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D:B-FRIEDOOLEAN-5-ENE-3β,29-DIOL, AN ANGULAR METHYL OXYGENATED D:B-FRIEDOOLEANENE FROM *ELAEODENDRON BALAE*

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Key Word Index—*Elaeodendron balae*; Celastraceae; D:B-friedoolean-5-ene-3β,29-diol.

Abstract—A new dioxygenated D:B-friedooleanene from *Elaeodendron balae* root bark was shown to be D:B-friedoolean-5-ene-3β,29-diol by relating it to 29-oxygenated D:A-friedooleanane. This is the first report of angular methyl oxygenation in the D:B-friedooleananes.

INTRODUCTION

Angular methyl oxygenated D:A-friedooleananes have been found to occur in the stem bark of the two *Elaeodendron* species studied, *E. glaucum* [1, 2] and *E. balae* [3]. Although angular methyl oxygenation commonly occurs in the oleananes and the D:A-friedooleananes [4, 5], there have been no reports of angular methyl oxygenation in the D:B-friedooleanane series. The root bark of *E. balae* Kosterm., a tree found in south-east Sri Lanka, is now shown to contain an angular methyl oxygenated D:B-friedooleanane, D:B-friedoolean-5-ene-3β,29-diol (**1**).

RESULTS AND DISCUSSION

The petrol extract of the root bark of *E. balae* on chromatographic separation yielded D:B-friedoolean-5-ene-3β,29-diol (**1**). Its ^{1}H NMR spectrum (Table 1) suggested it to be an unsaturated triterpene with a hydroxymethylene and a secondary hydroxyl group. Its molecular formula, $C_{30}H_{50}O_2$, was consistent with a pentacyclic structure, while its mass spectrum showed intense peaks at *m/z* 290, 275, 221 and a base peak at *m/z* 259.

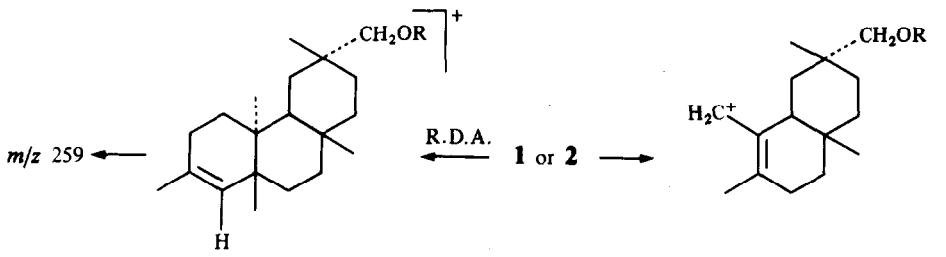
Acetylation gave a diacetate, **2**, whose mass spectrum showed intense peaks at *m/z* 273 and 259 with a base peak at *m/z* 332. The peaks at *m/z* 259 and 275 in the mass spectrum of the diol **1**, represented losses of hydroxymethylene and methyl groups, respectively, from the fragment ion at *m/z* 290. The base peak fragment ion in the mass spectrum of the diacetate **2**, lost acetoxymethylene to give the intense peak at *m/z* 259. This suggested that the peak at *m/z* 290 in the diol **1** and the base peak in the diacetate **2** were due to fragment ions **3a** and **3b** which arose from retro-Diels–Alder cleavage. These fragmentations could be rationalized by a triterpene-5-ene structure in which the A-ring contained the secondary oxygenated function and two methyl groups, suggesting it to be D:B-friedoolean-5-ene with a hydroxyl group probably at C-3. The fragment ions **4a** and **4b** also indicated that the hydroxymethylene group was likely to be located in the C-, D- or E-rings.

The skeletal structure was confirmed by chemically relating the diacetate **2** to D:B-friedoolean-5-ene-3β-ol (**5**). The diacetate **2** was selectively deacetylated to give a

Table 1. ^{1}H NMR chemical shifts [δ (ppm), $CDCl_3$, 60 MHz]

	1	2	6	7	9	12	13	14	15
H-29	3.28	3.60	3.27	9.33	3.76	3.72	3.73	3.27	9.41
H-3	3.46*	4.62*	4.66*	4.70*	—	3.60†	3.48‡	3.67†	—
H-6§	5.56	5.50	5.63	5.56	—	5.66	—	5.67	5.66
OAc	—	2.00	2.00	2.00	2.06	2.03	2.06	—	—
		1.93							
Me	0.91	1.20	1.23	1.25	1.70	1.24	1.26	1.21	1.26
	0.86	1.13	1.16	1.10	1.23	1.22	1.23	1.13	1.24
	0.83	1.06	1.10	1.06	1.06	1.12	1.05	1.13	1.07
	0.83	1.02	1.03	1.03	1.06	1.03	1.05	1.01	1.07
	0.73	1.02	1.01	0.96	1.02	0.98	1.02	1.01	1.03
	0.73	0.96	1.01	0.87	0.96	0.93	0.93	0.94	0.96
	0.70	0.83	0.84	0.82	0.90	0.76	0.93	0.77	0.83

*m, $W_{1/2}$ = 5–6 Hz.
†m, $W_{1/2}$ = 12 Hz.
‡dd, J = 12, 4 Hz.
§m, $W_{1/2}$ = 8 Hz, all other signals s.



3a *m/z* 290, R = H
3b *m/z* 332, R = Ac

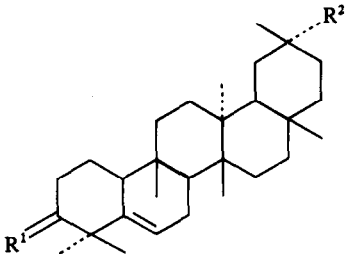
4a *m/z* 221, R = H
4b *m/z* 273, R = Ac

monoacetate (**6**). Oxidation of the monoacetate **6** with chromium trioxide–pyridine gave an aldehyde **7**, Huang–Minlon reduction of which afforded D:B-friedoolean-5-ene-3β-ol (glutinol, **5**) which was identical with an authentic sample [6].

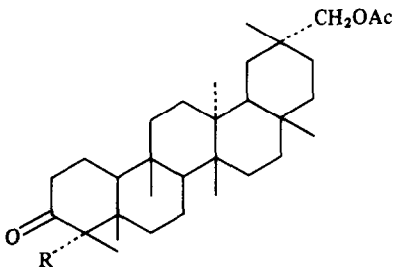
The diol **1** was, therefore, a D:B-friedoolean-5-ene-3β-ol with a hydroxymethylene group in rings C, D or E. Comparison of the chemical shifts of the hydroxymethylene, acetoxymethylene and aldehydic proton in diol **1** and its derivatives **2** and **7** with those reported for similarly functionalized compounds in the D:A-friedooleanane series (Table 2), which have a similar C-, D- and E-ring system, suggested that oxygenation in diol **1** was unlikely to be at the Me-13α or Me-14β positions and that it was most probably at the Me-20α position.

The oxygenation was shown to occur at the Me-20α group by relating the compound to 3-oxo-D:A-friedooleanan-29-yl acetate (**8**) [7]. The acetate **8** was brominated with *N*-bromosuccinimide [8] to give the 4α-bromo derivative **9**. The Me-4β signal appeared at δ 1.70 in its ^{1}H NMR spectrum, while the characteristic double $[M]^+$ peaks occurred at *m/z* 562 and 564. Dehydrobromination with silver acetate in acetic acid [9] gave a mixture of the β,γ-unsaturated D:B-friedooleananes, **10** and **11**, which could not be separated. Reduction of the mixture with sodium borohydride yielded a mixture of alcohols which was separated into D:B-friedoolean-5-ene-3α,29-diol,29-acetate (**12**) and its 5(10)-ene isomer **13**. Hydrolysis of the acetate **12** gave a diol, **14**, whose physical and spectroscopic properties differed from those of the diol **1**. The spectral data (Table 1) suggested that the diols **1** and **14** were epimeric at C-3. Oxidation of the diol **1** with chromium trioxide–pyridine gave an aldehyde, **15**. Sodium borohydride reduction of the aldehyde **15** gave a diol identical with the diol **14**, confirming the angular oxygenation occurring in the diol at the Me-20α group. Compound **1** is, therefore, D:B-friedoolean-5-ene-3β,29-diol.

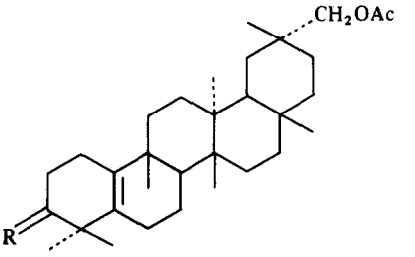
This is the first report of angular methyl oxygenation in the D:B-friedooleanane series.



1 R^1 = βOH, αH; R^2 = CH_2OH
2 R^1 = βOAc, αH; R^2 = CH_2OAc
5 R^1 = βOH, αH; R^2 = Me
6 R^1 = βOAc, αH; R^2 = CH_2OH
7 R^1 = βOAc, αH; R^2 = CHO
10 R^1 = O; R^2 = CH_2OAc
12 R^1 = αOH, βH; R^2 = CH_2OAc
14 R^1 = αOH, βH; R^2 = CH_2OH
15 R^1 = O; R^2 = CHO



8 R = H
9 R = Br



11 R = O
13 R = αOH, βH

Table 2. ^{1}H NMR chemical shifts of angular methyl oxygenated groups in friedooleananes [δ(ppm), $CDCl_3$, 60 MHz]

Position*	13α[10]	14β[12]	17β[1]	20α[3]	20β	X
CH_2OH	4.13 (*br s*)	4.03 (*dd*)	3.66 (*s*)	3.28 (*s*)	3.45 (*s*)	3.28 (*s*)
CH_2OAc	4.51 (AB *dd*) [11]	4.45 (*s*)	4.13 (AB *dd*)	3.74 (*s*)	3.90 (*s*)	3.60 (*s*)
CHO	10.30 (*s*) [11]	—	9.50 (*s*)	9.37 (*s*)	9.45 (*s*) [7]	9.33 (*s*)

*In D:A-friedooleananes, except X which refers to an unknown position in the D:B-friedooleanene diol, **1**, and its derivatives **2** and **7**.

EXPERIMENTAL

Mps were determined on a Kofler hot-stage apparatus and are uncorr. Identities of compounds were established by mmp, IR, NMR and MS comparisons. Petrol refers to the fraction having bp 40–60° and prep. TLC was carried out on Merck kieselgel 60. ORDs were measured at 27° in $CHCl_3$. IR spectra were recorded on KBr discs, ^{1}H NMR spectra were recorded at 60 MHz in $CDCl_3$ with TMS as int. standard.

D:B-Friedoolean-5-ene-3β,29-diol (**1**). The root of *E. balae* was collected at Yala, Sri Lanka and a voucher specimen of the plant has been deposited at the Herbarium of the University of Peradeniya. The root bark (2.5 kg) was separated, dried, pulverized and extracted with petrol (10 l.). Evaporation of the extract gave a residue (20 g), chromatography of which on silica gel (500 g) ($CHCl_3$–MeOH, 99:1) gave D:B-friedoolean-5-ene-3β,29-diol (**1**) (0.26 g) which was recrystallized from $CHCl_3$–MeOH as needles: mp 276–279°; $[\alpha]_D$ +55.7° (*c* 1.0). (Found: C, 80.15; H, 11.08. $C_{30}H_{50}O_2$ requires: C, 81.39; H, 11.38%.) IR ν_{max}^{KBr} cm^{-1}: 3500–3300, 830; MS *m/z* (rel. int.): 442 $[M]^+$ (5), 427 (2), 424 (4), 290 (77), 275 (51), 259 (100), 221 (20).

D:B-Friedoolean-5-ene-3β,29-diol diacetate (**2**). This compound was obtained by stirring the diol **1** (0.2 g) with Ac_2O–pyridine (1:1) (6 ml) for 18 hr at 27°. The diacetate **2** (0.18 g) recrystallized from $CHCl_3$–MeOH as needles: mp 108–110°; $[\alpha]_D$ +48.6° (*c* 1.0). (Found: $[M]^+$ at *m/z* 526.3992. $C_{34}H_{54}O_4$ requires: $[M]^+$ at *m/z* 526.4002.) IR ν_{max}^{KBr} cm^{-1}: 1739, 1735, 1365, 1245, 830; MS *m/z* (rel. int.): 426 $[M]^+$ (8), 466 (23), 451 (9), 332 (100), 273 (17), 259 (84).

D:B-Friedoolean-5-ene-3β,29-diol,3β-acetate (**6**). This compound was obtained by stirring the diacetate **2** (150 mg) with KOH (100 g) in MeOH (4 ml) for 1 hr at 27°. The acetate **6** (98 mg), recrystallized from $CHCl_3$–MeOH as needles: mp 223–224°; $[\alpha]_D$ +72° (*c* 1.0). (Found: $[M]^+$ at *m/z* 484.3899. $C_{32}H_{52}O_3$ requires: $[M]^+$ at *m/z* 484.3893.) IR ν_{max}^{KBr} cm^{-1}: 3500–3200, 1738, 1450, 1245, 830; MS *m/z* (rel. int.): 484 $[M]^+$ (5), 453 (2), 424 (18), 409 (12), 393 (8), 290 (75), 259 (100), 221 (16).

29-Oxo-D:B-friedooleanan-5-ene-3β-yl acetate (**7**). CrO_3 (50 mg) was added to a soln of the acetate **6** (80 mg) in pyridine (3 ml) and the mixture was stirred for 18 hr at 27° and was then poured into dil. HCl. Work-up gave a residue which recrystallized from $CHCl_3$–MeOH as needles of 29-oxo-D:B-friedoolean-5-ene-3β-yl acetate (**7**) (47 mg): mp 137–139°; $[\alpha]_D$ +28°. (Found: $[M]^+$ at *m/z* 482.3736. $C_{32}H_{50}O_3$ requires: $[M]^+$ at *m/z* 482.3760.) IR ν_{max}^{KBr} cm^{-1}: 1730, 1712, 835; MS *m/z* (rel. int.): 482 $[M]^+$ (5), 453 (6), 423 (12), 273 (34), 259 (60), 134 (100).

D:B-Friedoolean-5-en-3β-ol (**5**). The aldehyde **7** (40 mg) was reduced under Huang–Minlon conditions with ethylene glycol (5 ml), hydrazine hydrate (1 g) and KOH (100 mg) under reflux for 3 hr followed by distillation until the temp. reached 200°. The residue was then heated at this temp. for a further 3 hr. The usual work-up, followed by recrystallization from $CHCl_3$–MeOH gave D:B-friedoolean-5-en-3β-ol (**5**) (20 mg) as needles: mp 208–211°; $[\alpha]_D$ +68° (*c* 0.5) (lit. [6] mp 210–212°; $[\alpha]_D$ +67°); identical with an authentic sample of D:B-friedoolean-5-en-3β-ol (glutinol) (mmp and IR).

4α-Bromo-3-oxo-D:A-friedooleanan-29-yl acetate (**9**). 3-Oxo-D:A-friedooleanan-29-yl acetate (200 mg) and *N*-Bromosuccinimide (275 mg) in CCl_4 (140 ml) were heated under reflux using an IR lamp for 30 min. Filtration followed by concn *in vacuo* and purification by prep. TLC (petrol–EtOAc, 24:1, developed twice) gave 4α-bromo-3-oxo-D:A-friedooleanan-29-yl acetate (**9**) (125 mg): mp 120–123°; $[\alpha]_D$ +62°. (Found: $[M]^+$ at *m/z* 564.3021 and 562.3009. $C_{32}H_{51}O_3Br$ requires: $[M]^+$ at *m/z* 564.3022 and 562.3002.) IR ν_{max}^{KBr} cm^{-1}: 1735, 1710, 760; MS *m/z* (rel. int.): 564, 562 $[M]^+$ (8), 482 (34), 353 (31), 351 (22), 271 (54), 123 (100).

D:B-Friedoolean-5-ene-3α,29-diol, 29-acetate (**12**) *and D:B-friedoolean-5(10)-ene-3α,29-diol 29-acetate* (**13**). The bromide **9** (120 mg) in Et_2O (50 ml) was added to AgOAc (120 mg) in H_2O (1 ml) and HOAc (60 ml) and the mixture was distilled until the vapour temp. was 110° and then refluxed for 20 min. The usual work-up, followed by purification by prep. TLC (petrol–$CHCl_3$, 2:3) gave a product (49 mg) which was reduced with $NaBH_4$ (30 mg) in MeOH (5 ml). Work-up gave a residue which was separated by prep. TLC (C_6H_6–$CHCl_3$, 1:1, developed twice) into the less polar D:B-friedoolean-5(10)-ene-3α,29-diol 29-acetate (**13**) (25 mg), needles recrystallized from $CHCl_3$–MeOH: mp 203–206°; $[\alpha]_D$ −45°. (Found: $[M]^+$ at *m/z* 484.3902. $C_{32}H_{52}O_3$ requires: $[M]^+$ at *m/z* 484.3916.) IR ν_{max}^{KBr} cm^{-1}: 3570, 1715, 1250; MS *m/z* (rel. int.): 484 $[M]^+$ (18), 466 (28), 411 (8), 205 (46), 203 (100); the more polar D:B-friedoolean-5-ene-3α,29-diol 29-acetate (**12**) (25 mg), needles recrystallized from $CHCl_3$–MeOH: mp 210–212°; $[\alpha]_D$ −38°. (Found: $[M]^+$ at *m/z* 484.3917. $C_{32}H_{52}O_3$ requires: $[M]^+$ at *m/z* 484.3916.) IR ν_{max}^{KBr} cm^{-1}: 3430, 1710, 1250; MS *m/z* (rel. int.): 484 $[M]^+$ (8), 466 (36), 451 (23), 423 (14), 409 (44), 332 (16), 317 (16), 259 (40), 203 (85), 187 (100).

3-Oxo-D:B-friedoolean-5-en-29-al (**15**). CrO_3 (35 mg) was added to diol **1** (40 mg) in pyridine (2 ml) and the mixture stirred for 30 min at 0° and then for 18 hr at 27°. Work-up followed by crystallization from $CHCl_3$–MeOH gave 3-oxo-D:B-friedoolean-5-en-29-al (**15**) as needles (32 mg): mp 168–169°; $[\alpha]_D$ +26.6° (*c* 1.0); IR ν_{max}^{KBr} cm^{-1}: 2680, 1715, 1710, 830; MS *m/z* (rel. int.): 438 $[M]^+$ (37), 423 (4), 409 (4), 288 (63), 273 (68), 259 (100), 219 (21).

D:B-Friedoolean-5-ene-3α,29-diol (**14**). (a) D:B-Friedoolean-5-ene-3α,29-diol 29-acetate (**12**) (15 mg) was refluxed with KOH (35 mg) in MeOH (2 ml) for 3 hr. Work-up gave a residue which was recrystallized from $CHCl_3$–MeOH as needles of D:B-friedoolean-5-ene-3α,29-diol (**14**) (10 mg): mp 295–297°; $[\alpha]_D$ +32° (*c* 0.5). (Found: $[M]^+$ at *m/z* 442.3798. $C_{30}H_{50}O_2$ requires: $[M]^+$ at *m/z* 442.3811.) IR ν_{max}^{KBr} cm^{-1}: 3500–3120; MS *m/z* (rel. int.): 442 $[M]^+$ (6), 427 (4), 424 (8), 290 (75), 275 (43), 259 (86), 95 (100).

(b) $NaBH_4$ (20 mg) was added to 3-oxo-D:B-friedoolean-5-en-29-al (**15**) (25 mg) in MeOH (15 ml) with stirring. Work-up followed by recrystallization from $CHCl_3$–MeOH gave needles: mp 294–297°; $[\alpha]_D$ +33° (*c* 0.4) identical with the diol **14** (mmp and IR).

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