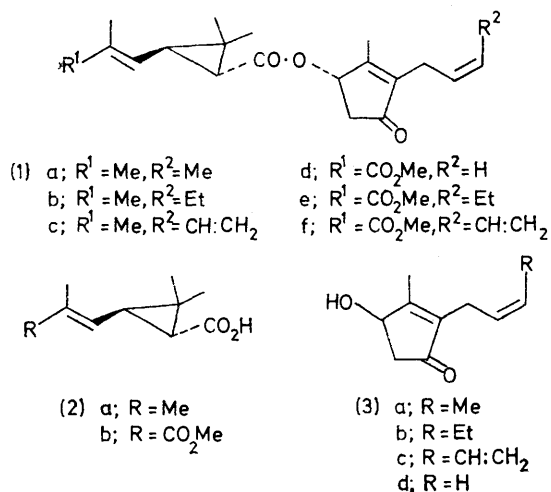


Carbon-13 Nuclear Magnetic Resonance Spectra of the Natural Pyrethrins and Related Compounds

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¹³C N.m.r. data for the naturally occurring insecticidal pyrethrin esters, synthetic allethrin, and the chrysanthemic acid and rethrolone molecules from which the esters are constituted, have been measured. Resonances were assigned by chemical shift comparisons, single frequency off-resonance proton decoupling, and specific ¹³C-¹H decoupling with proton resonances.

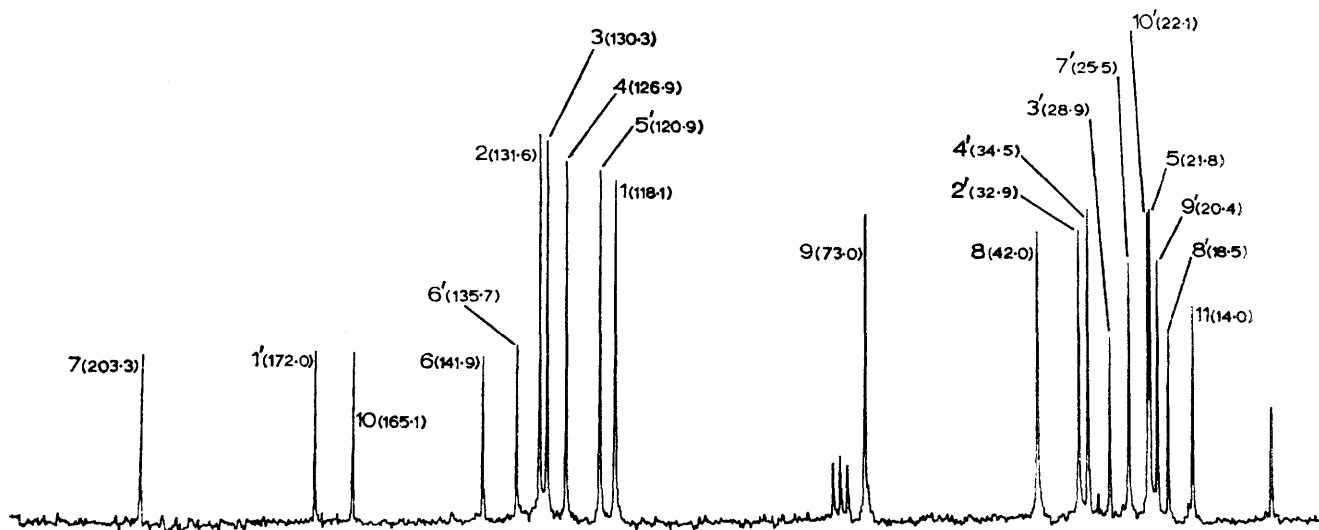
THE pyrethrins are insecticidal esters found in *Chrysanthemum cinerariaefolium*.¹ Their structures are based



on the common skeleton (1). The desirable insecticidal properties shown by the natural pyrethrins have resulted in the development of several useful synthetic

geometries, the development of satisfactory structure-activity relationships requires reliable information about the preferred conformations of the molecules in solution. With this in mind, and also in relation to our studies of the biosynthesis of the pyrethrins,³ we have examined the ¹³C magnetic resonance spectra of the natural pyrethrins (1a, c, e, and f), synthetic allethrin (1d), and the chrysanthemic acid (2a and b) and alcohol (3a-d) ('rethrolone') molecules from which the esters are constituted.

The ¹³C spectra of the esters were complex and not amenable to direct analysis. They were interpreted by comparison with the ¹³C magnetic resonance data of the acids and alcohols from which the esters are derived. Both noise- and off-resonance-decoupled spectra were collected for all these compounds and the Table lists the assignments (δ in p.p.m. from Me₄Si internal standard). The spectrum of any rethrin ester is almost a direct summation of the spectra of the acid and alcohol components [in this case chrysanthemic acid (2a) + pyrethrolone (3c) → pyrethrin I (1c)] and the Figure shows the fully assigned spectrum of pyrethrin I.



¹³C N.m.r. assignments for pyrethrin I

analogues, and much attention has been given to structure-activity relationships amongst this group of compounds.² Apart from a knowledge of absolute

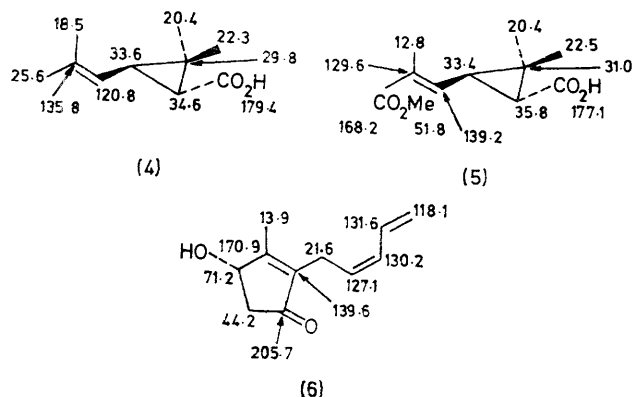
¹ See 'Pyrethrum, the Natural Insecticide,' ed. J. E. Casida, Academic Press, New York and London, 1973.

² M. Elliott, *Chem. and Ind.*, 1969, 776; *Bull. World Health Organisation*, 1971, **44**, 315.

¹³C Resonances for *trans*-chrysanthemic acid (2a) were readily assigned from inspection and comparison of shift data, and also from decoupled spectra; the assign-

³ (a) G. Pattenden and R. Storer, *Tetrahedron Letters*, 1973, 3473; (b) S. A. Abou-Donia, C. F. Doherty, and G. Pattenden, *ibid.*, p. 3477; G. Pattenden, C. R. Popplestone, and R. Storer, *J.C.S. Chem. Comm.*, 1975, 290.

ments are summarised on formula (4). The olefinic carbon signals were distinguished in the off-resonance

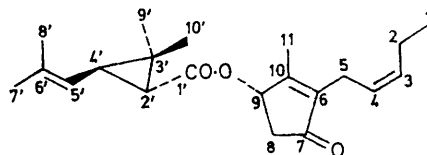


spectrum; one (at δ 135.8) was observed as a singlet, and the other (at δ 120.8) as a doublet. The off-resonance spectrum also distinguished the quaternary

experiments showed that the methyl carbon atom *cis* to the carboxy-function was the more shielded of the two (δ 20.4 and 22.3); this is the reverse of the differential shielding observed in ¹H n.m.r., where the methyl protons *cis* to the carboxy-function are more deshielded (τ 8.7 and 8.85).⁴ Interpretation of the ¹³C spectrum of pyrethric acid (2b) followed from comparison of data. As expected, those centres β (C-5') and δ (C-2' and C-3') to the methoxycarbonyl function in (2b) were significantly deshielded in comparison with the same centres in chrysanthemic acid [*cf.* δ values on formulae (4) and (5)].

¹³C Resonances associated with the carbon atoms of the 3-methylhydroxycyclopentenone rings in the alcohols (3a—d) (*i.e.* C-6—11) were closely similar, and furthermore were readily assigned from shift data and from off-resonance spectra. Two triplets and three doublets were observed in the off-resonance for the carbons associated with the pentadienyl side chain of pyrethrolone (3c). The triplets, due to the *sp*²- and *sp*³-hybridised

¹³C N.m.r. data (p.p.m. from Me₄Si)



Carbon atom	(2a) *	(2b) *	(3d)	(3a)	(3b)	(1d)	(1a)	(1b)	(1e)	(1f)
1					14.1			14.0	14.1	118.4
2				12.81	20.6		12.8	20.5	20.6	132.3
3			115.7	125.79	132.9	115.9	125.5	133.1	133.1	129.8
4			133.7	125.20	124.1	133.5	125.4	123.9	123.9	126.7
5			27.0	20.9	21.1	27.1	21.0	20.5	20.6	21.1
6			139.2	140.9	140.7	141.3	142.7	142.7	142.9	141.7
7			205.7	205.0	205.3	203.7	203.9	203.9	203.6	203.4
8			44.2	44.3	44.3	41.6	41.7	41.6	41.5	41.5
						42.0	42.0	42.0	42.0	42.0
9			71.3	71.6	71.5	72.6	72.7	72.6	73.1	73.1
						72.9	73.0	73.0	73.5	73.4
10			171.0	168.8	169.3	165.8	165.0	164.8	164.3	165.3
11			13.7	13.7	13.7	14.0	14.0	14.0	14.1	14.2
1'	172.7	171.7				172.2	172.3	172.3	171.2	171.1
2'	34.6	36.0				34.6	34.6	34.6	35.8	35.8
3'	28.4	30.1				29.1	29.1	29.1	30.5	30.6
4'	32.8	32.8				33.0	32.9	32.9	32.9	33.0
						33.1	33.1			
5'	121.3	139.4				120.8	120.8	120.8	138.9	138.9
6'	135.3	129.5				135.8	135.9	135.9	129.8	129.3
7'	25.6	168.1				25.6	25.6	25.6	168.0	168.0
8'	18.4	12.8				18.5	18.5	18.5	12.9	12.9
9'	20.4	20.5				20.4	20.4	20.5	20.6	20.5
10'	22.2	22.4				22.1	22.1	22.1	22.3	22.3
OMe	51.2	51.7							51.8	51.8

* Methyl ester.

cyclopropane carbon atom (C-3') from the two other cyclopropane carbon atoms (C-2' and C-4'), but a distinction between the latter was only possible by specific ¹³C-¹H decoupling experiments with the proton resonances.^{4,†} In a similar manner, ¹³C-¹H decoupling experiments were used to distinguish the geminal methyl groups attached to the cyclopropane ring. These

† We thank R. W. King for this information.

⁴ A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M. Elliott, and N. F. Janes, *Tetrahedron*, 1969, **25**, 1727.

carbon atoms C-1 and C-5 respectively, were readily assigned. The doublets due to the remaining *sp*²-hybridised carbon atoms C-2, C-3, and C-4 were distinguished by specific ¹³C-¹H decoupling with the proton resonances [see formula (6) for assignments].

The three triplets (δ 20.6, 21.1, and 44.3) observed in the off-resonance spectrum of jasmololone (3b), due to the *sp*³-hybridised carbon atoms C-2, C-5, and C-8 were assigned from ¹³C-¹H decoupled spectra. Assignment of the signals due to the *sp*²-hybridised carbon atoms C-3

and C-4 in the side chain of jasmololone is based on semiempirical relations derived by Brouwer and Stothers⁵ [calc. δ 122.1 (C-3) and 130.5 (C-4)]. The similar sp^2 carbon centres in the side chain of cinerolone (3a) (δ 125.79 and 125.20) could not be distinguished.

The interpretation of the ^{13}C resonance spectra of the pyrethrin esters followed from comparison of data obtained for the acids (2a and b) and alcohols (3a—d): see Table for assignments. Inspection of ^{13}C data for esters synthesised from (\pm)-alcohols and (+)-*trans*-chrysanthemic acids shows that certain resonances (notably those of C-8, C-9, and C-4') are duplicated in these spectra; the resonance duplications reflect differential shielding of epimerically related carbons, the effect falling off with distance from the dissymmetric centres responsible for the diastereoisomerism (*viz.* C-9 and C-2'). The observed duplication of the C-4' resonance is particularly noteworthy, and is to be contrasted

⁵ See J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, 1972, p. 75.

with the corresponding ^1H n.m.r. data: the proton attached to C-2' and not that attached to C-4', showed differential shielding in the diastereoisomers.⁴

EXPERIMENTAL

The materials used in this study were available from our previous synthetic work. Samples were rigorously purified by chromatography prior to analysis. Spectra were recorded at 20 °C on a JEOL-PS-100 spectrometer operating at 25.15 MHz interfaced with a Nicolet 1085 20 K computer. Deuterium lock was provided by the solvent (CDCl_3). Sample concentrations were in the range 30—90 mg ml⁻¹. The pulse width was 3 μs (22° tip) and the F.I.D.s were compiled using 8 K data points over a spectral width of 6 000 Hz.

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