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EUDESMANE SESQUITERPENES FROM *LAGGERA PTERODONTA*

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Key Word Index—*Laggera pterodonta*; Compositae; sesquiterpenoids; eudesmane derivatives; flavones.

Abstract—Seven new eudesmane sesquiterpenoids were isolated from the aerial parts of *Laggera pterodonta*. Their structures were elucidated by high-field NMR techniques and chemical evidence. They were named 4β,11-dihydroxyenantioeudesmane-1-one, pterodontriol C, *ent*-7(11)-selinen-4-ol, pterodontriol D, 2α-acetoxycostoate, 2β-acetoxypterodontic acid, and 5α,11-dihydroxy-3-ene-eudesman-2-one. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

Laggera pterodonta (DC) Benth (Compositae) is widely distributed in southwestern China, especially in Yunnan and Sichuan provinces. The green herbal plant has been traditionally used as a medicine by the natives for the treatment of a variety of conditions [1]. The natives named it as 'Chou Ling Dan', which means 'odorous panacea', because the fresh leaves of the plant produce a stimulating odour upon twisting. Pharmaceutical testing has shown that the plant possesses antileukaemia activity [1] as well as the ability to remove phlegm and to inhibit experimental acute bronchitis. Li *et al.* have previously reported several eudesmane derivatives from this plant [2–4] and Zhao *et al.* have also isolated eudesmane sesquiterpenes and flavones [5]. A thorough investigation of the title plant led to the isolation of five flavones and 13 eudesmane derivatives of which seven are new compounds.

RESULTS AND DISCUSSION

Repeated column chromatography and prep. TLC of the EtOAc extract of the title plant yielded seven new constituents (**1**–**7**), as well as 11 known compounds: pterodondiol (**8**) [2], pterodontriol B (**9**) [2], 2α,3β-dihydroxy pterodontic acid (**10**) [3], 3β-hydroxy pterodontic acid (**11**) [3], 1β-hydroxy pterodontic acid (**12**) [3], illicic acid (**13**) [6], penduletin [7], 5-hydroxy-3,4′,6,7-tetramethoxyflavone [7], chrysosplenetin B [7], artemitin [8] and 3′,4′,5-trihydroxy-3,5,6-trimethoxyflavone.

The ^{1}H and ^{13}C NMR spectra of compound **1** showed close similarities to those of pterodontriol B (**9**), an enantio-eudesmantriol [1]. However, the H-1 signal of compound **9** was absent in the ^{1}H NMR spectrum of **1** (Table 1) as was the tertiary carbon signal (δ 80.1, C-1) of **9**. The latter was replaced by a low-field quaternary carbonyl signal which appeared at δ 215.8 (Table 2). Such information indicated that the 1-hydroxy group of compound **9** was changed to a 1-oxo group in the case of compound **1**. The IR spectrum of compound **1** confirmed the presence of the 1-oxo group (1710 cm^{-1}); EI-mass spectrometry gave the $[M]^+$ peak at *m/z* 254, also in agreement with the proposed structure. Furthermore, $NaBH_4$ reduction of compound **1** followed by preparative TLC gave a main product, which was found to be identical to compound **9** ($[\alpha]_D$, mp, IR, NMR, and MS).

Compound 2 exhibited a weak $[M]^+$ peak at *m/z* 256, which has the same amu value as the M_r weight of compound **9**. Combining the results of elemental analysis, the molecular formula of compound **2** was deduced to be $C_{15}H_{28}O_3$, i.e. identical with that of pterodontriol B (**9**) [2]. This suggested that compound **2** was most likely an isomer of pterodontriol B. Because the ^{1}H NMR spectrum of compound **2** also showed three broad hydroxyl signals (δ 6.36, 6.06 and 5.35, each ^{1}H, disappearing on D_2O exchange), compound **2** was, apparently, also an eudesmantriol. The ^{1}H and ^{13}C NMR spectra confirmed this assumption. When comparing the ^{13}C NMR spectrum of compound **2** with that of **9**, the diagnostic lowfield signal for C-7 shifted from δ 42.80 to 48.37, *ca* 5.57 ppm and for C-9 from δ 39.0 to 52.0, *ca* 13.0 ppm which suggested the presence of

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Table 1. ^{1}H NMR spectral data of compounds **1–7** (400 MHz, Me_2CO-d_6)

H	**1**	**2**	**3**	**4***	**5**	**6**	**7**
1	–	1.20 *m*	1.32 *m*	3.67 *t* (6.6)	1.36 *m*	1.42 *m*	2.80 *d* (16.8)
1′	–	1.48 *m*	1.05 *m*	–	1.92 *m*	1.96 *m*	1.83 *d* (16.8)
2	2.55 *m*	1.32 *m*	1.38 *m*	1.02–1.98 *m*	5.25 *tt* (12.0, 4.1)	4.87 *ttd* (4.6, 4.6, 1.6)	–
2′	2.71 *m*	1.58 *m*	1.52 *m*		–	–	–
3	1.78 *m*	1.70 *m*	1.39 *m*		2.08 *m*	1.62 *m*	5.68 *br s*
3′	2.12 *m*	2.03 *m*	1.69 *m*	–	2.72 *m*	1.96 *m*	–
4	–	–	–	–	–	2.67 *m*	–
5	2.49 *m*	2.17 *dd* (13.6, 6.1)	1.15 *dd* (13.0, 2.7)	2.11 *d* (11.4)	1.99 *m*	–	–
6	1.69 *m*	1.74 *ddd* (13.4, 13.4, 13.2)	1.57 *br dd* (13.6, 10.4)	4.65 *ddd* (11.4, 4.6, 3.2)	1.46 *m*	5.30 *d* (2.0)	1.48 *dd* (13.3, 13.3)
6′	2.14 *m*	2.21 *m*	2.92 *ddd* (13.5, 2.6, 2.6)	–	1.94 *m*	–	2.09 *ddd* (13.3, 3.0, 3.0)
7	2.06 *m*	1.97 *m*	–	2.25 *ddt* (6.8, 4.6, 4.5)	2.58 *tt* (12.8, 3.0)	3.33 *m*	2.03 *m*
8	1.75 *m*	–	1.88 *t* (13.8)		1.34 *m*	1.49 *m*	
8′	1.82 *m*	4.56 *ddd* (6.0, 6.0, 6.0)	2.48 *dddd* (13.8, 12.0, 2.6, 2.6)		1.68 *m*	1.63 *m*	
9	2.62 *m*	2.20 *m*	1.01 *ddd* (12.0, 13.0, 1.0)	1.02–1.98 *m*	1.48 *m*	1.53 *m*	0.99–1.98 *m*
9′	2.09 *m*	2.01 *m*	1.55 *ddd* (13.0, 4.0, 1.0)		1.61 *m*	1.53 *m*	
11	–	–	–	1.96 *m*	–	–	–
12	1.44 *s*	1.43 *s*	1.62 *q* (1.6)	1.34 *d* (6.6)	–	–	1.18 *s*
13	1.49 *s*	1.51 *s*	1.64 *q* (1.6)	0.96 *d* (6.6)	6.15 *t* (0.9)	6.17 *t* (0.9)	1.17 *s*
13′	–	–	–	–	5.58 *br s*	5.66 *br s*	–
14	1.18 *s*	1.22 *s*	0.96 *d* (0.8)	1.22 *s*	0.79 *s*	1.22 *s*	0.93 *s*
15	1.39 *s*	1.37 *s*	1.07 *d* (0.6)	1.60 *s*	4.59 *q* (1.2)	1.23 *d* (7.6)	1.98 *d* (1.3)
15′	–	–	–	–	4.87 *q* (1.2)	–	–
OAc	–	–	–	–	1.97 *s*	1.97 *s*	–

*Measured in pyridine-d_6.

Table 2. ^{13}C NMR spectral data of compounds **1–7** (100 MHz, Me_2CO-d_6)

C	**1**	**2**	**3**	**4***	**5**	**6**	**7**
1	215.8	43.5	42.0	79.3	47.3	47.2	47.7
2	33.6	21.0	20.8	29.4	70.8	67.8	198.4
3	36.0	44.3	44.1	36.7	42.8	39.0	125.5
4	70.3	71.6	71.5	72.7	146.5	39.4	168.2
5	48.0	52.0	56.2	47.9	49.8	147.8	76.2
6	21.6	21.5	26.2	73.1	26.6	126.0	35.4
7	42.4	48.4	132.9	51.2	40.4	42.0	42.9
8	22.1	68.6	25.3	23.4	30.0	27.5	23.0
9	41.2	52.0	56.2	41.4	41.2	42.0	76.2
10	46.5	35.2	35.3	41.5	35.9	39.4	41.5
11	73.4	73.9	120.5	25.9	146.6	146.7	71.8
12	29.5	25.8	20.1	24.5	168.3	168.5	23.2
13	30.1	30.1	20.1	25.1	123.7	123.1	27.1
14	19.2	23.3	18.5	14.7	24.0	28.2	18.9
15	23.7	23.8	22.6	22.6	109.1	19.3	28.1
OAc	–	–	–	–	170.5	170.4	–
					21.2	21.2	

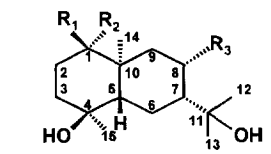
*Measured in pyridine-d_6.

an 8-hydroxyl group. Meanwhile, the multiplet at δ 3.62 found in compound **9** was absent, while a twofold doublet due to H-8β was visible at δ 4.56 (J = 6.0, 6.0, 6.0 Hz) (Table 1), confirming the occurrence of the hydroxy group at C-8 in the case of **2**. From the positive $[\alpha]_D$ value (+88.6°), compound **2** was apparently also an enantio-eudesmatriol [1], which was named pterodontriol C.

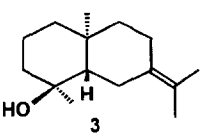
The EI-mass spectrum of compound **3** contained the $[M]^+$ peak at m/z 222, which is 18 amu lower than that of pterodondiol (**8**) [2]. The ^1H NMR spectrum of compound **3** showed four methyl singlets, two of which were olefinic methyls (Table 1). The ^{13}C NMR spectrum of compound **3** exhibited two olefinic quaternary carbon signals at δ 132.9 and δ 120.5 (Table 2), suggesting the presence of a 7(11)-en-12,13-dimethyl moiety in compound **3**. ^1H–^1H COSY and ^1H–^{13}C COSY experiments finally led to the assignment of the present structure. Biogenetically, compound **3** is probably formed by enzymic dehydration. Treatment of compound **8** with p-toluene sulphonic acid, then KI/DBU (1,8-diazabicyclo[5.4.0.] undec-7-ene) also yielded the dehydrated product, which was identical to compound **3** (by comparison of $[\alpha]_D$, ^1H, ^{13}C, mp and IR data). According to the literature [9], compound **3** was unambiguously the enantiomer of the known eudesmane derivative 7(11)-eudesmen-4-ol (**19**) [9] and was named *ent*-7(11)-eudesmen-4-ol.

The EI-mass spectrum of compound **4** showed a $[M]^+$ peak at m/z 256, and three fragments indicative of the sequential loss of three molecules of water (m/z 238, 220 and 202). This suggested that compound **4** probably possessed three hydroxyl groups. Unlike compounds **1–3**, compound **4** possessed two methyl doublets at δ 1.34 and 0.96 (J = 6.6 Hz) and two other methyl singlets appeared at δ 1.22 and δ 1.60 (Table 1). Therefore, the presence of an isopropenyl group in the molecule was suggested. The ^{13}C NMR spectrum of compound **4** also exhibited a highfield methine signal at δ 25.9 (CH), which was typically attributable to C-11, the methine of the isopropenyl group. Furthermore, two oxygenated methine signals were visible at δ 3.67 and δ 4.65. The former could be assigned to H-1 by comparing the ^1H and ^{13}C NMR resonances with those of the enantio-eudesmane derivatives **1–3**. Biogenetically, such derivatives probably possess the same skeleton, therefore the Me-14 and Me-15 could be reasonably assigned α-orientation, and consequently the 1-hydroxyl group must have β-orientation in this case. This agreed with the coupling constants of H-1 (Table 1). The second oxygenated methine, appeared as a twofold doublet at δ 4.65 (J = 11.4, 4.4 and 3.2 Hz). H-5 was found to be coupled with it by the occurrence of a doublet at δ 2.11 (J = 11.4 Hz). Therefore, this hydroxyl group was unambiguously present at C-6, and H-6 possessed an axial α-orientation, which allowed a large coupling with H-5β. The ^{13}C NMR spectrum also indicated that C-7 was somewhat low-field shifted when compared with C-7 of compounds **1–3**, and supported this assumption. However, the coupling of H-6α with H-7 was found to be a small one (4.6 Hz) (Table 1), which suggested the presence of a H-7α. Checking the coupling pattern of H-7 also supported this deduction, for H-7 gave a double-fold triplet, all with small coupling constants (J = 4.6, 6.8, 4.5 Hz), thus eliminating the possibility of an axial H-7 (H-7β). Therefore, the above-mentioned isopropenyl at C-7 was definitely assigned β-orientation. Considering that the methyl singlet due to Me-15 appeared low-field at δ 1.60, the third hydroxyl was correspondingly assigned as a 4β-one.

Compounds **5** and **6** were obtained as a mixture, which could not easily be separated by various solvent systems and reverse-phased materials. However, the GC–mass spectrometry showed two near peaks having the same $[M]^+$ ion, thus indicating a pair of isomers. In addition, the ^1H NMR spectrum of compounds **5** and **6** showed, apart from three high-field methyl signals appearing at δ 0.79 (*s*, 3H), 1.23 (*d*, J = 7.6 Hz, 3H) and 1.22 (*s*, 3H), the presence of three other olefinic methylene signals. Two triplets at δ 4.87 (J = 1.2 Hz) and 4.59 (J = 1.2 Hz) were diagnostically attributable to an exomethylene at C-15, while another two pairs of olefinic methylene signals i.e. δ 6.15 (*t*, J = 0.9 Hz) with 5.58 (*br s*), and δ 6.17 (*t*, J = 0.9 Hz) with 5.66 (*br s*) were apparently due to two C-13 methylenes of compounds **5** and **6**, respectively. The presence of a 12-carbonyl group was identified by the ^{13}C resonance at δ 168.3/168.5 and the IR absorption band at 1676 cm^{-1}, which were the typical signals of an α,β-unsaturated carboxyl group. Furthermore, another trisubstituted double bond was visible at δ 147.8 (C) and 126.0 (CH) (due to C-5 and C-6 of compound **6**, respectively) in the ^{13}C NMR spectrum, while H-6 of **6** was found at δ 5.30 (*d*, J = 2.0 Hz), and had a small coupling with



1 R_1, R_2=oxo
2 R_1=R_2=H, R_3=OH
8 R_1=R_2=R_3=H
9 R_1=R_3=H, R_2=OH



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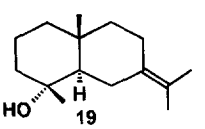

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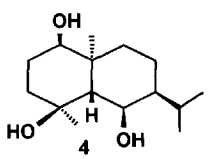

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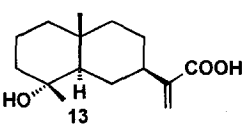

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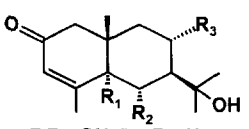
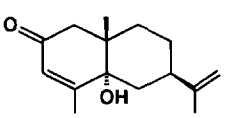


7 R_1=OH, R_2=R_3=H
20 R_1=R_3=H, R_2=OH
21 R_1=R_2=H, R_3=OH



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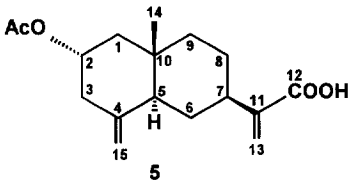

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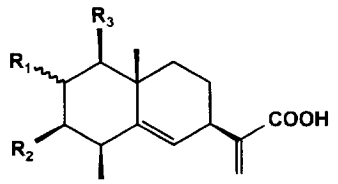

6 R_1=ß-OAc, R_2=R_3=H
10 R_1=α-OH, R_2=OH, R_3=H
11 R_1=R_3=H, R_2=OH
12 R_1=R_2=H, R_3=OH

H-7. Hence compound **6** was the same kind of pterodontic acid as compounds **10**–**12**. ^1H–^{13}C COLOC, ^1H–^{13}C COSY and ^1H–^1H COSY experiments led to the assignment of all of ^1H and ^{13}C resonances of compound **6** (Tables 1 and 2). An oxygenated methine double triple triplet appeared at δ 4.87 (J = 1.6, 4.6, 4.6 Hz) together with an acetoxyl group at δ 1.97, indicating the presence of an acetoxyl group at C-2. According to a molecular model, H-2 should adopt an α-orientation, which permits the observed coupling constants with H-1, H-3 and H-4α (Table 1).

For compound **5**, in addition to the presence of the 4,15-ene and the 11,13-ene-12-acid moiety mentioned above, another oxygenated methine was visible at δ 5.25 as a triple triplet (J = 12.0, 4.1 Hz); therefore, it could only be assigned to H-2β, which must be coupled with H-1 and H-3. The somewhat low-field resonances of C-1 and C-3 (at δ 47.3 and 42.8, respectively) agreed with this assumption. Other ^1H and ^{13}C assignments were based on the 2 two-dimensional-NMR experiments.

The EI-mass spectrum of compound **7** exhibited a $[M]^+$ peak at m/z 252 and, combined with the results of elemental analysis, the molecular formula $C_{15}H_{24}O_3$ could be deduced. The UV spectrum showed an absorption band at 235 nm, suggesting the presence of a α,β-unsaturated ketone group, which was further supported by the IR absorption band at 1675 cm^{-1}, as well as the ^{13}C resonances at δ 198.4 (C), 125.5 (CH) and 168.2 (C). Its ^1H NMR spectrum showed resemblance to those of the known eudesmane sesquiterpenes (**20**–**22**) [10–12]. However, unlike compounds **20** and **21** compound **7** did not give rise to a tertiary oxygen-bearing carbon signal in its ^{13}C NMR spectrum (Table 2), but showed two oxygen-bearing quaternary carbon signals at δ 71.8 and δ 76.2, which could only be assigned to C-11 and C-5, respectively (Table 2). The other ^1H and ^{13}C resonances of compound **7** could be assigned by comparing them with those of **20**–**22** [10–12]. The absolute configuration of compound **7** remains undetermined. Results from this work, in combination with those of other groups [2–5], show that the principal chemical components of this plant are eudesmane derivatives and flavones; also, all of the flavones found in this plant to date have the same A and C ring characteristics and vary only in the B ring features.

EXPERIMENTAL

General. Mps: uncorr; NMR: TMS as int. standard; EI-MS: 70 eV, direct inlet; IR: KBr.

Plant material. The whole plant of *L. pterodonta* (DC) Benth was collected in Qiubei county, southeastern Yunnan province, China, in November (1994), and samples were identified by Professor Z . W. Lin of our institute, where a voucher specimen has been deposited.

Extraction and isolation. The air-dried aerial parts of the whole plant (10.2 kg, dry wt.) were powdered and extracted twice with hot 95% EtOH at 70° (2 hr each). The residue (486 g) obtained by removal of the solvent *in vacuo* was triturated with H_2O (to 1500 ml). The aq. soln was throughly defatted with petrol and then succesively extracted with EtOAc (100 ml × 4) and *n*-BuOH (1000 ml × 4). The EtOAc layer was evapd to give a residue (242 g), which was subjected to CC over 1600 g silica gel with $CHCl_3$ containing gradually increasing amounts of Me_2CO (1:0–0:1). The eluates were monitored by TLC and were then combined to yield 30 crude frs (Fr.1–Fr.30). 100 ml petrol (60–90°)–Me_2CO (1:1) soln was added to Fr. 3 (3.5 g), and yielded 915 mg crude yellow crystals; recrystallization using the same solvent gave compound **17** (802 mg) ($CHCl_3$–Me_2CO 6:1, R_f 0.66). Fr. 8 (2.8 g) was subjected to CC on 150 g silica gel (200–300 mesh), using $CHCl_3$–Me_2CO (50:1-2:1) as eluents. Eluates **5** and **6** (860 mg) were combined and passed through a small column (10 g silica gel, with $CHCl_3$–Me_2CO, 15:1–5:1) From frs 7–10, we obtained 560 mg crystals of compound **16**. Fr. 13 (2.3 g) was subjected to CC on 200 g silica gel (C_6H_6–Et_2O 5:1–0:1 as gradient system); combination of eluates 6 and 7 (350 mg) and purification by prep. TLC (C_6H_6–Et_2O 3:1, two developments) yielded 80 mg of **5** and **6**; eluates 15–17 (375 mg) were combined and purified by CC (10 g silica gel H, $CHCl_3$–MeOH 50:1-3:1), **12** (9 mg) was obtained from eluate 10. Fr. 14 (14.2 g) was further chromatographed on silica gel (column, 500 g) eluted with petrol–Me_2CO (5:1–1:2). From eluate 3, we obtained crude crystals (50 mg), prep. TLC purification of which afforded compound **3** (44 mg) (C_6H_6–Et_2O 1:1.5, *Rf* 0.75). Eluate **6** (1.8 g) was subjected to CC (100 g silica gel with C_6H_6–Et_2O 5:1–1:1) prep. TLC purification of frs 3 and 4 ($CHCl_3$–MeOH, 10:1) yielded compound **11** (36 mg) (R_f 0.45); frs 12 and 13 gave yellowish crystals, which were purified by prep. TLC (C_6H_6–Et_2O, 1:1) and yielded 20 mg of compound **18**. CC of fr. 15 (2.0 g) with C_6H_{12}–Me_2CHOH (20:1–1:1) gave 10 frs, from fr. 6 we obtained

compound **15** (8 mg), while compound **14** (12 mg) was obtained from fr. 8 (C_6H_6–Et_2O). Combined fr. 16 and fr. 17 (5.8 g) were further separated by CC ($CHCl_3$–MeOH, 50:1–10:1) and crude crystals were obtained from eluates 8–10. The crystals were combined and purified by CC (10 g silica gel H, C_6H_6–MeOH 20:1–10:1) and yielded 220 mg of white prisms (in MeOH) of **8**. A total of 1.5 g of eluent 11 was gradient eluted (MeOH–H_2O, 5:5–1:0) on a RP-18 column (100 g) and 16 mg of compound **4** was obtained after recrystallization in MeOH. Compound **13** (1.2 g) was recovered from the eluates 12–15 ($CHCl_3$–MeOH, 15:1). The residue of eluates 6 and 7 (580 mg) on prep. TLC ($CHCl_3$–MeOH 50:1, 3 developments) gave 28 mg of compound **7** ($CHCl_3$–Me_2CHOH, 20:1). 6.0 g of fr. 18 was subjected to CC (300 g silica gel) using a $CHCl_3$–Me_2CHOH (50:1–1:1) gradient; eluates 7 and 8 (1.55 g) on further CC ($CHCl_3$–MeOH, 20:1–10:1) yielded 44 mg of compound **2**; eluates 9 and 10 (550 mg) on crystallization gave 56 mg of compound **10**. Fr. 19 (8.0 g) was subjected to CC (250 g silica gel with $CHCl_3$–Me_2CHOH, 50:1–1:1) and eluates 5 and 6 (1.8 g) were further sepd by CC (200 g silica gel H with petrol–Me_2CO, 5:1–1:2) to give 51 mg of compound **1**. Finally, we chromatographed fr. 25 (3.2 g) on a silica gel column (300 g) $CHCl_3$–MeOH, 30:1–1:1). Combination of eluates 13–15 (930 mg) and CC (20 g silica gel H, C_6H_6–MeOH 20:1–1:1) yielded needles of compound **9** (354 mg).

4β,11-*Dihydroxyenantioeudesmane*-1-*one* (**1**). Needles, mp 121–122° (Me_2CO), $[\alpha]_D^{24}$ + 42.4° (MeOH, *c* 0.67). Found: C, 70.82; H, 10.20. $C_{15}H_{26}O_3$ requires: C, 70.87, H, 10.24%. UV λ_{max}^{MeOH} (log ε) nm: 262 (3.81), 284 (3.74); IR ν_{max}^{KBr} cm^{-1}: 3428 (OH), 2958, 2936, 1710, 1459, 1403, 1372, 1351, 1158, 1129, 1073, 822, 604; EI-MS *m/z* (rel. int.): 254 $[M]^+$ (1), 236 $[M-H_2O]^+$ (9), 218 $[M-2\times H_2O]^+$ (38), 203 (30), 191 (29), 178 (68), 163 (59), 145 (64), 135 (66), 123 (67), 107 (64), 99 (42), 91 (76), 55 (100).

Reduction of compound **1**. A soln of compound **1** (20 mg) in 2.5 ml of MeOH was red. with 16 mg $NaBH_4$ by stirring for 30 min (room temp.), diluting with 2 M HCl and extracting with Et_2O (5 ml × 3). The washed and dried Et_2O layer was evapd and the residue (14 mg) was purified by prep. TLC (C_6H_6–MeOH, 5:1) to yield 10 mg of compound **1a**, whose $[\alpha]_D$, mp, IR, ^1H and ^{13}C NMR, MS data, were identical to those of compound **9**.

Pterodontriol C (4β,8α, 11-*enantioeudesmantriol*) (**2**). Prisms, mp 193–194° (MeOH), $[\alpha]_D^{24}$ + 88.6° (MeOH, *c* 0.7). Found: C, 70.26; H, 10.96. $C_{15}H_{28}O_3$ requires: C, 70.31; H, 10.94%. IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 3221 (OH), 2965, 2919, 2847, 1466, 1450, 1379, 1363, 1290, 1220, 1167, 1036, 918, 587; EI-MS *m/z* (rel. int.): 256 $[M]^+$ (0.3), 238 $[M-H2O]^+$ (31), 223 (28), 220 $[M-2\times H_2O]^+$ (28), 205 (37), 187 (14), 180 (42), 177 (47), 165 (55), 162 (85), 147 (60), 137 (49), 122 (71), 109 (71), 95 (86), 59 (100).

Ent-7 (11)-*selinen*-4-*ol* [*enantio*-7(11)-*eudesmen*-4-*ol*] (**3**). Needles, mp 76–77° ($CHCl_3$); $[\alpha]_D^{24}$ = +4° (MeOH, *c* 0.5); Found: *C*, 81.01; H, 11.67. $C_{15}H_{26}O$ requires: C, 81.08; H, 11.71%. UV λ_{max}^{MeOH} (log ε) nm: 203.5 (3.56); IR ν_{max}^{KBr} cm^{-1}: 3200 (OH), 2938, 2790, 1620, 1510, 1200, 1075, 774, 752; EI-MS *m/z* (rel. int.): 222 $[M]^+$ (37), 204 $[M-H_2O]^+$ (43), 197 (54), 189 (48), 179 (52), 163 (51), 161 (58), 149 (48), 147 (48), 137 (49), 135 (59), 133 (45), 121 (66), 109 (94), 95 (73), 81 (73), 69 (78), 55 (100).

Dehydration of compound **8** *to* **3**. Compound **8** (30 mg) was dissolved in MeOH (4 ml), 25 mg of *p*-toluene sulphonic acid were added with stirring at 45° on a water bath for 30 min. Three ml of MeOH containing 8 mg of KI and 30 mg of DBU was added slowly, before heating at 75° for 1 hr. The soln was evapd *in vacuo*, the residue was further purified by prep. TLC and recrystallized from Me_2CO and 6 mg of compound **8a** was obtained. ^1H, ^{13}C NMR spectra, $[\alpha]_D$, mp value and IR data of compound **8a** were identical to those of compound **3**.

Pterodontriol D (6β-*isopropyl* 4α,8aα-*dimethyl*-1,2,3,4,4*a*,5,6,7,8,8*a*-*decahydronaphthylene* 1β,4β,5β-*triol*) (**4**). Needles, mp 183.5–184.5° (MeOH); $[\alpha]_D^{23}$ = +0.4° (MeOH, *c* 0.2). Found: C, 70.27; H, 10.92. $C_{15}H_{28}O_3$ requires: C, 70.3; H, 10.94%. IR ν_{max}^{KBr} cm^{-1}: 3225 (OH), 2917, 1504, 1374, 1330, 1271, 1143, 1074, 1039, 908, 863, 833, 656; EI-MS *m/z* (rel. int.): 256 $[M]^+$ (6), 238 (21), 220 (18), 202 (9), 195 (16), 177 (19), 163 (15), 149 (25), 123 (40), 109 (51), 95 (62), 81 (64), 69 (69), 55 (100); FAB-MS (pos.) *m/z* (rel. int.): 257 $[M+H]^+$ (16), 239 $[M-H_2O+H]^+$ (57), 221 $[M-2\times H_2O+H]^+$ (100), 203 (51), 177 (14), 163 (14), 147 (21), 133 (14), 123 (21), 109 (38), 95 (53), 81 (58), 69 (68).

2α-*Acetoxycostoate* (**5**) *and* 2β-*acetoxy pterodontic acid* (**6**). Gum, Found: C, 69.79; H, 8.0. $C_{17}H_{24}O_4$ requires: C, 69.86; H, 8.2% UV λ_{max}^{MeOH} (log ε) nm: 228 (3.74), 269 (3.53). IR ν_{max}^{KBr} cm^{-1}: 3430, 2924, 2862, 1715 (*br*), 1612, 1435, 1375, 1364, 1241, 1141, 1026, 960, 890, 600; EI-MS *m/z* (rel. int.): [(peak A): 292 $[M]^-$ (1), 264 (1), 248 (8), 232 $[M-AcOH]^+$ (100), 217 (35), 202 (26), 199 (28), 171 (30), 161 (32), 145 (40), 119 (53), 105 (52), 91 (61), 79 (41); (peak B): 292 $[M]^+$ (3), 248 (13), 232 $[M-AcOH]^+$ (57), 217 (32), 202 (36), 187 (63), 171 (52), 161 (100), 145 (77), 119 (80), 105 (78), 91 (84), 79 (83), 69 (65)].

5α,11-*Dihydroxy*-3-*ene*-*eudesman*-2-*one* (**7**). Oil, $[\alpha]_D^{24}$ = +34° (MeOH, *c* 0.75), Found: C, 71.41; H, 9.15. $C_{15}H_{24}O_3$ requires: C, 71.43; H, 9.5%. UV λ_{max}^{MeOH} (log ε) nm: 235 (3.91); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2925, 2976, 2673, 2130, 1480, 1365, 1063, 926; EI-MS *m/z* (rel. int.): 252 $[M]^+$ (12), 234 $[M-H_2O]^+$ (26), 219 (66), 204 (27), 201 (45), 192 (43), 190 (48), 187 (16), 186 (18), 177 (53), 176 (30), 159 (35), 158 (32), 130 (33).

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