Tetrahedron. Vol. 25, pp. 1727 to 1741. Pergamon Press 1969. Printed in Great Britain

NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE NATURAL PYRETHRINS AND RELATED COMPOUNDS

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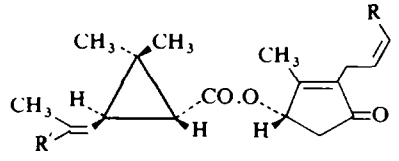
(*Received in the UK* 29 *October* 1968; *accepted for publication* 20 *November* 1968)

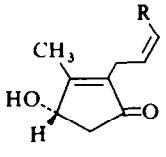
Abstract—The NMR spectra of the natural pyrethrins, allethrin, and the alcohols and acids from which these esters are separately constituted are presented and discussed.

THE pyrethrins are a group of insecticidal esters found in the flower heads of pyrethrum *Chrysanthemum cinerariaefolium*. Six compounds are now recognized as being responsible for the insecticidal activity of pyrethrum extract; these are cinerin I (**1a**), jasmolin I (**1b**), pyrethrin I (**1c**), grouped collectively as the "pyrethrin I's", and cinerin II (**1d**), jasmolin II (**1e**), pyrethrin II (**1f**), grouped as the "pyrethrin II's".[1,2] Degradation of the mixed esters gives a mixture of alcohols, the rethrolones, cinerolone (**2a**),



1

a: R = CH_3; R′ = $-CH_3$.
b: R = C_2H_5; R′ = $-CH_3$.
c: R = $-CH{=}CH_2$; R′ = $-CH_3$.
d: R = $-CH_3$; R′ = $-CO_2CH_3$.
e: R = $-C_2H_5$; R′ = $-CO_2CH_3$.
f: R = $-CH{=}CH_2$; R′ = $-CO_2CH_3$.



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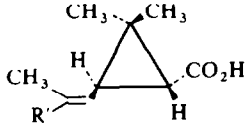
a: R = CH_3.
b: R = $-C_2H_5$.
c: R = $-CH{=}CH_2$.



3

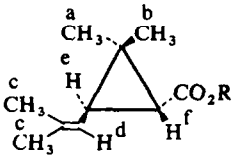
a: R′ = $-CH_3$.
b: R′ = $-CO_2CH_3$.

jasmololone (**2b**), pyrethrolone (**2c**), and of acids, chrysanthemic acid (**3a**) and pyrethric acid (**3b**). The stereochemical detail now accepted for the pyrethrins, the rethrolones, and the naturally derived acids is indicated in the appropriate formulae.[1] This paper

describes the NMR spectra of these important natural insecticides, and also of the natural rethrolones (2) and acids (3) from which they are constituted. The NMR spectrum of allethrin (1; R = H; R′ = —CH_3),[3] a commercially important insecticide with a structure similar to that of the natural pyrethrins, is also included.

The NMR spectra of the pyrethrins are reproduced in Figs 3 and 4. The spectra are complex, so direct analyses are not possible. However, the spectrum of any pyrethrin is almost a direct summation of the spectra of the alcohol and acid from which it is derived; the NMR spectra of the separate alcohols (2) and acids (3) are, therefore, discussed first.

The NMR spectra of *trans*-**4a**, and *cis*-chrysanthemic acid (**5a**) have been reported previously by Hutton and Schaefer[4] for benzene and carbon disulphide solutions



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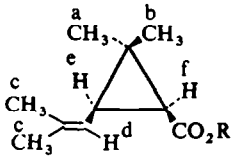

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a R = H; **b** R = —CH_3.

respectively. The cyclopropane ring protons ^eH, ^fH, and the olefinic proton ^dH in both isomers constitute ABX-type systems, which approximate to the AMX-case with $J_{AX} \sim 0$ c/s. Hutton and Schaefer have calculated J 5·4 (*trans*) and J 8·7 (*cis*) c/s for the cyclopropane ring proton (J ^eH–^fH) couplings in the two isomers, which are in reasonable agreement with calculations based on the Karplus equation.[5] Table 1

TABLE 1. NMR DATA* FOR *cis*-, AND *trans*-CHRYSANTHEMIC ACIDS AND THEIR METHYL ESTERS

	$^aCH_3$	$^bCH_3$	$^cCH_3$ d($J \sim 1·5$)	^dH dm($J \sim 8$)	^eH dd(J 5·5 and 8)	^fH d($J \sim 5·5$)†	—OH or —OCH_3
4a	8·7	8·85	8·30	5·1	7·9	8·62	−1·64
4b	8·75	8·89	8·31	5·09	7·9	8·63	6·33
5a	8·74	8·79	8·23; 8·29	4·63	~8·02‡	~8·36‡	—
5b	8·77	8·80	8·26; 8·32	4·62	~8·12‡	~8·40‡	6·38

* For abbreviation see Experimental.
† J applies only to *trans*-isomers.
‡ Resonance partly obscured.

summarizes the NMR data for *cis*-, and *trans*-chrysanthemic acids, and their Me esters in deuteriochloroform solution; the spectra of the two esters are reproduced in Fig. 1. The quoted J-values are the result of a simple AMX-analysis; the cyclopropane ring proton couplings (J ^eH–^fH) in the *cis* isomers (**5**) could not be obtained because these resonances are partly obscured by the corresponding vinyl-methyl signals

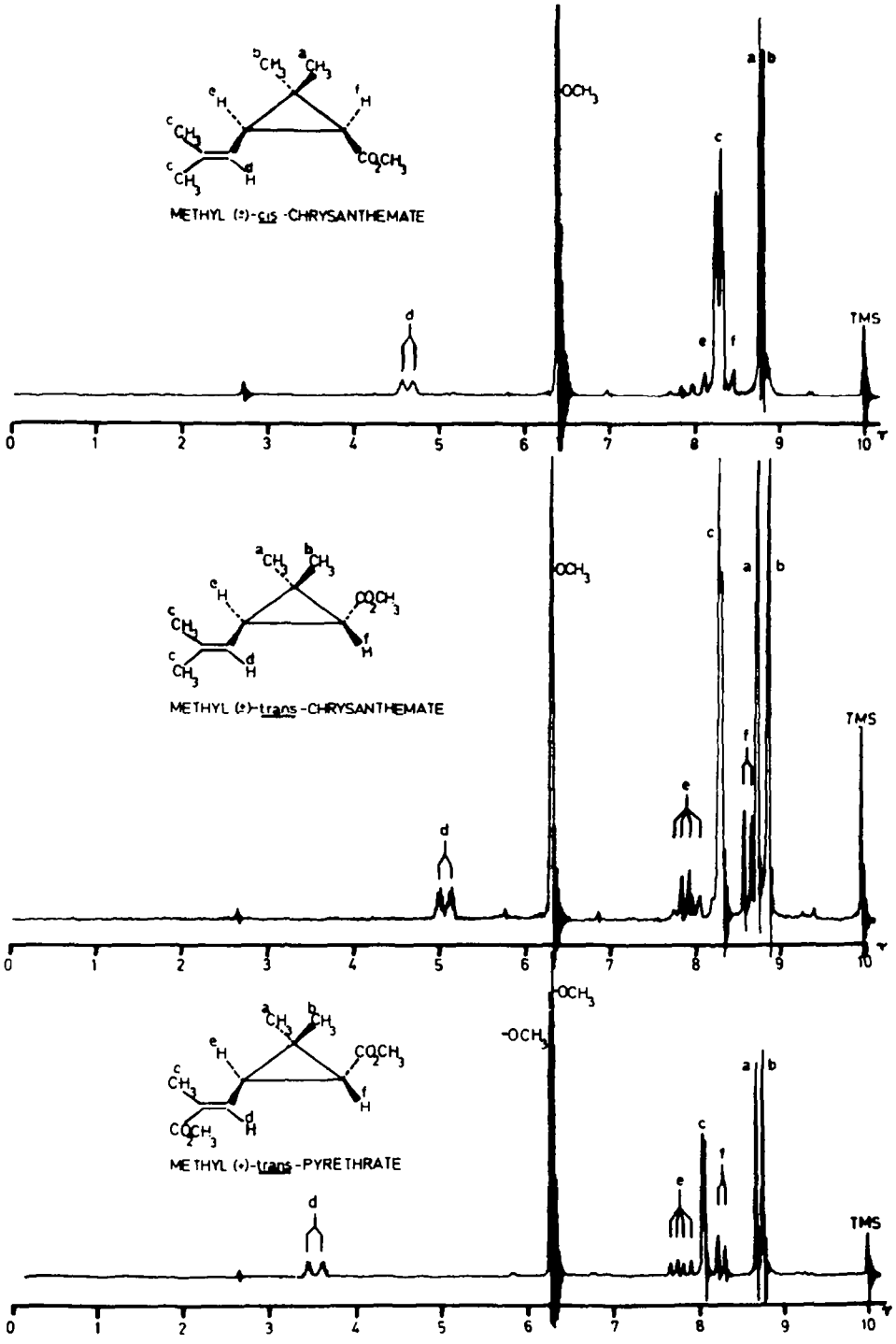
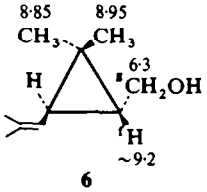


FIG. 1 NMR spectra of methyl (±)-*cis*-, and (±)-*trans*-chrysanthemate, and methyl (+)-*trans*-pyrethrate.

(Fig. 1). The olefinic protons (^{d}H) in both isomers are observed as doublets ($J \sim 8$) of partially resolved multiplets; the complex multiplicity of each component of the doublets results from coupling ($J \sim 1{\cdot}5$) to the neighbouring *gem*-dimethyl protons. The olefinic protons (^{d}H) in the *cis* isomers (**5**) resonate at lower field ($\sim \tau$ 4·62) than the corresponding protons in the *trans* isomers (**4**; $\sim \tau$ 5·1). These differences, which are associated with the relative situation of the protons with respect to the neighbouring carboxy function in the two isomers, are useful in determining percentage compositions of chrysanthemic acid isomer mixtures.[6] The ^{e}H-protons in the *trans* isomers are likewise deshielded, relative to those in the *cis* isomers (τ 8·02–8·12), by the neighbouring *cis* (to them) carboxy function, and resonate at lower field (τ 7·9). It is interesting to note that the ^{f}H-protons in the *trans* isomers (**4**) resonate at higher field (τ 8·62) than the corresponding protons ($\sim \tau$ 8·36) in the *cis* isomers (**5**); clearly the neighbouring isobutenyl group adopts conformations whereby the double bond shields these protons in the *trans* isomers. The corresponding protons in *trans*-**6**, and *cis*-chrysanthemyl alcohol (**7**) show a similar chemical shift difference (for discussion of conformational equilibrium in vinylcyclopropanes see refs 7 and 8, and refs cited therein).



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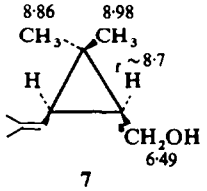

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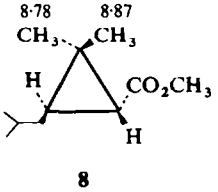

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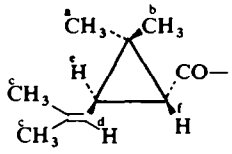
The saturated Me protons (^{a}CH$_3$:^{b}CH$_3$) resonate at different chemical shifts in both the chrysanthemate isomers. These differences, which are more pronounced in the *trans* isomers (**4**; τ 8·75; 8·89) than in the *cis* compounds (**5**; τ 8·77; 8·8) are associated with the situation of these protons with respect to the adjacent carboxy functions and isobutenyl groups. The NMR spectra of (±)-*trans*-**6**, and (±)-*cis*-chrysanthemyl alcohol (**7**), and of methyl (±)-*trans*-dihydrochrysanthemate (**8**) show similar differential shielding of the two Me groups to that observed in the *trans* ester (**4b**). On this basis it is not possible to unambiguously assign the two Me groups in **4b**, but evidence presented later strongly supports an assignment where those Me protons (^{a}CH$_3$) which resonate at lowest field in the *trans* isomers (**4**) are *cis* to the neighbouring carboxy functions. The saturated Me protons in the *cis* isomers (**5**) resonate at approximately the same field. Although the adjacent carboxy function seemingly deshields those methyl protons (^{a}CH$_3$) *cis*- to it, the isobutenyl group which is also *cis* to these protons, shields them, thereby making the effective deshielding by the carboxy function less than that observed in the *trans* compounds. It is recalled that the ^{f}H-protons in the *trans* isomers (**4**) are also shielded by the neighbouring isobutenyl group, relative to the same resonances in the *cis* compounds. It is interesting to note, that protons (^{f}H or ^{g}CH$_2$) *cis* to the isobutenyl group in *trans*-**6**, and *cis*-chrysanthemyl alcohols (**7**) are also shielded relative to the same protons *trans* to this group, in the corresponding isomer (see Refs 7 and 8).

The isobutenyl Me protons (—^{c}CH$_3$) are observed as doublets ($J \sim 1{\cdot}5$) in both isomers. Although these protons have the same chemical shift in the *trans* isomers

(**4**; τ 8·30), one of the Me groups in the *cis* isomers is deshielded relative to the other, by virtue of its proximity to the neighbouring carboxy function, and two resonances are observed (τ 8·23; 8·29).

In natural pyrethrin I's (+)-*trans*-chrysanthemic acid is esterified with a rethrolone (**2**). The NMR data for the chrysanthemate protons in natural pyrethrin I's and

TABLE 2. NMR DATA FOR [(+)-*trans*-] CHRYSANTHEMATE PROTONS IN NATURAL PYRETHRIN I'S AND RELATED COMPOUNDS



	$^{a}CH_3$	$^{b}CH_3$	$^{c}CH_3$	^{d}H dm ($J \sim 8$)	^{e}H*	^{f}H d ($J \sim 5{\cdot}5$)
Cinerin I (**1a**)	8·73	8·86	8·27	5·07	~7·9	8·59
(±)-Jasmolin I (**1b**)†	8·72; 8·74	8·85	8·28	5·06	~7·9	8·59
Pyrethrin I (**1c**)	8·76	8·88	8·29	5·07	~7·9	8·62
Allethrin (1. R = H; R′ = CH_3)‡	8·74	8·87	8·30	~5·07*	~7·9	8·6

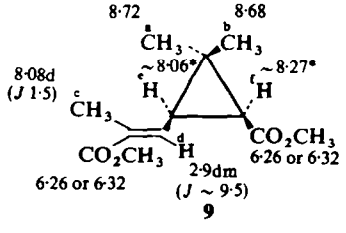
* Resonances obscured.

† Reconstituted from (±)-alcohol, and chloride of (+)-*trans*-acid.

‡ Reconstituted from (+)-alcohol, and chloride of (+)-*trans*-acid.

related compounds (Table 2; Figs 3 and 5) closely resemble those obtained for methyl (±)-*trans*-chrysanthemate (**4b**; Table 1).

The NMR data for methyl *cis*- **9**, and *trans*-pyrethrate (**10**) are summarized in the accompanying formulae; the spectrum of the *trans*-di-ester (**10**) is reproduced in Fig. 1. The chemical shift differences between the protons (^{d}H, ^{e}H, ^{f}H) of the ABX-systems in the two isomers resemble those observed previously in the isomers of chrysanthemic acid; the magnitude of the splittings are also comparable. The appearance of the olefinic proton (^{d}H) in the *trans* isomer (**10**; which is the established configuration of the naturally derived acid), as a doublet ($J \sim 9{\cdot}5$) of multiplets at τ 3·53 has been used as strong support for the assignment of the *trans*-(*E*) side-chain configuration in natural pyrethric acid.[9]



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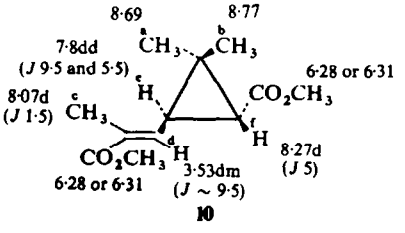
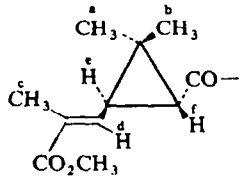


10

The vinyl-methyl protons in *cis*-, and *trans*-pyrethrates resonate at similar chemical shifts ($\sim \tau$ 8·08). This observation suggests that in methyl *cis*-chrysanthemate (**5b**) where two vinyl-methyl group signals are observed, it is the vinyl-methyl group *cis* to the olefinic proton that is preferentially deshielded (τ 8·26 versus 8·32) in this compound. The saturated Me protons in the pyrethrates resonate at different chemical shifts in both isomers, although these differences are not as marked as was observed previously with the chrysanthemic acid isomers. The data in Table 3 summarize the

TABLE 3. NMR DATA FOR [(+)-*trans*-] PYRETHRATE PROTONS IN NATURAL PYRETHRIN II'S AND RELATED COMPOUNDS



	$^{a}CH_3$	$^{b}CH_3$	^{c}CH d ($J \sim 1{\cdot}5$)	^{d}H dm ($J \sim 9$)	^{e}H dd ($J = 9$ and 5)	^{f}H d ($J = 5$)	$-OCH_3$
Cinerin II (**1d**)	8·7	8·77	8·07	3·47	~7·79*	8·26*	6·26
(±)-Jasmolin II (**1e**)†	8·64; 8·66	8·74	8·05	3·50	~7·8*	8·25	6·25
Pyrethin II (**1f**)	8·70	8·77	8·07	~3·52*	7·79	8·27	6·25

* Resonances partly obscured.

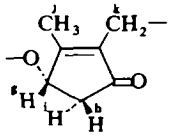
† Reconstituted from (±)-alcohol, and chloride of (+) *trans*-acid. The prefix (±) attached to a rethrin thus implies a mixture of two diastereoisomers and not a racemic mixture.

resonances of the pyrethrate protons in natural pyrethrin II's and related compounds (Fig. 4); the data agree with those obtained for methyl (+)-*trans*-pyrethrate, containing a *trans*-(*E*)-side-chain configuration.

The NMR data for the cyclopentenone ring protons of natural rethrolones, and related compounds are summarized in Table 4. The spectra of natural cinerolone (**2a**), natural pyrethrolone hydrate (**2c**), synthetic (±)-jasmololone (**2b**) and synthetic allethrolone (**2**; R = H) are reproduced in Figs 2 and 5. Natural jasmololone (**2b**) has not been isolated from the hydrolysis of pyrethrum extract, principally because it is present only in a small quantity, and also because it is separated only with difficulty from natural cinerolone (**2a**). The data in Table 4 were obtained from a recent synthetic sample of racemic jasmololone.[10]

The cyclopentenone ring protons (^{g}H, ^{h}H, ^{i}H) in the compounds collected in Table 4, form ABX-type systems, although parts of the multiplets due to the ^{h}H and ^{i}H-protons, are obscured in some spectra. Only four of the expected eight lines (due to ^{h}H, and ^{i}H) are clearly visible in the AB-regions of the spectra (five lines are seen in the case of pyrethrolone). The two outer lines of the ^{h}H-protons are partly masked by the doublets due to the exocyclic methylene protons (—$^{k}CH_2$—; split by adjacent olefinic proton in side-chain), and the outer lines of the ^{i}H-protons are completely hidden by the singlet signals due to the vinyl-methyl protons (—$^{j}CH_3$). In the 100 Mc/s NMR spectrum of pyrethrolone, determined in CCl_4 solution, however, the

TABLE 4. NMR DATA FOR THE CYCLOPENTENONE RING PROTONS IN NATURAL RETHROLONES AND RELATED COMPOUNDS



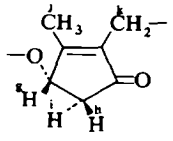
	^{g}H dm (J = 6)	^{h}H dd (J = 6 and 18)	^{i}H* dd (J = 2 and 18)	$^{j}CH_3$	$^{k}CH_2$ d (J = 6–7)	—O<u>H</u> or —O·CO<u>CH</u>$_3$
Cinerolone (**2a**)	5·31	7·22	7·76	7·9	7·06	6·24
(±)Jasmololone (**2b**)	5·33	7·24	7·81	7·91	7·09	6·27
Pyrethrolone (**2c**)	5·31	7·22	7·76	7·9	6·91	6·77
Pyrethrolone (**2c**)†	5·49	7·45	7·85	8·0	7·05	5·78
(**2a**)-acetate	4·32	7·12	7·76	7·96	7·02	7·9
(**2c**)-acetate	4·32	7·10	7·75	7·96	6·86	7·89
Allethrolone (2; R = H)	~5·25*	7·22	7·76	7·9	7·06	5·73
(2; R = H)-acetate	~4.31*	7·11	7·78	7·96	7·01	7·88

* Resonances partly obscured.

† 100 Mcs (CCl_4) spectrum.

^{h}H-proton resonates at τ 7·45, and a clear four line signal is observed. The ^{g}H-protons, which make up the X-parts of the ABX-systems in these spectra, are observed as poorly resolved doublets (J = 6) of multiplets; the multiplicities of these doublets result from additional coupling of the protons to the adjacent vinyl-methyl and vinyl-methylene protons, and also with some of the keto-alcohols, to the hydroxyl protons.

TABLE 5. NMR DATA FOR THE CYCLOPENTENONE RING PROTONS IN NATURAL PYRETHRINS AND RELATED COMPOUNDS



	^{g}H dm (J = 6)	^{h}H dd (J = 6 and 18)	^{i}H* dd (J = 2 and 18)	$^{j}CH_3$	$^{k}CH_2$ d (J = 6)
Cinerin I	4·32	7·11	7·81	7·95	7·02
(±)-Jasmolin I†	4·23; 4·33	7·13	~7·8	7·95	7·0
Pyrethrin I	4·31*	7·12	7·81	7·97	6·88
Cinerin II	4·29	7·10	7·80	7·97	7·02
(±)-Jasmolin II†	4·21; 4·31	7·07; 7·10	~7·8	7·95	7·01
Pyrethrin II	4·31	7·10	7·81	7·97	6·88
Allethrin (1, R = H, R′ = CH_3)‡	~4·28*	7·10	7·80	7·97	7·02

* Resonances partly obscured.

† Reconstituted from (±)-alcohol and chloride of (+)-*trans*-acid.

‡ Reconstituted from (+)-alcohol and chloride of (+)-*trans*-acid.

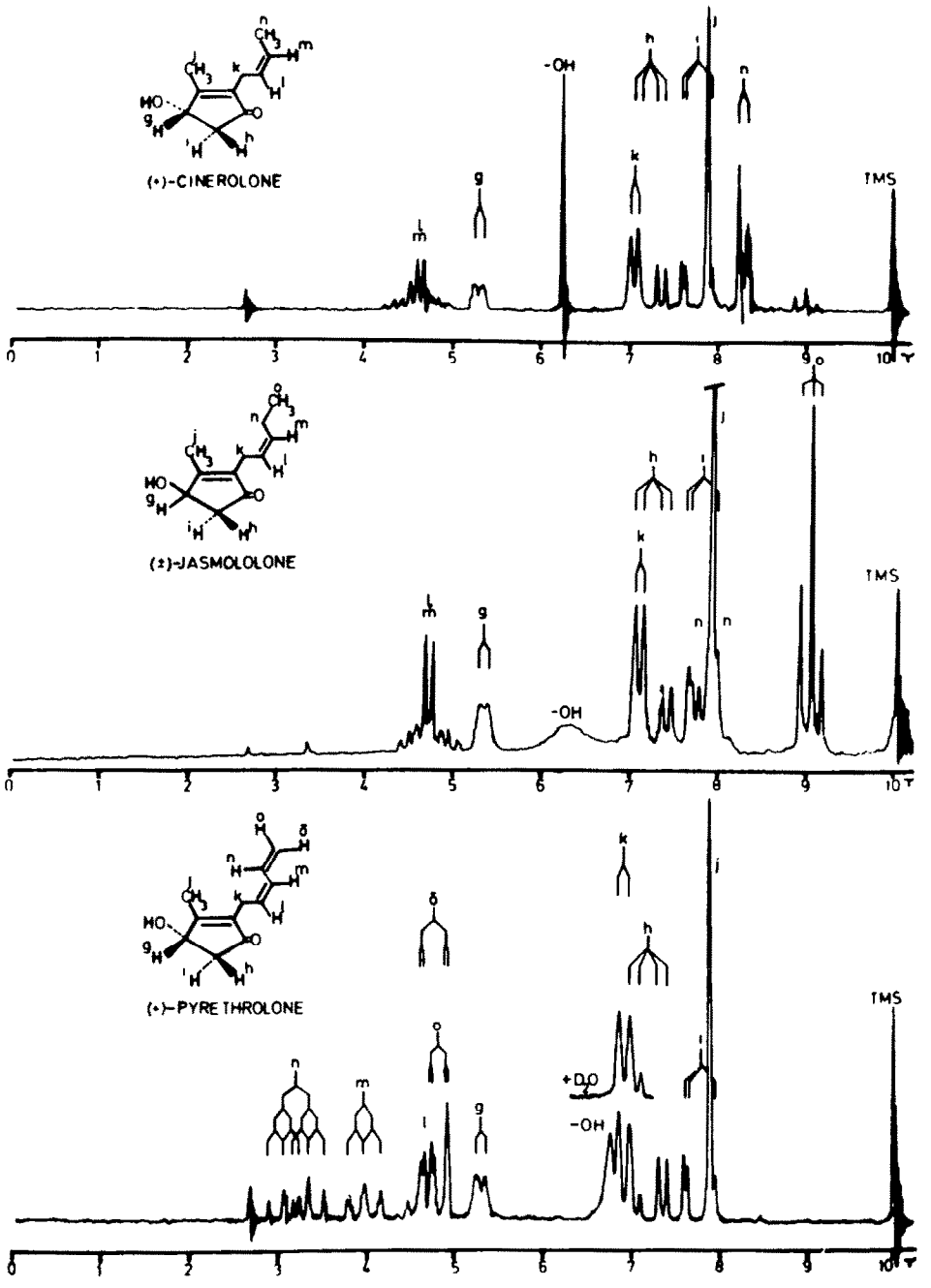


FIG. 2 NMR spectra of (+)-cinerolone, (±)-jasmololone, and (+)-pyrethrolone.

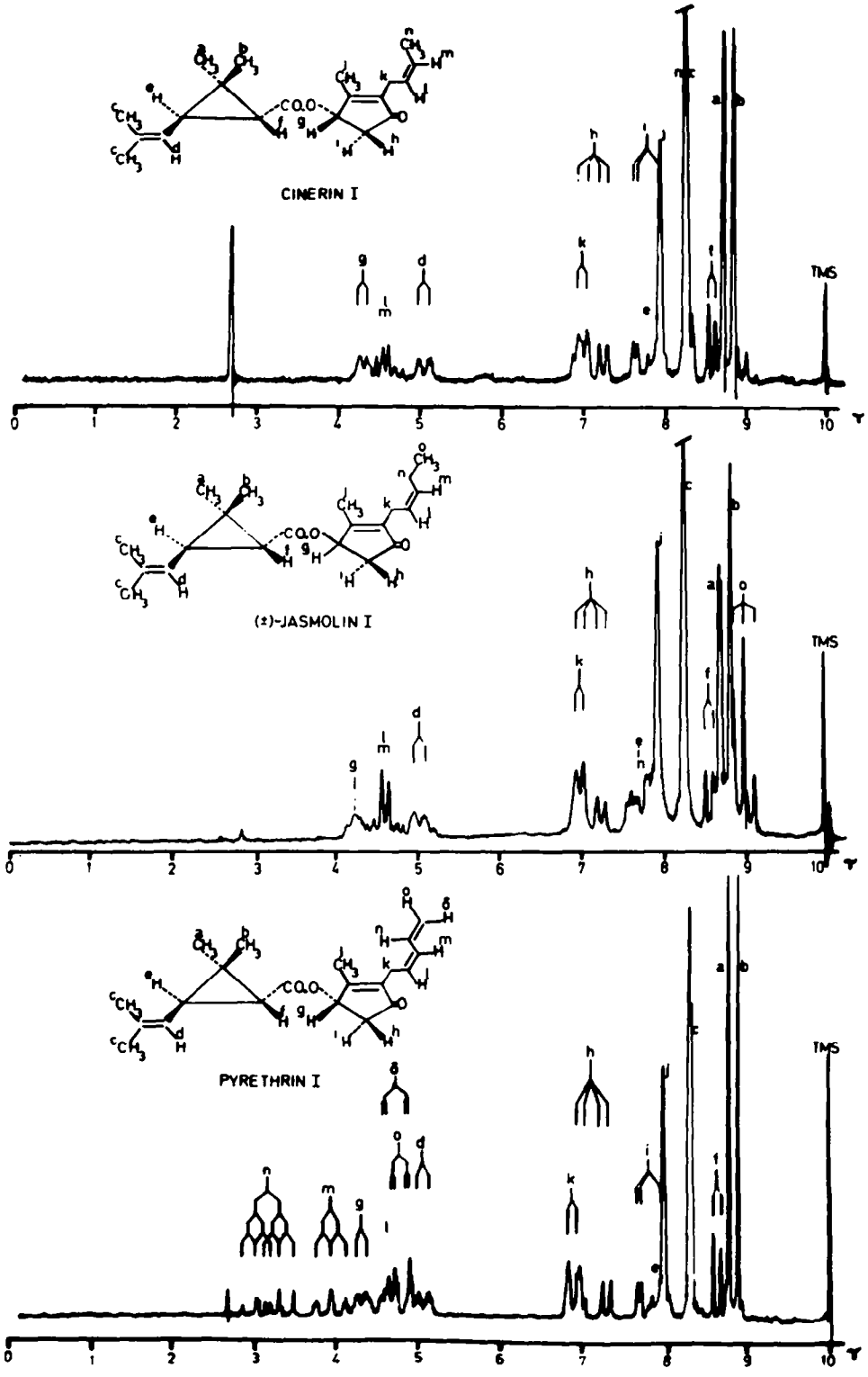


FIG. 3 NMR spectra of cinerin I, (±)-jasmolin I, and pyrethrin I.

The observed vicinal-couplings of the ^{h}H, and ^{i}H-protons are 6 and 2 c/s. Calculations based on the Karplus equation[5] give J (*cis*) (ϕ, 0°) 8 c/s, and J (*trans*) (ϕ, 120°) 2 c/s, for these two couplings suggesting that the upfield proton (J *vicinal*, 2 c/s) (^{i}H) in the compounds collected in Table 4 are *trans* to the ^{g}H-protons. The observed *geminal*-coupling (J^{h}H–^{i}H) is 18 c/s. Irradiation at the frequency (τ 5·49) due to the ^{g}H-proton in the 100 Mc/s spectrum of pyrethrolone, collapsed the 8-line (observed 6) signal due to the ^{h}H, ^{i}H-protons, to a simple 4-line (observed 3) AB-quartet (J = 18).

In the acetates of cinerolone, pyrethrolone, and allethrolone (Table 4), protons ^{g}H ($\sim \tau$ 4·3) next to the acetate grouping are significantly deshielded ($\Delta\tau \sim$ 1·0) relative to those in the parent alcohols ($\sim \tau$ 5·3); protons—^{h}H are also shifted downfield (τ 7·22 to 7·12). The data for the cyclopentenone ring protons in natural pyrethrins and related compounds (Table 5) are closely similar to those of the acetates of the corresponding rethrolones.

The olefinic protons (designated ^{l}H, and ^{m}H in Fig. 2) in the side-chains of cinerolone and jasmololone are observed as complex partially resolved multiplets centred at 4·63 and τ 4·72 respectively. In addition, the side-chain vinyl methyl ($^{n}CH_3$) in cinerolone appears as a diffuse doublet ($J \sim 6$) at τ 8·28, and jasmololone shows a methylene-proton multiplet (—$^{n}CH_2$—) centred at τ 7·85, and a saturated methyl (—$^{o}CH_3$) triplet (J = 7·3) at τ 9·04 for the protons in its side-chain. The same protons (^{l}H, ^{m}H, ^{n}H, ^{o}H) (some are obscured by other resonances) are observed at similar chemical shifts, and with comparable multiplicities in the spectra of the natural cinerins, and synthetic jasmolins (Figs 3 and 4). It is interesting to note that both the spectra of natural cinerolone (Fig. 2), and of the natural cinerins (Figs 3 and 4) show saturated Me triplets at $\sim \tau$ 9·0, indicating minor contamination of these materials with jasmololone, and the corresponding jasmolins, respectively. The spectra of synthetic samples of (±)-cinerolone and (±)-cinerins did not show these impurities.[10]

The olefinic proton region of the 100 Mc/s NMR spectrum (CCl_4) for natural pyrethrolone hydrate (**2c**) is reproduced in Fig. 6; the assignments are summarized in the accompanying diagram. The *geminal* protons (^{o}H, ^{o}H) resonate at highest field, and both are observed as double doublets with *geminal* coupling ~1·5 c/s, and vicinal couplings 10·4 (*cis*) and 16·5 (*trans*) c/s. Proton-^{n}H should be observed as a doublet of double doublets, but because two of the vicinal couplings are of comparable magnitude (~10·4 c/s) only six lines are seen for this resonance. Significantly, proton-^{m}H is observed as a doublet of doublets with the two vicinal couplings of the same magnitude; the observed *cis*-vicinal coupling (10·4 c/s) is characteristic of *cis* disubstituted double bonds.[11] Proton-^{l}H resonates as a doublet ($J \sim$ 10·4) of triplets ($J \sim 7$) centred at approximately τ 4·78, although this resonance is partly obscured by the *geminal* proton signals. Irradiation at the resonance (τ 7·05) of the allylic-methylene protons (^{k}H) collapses the doublet of triplets (due to ^{l}H) centred at τ 4·78 to a doublet ($J \sim 10$), and also sharpens the triplet signal (due to ^{m}H) at τ 4·15. Similar irradiation at the resonance (τ 4·15) due to ^{m}H simplifies the multiplicity of the signals between τ 4·5 and τ 5·5, and also sharpens the doublet due to the allylic methylene protons (^{k}H) at τ 7·05. These experiments confirmed the assignments presented in the diagram; they also indicate small (<1 c/s) coupling between protons ^{k}H and ^{m}H. The corresponding τ-values for these olefinic protons in natural pyrethrolone hydrate at

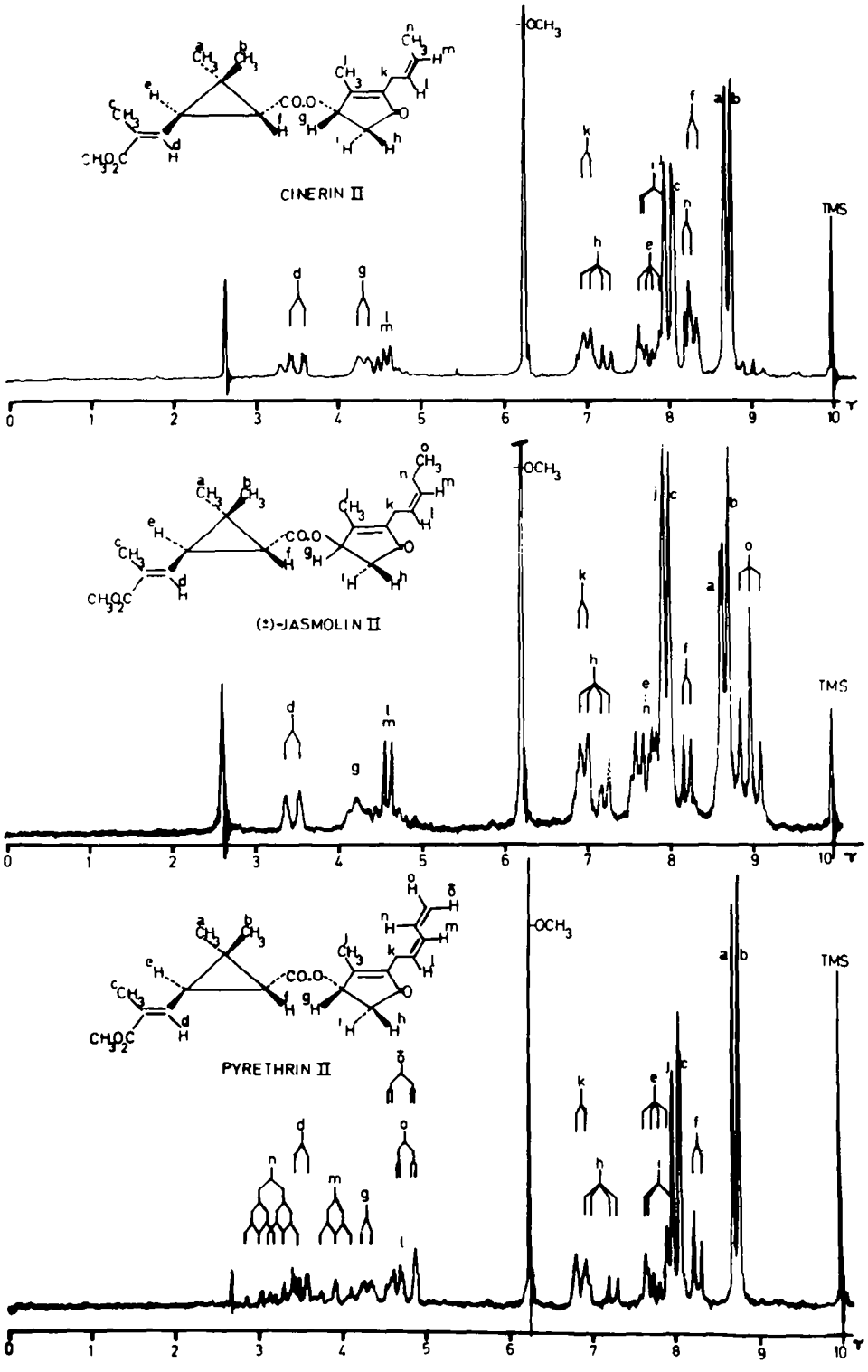


FIG. 4 NMR spectra of cinerin II, (±)-jasmolin II, and pyrethrin II.

same chemical shifts were observed for the olefinic protons in the side-chains of pyrethrolone acetate, pyrethrin I (Fig. 3) and pyrethrin II (Fig. 4).

The geminal olefinic protons (^{m}H, ^{n}H) in the side-chain of allethrolone (2, R = H) give rise to a complex signal pattern between τ 4·8 and τ 5·3, which overlaps the doublet signal due to the ^{s}H-proton of the cyclopentenolone ring (Fig. 5). Proton-^{1}H gives rise to a 12-line signal (τ 4·20) composed of a double-doublet of triplets, with $J^{m}H{-}^{1}H \sim 10$, $J^{n}H{-}^{1}H \sim 17$, and $J^{s}H{-}^{1}H = 6$ c/s. Irradiation at the frequency (τ 7·06) due to the allylic methylene protons (^{k}H) collapses this resonance to a 4-line signal. In the olefinic proton region of the corresponding acetate (Fig. 5; inset), proton-^{s}H is shifted to $\sim \tau$ 4·3, and the resonances for the *geminal* protons (^{m}H,

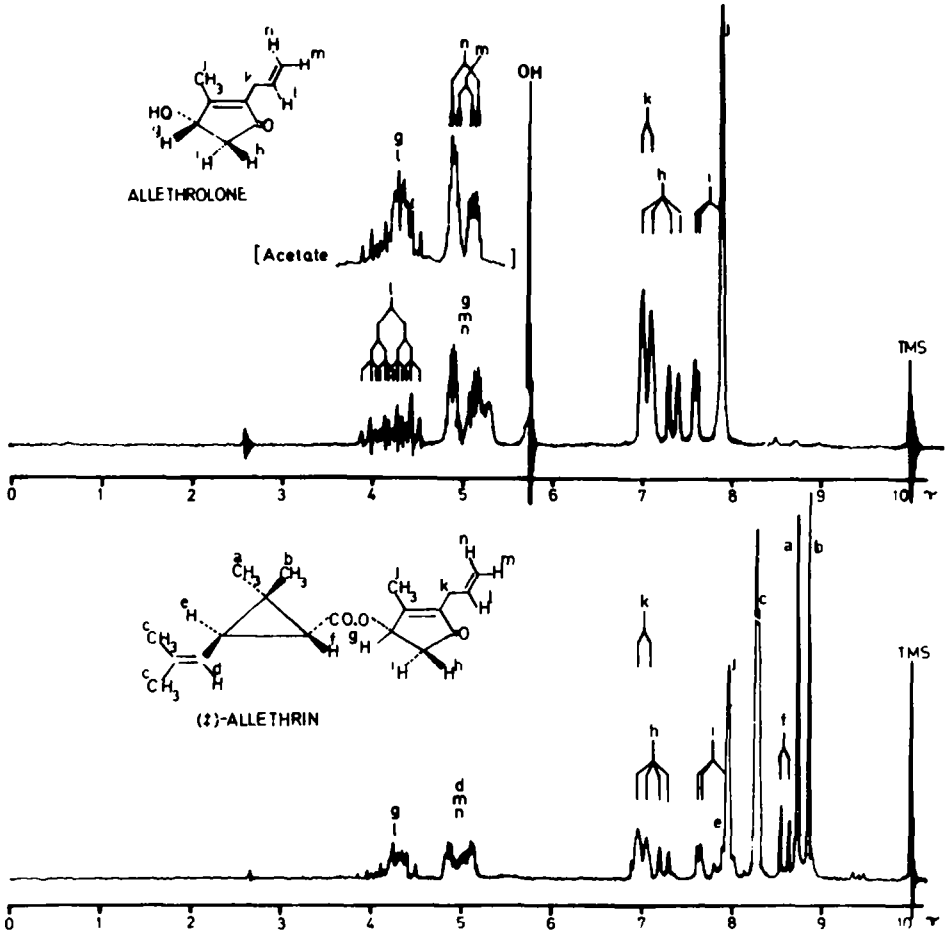


FIG. 5 NMR spectra of allethrolone, and (±)-allethrin.

^{n}H) are clearly observed in this spectrum [^{n}H $\sim \tau$ 5·01 dd (J = 17 and 2); ^{m}H $\sim \tau$ 5·02 dd (J = 9 and 2)]. The NMR spectrum of allethrin [re-constituted from (+)-allethrolone and chloride of (+)-*trans* acid], shown in Fig. 5, is almost identical

to the combined spectra of allethrolone acetate, and methyl (±)-*trans*-chrysanthemate.

The NMR spectra of the synthetic (±)-jasmolins differ from those of the related (+)-cinerins, in that certain proton resonances common to the four compounds,

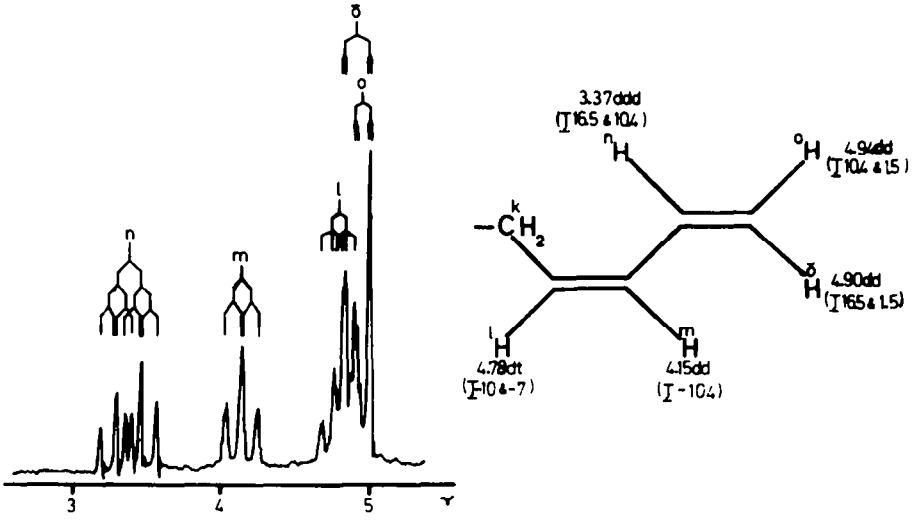


FIG. 6 NMR spectrum (100 Mc) of olefinic-proton region in natural pyrethrolone.

are doubled in the spectra of the jasmolins (compare Figs 3 and 4). Duplication of resonances in the (±)-jasmolins, are chemical shift differences resulting from NMR non-equivalence of signals from epimerically related protons. Chemical shift differences between diastereoisomers of this type are well known, and in some compounds such differences are large enough for the quantitative determination of diastereoisomers.[12, 13]

In (±)-jasmolin I (Fig. 3) one of the saturated Me groups (—$^{a}CH_3$) of the chrysanthemate moiety shows a chemical shift difference between the diastereoisomers of 1·8 c/s (τ 8·71; 8·74). In addition, protons-^{i}H show a 3-c/s difference, and the protons-^{g}H attached to the asymmetric centre of the cyclopentenone ring, a 6-c/s difference (~ τ 4·23; 4·33). The spectra of synthetic (±)-cinerin I, and (±)-pyrethrin I, show similar chemical shift differences between these same three (—$^{a}CH_3$, ^{i}H, ^{g}H) proton resonances. Resonances due to the ^{h}H-protons were visibly broadened in the spectra of the synthetic pyrethrins, but the signals were not actually split. Protons-^{f}H clearly had different chemical shifts in the diastereoisomeric pairs, but the differences could not be distinguished from long-range coupling of these protons to the ^{d}H-protons.

The same protons grouped around the dissymmetric centres responsible for the diastereoisomerism (—$^{a}CH_3$, ^{h}H, ^{i}H, ^{g}H, ^{f}H) show similar chemical shift differences in the synthetic (±)-pyrethrin II's as was observed with the (±)-pyrethrin I's, except here some of these resonances are obscured. It is significant that the ^{h}H-proton in

the spectrum of (±)-jasmolin II is observed at different chemical shifts (ca. 1·5 c/s difference) in the diastereoisomers; this difference is not clearly defined in the spectra of the other pyrethrin II's or the pyrethrin I's.

The magnitude of chemical shift differences between resonances from epimerically related protons becomes smaller the more distant the proton is from the disymmetric centre responsible for the diastereoisomerism; this is clearly reflected in the proton resonances from the diastereoisomers described above. Only one signal ($^{a}CH_3$) from the two cyclopropane methyl group resonances in the diastereoisomeric pyrethrins, shows a chemical shift difference (~1·8 c/s) in the diastereoisomers. These Me protons are clearly nearer the centre of change in the two diastereoisomers than those which show little chemical shift difference; accordingly these methyl protons are assigned *cis* to the carbonyl function. The same Me protons resonate at lowest field. It follows that those Me protons which resonate at lowest field in the *trans*-chrysanthemate (4) must be *cis* to the carboxy functions; it is recalled that these resonances could not be adequately assigned previously.

NMR cannot distinguish between enantiomers[12] in optically inactive solvents, and the NMR spectrum of (+) (+)-allethrin (**1**, R. = .H, R′ = CH_3) was identical with that of the (−)(−)-material ($CDCl_3$); also that of the (+)(−)-isomer was identical with that of the (−) (+)-isomer. Although there should be differences between the spectra of the (+) (+)-[or (−) (−)-], and the (+) (−)-[or (−) (+)-] isomers of allethrin, examination of these spectra, for deuteriochloroform solution, showed that the only proton resonance to differ much in the two spectra was that proton (^{g}H) attached to the asymmetric centre of the cyclopentenone ring [~ τ 4·28 in the (+)(+)-, and (−)(−)-isomers, and ~ τ 4·2 in the (+)(−)-(−)(+)-isomer mixture].

EXPERIMENTAL

Unless stated otherwise, N.M.R. spectra were determined on a Perkin–Elmer R.10 spectrometer, using dilute solns in $CDCl_3$ and TMS as internal standard. Bands were observed as singlets, except where one of the following designations is used: d, doublet; dd, doublet of doublets; ddd, doublet of double doublets; dt, doublet of triplets; dm, doublet of multiplets. Resonances marked by an asterisk, indicate that these resonances are partly obscured. Band positions are given on the τ-scale, and coupling constants (J) in c/s. The J-values quoted refer to the observed separation between appropriate lines.

Most of the compounds required in the present study were available from previous studies of the authors of this paper, and their collaborators.

(±)-*cis*, and (±)-*trans*-Chrysanthemic acids, and their methyl esters were obtained by separation[14,15] from the commercial mixed esters. Dimethyl (±)-*cis*-, and (±)-*trans*-chrysanthemumdicarboxylates were available from studies of Crombie, *et al.*[16] Methyl (±)-*trans*-dihydrochrysanthemate was prepared by hydrogenation.[17] (±)-*cis*-, and (±)-*trans*-Chrysanthemyl alcohols were obtained by reduction, with LAH, of the corresponding methyl esters;[18] their spectra were determined in carbon tetrachloride solution.

(+)-Cinerolone, and (+)-pyrethrolone were isolated from pyrethrum extract according to the method of Elliott;[19] the corresponding acetates are described in the same paper.

Cinerin I, cinerin II, pyrethrin I, and pyrethrin II were reconstituted from the naturally derived (+)-rethrolones, and the corresponding (+)-*trans*-acids as described by Sawicki *et al.*[20]

(±)-Jasmololone, and (±)-pyrethrins reconstituted from the (±)-rethrolones and (+)-*trans*-acids were available from recent synthetic studies.[10]

(±)-Allethrolone was of commercial origin, and the corresponding acetate was prepared according to the method of LaForge *et al.*[21] Diastereoisomeric allethrins were available from the work of LaForge *et al.*[22,23]

Acknowledgements—We thank the Science Research Council for providing NMR spectroscopic equipment and two of the authors (A.F.B. and P.H.) also thank the S.R.C. for research studentships. We appreciate

the help of Dr. J. Feeney (Varian Associates) who made spin-decoupling experiments involving the 100 Mc/s spectrum of natural pyrethrolone. Gifts of mixed chrysanthemic esters and allethrolone from Benzol Products Ltd., Newark, N.J., and of (+)-*trans*-chrysanthemic acid from Roussell Uclaf, Paris-7 ème are gratefully acknowledged.

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