# Assignment of Carbon-13 Nuclear Magnetic Resonance Spectra of Some Friedelanes

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Carbon-13 resonance assignments of cerin acetate,  $2\alpha$ -pyridine-*N*-oxyfriedelan-3-one, *epi*-cerin and its acetate,  $3\alpha$ -hydroxyfriedelan-2-one and its acetate,  $3\beta$ -hydroxyfriedelan-2-one and its acetate,  $3\beta$ -hydroxyfriedelan-7-one, canophyllol, friedelolactone and friedelolactone- $2\alpha$ -yl acetate, friedelane- $2\alpha$ ,  $3\alpha$ -diol and its diacetate, friedelane- $2\beta$ ,  $3\alpha$ -diyl diacetate, pachysandiyl-A diacetate and friedelane- $2\beta$ ,  $3\beta$ -diyl diacetate have been made. The carbon signals of 3-oxofriedelan-29-ol and its acetate, methyl 3-oxofriedelan-29-oate, 3-oxofriedelan-30-ol, maytenfoliol, maytensifolin-A, maytensifolin-B, pachysonol and pristimerin reported in the literature have also been considered for their specific resonance assignments. A few signal assignments of some friedelanes, viz. friedelan-28-ol, friedelan-29-ol, friedelan-30-ol, friedelan-29-ol, 3-oxofriedelan-29-ol, and zeylasterone, reported recently by others, are unusual and have been reviewed.

KEY WORDS <sup>13</sup>C NMR Friedelanes Revised assignments

## **INTRODUCTION**

Since the appearance of ambiguous resonance assignments of some friedelanones<sup>1</sup> and the subsequent revision of their resonance assignments by us,<sup>2</sup> a few more publications in the series have appeared.<sup>3-7</sup> We were interested in providing alternative support for our resonance assignments of friedelin<sup>2</sup> (1). For this purpose we obtained cerin acetate (3),  $2\alpha$ -pyridine-Noxyfriedelan-3-one (4), epi-cerin (5) and its acetate (6),  $3\alpha$ -hydroxyfriedelan-2-one (7) and its acetate (8), 3hydroxyfriedel-3-en-2-one (9) and its acetate (10), friedelane-3,7-dione (11),  $3\beta$ -hydroxyfriedelan-7-one (12), canophyllol (13), friedelolactone<sup>8</sup> (14), friedelane- $2\alpha, 3\alpha$ -diol (15) and its diacetate (16), friedelane- $2\beta, 3\alpha$ diyl diacetate (17), pachysandiyl-A diacetate (18), friedelane- $2\beta$ ,  $3\beta$ -diyl diacetate (19) and friedelolactone-2 $\alpha$ -yl acetate (19a), and recorded their <sup>13</sup>C NMR



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 $R^1 = R^2 = R^4 = H, R^3 = -OCOCH_3$  $R^1, R^2 = O, R^3 = H, R^4 = -OH$  $R^1, R^2 = O, R^3 = H, R^4 = -OCOCH_3$  $R^1 = R^3 = H, R^2 = R^4 = -OH$  $R^1 = R^3 = H, R^2 = R^4 = -OCOCH_3$  $R^1 = R^4 = -OCOCH_3, R^2 = R^3 = H$  $R^1 = R^4 = H, R^2 = R^3 = -OCOCH_3$  $R^1 = R^3 = -OCOCH_3, R^2 = R^4 = H$ 



9 R = H10  $R = -COCH_3$ 



 $R^1, R^2 = O, R^3 = O, R^4 = H_2$  $R^1 = -OH, R^2 = H, R^3 = O, R^4 = H_2$  $R^1, R^2 = O, R^3 = H_2, R^4 = H, -OH(\beta)$  $R^1, R^2 = O, R^3 = H_2, R^4 = O$ 

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14 R = H19a R = -OAc



**20**  $R^1 = -CH_2OCOCH_3$ ,  $R^2 = R^3 = H$ ,  $R^4 = O$  **21**  $R^1 = -COOCH_3$ ,  $R^2 = R^3 = H$ ,  $R^4 = O$  **22**  $R^1 = -CH_3$ ,  $R^2 = H$ ,  $R^3 = -OH$ ,  $R^4 = H_2$  **23**  $R^1 = -CH_3$ ,  $R^2 = -OH$ ,  $R^3 = H$ ,  $R^4 = H_2$  **24**  $R^1 = -CH_2OH$ ,  $R^2 = R^3 = H$ ,  $R^4 = H_2$  **25**  $R^1 = -CH_0$ ,  $R^2 = R^3 = H$ ,  $R^4 = H_2$  **29**  $R^1 = -CH_2OH$ ,  $R^2 = R^3 = H$ ,  $R^4 = O$  **30**  $R^1 = -CH_2OH$ ,  $R^2 = H$ ,  $R^3 = -OH$ ,  $R^4 = O$ **31**  $R^1 = -CH_3$ ,  $R^2 = -OH$ ,  $R^3 = H$ ,  $R^4 = O$ 



**26**  $R^1 = R^3 = -OH, R^2 = \beta - CH_3$ **32**  $R^1 = R^3 = H, R^2 = \alpha - OOH$ 





spectra which, to our knowledge, have not been published. We also present some signal assignments for friedelan-28-ol<sup>5</sup> (22), friedelan-30-ol<sup>5</sup> (23), friedelan-29ol<sup>5</sup> (24), friedelan-29-al<sup>5</sup> (25), 3-oxofriedelane-21 $\alpha$ ,26diol<sup>7</sup> (26) and zeylasterone<sup>6</sup> (33) reported recently which are inconsistent and require reconsideration. The carbon signals of methyl 3-oxofriedelan-29-oate<sup>9</sup> (21), pachysonol<sup>10</sup> (27), maytensifolin-B<sup>10</sup> (28), 3-oxofriedelan-29ol<sup>10</sup> (29) and its acetate<sup>9</sup> (20), maytenfoliol<sup>10</sup> (30), 3oxofriedelan-30-ol<sup>10</sup> (31), maytensifolin-A<sup>10</sup> (32) and pristimerin<sup>11</sup> (34) recorded in the literature<sup>9-11</sup> have been analysed for the purpose of making specific assignments.

### **RESULTS AND DISCUSSION**

The complete signal assignments for the friedelanes 1-19 and 19a are reported in Table 1. The assignments are based on the determination of the degree of protonation of each carbon from the corresponding SFORD and APT spectra, as well as from the chemical shift changes on change of functionalities using chemical shift theory,<sup>12</sup> in particular the effect of carbonyl or hydroxy (axial or equatorial) incorporation into a rigid framework. Finally, the friedelane resonances so derived were confirmed in appropriate cases by lanthanideinduced shift studies using either  $Pr(fod)_3$ - $d_{27}$  or  $Eu(fod)_3$ - $d_{27}$ .

The spectra of 3-10, 14 and 19a were of help in identifying the signals associated with C-1 to C-6 and C-10 in friedelin (1) and friedelan- $3\beta$ -yl acetate (2). The axial acetoxy function in 3 deshielded the methylene signal for C-1 (ca 5.8 ppm) and shielded considerably (due to its  $\gamma$ -effect) the signals for C-4 and C-10 by approximately 4.9 and 5.2 ppm, respectively. The equatorial hydroxy or acetoxy functions in 5 and 6 deshielded the C-1 resonances significantly (10.3 and 6.3 ppm, respectively) but marginally shielded the signals associated with C-4 and C-10 (ca 2.0-2.8 ppm) relative to the appropriate carbon resonances in 1. The change from 1 to 7 or 8 led to a downfield shift of the most upfield methyl signal ( $\delta$  6.7) in 1 by about 3.9-4.0 ppm, necessitating its relationship with C-23. A large downfield shift of the C-1 resonance (ca 13.8-14.9 ppm) was also noted. Further, the C-4 methine resonance at  $\delta$  58.1 and the non-protonated carbon resonance for C-5 at  $\delta$  42.0 in the spectrum of 1 were replaced in 7 by analogous resonances at  $\delta$  54.4 (further shifted upfield to  $\delta$  50.2 in 8) and 38.0. The assignments of 3-hydroxyfriedel-3-en-2-one (9) and its acetate (10) gave further support for the signals of C-1 to C-5 and C-10, and also an idea about the resonance positions for C-6 and C-24 in 1. Carbons C-4, C-10, C-23 and C-24 in 14 resonated downfield (by 26.7, 4.5, 6.6 and 1.5 ppm, respectively) while C-1, C-2, C-5 and C-6 experienced upfield shifts on going from 1 to 14.

The spectrum of friedelane-3,7-dione (11) was studied to identify the signals associated with C-5 to C-9 and C-14 in 1. The carbonyl function at C-7 in 11 was found to exert a strong deshielding influence on the adjacent carbons C-6 (*ca* 15.7 ppm) and C-8 (*ca* 10.4 ppm), and gave appreciable downfield shifts for C-5 and C-9 (5.0 ppm). Further, C-14, being equatorial to ring B and

Table 1. Carl	bon-13 signals	(8) of t	he friedelanes	1-19 an	d 19a															
Carbon	1 <sup>2.а</sup>	<b>2</b> <sup>2</sup>	ар З	<b>4</b> °	ŝ	9	7	р <b>8</b>	6	10	11	12	13	14	15	16	17	18	19	19a
C-1	22.2 (2.20)	16.3	28.0 (1.48)	30.5	32.5	28.5	36.0	37.1 (0.51)	32.0	33.9	21.6	16.8	22.1	18.4	26.6	24.8	25.5 2	1.5 2	2.2	23.1
C-2	41.4 (4.60) <sup>f</sup>	32.1	76.4 (3.71)	76.9	75.0	76.4	211.6	204.4 (1.11)	194.9	191.7	40.8	34.7	41.3	34.2	69.6 (	39.6	75.4 7	T 10.7	3.4	73.9
C-3	212.8 (5.75)	74.5	207.8 (4.11)	203.4	212.0	205.1	76.9	78.7 (0.94)	142.5	156.8	210.6	72.0	212.6 1	75.9	73.2	73.5	75.8 7	3.8 7	3.4 17	73.5
C-4	58.1 (3.12)	48.0	53.2 (1.05)	56.4	55.5	56.1	54.4	50.2 (0.51)	140.6	140.8	57.8	48.8	57.8	84.8	45.6	43.7 4	18.3 4	13.7 4	6.4 8	84.4
C-5	42.0 (2.19) <sup>f</sup>	37.8	43.0 (1.13)	42.9	43.0	42.4	38.0	38.1 (0.31)	39.7°	40.4	47.0	43.4	41.9	40.7	37.8	38.1	37.9 3	1.4 3	1.3 4	40.9
C-6	41.2 (1.14)	41.6	40.9 (0.59)	40.4	41.2	41.0	40.6	40.7 (0.16)	38.4	37.8	56.9	58.2	41.0	38.3	41.0	t0.8 <sup>4</sup>	t0.9 4	1.2 4	1.2	38.5
C-7	18.1 (0.71)	17.6	18.1 (0.41)	18.1	18.1	18.1	17.5	17.6 (0.08)	17.9	17.8	210.2	210.3	18.1	17.9	17.8	18.0	17.9 1	7.9 1	8.2	17.8
C-8 C	53.0 (0.65)	53.1	53.1 (0.41)	52.4	53.1	53.1	53.1	52.9 (0.03)	52.6	52.3	63.4	63.9	52.2	52.6	52.9	52.8	53.0 E	52.9° 5	3.1	52.6
6-0 C	37.4 (0.84)	37.0	36.7 (0.49)	37.3	37.3	37.4	37.6	37.4 (0.12)	36.7	36.8	42.4	43.4	37.3	38.0	36.4	36.3	36.9 3	6.3 3	0.7	37.7
C-10	59.4 (1.68)	60.9	54.2 (1.58)	56.7	56.6	57.2	60.3	59.6 (0.33)	55.7	54.5	59.0	61.1	59.1	63.9	51.3	52.4 E	56.8 E	3.0° 5	8.4 5	55.2
C-11	35.5 (0.54)	35.5	35.3 (0.39)	35.6	35.6	35.6	35.0	34.9 (0.04)	34.7	34.4	35.5	35.6	35.3	35.2	35.2	35.2	35.3° 3	5.2 3	5.5	35.1
C-12	30.4 (0.34)	30.5	30.2 (0.22)	30.1	30.4	30.4	30.2	30.1 (0.01)	30.2	30.1	29.8	30.1	29.9	30.4	30.5	30.2	30.2 3	0.2 3	0.5	30.5
C-13	39.6 (0.29)	39.6	39.5 (0.19)	39.4	39.7	39.7	39.6	39.5 (0.01)	39.6°	39.6	39.4	38.8	39.1	39.2	39.6	39.6	39.6 3	9.5 3	9.6	39.1
C-14	38.2 (0.38)	38.3	38.2 (0.25)	38.0	38.3	38.3	38.2	38.1 (0.00)	38.3	38.1	37.5	37.6	38.0	38.3	38.2	38.2	38.2 3	8.3 3	8.3	38.3
C-15	32.3 (0.32)	32.3	32.2 (0.17)	32.1	32.4	32.4	32.3	32.2 (0.03)	32.3	32.1	31.6	31.6	31.3°	32.2	32.3 3	32.2 3	12.3 3	2.1 3	2.3 3	32.2
C-16	35.9 (0.23)	36.0	35.9 (0.23)	35.8	35.9	35.9	35.9	35.8 (0.02)	35.9	35.8	36.3	36.3	29.0	35.8	35.9 3	36.0 3	5.9 3	6.0 3	5.9 3	35.9
C-17	29.9 (0.20)	29.9	29.8 (0.09)	29.7	29.9	29.9	29.9	29.9 (0.01)	30.0	29.9	30.1	30.1	35.1	29.9	29.9	9.9 2	9.9 2	9.9 2	9.9 2	29.9
C-18	42.8 (0.21)	42.8	42.7 (0.09)	42.5	42.8	42.8	42.7	42.6 (0.00)	42.8	42.7	41.8	41.9	39.2	42.6	42.7 4	12.7 4	12.7 4	2.7 4	2.7 4	12.6
C-19	35.2 (0.18)	35.3	35.1 (0.11)	35.0	35.3	35.3	35.2	35.2 (0.02)	35.3	35.2	34.9	35.0	34.4	35.2	35.2 3	35.2 3	35.2° 3	5.2 3	5.2 3	35.3
C-20	28.0 (0.11)	28.1	28.0 (0.09)	27.8	28.1	28.1	28.1	28.0 (0.01)	28.1	28.0	28.0	28.1	27.9	28.0	28.0	8.0 2	8.0 2	8.0 2	8.1 2	28.0
C-21	32.7 (0.12) <sup>f</sup>	32.8	32.7 (0.04)	32.5	32.8	32.7	32.7	32.6 (0.00)	32.7	32.6	32.8	32.9	31.4 <sup>°</sup>	32.6	32.7	32.7 3	32.7 3	2.7 3	2.7 3	32.7
C-22	39.2 (0.14) <sup>†</sup>	39.2	39.1 (0.08)	39.0	39.2	39.2	39.1	39.1 (0.00)	39.2	39.1	38.6	39.4	33.2	39.1	39.2 3	39.1 3	1 <u>3</u> 3.	9.1 3	9.1 3	39.1
C-23	6.7 (3.40)	11.2	6.3 (1.32)	6.6	6.5	6.5	10.7	10.6 (0.35)	10.3	11.3	6.8	11.6	6.7	13.3	9.6	9.3	9.7 1	0.3 1	0.8	12.6
C-24	14.5 (1.90)	15.7	13.9 (0.90)	14.7	14.7	14.5	14.0	13.9 (0.17)	17.6	17.5	15.1	16.3	14.5	16.0	13.4 1	3.5 1	4.4 1	5.1 1	5.8 1	6.2
C-25	17.8 (0.61)	18.1	17.7 (0.36)	17.8	18.0	17.9	17.3	17.3 (0.06)	18.4	18.4	18.2	18.3	18.0	17.8	1.8 1	8.0 1	7.7 1	7.5 1	7.5 1	1.8
C-26	18.5 (0.32)	18.5	18.5 (0.26)	18.3	18.6	18.5	18.4	18.4 (0.04)	18.8	19.0	19.2	19.5	18.9	18.4	18.6 1	8.4 1	8.5	8.4 1	8.5 1	8.3
C-27	20.1 (0.27)	20.0	19.9 (0.18)	19.9	20.1	20.1	20.1	20.0 (0.02)	20.0	20.0	19.4	19.5	19.1	20.0	20.1 2	0.0	0.0	9.9 2	0.0	0.0
C-28	32.0 (0.14)	32.0	32.0 (0.09)	31.8	32.0	32.0	32.0	31.9 (0.00)	32.1	32.0	32.1	32.1	67.0	31.9	32.0 3	2.0 3	2.0 3	2.0 3	2.0 3	32.0
C-29	31.7 (0.08)	31.7	31.7 (0.05)	31.5	31.7	31.7	31.7	31.6 (0.01)	31.7	31.6	31.8	31.9	32.9	31.6	31.6 3	1.7 3	1.9 3	1.7 3	1.6 3	31.7
C-30	34.9 (0.09)	34.9	34.8 (0.07)	34.8	34.9	34.9	34.9	34.9 (0.00)	34.9	34.9	34.6	34.9	34.2	34.8	34.9 3	4.8 3	4.9 3.	4.8 3	4.9 3	34.8
ососн3		170.7	169.5			169.9		170.4		173.5					1	0.2 17	0.7 16	9.8 17	0.5 16	<b>39.4</b>
															17	0.0 17	0.5 16	9.5 17	0.1	
OCOCH3		21.2	20.9			20.7		20.5		20.2					7	1.1 2	0.8 2	1.1 2	0.9 2	0.7
															2	0.8 2	1.0 2(	0.9 21	<b>J.</b> 8	
Values in pare	entheses are up	ofield shi	fts for the add	tion of 0	.182 mol	equiv. P	r(fod) <sub>3</sub> -d	27.												

<sup>b</sup> Values in parentheses are upfield shifts for the addition of 0.197 mol equiv. Pr(fod)<sub>3</sub>- $d_{27}$ . <sup>c</sup> Other signals present were at  $\delta$  144.9 (C- $\alpha$ ), 127.8 (C- $\beta$ ) and 145.7 (C- $\gamma$ ). <sup>d</sup> Values in parentheses are upfield shifts for the addition of 0.089 mol equiv. Pr(fod)<sub>3</sub>- $d_{27}$ . <sup>e</sup> Values bearing the same superscript are interchangeable. <sup>f</sup> C-2, C-5, C-21 and C-22 are related in Ref. 13 with  $\delta$  42.2, 41.5, 39.3 and 32.8 resonances, respectively. 97

ASSIGNMENT OF <sup>13</sup>C NMR SPECTRA OF SOME FRIEDELANES

adjacent to the C-7 carbonyl function, experienced a minor upfield shift (0.7 ppm). An analogous observation was made on comparison of the spectra of 12 and 2. However, C-17 in 11 resonates at  $\delta$  30.1, and not at  $\delta$  34.7 as has been reported recently.<sup>4</sup>

The change from 1 to canophyllol (13) significantly affected the resonances at  $\delta$  35.9 (CH<sub>2</sub>), 29.9 (-C-), 42.8 (CH), 39.2 (CH<sub>2</sub>) and 32.0 (CH<sub>3</sub>) which are replaced by the signals at  $\delta 29.0$  (CH<sub>2</sub>), 35.1 (-C-), 39.2 (CH), 33.2 (CH<sub>2</sub>) and 67.0 (CH<sub>2</sub>OH), respectively, in 13. They are thus associated with C-16, C-17, C-18, C-22 and C-28, as appropriate. The <sup>13</sup>C spectra of 3-oxofriedelan-29-yl acetate (20) and methyl 3oxofriedelan-29-oate (21) reported by Betancor et al.<sup>9</sup> have also been analysed. Both these spectra are more or less superimposable with the spectrum of 1, except for the resonances associated with C-19, C-20, C-21, C-29 and C-30. The functionalization of 1 at C-29 as in 20 and 21 caused appropriate downfield shifts of the C-20 and C-29 and upfield shifts of the C-19, C-21 and C-30 resonances (ca 4.5-5.4 ppm in 20; ca 3.1-4.1 ppm in 21). The spectrum of 27-hydroxyfriedelane<sup>3</sup> was of help in assigning resonances for C-12 and C-13 in 1, leaving only the resonances of C-11 and C-15 for identification. C-12 and C-15 in 1 should have similar resonance positions as their magnetic environments are similar while C-11, experiencing one less  $\gamma$ -interaction from an axial methyl group, is likely to absorb relatively downfield of C-15.

The acetoxy function at C-2 in pachysandiyl diacetate (18) and friedelan- $2\beta$ ,  $3\beta$ -diyl diacetate (19) had similar effects on the C-1 resonance (downfield shifts relative to 2 by 5.2 and 5.9 ppm, respectively); however, the axial group in 18 caused stronger upfield shifts for the C-4 and C-10 (4.3 and 7.9 ppm, respectively, relative to 2) resonances than the equatorial group in 19 (1.6 and 2.5 ppm, respectively, compared with 2). Similarly, a  $3\alpha$ -hydroxyfriedelan-2-one (7) from change to friedelane- $2\alpha$ ,  $3\alpha$ -diol (15) led to upfield shifts of the C-4 and C-10 signals by 8.8 and 9.0 ppm, respectively, and of those of the C-1 and C-3 resonances by 9.4 and 3.7 ppm, respectively. A  $3\beta$  (axial) substituent is involved in a gauche-butane type of interaction with the C-1 methylene in 18 and 19, causing its strong upfield shift relative to that in 6 and 3, respectively. For a  $3\alpha$  substituent (as in 15-17 relative to 3 and 6 as appropriate) such a strong upfield shift was not found.

The observation described above draws attention to the resonance assignments for C-16 and C-17 in friedelan-28-ol (22) and of C-19, C-21 and C-22 in friedelan-30-ol (23), friedelan-29-ol (24) and friedelan-29-al (25) reported recently by other workers.<sup>5</sup> The hydroxy group on C-28 in 22 was reported <sup>5</sup> to have a minor influence on the C-16 and C-17 resonances. We, however, feel from our experience on canophyllol (13) that the assignments should be reversed, and thus C-16 and C-17 in 22 are likely to be related to the resonances at  $\delta$  29.2 and 34.2, respectively. [The numbers of attached protons at C-16 and C-17 are different (2 and 0). These assignments would be more unambiguous if the multiplicities of these carbons were to be observed.] It was also reported that the incorporation of a hydroxy function at C-29 or C-30, as in 23 and 24, led to an unusual upfield shift for the C-22 signal ( $\delta$ -carbon with

respect to the oxygen substituent) of 11.0-11.4 ppm relative to the C-22 resonance in 1. Again, C-19 in 23 and 24 was reported to undergo a downfield shift (2.9-4.3 ppm) relative to 1, while C-21 experienced an upfield shift (3.0-3.4 ppm) for a similar functionalization at C-29 or C-30. Further, the formyl group at C-20 in 25 was reported<sup>5</sup> to exert opposing influences on the  $\beta$ carbons C-19 and C-21 (deshielding the former by 7.2 ppm while shielding the latter by 7.8 ppm), concommitant with a strong upfield shift of the C-22 resonance (9.9 ppm) relative to 1. It thus becomes apparent that a reassignment of these resonances in 23, 24 and 25 is needed, and that the resonances at  $\delta$  39.5 ( $\delta$  38.1 and 42.4 in 24 and 25, respectively), 29.7 ( $\delta$  29.3 in 24 and **25**) and 27.8 (δ 28.2 in **24** and 24.9 in **25**) in **23** are more likely to be related to C-22, C-19 and C-21, respectively, for a better correspondence with substituent effects. The hydroxy group on C-26 in 26 should affect C-15 instead of C-12. Thus, the  $\delta$  23.4 methylene resonance in 26 is probably associated with C-15, while C-12 should resonate in the same region ( $\delta$  30.0) as in 1.

The carbon spectra of pachysonol (27), maytensifolin-B (28), 3-oxofriedelan-29-ol (29), maytenfoliol (30), 3oxofriedelan-30-ol (31) and maytensifolin-A (32) recently reported by Nozaki *et al.*<sup>10</sup> have been considered in this context, and the probable assignments are given in Table 2. The C=O function at C-16 in 28 was found to exert strong deshielding effects on the  $\alpha$ -carbons, and also on the  $\beta$ -carbons of the cyclohexanone ring. A large upfield shift (about 8.4 ppm relative to 1) noted for the other  $\beta$ -carbon, peri to the carbonyl, is reminiscent of the influence of a carbonyl function at C-6 or C-22 in friedelane systems.<sup>2,4</sup> The hydroxy group at C-16 in 27 had, however, an unusual deshielding effect on C-15 (ca 12.1 ppm relative to 1) and also affected the C-22 resonance (ca 3.2 ppm upfield shift through a  $\gamma$ -interaction). The C-29 methyl carbon in 31 resonanted slightly upfield ( $\delta$  25.87) of the C-30 methyl carbon in 29 and **30** ( $\delta$  28.60–28.96), further supporting the association of the  $\delta$  31.7 and 34.9 resonances with C-29 and C-30, respectively, in 1. The apparent upfield position of C-22 in 30 ( $\delta$  28.32 or 29.17) compared with a similar carbon in 13 ( $\delta$  33.2) is not, however, readily accountable. The contention of Nozaki *et al.*<sup>10</sup> that C-17 in 32 is related to a  $\delta 203.71$  (s) resonance rather than the signal at  $\delta$  82.79 (s) is strange. A few other anomalies noted during the analysis are given as footnotes in Table 2.

The resonance at  $\delta$  173.7 assigned to C-2 in zeylasterone<sup>6</sup> (33) is too downfield for an oxygenated carbon of a catechol system, even if the deshielding effect of the para carbonyl at C-6 is considered. Again, the resonance at  $\delta$  153.8 related<sup>6</sup> to C-8 in 33 is too far upfield considering that it is  $\beta$ - and conjugated to a carbonyl, and also has deshielding effects from several  $\alpha$ - and  $\beta$ -substituents. An interchange of the resonance assignments between C-2 and C-8 in 33, however, gives a better correspondance. The C-27 and C-28 resonance assignments<sup>6</sup> in 33 to the signals at  $\delta$  32.7 and 18.3, respectively, are inconsistent when compared with those in 1 as well as in 20, and should be reversed. Again, the carbomethoxy substituent in 33 and 34 should affect, as in 20, the C-20 resonance (relative to 1) while C-17 should be more or less unaffected. The assignment of the  $\delta$  30.5 non-protonated carbon resonance in 33<sup>6</sup> and

Table 2.	Carbon-1	3 signals	(d) of the frie	delanes 20-34											
Carbon	20 <sup>9</sup>	21 <sup>8</sup>	22ª	23 <sup>a</sup>	24ª	25 <sup>ª</sup>	26"	27	28	ន	8	31	22	33°	æ
<u>د</u> ۔	22.26	22.27	20.7	20.7	20.7	20.7	22.3	22.29	22.23	22.32	22.29	22.32	22.35	113.8	110.5
C-2	41.48	44.49°	27.4	27.4	27.4	27.4	41.4	41.55	41.42	41.55	41.51	41.55	41.55	173.7 (155.5)	178.4 <sup>d</sup>
C-3	212.62	212.58	30.9	30.9	30.9	30.9	213.0	212.48	212.48	212.90	212.93	212.20 <sup>g</sup>	212.87	155.5 (152.8 <sup>d</sup> )	146.0
C-4	58.22	58.28	46.1	46.1	46.1	46.2	58.1	58.32	58.17	58.32	58.32	58.31	58.32	113.3	127.2 <sup>e</sup>
C-5	42.10	42.05	37.5	37.6	37.5	37.6	42.2	42.27	42.09	42.15	42.12	42.18	42.15	119.4	117.1°
C-6	41.37	41.31	41.4	41.5	41.5	41.4	42.4	41.36	41.03	41.42	41.36	41.37	41.30	188.0	133.8
C-7	18.25	18.21	18.1	18.1	18.1	18.1	20.7	18.56	18.62	18.31	18.31	18.29	18.04	124.4	118.0
C-8	53.14	53.15	52.5	53.5	53.1	53.3	51.2	53.49	52.37	53.10	52.49	53.47	49.89	153.8 (173.7)	164.0 <sup>f</sup>
C-9	37.46	37.53	37.1	37.0	37.0	37.1	37.5	37.63	37.66	37.54 <sup>g</sup>	37.54	37.51	37.78	45.6	44.9
C-10	59.56	59.50	60.7	60.7	60.8	60.7	59.9	59.65	59.35	59.65	59.65	59.58	59.74	152.8 (153.8 <sup>d</sup> )	169.8 <sup>†</sup>
C-11	35.56	35.53	35.3	35.5	35.4	35.4	35.4	35.78	35.42	35.66	35.48	35.72 <sup>h</sup>	34.54	36.2 (34.8)	33.5
C-12	30.39	30.27	30.2	30.7	30.7	30.5	23.4 (30.0)	30.81	29.11	29.44	29.96	29.82	27.84	28.6 (29.8)	29.6
C-13	39.84	39.67	38.2 (39.3)	38.3 (39.9)	38.4 (39.7)	38.1 (39.8)	39.6	39.33 <sup>d</sup>	39.15	39.91	39.59	40.03	39.82	39.7	39.3
C-14	38.32	38.08	39.3 (38.2)	39.9 (38.3)	39.7 (38.4)	39.8 (38.1)	42.7	40.09 <sup>d</sup>	40.45	38.18	38.39	38.31		40.5 (43.0)	38.3
C-15	32.27	32.83	31.2	32.6	32.1	32.6	30.0 (23.4)	44.43	50.22	32.20	31.11	32.81	27.75	30.9 (29.8)	29.8
C-16	35.89	35.53	34.2 (29.2)	35.9	36.0	36.2	36.3	75.57	218.84	29.66 <sup>h</sup>	29.17	35.96	33.24	34.8 (36.2)	36.4
C-17	29.96	29.53	29.2 (34.2)	30.5	30.0	29.4	32.9	32.05	45.31	30.05	35.15	29.82	82.79	43.0 (30.5)	30.5
C-18	42.60	42.49	39.5	41.8	42.7	44.4	44.9	44.79	44.00	42.88	38.88	41.97	43.43	44.2	44.2
C-19	30.21	31.43	34.5	39.5 (29.7)	38.1 (29.3)	42.4 (29.3)	36.0	35.78	35.48	30.57	31.51	30.63	32.08	29.8 (30.9)	30.4
C-20	31.97	40.47	28.1	33.1	33.4	38.0	34.5	28.02	27.59	33.45	33.30	33.17	30.84	30.5 (40.5)	40.3
C-21	28.24	28.55	32.8	29.7 (27.8)	29.3 (28.2)	24.9	74.3	32.05	31.66	28.26	30.20	27.87	27.20	29.8	28.6
C-22	38.03	38.32	33.4	27.8 (39.5)	28.2 (38.1)	29.3 (42.4)	46.6	36.03	30.78	39.91	28.32	39.56	35.69	34.4	34.8
C-23	6.78	6.78	15.1	15.1	15.1	15.1	6.7	6.82	6.79	6.79	6.82	6.82	6.79	178.7	10.2
C-24	14.65	14.64	13.5	13.5	13.5	13.5	14.4	14.70	14.67	14.70	14.70	14.70	14.64	-	1
C-25	18.00	17.64	18.3	18.1	18.2	17.6	17.9	18.19	17.34	18.04	18.19	17.90	16.49	36.8	38.2
C-26	18.54	17.64	19.2	18.4	18.6	17.9	63.2	20.07	20.29	18.56	18.65	18.44	15.52	20.2	21.5
C-27	20.12 <sup>d</sup>	20.87	19.0	20.7	19.9	20.7	20.2	21.47	16.22	19.95	19.13	20.77	19.47	32.7 (18.3)	18.3
C-28	32.10	31.91	68.0	32.1	32.1	31.1	32.7	24.86	27.38	32.20	69.02	32.14	1	18.3 (32.7)	31.5
C-29	72.73	179.43	31.3	25.8	72.0	207.0	24.9	30.75	31.11	72.09	73.36	25.87	33.36	31.6	30.8
C-30	29.52	31.79	35.1	74.8	28.9	27.1	32.0	35.48	35.21	28.96	28.60	74.79	25.35	179.8	178.1 <sup>d</sup>
осн <sub>з</sub>		51.77												51.6	51.4
ососн	171.20														
	20.92 <sup>d</sup>														

<sup>a</sup> Values in parentheses represent revised assignments.

<sup>b</sup> The methy parameter option consignments are those of earlier workers<sup>11</sup> who also related the  $\delta$ 30.5 (s) resonance with C-20 instead of C-17. <sup>c</sup> The sequence of signal representation in Ref. 9 indicates this value to be a misprint, and it should be replaced by 41.79. <sup>c</sup> The sequence of signal representation in Ref. 9 indicates this value to be a misprint, and it should be replaced by 41.79. <sup>d.e.f</sup> Values bearing the same superscript are interchangeable. <sup>g</sup> The multiplicity reported in Ref. 10 is a triplet, and is questionable. The  $\delta$  29.66 (s) resonance in **29** is upfield for C-9, which is more likely to resonate at  $\delta$  *ca* 37. <sup>h</sup> The multiplicity (singlet) reported in Ref. 10 is questionable. The  $\delta$  37.54 (t) resonance is slightly low field for C-16 in **29**.

pristimerin<sup>11</sup> (34) is thus untenable. Hence C-20 is likely to be linked with the resonance at  $\delta ca 40.3-40.5$ , and C-17 with the signal at  $\delta 30.5$ . A partial carbon shift assignment of 34 was made by earlier workers.<sup>11</sup> The assignments of the remaining signals of 34 given in Table 2 followed from comparison with the revised assignment of zeylasterone, which were deduced by comparison with the carbon chemical shifts of 20 and other friedelanes.

#### **EXPERIMENTAL**

The <sup>13</sup>C NMR spectra were recorded on a Varian 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 recorded in 5 mm o.d. tubes using CDCl<sub>3</sub> as solvent as well as internal lock and internal standard. All solutions were ca 5-10% in concentration. The chemical shifts reported are in  $\delta$  (ppm) downfield from TMS;  $\delta_{TMS} = \delta_{CDCl_3} + 76.9$  ppm. The spectra were run with sweep width 4500 Hz, pulse width 6  $\mu$ s (approximately 45° flip angle) and approximately 1.5 s delay between pulses. The attached proton test (APT) experiment was also carried out using the pulse sequence  $D_{1-}(\pi/4) - \tau - \pi - \tau + 1 - \pi - D_2$ -FID, where  $D_1 = 0.6$  s,  $\tau =$ 8 ms and  $D_2 = 1500 \ \mu$ s for 5, 6, 9 and 19a. The shift studies were carried out using approximately 0.05, 0.10 and 0.15 molar equivalents of LSR.  $Pr(fod)_3 - d_{27}$  was employed for 3, 7 and 8 and  $Eu(fod)_3$ - $d_{27}$  was used for 14.

Cerin, 5, 7, 9 and 13 were isolated<sup>13,14</sup> from the bark of *Quercus suber* (Cork waste). Acetylation of cerin, 5,

7 and 9 with  $Ac_2O$  in  $C_5H_5N$  at room temperature for 12 h afforded 3 (and also 4 in one run), 6, 8 and 10, respectively. NaBH<sub>4</sub> reduction of 3 and 5 in MeOH and subsequent treatment of the products with Ac<sub>2</sub>O in  $C_5H_5N$  as above afforded 18 and 19, respectively. NaBH<sub>4</sub> reduction of 11 gave 12, while similar reduction of 7 afforded 15 and friedelane- $2\beta$ ,  $3\alpha$ -diol which, on acetylation as above, furnished 16 and 17, respectively. Friedelin (1) yielded 14 on treatment with *m*-chloroperbenzoic acid (*m*-CPBA) in  $CH_2Cl_2$  at -5 °C for 24 h, or by refluxing with  $H_2O_2$  and  $SeO_2$  in *t*-BuOH for 35 h. Treatment with  $Ac_2O$  and  $C_5H_5N$  of the product from the reaction of *m*-CPBA with cerin, as above, afforded **19a**. These compounds were purified by chromatography over silica gel and subsequent recrystallization from suitable solvent mixtures, and were identified<sup>14</sup> from their spectral (IR, <sup>1</sup>H NMR and MS) characteristics and also by direct comparison with authentic samples in appropriate cases. Compound 4,  $C_{35}H_{54}O_2N^+Cl^ (M^{+} m/z 520)$ , m.p. 178-80 °C,  $[\alpha]_{D}^{25} + 20^{\circ}$  (CHCl<sub>3</sub>) exhibits IR bands (KBr) at 1725, 1620, 1502, 1485, 1455, 1385, 1180, 1000 and  $690 \text{ cm}^{-1}$  and <sup>1</sup>H NMR signals (360 MHz, CDCl<sub>3</sub>) at  $\delta$  9.08 (2H, d, J = 5.8 Hz,  $H_2$ - $\alpha$ ), 8.49 (1H, t, J = 7.8 Hz,  $H-\gamma$ ), 8.06 (2H, dd, J = 5.8 and 7.8 Hz,  $H_2$ - $\beta$ ), 6.70 (1H, m, H-2), 1.17 (3H, s), 1.08 (3H, s), 1.00 (3H, s), 0.98 (3H, s), 0.96 (3H, d, J = 7.0 Hz, $H_3$ -23), 0.94 (3H, s), 0.90 (3H, s) and 0.86 (3H, s).

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