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^{13}C NMR SPECTRA OF β-DIKETONES FROM WAXES OF THE GRAMINEAE*

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Key Word Index—Gramineae; epicuticular wax, β-diketones; hydroxy β-diketones; oxo β-diketones; ^{13}C NMR; structure determination.

Abstract—The ^{13}C NMR spectra of six β-diketones and seven oxygenated β-diketones have been measured. The β-dicarbonyl grouping has the following effects on the chemical shifts of the neighbouring carbons: α-, +8.72; β-, −3.98; γ-, −0.42; δ-, −0.33; ε-, −0.20; ζ-, −0.09; η-, −0.05; θ-, −0.03 ppm. The effects indicate the position of the grouping up to the 10,12-position. The positions of hydroxyl and oxo groups, up to the eighth carbon from the end of the chain, are also shown by long-range effects. The relative positions of a β-diketone grouping and another oxygen-containing group can be established from the ^{13}C NMR spectrum with little ambiguity when they are separated by six or fewer methylene groups. For these structures NMR spectroscopy is more reliable than mass spectroscopy, which gives results which are difficult to interpret when groups are close together. Components of mixtures of hydroxy β-diketones, from grass waxes, are identified and proportions indicated by the NMR spectra.

INTRODUCTION

β-Diketones are relatively common constituents of plant waxes [1–3]. In waxes from the Gramineae they are sometimes accompanied by hydroxy β-diketones [1] and oxo β-diketones and even occasionally, in waxes from *Agropyron* species, by hydroxyoxo β-diketones [4, 5]. The structures of these compounds were originally determined by GC analysis of the methyl ketones and acids resulting from alkali cleavage [2, 3, 6]; more recently, the iodoform reaction, which yields only acidic products, has been used [7].

Mass spectrometry of the β-diketones, although it gives numerous fragments, has since been employed [4, 8–10]; it was also carried out on the TMSi ethers of the diols obtained by reduction [11]. GC/MS, particularly useful in surveying a number of waxes, has been applied, without derivatization to *Rhododendron* waxes [12]. GC/MS after conversion of β-diketones to TMSi ethers leads to simpler spectra and better resolution [13, 14]. It is not always possible, however, to interpret the mass spectra of new β-diketones containing additional oxo groups unambiguously [4, 13] and such methods are not satisfactory when mixtures of oxo or of hydroxy β-diketones are present because fragmentation pathways may differ and the relative intensities of ions from isomers vary [4, 5, 9].

For this reason, ^{13}C NMR spectroscopy, which is a complementary, relatively quantitative and non-destructive procedure, has been investigated. The principal disadvantage of NMR is that, compared to mass spectrometry, a relatively large sample (at least 1 mg depending on the spectrometer employed) is required. Examination of ^{13}C NMR spectra of methyl octadecanoate [15] and of all the isomeric oxo [16], hydroxy and acetoxy octadecanoates [17] has shown that these oxygen-containing groups have small long-range effects on the chemical shifts of neighbouring carbons extending to carbons separated from the substituted carbon by seven or eight methylene groups. Long-range effects of the β-dicarbonyl group have not been reported previously but ^{13}C NMR has been applied to analysis of methyl hydroxy esters from hydrolysis of hydroxy β-diketones from *Avena sativa* [9] and from *Agropyron* species [4, 18]. A brief description of the spectrum of the hydroxy β-diketone from spring wheat wax has been given [1] and that of a hydroxyoxo β-diketone was reported recently [5]. Spectra of a number of β-diketones from plant waxes have now been measured and effects of substitution determined.

RESULTS AND DISCUSSION

Unsubstituted β-diketones

^{13}C NMR spectra of unsubstituted β-diketones were examined first to investigate the possibility of using long-range effects on the γ- to η-carbons to establish the position of the β-dicarbonyl group in an aliphatic chain. Since only two unsubstituted β-diketones, hentriacontane-14,16-dione and tritriacontane-12,14-dione, which have the carbonyl groups relatively close to the centre of the chain, were available from plant waxes, six β-diketones were synthesized. These were docosane-5,7-dione, tricosane-6,8-dione, tetracosane-7,9-dione, pentacosane-8,10-dione, hexacosane-9,11-dione and heptacosane-10,12-dione. The diketones were selected with an alkyl group on one side of the β-diketone grouping ranging in length from four (docosane-5,7-dione) to nine carbons (heptacosane-10,12-dione) and a pentadecyl group on the other side. Effects of the diketone grouping on the last three carbons of the shorter alkyl group were then observed as differences between shifts of these carbons and the corresponding last three carbons of the pentadecyl group. Thus the latter group was used as an

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internal standard and very small effects were detected more easily than in studies of spectra of long-chain methyl esters when standards, such as methyl octadecanoate, had to be added [15].

Shifts of resolved signals in the spectrum of pentacosane-8,10-dione are listed in Table 1; those due to C-13 to C-22 were not resolved. The ^{1}H NMR spectra of β-diketones show that they exist in solution principally (*ca* 80%) in the enol form [4, 6] but signals due to C-6 to C-12 of the keto form can also be seen in the ^{13}C NMR spectra. Those of other carbons of the keto form are not observed, probably because long-range effects in this form are quite similar to the effects in the enol form.

Shifts of carbons of the keto form can be calculated by adding effects of a carbonyl, β to another carbonyl on the neighbouring carbons, from the shifts of carbons of methyl 11-oxooctadecanoate [16] (as an example of a long-chain compound with an isolated carbonyl group). The results obtained were C-6 and C-12, 24 ppm; C-7 and C-11, 43 ppm; C-8 and C-10, 205 ppm and C-9, 56 ppm; quite close to those observed. Shifts of carbons of the enol form are not so readily predicted because there is considerable delocalization with redistribution of electron density in the hydrogen-bonded chelate ring [19, 20]

Table 1. Chemical shifts of the resolved signals in the ^{13}C NMR spectrum of pentacosane-8,10-dione

Carbon	Enol form	Keto form
1	14.09	—
2	22.67	—
3	31.75	—
4	29.09*	—
5	29.28*	—
6	25.81	23.49
7	38.48	43.85
8	194.52	204.29
9	99.04	57.27
10	194.52	204.29
11	38.48	43.85
12	25.81	23.49
23	31.99	—
24	22.76	—
25	14.13	—

*Tentative assignment.

Table 1 shows that the shifts of C-1, C-2 and C-3 are upfield of those of C-25, C-24 and C-23. Differences between the shifts of C-1 and of C-25, of C-2 and of C-24, and of C-3 and C-23 gave values for some of the long-range effects. Effects observed in the spectra of the six β-diketones were calculated in this way and are listed in Table 2. Where signals due to C-4 and C-5 could be assigned, effects were also calculated using shifts of C-15 and C-14 of methyl octadecanoate [21] as reference. Effects on carbons α and β to the dicarbonyl group were obtained by comparison with the shifts of carbons of methyl octadecanoate which have the corresponding chain position (from the terminal methyl group, since C-11 to C-18 of octadecanoate are unaffected by the ester group [15, 16]).

Average values for the long-range effects of the β-dicarbonyl were calculated and are listed in Table 3 along with those due to the oxo [15, 16], acetoxyl and hydroxyl groups [17]. The α- and β-effects are smaller than those of the oxo group but similar to those of the hydroxyl group. The γ- to ε-effects are relatively large like those of the oxo group but the ζ- to θ-effects are small like those of the hydroxyl group. Thus the β-dicarbonyl grouping has its own set of characteristic effects different from those of the other three oxygen-containing groups.

The results in Tables 2 and 3 show that ^{13}C NMR spectroscopy can determine the position of a β-dicarbonyl grouping in a long aliphatic chain up to that in a 10,12-dione from the separations between the shifts of the first three carbons and those of the corresponding last three carbons. An example of these effects appears in the spectrum of the β-diketones from *Andropogon scoparius*, which showed a partial separation of the C-3 and C-29 signals in agreement with chemical evidence that these β-diketones were a mixture of 10,12- and 12,14-diones [22].

Application of these effects in interpretation of spectra of naturally occurring hydroxy and oxo β-diketones will now be discussed. In making reasonable signal assignments four factors have been considered: shifts of the last six carbons of a hydrocarbon chain, derived from shifts of these carbons in the spectrum of methyl octadecanoate [16, 21]; long-range effects of the β-diketone group discussed above; long-range effects of the hydroxyl group [17] and of the oxo group [16]. Since there have been no NMR studies of series of long-chain secondary alcohols or ketones, the last two factors have had to be derived from spectra of isomeric hydroxy- and oxo-octadecanoates introducing occasional uncertainty about assignments of carbons α and β to the oxygenated carbon.

Table 2. Effect of the β-diketone grouping on the ^{13}C chemical shifts of carbons between the grouping and the closer end of the chain

	β-Diketone					
Effect	C_{22}-5,7	C_{23}-6,8	C_{24}-7,9	C_{25}-8,10	C_{26}-9,11	C_{27}-10,12
α	+8.75	+8.74	+8.70	+8.71	+8.70	+8.70
β	−4.09	−3.93	−3.93	−3.96	−3.97	−3.96
γ	−0.32	−0.50	−0.43	−0.43	?	?
δ	−0.31	−0.29	−0.38	−0.32	?	?
ε		−0.21	−0.20	−0.24	?	?
ζ			−0.08	−0.09	−0.11	?
η				−0.04	−0.05	−0.06
θ					−0.03	−0.03

Table 3. Average values of the effects of the β-diketone grouping on the ^{13}C chemical shifts compared with the effects of the oxo, acetoxyl and hydroxyl groups

	Group			
Effect	β-Diketone	Oxo [16]	Acetoxyl [17]	Hydroxyl [17]
α	+8.72	+13.00	+4.40	+7.80
β	−3.98	−5.80	−4.40	−4.05
γ	−0.42	−0.46	−0.20	+0.01
δ	−0.33	−0.30	−0.20	−0.09
ε	−0.20	−0.27	−0.16	−0.11
ζ	−0.09	−0.13	−0.11	−0.06
η	−0.05	−0.09	−0.08	−0.05
θ	−0.03	−0.06	−0.07	−0.04

Hydroxy β-diketones

When a hydroxyl substituent is present in a β-diketone, the position of the hydroxyl relative to the end of the chain may be deduced from the ^{13}C NMR spectrum without at first considering the effects due to the β-dicarbonyl grouping. The spectra are similar to those of the hydroxyoctadecanoates in which the hydroxyl is close to the terminal methyl group [15, 17]. Thus the shifts of C-1 to C-4 in the spectra of 5-hydroxytritriacontane-12,14-dione (**1**) and 5-hydroxyhentriacontane-14,16-dione (**2**) (Table 4) show that the hydroxyl is at C-5. The hydroxyl position in 25-hydroxyhentriacontane-14,16-dione (**3**) is also shown by the spectrum though not as clearly since the effects are smaller. The CHOH has δ- and ε-effects on C-29 and C-30 of −0.06 ppm and Table 3 shows that while these two effects are similar the ζ-effect is smaller. Thus a hydroxyl at C-24 would be indicated by a smaller effect on C-30 than on C-29. These differences are discussed further, later, when a β-diketone with the hydroxyl at C-8 (which corresponds to C-24 relative to the end of the chain) is considered.

When hydroxyl and β-dicarbonyl groups are sufficiently close together, each has long-range effects on the characteristic α- and β-signals associated with the other. Comparison of the signals of hydroxy β-diketones **1** and **2** (Table 4) shows distinct differences. The effects of the β-dicarbonyl group on C-5, C-6 and C-7 of **1** are η-, −0.07; ζ-, −0.07 and ε-, −0.10; the ε-effect of the CHOH on C-10 is −0.10 but there is no ζ-effect on C-11. Since, as shown in Table 3, the ε-effect of the β-diketone grouping is usually larger than the ζ- and η-effects, the upfield displacements of the signals of C-5 to C-7 are probably sufficient to establish relative positions of the substituents in **1**. From the spectrum of **2**, however, it can only be concluded that the diketone group is further along the chain than C-12 and C-14. Similarly, in **3**, the CHOH and

Table 4. Chemical shifts of the resolved signals in the ^{13}C NMR spectra of 5-hydroxytritriacontane-12,14-dione (**1**), 5-hydroxyhentriacontane-14,16-dione (**2**) and 25-hydroxyhentriacontane-14,16-dione (**3**)

Carbon	Effect of CHOH	1	Effect of $COCH_2CO$	Carbon	2	Carbon	3	Effect of CHOH
1	δ −0.03	14.10		1	14.10	31	14.11	ζ −0.03
2	γ +0.08	22.81		2	22.81	30	22.67	ε −0.06
3	β −4.09	27.90		3	27.90	29	31.91	δ −0.06
4	α +7.88	37.29		4	37.27	28	?	
5		71.91	η −0.07	5	71.98	27	25.68	
6		37.47	ζ −0.07	6	37.54	26	37.61	
7		25.53	ε −0.14	7	25.67	25	72.03	
8		?				24	37.55	
9		?				23	25.68	
10	ε −0.10	25.69		12	25.76	18	25.77	
11		38.43		13	38.45	17	38.48	
12		194.50		14	194.53	16	194.56	
13		99.04		15	99.05	15	99.07	
14		194.50		16	194.53	14	194.56	
15		38.43		17	38.45	13	38.48	
16		25.79		18	25.79	12	25.80	
31		31.99		29	31.97	3	31.97	
32		22.73		30	22.73	2	22.73	
33		14.13		31	14.13	1	14.14	

the β-diketone group are also separated by eight CH_2 groups so that neither can significantly affect the signals of carbons α or β to the other.

When CHOH and β-diketone groups are separated by five and four CH_2 groups some unexpectedly different effects are observed. Table 5 lists the shifts of 8-hydroxyhentriacontane-14,16-dione (**4**) and 9-hydroxyhentriacontane-14,16-dione (**5**). The spectra were obtained using the 1:1 mixture of these components which occurs in the wax from some *Triticum* species [6, 23] so that differences between similar shifts, such as those of C-3 of **4** and **5**, would be clearly seen. The larger ε-effect (-0.09 ppm on C-3) of the CHOH in **4** compared to the ζ-effect (-0.05 ppm) in **5** indicates the different positions of the hydroxyl groups. In **5**, only four CH_2 groups separate the β-diketone and CHOH groups, resulting in relatively large γ-, δ- and ε-effects on C-11, C-10 and C-9. The separation is five CH_2 groups in **4** so that the corresponding carbons (C-10, C-9 and C-8) undergo smaller δ-, ε- and ζ-effects.

In the spectrum of **5**, the δ-effect (-0.47 ppm on C-10) is unexpectedly larger than the γ-effect (-0.35 ppm on C-11); in **4**, the ε-effect is slightly larger than the δ-effect on the corresponding carbons. The carbon most affected in the spectra of both **4** and **5** is α to the CHOH. In **1**, however, the two groups are separated by six CH_2 groups and no unusual reversal of long-range effects was observed (Table 4). No compounds with analogous structures were available for comparison and hence a possible explanation of the unusual effects cannot be derived. They may be restricted to the spectra of β-diketones since in the spectrum of methyl 6-hydroxyoctadecanoate (which has CHOH and carbonyl the same distance apart as in **5**) the δ-effect on C-5 was not larger than the γ-effect on C-4 [17]. Perhaps the greater δ-effect in **5** is due to an interaction between CHOH and β-diketone groups bringing C-10 closer to the carbonyls so that it is subject to some type of 'through space effect'.

Oxo β-diketones

The spectra of two oxo β-diketones, 25-oxohentriacontane-14,16-dione (**6**) and 10-oxohentriacontane-14,16-dione (**7**), have also been examined and the shifts of resolved signals are listed in Table 6. The position of the oxo group at C-25 in **6** is unambiguously established by the effects on C-28 to C-31 which are the same as those on the corresponding signals in the spectrum of methyl 12-oxooctadecanoate [15, 16]. The β-diketone and oxo groups are separated by eight CH_2 groups, resulting in only very small effects of the oxo group on C-18 and of the β-diketone on C-23 and C-24. These are too small to indicate the relative positions of the two groups unambiguously.

In **7** only three CH_2 groups separate the two groups and, in consequence, much larger effects are seen on carbons between the groups and also on the three carbonyl groups. The oxo carbonyl has γ- to ζ-effects on the dicarbonyl grouping mainly analogous to those of the carbonyl noted in the spectra of 5-oxo- and 7-oxooctadecanoates on C-1 and C-2 [16]; i.e. the effects on the carbonyl carbons are greater than those on the methylene carbons. The one unusual effect is the small downfield displacement ($+0.15$ ppm) of the signal due to C-15. Thus the spectrum of **7** clearly establishes the relative positions of the oxo and β-diketone groups; ketones in which the

Table 5. Chemical shifts of the resolved signals in the ^{13}C NMR spectra of 8-hydroxyhentriacontane-14,16-dione (**4**) and 9-hydroxyhentriacontane-14,16-dione (**5**)

Carbon	Effect of CHOH*	4	Effect of $COCH_2CO$*	Effect of CHOH*	5	Effect of $COCH_2CO$*
1		14.14			14.14	
2	ζ -0.03	22.70			22.73	
3	ε -0.09	31.88		ζ -0.05	31.92	
4		?			?	
5		?			?	
6		25.71			?	
7		37.63			25.71	
8		71.91	ζ -0.12		37.63	
9		37.31	ε -0.32		71.77	ε -0.26
10		25.43	δ -0.28		37.16	δ -0.47
11		29.10†			25.36	γ -0.35
12	δ -0.09	25.71		γ -0.09	25.71	
13	ε -0.04	38.39		δ -0.04	38.39	
14		194.49			194.49	
15		99.12		ζ -0.04	99.08	
16		194.49			194.49	
17		38.43			38.43	
18		25.80			25.80	
29		31.97			31.97	
30		22.73			22.73	
31		14.14			14.14	

* Effects calculated by comparison with the corresponding signals in the lower half of the molecule.

† Tentative assignment.

Table 6. Chemical shifts of the resolved signals in the ^{13}C NMR spectra of 25-oxohentriacontane-14,16-dione (**6**) and 10-oxohentriacontane-14,16-dione (**7**)

Carbon	**6**	Effect of CO	Carbon	Effect of CO*	**7**	Effect of $COCH_2CO$*
1	14.14		1		14.14	
2	22.73		2		22.74	
3	31.97		3	η −0.05	31.94	
12	25.79		4		?	
13	38.45		5		?	
14	194.50		6		?	
15	99.04		7		?	
16	194.50		8		23.94	ζ +0.02
17	38.45		9		42.96	ε +0.10
18	25.74	η −0.05	10		210.42	δ −0.96
23	23.88†		11		41.54	γ −1.32
24	42.78†		12	β −6.13	19.66	β −4.26
25	211.38		13	γ −1.00	37.45	
26	42.86†		14	δ −0.68	193.82	
27	23.92†		15	ε +0.15	99.19	
28	29.01	γ −0.40	16	ζ −0.31	194.29	
29	31.67	δ −0.30	17	η −0.09	38.36	
30	22.55	ε −0.18	18		25.80	
31	14.05	ζ −0.09	29		31.99	
			30		22.74	
			31		14.14	

*The effects of one group are regarded as superimposed on the effects due to the other on the hydrocarbon chain and are calculated with reference to the corresponding unaffected signals in the spectrum of **6**.

†Tentative assignment.

groups were separated by four or five CH_2 groups would also be expected to have spectra which could be clearly interpreted. The position of the oxo group relative to the end of the chain is not shown with certainty, though there is an η-effect on the signal due to C-3 of −0.05 ppm, the ζ-effect of carbonyl at C-9 might be similar. The position of the β-diketone grouping is, of course, not shown by the spectrum either.

Estimation of the composition of a mixture of hydroxy β-diketones

The chemical shifts of the 5-hydroxy β-diketone **2** were listed in Table 4 but **2** occurs in the wax from *Poa ampla* as the major component of a mixture with 4-hydroxyhentriacontane-14,16-dione (**8**) and 6-hydroxyhentriacontane-14,16-dione (**9**) [24]. The spectrum of the mixture (Fig. 1) shows separate signals indicating the position of the hydroxyl group in each isomer. Thus C-2 of **8** appears at 18.88 ppm and C-2 of **2** at 22.82 ppm (downfield of C-30 because of the positive γ-effect of a hydroxyl at C-5 on a penultimate carbon of a chain [17]). C-3 of **2** is at 27.90 ppm and C-3 of **8** at 39.77 ppm; C-4 of **9** is at 25.38 ppm and C-4 of **2** at 37.27 ppm.

Integration of ^{13}C NMR signals can also indicate the compositions of mixtures, particularly of long-chain compounds ([21] and references cited therein). Also it was shown previously that the relative intensities of appropriate signals in spectra of mixtures of known composition of synthetic long-chain hydroxy esters (hydroxyls in the same positions from the end of the chain as in the hydroxy β-diketones) satisfactorily measure the proportions of the components [9, 18]. Comparing the average of the three signals of **2** with the average of the two signals of **8** and with the one signal of **9** gave percentages of 75, 12 and 13% for **2**, **8** and **9**, respectively. Previously, integration of the ^{13}C NMR spectrum of the mixed hydroxytetradecanoates (from alkali cleavage of the hydroxy β-diketones) gave similar percentages: 70, 15 and 15% for **2**, **8** and **9** [24].

It is useful to consider other isomers which might be distinguished. A separate signal for C-3 of **9** does not appear in the spectrum because the γ-effect of CHOH is usually close to zero (Table 3), except on the last two carbons of a chain [17]. A 7-hydroxy β-diketone, as occurs in the wax of *Avena sativa* [8, 9], would show separate upfield signals for C-3 due to the δ-effect. The absence of such a signal shows that the 7-hydroxy isomer is absent from the wax of *P. ampla*. The expected differences between the spectra of a 7-hydroxy β-diketone and **9** are, in fact, seen in the spectrum of the mixture of the 25-hydroxy isomer (**3**), with CHOH at the same distance from the end of the chain as the 7-hydroxy isomer, and the 26-hydroxy isomer, substituted on the sixth carbon from the end of the chain like **9**, which compose the hydroxy β-diketones from waxes of some *Agropyron* species [4, 5, 18]. As mentioned earlier, isomers with a hydroxyl at C-8 and C-9, such as **4** and **5**, are also distinguishable.

Thus ^{13}C NMR spectra can identify many of the naturally occurring β-diketones and oxygenated β-diketones. The position of the β-diketone grouping can be established up to the 10,12-position and the position of

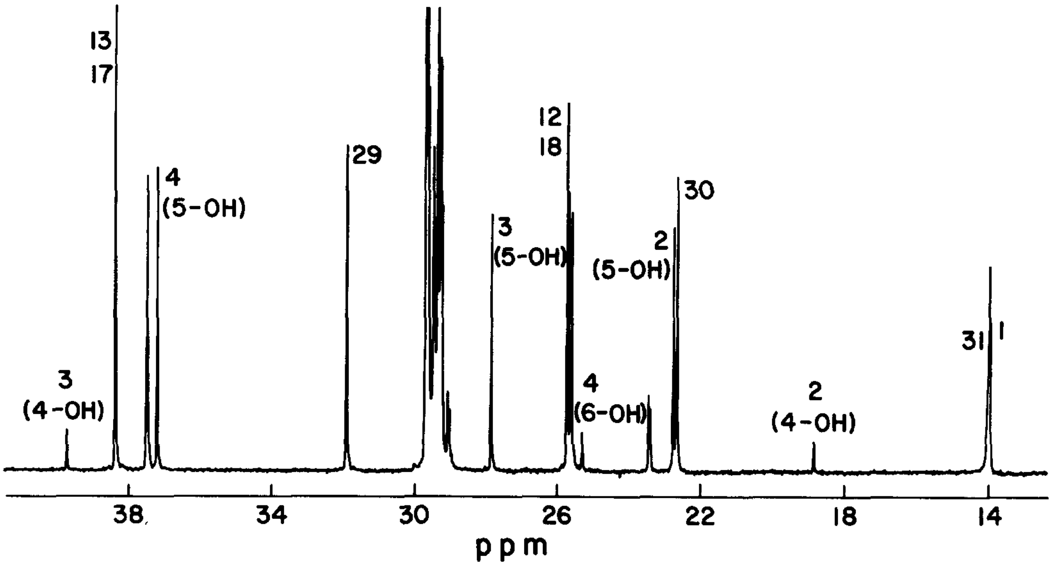

Fig. 1. ^{13}C NMR spectrum (10–40 ppm region) of the mixture of 5-hydroxyhentriacontane-14,16-dione (**2**), 4-hydroxyhentriacontane-14,16-dione (**8**) and 6-hydroxyhentriacontane-14,16-dione (**9**) from the wax of *Poa ampla*. Signal numbers indicate assignments.

hydroxyl and carbonyl up to C-7 or C-8. Relative positions of the two functional groups can be shown when they are separated by up to six CH_2 groups. The method is most useful for determination of the structure of components with functional groups relatively close together, such as **4**, **5** and **7**. These are the structures which are least well identified by mass spectrometry, either because important ions have low intensities or because fragmentation is difficult to interpret with certainty [4, 13].

EXPERIMENTAL

Spectra were measured at 25.16 MHz with proton noise decoupling, 15% solns in $CDCl_3$ (300 mg in 2 ml in 12 mm tubes) were used and the solvent provided the internal deuterium lock; chemical shifts are downfield from TMS. Complete spectra were measured with a sweep width of 6000 Hz, data length was 16 384 points, acquisition time was 1.36 sec and the number of scans 20 000. The 10–50 ppm region was measured with a sweep width of 1000 Hz using 16 384 data points, acquisition time was 8.19 sec and the number of scans 10 000. To integrate spectra from mixtures, the 1000 Hz sweep width spectra were expanded to 4 Hz/cm and peak intensity measured by triangulation [21].

The C_{22} to C_{26} β-diketones were prepared by reaction of Me hexadecanoate with the Na enolate of the appropriate Me ketone, prepared using NaH [25]. The product was isolated as the Cu complex [3, 6], crystallized from hexane and from Me_2CO; yields of purified β-diketone were 5% or less. Heptacosane-10,12-dione was prepared from Me hexadecanoate and the Li enolate of 2-undecanone, formed using Li diisopropylamide as previously described [5, 26]. After reaction at −78°, the reactants were refluxed for 5 hr, the product was purified as the Cu complex, crystallized from EtOAc and from Me_2CO; the yield was 20%.

Docosane-5,7-dione had mp 34.5–36.5° (Found: C, 78.1; H, 12.6. $C_{22}H_{42}O_2$ requires: C, 78.0; H, 12.5%). Tricosane-6,8-dione had mp 39–40° (Found: C, 78.6; H, 12.8. $C_{23}H_{44}O_2$ requires: C, 78.3; H, 12.6%). Tetracosane-7,9-dione had mp 41.5–42.5° (Found: C, 78.7; H, 12.7. $C_{24}H_{46}O_2$ requires: C, 78.6; H, 12.7%). Pentacosane-8,10-dione had mp 44–45° (Found: C, 79.4; H, 12.7. $C_{25}H_{48}O_2$ requires: C, 78.9; H, 12.7%). Hexacosane-9,11-dione had mp 47–48° (Found: C, 79.4; H, 12.9. $C_{26}H_{50}O_2$ requires: C, 79.1; H, 12.8%). Heptacosane-10,12-dione had mp 50–51° (Found: C, 79.6; H, 12.9. $C_{27}H_{52}O_2$ requires: C, 79.3; H, 12.8%).

5-Hydroxytritriacontane-12,14-dione (**1**) was from the wax of *Andropogon scoparius* [22]; 25-hydroxyhentriacontane-14,16-dione (**3**) was from the wax of *Secale cereale* [27]; the mixture of 8- and 9-hydroxyhentriacontane-14,16-diones (**4** and **5**) was from the wax of *Triticum aestivum* var. Manitou [23]; 25-oxohentriacontane-14,16-dione (**6**) was from the wax of *Agropyron elongatum* [5], 10-oxohentriacontane-14,16-dione (**7**) was from the wax of *A. riparium* [5] and the mixture of 5-hydroxyhentriacontane-14,16-dione (**2**) and 4- and 6-hydroxyhentriacontane-14,16-diones was from the wax of *Poa ampla* [24].

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