 of whom 110,000 were Jews. On September 17, 1939, the Soviets entered Lvov, imposing their system on the city. Some 100,000 Jewish refugees from the German - occupied areas of Poland crowded into Lvov; in the summer of 1940 many of them were expelled to the remote regions of the Soviet Union.

On June 22, 1941, about 10,000 Jews escaped from the city with the Red Army and nine days later, the Germans occupied Lvov. With the German entry, the rumor was spread that Jews had taken part in the execution of Ukrainian political prisoners and the killing of Jews by Einsatzgruppe C, German soldiers, Ukrainian nationalists, and rabble, began. By July 3, 1941, 4,000 Jews had been murdered. On July 8, the wearing of the JEWISH BADGE was ordered. From July 25 to 27, the Ukrainians murdered 2,000 Jews in pogroms that came to be known as the PETLIURA DAYS.

The First Judenrat and its Attempts to Stand Up to the Nazis.

At the end of July a temporary committee was established, that soon became the JUDENRAT, with Dr. Joseph Parnes as chairman. Parnes tried to stand up for the community. Nonetheless, in August, the Jews were forced to pay a 20 million ruble ransom and to ensure the payment, hostages were taken. Even though the money was paid on time, the hostages were killed. During that summer, Jewish property was plundered, Jews were drafted for forced labor, and synagogues were burned down. In September a Jewish police force was established. Parnes was killed in the end of October, when he refused to hand over Jews to the JANOWSKA camp. His place was taken by Abraham Rotfeld.

The Establishment of a Ghetto and the Murder of the Weakest Jews.

On November 8, 1941, the Germans ordered a ghetto be established by December 15; not all the Jews were concentrated there, but tens of thousands were. In the course of the move 5,000 elderly and sick Jews were killed. That winter, the Germans began sending Jews to labor camps. In February 1942, Rotfeld died and Henryk Landsberg took his place. In March 1942, the Judenrat was ordered to prepare lists allegedly to send Jews east to work. A delegation of rabbis appealed to Landsberg not to cooperate, but he did, believing if the Germans were to carry out the deportation, more Jews would be killed. From March 19, 1942 for a month, 15,000 Jews were sent to BELZEC.

The Destruction of Lvov Jewry.

On July 8, 1942, 7,000 Jews without certificates of employment were put in Janowska. From August 10, until August 23, 50,000 Jews were sent to Belzec. In September the remaining Jews outside the ghetto were herded into a greatly reduced ghetto. Landesberg and a group of Jewish employees were hanged by the Germans, and Eduard Eberson was made Judenrat chairman. In November, 5,000 "unproductive" persons were put in Janowska or sent to Belzec. Unemployed Jews were hunted down systematically. In January 1943 the ghetto was officially designated a Judenlager (Jewish camp), 10,000 Jews without work cards were killed, and the Judenrat was disbanded. On March 17, 1,500 Jews were murdered near the city at Piasky, and 800 were sent to AUSCHWITZ. Beginning on June 1, 1943, the Germans and Ukrainians sent 7,000 Jews to Janowska, where they were soon put to death, and some 3,000 were murdered in the ghetto. When Jews resisted with arms, killing nine and wounding twenty, buildings in the ghetto were blown up to force Jews out into the open. Attempts to organize armed resistance in the ghetto had been made earlier, but had generally failed, as had attempts to flee to the forest and establish resistance centers. One small group, did kill a German policeman, and some individuals did reach the forests where they contacted partisans.

Courtesy of:
"Encyclopedia of the Holocaust"
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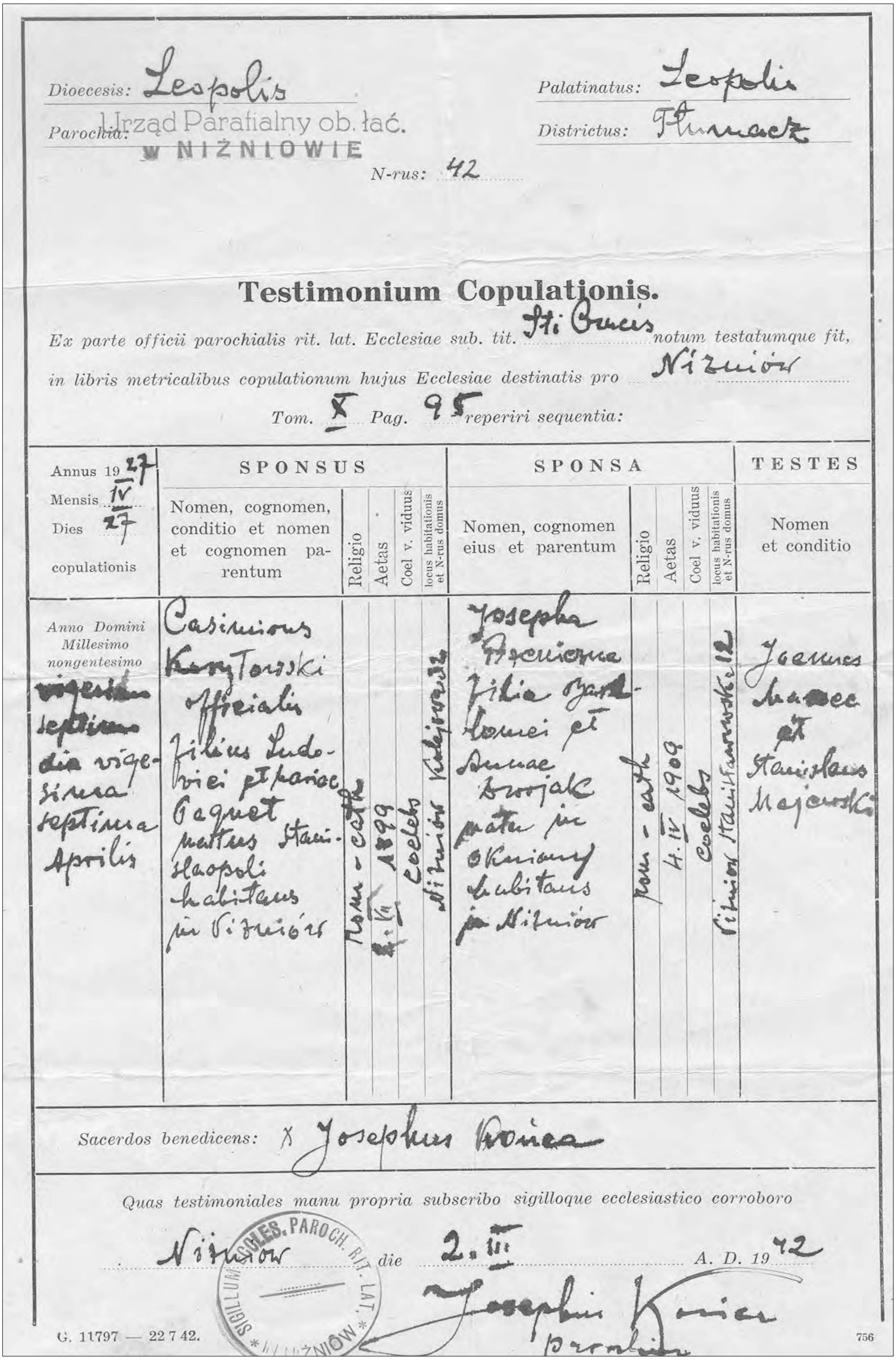
New York, NY 10022



Dioecesis: Leopolis

Palatinatus: Leopolis

Parochia: Urząd Parafialny ob. łać. w NIŻNIOWIE

Districtus: Tłumacz

N-rus: 42

Testimonium Copulationis.

Ex parte officii parochialis rit. lat. Ecclesiae sub. tit. Sti Crucis *notum testatumque fit, in libris metricalibus copulationum hujus Ecclesiae destinatis pro* Niżniów

Tom. X *Pag.* 95 *reperiri sequentia:*

Annus 19 27 Mensis IV Dies 27 copulationis	SPONSUS Nomen, cognomen, conditio et nomen et cognomen parentum	Religio	Aetas	Coel v. viduus	locus habitationis et N-rus domus	SPONSA Nomen, cognomen eius et parentum	Religio	Aetas	Coel v. viduus	locus habitationis et N-rus domus	TESTES Nomen et conditio
Anno Domini Millesimo nongentesimo ~~vigesimo septimo~~ die vigesima septima Aprilis	Casimirus Korytowski officialis filius Ludovici et Mariae Paquet natus Stanislaopoli habitans in Niżniów	rom.-cath.	4.VII 1899	Coelebs	Niżniów Kolejowa 32	Josepha [illegible] filia Bartolomei et Annae Dworjak nata in Okniany habitans in Niżniów	rom.-cath.	4.IV 1909	Coelebs	Niżniów Stanisławowska 12	Joannes [illegible] et Stanislaus Majewski

Sacerdos benedicens: X Josephus Konica

Quas testimoniales manu propria subscribo sigilloque ecclesiastico corroboro

Niżniów *die* 2.VII *A. D. 19*42

SIGILLUM ECCLES. PAROCH. RIT. LAT. IN NIŻNIÓW

Josephus Konica parochus

G. 11797 — 22 7 42.

756

A sample of Aryan papers: the false marriage certificate of Sev’s parents on the name of Casimir (Kazimierz or Kazik) Korytowski and Josepha P……..?

Huszt Koronaváros
Nagyközség
Jegyzői Hivatala

Igazoló-jegy

Sternhell Szeverin,
tanuló.huszti lakos részére.
Születési helye és éve :
Lemberg.1930.
Állapota,vallása :nőtlen,xz
izr.
Állampolgársága :magyar
Állandó lakhelye : Huszt

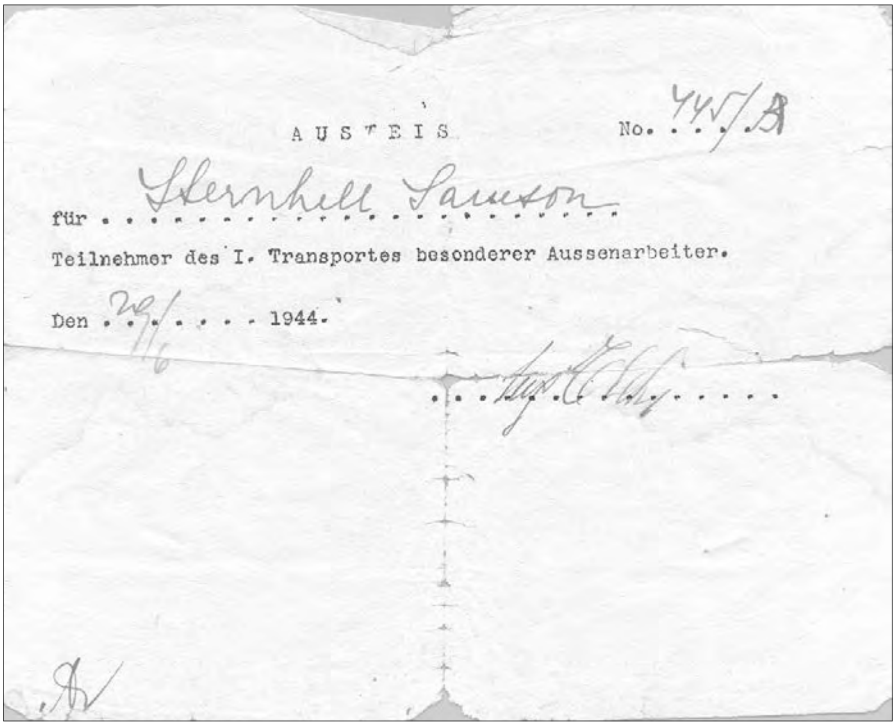
Személyleirása
Termete : növésben
Arca : hosszas
Haja : szőke
Bajusza: ----------
Szakálla:----------
Szeme : kék
Szája : rendes
Különös ismertető jelei
nincsnek .
Nyelvismerete : magyar,
német

Igazolom, hogy az igazolójegy tulajdonosa arcképét sajátkezüleg irta alá.

Kelt,1943,augusztus hó 12,

főjegyző

Jew again! Identity paper (in Hungarian) for Severin Sternhell produced before boarding the transport which finished up in Bergen-Belsen.



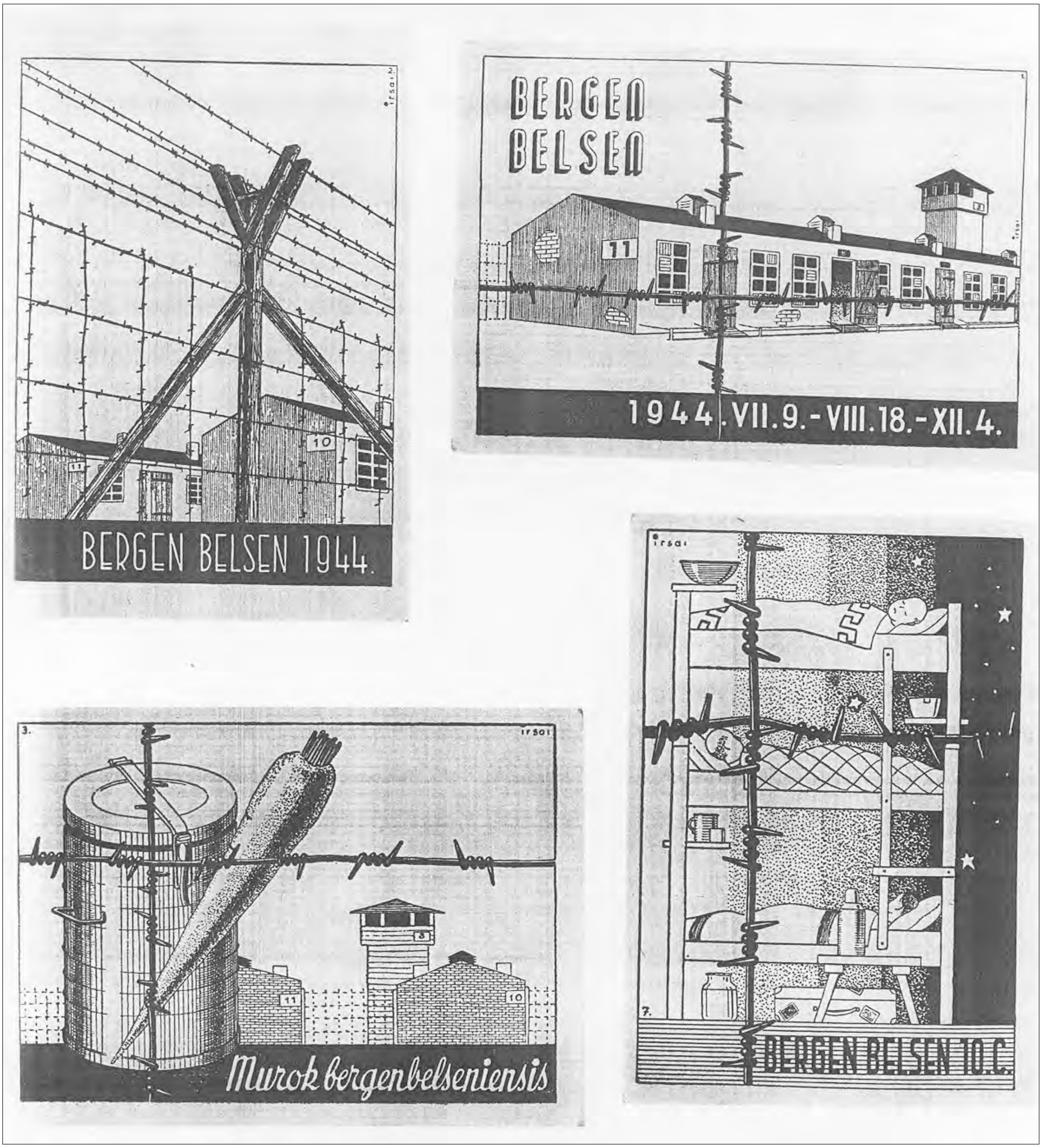
AUSWEIS No. 445/B

für Sternhell Samson

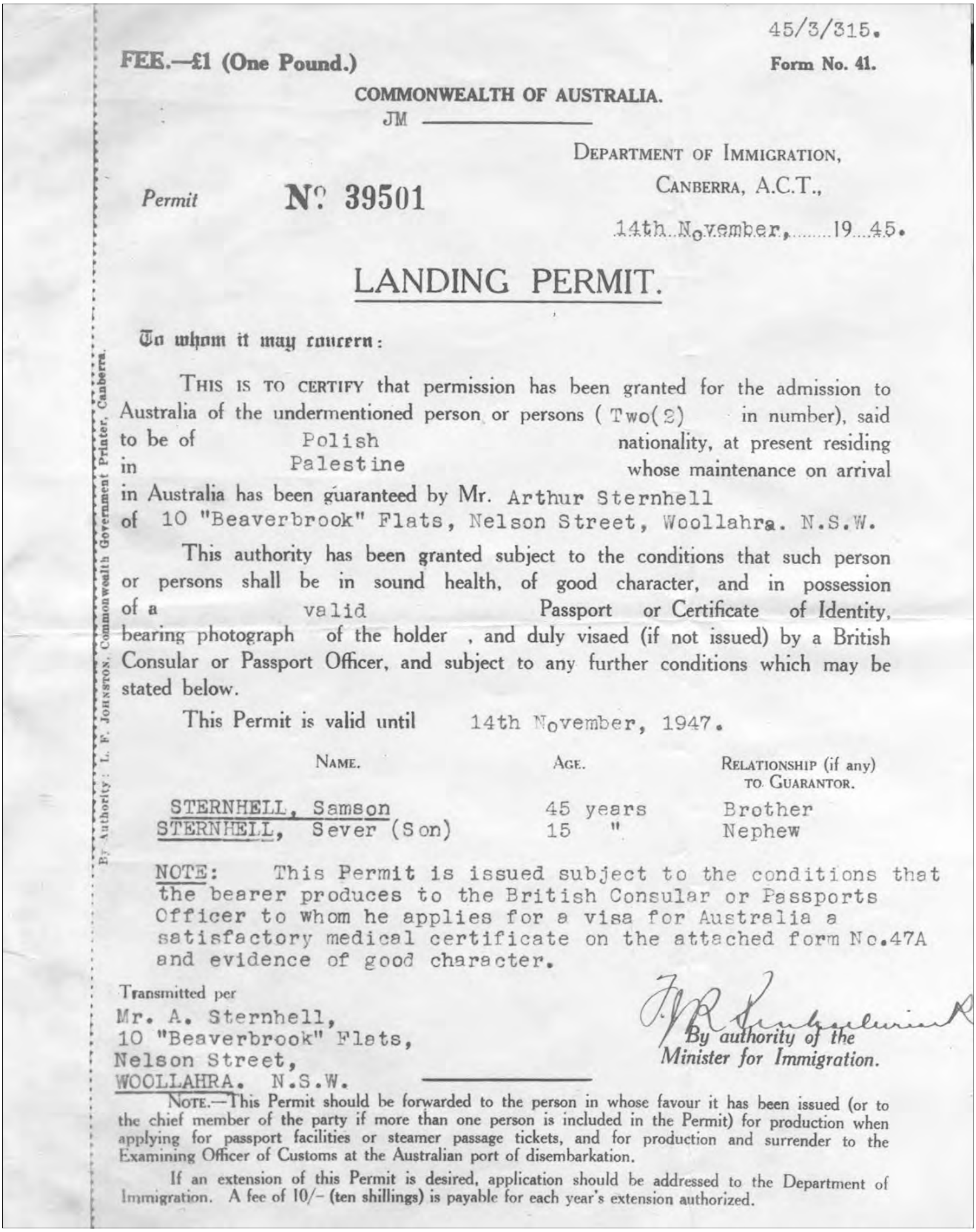
Teilnehmer des I. Transportes besonderer Aussenarbeiter.

Den 29/6 1944.

Authorisation for Samson Sternhell to join the transport.



**A fellow prisoner in Belsen, an architect named Irsai, made these sketches in Switzerland.
I believe he got some dates wrong by a few days.**



45/3/315.

FEE.—£1 (One Pound.) **Form No. 41.**

COMMONWEALTH OF AUSTRALIA.

JM

DEPARTMENT OF IMMIGRATION,
CANBERRA, A.C.T.,
14th November, 1945.

Permit **No. 39501**

LANDING PERMIT.

To whom it may concern:

THIS IS TO CERTIFY that permission has been granted for the admission to Australia of the undermentioned person or persons (Two(2) in number), said to be of Polish nationality, at present residing in Palestine whose maintenance on arrival in Australia has been guaranteed by Mr. Arthur Sternhell of 10 "Beaverbrook" Flats, Nelson Street, Woollahra. N.S.W.

This authority has been granted subject to the conditions that such person or persons shall be in sound health, of good character, and in possession of a valid Passport or Certificate of Identity, bearing photograph of the holder , and duly visaed (if not issued) by a British Consular or Passport Officer, and subject to any further conditions which may be stated below.

This Permit is valid until 14th November, 1947.

NAME.	AGE.	RELATIONSHIP (if any) TO GUARANTOR.
STERNHELL, Samson	45 years	Brother
STERNHELL, Sever (Son)	15 "	Nephew

NOTE: This Permit is issued subject to the conditions that the bearer produces to the British Consular or Passports Officer to whom he applies for a visa for Australia a satisfactory medical certificate on the attached form No.47A and evidence of good character.

Transmitted per
Mr. A. Sternhell,
10 "Beaverbrook" Flats,
Nelson Street,
WOOLLAHRA. N.S.W.

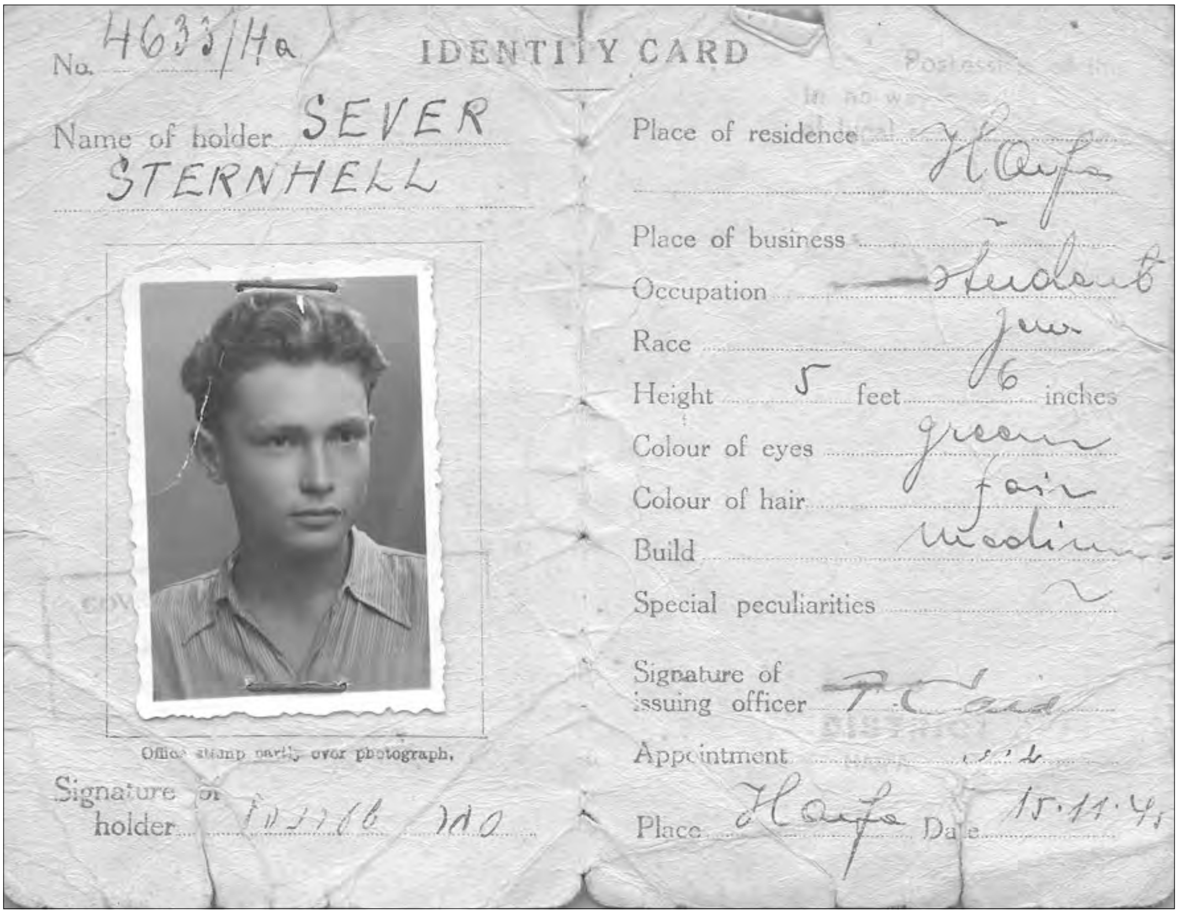
By authority of the
Minister for Immigration.

NOTE.—This Permit should be forwarded to the person in whose favour it has been issued (or to the chief member of the party if more than one person is included in the Permit) for production when applying for passport facilities or steamer passage tickets, and for production and surrender to the Examining Officer of Customs at the Australian port of disembarkation.

If an extension of this Permit is desired, application should be addressed to the Department of Immigration. A fee of 10/- (ten shillings) is payable for each year's extension authorized.

By Authority: L. F. JOHNSTON, Commonwealth Government Printer, Canberra.

Passport to the future: the Australian Landing Permit for Samson and Sever Sternhell.



No. 4633/Ha **IDENTITY CARD**

Name of holder SEVER STERNHELL

Office stamp partly over photograph.

Signature of holder

Place of residence Haifa

Place of business –

Occupation Student

Race Jew

Height 5 feet 6 inches

Colour of eyes green

Colour of hair fair

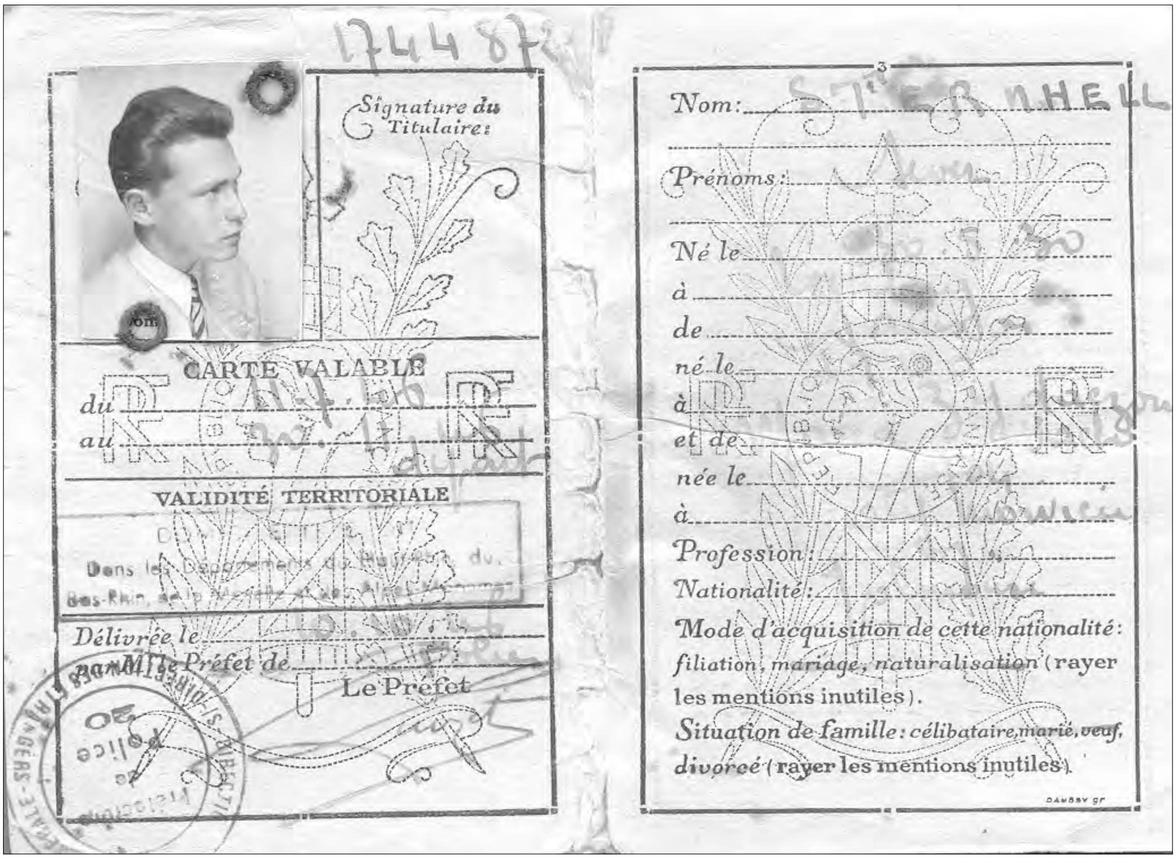
Build medium

Special peculiarities ~

Signature of issuing officer

Appointment

Place Haifa Date 15.11.45



174487

Signature du Titulaire:

CARTE VALABLE

du

au

VALIDITÉ TERRITORIALE

Dans les Départements du [illegible] du Bas-Rhin, de la Moselle et [illegible]

Délivrée le

par M. le Préfet de

Le Préfet

Nom: STERNHELL

Prénoms:

Né le

à

de

né le

à

et de

née le

à

Profession:

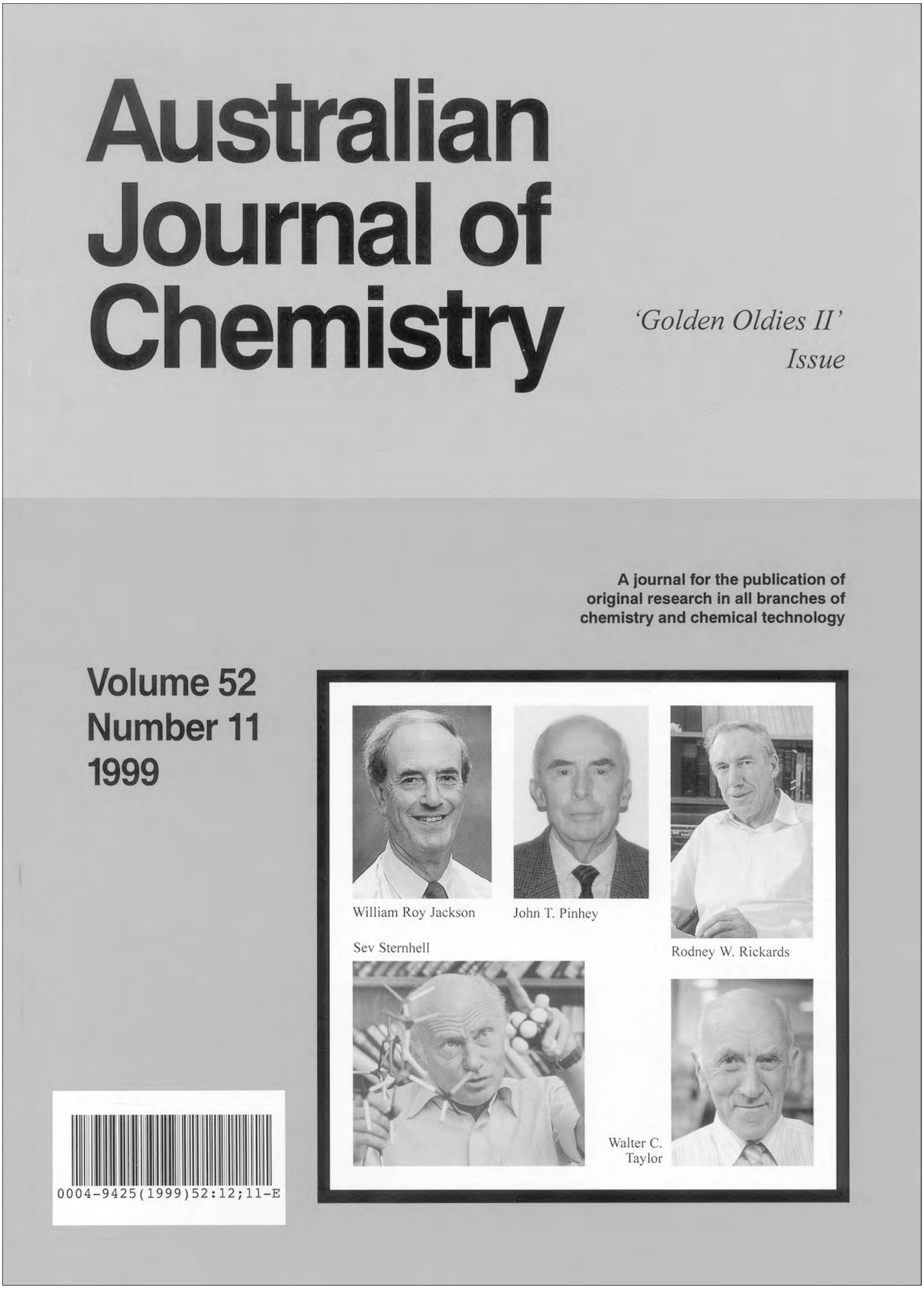
Nationalité:

Mode d'acquisition de cette nationalité: filiation, mariage, naturalisation (rayer les mentions inutiles).

Situation de famille: célibataire, marié, veuf, divorcé (rayer les mentions inutiles).

DAUSSY gr

An old Czarist Russian saying stated that “a person consists of a body, a soul and a passport”. Sev’s identity papers in the British Mandate of Palestine issued in 1945 and in France in 1946.



Australian Journal of Chemistry

'Golden Oldies II'
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Volume 52
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1999

William Roy Jackson

John T. Pinhey

Rodney W. Rickards

Sev Sternhell

Walter C.
Taylor

0004-9425(1999)52:12;11-E

Aust. J. Chem., 1999, **52**, 1001–1002

Professor Sev Sternhell

Sev Sternhell has been active in Australian chemistry over a period of well over 40 years and has been very influential, not only directly through his work, but also indirectly because of the graduates that he has inspired and various positions he has held.

Sev was born in 1930 in Lwów, then a large city in eastern Poland, now part of Ukraine. His early education was interrupted at the primary school stage by the outbreak of World War II which he barely survived (his family was Jewish) and his education was not resumed until the age of 16 in 1947 when he was enrolled into the final year of High School at Newington College, Stanmore, New South Wales. In 1948 he enrolled into the Faculty of Science at the University of Sydney. He graduated with First Class Honours in 1951 under the supervision of Dr Francis Lions, Reader in Organic Chemistry. He graduated with an M.Sc. supervised by the newly arrived Professor Arthur Birch in 1952, and then left for 'the real world' of chemical industry, although he held a continuing scholarship which would have funded him to a Ph.D. The real world, which was the plastics and polymer factory of Beetle Elliott in Rozelle, proved disappointing and Sev left in 1955 to take up a position with the CSIRO (Division of Coal Research) at North Ryde where he worked until 1964. Between September 1958 and November 1960 he was granted a leave of absence and an overseas CSIRO scholarship tenable anywhere. He chose to enrol for a Ph.D. at the Imperial College in the laboratory of D. H. R. Barton, FRS (later Sir Derek and a Nobel Laureate), who proved to be the critical influence in Sev's professional life. His Ph.D. topic was the structure of the major bitter principle of citrus fruit, Limonin, work which he completed successfully as a junior member of a star-studded research team which included E. J. Corey (later Nobel Laureate), D. Arigoni and O. Jeger. Sev later joked that 'at least I started off as an honest natural-product organic chemist'. He also liked to point out that he 'held degrees from the University of Sydney, Imperial College London and Bergen–Belsen' the last 'a very rare degree—large enrolment, few graduations'.

Sev became attracted to the academic life and in April 1964 he was appointed to a Senior Lectureship in Organic Chemistry at the University of Sydney, his old *alma mater*, where he remained till his formal retirement in July 1998. He was appointed to a Readership in 1967 and, following the premature death of Ern Ritchie, he was appointed Professor of Organic Chemistry and Head of Department of Organic Chemistry in 1977. By the time of his retirement, he was the last Professor at the University of Sydney who held a managerial position (Head of the Division of Organic Chemistry) by virtue of his appointment to a Chair!

Sev's work with Lions dealt mainly with aspects of the Mannich reaction while his M.Sc. work with Birch was concerned with the classical Birch reduction. While at Imperial College he developed the unusual conversion of hydrazones into vinyl iodides and/or geminal diiodides—a reaction now known as the Barton–Sternhell reaction. His work as an independent researcher started with a long series of papers on coal chemistry, but already, while at CSIRO, he developed a lifelong interest in the then new area of n.m.r. spectroscopy. He lobbied successfully for the purchase of the first commercial n.m.r. spectrometer installed in Australia (a Varian A60). Much of his next 30 years was spent establishing correlations between n.m.r. parameters and molecular structure, particularly between the magnitudes of spin–spin coupling constants and the stereochemistry and electronic nature of the coupling paths. This work resulted in well over 100 publications including some reviews which became highly influential and the textbook (with L. M. Jackman) 'Applications of NMR Spectroscopy in Organic Chemistry', which still has an honoured place on many a chemist's bookshelf.

Besides this work, there were a number of minor themes including keto–enol tautomerism, photochemistry of Schiff's bases, quinone chemistry, the Wessely acetoxylation, the Barton–Sternhell reaction, dynamic n.m.r. spectroscopy, steroid chemistry, organolead chemistry (with J. T. Pinhey), non-bonding interactions, porphyrin chemistry (with M. J. Crossley), induction of chirality in mesophases (with L. D. Field) and mechanochemistry.

Sev spent a number of sabbaticals as a visiting Professor at the University of Tennessee, the University of Arizona (where he began a long collaboration with M. Barfield), the ETH Zurich and Oxford. His scientific contributions were acknowledged by a D.Sc. from London (in 1966) and Fellowship of the Australian Academy of Science in 1992.

Over the years, Sev supervised a large number of Honours and Postgraduate students, several of whom went on to academic careers in chemistry including two later appointed to Chairs in Australia (L. D. Field and R. K. Norris) and two appointed to Chairs overseas (A. Pross and P. W. Westerman). During his long period (1977–1998) as Head of Organic Chemistry at the University of Sydney, Sev presided over a flourishing Department, made a number of outstanding academic appointments and fought long and hard to obtain resources for teaching and research in organic chemistry.

Sev was very active in the affairs of the School of Chemistry at Sydney University, where he served twice as

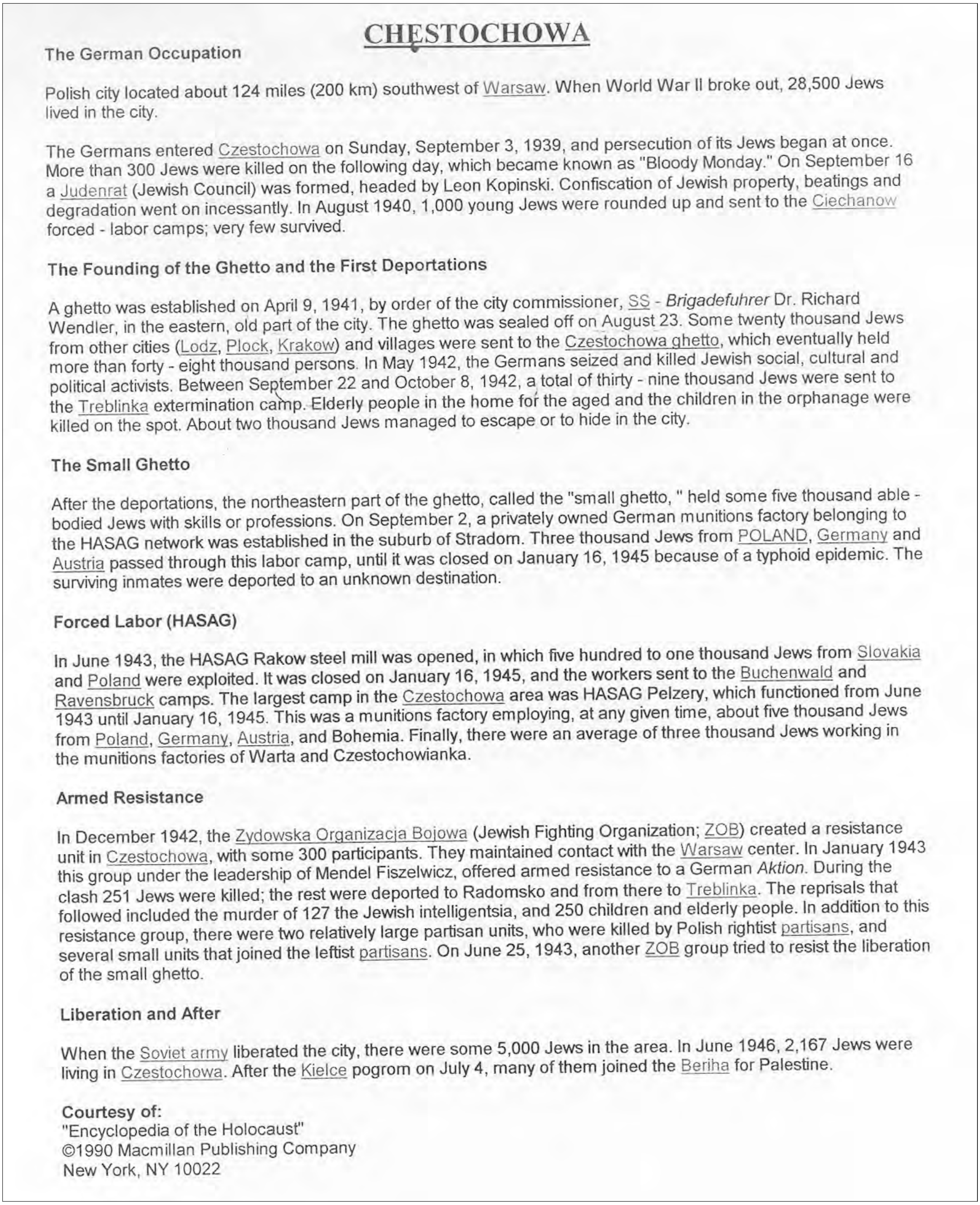
Manuscript received 3 September 1999

10.1071/CH99107 0004-9425/99/111001

Head of School, and the affairs of the University where he was, *inter alia*, the foundation Chairman of the Committee of Graduate Studies. He was often asked 'if there was any committee he has not served on?' He also served for 5 years on the Chemistry Panel of the Australian Research Council, 2 years as its Chairman.

Outside his professional activities, Sev's life has been devoted to his wife Alice whom he married in 1953 and his sons Peter, James and Roger, all of whom are now graduates of the University of Sydney. He was also an enthusiastic surfer, squash player, bushwalker, canyoneer, teller of dubious jokes and writer of political essays. Some of the essays achieved wide circulation, particularly those dealing with 'Chemophobia' and risk, while one of them ('The Class that Cried Wolf' dealing with environmental issues), which appeared in the *Quadrant* magazine, won the prestigious Watson prize. In several essays and letters to editor to *The Australian*, *The Sydney Morning Herald* and to the *Canberra Times* he expressed strong and cogent criticisms of the policies of successive Governments towards Australian Universities, while his oft-expressed opinions of a former Minister simply cannot be quoted in print. Later in life he developed a positive mania for trekking in the Nepal Himalayas to which he has made nine expeditions so far (mostly led by himself). None of his many activities have diminished much since his formal retirement in July 1998, although he occasionally complains of some geological changes in the gradients of hills!

Les Field
School of Chemistry
University of Sydney



CHĘSTOCHOWA

The German Occupation

Polish city located about 124 miles (200 km) southwest of Warsaw. When World War II broke out, 28,500 Jews lived in the city.

The Germans entered Czestochowa on Sunday, September 3, 1939, and persecution of its Jews began at once. More than 300 Jews were killed on the following day, which became known as "Bloody Monday." On September 16 a Judenrat (Jewish Council) was formed, headed by Leon Kopinski. Confiscation of Jewish property, beatings and degradation went on incessantly. In August 1940, 1,000 young Jews were rounded up and sent to the Ciechanow forced - labor camps; very few survived.

The Founding of the Ghetto and the First Deportations

A ghetto was established on April 9, 1941, by order of the city commissioner, SS - *Brigadefuhrer* Dr. Richard Wendler, in the eastern, old part of the city. The ghetto was sealed off on August 23. Some twenty thousand Jews from other cities (Lodz, Plock, Krakow) and villages were sent to the Czestochowa ghetto, which eventually held more than forty - eight thousand persons. In May 1942, the Germans seized and killed Jewish social, cultural and political activists. Between September 22 and October 8, 1942, a total of thirty - nine thousand Jews were sent to the Treblinka extermination camp. Elderly people in the home for the aged and the children in the orphanage were killed on the spot. About two thousand Jews managed to escape or to hide in the city.

The Small Ghetto

After the deportations, the northeastern part of the ghetto, called the "small ghetto, " held some five thousand able - bodied Jews with skills or professions. On September 2, a privately owned German munitions factory belonging to the HASAG network was established in the suburb of Stradom. Three thousand Jews from POLAND, Germany and Austria passed through this labor camp, until it was closed on January 16, 1945 because of a typhoid epidemic. The surviving inmates were deported to an unknown destination.

Forced Labor (HASAG)

In June 1943, the HASAG Rakow steel mill was opened, in which five hundred to one thousand Jews from Slovakia and Poland were exploited. It was closed on January 16, 1945, and the workers sent to the Buchenwald and Ravensbruck camps. The largest camp in the Czestochowa area was HASAG Pelzery, which functioned from June 1943 until January 16, 1945. This was a munitions factory employing, at any given time, about five thousand Jews from Poland, Germany, Austria, and Bohemia. Finally, there were an average of three thousand Jews working in the munitions factories of Warta and Czestochowianka.

Armed Resistance

In December 1942, the Zydowska Organizacja Bojowa (Jewish Fighting Organization; ZOB) created a resistance unit in Czestochowa, with some 300 participants. They maintained contact with the Warsaw center. In January 1943 this group under the leadership of Mendel Fiszelwicz, offered armed resistance to a German *Aktion*. During the clash 251 Jews were killed; the rest were deported to Radomsko and from there to Treblinka. The reprisals that followed included the murder of 127 the Jewish intelligentsia, and 250 children and elderly people. In addition to this resistance group, there were two relatively large partisan units, who were killed by Polish rightist partisans, and several small units that joined the leftist partisans. On June 25, 1943, another ZOB group tried to resist the liberation of the small ghetto.

Liberation and After

When the Soviet army liberated the city, there were some 5,000 Jews in the area. In June 1946, 2,167 Jews were living in Czestochowa. After the Kielce pogrom on July 4, many of them joined the Beriha for Palestine.

Courtesy of:
"Encyclopedia of the Holocaust"
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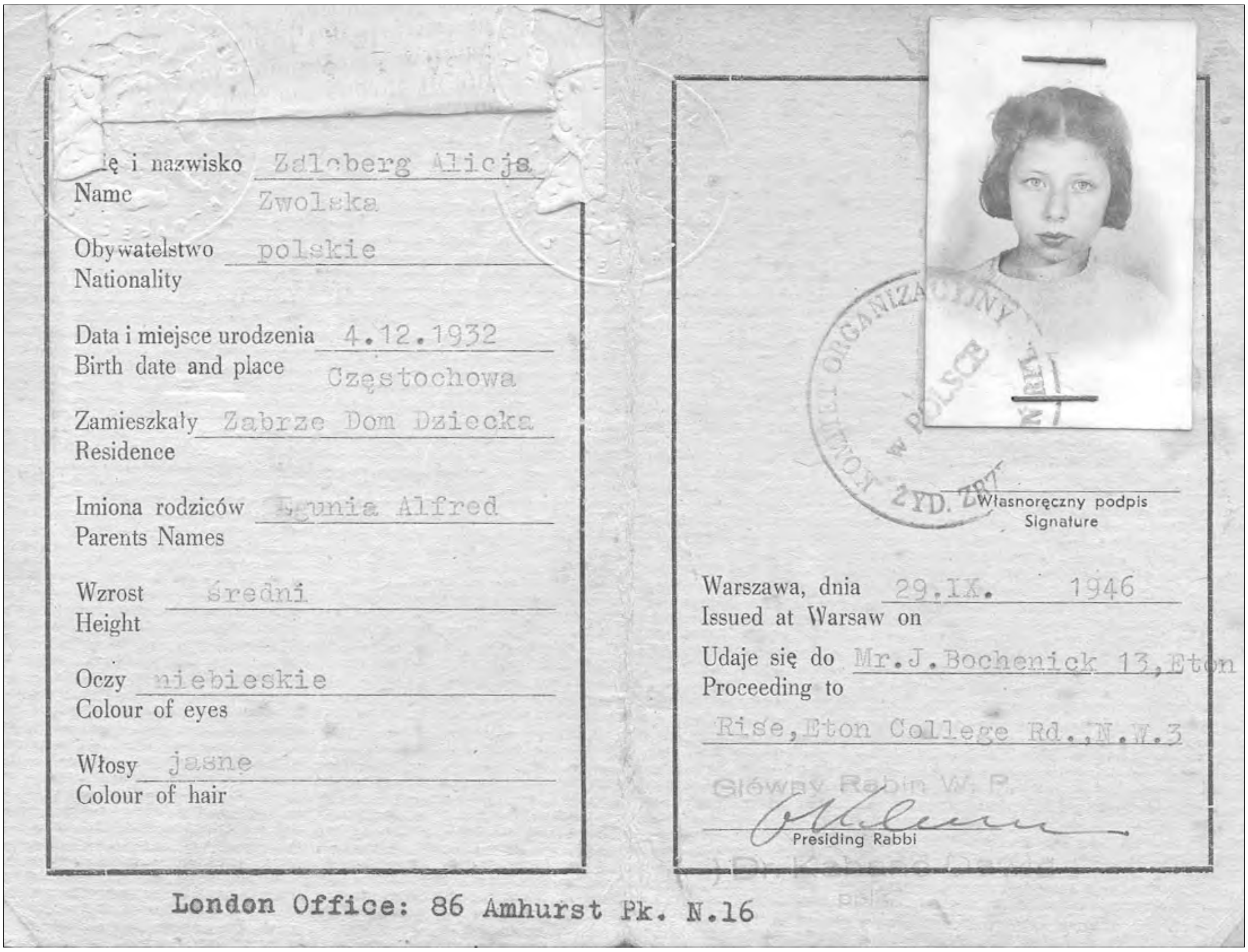
New York, NY 10022



Imię i nazwisko Zdlcberg Alicja
Name Zwolska

Obywatelstwo polskie
Nationality

Data i miejsce urodzenia 4.12.1932
Birth date and place Częstochowa

Zamieszkały Zabrze Dom Dziecka
Residence

Imiona rodziców Egunia Alfred
Parents Names

Wzrost średni
Height

Oczy niebieskie
Colour of eyes

Włosy jasne
Colour of hair

London Office: 86 Amhurst Pk. N.16

KOMITET ORGANIZACYJNY ŻYD. ZRZ. W POLSCE

Własnoręczny podpis
Signature

Warszawa, dnia 29.IX. 1946
Issued at Warsaw on

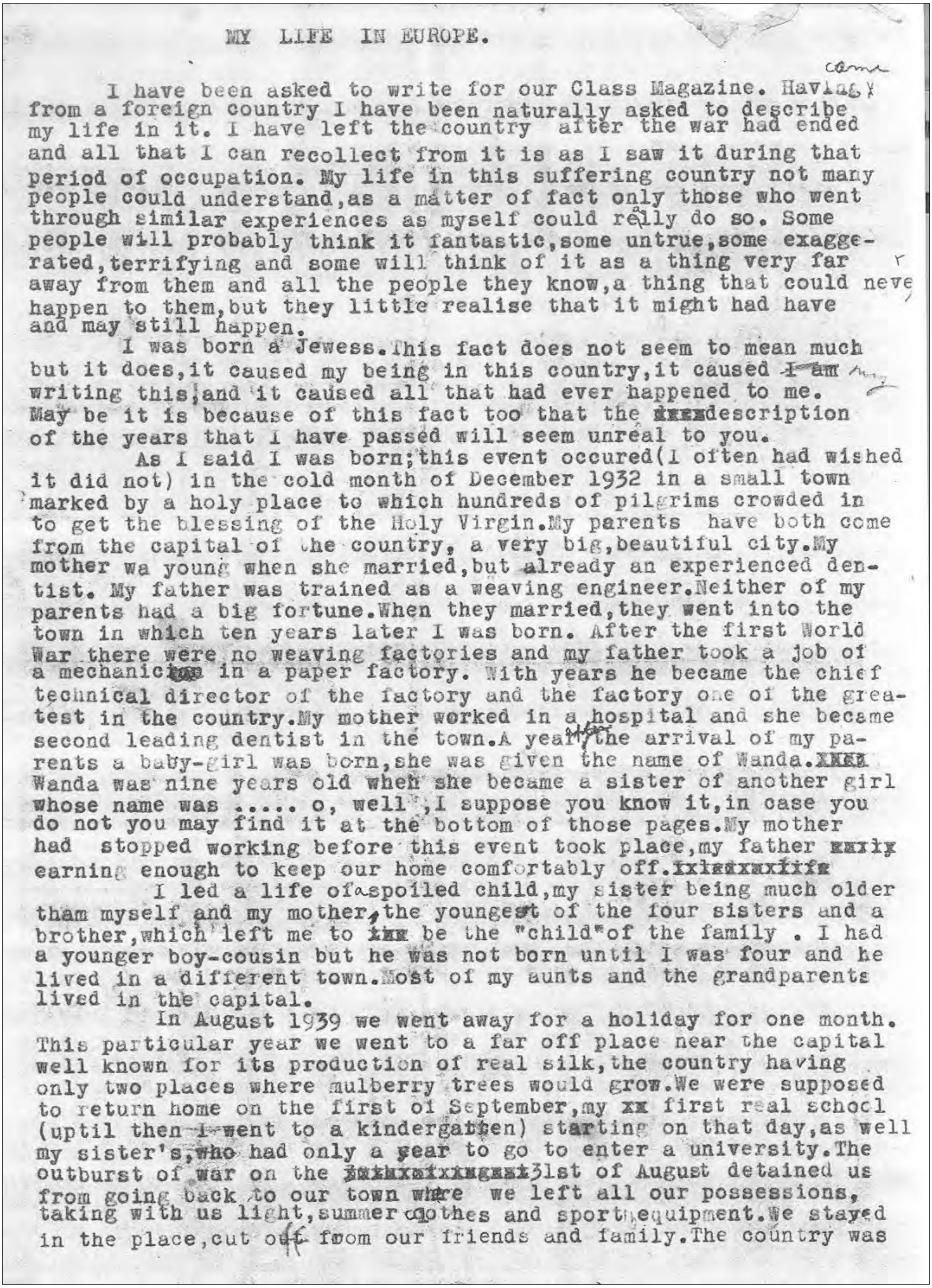
Udaje się do Mr.J.Bochenick 13,Eton
Proceeding to
Rise,Eton College Rd.,N.W.3

Główny Rabin W. P.

Presiding Rabbi

Dr. Kahane Dawid
ppłk.

Out of the shadows! Alice’s identity papers issued in Poland in 1946 to enable her to travel to the United Kingdom. Note the Zwolska (her Aryan name) which was to trail after her for years.



MY LIFE IN EUROPE.

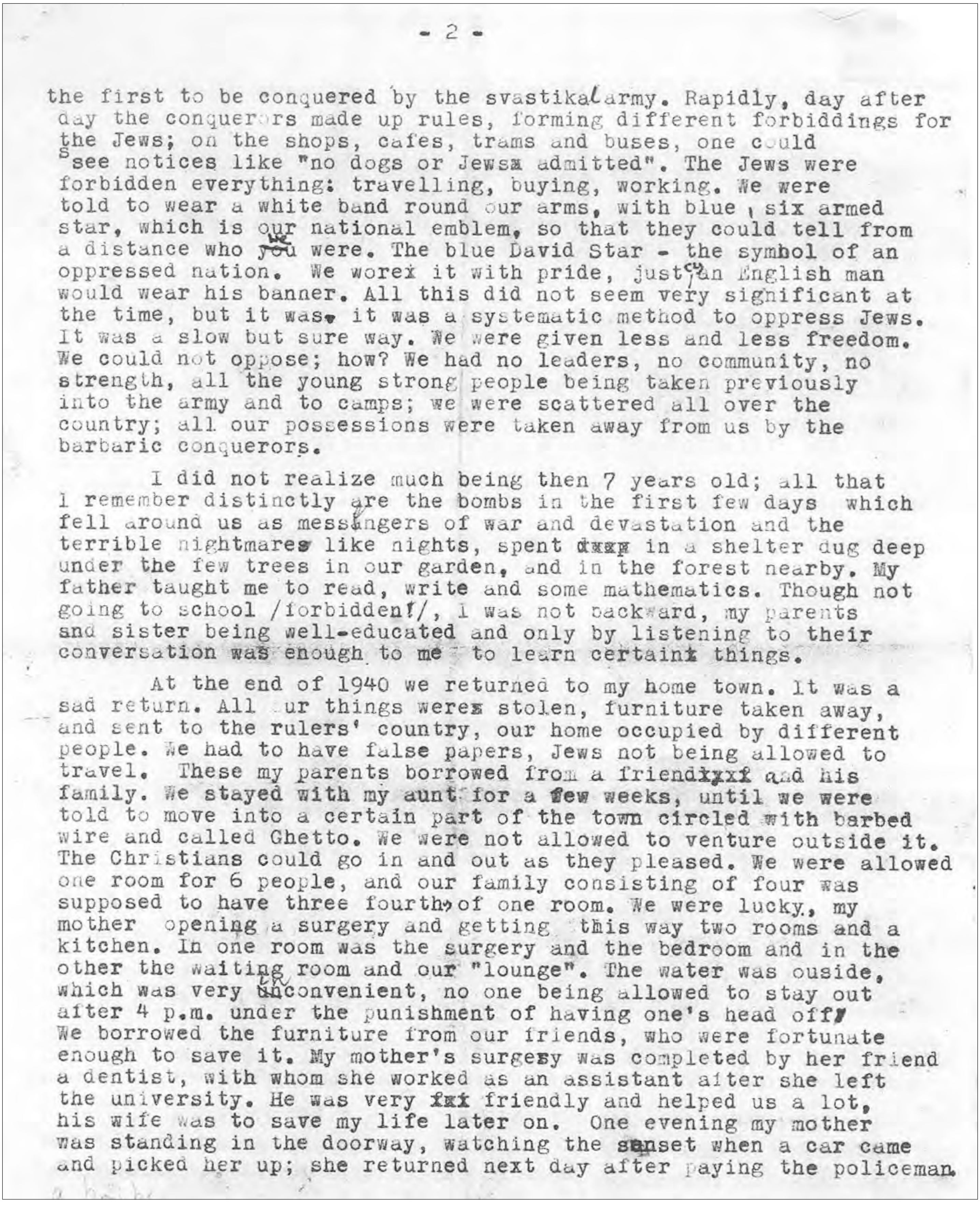
I have been asked to write for our Class Magazine. Having came from a foreign country I have been naturally asked to describe my life in it. I have left the country after the war had ended and all that I can recollect from it is as I saw it during that period of occupation. My life in this suffering country not many people could understand,as a matter of fact only those who went through similar experiences as myself could really do so. Some people will probably think it fantastic,some untrue,some exaggerated,terrifying and some will think of it as a thing very far away from them and all the people they know,a thing that could never happen to them,but they little realise that it might had have and may still happen.

I was born a Jewess.This fact does not seem to mean much but it does,it caused my being in this country,it caused ~~I am~~ my writing this,and it caused all that had ever happened to me. May be it is because of this fact too that the ~~xxxx~~description of the years that I have passed will seem unreal to you.

As I said I was born;this event occured(I often had wished it did not) in the cold month of December 1932 in a small town marked by a holy place to which hundreds of pilgrims crowded in to get the blessing of the Holy Virgin.My parents have both come from the capital of the country, a very big,beautiful city.My mother wa young when she married,but already an experienced dentist. My father was trained as a weaving engineer.Neither of my parents had a big fortune.When they married,they went into the town in which ten years later I was born. After the first World War there were no weaving factories and my father took a job of a mechanic~~xx~~ in a paper factory. With years he became the chief technical director of the factory and the factory one of the greatest in the country.My mother worked in a hospital and she became second leading dentist in the town.A year after the arrival of my parents a baby-girl was born,she was given the name of Wanda.~~XXXX~~ Wanda was nine years old when she became a sister of another girl whose name was ..... o, well ,I suppose you know it,in case you do not you may find it at the bottom of those pages.My mother had stopped working before this event took place,my father ~~xxxxx~~ earning enough to keep our home comfortably off.~~xxxxxxxxxx~~

I led a life of a spoiled child,my sister being much older tham myself and my mother, the youngest of the four sisters and a brother,which left me to ~~xxx~~ be the "child"of the family . I had a younger boy-cousin but he was not born until I was four and he lived in a different town.Most of my aunts and the grandparents lived in the capital.

In August 1939 we went away for a holiday for one month. This particular year we went to a far off place near the capital well known for its production of real silk,the country having only two places where mulberry trees would grow.We were supposed to return home on the first of September,my ~~xx~~ first real school (uptil then ~~I went~~ to a kindergarten) starting on that day,as well my sister's,who had only a year to go to enter a university.The outburst of war on the ~~xxxxxxxxxxxxxx~~31st of August detained us from going back to our town where we left all our possessions, taking with us light,summer clothes and sport equipment.We stayed in the place,cut off from our friends and family.The country was



the first to be conquered by the svastikal army. Rapidly, day after day the conquerors made up rules, forming different forbiddings for the Jews; on the shops, cafes, trams and buses, one could see notices like "no dogs or Jews admitted". The Jews were forbidden everything: travelling, buying, working. We were told to wear a white band round our arms, with blue, six armed star, which is our national emblem, so that they could tell from a distance who ~~you~~ we were. The blue David Star - the symbol of an oppressed nation. We wore it with pride, just as an English man would wear his banner. All this did not seem very significant at the time, but it was. it was a systematic method to oppress Jews. It was a slow but sure way. We were given less and less freedom. We could not oppose; how? We had no leaders, no community, no strength, all the young strong people being taken previously into the army and to camps; we were scattered all over the country; all our possessions were taken away from us by the barbaric conquerors.

I did not realize much being then 7 years old; all that I remember distinctly are the bombs in the first few days which fell around us as messangers of war and devastation and the terrible nightmares like nights, spent in a shelter dug deep under the few trees in our garden, and in the forest nearby. My father taught me to read, write and some mathematics. Though not going to school /forbidden!/, I was not backward, my parents and sister being well-educated and only by listening to their conversation was enough to me to learn certain things.

At the end of 1940 we returned to my home town. It was a sad return. All our things were stolen, furniture taken away, and sent to the rulers' country, our home occupied by different people. We had to have false papers, Jews not being allowed to travel. These my parents borrowed from a friend and his family. We stayed with my aunt for a few weeks, until we were told to move into a certain part of the town circled with barbed wire and called Ghetto. We were not allowed to venture outside it. The Christians could go in and out as they pleased. We were allowed one room for 6 people, and our family consisting of four was supposed to have three fourths of one room. We were lucky, my mother opening a surgery and getting this way two rooms and a kitchen. In one room was the surgery and the bedroom and in the other the waiting room and our "lounge". The water was ouside, which was very ~~un~~inconvenient, no one being allowed to stay out after 4 p.m. under the punishment of having one's head off! We borrowed the furniture from our friends, who were fortunate enough to save it. My mother's surgery was completed by her friend a dentist, with whom she worked as an assistant after she left the university. He was very friendly and helped us a lot, his wife was to save my life later on. One evening my mother was standing in the doorway, watching the sunset when a car came and picked her up; she returned next day after paying the policeman.

Months passed. One terrible morning there were notices that all the men from 11 upwards were to go to a meeting place, if any did not do so they would be shot immediately. My father and our friends went - we thought that we would not see them again. However, they came back, they were given work. People who would not or could not come were killed. This event took place in September 1942. On September 18th there was a great Jewish holiday. We knew that the occupating murderers were preparing for great mass-killing action. I was sick at the time. On the well-remembered day a friend of my mother, wife of the dentist who helped to provide my mother with dental instruments, came to take me away. She was also a dentist, but not such a good one as her husband. She was also very religious and devoted catholic, but that not only did not stop her, but encouraged her to save many Jewish children's lives, ~~xx~~ with the risk of her own. I would not go at first, but after a long persuasion and my sisters's promise to join me soon, I went away in tears with my belongings wrapped in few minutes in my hand. As soon as we walked out I controlled myself and even managed to say that it was a fine evening when we passed someone in the street. We simply walked out of the Ghetto to this lady's house which was not very far off and no one ~~could~~ had stopp us, police being busy preparing for the next day.

Here begins a great change in my life. Until then I was the most important person at home, the only child, my sister being by then almost one of the grown-ups. I was very spoiled and even all the terrors of Ghetto did not stop me from having things I wanted, my parents doing all they could to provide them. Now I was left with a person whom I hardly knew, who taught me to kneel and pray. I stayed with the lady for a week, curing ~~out of~~ a bad cold I had, crying my eyes out in the pillow, not daring to make any sound in fear someone might hear me. I was given many different names until my patroness bought special papers for me. I had to learn by heart my name, the date of birth as well as that of my parents', and name of the place where I was supposed to come from, plus a long tale of my life and loss of parents.

I was then taken to a village where I stayed for 8 weeks, as the people recognized me as a Jewess, calling me names and in the end nearly reporting me to the Gestapo - the conquerors' police. I went to another town, where I was a week, then I went to the oldest city of my country. First thing I have learned after leaving the Ghetto was the prayer, while learning it I hardly realized that one day it would save my life. When my benefactoress and myself arrived in the city, an officer took us to a police building accusing us of being Jewesses. He looked through the lady's papers and thinking that I was her daughter, luckily did not ask for mine. It was late in the evening and in the doorway of the police station was dark. The "SS man" took little notice of me and I knew that he would soon turn his torch on my face. The fear was strangling me, but I understood well and my face was covered with a most innocent looking smile; this smile cost me a lot, but it probably saved my life. The man asked me then to kneel down and pray - I did so and he let us go. The lady went back to her, as well as mine, hometown, leaving me with her parents, with whom I stayed three months. They were old people very nervous and frightened, they shared their fear with me. I did not know their name or the name of the street I lived on. I was never allowed to look through the window or walk quickly, I had to speak in whisper. All daylong - I stayed on a carpet behind a bed in the bedroom. If i heard any steps or a knock I hid myself underneath it. The maid of the couple did not know of my existence and you can imagine the state of my nerves when she was dusting in the room in which I sat in, sewing behind a flower-pot. My hiding place was then under the window and the winter being very severe, I caught a bad cold. One day the maid was making the fire, when I suddenly sneezed. She jumped as if she ~~would~~ have seen a ghost, but the lady hearing the sneeze, came hurriedly into the room, sneezing rapidly. This life could not go on for long - me sitting all the time mending stockings, half dead with fear and the people worrying themselves greatly. /

The people had a friend who ~~had~~ was a Protestant ~~friend~~ priest and his wife a professional singer. I went to her sister, a widow with a dagghter, a young clever girl, who had an office position, keeping her mother and herself. The lady died after a year, having a lung and heart trouble. I stayed with her daughter. My patroness came to visit us from time to time, but she never told me what happened in Ghetto after we left it.

The life became very "hot" for me. The police were asking me questions on the street, and I could hear allround me "Jewess, Jewess". I naturally did not want anyone to know where I lived so I circled around the block for a few times, any time I wished to enter the house. I said nothing of it at home, being afraid of being thrown out; but this situation could not go on for very long. I had to leave the place. I went to the girl's aunt, a very nice lady. I did all the work at home, including washing, and even tried to earn some money, by selling newspapers and cigarettes, but this was too dangerous and I gave it up.

The people were frightened to keep me any longer and they returned me to the ~~Protestant~~ priest who took me into his home. His wife was a real shrew and I had a very bad time. I acted as her niece, hoping the real one would not come to visit her

When the liberating armies came, we saw a lot of fighting, our house being next to a bridge andit being used as a fortress of the withdrawing army. We were left without water, food, windows or doors, which were broken by the explosion of mines on the bridge, which has been destroyed, our only communication with the rest of the town being through the thick ice on the river /luckily the weather was very cold this year./ In Spring when the snow and ice melted many people were drowned trying to row across over the overflowing river. The lady being injured and the priest busy looking for a place to live in, the house being ruined, /we lived in the cellar/ I had to do all the work, trying to keep the place warm, without windows and very little fuel and carrying water from a well a mile away, which was always surrounded by a great crowd. After a few days or weeks, which seemed to me like months, of cold and hunger, we moved to a house, and dug out some potatoes from a cellar. The priest got a job as a clerk and food came from the country. The people did not want to give me back, to my patroness, who, they said, wanted to make me a nun in a convent. I went to some evening classes for 4 months, ending this way my elementary school, I could go to second year in High School. But just as I did so in 1945 my aunt, after finding out where I was, took me from the people.

I knew nothing about my family and I was almost sure nobody has survived. My cousins /five of them/ some of them married, have gone abroad in 1939 when the War started. After this terrible massacre of war each of them found himself in a different country, and even on a different continent, with their wifes far away from them. They all wrote to the Mother-Country, asking about their family, and found that their mothers fathers, friends and homes were all gone. My aunt and myself were the only lucky survivers.

My aunt took me to the Capital City.- It was the most terrifying sight: blocks, streets, all consisted of blood splashed bits of stone, bricks, furniture, dead bodies and fragments of cloths. Ruin and death. In this picture of destruction between the fallen houses, the few survivers swarmed seeking a home and between those ruins one could see in a not quite to the ground bombed house, a sprinkle of life - a blanket in a door or a window. My aunt's son, a little innocent boy, of six, was in her eyes taken by ~~the~~ one of ruthless, pitiless conquerors by his legs and smashed against the wall of his home to death.

My cousin who was in a different country wanted to bring me to him as well as his wife who was somewhere else. While I was awaiting my passport I stayed in a children's home. I had a very good time there. My passport came after 2 months. And so I left my Mother Country, in November 1945. I was rather glad to leave the scene of so many tragedies, the grave of all my friends and family, however I felt some pain inside of me, for I knew that I would never see the Country again.

I arrived to my new country, dizzy, after a very rough passage through a stormy sea. I went to the Capital City of this country, new to me in every respect. This town is the biggest town of the world. The language was terribly difficult for me, but I overcame it /not quite, this difficulty still far from being mastered./ when my cousin sent me to a boarding school, where I was for five months. When I came back I went to a high school into 3rd year. Meanwhile my cousin decided to emigrate into this country, where he had relatives and so after 6 months and finishing 3rd year, in August 1948 I left the school and the country by myself, My cousin not being able to get transport so soon was to follow me with his wife.

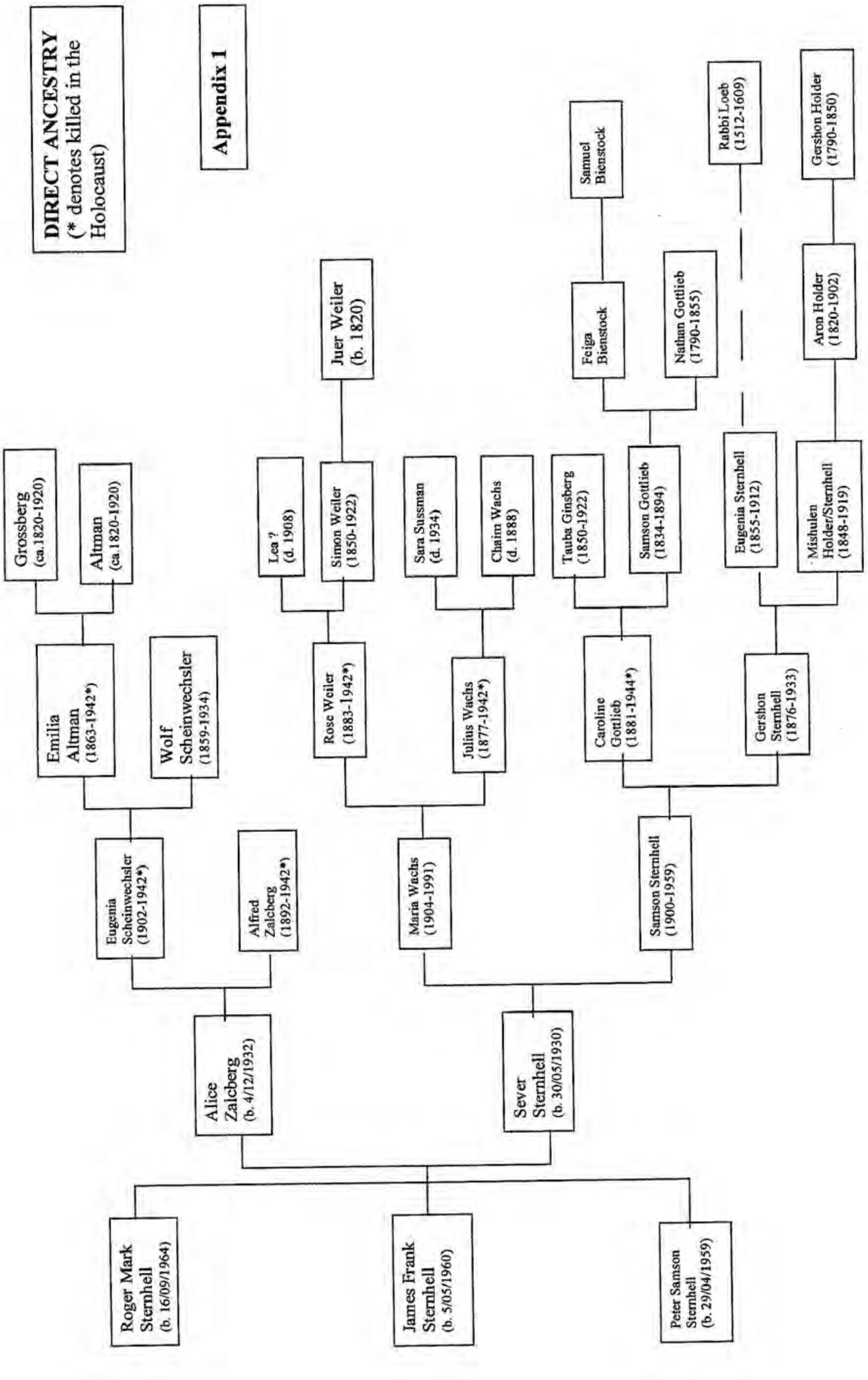
I arrived here 4 months ago, after a long and very interesting voyage. I am hoping that this the end of my gipsy-like life, though I have changed the place of living four times already here. However I think that I will soon settle down for good, finish my school and become a dentist.

Sydney, 2nd April 1949. Alice Zalcber

APPENDICES

Appendix 1

DIRECT ANCESTRY
(* denotes killed in the Holocaust)

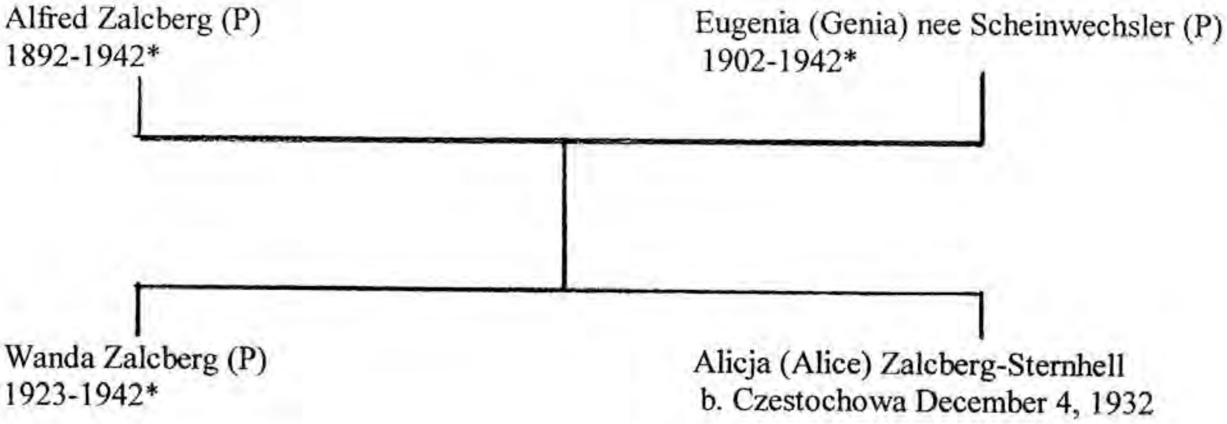


Appendix 2

THE ZALCBERGS came from Czestochowa, a holy city in Western Poland and the site of the monastery "Klasztor Jasnogorski", which withstood a siege by the Swedes during the Thirty Years War in the XVIIth century, protected by a miraculous icon "The Black Madonna", which is still in existence.

We know very little about the Zalcbergs. The parents of your **direct ancestor, Alfred (Fred) Zalcberg** lived in Chestochowa. His mother (whom Alice knew before 1942) was a sister of a Mrs Imich and some Imichs [she had 3 sons: Jerzy (George), Alexander and Stanislaw] now live in Israel, France and Canada. His father died before the war and Alice does not remember him.

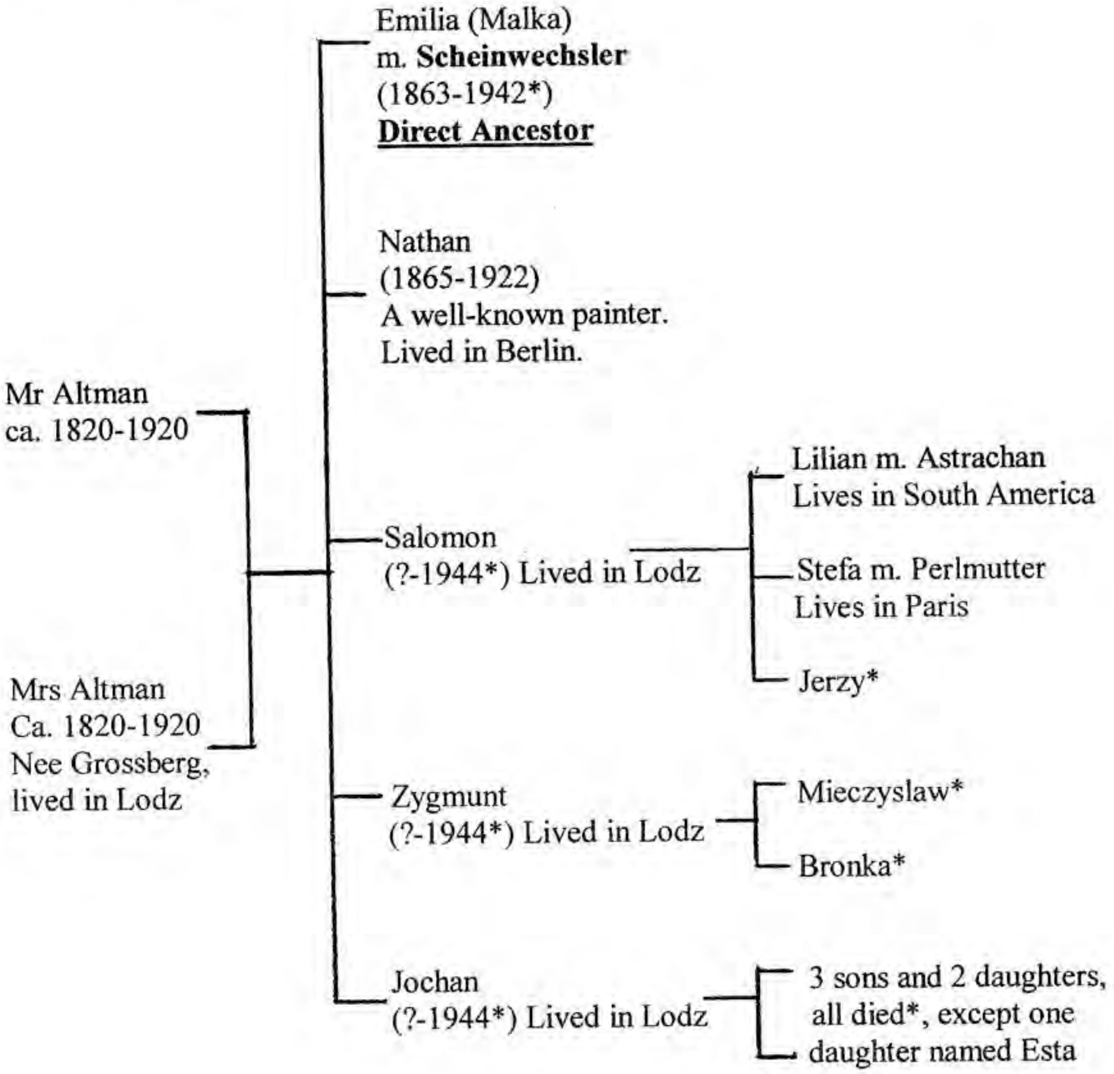
Alfred Zalcberg had only one sibling, a sister named Hanka who was a poetess, married a Polish Catholic who left her before the war and who had one daughter, Irena. Alice knew both Hanka and Irena. Their fate is unknown.



* denotes: killed in the Holocaust
(P) denotes that a photograph is reproduced in this book

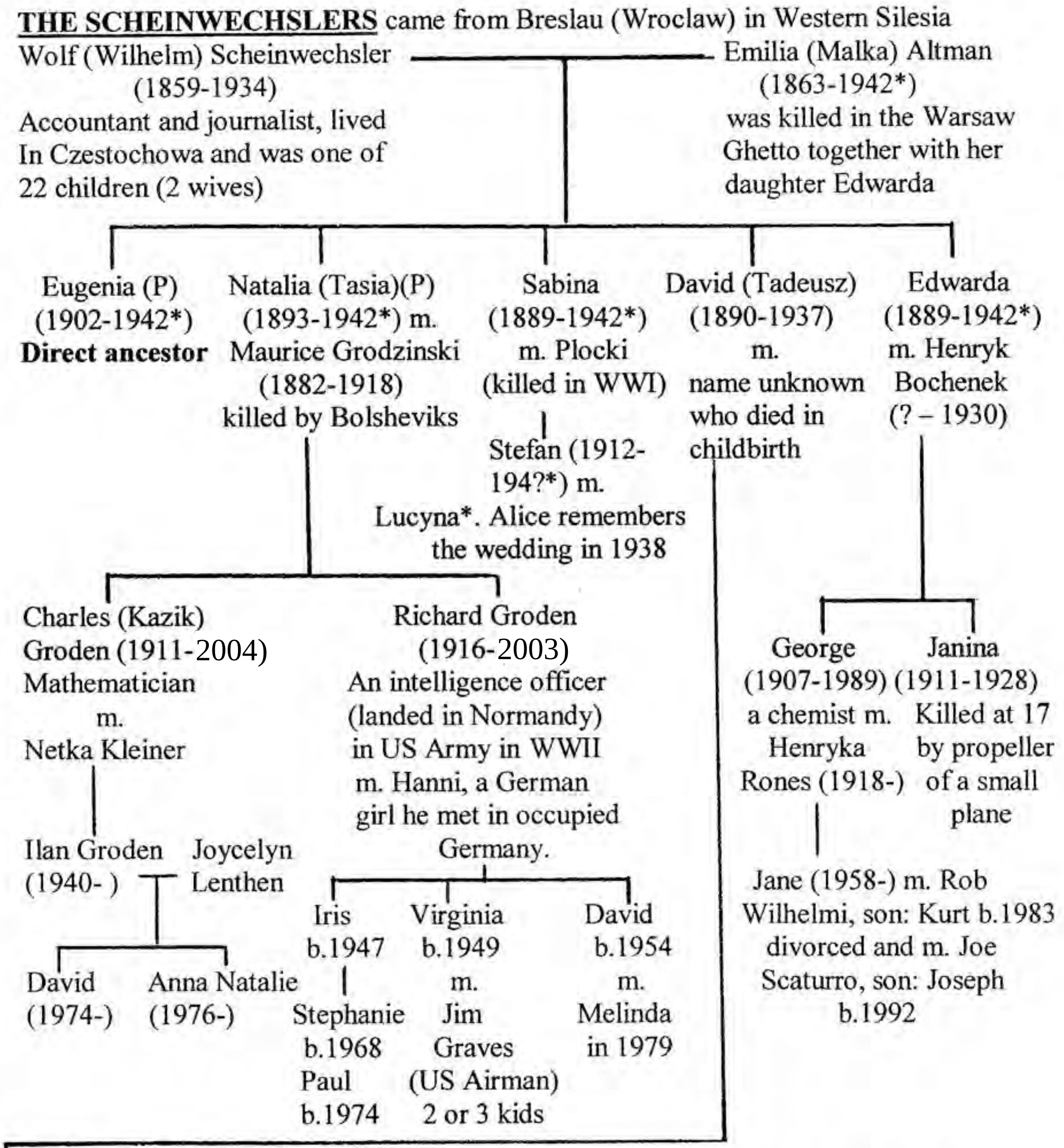
Appendix 3

THE ALTMANS were a well-established family who lived in Western Poland. Legend has it that a remote ancestor, a rabbi in ca. 11th century, was "King for a day" (really a regent) of Poland. Alice's great grandparents (whose given names we don't know) lived in Chestochowa. They both lived to a great age.



* denotes: killed in the Holocaust

Appendix 4



THE SCHEINWECHSLERS came from Breslau (Wroclaw) in Western Silesia

Wolf (Wilhelm) Scheinwechsler
(1859-1934)
Accountant and journalist, lived
In Czestochowa and was one of
22 children (2 wives)

Emilia (Malka) Altman
(1863-1942*)
was killed in the Warsaw
Ghetto together with her
daughter Edwarda

Eugenia (P)
(1902-1942*)
Direct ancestor

Natalia (Tasia)(P)
(1893-1942*) m.
Maurice Grodzinski
(1882-1918)
killed by Bolsheviks

Sabina
(1889-1942*)
m. Plocki
(killed in WWI)

Stefan (1912-
194?*) m.
Lucyna*. Alice remembers
the wedding in 1938

David (Tadeusz)
(1890-1937)
m.
name unknown
who died in
childbirth

Edwarda
(1889-1942*)
m. Henryk
Bochenek
(? – 1930)

Charles (Kazik)
Groden (1911-2004)
Mathematician
m.
Netka Kleiner

Ilan Groden
(1940-)

Joycelyn
Lenthen

David
(1974-)

Anna Natalie
(1976-)

Richard Groden
(1916-2003)
An intelligence officer
(landed in Normandy)
in US Army in WWII
m. Hanni, a German
girl he met in occupied
Germany.

Iris
b.1947

Stephanie
b.1968
Paul
b.1974

Virginia
b.1949
m.
Jim
Graves
(US Airman)
2 or 3 kids

David
b.1954
m.
Melinda
in 1979

George
(1907-1989)
a chemist m.
Henryka
Rones (1918-)

Jane (1958-) m. Rob
Wilhelmi, son: Kurt b.1983
divorced and m. Joe
Scaturro, son: Joseph
b.1992

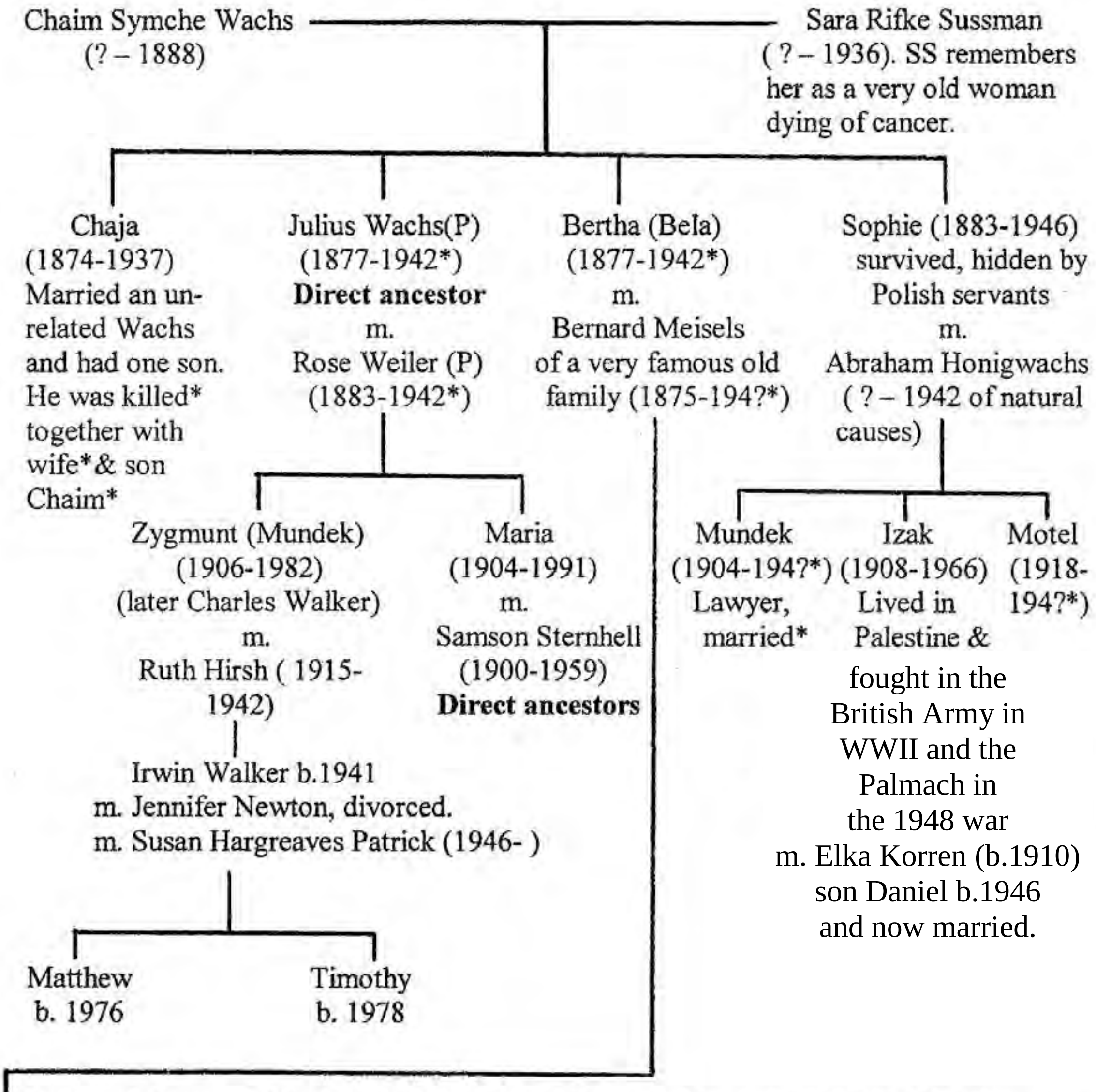
Janina
(1911-1928)
Killed at 17
by propeller
of a small
plane

They had one son, Henryk (Henio) (1911-1955) who was a lawyer, married Lydia (divorced) and survived the war in Roumania. Married Lucyna Berland and took on the name of Stanicki. They had one daughter Joanna, b.1953 who in 1979 was a student in Lyon, France. David Scheinwechsler had a second marriage to Franka (see "Your Mother's Story") who was alive in Warsaw in 1979. They had a son Wojtek (1935-1942*) whom Alice remembers as a little boy and who was murdered by the Germans in the Warsaw Ghetto by having his skull smashed against a wall.

* denotes: killed in the Holocaust. (P): denotes photograph reproduced in this book.

Appendix 5

<u>**THE WACHSES**</u> came from Grodek Jagielonski, a small town about 30km from Lwow



Chaim Symche Wachs
(? – 1888)

Sara Rifke Sussman
(? – 1936). SS remembers her as a very old woman dying of cancer.

Chaja
(1874-1937)
Married an unrelated Wachs and had one son. He was killed* together with wife*& son Chaim*

Julius Wachs(P)
(1877-1942*)
Direct ancestor
m.
Rose Weiler (P)
(1883-1942*)

Bertha (Bela)
(1877-1942*)
m.
Bernard Meisels
of a very famous old family (1875-194?*)

Sophie (1883-1946)
survived, hidden by Polish servants
m.
Abraham Honigwachs
(? – 1942 of natural causes)

Zygmunt (Mundek)
(1906-1982)
(later Charles Walker)
m.
Ruth Hirsh (1915-1942)

Maria
(1904-1991)
m.
Samson Sternhell
(1900-1959)
Direct ancestors

Mundek
(1904-194?*)
Lawyer, married*

Izak
(1908-1966)
Lived in Palestine & fought in the British Army in WWII and the Palmach in the 1948 war
m. Elka Korren (b.1910)
son Daniel b.1946
and now married.

Motel
(1918-194?*)

Irwin Walker b.1941
m. Jennifer Newton, divorced.
m. Susan Hargreaves Patrick (1946-)

Matthew
b. 1976

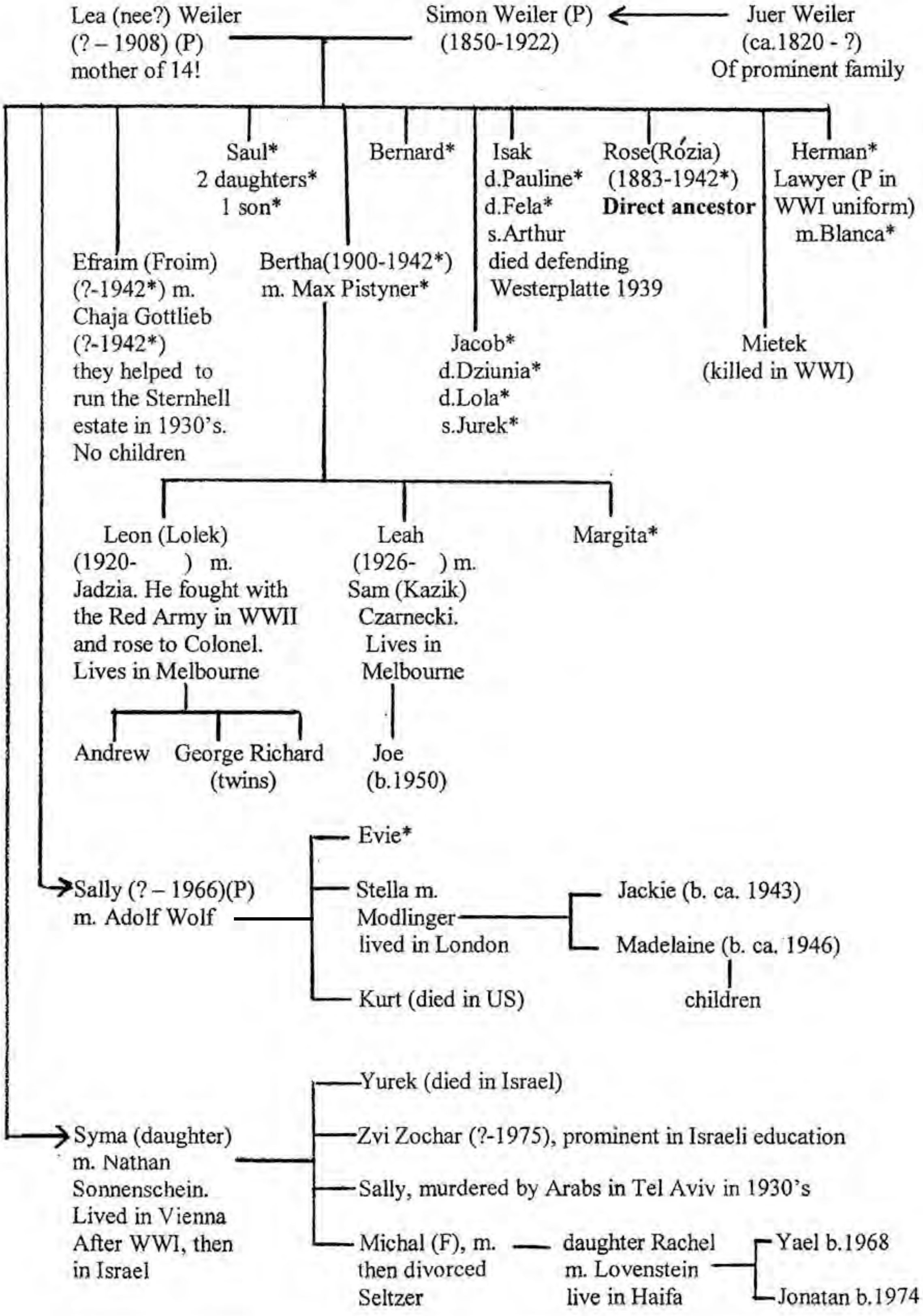
Timothy
b. 1978

<u>**Bela and Bernard (Dov) Meisels**</u> had five children. **1.Mundek** (1900-194?*) who never married. **2.Rose** (1898-1942*), who married Maurice Schlager* They had a daughter, Elizabeth who was killed* at 19 years of age. **3&4 Twins, Malie** (1909-1941*) **and Miriam** b.1909 who lives in Tel Aviv and married late in life (1984) Fred Lind. **5.Fanny** (1899-1995) m. Otto Lederer (1900-1991). They changed their name to **Lidror** and lived in Israel together with their 3 children: **(i) Rafael (Rafi)** (b.1927) who married Ruth (b.1930) and they have 3 children, <u>Nurit</u> (b.1958), who married Enrico Attas in 1984 daughter Niva b.1990; <u>Nitza</u> (b.1959) married Yoram Barhalevi; and <u>Ghadi</u> (b.1963). **(ii) Michal** (b.1920) who married David Seidman. They have two girls. Jael (b.1962, married Hosik 1983, two children :Noa(F), b.1988 and Jonathon, b.1992) and Wered, b.1963. **(iii) Amos** b.1935 who married Aliza. They have a daughter Idit, b.1969. **(iv) Nadev** (b.1941) who married Harriet ? (divorced). They have 3 daughters: Anat (b.1974), Hagid (b.1976) and Zeva (b.1981). ***You have met many of these members of the Israeli branch of the family.***

* denotes: killed in the Holocaust. (P): denotes photograph reproduced in this book

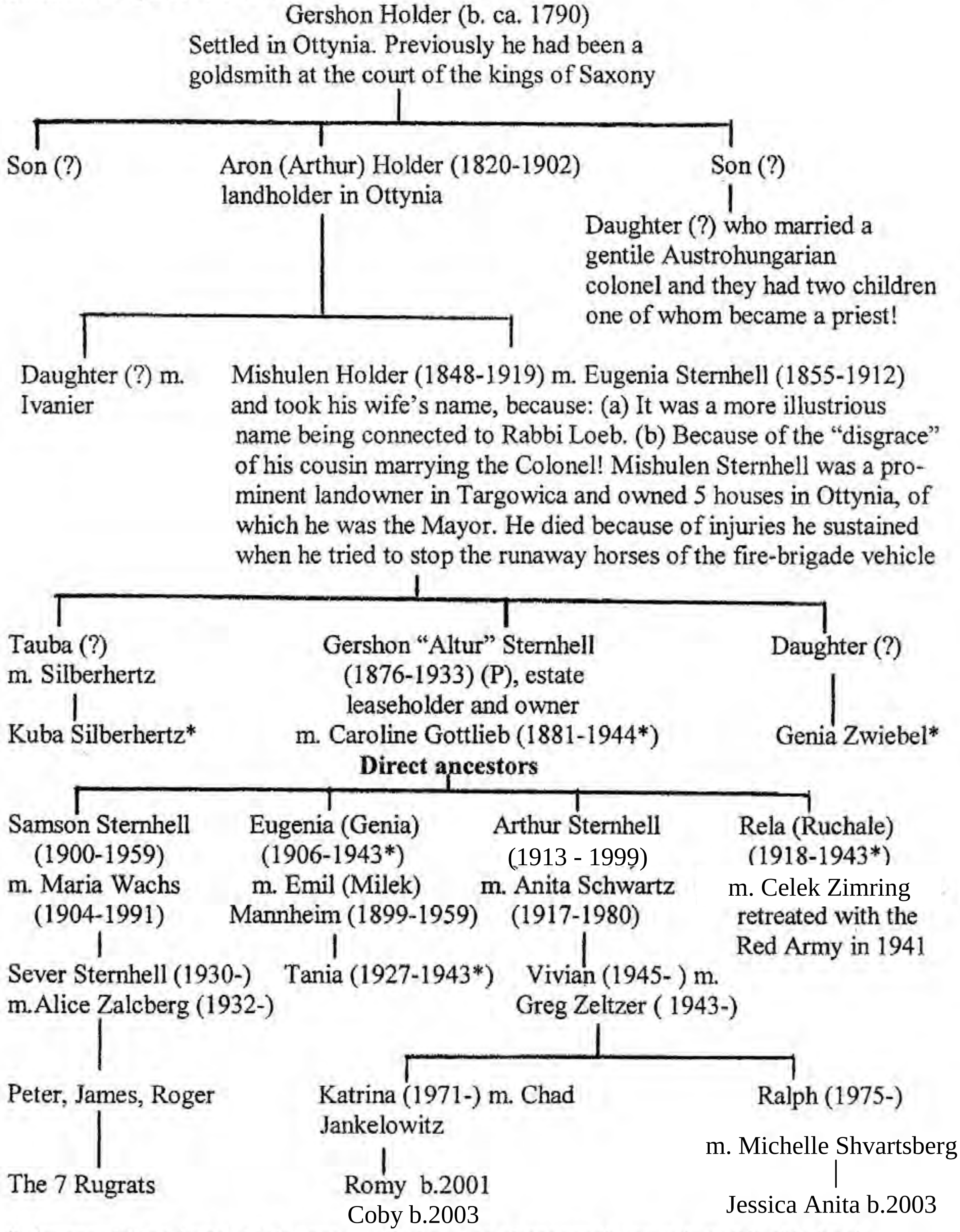
Appendix 6

THE WEILERS came from Ottyniowice, a small town on the river Stryj, East of Lwow.



*denotes: killed in the Holocaust. (P) denotes photograph reproduced in this book

THE STERNHELLS AND THE HOLDERS lived in Ottynia, a small town near Stanislawow, East of Lwow.



Gershon Holder (b. ca. 1790)
Settled in Ottynia. Previously he had been a goldsmith at the court of the kings of Saxony

Son (?)

Aron (Arthur) Holder (1820-1902)
landholder in Ottynia

Son (?)

Daughter (?) who married a gentile Austrohungarian colonel and they had two children one of whom became a priest!

Daughter (?) m.
Ivanier

Mishulen Holder (1848-1919) m. Eugenia Sternhell (1855-1912) and took his wife's name, because: (a) It was a more illustrious name being connected to Rabbi Loeb. (b) Because of the "disgrace" of his cousin marrying the Colonel! Mishulen Sternhell was a prominent landowner in Targowica and owned 5 houses in Ottynia, of which he was the Mayor. He died because of injuries he sustained when he tried to stop the runaway horses of the fire-brigade vehicle

Tauba (?)
m. Silberhertz

Kuba Silberhertz*

Gershon "Altur" Sternhell
(1876-1933) (P), estate
leaseholder and owner
m. Caroline Gottlieb (1881-1944*)

Daughter (?)

Genia Zwiebel*

Direct ancestors

Samson Sternhell
(1900-1959)
m. Maria Wachs
(1904-1991)

Sever Sternhell (1930-)
m.Alice Zalcberg (1932-)

Peter, James, Roger

The 7 Rugrats

Eugenia (Genia)
(1906-1943*)
m. Emil (Milek)
Mannheim (1899-1959)

Tania (1927-1943*)

Arthur Sternhell
(1913 - 1999)
m. Anita Schwartz
(1917-1980)

Vivian (1945-) m.
Greg Zeltzer (1943-)

Katrina (1971-) m. Chad
Jankelowitz

Romy b.2001
Coby b.2003

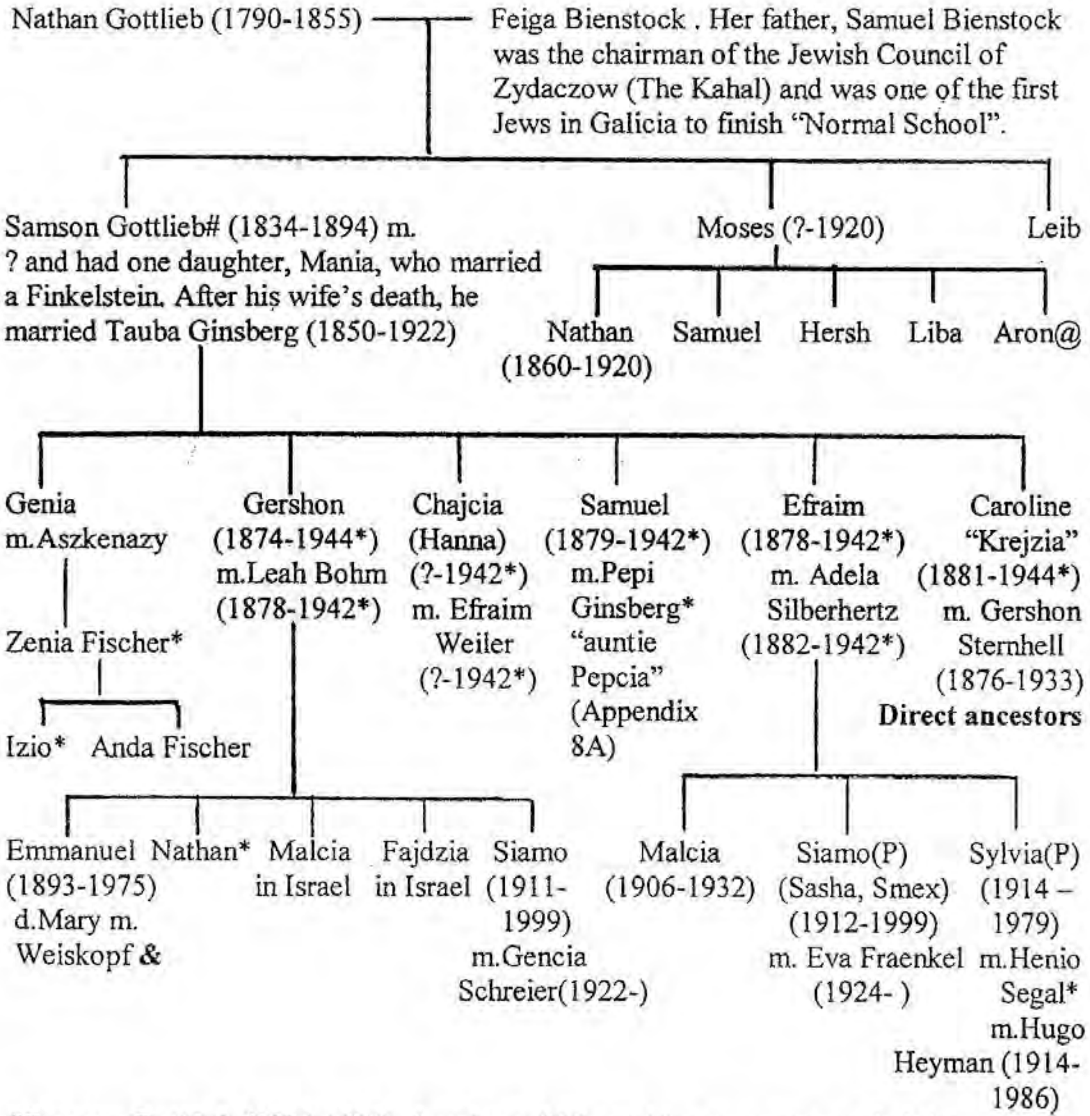
Ralph (1975-)
m. Michelle Shvartsberg

Jessica Anita b.2003

Rela (Ruchale)
(1918-1943*)
m. Celek Zimring
retreated with the
Red Army in 1941

* denotes killed in the Holocaust. (P) denotes photograph reproduced in this book

THE GOTTLIEBS lived in a Zydaczow, a small town in Eastern Galicia.



Nathan Gottlieb (1790-1855)

Feiga Bienstock . Her father, Samuel Bienstock was the chairman of the Jewish Council of Zydaczow (The Kahal) and was one of the first Jews in Galicia to finish "Normal School".

Samson Gottlieb# (1834-1894) m. ? and had one daughter, Mania, who married a Finkelstein. After his wife's death, he married Tauba Ginsberg (1850-1922)

Moses (?-1920)

Leib

Nathan (1860-1920)

Samuel

Hersh

Liba

Aron@

Genia m.Aszkenazy

Zenia Fischer*

Izio* Anda Fischer

Gershon (1874-1944*) m.Leah Bohm (1878-1942*)

Emmanuel (1893-1975) d.Mary m. Weiskopf &

Nathan*

Malcia in Israel

Fajdzia in Israel

Siamo (1911-1999) m.Gencia Schreier(1922-)

Chajcia (Hanna) (?-1942*) m. Efraim Weiler (?-1942*)

Samuel (1879-1942*) m.Pepi Ginsberg* "auntie Pepcia" (Appendix 8A)

Efraim (1878-1942*) m. Adela Silberhertz (1882-1942*)

Malcia (1906-1932)

Siamo(P) (Sasha, Smex) (1912-1999) m. Eva Fraenkel (1924-)

Sylvia(P) (1914 – 1979) m.Henio Segal* m.Hugo Heyman (1914-1986)

Caroline "Krejzia" (1881-1944*) m. Gershon Sternhell (1876-1933) **Direct ancestors**

#Samson Gottlieb (1834-1894). As a boy of 16, working as a grocery clerk in Czerniowce, he caught the eye of a Habsburg duke, who took him on a world tour. The duke died on the tour stranding the young (ca.18) Samson in Istanbul, where he lost all his money gambling. Back in Zydaczow, he became a successful merchant (grocer, bottler of liquor, tobacco wholesaler and "Keiserlich und Koninglich Haupttrafficant"). He was an officer in the district (powiat) administration and an alderman.

@Aron Gottlieb (dates unknown) was a mayor of Zydaczow. He owned the brickworks (SS remembers them), a restaurant and other businesses. He was childless, but had two illegitimate children by a Ukrainian woman, whom he educated. The boy, Adam, became the Chief of Police in Katowice. Samson Sternhell recalled visiting him in Katowice and playing poker with him. The girl, Eva, married a judge.

& Mary Weiskopf lives in Israel. She has a daughter Cyla and a son Gad. The son is married and has a daughter Ayalah (b.1970), a son Elad (b.1973) and a son Itzhak (b.1977).

*denotes killed in the Holocaust. (P) denotes that a photograph is reproduced in this book

Appendix 8A

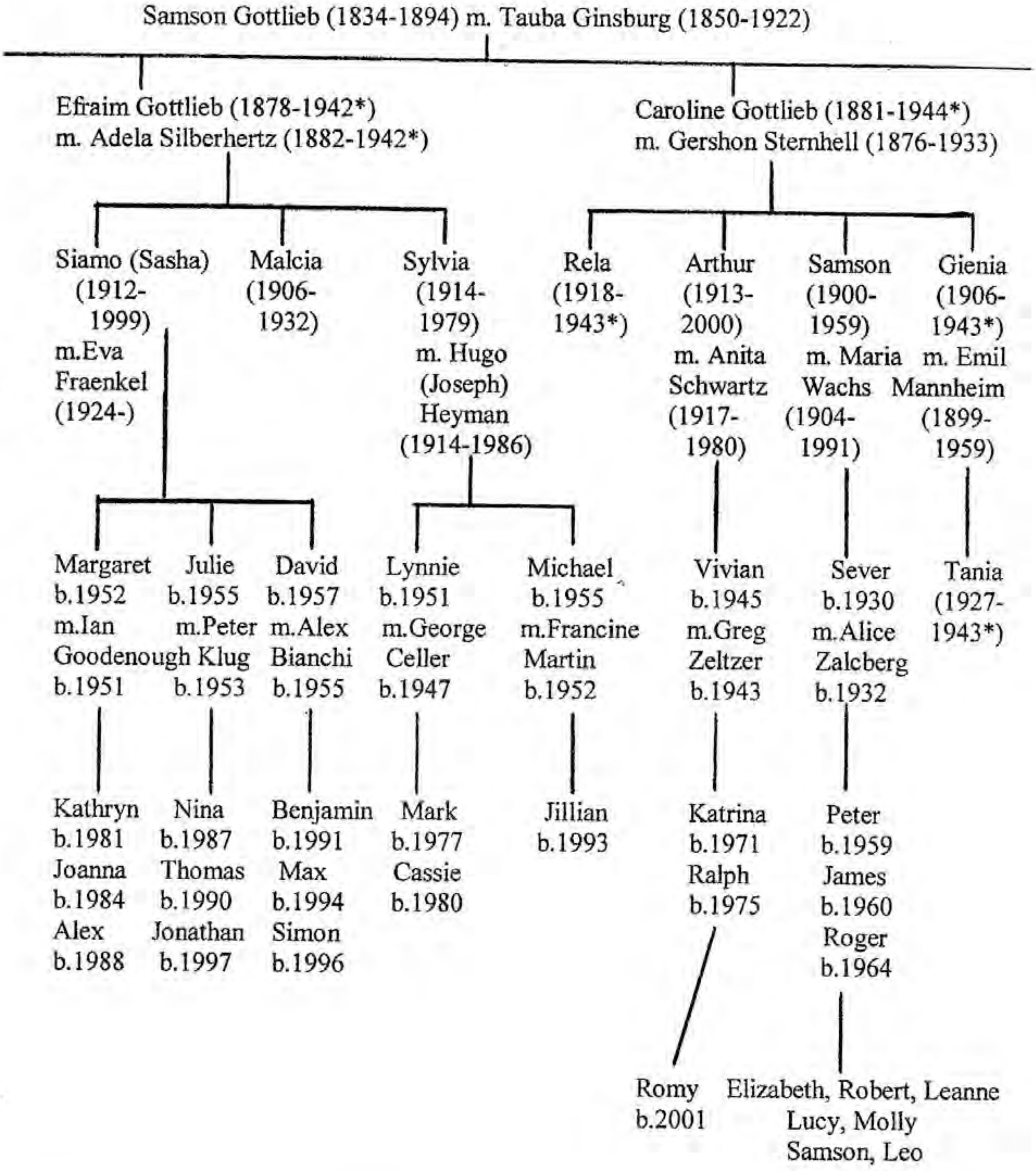
INFORMATION FROM GENCIA GOTTLIEB (nee SCHREIER), February 2002
The brother of Tauba Ginsberg (Appendix 8), Israel Ginsberg (son of the rabbi of Chodorow), was the father of **The Ginsberg sisters.** There were 6 of them and I think of them as the Stanislawow branch:

1. Pepi (?-1942*) married Samuel Gottlieb* (see Appendix 8). I remember her well, as “my auntie Pepcia”. They lived in Stanislawow and had 3 sons, all of whom I remember as young men. Kuba* (a ginger-headed, pleasant young “uncle”), Gustav* (slightly older) and Siamo*, who was a schizophrenic. All perished.
2. Amalia (Malcia) (1890-1943*), married Marcus Schreier and was the mother of Gencia (Appendix 8) and Salomea (Salka) (1920-1943*).
3. Zenia* (pronounced Zhenia), married Wiesner and was the mother of Klara (1922-1942*) and Sydzia (1927-1942*), whom I remember well from both Stanislawow, where she lived and from shared vacations at my grandmother Carolina’s place.
4. Henia*, married Fingerman and was the mother of Ulek, diminutive of “Srulek”, which is diminutive of Israel, (1933-1942*). They lived in Stanislawow and I remember him together with Sydzia (in fact, I always thought of them as siblings!). Most of the Stanislawow branch perished early at the hands of Einsatzgruppe C (Erhardt Kroeger’s Sonderkommando 6 was headquartered in Stanislawow) and the dates of their deaths given as “1942*” were just as likely “1941*”. There is a horrible story of Ulek being pushed alive into a mass grave and of his grandmother trying to save him by lying on top of him. Needless to say, both perished.
5. Sophie*, married Max Bohm*. Their daughter Gustie married Emmanuel Gottlieb and was the mother of Mary Weiskopf, whose descendents live in Israel (see Appendix 8).
6. Karolina* married Marcus Wolin and was the mother of Lusia (b.1920) who married Karol Celler. They survived on Aryan papers and in post-war Poland he changed his name to Marian Wajda. The Wajdas live in Vienna, visited Australia and are the parents of George Celler, the husband of Lynnie Hayman (the American branch, Appendix 9). There is also a connection between the Wajdas and Riky Thieben.

The children of Zenia Fischer. In addition to information in Appendix 8:
Izio Fischer* was murdered by Ukrainians in July 1941 after the Red Army withdrew, in a local mass murder of many Jewish professionals in Zydaczow. There was also another brother, Wisio,* who perished later. Anda Fischer (whom I remember) survived on Aryan papers close to where my grandmother Caroline Sternhell (nee Gottlieb) was also living on Aryan papers. At one stage (1943 or 1944) all Poles and Ukrainians above the age of 14, had to obtain identity documents, the so-called Kennkarte. Anda applied for a Kennkarte and was not detected. My grandmother (then 62 or 63 years old) could not face this, was denounced and shot by the SS. When the Red Army returned in 1944, Anda returned to Zydaczow and found Siamo and Gencia (who survived by being hidden in a loft by a Pole). Tragically, Anda lost a leg in a train accident, but survived this as well and finished up in Palestine, where she married.

Appendix 9

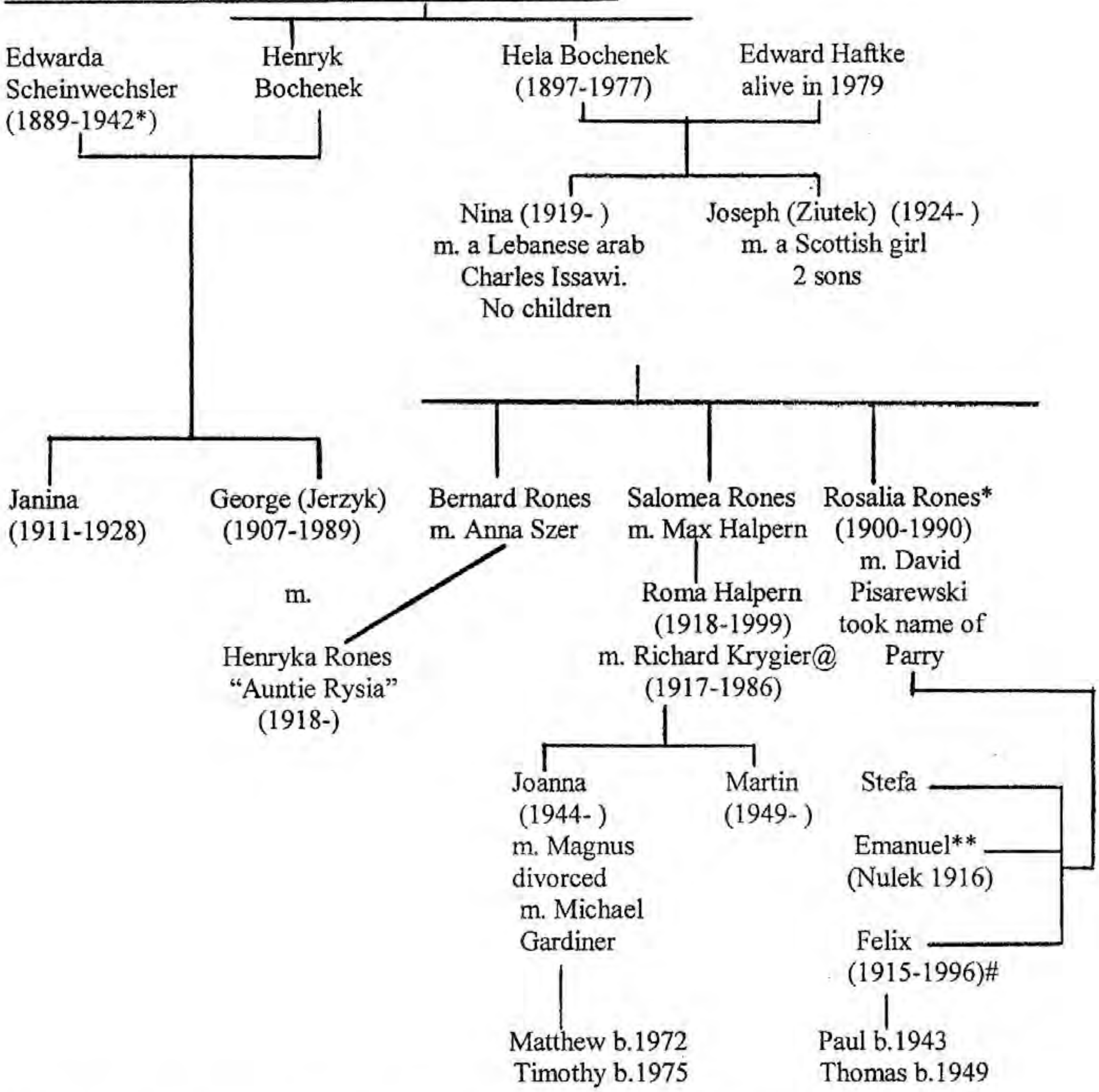
THE CONNECTION BETWEEN GOTTLIEBS AND STERNHELLS



* Denotes killed in the Holocaust

Appendix 10

CONNECTIONS via BOCHENEKS and RONESES



*Another of the Rones sisters, Eleonora (Lonia) married Mark Segal. They have a son, Bogdan (Robert) b.1932 who married Pat. They have a son Mark and a daughter Donna. Robert Segal served in the US Navy (submarines) and retired as a Lt. Commander.

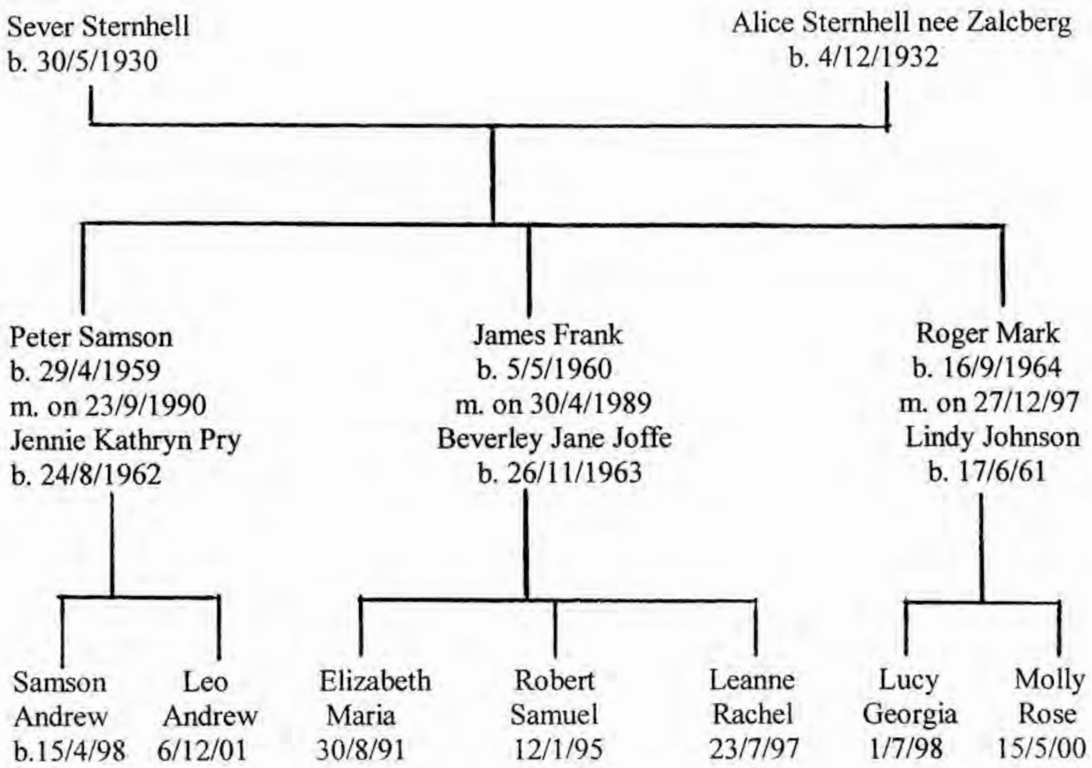
** Fought in General Anders' Polish Army and took part in the battle of Monte Casino

@ Founder of the *"Quadrant"* magazine.

Hero of Polish WWII Resistance. Awarded the highest military decoration (Virtuti Militari). This is described in his book *"Life in three dimensions"*.

Appendix 11

THE NEW TREE



Left to right: Standing: Beverley; Sitting: James holding Leanne (6),
Sitting in front: Robert (8); Standing behind James: Elizabeth (11);
Sitting centre: Jennie with Leo (1.5) and Peter with Samson (5); Lindy with Molly (3);
Roger with Lucy (5); Sitting in the back: Sever and Alice.
Photo taken at Alice and Sever's 50th wedding anniversary party on March 22, 2003.