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ENDOPEROXIDE DITERPENOIDS AND OTHER CONSTITUENTS FROM *ABIES MAROCANA*

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Key Word Index—*Abies marocana*; Pinaceae; endoperoxide diterpenoids; triterpenoids.

Abstract—From the acid fraction of the hexane extract of the needles of *Abies marocana* three endoperoxide diterpenoids, methyl 12α-hydroxyabietate and a triterpenoid, in addition to other resin acids have been isolated.

INTRODUCTION

As a part of our research program on the chemical composition of different species of the genus *Abies* [1] we have studied the acid fraction of the hexane extract from the needles of *Abies marocana* Trabut, which grows on the calcareous chain of Yebala (northern Morocco). The chemical composition of this plant has not been published, except a brief study on the polar extract of its heartwood [2].

RESULTS AND DISCUSSION

The acid fraction of the hexane extract from the needles of *A. marocana* was esterified, after which the endoperoxide diterpenoids **1–3**, methyl 12α-hydroxyabietate (as its acetyl derivative **4**) and triterpenoid **5**, were isolated, in addition to the well-known methyl dehydroabietate, methyl abietate, methyl 7-oxodehydroabietate and methyl 15-hydroxydehydroabietate.

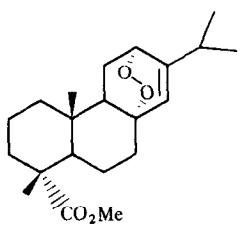
The molecular formula $C_{21}H_{32}O_4$ for compound **1** was assigned on the basis of MS, ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2). Absorptions in the IR region at 1721 and 1248 cm^{-1} were attributed to the presence of a methoxycarbonyl group equatorially attached to a cyclohexane ring [3] and the one at 1655 cm^{-1} revealed a trisubstituted double bond. The ^{1}H NMR spectrum showed three methyl singlets at δ0.5, 1.1 and 3.60 and an isopropyl group as a doublet at δ1.03. The above NMR data coupled with the carbon distribution in the ^{13}C NMR suggest that the structure of **1** consists of an abietane skeleton. The endoperoxide function was located between C-8 and C-12, as deduced from the signals in the ^{1}H NMR spectrum at δ4.58 (*m*) due to the allylic H-12 and to the signals at δ74.0 (tertiary) and at δ77.0 (quaternary) in the ^{13}C NMR spectrum. The trisubstituted double bond was located at Δ^{13} because of the above considerations and the presence of a broad singlet in the ^{1}H NMR spectrum at δ5.85, corresponding to one proton. The α-orientation of the endoperoxide bridge was deduced from the analysis of the ^{1}H NMR spectrum. The anomalously low δ value for Me-20 (0.5 ppm) was attributed to its shielding by the double bond.

The structures of compounds **2** and **3** were established by comparison of their properties with the reported data [4]. We have unambiguously assigned their ^{13}C NMR spectra by 2D H–C correlation experiments and differences with the literature assignments have been found.

These three compounds could be artefacts produced through oxidation of levopimaric and palustric acids during extraction and isolation procedure. This is supported by the results reported in the literature [5, 6] and those obtained by us in the photooxidation reaction of the resin from *Pinus pinea*, which contains 39.1% of a mixture of palustric and levopimaric acids and from which **1–3** originated (Experimental).

Compound **4**, isolated by column chromatography after acetylation of a polar fraction exhibited IR, MS and ^{1}H NMR data in agreement with the literature [7, 8]. Assignment of the relative stereochemistry at C-12, which was not unambiguously established in refs [7, 8], has received greater attention by chemical and spectroscopic study. Reduction of **4** with $LiAlH_4$ gave **6**, identical to the product obtained by treatment of the endoperoxide diterpenoid **1** with the same reducing agent. The C-12 α-configuration in **4** was confirmed by the H-12 multiplicity and $J_{11,12}$ value in its ^{1}H NMR spectrum, analysis of which was achieved with the aid of the spectrum of **7** (for preparation of this substance see Experimental).

Acetylation of the most polar fraction of the column chromatography of the extract allowed us to isolate **5**. From its mass spectrum ($[M]^+$ at *m/z* 528), together with the ^{1}H and ^{13}C NMR data, a molecular formula of $C_{33}H_{52}O_5$ was deduced. Its IR spectrum showed ketone and methoxycarbonyl groups (1718, 1730 cm^{-1}) and a double bond (1635 cm^{-1}). The ^{1}H NMR spectrum (Table 3) exhibited the following signals corresponding to methyls: two doublets at δ0.84 (J = 6.8 Hz) and 1.16 (J = 7.0 Hz), five singlets at δ0.86, 0.94, 0.95, 0.99 and 1.05, as well as others corresponding to an acetoxyl group (δ2.03) and methoxyl group (δ3.66). We also observed the presence of a proton geminal to an acetoxyl group, as a triplet (J = 3.4 Hz) at δ4.63 and that of an olefinic proton at 5.54, as a multiplet. The above data allowed us to propose a lanostane skeleton for **5**. The 3α-location of the acetoxy group followed from the ^{1}H NMR signal of H-3



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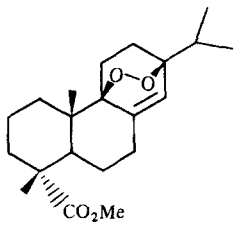

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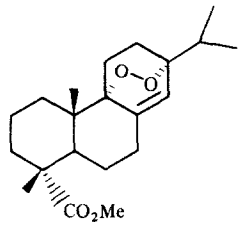

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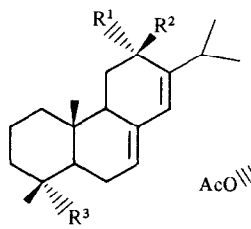

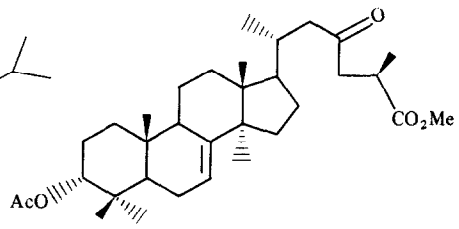

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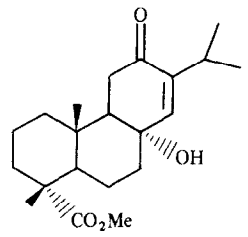

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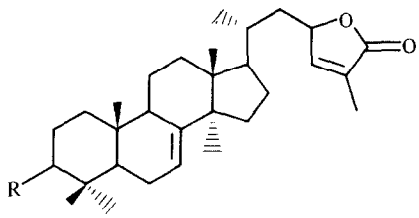
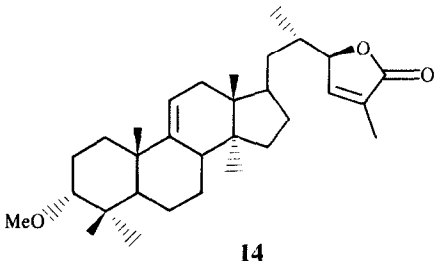
4 R^1 = OAc, R^2 = H, R^3 = CO_2Me
6 R^1 = OH, R^2 = H, R^3 = CH_2OH
7 R^1 = H, R^2 = OAc, R^3 = CO_2Me
9 R^1, R^2 = O, R^3 = CO_2Me
10 R^1 = H, R^2 = OH, R^3 = CO_2Me
11 R^1 = H, R^2 = OH, R^3 = CH_2OH



12 R = β-OH
13 R = α-OMe



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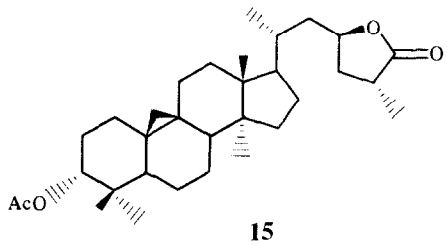

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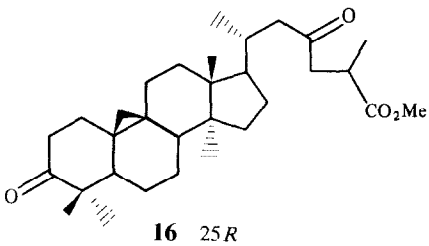
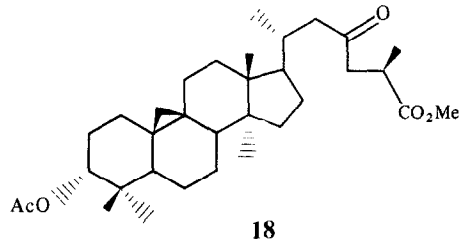


16 25*R*
17 25*S*



18

and the δ values for the methyl groups attached to C-4. A Δ^7-double bond was confirmed by comparison of the ^1H and ^{13}C NMR data with those of the abieslactones **12** and **13** [10] and of the derivatives of grandisolide **14** [11] which possesses a $\Delta^{9(11)}$-double bond. The doublet at δ1.16, in the ^1H NMR spectrum for H-27, located the ester group at C-26. Finally, the ^{13}C NMR spectrum revealed the presence of two methylenes resonating at δ50.13 and 46.62, thus fixing the carbonyl group at C-23.

Location of the γ-ketoester at the side chain was confirmed by means of chemical correlations. For this purpose we treated **15** [12] with 2 M KOH–methanol at room temperature, neutralization, esterification with diazomethane and subsequent oxidation with Jones reagent yielded the mixture of **16** and **17**. Its ^{13}C NMR spectrum showed splitting of some signals, mainly the ones corresponding to the carbons near the epimerization centre C-25. When we carried out a basic treatment of **15** in

Table 1. ^{1}H NMR spectral data of compounds **1–4** and **6–11** ($CDCl_3$, TMS as int. standard)*

H	1	2	3	4	6	7	8	9	10	11
7				5.56 *m*	5.55 *m*	5.49 *m*		6.00 *m*	5.46 *m*	5.50 *m*
11							2.62 *m*	2.20 *m*		
12	4.58 *m*			5.48 *t* (3.0)	4.25 *t* (3.0)	5.60 *dd* (5.6) (11.0)			4.41 *dd* (4.7) (10.0)	4.42 *m*
14	5.85 *t* (2.0)	6.11 *t* (2.2)	6.05 *t* (2.0)	5.98 *s*	5.83 *s*	5.86 *s*	6.32 *s*	6.70 *s*	5.76 *s*	5.75 *s*
15		1.87 *hp*† (6.9)	1.87 *hp* (6.9)							
16	1.04 *d*[a] (7.0)	0.95 *d*[b] (6.9)	0.94 *d* (7.2)	1.00 *d* (7.3)	1.07 *d* (7.0)	0.94 *d* (6.8)	0.98 *d* (7.0)	1.01 *d* (7.0)	1.03 *d* (6.8)	1.04 *d* (7.0)
17	1.08 *d*[a] (7.0)	0.96 *d*[b] (6.9)	0.94 *d* (7.2)	1.02 *d* (7.3)	1.11 *d* (7.0)	1.04 *d* (6.8)	1.02 *d* (7.0)	1.04 *d* (7.0)	1.05 *d* (6.7)	1.06 *d* (7.0)
18	—	—	—	—	3.11; 3.36 AB (11.0)	—	—	—	—	3.12; 3.40 AB (11.0)
19	1.10 *s*	1.29 *s*	1.24 *s*	1.24 *s*	0.86 *s*	1.23 *s*	1.10 *s*	1.27 *s*	1.23 *s*	0.87 *s*
20	0.50 *s*	1.11 *s*	1.03 *s*	0.78 *s*	0.81 *s*	0.79 *s*	0.62 *s*	0.87 *s*	0.81 *s*	0.82 *s*
OMe	3.63 *s*	3.63 *s*	3.58 *s*	3.63 *s*		3.61 *s*	3.65 *s*	3.65 *s*	3.61 *s*	
OAc				2.05 *s*		2.07 *s*				

Coupling constants (J in Hz) are given in parentheses.
*Compound **1**: 80 MHz; **2–4** and **6** 300 MHz, **7**: 300 MHz; **8–11**: 80 MHz.
† *hp*: Heptuplet.
[a,b]Interchangeable values.

Table 2. ^{13}C NMR chemical shifts of compounds **1–4** (75 MHz, $CDCl_3$, TMS as int. standard)

C	1	2	3	4
1	32.13	33.62	30.93	37.96
2	17.04	17.62	17.64	17.88
3	36.83	37.45	36.72	37.00
4	47.09	47.45	46.81	46.35
5	49.23	40.50	38.22	44.86
6	21.65	20.61	19.91	25.81
7	36.75	27.45	25.01	125.16
8	76.97	143.95	144.34	134.00
9	50.10	82.22	80.82	44.15
10	36.30	38.67	39.18	33.87
11	25.00	23.59	21.78	27.71
12	74.69	25.26	24.26	68.62
13	149.07	79.79	79.22	139.54
14	124.60	127.00	126.99	128.16
15	31.08	32.26	32.18	32.53
16	20.16	17.54[a]	17.49[b]	16.77
17	20.44	17.21[a]	17.11[b]	17.88
18	178.94	178.96	178.54	178.73
19	16.57	17.68	17.87	21.37
20	15.20	18.13	19.19	14.13
OMe	52.06	52.14	51.99	51.79
OCOMe				170.88
OCOMe				21.71

[a,b]Interchangeable values.

softer conditions, with K_2CO_3 in ethanol–water, only the opening of the lactone occurred, without epimerization at C-25. Later, esterification with diazomethane and oxidation with the Jones reagent, gave **18**, the ^{13}C NMR spectrum of which did not show split signals. The chemical shifts of C-17, C-21, C-24, C-25 and C-26 were similar to those of the **16** and **17** mixture. As these values were similar to the ones of the same carbons for compound **5**, we proposed the *R*-configuration for the chiral centre at C-25.

EXPERIMENTAL

The needles of *A. marocana* were collected in Mont Talasmtane (calcareous chain of Yebala, Western Rif, Morocco) in Mars, 1987. The plant was identified by Professor F. Valle (Departamento de Biología Vegetal, Universidad de Granada, España. The air-dried needles (3 kg) were crushed and extracted with hexane in a Soxhlet apparatus for 12 hr. The extract (43.0 g) was defatted and after dissolving in Et_2O, extracted with an aq. NaOH soln (10%), giving 28.9 g of a neutral fr. and 10.8 g of an acid fr. The later was treated with CH_2N_2 and then chromatographed under pressure on a silica gel column eluted with hexane–Et_2O mixts, giving frs A_1–A_6. Further chromatographies on a silica gel column yielded different compounds, which, finally, were purified by prep. TLC or recrystallization. Fraction A_1 (2.1 g, eluted with hexane–Et_2O, 24:1) consisted basically of fatty acids. Fr. A_2 (1.1 g, eluted with hexane–Et_2O, 93:7) contained, besides fatty acids, methyl dehydroabietate (635 mg) and methyl abietate (404 mg). Fr. A_3 (1.2 g, eluted with hexane–Et_2O, 23:2, 9:1) gave by rechromatography **1** (192 mg), **2** (88 mg) and **3** (375 mg). The most polar frs from A_3 were acetylated and by rechromatography **4** was isolated (25 mg). Fr. A_4 (0.8 g, eluted with hexane–Et_2O, 4:1) contained methyl 7-oxodehydroabietate (83 mg). Fr. A_5 (1.2 g, eluted with hexane–Et_2O, 7:3) was methyl 15-hydroxydehydroabietate (65 mg). Fr. A_6. It was acetylated (0.87 g, eluted with hexane–Et_2O, 13:7); after prep. TLC, **5** was isolated (26 mg).

Methyl 8,12α-epidioxy-13-abieten-18-oate (**1**). Solid, mp (uncorr): 91–93° (hexane); $[\alpha]_D^{25}$ +50.8° ($CHCl_3$; *c* 1.40); IR ν_{max}^{film} cm^{-1}: 2927, 2868, 1721, 1655, 1463, 1443, 1385, 1367, 1248,

Table 3. ^{1}H NMR spectral data of compounds **5**, **16/17** and **18** (300 MHz, $CDCl_3$, TMS as int. standard)

H	5	16/17	18
3	4.63 *t* (3.42)		4.67 *t* (2.75)
7	5.54 *m*		
18	0.94 *s*	1.03 *s*	0.90 *s*
19	0.99 *s*	0.56; 0.77	0.34; 0.50
		AB (4.4)	AB (4.2)
20	0.99 *s*		
21	0.84 *d* (6.7)	0.86 *d* (6.3)	0.85 *d* (6.4)
24	2.45 *dd* (5.6, 17.6)	2.45 *dd* (5.6, 17.6)	2.45 *dd* (5.6, 17.6)
24′	2.82 *dd* (8.0, 17.6)	2.82 *dd* (8.0, 17.6)	2.82 *dd* (8.0, 17.6)
25	2.92 *m*	2.92 *m*	2.92 *m*
27	1.16 *d* (7.0)	1.16 *d* (7.0)	1.16 *d* (7.0)
28	1.05 *s*	1.08 *s*	0.98 *s*
29	0.95 *s*	1.01 *s*	0.90 *s*
30	0.86 *s*	0.89 *s*	0.83 *s*
OMe	3.66 *s*	3.66 *s*	3.65 *s*
OCOMe	2.03 *s*		2.06 *s*

Coupling constants (J in Hz) are given in parentheses.

Table 4. ^{13}C NMR chemical shifts of compounds **5** and **16–18** (75 MHz, $CDCl_3$, TMS as int. standard)

C	5	16	17	18
1	30.60	37.54	37.54	28.37
2	22.87	33.50	33.50	26.23
3	78.53	216.67	216.67	79.15
4	36.60	45.51	45.51	38.79
5	43.45	47.90	47.90	42.25
6	23.32	21.55	21.55	21.06
7	121.60	25.91	25.91	25.70
8	148.66	48.49	48.49	48.91
9	48.51	21.07	21.07	19.88
10	35.69	26.05	26.05	26.37
11	23.06	26.71	26.71	26.21
12	33.38	32.75	32.75	32.80
13	43.73	48.49	48.49	45.41
14	53.02	50.30	50.30	49.09
15	35.17	35.54	35.54	35.52
16	28.81	28.38	28.38	28.23
17	53.63	52.40	52.37	52.40
18	24.39	18.21	18.21	18.20
19	23.12	29.62	29.62	29.89
20	33.12	33.02	33.02	33.07
21	19.50	19.37	19.37	19.37
22	50.13	50.39	50.39	50.44
23	209.14	209.30	209.30	209.33
24	46.62	46.66	46.73	46.60
25	34.66	34.67	34.58	34.64
26	176.35	176.44	176.44	176.43
27	17.16	17.19	17.22	17.18
28	28.32	22.25	22.25	25.52
29	23.80	20.84	20.84	20.85
30	30.90	19.40	19.40	19.37
OMe	51.88	51.92	51.92	51.91
$MeCO_2$	170.72			170.86
$MeCO_2$	21.34			21.42

1183, 1149, 1029. MS (probe) 70 eV, *m/z* (rel. int.): 348 $[M]^+$. (4.0), 330 (14.0), 316 (12.0), 305 (13.0), 255 (28.0), 173 (22.0), 123 (36.0), 121 (100.0) 113 (39.0), 109 (30.0), 91 (40.0).

Methyl 9,13*β-epidioxy*-8(14)-*abieten*-18-*oate* (**2**). Solid, mp (uncorr): 115–117° (hexane); $[\alpha]_D^{25} - 32.0°$ ($CHCl_3$; *c* 0.62); IR ν_{max}^{film} cm^{-1}: 2929, 2872, 1725, 1642, 1453, 1432, 1386, 1367, 1248, 1208, 1185, 1148, 1103, 1034, 984, 946, 910, 890. MS (probe) 70 eV, *m/z* (rel. int.): 348 $[M]^+$. (1.0), 330 (11.0), 316 (80.0), 301 (69.0), 245 (60.0), 241 (36.0), 227 (34.0), 159 (33.0), 149 (38.0), 121 (100.0), 107 (54.0), 105 (65.0), 91 (77.0), 79 (57.0), 43 (80.0).

Methyl 9,13*α-epidioxy*-8(14)-*abieten*-18-*oate* (**3**). Solid. Mp. (uncorr): 116–118° (hexane); $[\alpha]_D^{25} - 19.0°$ ($CHCl_3$; *c* 0.64). IR ν_{max}^{film} cm^{-1}: 2952, 2878, 1722, 1461, 1437, 1389, 1367. MS (probe) 70 eV, *m/z* (rel. int.): 348 $[M]^+$. (3.0), 330 (28.0), 316 (25.0), 301 (23.0), 237 (26.0), 162 (44.0), 149 (66.0), 147 (46.0), 133 (36.0), 121 (100.0), 107 (56.0), 105 (54.0), 91 (83.0), 79 (40.0), 77 (32.0).

Methyl 12*α-acetoxyabietate* (**4**). Syrup, IR and MS data were in agreement with lit. [7, 8].

Methyl (25R)-3*α-acetoxy*-23-*oxo*-9*β-lanost*-7-*en*-26-*oate* (**5**). Syrup, IR ν_{max}^{film} cm^{-1}: 2947, 2863, 1718, 1458, 1375, 1246, 1178, 1030, 979, 885, 835, 756. MS (probe) 70 eV, *m/z* (rel. int.): 528 $[M]^+$. (3.0), 513 (7.0), 453 (27.0), 309 (54.0), 187 (55.0), 171 (52.0), 139 (100.0), 129 (93.0), 69 (77.0), 59 (86.0).

Preparation of the endoperoxide diterpenoids **1–3**, *by fotooxygenation. Pinus pinea* resin (25 g) was esterified with CH_2N_2 and the corresponding methyl esters separated by flash chromatography on a silica gel column (hexane–Et_2O, 99:1), 22 g of these in *i*-PrOH (1.1 l) were photooxidized with rose bengal as photosensitizer (146 mg). After 5 hr under sunlight, solvent was evapd and **1** (3.82 g), **2** (0.54 g) and **3** (2.68 g) were isolated by flash chromatography on a silica gel column.

12*α*,18-*Dihydroxy*-7,13-*abietadiene* (**6**). To a soln of **1** (220 mg) in Et_2O (6 ml), 315 mg of $LiAlH_4$ were slowly added. Reduction was performed at room temp for 4 hr. Then H_2O was added and the mixt. was extracted with Et_2O. The extracts were washed, dried over Na_2SO_4 and then evapd to give a crude material (200 mg) which was chromatographed on a silica gel column, eluted with hexane–Et_2O (9:11), 40 mg of **6** was obtained. Syrup, IR ν_{max}^{film} cm^{-1}: 3383, 2928, 2880, 1675, 1620, 1461, 1383, 1259,

1040, 757. MS (probe) 70 eV, *m/z* (rel. int.): 304 $[M]^+$. (1.0), 273 (1.0), 271 (2.0), 261 (4.0), 255 (5.0), 167 (6.0), 149 (32.0), 107 (9.0), 91 (16.0), 83 (35.0), 55 (40.0), 43 (100.0).

Compound **6** was also obtained by $LiAlH_4$ reduction of **4**, as follows: a mixt. of $LiAlH_4$ (10 mg), and **4** (25 mg) in Et_2O (3 ml) was stirred for 1 hr at room temp. After adding H_2O, Et_2O extraction and solvent evapn, 20 mg of **6** was obtained.

Methyl 8α-hydroxy-12-oxo-13-abieten-18-oate (**8**). Compound **1** (5 g) was dissolved in 1 M NaOH–EtOH and refluxed for 10 min. After cooling at room temp., EtOH was evapd and the soln neutralized with HOAc; then H_2O was added and extracted with Et_2O. After drying with Na_2SO_4, **8** was obtained (4.8 g). Solid, mp (uncorr): 107–108° (hexane), IR ν_{max}^{film} cm^{-1}: 3466, 2932, 2870, 1722, 1668, 1449, 1408, 1385, 1345, 1247, 1192, 1168, 1109, 1016, 978, 897, 830. MS (probe) 70 eV, *m/z* (rel. int.): 348 $[M]^+$, (4.0), 330 (5.0), 271 (5.0), 255 (12.0), 149 (29.0), 121 (31.0), 107 (25.0), 91 (31.0), 85 (33.0), 79 (35.0), 59 (86.0), 55 (65.0), 43 (100.0).

Methyl 12β-hydroxyabietate (**10**). Compound **8** (3 g) in glacial HOAc (30 ml) was heated under refluxing for 10 min, neutralized with 5% NaOH and extracted with Et_2O. The extracts were dried and evapd giving a crude material, constituted mainly by **9**. To a stirred soln of this material (215 mg) in MeOH (6 ml), $NaBH_4$ (60 mg) was added for 2 hr at room temp. and then the solvent was evapd. To the resulting residue, H_2O, was added, neutralized with 2 M HCl and extracted with Et_2O. The organic soln was dried, giving a mixt. which by column chromatography on silica gel, eluted with hexane–Et_2O, yielded **10**. Solid, mp (uncorr): 66–67° (hexane). IR ν_{max}^{film} cm^{-1}: 3427, 2952, 2871, 1722, 1669, 1630, 1386, 1247, 1247, 980, 894.

Acetylation of compound **10**. To a soln of **10** (144 mg) in 2 ml pyridine, Ac_2O (2 ml) was added and kept at room temp. overnight. The reaction mixt. was poured onto ice and extracted with Et_2O. The organic phase was successively washed with HCl 5%, satd soln of $NaCO_3H$ and H_2O, dried and evapd, giving **7** (140 mg).

Methyl 12β-acetoxyabietate (**7**). Syrup, IR ν_{max}^{film} cm^{-1}: 2933, 1738, 1721, 1630, 1459, 1369, 1238, 1108, 1034, 966, 918.

Reduction of **8** *with* $NaBH_4$. To a soln of **8** (826 mg) in MeOH (10 ml), $NaBH_4$ was added (90 mg) and the mixt. was stirred for 2 hr at room temp. After solvent evapn, neutralization with 2 M HCl, and Et_2O extraction a material was obtained (810 mg) which was column chromatographed on silica gel, eluting with hexane–Et_2O (9:1) to give **10** (192 mg).

12β,18-Dihydroxy 7,13-abietadiene (**11**). $LiAlH_4$ (77 mg) was added to a soln of **8** (126 mg) in Et_2O (6 ml). After stirring at room temp. for 3 hr, H_2O was added and extracted with Et_2O, this was dried and evapd, yielding **11** quantitatively. IR ν_{max}^{film} cm^{-1}: 3383, 2928, 2880, 1675, 1620, 1461, 1383, 1259, 1040.

Methyl 3,23-dioxo-9,19-cyclo-9β-lanost-26-oate (25R-**16** *and* 25S-**17**). Compound **15** (100 mg) was dissolved in 6 ml of 2 M KOH–MeOH soln. After 1.5 hr solvent was evapd, H_2O was added and extracted with Et_2O. The aq. phase was acidified until pH 2 and extracted with Et_2O and then esterified with CH_2N_2. A crude material was obtained (95 mg) which was dissolved in Me_2CO at 0°. Jones reagent was added dropwise until the colour did not change (orange). The soln was evapd, washed and dried to yield 90 mg **16** and **17**. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2945, 2872, 1736, 1707, 1462, 1379, 1362, 1254, 1215, 1112, 1033, 1006, 979, 933, 911.

Methyl (25R)-3α-Acetoxy-23-oxo-9,19-cyclo-9β-lanost-26-oate (**18**). To 100 mg of **15**, dissolved in 10 ml of EtOH with 5% H_2O, K_2CO_3 was gradually added until saturation of the soln. Reaction was monitored by TLC and after 5 hr worked-up as above, 90 mg of **18** were obtained. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2942, 2869, 1729, 1612, 1372, 1247, 1174, 1042, 995, 909. MS (probe) 70 eV, *m/z* (rel. int.): 528 $[M]^+$ (1.6), 510 (1.9), 470 (8.9), 455 (3.3), 384 (5.2), 324 (6.9), 309 (7.9), 202 (17.3), 187 (19.3), 175 (29.8), 170 (21.4), 162 (26.0), 147 (28.3), 135 (17.0), 128 (33.8), 121 (39.5), 107 (26.6), 95 (26.2), 91 (20.9), 81 (20.0), 59 (22.3), 43 (100.0).

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