Carbon-13 Resonance Assignments of some Friedelanes and Taraxasteranes

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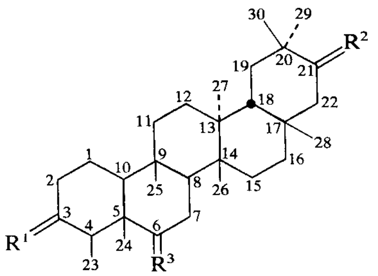
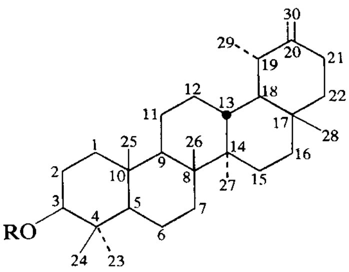
Carbon-13 signal assignments of taraxasteryl acetate, taraxasteryl palmitate, taraxasterol and *epi*-friedelinyl acetate are reported. Some signal assignments of the friedelanones, reported recently by others, are inconsistent and require revision.

In a recent communication[1] Sultanbawa, Wazeer and their co-workers reported the ^{13}C NMR signal assignments of six friedelanones viz. friedelin (**1**), 21-oxofriedelane (**2**), 6-oxofriedelane (**3**), 3,21-dioxofriedelane (**4**), 3,6-dioxofriedelane (**5**) and 3,6,21-trioxofriedelane (**6**). Some of these signal assignments are, however, inconsistent and require reconsideration. Some examples are presented here, along with the ^{13}C chemical shift assignments of *epi*-friedelinyl acetate (**7**), taraxasteryl acetate[2] (**8**), taraxasteryl palmitate (**9**) and taraxasterol (**10**). The assignments of the various chemical shifts of **8–10** were made by comparison with the resonances for germanicol acetate[3] (**11**) and lupeol[4] (**12**).

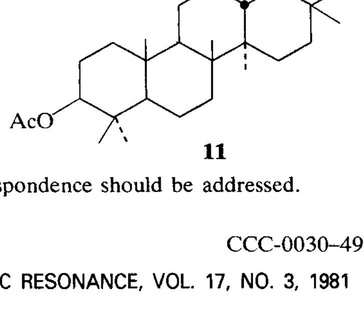
It was reported[1] that the incorporation of a carbonyl function at C-21 deshielded C-20 by approximately 4.9–5.2 ppm, whereas the signal of C-17 experienced a much stronger downfield shift by approximately 12.6–12.8 ppm in **2**, **4** and **6** when compared with similar carbon resonances in **1**, **3** or **5**. The carbonyl function at C-6 in **3** was reported[1] to have almost no influence on the adjacent carbon, C-5, whereas it influenced the C-9 resonance remarkably (deshielded by 14.9 ppm) when compared with similar resonances in **2**. Furthermore, C-5 in **5** and **6** were shielded (by ~3.7–3.9 ppm) relative to C-5 in **1** and **4**, which is the opposite effect to that expected, and the C-9 signal in **5** and **6** had an unusual downfield shift (19.0–19.1 ppm) relative to that in **4**. The pronounced effect of a carbonyl function of an adjacent carbon is well



1 $R^1 = O$; $R^2 = R^3 = H_2$
2 $R^1 = R^3 = H_2$; $R^2 = O$
3 $R^1 = R^2 = H_2$; $R^3 = O$
4 $R^1 = R^2 = O$; $R^3 = H_2$
5 $R^1 = R^3 = O$; $R^2 = H_2$
6 $R^1 = R^2 = R^3 = O$
7 $R^1 = \overset{H}{\underset{OAc}{<}}$; $R^2 = R^3 = H_2$
13 $R^1 = \overset{H}{\underset{OH}{<}}$; $R^2 = R^3 = H_2$



8 $R = Ac$
9 $R = -\overset{1'}{C}O(CH_2)_{14}\overset{16'}{C}H_3$
10 $R = H$



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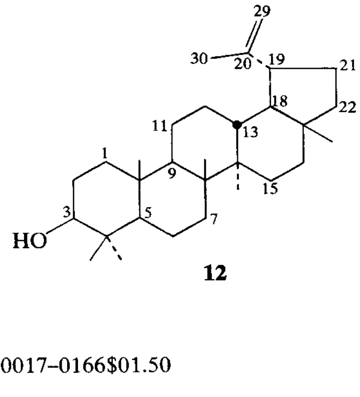

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CCC-0030-4921/81/0017-0166$01.50

Table 1. Carbon-13 NMR signals (δ, revised assignments in parentheses) of some friedelanes (1–7), taraxasteranes (8–10) and of germanicol acetate (11) and lupeol (12)

Carbon	1[1]	2[1]	3[1]	4[1]	5[1]	6[1]	7	8	9[a]	10	11[2]	12[3]
C-1	41.3 (22.3)	20.7	31.4	41.3 (22.4)	35.5 (35.1)	35.5	16.3	38.4	38.4	38.7	38.6	38.7
C-2	41.5	30.9 (27.4)	35.6	41.6	41.6	41.5	32.1	23.6	23.7	27.3	23.6	27.4
C-3	213.0	27.4 (30.9)	30.4	213.0	212.9	212.2	74.5	80.8	80.5	78.9	80.8	78.8
C-4	59.5 (58.2)	46.0	37.6	59.5 (58.2)	51.5	51.4	48.0	37.7	37.7	38.7	37.7	38.8
C-5	42.1	37.6	38.0 (53.1)	42.2	38.4 (56.6)	38.3 (56.5)	37.8	55.4	55.4	55.3	55.5	55.2
C-6	35.6 (41.3)	41.4	217.0	35.6 (41.3)	214.4	213.6	41.6	18.1	18.1	18.2	18.0	18.3
C-7	30.5 (18.2)	18.2	36.4 (32.7)	30.7 (18.4)	36.1 (32.7)	36.0 (32.2)	17.6	33.9	33.9	34.0	33.3	34.2
C-8	53.1	53.4	55.3	53.4	55.5	55.5	53.1	40.8	40.9	40.8	40.7	40.8
C-9	37.4	38.2 (37.1)	53.1 (38.0)	37.5	56.6 (38.4)	56.5 (38.3)	37.0	50.3	50.3	50.4	51.0	50.4
C-10	58.2 (59.5)	60.7	62.1	58.2 (59.5)	60.9	60.7	60.9	37.0	37.0	37.0	37.0	37.1
C-11	32.4 (35.6)	35.4	32.7 (36.4)	22.4[b] (35.6)	32.7 (36.1)	30.9 (36.0)	35.3	21.4	21.4	21.3	21.1	20.9
C-12	36.0 (30.5[c])	32.7[c]	31.7[c]	32.9[c]	32.1[c]	32.2 (30.9[c])	30.5[c]	25.5[c]	25.6	25.5[c]	26.0	25.1
C-13	38.3[d]	37.1 (38.2[d])	39.1[d]	38.3[d]	39.2[d]	39.1[d]	38.3[d]	38.8	38.8	38.7	38.3	38.0
C-14	39.7[d]	39.8[d]	40.2[d]	40.0[d]	40.2[d]	40.5[d]	39.6[d]	41.9	42.0	41.9	43.2	42.8
C-15	31.8[b] (32.4[c])	30.8[c]	31.8[c]	18.4[b] (30.7[c])	30.3[c]	30.3[c]	32.3[c]	26.6	26.6	26.6	27.4	27.4
C-16	32.8[b] (36.0)	37.0	35.4	37.1	35.1 (35.5)	37.0	36.0	39.1[d]	39.1[c]	39.1[d]	37.3	35.5
C-17	30.0	42.7 (33.2)	30.0	42.8 (33.3)	30.0	42.6 (33.1)	29.9	34.4	34.4	34.4	34.2	42.9
C-18	42.8	41.9	42.9	42.0	43.0	42.2	42.8	48.6	48.6	48.5	142.5	48.2
C-19	39.2 (35.3)	35.2	39.1 (35.7)	35.1	39.2 (35.7)	34.2	35.5	38.3	38.4	38.2	129.6	47.9
C-20	28.1	33.2 (42.7)	28.1	33.3 (42.8)	28.2	33.1 (42.6)	28.1	154.4	154.3	154.4	32.2	150.6
C-21	35.0 (32.8)	219.2	35.0[b]	218.8	35.7	218.2	32.8	25.4[c]	25.6	25.4[c]	34.5	29.8
C-22	35.3[b] (39.2)	55.0	35.7[b] (39.1)	55.1	35.7 (39.2)	54.8	39.2	39.3[d]	39.2[c]	39.2[d]	37.6	39.9
C-23	6.8	15.1 (13.6)	20.4 (11.9)	6.9	9.6	9.6	11.2	27.8	27.9	27.9	27.8	28.0
C-24	22.3 (14.6)	13.6 (15.1)	17.9	17.9 (14.8)	18.0 (13.4)	17.8 (13.4)	15.7	16.4	16.5	15.2	16.6	15.4
C-25	14.6 (17.9)	17.9	11.9 (18.1)	14.8 (17.9)	13.4 (18.0)	13.4 (17.8)	18.1	15.8	15.9	15.8	16.0	16.1
C-26	17.9 (18.6)	33.5 (18.4)	26.7 (18.5)	33.6 (18.6)	31.7 (18.6)	33.5 (18.4)	18.5	16.2	16.2	16.1	16.4	15.9
C-27	18.2 (20.3)	21.1	18.1 (20.4)	21.4	21.1	21.1	20.0	14.6	14.7	14.6	14.4	14.5
C-28	20.3 (32.1)	18.4 (33.5)	20.1 (26.7)	18.6 (33.6)	20.0 (32.0)	18.4 (33.5)	32.0	26.1	26.1	26.1	25.1	18.0
C-29	32.1 (35.0)	28.8	32.0	28.9	32.0 (20.0)	28.7	34.9	19.4	19.4	19.3	31.2	109.2
C-30	18.6 (31.8)	25.0	18.5 (20.1)	25.1	18.6 (31.7)	24.9	31.7	107.0	107.1	107.0	29.1	19.3
$OCOCH_3$							170.7	170.8			170.7	
							21.2	21.1			21.0	

[a] Other signals present were at δ173.4 (CO), 34.7 (C-2′), 31.9 (C-14′), 29.6 (C-4′ to C-13′), 25.1 (C-3′), 22.6 (C-15′) and 18.1 (C-16′).
[b] Values are interchangeable as in Ref. 1.
[c,d] Values bearing the same superscript may be interchanged.

established[5] and, as such, interchange of the assignments between C-5 and C-9 in **3**, **5** and **6** and between C-17 and C-20 in **2**, **4** and **6**, as shown in parentheses in Table 1, should give a better correspondence.

Furthermore, C-11, C-12, C-15 and C-16, being remote from C-3, C-6 and/or C-21, should have approximately the same chemical shifts in **1**–**6**. Surprisingly, C-11 and C-15 in **4** were assigned[1] to remarkably high field resonances compared to similar carbon resonances in **1**–**3**, **5** and **6** (see Table 1). In addition, the positions of the C-12 and C-16 signals in **1** varied from those in **2**–**6**. The C-1 resonance assignments in **1**–**6**[1] were also quite inconsistent. The signal of C-1 in **1** and **4** had[1] an unusual downfield shift (20.6 ppm) relative to that in **2** for the incorporation of a carbonyl function at C-3, whereas the C-1 signal in **5** and **6** experienced only a 4.1 ppm downfield shift relative to that in **3**. Again, C-1 in **3** was related[1] to a 10.7 ppm downfield signal relative to that in **2**, but in **5** and **6** C-1 was linked to a signal 5.8 ppm upfield to that in **4**, reflecting strong but opposite effects of the carbonyl at C-6 on the somewhat remote C-1. Furthermore, the downfield shift of C-22 (19.1–19.8 ppm) and upfield shift of C-19 (4.0–5.0 ppm) in **2**, **4** and **6**, relative to the respective carbons in **1**, **3** and **5**, were also somewhat higher than that expected for the incorporation of a carbonyl at C-21.

It has, however, been observed that of the two low field methylene resonances appearing around 41.3–41.5 ppm in the spectrum of **1**, one moved to high field when there was no carbonyl at C-3 (as in **2**, **3** and **7**) while the other disappeared when there was a carbonyl at C-6 (as in **3**, **5** and **6**). Thus, the signals at δ41.5 in **1**, δ41.6 (or 41.3) in **4**, δ41.6 in **5** and δ41.5 in **6** should be related to C-2, whereas the signals at δ41.3 in **1**, δ41.4 in **2**, δ41.3 (or 41.6) in **4** and δ41.6 in **7** should be associated with C-6. The methylene resonances similar to δ18.2 in **2**, δ18.4 in **4** and δ17.6 in **7** were absent in **3**, **5** and **6**, and these resonances in **2**, **4** and **7** should, thus, be assigned to C-7. The environment of C-7 in **1**, **2**, **4** and **7**, being similar to that of C-6 in **8**–**12** (resonating at δ18.0–18.3), further supported the association of the methylene signal at δ17.6–18.4 in **2**, **4** and **7** to C-7. Again, the methylene resonance at δ22.4 (assigned[1] to C-11) in **4** was analogous to the δ20.7 signal (assigned[1] to C-1) in **2**; the appearance of a methylene signal at a relatively high field position at δ16.3 in **7** was in conformity with the influence of an axial acetate function at C-3 and, thus, the above-mentioned methylene signals in **2**, **4** and **7** should be associated with C-1. The methylene signals at δ30.7 (or 32.9) and 35.6 in **4** should, thus, be linked to C-15 and C-11, respectively. The C-7 and C-11 resonance assignments[1] in **3** and in **5** should also be reversed to provide a better fit with the resonances now assigned to these carbons in **2**, **4** and **7**. Furthermore, an interchange of the resonances assigned[1] to C-19 and C-22 in **1**, **3** and **5** would also give better correspondence between the substituent effects and the change in chemical shifts on-going to **2**, **4** and **6**.

Thus, the signals at δ32.4 (or 30.5), 35.3, 35.6, 36.0 and 39.2 in **1** should preferably be related to C-12, C-19, C-11, C-16 and C-22, respectively.

In addition to the methylene resonances at δ16.3 and 17.6, six methyl resonances appeared in the region δ10–23 in the spectrum of **7**. Three other methyls in **7** resonated in the region δ30–35. The absence of the high field methylene signals in **1**, **3**, **5** and **6** in Ref. 1 should be noted, two additional methyls being, instead, present in this range. Furthermore, only one methyl signal was assigned[1] to the region δ30–35, along with two additional methylene resonances in **1**, **3** and **5**. The still anomalous resonance positions for C-1, C-2, C-28 and C-30 in **3** and C-1 and C-29 in **5** are probably connected with these observations, since a reinvestigation on the ^{13}C NMR studies of **1** revealed that the signals at δ18.2 and 22.3 were due to methylenes and those at δ31.8 and 35.0 for methyl groups. The lanthanide shift studies employing $Pr(FOD)_3$-d_{27} established the association of C-1 with the δ22.3 signal and C-7 with the δ18.2 signal. The methyl signal at δ32.1 was shifted upfield by the LSR at a faster rate than the other two in its vicinity, thus indicating its relationship with C-28, and those of the δ31.8 and 35.0 signals with C-30 and C-29, respectively. Furthermore, the methylene signal at δ30.5 moved slightly faster than the δ32.4 signal, indicating the probable association of the former with C-12 and the latter with C-15. The LSR studies also confirmed the association of the remaining carbons in **1** with the new signal assignments given in Table 1. Thus, the calculated values, using β-effects, for all the seven reported[5] carbons in **1** fitted well with the present assignment. This rules out the claim of Sultanbawa and Wazeer *et al.*[1] on the inability of β-effects alone in predicting[6] chemical shifts in friedelane systems.

Earlier workers also correlated[1] the rate of the $Eu(fod)_3$ induced shift of the peaks with the distance from the carbonyl oxygen to the relevant carbon. Since the shift reagent is likely to be co-ordinated with the carbonyl oxygen lone pair *anti* to C-4, C-5 or C-20, where appropriate in **1**, **2** and **3**, the rate of movement of the signals on addition of LSR should be proportional to the distance between the reagent and the relevant carbon, but it may not be exactly related in the way employed earlier.[1]

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a Varian Associates CFT-20 NMR spectrometer operating at 20.1 MHz in the FT mode. The compounds were submitted to noise decoupling and single frequency off-resonance decoupling to establish the carbon shifts and the degree of protonation. The samples were run in 5 mm o.d. tubes using $CDCl_3$ as solvent as well as internal lock and internal standard. All solutions were *c.* 5–10% in concentration. The chemical shifts reported are in δ (ppm) downfield from TMS; $\delta_{TMS} = \delta_{CDCl_3} + 76.9$ ppm. The spectra were run with sweep width 4000 Hz, pulse width 6 μs (approximately 45° flip angle) and approximately 2 s delay between pulses.

The spectra of **1** were run in a 10 mm o.d. tube with sweep width 4500 Hz, pulse width 12 μs (approximately 60° flip angle) and approximately 1.5 s delay between pulses; the positions of the signals were within -0.1 ppm, as were those in Ref. 1. The shift studies were made using approximately 0.05, 0.10 and 0.15 mol equivalents of LSR.

8, **9** and *epi*-Friedelinol (**13**) were isolated[7,8] from *Eupatorium riparium*. Basic hydrolysis of **8** afforded **10** and acetylation of **13** furnished **7**. CrO_3 oxidation of **13** afforded **1**. These compounds were purified by chromatographic separation over silica gel and subsequent recrystallizations from suitable solvent mixtures, and were identified from their spectral (IR, ^{1}H NMR and high resolution mass) characteristics and also by direct comparison with authentic samples.

Acknowledgements

The authors are grateful to the University Grants Commission, New Delhi for financial assistance and to Professor A. K. Barua (Bose Institute, Calcutta) for authentic samples of *epi*-friedelinol and taraxasterol.

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Received 16 March 1981; accepted (revised) 15 May 1981