Liversidge Research Lecture

No. 22
1980

NUCLEAR MAGNETIC RESONANCE IN POLYMER STUDIES

STANLEY R. JOHNS

The Royal Society of New South Wales

Stanley Roy Johns

Liversidge Research Lecturer No. 22, 1980.

STANLEY ROY JOHNS 1935-1986

Stanley Roy Johns was born in Cessnock, N.S.W. on 8 July, 1935. His secondary education was at Cessnock High School, and then he went to the University of New England, graduating B.Sc. (Hons) in 1957. In 1957 he was a Teaching Fellow at the University of New South Wales, then he proceeded to the University of Sydney as a NSW State Cancer Council Research Student (1958-1960) to work for his Ph.D. degree under Professor C.W. Shoppee. After graduating Ph.D. in 1961, he was a Burroughs Wellcome Research Fellow for the period 1961-1962 at the Department of Pharmaceutical Chemistry, University of Sydney where he worked in collaboration with Professor S.E. Wright. During 1962-1964 he was a Postdoctoral Fellow at the NRC (National Research Council) Ottawa, Canada where he worked with Dr. Leo Marion. In 1964 he was appointed as Research Scientist at the CSIRO Division of Organic Chemistry that later became the Division of Chemicals and Polymers. He was a Visiting Associate at the California Institute of Technology for six months during 1972 with J.D. Roberts. In a highly productive collaboration with Dr. J.A. Lamberton on the Chemistry of Australian plant extractives, Stan Johns' contribution was mainly in the applications of ^{1}H and ^{13}C n.m.r. spectroscopy in structure determination. He also applied ^{13}C n.m.r. spectroscopy in a study of the structure and shape changes in biomembranes, and used various n.m.r. spectroscopic techniques in studies of the structure and stereochemistry of polymers. In 1983 he was one of six Australian scientists invited to participate in a joint Australian, West German Science Agreement Workshop on the "Biophysics and Biochemistry of Photosynthesis" held at Osnabruck in West Germany.

Stan Johns was very active in affairs of the Royal Australian Chemical Institute (RACI) - from 1978 to 1984 he was a member of the Executive Council, and in 1979 he was President of the Victorian Branch. His death from cancer at the relatively young age of 51 deprived CSIRO of an excellent chemist, and a popular colleague.

Honours and Awards

1980 Liversidge Research Lecture, Royal Society of New South Wales

Biographical Source

(1) Willing, R.I. and Spurling, T.H., 'Dr Stanley R. Johns 1935-1986', *Chem. in Aust.*, 1986, **53**, 437.

(2) Willing, R.I., personal communication.

Scientific Publications of S.R. Johns

A list of 157 publications by S.R. Johns is given here. A large number of these were on the structure determination of alkaloids from Australian plants, carried out in collaboration with his CSIRO colleague Dr. J.A. Lamberton.

Scientific Publications of S.R. Johns

(A) Pre-CSIRO

1. Johns SR and Stimson VR. The kinetics of alkyl-oxygen fission in ester hydrolysis. VII. *p*-Methoxydiphenylmethyl Benzoate. *J. Chem. Soc*., 1960, 467-8.

2. Johns SR and Wright SE. Metabolism of carbazole. *Experientia,* 1962, **18**, 416-7.

3. Cymerman-Craig J, Johns SR, and Moyle M. Amine exchange reactions. Mannich bases from primary aliphatic amines and from amino acids. *J. Org. Chem.*, 1963, **28**, 1779-83.

4. Johns SR and Wright SE. Metabolism of carbazole in rats and rabbits. *J. Med. Chem.*, 1964, **7**, 158-61.

(B) CSIRO - Papers on Natural Products Chemistry

5. Johns SR and Lamberton JA. Alkaloids of *Mackinlaya* species (Family Araliaceae). *J. Chem. Soc., Chem. Commun*., 1965, 267.

6. Johns SR and Lamberton JA. Magnetic non-equivalence of the epoxide ring (C-6 and C-7) protons of scopolamine. *J. Chem. Soc., Chem. Commun*., 1965, 458-9.

7. Johns SR, Russel JH and Heffernan ML. Ficine, a novel flavonoidal alkaloid. *Tetrahedron Lett*., 1965, 1987-91.

8. Fitzgerald JS, Johns SR, Lamberton JA and Redcliffe AH. 6,7,8,9-Tetrahydropyridoquinazolines, a new class of alkaloids from *Mackinlaya* species (Araliaceae). *Aust. J. Chem*., 1966, **19**, 151-9.

9. Johns SR and Lamberton JA. New histamine alkaloids from a *Glochidion* species. *J. Chem. Soc., Chem. Commun*., 1966, 312-3.

10. Johns SR and Lamberton JA. *Uncaria* alkaloids: two stereoisomers of mitraphylline from *Uncaria bernaysii* F.v. Muell and *U. ferra* D.C. *Tetrahedron Lett.*, 1966, 4883-8.

11. Johns SR and Lamberton JA. Alkaloids of *Geijera salicifolia* Schott. (family Rutaceae): the identification of platydesmine and platydesmine acetate. *Aust. J. Chem*., 1966, **19**, 1991-4.

12. Johns SR and Lamberton JA. *Cassytha* alkaloids. I. New aporphine alkaloids from *Cassytha filiformis* L. *Aust. J. Chem*., 1966, **19**, 297-302.

13. Johns SR and Lamberton JA. Alkaloids of *Euodia alata* F.Muell. *Aust. J. Chem*., 1966, **19**, 895-6.

14. Johns SR, Lamberton JA, and Occolowitz JL. An indole alkaloid from *Dracontomelum mangiferum* Bl. (Family Anacardiaceae). *J. Chem. Soc., Chem. Commun*., 1966, 421-2.

15. Johns SR, Lamberton JA and Occolowitz JL. 1,2,3,4,6,7-Hexahydro-12*H*-indolo[2,3a] quinolizine, an alkaloid from *Dracontomelum mangiferum* Bl. (family Anacardiaceae). *Aust. J. Chem*., 1966, **19**, 1951-4.

16. Johns SR, Lamberton JA and Sioumis AA. A splitting of aryl proton signals in the N.M.R. spectra of N-alkyl-N-arylamides. *J. Chem. Soc., Chem. Commun*., 1966, 480-1.

17. Johns SR, Lamberton JA and Sioumis AA. Alkaloids of the Australian Leguminosae. VII. Nb-Methyltetrahydroharman from *Acacia complanata* A. Cunn. ex Benth. *Aust. J. Chem.,* 1966, **19**, 1539-40.

18. Johns SR, Lamberton JA and Sioumis AA. *Cassytha* Alkaloids II. Alkaloids of *Cassytha pubescens* R.Br. *Aust. J. Chem*., 1966, **19**, 2331-8.

19. Johns SR, Lamberton JA and Sioumis AA. *Cassytha* alkaloids. III. Aporphine alkaloids from *Cassytha melantha* R.Br. *Aust. J. Chem*., 1966, **19**, 2339-45.

20. Johns SR, Lamberton JA and Sioumis AA. Alkaloids of the Australian Leguminosae. VI. Alkaloids of *Petalostylis labicheoides* var. *casseoides* Benth. *Aust. J.Chem*., 1966, **19**, 893.

21. Arthur HR, Johns SR, Lamberton JA, and Loo SN. A new monoterpenoid alkaloid (RW47) from *Rauwolfia verticillata* of Hong Kong. *Aust. J. Chem.*, 1967, **20**, 2505-8.

22. Beecham AF, Hart NK, Johns SR and Lamberton JA. The stereochemistry of formosanine (uncarine B) and uncarine A *J. Chem. Soc., Chem. Commun*., 1967, 535-6.

23. Beecham AF, Hart NK, Johns SR and Lamberton JA. A Study of the C3/C7 stereochemistry of uncarines C, D, E and F by circular dichroism. *Tetrahedron Lett.*, 1967, 991-3.

24. Beecham AF, Johns SR and Lamberton JA. The absolute configuration of (+)-9-aza-1-methylbicyclo[3,3,1]- nonan-3-one, an alkaloid from *Euphorbia atoto* Forst. *Aust. J. Chem.,* 1967, **20**, 2291.

25. Hart NK, Johns SR and Lamberton JA. Uncarine C, D (speciophylline), E, and F: C-3 and C-7 epimeric oxindoles related to tetrahydroalstonine. *J. Chem. Soc., Chem. Commun*., 1967, 87-8.

26. Hart NK, Johns SR and Lamberton JA. (+)-9-Aza-1-methylbicyclo[3,3,1]nonan-3-one, a new alkaloid from Euphorbia atoto Forst. *Aust. J. Chem*., 1967, **20**, 561-3.

27. Johns SR and Lamberton JA. Alkaloids of *Phoebe clemensii* Allen (family Lauraceae). *Aust. J. Chem*., 1967, **20**, 1277-81.

28. Johns SR and Lamberton JA. Meteloidine from *Erythroxylum australe* F.Muell. *Aust. J. Chem*., 1967, **20**, 1301.

29. Johns SR and Lamberton JA. New imidazole alkaloids from a *Glochidion* species (family Euphorbiaceae). *Aust. J. Chem.,* 1967, **20**, 555-60.

30. Johns SR, Lamberton JA and Occolowitz JL. Antirhine, a new indole alkaloid from *Antirhea putaminosa* (F.v. Muell.) Bail. *J. Chem. Soc., Chem. Commun*., 1967, 229-30.

31. Johns SR, Lamberton JA and Occolowitz JL Antirhine, a new indole alkaloid from *Antirhea putaminosa* (F.Muell.) Bail. (family Rubiaceae). *Aust. J. Chem*., 1967, **20**, 1463-71.

32. Johns SR, Lamberton JA and Occolowitz JL. 1,5-Dimethoxy-3-(dimethylaminomethyl)indole, the major alkaloid from *Gymnacranthera paniculata* (A.DC.) Warb. var. *zippeliana* (Miq.) J. Sinclair (Family Myristicaceae). *Aust. J. Chem*., 1967, **20**, 1737-42.

33. Johns SR, Lamberton JA and Price JR. (±)-*N*-Benzoyl[2-hydroxy-2-(4'-methoxyphenyl)]ethylamine from *Clausena brevistyla* Oliver (Family Rutaceae). *Aust. J. Chem*., 1967, **20**, 2795-7.

34. Johns SR, Lamberton JA and Sioumis AA. The occurrence of (+)-hygroline in *Gynotroches axillaris* Bl. (Rhizophoraceae). *Aust. J. Chem*., 1967, **20**, 1303-4.

35. Johns SR, Lamberton JA and Sioumis AA. *Cassytha* alkaloids. IV. The alkaloids of *Cassytha racemosa* Nees (Family Lauraceae). *Aust. J. Chem*., 1967, **20**, 1457-62.

36. Johns SR, Lamberton JA and Sioumis AA. 1-Benzyl-1,2,3,4-tetrahydroisoquinoline alkaloids from *Alseodaphne archboldiana* (Allen) Kostermans (Family Lauraceae). *Aust. J. Chem*., 1967, **20**, 1729-35.

37. Johns SR, Lamberton JA and Sioumis AA. Laurotetanine and *N*-methyllaurotetanine from *Palmeria fengeriana* Perk. (Family Monimiaceae). *Aust. J. Chem*., 1967, **20**, 1787.

38. Johns SR, Lamberton JA and Sioumis AA. Alkaloids of *Choisya ternata* H.B. & K. (Family Rutaceae). The structure of choisyine. *Aust. J. Chem*., 1967, **20**, 1975-81.

39. Arthur HR, Johns SR, Lamberton JA and Loo SN. Alkaloids of *Rauwolfia verticillata* of Hong Kong. Identification of vellosamine and peraksine, and demonstration from N.M.R. data that peraksine is a mixture of two epimers. *Aust. J. Chem*., 1968, **21**, 1399-401.

40. Beecham AF, Hart NK, Johns SR and Lamberton JA. The absolute configuration of (-)-floramultine, an alkaloid from *Kreysigia multiflora* Reichb. *Aust. J. Chem*., 1968, **21**, 2829-30.

41. Beecham AF, Hart NK, Johns SR and Lamberton JA. The stereochemistry of oxindole alkaloids: uncarines A, B (formosanine), C (pteropodine), D (speciophylline), E (isopteropodine), and F. *Aust. J. Chem*., 1968, **21**, 491-504.

42. Hart NK, Johns SR and Lamberton JA. Alkaloids of *Lamprolobium fruticosum* Benth. (Leguminosae). *J. Chem. Soc., Chem. Commun*., 1968, 302.

43. Hart NK, Johns SR and Lamberton JA. A new monoterpenoid alkaloid from *Jasminum* species and from *Ligustrum novoguineense* (Family Oleaceae). *Aust. J. Chem*., 1968, **21**, 1321-6.

44. Hart NK, Johns SR and Lamberton JA. Alkaloids of the Sapotaceae: *trans*-β-methylthioacrylate and tiglate esters of (-)-isoretronecanol from a *Planchonella* species. *Aust. J. Chem*., 1968, **21**, 1393-5.

45. Hart NK, Johns SR and Lamberton JA. 3,4-Dimethoxy-ω-(2'-piperidyl)acetophenone, a new alkaloid from *Boehmeria platyphylla* Don. (Family Urticaceae). *Aust. J. Chem*., 1968, **21**, 1397-8.

46. Hart NK, Johns SR and Lamberton JA. The akaloids of *Lamprolobium fruticosum* Benth. (Family Leguminosae). *Aust. J. Chem*., 1968, **21**, 1619-24.

47. Hart NK, Johns SR and Lamberton JA. Minor alkaloids of *Boehmeria platyphylla* Don. (Family Urticaceae). II. Isolation of cryptopleurine and a new seco-phenanthroquinolizidine alkaloid. *Aust. J. Chem*., 1968, **21**, 2579-81.

48. Hart NK, Johns SR, Lamberton JA and Price JR. Alkaloids of the Australian Rutaceae: *Lunasia quercifolia*. IV. Identification of a minor constituent as 5- hydroxy-1-methyl-2-phenyl-4-quinolone and the preparation of an angular isomer of (-)-lunine. *Aust. J. Chem*., 1968, **21**, 1389-91.

49. Hart NK, Johns SR, Lamberton JA and Saunders JK. Kreysiginine, a homo-morphine alkaloid from *Kreysigia multiflora* Reichb. *Tetrahedron Lett*., 1968, 2891-4.

50. Johns SR, Kowala C, Lamberton JA, Sioumis AA and Wunderlich JA. "Homoerythrina" alkaloids from *Schelhammera pedunculata* F.Muell. (family Liliaceae). *J. Chem. Soc., Chem. Commun*., 1968, 1102-4.

51. Johns SR, Lamberton JA, Price JR and Sioumis AA. Identification of coumarins isolated from *Lepiniopsis ternatensis* (Apocynaceae), *Pterocaulon sphacelatum* (Compositae), and *Melicope melanophloia* (Rutaceae). *Aust. J. Chem*., 1968, **21**, 3079-80.

52. Johns SR, Lamberton JA and Sioumis AA. Three new indolizidine alkaloids related to elaeocarpine and isoelaeocarpine. *J. Chem. Soc., Chem. Commun*., 1968, 1324-5.

53. Johns SR, Lamberton JA and Sioumis AA. Elaeocarpidine, and new indole alkaloid from *Elaeocarpus archboldianus* A.C. Sm. *J. Chem. Soc., Chem. Commun*., 1968, 410.

54. Johns SR, Lamberton JA and Sioumis AA. Alkaloids of *Xylopia papuana* Diels (Family Annonaceae). *Aust. J. Chem*., 1968, **21**, 383-6.

55. Johns SR, Lamberton JA and Sioumis AA. Alkaloids of a *Phaeanthus* species from New Guinea. Isolation of phaeanthine and limacine. *Aust. J. Chem*., 1968, **21**, 1387-8.

56. Johns SR, Lamberton JA and Sioumis AA. Furoquinoline alkaloids from *Evodia elleryana* F.Muell. The structure of evellerine. *Aust. J. Chem*., 1968, **21**, 1897-901.

57. Johns SR, Lamberton JA, Sioumis AA and Wunderlich JA. Alkaloids of a new type from *Elaeocarpus polydactylus* Schl. (Family Elaeocarpaceae). *J. Chem. Soc., Chem. Commun*., 1968, 290-1.

58. Farnsworth NR, Hart NK, Johns SR, Lamberton JA and Messmer W. Alkaloids of *Boehmeria cylindrica* (Family Urticaceae): identification of a cytotoxic agent, highly active against Eagle's 9KB carcinoma of the nasopharynx in cell culture, as cryptopleurine. *Aust. J. Chem*., 1969, **22**, 1805-7.

59. Fitzgerald JS, Johns SR, Lamberton JA and Sioumis AA. Alkaloids of *Schelhammera pedunculata* (Liliaceae). I. Isolation of the alkaloids and the structures of the Homoerythrina alkaloids schelhammerine and schelhammeridine. *Aust. J. Chem*., 1969, **22**, 2187-201.

60. Hart NK, Johns SR and Lamberton JA. Hexahydroimidazo-pyrimidines, a new class of alkaloids from *Alchornea javanensis*. *J. Chem. Soc., Chem. Commun*., 1969, 1484-5.

61. Hart NK, Johns SR and Lamberton JA. Alkaloids of *Jasminum* species (family Oleaceae). II. Isolation of a new monoterpenoid alkaloid and other constituents. *Aust. J. Chem*., 1969, **22**, 1283-90.

62. Hart NK, Johns SR, Lamberton JA, Loder JW, Moorhouse A, Sioumis AA and Smith TK. Alkaloids of several *Litsea* species from New Guinea. *Aust. J. Chem*., 1969, **22**, 2259-62.

63. Johns SR and Lamberton JA. Isolation of simple acid amides from *Allophylus cobbe* (Sapindaceae), *Homalium foetidum* (Flacourtiaceae) and from an *Aglaia* species (Meliaceae). *Aust. J. Chem*., 1969, **22**, 1315-6.

64. Johns SR, Lamberton JA, Loder JW, Redcliffe AH and Sioumis AA. Alkaloids of *Argyrodendron peralatum* (Sterculiaceae): identification of *N*α-cinnamoylhistamine. *Aust. J. Chem*., 1969, **22**, 1309-10.

65. Johns SR, Lamberton JA and Sioumis AA. The alkaloids of *Neolitsea pubescens* (Lauraceae). *Aust. J. Chem*., 1969, **22**, 1311-2.

66. Johns SR, Lamberton JA and Sioumis AA. Alkaloids of *Lycopodium volubile* (Lycopodiaceae). *Aust. J. Chem*., 1969, **22**, 1317.

67. Johns SR, Lamberton JA and Sioumis AA. Alkaloids of *Schelhammera pedunculata* (Liliaceae). III. The structures of schelhammericine and alkaloids A, B, E, G, H, J, and K. *Aust. J. Chem*., 1969, **22**, 2219-31.

68. Johns SR, Lamberton JA and Sioumis AA. Alkaloids of *Actinodaphne nitida* (Lauraceae). *Aust. J. Chem.*, 1969, **22**, 2257.

69. Johns SR, Lamberton JA and Sioumis AA. *Elaeocarpus* alkaloids. II. (+)-Elaeocarpiline and (-)-Isoelaeocarpiline, new indolizidine alkaloids from *Elaeocarpus dolichostylis*. *Aust. J. Chem*., 1969, **22**, 793-800.

70. Johns SR, Lamberton JA and Sioumis AA. *Elaeocarpus* Alkaloids. III. The structure of elaeocarpidine, a new indole alkaloid. *Aust. J. Chem*., 1969, **22**, 801-6.

71. Johns SR, Lamberton JA, Sioumis AA and Suares H. The formation of optically active biphenyls from schelhammeridine. *J. Chem. Soc., Chem. Commun*., 1969, 646-7.

72. Johns SR, Lamberton JA, Sioumis AA and Suares H. Alkaloids of *Schelhammera pedunculata* (Liliaceae). II. Reactions of schelhammeridine. *Aust. J. Chem*., 1969, **22**, 2203-18.

73. Johns SR, Lamberton JA, Sioumis AA and Tweeddale HJ. New aporphine alkaloids from *Beilschmiedia podagrica*. *Aust. J. Chem*., 1969, **22**, 277-81.

74. Johns SR, Lamberton JA, Sioumis AA and Willing RI. *Elaeocarpus* alkaloids. I. The structures of (+-)-elaeocarpine, (+-)-isoelaeocarpine, and (+)-isoelaeocarpicine, three new indolizidine alkaloids from *Elaeocarpus polydactylus*. *Aust. J. Chem*., 1969, **22**, 775-92.

75. Johns SR, Lamberton JA and Tweeddale HJ. Identification of (-)-armepavine as the major leaf alkaloid of *Cryptocarya archboldiana* (Lauraceae). *Aust. J. Chem.*, 1969, **22**, 1313.

76. Johns SR, Lamberton JA, Tweeddale HJ, and Willing RI. Alkaloids of *Zanthoxylum conspersipunctatum* (Rutaceae): the structure of a new alkaloid isomeric with protopine. *Aust. J. Chem*., 1969, **22**, 2233-6.

77. Crow WD, Hancox NC, Johns SR and Lamberton JA. New alkaloids of *Alstonia constricta*. *Aust. J. Chem*., 1970, **23**, 2489-501.

78. Culvenor CCJ, Johns SR, Lamberton JA and Smith LW. The isolation of calycanthine and pyrrolizidine alkaloids from *Bhesa archboldiana* (Celastraceae): an unusual co-occurrence of alkaloidal types. *Aust. J. Chem*., 1970, **23**, 1279-82.

79. Hart NK, Johns SR, Lamberton JA, Loder JW and Nearn RH. New imidazole alkaloids from *Cypholophus friesianus*. *J. Chem. Soc., Chem. Commun*., 1970, 441.

80. Hart NK, Johns SR, Lamberton JA and Willing RI. Alkaloids of *Alchornea javanensis* (Euphorbiaceae): the isolation of hexahydroimidazo[1,2a]pyrimidines and guanidines. *Aust. J. Chem*., 1970, **23**, 1679-93.

81. Johns SR and Lamberton JA. The identification of a new alkaloid from *Timonius kaniensis* (Rubiaceae) as dihydrocupreine. *Aust. J. Chem*., 1970, **23**, 211-2.

82. Johns SR, Lamberton JA, Li CS and Sioumis AA. New alkaloids from a *Popowia* species (Annonaceae). *Aust. J. Chem*., 1970, **23**, 363-8.

83. Johns SR, Lamberton JA, Li CS and Sioumis AA. Alkaloids from *Pseuduvaria* species, *Schefferomitra subaequalis,* and *Polyalthia nitidissima* (Annonaceae): isolation of a new alkaloid shown to be 1,2,9,10-tetramethoxynoraporphine (norglaucine). *Aust. J. Chem*., 1970, **23**, 423-6.

84. Johns SR, Lamberton JA, Loder JW and Sioumis AA. Alkaloids of three *Palmeria* species (Monimiaceae). *Aust. J. Chem*., 1970, **23**, 1919-20.

85. Johns SR, Lamberton JA and Price JR. Isolation of isomultiflorenol, a possible triterpenoid artefact, from *Pleiococca wilcoxiana* (Rutaceae). *Aust. J. Chem*., 1970, **23**, 1283-4.

86. Johns SR, Lamberton JA and Sioumis AA. The identification of a leaf alkaloid of *Neonauclea schlechteri* (Rubiaceae) as gambirine (9-hydroxydihydrocorynantheine). *Aust. J. Chem*., 1970, **23**, 1285-6.

87. Johns SR, Lamberton JA and Sioumis AA. *N*b-Methyltetrahydroharman from *Spathiostemon javensis* (Euphorbiaceae). *Aust. J. Chem*., 1970, **23**, 213.

88. Johns SR, Lamberton JA and Sioumis AA. The identification of a quinolone alkaloid from *Citrus macroptera* (Rutaceae). *Aust. J. Chem.*, 1970, **23**, 419-20.

89. Johns SR, Lamberton JA and Sioumis AA. Tropine 3,4,5-trimethoxycinnamate, a new alkaloid from *Erythroxylum ellipticum* (Erythroxylaceae). *Aust. J. Chem*., 1970, **23**, 421-2.

90. Johns SR, Lamberton JA and Sioumis AA. 4-Methoxy-1-vinyl-b-carboline, a new alkaloid from *Picrasma javanica* (Simaroubaceae). *Aust. J. Chem*., 1970, **23**, 629-30.

91. Johns SR, Lamberton JA, Sioumis AA, Suares H, and Willing RI. The structures and absolute configurations of seven alkaloids from *Elaeocarpus sphaericus*. *J. Chem. Soc., Chem. Commun*., 1970, 804-5.

92. Johns SR, Lamberton JA, Sioumis AA and Willing RI. New alkaloids from *Cryptocarya pleurosperma* (Lauraceae): the structures of cryptopleuridine and cryptopleurospermine. *Aust. J. Chem*., 1970, **23**, 353-61.

93. Beecham AF, Mathieson AMcL, Johns SR, Lamberton JA, Sioumis AA, Batterham TJ and Young IG. The influence of allylic oxygen on the CD of skew dienes. *Tetrahedron*, 1971, **27**, 3725-38.

94. Denne WA, Johns SR, Lamberton JA and Mathieson AMcL. The absolute structure of porantherine. *Tetrahedron Lett.*, 1971, 3107-8.

95. Hart NK, Johns SR, and Lamberton JA. New alkaloids from *Elaeocarpus kaniensis* Schltr.: nuclear magnetic resonance study. *J. Chem. Soc., Chem. Commun*., 1971, 460-1.

96. Hart NK, Johns SR, andLamberton JA. The isolation of the alkaloid jasminine from *Olea paniculata* (Oleaceae). *Aust. J. Chem*., 1971, **24**, 1739-40.

97. Hart NK, Johns SR and Lamberton JA. The identification of a minor alkaloid of *Mackinlaya macrosciadia* (Araliaceae) as deoxyvasicinone. *Aust. J. Chem*., 1971, **24**, 223-4.

98. Hart NK, Johns SR, Lamberton JA, Loder JW and Nearn RH. New imidazole alkaloids from *Cypholophus friesianus* (Urticaceae). The structures and synthesis of cypholophine and *O*-acetylcypholophine. *Aust. J. Chem*., 1971, **24**, 857-64.

99. Hart NK, Johns SR, Lamberton JA, Suares H and Summons RE. The identification of the major alkaloid of *Strychnos ledermannii* as diaboline. *Aust. J. Chem*., 1971, 24, 1741.

100. Johns SR, Lamberton JA and Sioumis AA. New tropane alkaloids (+)-(3R, 6R)-3α-acetoxy-6β-hydroxytropane and (R)-2α-benzoyloxy-3β-hydroxynortropane, from *Peripentadenia mearsii* (Euphorbiaceae). *Aust. J. Chem*., 1971, **24**, 2399-403.

101. Johns SR, Lamberton JA and Sioumis AA. The major alkaloid of *Aotus subglauca* (Leguminosae), S-(+)-*N*b-methyltryptophan methyl ester. *Aust. J. Chem*., 1971, **24**, 439-40.

102. Johns SR, Lamberton JA, Sioumis AA, Suares H and Willing RI. *Elaeocarpus* alkaloids. IV. The alkaloids of *Elaeocarpus sphaericus*. *Aust. J. Chem*., 1971, **24**, 1679-94.

103. Denne WA, Johns SR, Lamberton JA, Mathieson AMcL, and Suares H. The molecular structure and absolute configuration of porantheridine and porantheridine. *Tetrahedron Lett.*, 1972, 1767-70.

104. Denne WA, Johns SR, Lamberton JA, Mathieson AMcL and Suares H. The absolute structure of anopterine. *Tetrahedron Lett.*, 1972, 2727-30.

105. Fitzgerald JS, Johns SR, Lamberton JA, Redcliffe AH, Sioumis AA, and Suares H. Alkaloids of *Hovea longipes* (Leguminosae): the structure of a hypotensive alkaloid (-)-hoveine. *An. Quim*., 1972, **68**, 737-42.

106. Hart NK, Johns SR and Lamberton JA. Tertiary alkaloids of *Alstonia spectabilis* and *Alstonia glabriflora* (Apocynaceae). *Aust. J. Chem*., 1972, **25**, 2739-41.

107. Hart NK, Johns SR and Lamberton JA. *Elaeocarpus* alkaloids. V. The alkaloids of *Elaeocarpus kaniensis*. *Aust. J. Chem*., 1972, **25**, 817-35.

108. Hart NK, Johns SR, Lamberton JA, Mackay MF, Mathieson AMcL and Satzke L. The absolute molecular structure of podopetaline. *Tetrahedron Lett.*, 1972, 5333-6.

109. Hart NK, Johns SR, Lamberton JA and Suares H. Alkaloids of *Pachygone pubescens* (Menispermaceae). *Aust. J. Chem*., 1972, **25**, 2289-90.

110. Hartley TG, Dunstone EA, Fitzgerald JS, Johns SR and Lamberton JA. A survey of New Guinea plants for alkaloids. *Lloydia*, 1973, **36**, 217-319.

111. Johns SR and Lamberton JA. *Elaeocarpus* alkaloids. In 'The Alkaloids, Chemistry and Pharmacology', 1973, **14**, 325-46.

112. Hart NK, Johns SR, Lamberton JA and Summons RE. Psychotridine, a $C_{55}H_{62}N_{10}$ alkaloid from *Psychotria beccarioides* (Rubiaceae). *Aust. J. Chem*., 1974, **27**, 639-46.

113. Johns SR, Lamberton JA, Sioumis AA, and Suares H. The alkaloids of *Poranthera corymbosa* (Euphorbiaceae). *Aust. J. Chem*., 1974, **27**, 2025-34.

114. Battersby AR, McDonald E, Milner JA, Johns SR, Lamberton JA and Sioumis AA. Biosynthesis of schelhammeridine: mode of specific incorporation of [2-^{14}C]tyrosine. *Tetrahedron Lett*., 1975, 3419-22.

115. Culvenor CCJ, Johns SR and Smith LW. Acetyllasiocarpine, an alkaloid from *Heliotropium europaeum. Aust. J. Chem*., 1975, **28**, 2319-22.

116. Johns SR, Lamberton JA, Moore BP and Sioumis AA. Alkaloids of *Ochrosia poweri* Bail. The stereochemistry of poweridine and the identity of elliptamine and reserpiline. *Aust. J. Chem*., 1975, **28**, 1627-9.

117. Hart NK, Johns SR, Lamberton JA, Suares H and Willing RI. New alkaloids of the *ent*-kaurene type from *Anopterus* species (Escalloniaceae). I. The structure and reactions of anopterine. *Aust. J. Chem*., 1976, **29**, 1295-318.

118. Hart NK, Johns SR, Lamberton JA, Suares H and Willing RI. New alkaloids of the *ent*-kaurene type from *Anopterus* species. II. The structure of the minor alkaloids. *Aust. J. Chem*., 1976, **29**, 1319-27.

119. Banfield JE, Black DStC, Johns SR and Willing RI. Constituents of *Endiandra* species. IV. Isolation of 2-(8'-[(E,E)-5"-Phenylpenta-2",4"-dien-1"-yl] bicyclo[4,2,0]octa-2',4'- dien-7'-yl)acetic acid, a biogenetically predicted metabolite of *Endiandra introrsa* (Lauraceae) and its structure determination by means of 1D and 2D N.M.R. spectroscopy. *Aust. J. Chem.*, 1982, **35**, 2247-56.

120. Johns SR, Lamberton JA, Morton TC, Suares H and Willing RI. 22β-[(S)-2-Methylbutanoyloxy]-3-oxoolean-12-en-28-oic acid, a new constituent of *Lantana camara. Aust. J. Chem*., 1983, **36**, 1895-902.

121. Johns SR, Lamberton JA, Morton TC, Suares H and Willing RI. Triterpenes of *Lantana tiliaefolia.* 24-Hydroxy-3-oxours-12-en-28-oic acid, a new triterpene. *Aust. J. Chem*., 1983, **36**, 2537-47.

122. Johns SR, Lamberton JA and Suares H. 3,4,5,6,7,8-Hexahydro-1,7-benzodiazecin-2(1H)-one from extracts of *Mackinlaya* species. *Aust. J. Chem*., 1985, **38**, 1007-8.

123. Johns SR, Lamberton JA, Suares H and Willing RI. New alkaloids of the *ent*-kaurene type from *Anopterus* species. III. A 2D-N.M.R. study of anopterine and the determination of structure of six minor alkaloids by N.M.R. *Aust. J. Chem*., 1985, **38**, 1091-106.

124. Johns SR, Lamberton JA, Morton TC, Suares H and Willing RI. *Campnosperma* exudates. The optically active long-chain 5-hydroxycyclohex-2-enones and long-chain bicyclo[3.3.1]nonane-3,7-diones. *Aust. J. Chem*., 1987, **40**, 79-96.

(C) CSIRO - Papers on Polymers - NMR Studies

The following list of papers on nuclear magnetic resonance studies of polymers was kindly supplied by Mr Ian Willing.

125. Hawthorne DG, Johns SR, Solomon DH, and Willing RI. Cyanoisopropyl radical induced cyclization and cyclopolymerization of *N*-methyl-*N*- allyl-*N*-(2-alkylallyl)amines and *N*-methyl-*N,N*-bis(2 alkylally)amines. A ^{13}C NMR study. *J. Chem. Soc., Chem. Commun.,* 1975, 982-3.

126. Johns SR, and Willing RI. Cyclopolymerization V. The ^{13}C NMR spectrum and structure of the low molecular weight product from the reaction of *N*-methyl-*N,N*-diallylamine with azobisisobutyronitrile. *J. Macromol. Sci.-Chem*., 1975, **A9**, 169-81.

127. Hawthorne DG, Johns SR, and Willing RI. ^{13}C NMR Spectra of pyrrolidines and piperidines. Structure of the perhydroisoindol-5-ones and 3-azabicyclo(3,3,1)nonan-6-imes formed by the cyanoisopropyl radical induced cyclization of N-methyl-*N,N*-bis(2-alkylallyl) amines. *Aust. J. Chem*., 1976, **29**, 315-26.

128. Kissane PJ, Johns SR, Willing RI, and Sasse WHF. 2,7-Bis(dimethylamino)anthracene and 2,2',7,7'-tetrakis(dimethylamino)-9,9'-bianthracene. *Aust. J. Chem*., 1976, **29**, 1613-6.

129. Johns SR, Willing RI, Middleton S, and Ong AK. Cyclopolymerization. VII. The ^{13}C NMR spectra of cyclopolymers obtained from *N,N*-diallylamines. *J. Macromol. Sci.-Chem.*, 1976, **A10**, 875-891.

130. Hawthorne DG, Johns SR, Solomon DH, and Willing RI. The Cyclopolymerization of *N*-allyl-*N*-methyl(2-substituted allyl)amines. The structure of the polymers and low molecular weight products. *Aust. J. Chem*., 1976, **29**, 1955-74.

131. Johns SR, and Willing RI. ^{13}C NMR Spectra of quinoline and methylquinolines. The magnitude of the Vicinal (peri) $^{3}J_{CCCH}$ Coupling constants. *Aust. J. Chem*., 1976, **29**,1617-22.

132. Johns SR, Leslie DR, Willing RI, and Bishop DG. Studies on chloroplast membranes. I. ^{13}C chemical shifts and longitudinal relaxation times of carboxylic acids. *Aust. J. Chem*., 1977, **30**, 813-822.

133. Johns SR, Leslie DR, Willing RI, and Bishop DG. Studies on chloroplast membranes. II. ^{13}C Chemical shifts and longitudinal relaxation times of 1,2-di((9Z,12Z,15Z)-octadeca-9,12,15-trienoyl)-3-galactosyl-*sn*-glycerol and 1,2-di((9Z,12Z,15Z)-octadeca-9,12,15-trienoyl)-3-digalactosyl-*sn*-glycerol. *Aust. J. Chem*., 1977, **30**, 823-34.

134. Johns SR, Leslie DR, Willing RI, and Bishop DG. Studies on chloroplast membranes. III. ^{13}C chemical shifts and longitudinal elaxation times of 1,2-diacyl-3-(6-sulpho- quinovosyl)-*sn*-glycerol. *Aust. J. Chem*.,1978, **31**, 65-72.

135. Bishop DG, Johns SR, Nolan WG, and Willing RI. Evolution of the lipid components of chloroplast membranes: The role of lipid fluidity in membrane associated reactions. In *Light Transducing Membranes*, Academic Press (1978).

136. Johns SR, Willing RI, Claret PA, and Osborne AG. Single frequency proton decoupling in ^{13}C NMR spectra. ^{13}C Chemical shifts and methyl substituent chemical shifts in methylquinolines. *Aust. J. Chem*., 1979, **32**, 761-8.

137. Hawthorne DG, Johns SR, Solomon DH, and Willing RI. Initiation and termination group identification in polymers by ^{13}C NMR spectroscopy. *Aust. J. Chem*., 1979, **32**, 1133-7.

138. Johns SR, Willing RI, Thulborn KR, and Sawyer WH. ^{13}C NMR studies on fluorescent probes. ^{13}C Chemical shifts and longitudinal relaxation times of n-hydroxy-fatty (n=2,6,9,12) acids and n-(9-anthroyloxy)-stearic (n = 6,12) acids. *Chemistry and Physics of Lipids,* 1979, **24**, 11-16.

139. Bishop DG, Kenrick JR, Bayston JH, Macpherson AS, Johns SR, and Willing RI. The influence of fatty acid unsaturation on fluidity and molecular packing of chloroplast membrane lipids. In *Low Temperature Stress in Crop Plants*, Academic Press (1979).

140. Johns SR, Leslie DR, Willing RI, and Yabsley MA. A two-pulse sequence for the analysis of unresolved multiline resonances in ^{13}C Fourier transform NMR spectra. *Mag. Reson*., 1980, **40**, 283-291.

141. Coddington JM, Johns SR, Leslie DR, Willing RI, and Bishop DG. Studies on chloroplast membranes. IV. ^{13}C NMR Chemical shifts and longitudinal relaxation times of 1,2-diacyl-3-phosphatidyl-*sn*-glycerol. *Aust. J. Chem*., 1981, **34**, 357-63,

142. Coddington JM, Johns SR, Leslie DR, Willing RI, and Bishop DG. ^{13}C Nuclear magnetic resonance studies of the composition and fluidity of several chloroplast monogalactosyl diacyl glycerols. *Biochim. Biophys. Acta*., 1981, **663**, 653-660.

143. Hodgkin JH, Johns SR, and Willing RI. Cyclopolymerization of Diallylamides and Diallylsulphonamides. *Polymer Bulletin*, 1982, **7**, 353-359.

144. Coddington JM, Johns SR, Willing RI, Kenrick JR, and Bishop DG. Preparation and comparison of model bilayer systems from chloroplasts thylakoid membrane lipids for ^{13}C-NMR studies. *J. Biochem., Biophys., Methods*, 1982, **6**, 351-356.

145. Bishop DG, Kenrick JR, Coddington JM, Johns SR and Willing RI. The role of membrane fluidity in the maintenance of chloroplast function. In *Biochemistry and Metabolism of Plant Lipids*, Elsevier Biomedical Press B.V. (1982).

146. Moad GM, Solomon DH, Johns SR and Willing RI. Structure of benzoyl peroxide initiated polystyrene: Determination of the initiator-derived functionality by ^{13}C NMR. *Macromolecules*, 1982, **5**, 1188.

147. Bendall MR, Pegg DT, Doddrell DM, Johns SR and Willing RI. Pulse sequence for the generation of a ^{13}C subspectrum of both aromatic and aliphatic quaternary carbons. *J. Chem. Soc., Chem. Commun*., 1982, 1138-1140.

148. Coddington JM, Johns SR, Willing RI, Kenrick JR and Bishop DG. Monolayer and ^{13}C NMR studies on the interaction between Melittin and chloroplast lipids. *Biochim. Biophys. Acta*, 1983, **727**,1-6.

149. Johns SR, Rizzardo E, Solomon DH, and Willing RI. Identification of end groups in polymers by a spin-echo NMR technique. *Makromol. Chem., Rapid Commun*., 1983, **4**, 29-32.

150. Moad G, Solomon DH, Johns SR, and Willing RI. Fate of the initiator in the azobis(isobutyronitrile)-initiated polymerizaiton of styrene. *Macromolecules*, 1984, **17**,1904-9.

151. Moad G, Rizzardo E, Solomon DH Johns SR, and Willing RI. Application of ^{13}C-labelled initiators and ^{13}C NMR to the study of kinetics and efficiency of initiation of sytrene polymerization. *Makromol. Chem., Rapid Commun*., 1984, **5**, 793-798.

152. Johns SR, and Willing RI. ^{13}C Chemical shift and $^{13}C,^{13}C$ coupling constant assignment of quaternary carbons by double quantum coherence. Use of the doubtful pulse sequence in natural abundance ^{13}C NMR spectra. *Magn. Reson. in Chemistry*, 1985, **23**,16-17.

153. Cacioli P, Hawthorne DG, Johns SR, Solomon DH, Rizzardo E, and Willing RI. The detection of preferred conformation in oligomers of methyl methacrylate in solution by ^{1}H NMR 2D-correlation spectroscopy. *J. Chem. Soc., Chem. Commun*., 1985, 1355.

154. Moad G, Solomon DH, Spurling TH, Johns SR and Willing RI. Tacticity of poly(methyl methacrylate). Evidence for a penpenultimate group effect in free-radical polymerization. *Aust. J. Chem*., 1986, **39**, 43-50.

155. Moad G, Rizzardo E, Solomon DH, Johns SR, and Willing RI. ^{13}C-^{1}H Heteronuclear chemical shift correlation spectroscopy applied to poly(methyl(carbonyl-^{13}C) methacrylate: An unambiguous method for assigning resonances to configurational sequences. *Macromolecules*, 1986, **19**, 2494-7.

156. Johns SR, Willing RI, and Winkler DA. Conformational studies of methyl methacrylate by NMR and potential energy calculations: The origin of the acyclic "W" coupling. *Makromol. Chem., Rapid Commun.*, 1987, **8**,17-22.

157. Newman RH, Porter LJ, and Foo LY, Johns SR, and Willing RI. High-resolution ^{13}C NMR studies of proanthocyanidin polymers (condensed tannins). *Magn. Reson. in Chemistry*, 1987, **25**, 118-124.

NUCLEAR MAGNETIC RESONANCE IN POLYMER STUDIES*

STANLEY R. JOHNS

Division of Applied Organic Chemistry, C.S.I.R.O., Melbourne, Victoria

ABSTRACT. ^{13}C nmr spectroscopy is now extensively used in both synthetic and biological polymer studies. Structural and dynamic properties of a polymer can be determined from the ^{13}C nmr chemical shift and relaxation time parameters. Examples from both the synthetic and biological fields are presented together with descriptions of new techniques for the analysis of end groups and the determination of tacticity in synthetic polymers.

Introduction

In his will the late Professor A. Liversidge requested that this lecture should be "for the encouragement of research in Chemistry.... and shall not be such as are termed popular lectures dealing with generalities.... but shall be such as will primarily encourage research and stimulate the lecturer and the public to think and acquire new knowledge by research instead of merely giving instructions". Further he directed that "the lecture shall be upon recent researches and discoveries and the most important part of the lecturers' duty shall be to point in which direction further researches are necessary and how he thinks they can best be carried out".

I hope to fulfill these requirements in this lecture by describing some of our recent work in the field of synthetic and biological polymers using the versatile physical technique, nuclear magnetic resonance (nmr) spectroscopy. In the past 35 years the nmr technique has crossed many discipline barriers. After its discovery and initial description by physicists in the mid 1940's (Block, 1946; Purcell, 1946), chemists and particularly organic chemists, have developed the technique over the next 30 years into a powerful tool for the study of structure and motion within organic molecules. The method is now used extensively in the fields of polymer and biological sciences and it is some of these applications I wish to discuss today.

I shall concentrate on ^{13}C nmr and after an initial introduction to the technique and a description of the two most important parameters of chemical shift and relaxation time, I shall discuss some of our recent research. Firstly I shall describe our work dealing with structural studies of synthetic polymers, and with new methods for the analysis of end groups and for the determination of the tacticity of synthetic polymers. I shall then turn to our studies of biological polymers, and in particular to the use of relaxation times in the study of motion and interaction in lipid bilayers. We expect that this work should lead to an understanding of lipid/protein interactions and the overall function of biological membranes.

---

* The Liversidge Research Lecture, delivered before the Royal Society of New South Wales, 19th June., 1980. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1980, **113**, 69-80.

^{13}C Nmr Theory

The ^{13}C nucleus has a quantum spin number of 1/2 and when a nucleus is placed in an applied magnetic field (H_0) it precesses about the field with a characteristic frequency, ω_0, (its Larmor frequency) such that $\omega_0 = -\gamma H_0$ where γ is the gyromagnetic ratio of the ^{13}C nucleus (Figure 1).

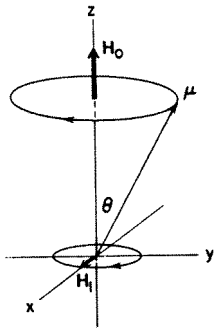


FIGURE 1. Precession of a magnetic moment μ about a fixed magnetic field H_0

In practice we never study a single nucleus but rather a collection of nuclei. Some nuclei precess in the direction of the applied field and some opposed to the field. At thermal equilibrium there are more aligned in the direction of the field (the lower energy state) than opposed which results in a net magnetisation (M) along the direction of H_0 (conventionally the z axis). (Figure 2).

The resonance condition in an nmr experiment is achieved by applying a second oscillating radio-frequency (rf) field (H_1) at right angles to H_0 . Resonance occurs with an absorption of energy when the frequency of H_1 equals the Larmor frequency of the nucleus.

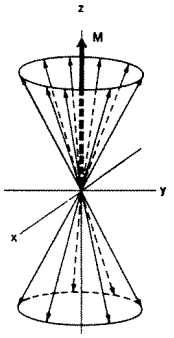


FIGURE 2. Precession of a collection of identical nuclei with net macroscopic magnetisation (M) along the z axis.

The motion of the net magnetisation under the influence of two different fields, H_0 and H_1, is extremely complicated in the normal laboratory frame of reference and to simplify the discussion of pulsed nmr and relaxation times, it is convenient to consider the motion of M in a co-ordinate system rotating about H_0 at the angular frequency ω_0. This new co-ordinate system, designated x', y', z', is called the rotating frame. In the laboratory frame, H_1 is rotating in the xy plane but in the rotating frame this second field is fixed and, by convention, fixed along the x' axis. Again, by convention, the receiver is placed at right angles to the transmitter i.e. along the y' axis.

When an intense rf pulse (H_1) is applied for time t_p the magnetisation M_0 along z' will begin to precess about the new field (H_1) and in fact rotate through an angle θ radians

where $\theta = \gamma H_1 t_p$ (Figure 3). By varying t_p it is possible to rotate the magnetisation through any desired angle.

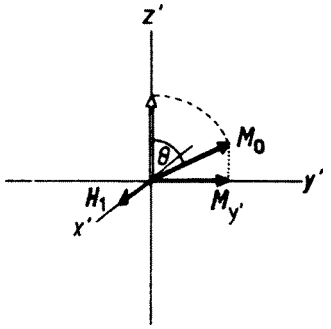


FIGURE 3. Rotation of magnetisation (M_0) around H_1 field.

After the pulse is turned off the spin system will relax back to its equilibrium position (M_0) according to two rate equations.

$$\frac{dM_{z'}}{dt} = -\frac{(M_{z'} - M_0)}{T_1}$$

$$\frac{dM_{y'}}{dt} = -\frac{M_{y'}}{T_2^*}$$

where T_1 and T_2^* are the longitudinal and transverse relaxation times respectively.

The signal in the Pulsed Fourier Transform (PFT) experiment is detected in the y' axis and is given by

$$M_{y'} = M_0 \sin\theta \, e^{-t/T_2^*}$$

Obviously, the maximum signal is observed when $\theta = \pi/2$ (90°) i.e. when $\sin\theta = 1$. If we plot the signal strength versus time we have a free induction decay (FID) or time domain spectrum (Figure 4), which on Fourier transformation gives a frequency domain spectrum. This is the case for a collection of nuclei irradiated at the Larmor frequency (ω_0).

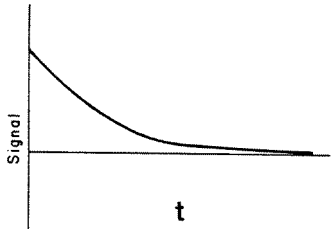


FIGURE 4. Experimental FID of magnetisation along y' axis

However, if the pulse frequency is slightly off-resonance by $\Delta\nu$ (as is the usual case) the FID will be modulated by a term $\cos 2\pi\Delta\nu t$ which gives a modulated FID (Figure 5) given by

$$M_{y'} = M_0 \sin\theta \, e^{-t/T_2^*} \cos 2\pi\Delta\nu t$$

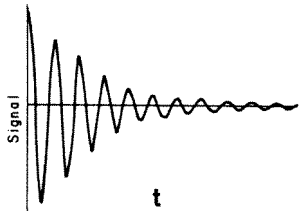


FIGURE 5. Modulated FID for off-resonance signal.

Because of the non-uniform distribution of electrons within an organic molecule, nuclei in different chemical environments within the molecule resonate at slightly different frequencies.

Therefore, in a normal nmr experiment, we obtain a series of modulated FID's i.e. an interferrogram and this signal is given by

$$M_{y'} = \sum_i M_0 \sin\theta_i \, e^{-t/T_2^*} \cos 2\pi\Delta\nu_i t$$

Fourier transformation of such an interferrogram gives a frequency domain spectrum made up of a number of resonance signals. These chemically induced differences in frequency, the chemical shift, are not recorded in absolute frequency units, but rather, in the form of a dimensionless quantity (δ) defined with respect to the observing frequency

$$\delta = \frac{H_C - H_R}{H_0} \times 10^6 \text{ ppm}$$

The reference standard is usually tetramethylsilane, arbitrarily set at $\delta = 0.00$ ppm.

Experimentally, it is easier to measure the longitudinal relaxation time, T_1 than the transverse relaxation time T_2^*. A number of multiple pulse sequences can be used but the most common is the so-called 'inversion/recovery' method (Vold, 1968) which involves a 180° - τ - 90° pulse sequence (Figure 6).

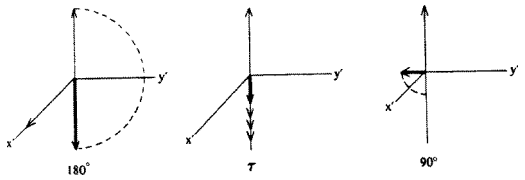


FIGURE 6. Determination of T_1 by 180° - τ - 90° pulse sequence.

The first 180° pulse applied along the x' axis inverts the magnetisation into the -z' axis. Longitudinal relaxation occurs causing $M_{z'}$ to change from a value of $-M_0$ through zero to the equilibrium value M_0 with time. If at a time t, after the 180° pulse, a 90° pulse is applied along x', M_z, (t) is rotated into the y' axis and a FID is detected. For signal averaging purposes, relaxation must be complete before the pulse train is repeated. Usually a time T is set such that $T = 5 \times T_1$ and the pulse train $(180°\text{-}\tau\text{-}90°\text{-}T)_n$ is used. The equation of motion of $M_{z'}$ is given by

$$\frac{dM_{z'}}{dt} = \frac{(M_{z'} - M_0)}{T_1}$$

At time $t = 0$, $M_{z'} = -M_0$

Integration yields $$M_{z'}(t) = M_0(1 - 2e^{-t/T_1})$$

This equation is usually rewritten in the form

$$\ln(A_\infty - A_t) = \ln 2 \; A_\infty - t/T_1$$

where A_t = signal amplitude at time t and A_∞ = limiting amplitude at time $5 \times T_1$

T_1 is determined from a series of spectra (Figure 7) recorded at different t settings using either an exponential fit (Figure 8) or a linear fit and measurement of slope (Figure 9). It is possible to measure T_1 values of all the different carbon nuclei in a molecule by careful selection of t values.

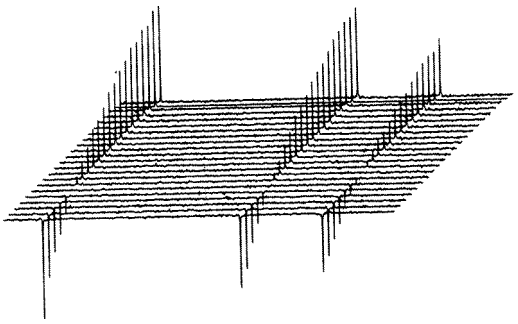


FIGURE 7. ^{13}C nmr (180° - τ - 90°) spectra of *n*-propanol for t = 0.4 to 13.0 sec. in 0.6 sec. steps.

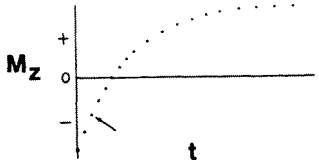


FIGURE 8. Exponential plot of signal intensity versus time in (180° - τ - 90°) sequence.

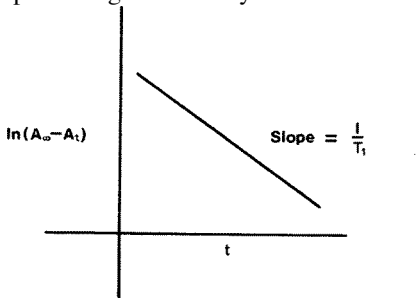


FIGURE 9. Linear plot of $\ln(A_\infty - A_t)$ versus time in (180°- τ - 90°) sequence.

In many cases the T_1 values, as measured, are inversely proportional to a correlation time (τ_c) which is defined as the time a particular nucleus spends in a particular position before moving through one radian. The correlation time is therefore a direct measurement of motion of the nucleus.

$$\frac{1}{T_1} = \frac{Nh^2\gamma_C^2\gamma_H^2}{r^6} \cdot \tau_c$$

where N is the number of directly bound hydrogen atoms, and r is the C-H interatomic distance.

The ^{13}C chemical shift and longitudinal relaxation time parameters will both be used in the subsequent discussions on the nmr of polymers.

Structure of Polymers

An organic molecule can be represented by a single structure and this structure can be readily determined by nmr measurements. In a polymer, the nmr spectrum represents an 'average molecule' from which we can determine overall structural features and also a monomer distribution e.g., the percentages of monomers as structural entities in homopolymers and a ratio of monomer A to monomer B in a copolymer (Randall, 1977).

As an example I wish to describe our work on the cyclopolymers used in the SIROTHERM process for the desalination of brackish water. Polymers for this process were derived by the cyanoisopropyl radical induced cyclopolymerization of diallylamines. Depending upon the initial position of attack and upon the subsequent cyclisation five, six or even seven membered ring structures are possible (Diagram 1). ^{13}C nmr can be used successfully to distinguish between these polymer possibilities. The proton decoupled ^{13}C nmr spectrum of the cyclopolymer from *N*-methyl-*N*,*N*-diallylamine (Diagram 1, $R_1 = R_2 = H$) is shown in Figure 10, (Johns, 1976).

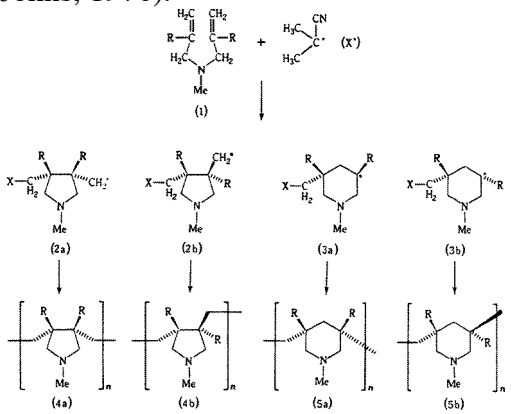


DIAGRAM 1. Possible structures from cyanoisopropyl-radical-induced cyclopolymerization of diallylamines.

Comparison of this spectrum with those of a series of β,β-substituted pyrrolidines and piperidines (Hawthorne, 1976*a*) shows that the cyclic moieties in the polymer structure are of the pyrrolidine type (4a, 4b) and no piperidine type units (5a, 5b) are present. Specifically, *N*-methyl signals in the region 42.5 - 42.8 ppm can be assigned to *N*-methyls of *cis*- and *trans*-pyrrolidine units and no signals are observed in the 47 ppm region for *cis*- and *trans*-piperidine. The overall structure is therefore that of a polypyrrolidine and not a polypiperidine.

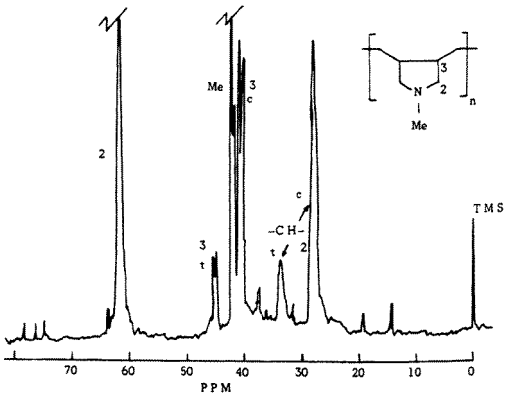


FIGURE 10. ^{13}C nmr spectrum of the polymer from *N*-methyl-*N*,*N*-diallylamine.

A full assignment of the spectrum indicates a 5:1 ratio of *cis*- and *trans*-polypyrrolidine. The downfield peak at 62.7 ppm can be assigned to the C2,5 methylene carbons of both *cis*- and *trans*-pyrrolidine rings while the two peaks at 41.9 and 41.5 ppm can be assigned to the C3,4 methine carbons of the *cis*-substituted rings and the peaks at 45.9 and 45.5 ppm to the *trans*-substituted rings. Similarly the remaining broadened peaks at 28.4 and 34.4 ppm can be assigned to the methylene carbons of the ethylene groups in the *cis*- and *trans*-pyrrolidines

respectively. The splitting of the C3,4 methine signals into pairs of signals in the *cis*- and *trans*-structures depends upon the different dyad structures (Diagram 2) possible.

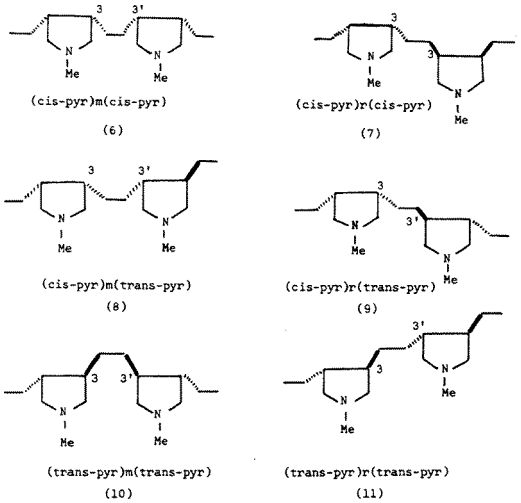


DIAGRAM 2. Dyad structures of polypyrrolidines (4a, 4b).

In considering the chemical shifts of the methine carbons in these different structures, it is convenient to focus attention on the "inner" methine carbons of each dyad (labelled 3 and 3' in each case). We propose that the chemical shift of any particular one of these carbons is determined primarily by the stereochemistry of the pyrrolidine unit in which it resides and secondarily by the relative chiralities of C3 and C3' of the appropriate dyad (Johns, 1976). On this basis, the methine carbons fall into two main groups, each of which has two sub-groups

Group 1: Methine of *cis*-pyrrolidine units.

(a) those in which there is a *meso* relationship between C3 and C3'

C3 of (6), C3' of (6), and C3 of (8)

(b) those in which there is a *racemic* relationship between

C3 of (7), C3' of (7), and C3 of (9)

Group 2: Methine of *trans*-pyrrolidine units.

(a) *meso* relationships between C3 and C3'

C3' of (8), C3 of (10), and C3' of (10)

(b) *racemic* relationships between C3 and C3'

C3' of (9), C3 of (11), and C3' of (11)

Two doublets are thus expected for the C3 signals in the average polymer spectrum.

A similar analysis of the spectrum (Figure 11) of the cyclopolymer from *N*-methyl-*N*,*N*-di-(2-methylallyl)amine (I, $R_1 = R_2 = Me$) reveals a mixture of both

polypyrrolidine and polypiperidine structures in approximately equal amounts with signals from *N*-methyl groups at both 44.2 and 47.1 ppm (Johns, 1976). The complexity of this spectrum can be explained and the different signals assigned when the possible combinations of the two structural types are considered.

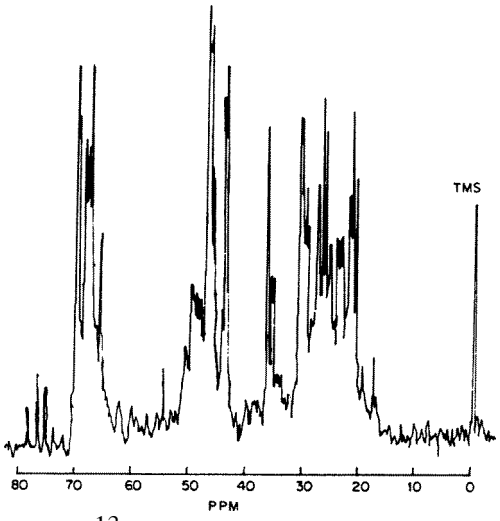


FIGURE 11. ^{13}C nmr spectrum of the cyclopolymer from *N*-methyl-*N*,*N*-di-(2-methylallyl) amine.

Further studies (Hawthorne, 1975; Hawthorne, 1976*b*), on a series of polymers from *N*-methyl-N-allyl-*N*-(2-substituted allyl)amines have been made to determine the preferred site of initial radical addition to the diallylamine and the subsequent direction of cyclization. Steric interactions induced by β-substituents tend to favour attack at the unsubstituted allyl group whereas conjugated substituents favour attack at the substituted group with the consequent formation of conjugate-stabilized radicals. In all monosubstituted diallylamines, cyclization to the polypyrrolidine occurs except in the case of the *t*-butyl derivative where steric interactions induce cyclizations to both pyrrolidine and piperidine structures.

End Group Analysis

The initiation and termination (end) groups can have a significant effect on the properties of a polymer. This is particularly so if the groups are reactive and can be involved in polymer degradation. However, the identification and estimation of the end groups is difficult because of their low overall concentration in our 'average' molecule as detected by nmr.

We have used an inversion/recovery technique similar to that employed in the determination of longitudinal relaxation times, to assign signals to those carbons of the initiation and termination groups (Hawthorne, 1979). Because of the restriction of motion along a polymer chain, the T_1 values of the backbone carbons of a cyclopolymer such as that from *N*-methyl-*N*,*N*-diallylamine (Figure 10) are expected to be quite short. By contrast the T_1 values of the carbons of the end groups of the polymer chain will be much longer because of their greater mobility.

By choosing a time t in an inversion/recovery, 180° - t - 90°, pulse sequence such that the backbone carbons with short T_1's have recovered their magnetisation in the positive z' axis, those signals will appear upright, while the signals from the carbons with the longer T_1 values i.e. those of the initiation and termination groups, will retain magnetisation in the negative z' axis and give inverted signals.

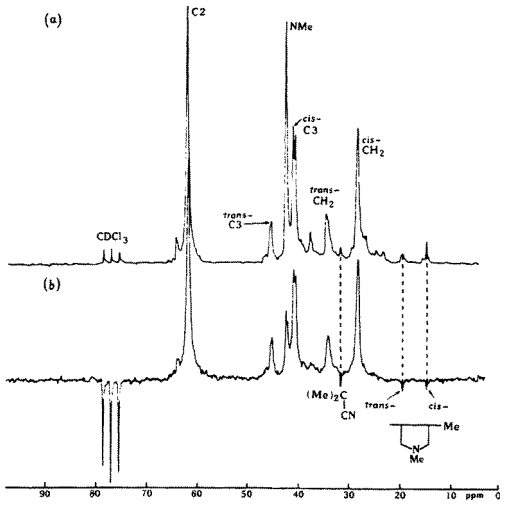


FIGURE 12. ^{13}C nmr (180° - t - 90°) spectra of cyclopolymer from *N*-methyl-*N*,*N*-diallylamine, t = 20 s. ; t = 0.2 s.

A comparison of the spectra of the cyanoisopropyl radical induced cyclopolymer from *N*-methyldiallylamine (MW ~ 2000, i.e. about 20 units) after t = 20 s. and t = 0.2 s. (Figures 12a and 12b) shows a number of inverted signals in Figure 12b that can be assigned to carbon atoms of the initiation and termination groups. Specifically, the signal at 31.7 ppm can be assigned to the methyl group of the initiating cyanoisopropyl radical and the signals at 14.6 ppm and 19.3 ppm to *cis*- and *trans*-methyl groups of terminating 3-methylpyrrolidine residues. The presence of the C-methyl groups on the terminating pyrrolidine indicates that termination occurs by an abstraction of hydrogen, probably from the solvent. These particular polymers are of low molecular weight but with state-of-the-art spectrometers that have greater dynamic range than our own the same approach should be possible with higher molecular weight polymers.

Tacticity Studies

In attempts to determine the sequencing of monomer units (tacticity) in a polymer it has been observed that the chemical shift sensitivity of a particular carbon may depend upon the configuration of from two (dyad) to seven (heptad) monomer units (Randall, 1977). The ensuing nmr signal from such a carbon can therefore consist of as many as thirty-six distinct resonance lines. The analysis of tacticity is important in relating polymer structure to polymer properties but is not easy since line shape analyses are unreliable. An example is the signal from the substituted aromatic carbon of polystyrene (Figure 13) which is obviously made up of a number of closely spaced individual lines.

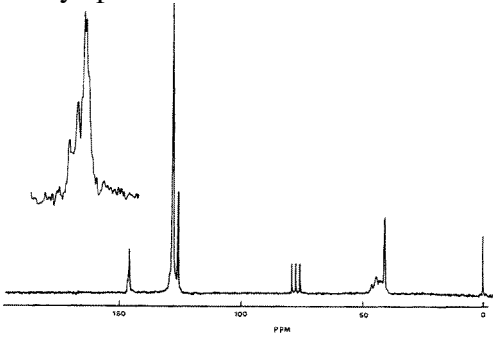


FIGURE 13. ^{13}C nmr spectrum of polystyrene (INSERT: Expanded region showing the fully substituted aromatic carbon signal).

I wish to describe a two pulse, inversion/recovery type $(\alpha - \tau - \delta - 5T_1)_n$ ^{13}C nmr sequence which induces different phase and intensity variations in the individual lines within such peaks and which, by varying the value of τ can produce a set of different peak shapes all of which must fit the same parameter set of chemical shifts and intensities (Johns, 1980).

The sequence (Figure 14) consists of an initial pulse which rotates the equilibrium magnetisation (M_0) through an angle (α) such that a significant component of the magnetisation exists in the xy plane (we use an angle of 220°). The time delay (τ) before the second pulse is set to less than the spin-spin relaxation time (T_2^*) so that a magnetisation component remains in the xy plane at the commencement of the second pulse which rotates the magnetisation through a further angle (δ). During the time τ, the xy component of magnetisation precesses about the z' axis and by varying the time τ a series of spectra can be obtained with phase and intensity variations arising from different excess precession angles. A series of different peak shapes can be experimentally produced.

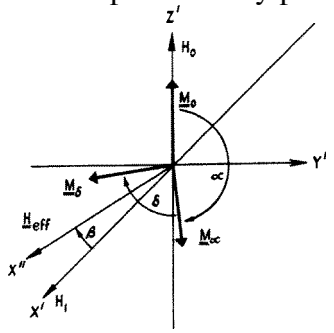


FIGURE 14. Two pulse sequence $(\alpha - \tau - \delta - 5T_1)_n$

The spin magnetisation during the two-pulse sequence can be described by the following equations:

$$M_\alpha = R_{y'}^{-1}(\beta)\, R_{x''}(\alpha)\, R_{y'}(\beta)\, M_0$$
$$M_\tau = R_{z'}(\theta K)\, \underline{S} M_\alpha + (1 - e_1^{-t/T_1})\, M_0$$
$$M_\delta = R_y^{-1}(\beta)\, R_{x''}(\delta)\, R_{y'}(\beta)\, M_\tau$$

where M_α and M_δ are the magnetisations after the α and δ pulses, M_τ the magnetisation following the time delay τ, $R_{y'}(\beta)$, $R_{x''}(\alpha)$ and $R_{z'}(\theta)$ are rotation matrices which rotate the magnetisation about the y', x'' and z' axis respectively. The angle θ is the precession angle of the magnetisation during the time τ about the z' axis and Θ is the excess precession angle defined as

$$\Theta = 2n\pi + \theta = (\Omega - \omega_1)r$$

where $(\Omega - \omega_1)r$ is the offset frequency

S is the relaxation matrix given by

$$S = \begin{bmatrix} e^{-\tau/T_2^*} & 0 & 0 \\ 0 & e^{-\tau/T_2^*} & 0 \\ 0 & 0 & e^{-\tau/T_1} \end{bmatrix}$$

Evaluation of M_δ gives a system of equations which provide the data necessary to define the spin state after the δ-pulse and these equations have been adapted to a Fortran programme to calculate a theoretical spectrum.

The simulation of a number of different peak shapes, derived from different τ values for a single set of chemical shifts and intensities should confirm the analysis of a multiline resonance peak.

Figures (15a, b, c) show the experimental ^{13}C nmr spectrum of the fully substituted aromatic carbon signal of polystyrene in $CDCl_3$ using a single FT pulse sequence, a $(220° - 0.2\ s. - 110° - 5 \times T_1)_n$ sequence and a $(220° - 0.35\ s. - 110° - 5 \times T_1)_n$ sequence.

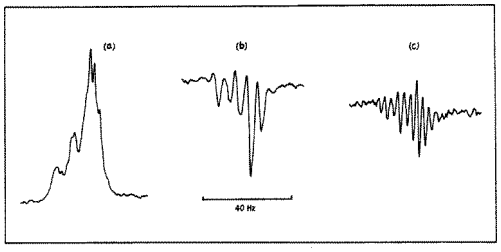


FIGURE 15. ^{13}C nmr spectrum of the fully substituted aromatic carbon signal of polystyrene in $CDCl_3$ using a

(a) Single FT pulse sequence.
(b) $(220° - 0.2\ s. - 110° - 5 \times T_1)_n$ pulse sequence
(c) $(220° - 0.35\ s. - 110° - 5 \times T_1)_n$ pulse sequence.

Figures (16a, b, c) show the theoretical ^{13}C nmr spectrum of the fully substituted aromatic carbon signal of polystyrene using 22 lines which correspond to the different chemical shifts and a $(220° - 20.0\ s. - 110° - 5 \times T_1)_n$ sequence, a $(220° - 0.2\ s. - 110° - 5 \times T_1)_n$ sequence and a $(220° - 0.35\ s. - 110° - 5 \times T_1)_n$ sequence.

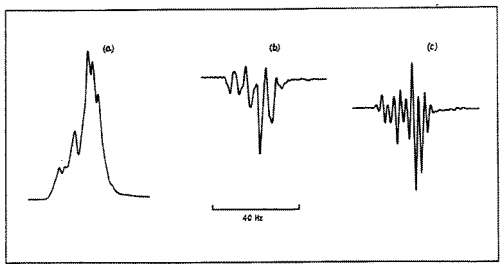


FIGURE 16. Theoretical ^{13}C nmr spectrum of fully substituted aromatic carbon signal of polystyrene using 22 lines and a

(a) $(220° - 20.0\ s. - 110° - 5 \times T_1)_n$ pulse sequence.
(b) $(220° - 0.2\ s. - 110° - 5 \times T_1)_n$ pulse sequence.
(c) $(220° - 0.35\ s. - 110° - 5 \times T_1)_n$ pulse sequence.

The good agreement between the experimental and simulated spectra confirms a heptad sensitivity to chemical shift for the fully substituted aromatic carbon of polystyrene although 14 of the 36 possible lines are coincident in shift within the experimental resolution.

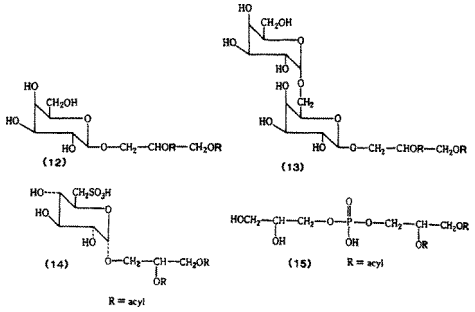
Of course the complete assignment of the tacticity broadened lines in the ^{13}C nmr spectrum of polymers will require the analysis of a number of samples prepared under different conditions with different monomer sequences, but the method should prove an excellent technique for the analysis of such spectra.

Biological Polymers

The ^{13}C nmr technique is equally suited to the study of biological polymers. Our own particular interest is in the use of ^{13}C nmr as a means of probing the structure and function of biological membranes. A membrane is considered to be made up of a mosaic of globular

proteins within a lipid bilayer (Singer, 1972) sometimes described as "icebergs in a lipid sea". The properties of the membrane depend particularly upon the fluidity of the lipid bilayer and the measurement of ^{13}C longitudinal relaxation times provides an excellent method for the study of motion within these lipid bilayers.

The particular membrane on which we have focussed our attention is the inner chloroplast membrane of green plants. This is where the light trapping, energy transfer and energy storage of photosynthesis takes place. The chloroplast membrane system, unlike most biological membranes, consists principally of neutral glycolipids rather than the charged phospholipids of other organelle and cellular membranes. The photosynthetic membranes are composed of approximately 50% protein and 50% lipid, the lipid composition comprising the four types; MGG (40%) (12), DGG (40%) (13), SL (10%) (14), and PG (10%) (15).



The fatty acid composition of the lipids shows a remarkably high concentration of(9Z,12Z,15Z)-octadeca-9,12,15-trienoic acid (α-linolenic acid) which may comprise over 90% of the acylating acids in DGG and MGG, 50% in SL and up to 30% in PG.

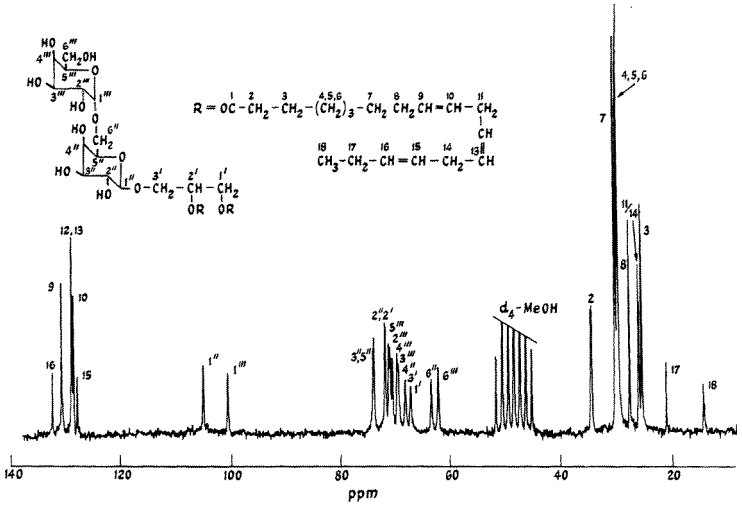


FIGURE 17. ^{13}C nmr of DGG in d_4-methanol.

We have isolated and purified these lipids and measurement of their ^{13}C nmr spectrum in d_4-methanol, e.g. that of DGG (Fig. 17) allows the assignment of all carbons in the molecules. We have measured the ^{13}C longitudinal relaxation times in different solvent systems, calculated the correlation times (τ_c) (Table 1) and interpreted these in terms of different secondary structures in the different solvents (Johns, 1977a). In methanol, correlation times

TABLE 1

^{13}C Longitudinal Relaxation Times (sec) and Correlation Times (x 10^{11} sec) in Brackets of DGG in Various Solvents.

Carbon	CD_3OD		$CDCl_3$		D_2O	
			α-Linolenic acid chain			
2	0.30	(7.8)	0.09	(26)		
	0.25	(9.3)				
3	0.53	(4.4)	0.26	(9.0)		
4	0.72[a]	(3.2)	0.47[a]	(5.0)	0.26[a]	(9.0)
5	0.72[a]	(3.2)	0.47[a]	(5.0)	0.26[a]	(9.0)
6	0.72[a]	(3.2)	0.47[a]	(5.0)	0.26[a]	(9.0)
7	0.91	(2.6)	0.72	(3.2)		
8	1.5	(1.6)	0.84	(2.8)		
9	2.1	(1.1)	1.2	(1.9)		
10	2.1	(1.1)	1.3	(1.8)		
11	2.9[b]	(0.80)	2.1	(1.1)	0.88[b]	(2.7)
12	3.9	(0.60)	2.6	(0.90)	0.83	(5.6)
13	3.9	(0.60)	2.6	(0.90)	0.83	(5.6)
14	2.9[b]	(0.80)	3.0	(0.78)	0.88[b]	(2.7)
15	7.6	(0.31)	7.1	(0.33)	2.3	(2.0)
16	7.4	(0.32)	6.9	(0.34)	2.3	(2.0)
17	11.1	(0.21)	9.5	(0.25)	3.0	(0.78)
18	8.9	(0.17)	7.8	(0.20)	3.6	(0.43)
			Glycerol chain			
1	0.10	(24)	0.03[c]	(100)	0.08[d]	(30)
2	0.16	(30)				
3	0.10	(24)				
			Galactoside groups			
1'	0.16	(30)	0.035	(800)		
2'	0.16	(30)				
3'	0.15	(32)	0.035	(800)		
4'	0.12	(40)				
5'	0.15	(32)	0.035	(800)		
6'	0.07	(32)			0.06	(100)
1"	0.19	(25)	0.035	(800)		
2"	0.17	(28)	0.04[d]	(200)		
3"	0.14	(34)	0.04[d]	(200)		
4"	0.18	(26)	0.04[d]	(200)		
5"	0.17	(28)	0.04[d]	(200)		
6"	0.19	(12)	0.03[c]	(100)	0.08[d]	(30)

[a,b,c,d] Averaged values obtained from unresolved signals.

of 2.8 ± 0.4 x 10^{-10} s. for all the glyceryl and galactosyl carbon atoms of DGG indicate that this portion of the lipid molecule undergoes rotation as a unit. The correlation times of the acyl chain carbon atoms however, decrease along the chain from C2 (8.0 x 10^{-11} s.) to the terminal methyl carbon (1.7 x 10^{-12} s.). This increase in motion arises from segmental motion in the acyl chain induced by β-coupled *trans-gauche* rotations about the C-C bonds. The total motion within the chain is derived from a combination of both molecular tumbling and segmental motion.

The longitudinal relaxation times and correlation times of the individual carbon atoms ofthe galactosyl and glyceryl moieties of DGG in chloroform are an order of magnitude different from the values in methanol. In chloroform, the motion of the carbon atoms in the polar regions of the molecules are severely restricted which indicates that the hydrophilic groups are associated and that the most likely secondary structure of the lipid molecule is one of an inverted micelle. The molecular tumbling of such a polymeric inverted micelle would be extremely slow which is consistent with the short relaxation times. By contrast, the motion of the acyl chain carbon atoms, which increase from C2 to the terminal methyl group carbons, are only slightly less than those of the monomeric form. Segmental motion along the acyl chain can again account for the observed values.

The correlation times of the glyceryl and galactosyl carbons of DGG in water correspond to a packing of the sugar moieties but in a structure in which the motion of the atoms is greater than in the inverted micellar structure. This is reflected in the broadened spectra of DGG in water (Figure 18). The relaxation times of the acyl chain carbons reveal a more restricted

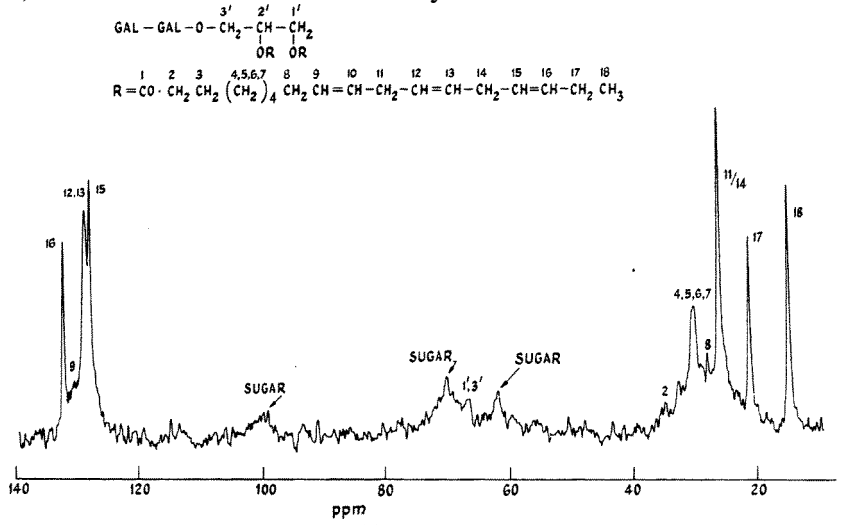


FIGURE 18. ^{13}C nmr of DGG in D_2O

motion than observed in the inverted micelles but once again segmental motion increases from the carbon atoms adjacent to the polar groups in the terminal methyl group carbons. The dynamic properties of the individual carbon atoms of DGG in water are therefore consistent with a bilayer structure with associated head groups at the water interface and a hydrophobic inner region comprised of acyl chains. Unlike the galactosyl lipids, SL is characterised by the presence of almost equimolar amounts of palmitic and α-linolenic acids. Comparison of the longitudinal relaxation times of the carbon atoms in the two chains (Table 2) (Johns, 1978) shows that at all equivalent positions that can be resolved (Figure 19) the motion of the α-linolenic acid chain is greater than that in the palmitic acid chain, but less than that of the same acid in DGG which contains two α-linolenic acid molecules. The presence of the saturated acyl chain in SL obviously restricts motion in the unsaturated acyl chain to a greater extent than does a second unsaturated chain.

Table 2

^{13}C Longitudinal Relaxation Times (sec) and Correlation Times (x 10^{11} sec) in Brackets of SL in Various Solvents.

Carbon	$CDCl_3$		CD_3OD		D_2O		$CDCl_3$		CD_3OD		D_2O	
	α-Linolenic acid chain						Palmitic acid chain					
2	0.14[a]	16.7)	0.29[a]	(8.0)	0.2[a]	(11.6)	0.14[a]	(16.7)	0.29[a]	(8.0)	0.2[a]	(11.6)
3	0.30[b]	(7.8)	0.44[b]	(5.3)			0.30[b]	(7.8)	0.44[b]	(5.3)		
4	0.53[c]	(4.4)	0.67[c]	(3.5)	0.3[c]	(7.8)	0.53[c]	(4.4)	0.67[c]	(3.5)	0.3[c]	(7.8)
5	0.53[c]	(4.4)	0.67[c]	(3.5)	0.3[c]	(7.8)	0.63[d]	(3.7)	0.71[d]	(3.3)	0.3[c]	(7.8)
6	0.53[c]	(4.4)	0.67[c]	(3.5)	0.3[c]	(7.8)	0.63[d]	(3.7)	0.71[d]	(3.3)	0.3[c]	(7.8)
7	0.77[e]	(3.0)	0.86[e]	(2.7)			0.77[e]	(3.0)	0.86[d]	(2.7)	0.3[c]	(7.8)
8	0.87	(2.7)	1.0	(2.3)	0.3	(7.8)	0.77[e]	(3.0)	0.86[e]	(2.7)	0.3[c]	(7.8)
9	1.2	(3.5)	1. 2	(3.5)			0.77[e]	(3.0)	0.86[e]	(2.7)	0.3[c]	(7.8)
10	1.2	(3.5)	1.2	(3.5)			0.77[e]	(3.0)	0.86[e]	(2.7)	0.3[c]	(7.8)
11	1.9[f]	(1.2)	2.6[f]	(0.90)	0.8[f]	(2.9)	0.77[e]	(3.0)	0.86[e]	(2.7)	0.3[c]	(7.8)
12	2.4	(1.7)	2.8	(1.5)	0.6	(7.0)	0.77[e]	(3.0	0.86[e]	(2.7)	0.3[c]	(7.8)
13	2.4	(1.7)	2.8	(1.5)	0.6	(7.0)	0.63[d]	(3.7)	0.71[d]	(3.3)	0.3[c]	(7.8)
14	1.9[f]	(1.2)	2.6[f]	(0.90)	0.8[f]	(2.9)	2.4	(0.97)	2.5	(0.93)	0.6	(3.9)
15	3.6	(1.2)	4.6	(0.91)	1.0	(4.2)	3.0	(0.78)	3.0	(0.78)	0.8	(2.9)
16	3.6	(1.2)	4.6	(0.91)	1.0	(4.2)	3.6	(0.43)	6.5[g]	(0.24)	2.0[g]	(0.78)
17	6.0	(0.39)	9.7	(0.24)	2.1	(1.1)						
18	5.7	(0.27)	6.5[g]	(0.24)	2.0[g]	(0.78)						
	Glycerol chain[h]						Sulphoquinovosyl group[h]					
1	0.03	(2500)	0.07	(34)			0.06	(2500)	0.14	(34)	0.05	(130)
2	0.06	(2500)	0.13	(37)	0.05	(130)	0.05	(2000)	0.14	(34)	0.05	(130)
3	0.03	(2500)	0.07	(34)			0.05	(2000)	0.13	(37)	0.04	(200)
4							0.04	(1400)	0.13	(37)	0.05	(130)
5							0.04	(1400)	0.13	(37)		
6							0.03	(2500)	0.08	(30)	0.03	(600)

[a-g] Averaged values obtained from unresolved signals.

[h] Correlation times in $CDCl_3$ are approximate.

This result indicates that the ^{13}C nmr technique can distinguish different motions in carbon atoms which are at the same distance from the polar head group in the different acyl chains of a lipid molecule, unlike the ESR spin label technique which only measures the motion of a reporter molecule.

We are using vesicles prepared from DGG in water and vesicles prepared from the total chloroplast membrane lipids in water to study the effect of added components such as antibiotics, anaesthetics, proteins and peptides to the lipid bilayers. The polyene antibiotic, amphotericin B, has been shown to inhibit a number of membrane-associated reactions in higher plant chloroplasts. That the inhibitions result from effects on membrane fluidity is

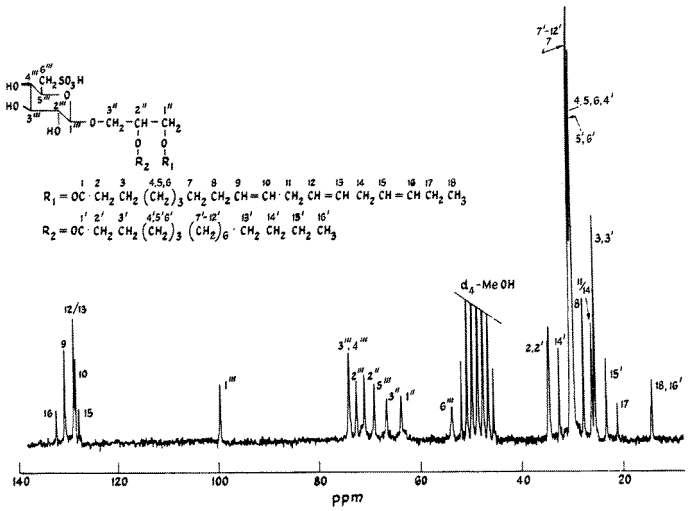


FIGURE 19. ^{13}C nmr of SL in d4 -methanol

clearly indicated by the relaxation time changes on addition of the antibiotic. (Table 3) (Bishop, 1978). The results indicate that the presence of the antibiotic causes a significant restriction in motion of the acyl chain carbons which is consistent with the occurrence of intercalation of the antibiotic between the acyl chains. Conversely, the addition of chloroform to the vesicles results in an increase in motion in the acyl chains.

TABLE 3

Effect of Amphotericin B on the Motion of Acyl chains of Aqueous Multibilayers of DGG

Carbon Atom	Longitudinal relaxatiom time (sec)	
	DGG	DGG plus Amphotericin B (10%)
4/5/6	0.26	0.27
11/14	0.88	0.91
12/13	0.83	0.91
15	2.3	1.2
16	2.3	1.4
17	3.0	2.5
18	3.6	2.7

Continuing experimentation on peptides and proteins, specifically membrane associated proteins such as the photosynthetic protein of the chloroplast, should lead to conclusive results on the interaction of proteins and lipids. These will be of importance in a variety of fields ranging from the mechanism of aging to the fundamental processes of colour vision and photosynthesis.

Future

^{13}C nmr and other magnetic resonance techniques promise an exciting future for study in the synthetic and the biological polymer fields. The examples given have been restricted to

^{13}C solution spectroscopy, however, current technological development of instrumentation is such that deuterium and phosphorus nmr now offer great potential in the biological/medical fields and the use of solid state nmr techniques offers unlimited opportunities. I trust that this short overview of our own work in the nmr of polymers might inspire you to use the technique in your own studies and apply the techniques in new areas of research.

Acknowledgements

I would finally like to thank my collaborators in the work described *viz*, Drs. D.G. Bishop, J.M. Coddington, D.G. Hawthorne, D.H. Solomon and M.A. Yabsley and Messrs. R.I. Willing and D.R. Leslie.

References

Bishop,.D.G., Nolan, W.G., Johns, S.R. and Willing, R.I., 1978. 'Evolution of the Lipid Components of Chloroplast Membranes. The Role of Lipid Fluidity in Membrane-Associated Reactions', in *Light Transducing Membranes*, pp. 269-288. Deamer, D.W. (Ed.). Academic Press Inc., New York.

Block, F., Hansen, W.W. and Packard, M., 1966. 'Nuclear Induction'. *Phys. Rev.,* **69**, 127.

Hawthorne, D.G., Johns, S.R., Solomon, D.H. and Willing, R.I., 1975. 'Cyanoisopropyl Radical Induced Cyclization and Cyclopolymerization of *N*-Methyl-*N*-allyl-*N*-(2-alkylallyl)amines and *N*-Methyl-*N,N*-bis(2-alkylallyl)amines. A ^{13}C Nuclear Magnetic Resonance Study'. *J. C. S. Chem. Commun.,* 982-3.

Hawthorne, D.G., Johns, S.R. and Willing, R.I., 1976a. '^{13}C NMR Spectra of Pyrrolidines and Piperidines. Structure of the Perhydroisoindol-5-ones and 3-Azabicyclo[3,3,1]nonan-6-imines Formed by the Cyanoisopropyl Radical Induced Cyclization of *N*-Methyl-*N,N*-bis-(2-alkylallyl)amines'. *Aust. J. Chem.,* **29**, 315-26.

Hawthorne, D.G., Johns, S.R., Solomon, D.H. and Willing, R.I., 1976b. 'The Cyclopolymerization of *N*-Allyl-*N*-methyl (2-substituted allyl) amines. The Structure of the Polymers and Low Molecular Weight Products'. *Aust. J. Chem.,* **29**, 1955-74.

Hawthorne, D.G., Johns, S.R., Solomon, D.H. and Willing, R.I., 1979. 'Initiation and Termination Group Identification in Polymers by ^{13}C NMR Spectroscopy'. *Aust. J. Chem.,* **32**, 1155-7.

Johns, S.R., Willing, R.I., Middleton, S. and Ong, A.L., 1976. 'Cyclopolymerization. VII. The ^{13}C NMR Spectra of Cyclopolymers Obtained from *N,N*-Diallylamines. *J. Macromol. Sci.-Chem.,* **A10**(5), 875-9.

Johns, S.R., Leslie, D.R., Willing, R.I. and Bishop, D.G., 1977. 'Studies on Chloroplast Membranes. II. ^{13}C Chemical Shifts and Longitudinal Relaxation Times of 1,2-Di[(9Z, 12Z,15Z)-octadeca-9,12,15-trienoyl]- 3-galactosyl-sn-glycerol and 1,2-Di[(9Z,12Z,15Z)-octadeca-9,12,15-trienoyl]-3-digalactosyl-*sn*-glycerol'. *Aust. J. Chem.,* **30**, 823-34.

Johns, S.R., Leslie, D.R., Willing, R.I. and Bishop, D.G., 1978. 'Studies on Chloroplast Membranes. III. ^{13}C Chemical Shifts and Longitudinal Relaxation Times of 1,2-Diacyl-3-(6-sulpho-α-quinovosyl)-*sn*-glycerol.' *Aust. J. Chem.,* **31**, 65-72.

Johns, S.R., Leslie, D.R., Willing, R.I. and Yabsley, M.A., 1980. 'A Two Pulse Sequence for the Analysis of Unresolved Multiline Resonances in ^{13}C Fourier Transform NMR Spectra'. *J. Magn. Reson.,* (In press).

Purcell, E.M., Torrey, H.C. and Pond, R.V., 1946. 'Resonance Absorption by Nuclear Magnetic Moments in a Solid'. *Phys. Rev.,* **69**, 37-38.

Randall, J.C., 1977. *Polymer Sequence Determination Carbon-13 NMR Method.* Academic Press, New York, 155 pp.

Singer, S.J. and Nicolson, G.L., 1972. 'The Fluid Mosaic Model of the Structure of Cell Membranes'. *Science,* **175**, 720-31.

Vold, R.L., Waugh, J.S., Klein, M.P. and Phelps, D.E., 1968. 'Measurement of Spin Relaxation in Complex Systems'. *J. Chem. Phys.,* **48**, 3831-2.