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ELAEODENDROL AND ELAEODENDRADIOL, NEW NOR-TRITERPENES FROM *ELAEODENDRON GLAUCUM*

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Key Word Index—*Elaeodendron glaucum*; Celastraceae; elaeodendrol; elaeodendradiol; D:A-friedo-oleananes; new nor-triterpenes.

Abstract—The isolation of six known and two new D:A-friedooleananes is reported from the bark of *Elaeodendron glaucum*. The structures of the new nor-triterpenes, elaeodendrol and elaeodendradiol, were established respectively as 17β-hydroxy-28-norfriedelan-3-one and 17β,25-dihydroxy-28-norfriedelan-3-one by a study of the methyl chemical shifts in their ^{1}H NMR spectra.

INTRODUCTION

The recent report of the isolation of a novel cytotoxic cardiac glycoside, elaeodendroside A, from the seeds of *Elaeodendron glaucum* [1] prompted a thorough investigation of all its parts. The isolation of ouratea-catechin and sitosterol from its heart-wood, and lupeol and sitosterol from its leaves have been reported [2]. We now report the isolation and identification from its bark of some known D:A-friedooleananes together with two new nor-derivatives, named as elaeodendrol and elaeodendradiol.

RESULTS AND DISCUSSION

The powered bark of *E. glaucum* collected locally was successively extracted with *n*-hexane, chloroform, ethyl acetate and methanol. The various extracts were concentrated and the residues chromatographed over Si gel to give seventeen compounds. The details of their physical characteristics, yields and their identification are given in the Experimental. Eleven of these were found to be triterpenes; four were steroids and the others were catechin, 4'-methoxyepigallocatechin (ouratea-catechin) [2, 3] and dulcitol [4].

Of the eleven triterpenes, six were characterized as the known friedelane derivatives, friedelin (**1**) [5], canophyllal (**2**) [6], friedelan-3-on-25-al (**6**) [7], friedelan-3β-ol [5], canophyllol (**3**) [6], and friedelan-3-on-25-ol (**7**) [8] by chemical and spectroscopic (^{1}H NMR and MS) evidence. Two more are new nor-friedelanes, elaeodendrol (**9**) and elaeodendradiol (**11**). The remaining three were obtained in very small quantities and could not be fully characterized. Two of the four steroid derivatives were identified as sitosterol and its β-D-glucoside [9]; the third one appeared to be a new steroid glycoside.

Structure of elaeodendrol (**9**)

Elaeodendrol, $C_{29}H_{48}O_2$, M^+ 428, mp 229–30°, $[\alpha]_D$ −26.2°, showed absorptions in its IR spectrum for a hydroxyl (3560 cm^{-1}) and a carbonyl (1700 cm^{-1}). It gave a positive Liebermann–Burchard test for triterpenes and a positive Zimmermann colour reaction for the 3-keto group, suggesting it to be a triterpene keto alcohol.

The presence of one secondary and six tertiary methyls at δ 0.69–1.04, three protons α to the carbonyl and the absence of any olefinic protons confine it to the friedelane series. The absence of a methine proton α to the hydroxyl between δ 3 and 4 suggested a tertiary hydroxyl. With Ac_2O–Py it furnished a mixture, a monoacetate (**10**), $C_{31}H_{50}O_3$, mp 204–206°, $[\alpha]_D$ −27.8°, which contained the carbonyls (>C=O and —O—C(=O)—Me) at 1705, 1740 cm^{-1} in its IR spectrum and an anhydro compound (**14**), $C_{29}H_{46}O$, mp 210–212°, $[\alpha]_D$ −32.2°, which contained only the keto carbonyl group at 1715 cm^{-1} but no hydroxyl. The ^{1}H NMR spectrum of the acetate showed one acetate at δ 2.02 and seven methyls, and a single proton at δ 3.40 (*dd*, J = 10, 2 Hz) which were absent in elaeodendrol. The anhydro compound, which was also obtained by $POCl_3$–Py dehydration of elaeodendrol, showed no protons in the olefinic region suggesting a tetrasubstituted double bond. This further suggested that the hydroxyl in elaeodendrol might be tertiary and in a relatively less-hindered position to give an acetate. Further, elaeodendrol was recovered unchanged after oxidation with CrO_3–Py, confirming the presence of a tertiary hydroxyl. Thus elaeodendrol was a nor-friedelan-3-keto alcohol in which the positions of the missing nor-methyl group and that of the tertiary hydroxyl remained to be established. The structure of elaeodendrol was ultimately determined to be

28-norfriedelan-3-on-17β-ol (**9**) by using the methyl chemical shift data (see later).

Structure of elaeodendradiol (**11**)

Elaeodendradiol, $C_{29}H_{48}O_3$, M^+ 444, mp 220–222°, $[\alpha]_D$ −24.8°, gave a positive Liebermann–Birchard test for triperpenes and resembled elaeodendrol in many of its reactions, e.g. no colouration with TNM, positive Zimmermann colour reaction and its behaviour during acetylation. It showed peaks for two hydroxyls (3510, 3400 cm^{-1}) and a carbonyl (1700 cm^{-1}) in its IR spectrum.

The ^1H NMR spectrum showed six methyls at δ 0.83–1.08 and two protons of $—CH_2OH$ at 3.87. On acetylation it gave a mixture of the anhydromonoacetate (**15**), $C_{31}H_{48}O_3$, mp 196–198°, $[\alpha]_D$ −28.6° and the diacetate (**12**), $C_{33}H_{52}O_5$, mp 214–216°, $[\alpha]_D$ −31.2°. The ^1H NMR spectrum of the diacetate showed two acetoxyl groups at δ 2.05 and the deshielded CH_2 of CH_2OAc at 4.33 (*d*, $J = 4$ Hz). One additional deshielded proton reminiscent of the one in elaeodendrol acetate appeared at 3.40 (*dd*, $J = 10$, 2 Hz). Elaeodendradiol on oxidation with CrO_3–Py gave a compound (**13**) which still showed the presence of the resistant tertiary hydroxyl and two carbonyls at 3410, 1710, 1700 cm^{-1}, respectively. Its ^1H NMR spectrum clearly showed the presence of an aldehydic proton singlet at δ 10.16. By comparison of the chemical shift of this aldehydic proton (Table 1) with those reported in literature [6, 10–12], it was inferred that the aldehyde group in the oxidation product, and therefore the hydroxymethyl in elaeodenendradiol, might be at C-9. Thus elaeodendradiol might be a dihydroxy-norfriedelan-3-one with $—CH_2OH$ at C-9 and one more tertiary hydroxyl. The positions of the missing methyl and the tertiary hydroxyl were fixed by using the methyl chemical shifts thus giving structure **11** for elaeodendradiol.

Methyl chemical shifts in the ^1H NMR spectra of D:A-friedooleananes

The individual chemical shifts of the various methyl groups in the ^1H NMR spectrum of friedelin have been assigned by Crawford *et al.* [13] by using $Eu(fod)_3$ shift reagent. However, it was suggested that the assignment of the most downfield signal at δ 1.18 to the C-28 methyl was tentative and might be alternatively assigned to one of the C-29 or C-30 methyls. Similarly, the assignments for C-26, C-27 and C-29, C-30 methyls, which differ by only 0.05 ppm, might be interchanged.

Table 1. Chemical shifts of aldehydic protons

Compound	CHO	Chemical Shift (δ) CHO	Ref.
1,3-Dioxofriedelan-24-al	24	10.35 *s*	10
Friedelan-3-on-25-al	25	10.16 *s*	—
O-Acetyltrichadenal	26	10.01 *s*	11
Canophyllal	28	9.50 *s*	6
Octandrolal	29	9.45 *s*	12
Oxidation product of elaeodendradiol (**13**)		10.16 *s*	

In view of the number of D:A-friedooleananes reported and their ^1H NMR spectra being available, the substituent effects have been used to assign the chemical shifts of the various methyls, C-26, C-27, C-28, C-29 and C-30 more definitely (Table 2). The original D/E *cis* all-chair conformation [14] suggested for friedelin has been changed to D/E *cis* twist-boat and boat forms by using three-dimensional X-ray analysis [15]. Examination of the Dreiding model of this conformation reveals that the C-28 methyl is the most deshielded and the signal at 1.18 can be assigned for it. Interestingly, this lowest field methyl is absent in canophyllal (**2**), methyl friedelan-3-one-28-oate (**5**), canophyllol (**3**) and its 28-acetate (**4**) which do not possess this C-28 methyl (Table 2). On the other hand, friedelan-3-one-25-al (**6**), 25-hydroxy-friedelan-3-one (**7**) and 25-acetoxyfriedelan-3-one (**8**), which possess a C-28 methyl, contain this lowest field signal but instead lack another methyl signal around 0.86 which must be assigned to C-25. These observations conclusively allow the C-28 methyl chemical shift to be assigned around 1.18.

The chemical shifts of the methyls C-26 (δ 1.01) and C-27 (1.05) assigned tentatively by Crawford *et al.* [13] may be regarded as correct in the light of the following observation. Only the higher field methyl signal due to C-26 is shielded since it is β-axial to the aldehyde group in both canophyllal (**2**) and friedelan-3-one-25-al (**6**) thus supporting the above assignment. It was also noticed that only the C-26 methyl was deshielded in the presence of the 25-alcohol or 25-acetate since it is in 1,3-diaxial position: this was not observed with the C-27 methyl. In canophyllol and its acetate the methyl at C-27, which is in the 1,3-*trans* diaxial position to the $—CH_2OH$ and $—CH_2OAc$, appeared deshielded at δ 1.12 (Table 2). Similar deshielding of the C-25 methyl was noticed in 23-hydroxy and 23-acetoxy oleanane derivatives [16].

The assignments made for the C-29 (0.96) and C-30 (1.01) methyl groups were considered to be interchangeable [13]. The following observations suggest that the higher field signal (0.96) might be assigned to C-30 and the latter to C-29. In canophyllal (**2**) with a C-28 aldehyde group, the two methyls (C-26 and C-29) which are in 1,4-*trans* diaxial positions, are likely to be shielded and the highest field signal which appeared at 0.67 might be assigned to one of these methyls. This signal was assigned to C-29 as the effect of the aldehyde group is felt more by C-29 which is nearer in view of the ring D twist-boat conformation. The other methyl signal at 0.94 was assigned for C-30 and remained unaffected. Similar shielding was also noticed on the C-29 methyl (0.72) in methyl friedelan-3-one-28-oate (**5**) while the C-30 signal remained unaffected.

Position of the hydroxyls and the normethyl groups in elaeodendrol and elaeodendradiol

The absence of the methyl signal around δ 1.18 in the ^1H NMR spectra of both elaeodendrol and elaeodendradiol proved that these were C-28 norfriedelane derivatives. Elaeodedradiol also lacked a second methyl around 0.86 showing the presence of C-25 as $—CH_2OH$ in place of CH_3 at C-25. It is not unreasonable to locate the tertiary hydroxyl at C-17

Table 2. Methyl chemical shifts in ^{1}H NMR spectra of D:A-friedooleananes

Compound	Methyl group							
	23*	24	25	26	27	28	29	30
Friedelin (**1**) [13]	0.88	0.73	0.87	1.01†	1.05†	1.18‡	0.96‡	1.01‡
Friedelin (**1**)	0.87	0.72	0.86	0.99	1.04	1.16	0.99	0.94
Canophyllal (**2**)	0.87	0.71	0.84	0.96	1.06	—	0.67	0.94
Canophyllol (**3**)	0.87	0.72	0.86	0.98	1.12	—	0.98	0.90
Canophyllol acetate (**4**)	0.87	0.72	0.88	0.99	1.12	—	0.99	0.95
Methylfriedelan-3-one-28-oate (**5**)	0.87	0.72	0.84	1.04	1.04	—	0.72	0.93
Friedelan-3-one-25-al (**6**)	0.90	0.63	—	0.94	1.05	1.14	0.94	0.94
25-Hydroxy-friedelan-3-one (**7**)	0.89	0.84	—	1.08	1.02	1.18	0.99	0.96
25-Acetoxy-friedelan-3-one (**8**)	0.90	0.76	—	1.06	1.02	1.17	0.98	0.94
Elaeodendrol (**9**)	0.86	0.69	0.90	0.94	1.04	—	0.90	0.90
Eaeodendrol acetate (**10**)	0.88	0.71	0.92	0.92	1.19	—	0.98	0.92
Anhydroelaeodendrol (**14**)	0.81	0.71	0.90	0.98	1.23	—	1.14	0.90
Elaeodendradiol (**11**)	0.84	0.83	—	0.96	1.08	—	0.96	0.96
Elaeodendradiol diacetate (**12**)	0.90	0.76	—	0.95	1.21	—	0.98	0.95
Anhydroelaeodendradiol acetate (**15**)	0.98	0.76	—	0.98	1.26	—	1.13	0.98
17β-Hydroxy-28-norfriedelan-3-one-25-al (**13**)	0.90	0.63	—	0.94	1.00	—	0.94	0.94

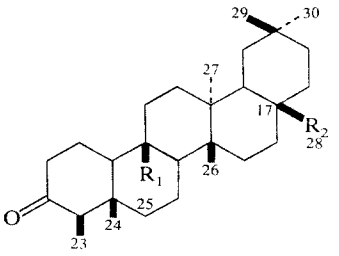
*Doublet J = 6-8 Hz.

†‡Methyl shifts may have to be interchanged.

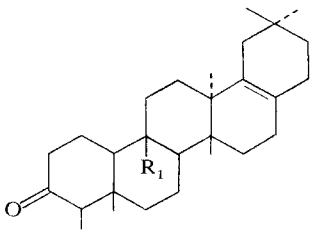
considering the absence of the C-28 methyl in both these compounds. The other possible position which can also give a tetrasubstituted anhydro compound is C-18. However this can be eliminated by considering its more hindered nature by virtue of the 1,3-diaxial interactions with the methyls at C-14 and C-20, where the ready formation of the acetate cannot be explained. The chemical shifts of the methyls in the hydroxy compounds and their acetates can be cited again in support of a C-17 hydroxyl. On acetylation significant deshielding (0.15 ppm) has been noticed in only one of the methyls, i.e. C-27. Such a large deshielding effect was noticed earlier in oleanane derivatives where the —Me and the acetate are in 1,3-diaxial positions. Thus the greater deshielding effect of a 2α-acetate over 2α-hydroxyl on the 25-methyl was 0.13 ppm while the deshielding effect of a 6α-acetate over the 6α-hydroxyl on the C-25 and C-26 methyls was 0.12 ppm [17]. The location of the 17β-hydroxyl satisfies this condition with a 1,3-axial methyl group at C-13 (i.e. 27-Me). Thus the structures of elaeodendrol and elaeodendradiol were fixed as 17β-hydroxy-28-norfriedelan-3-one (**9**) and 17β,25-dihydroxy-28-norfriedelan-3-one (**11**), respectively. With rings D and E in the boat form and the acetate at C-17, the proton which appeared deshielded after acetylation at δ 3.40 was obviously the 18-H which is split with the neighbouring C-19 axial and equatorial methylene protons to give a *dd*.

The MS of elaeodendrol, elaeodendradiol and their derivatives supported the above structures. The general fragmentation pattern conformed to the friedelane skeleton [18, 19]. In elaeodendrol the characteristic *m/e* 273 [16] peak ruled out the possibility of any hydroxyl in rings A, B or C. The base peak in the spectrum appeared at *m/e* 177 (18%) which might have been formed from the intermediate 17(18)-ene formed after the loss of H_2O as noticed in 28-nor-17(18)-oleanene [20] by initial retro Diels–Alder rearrangement followed by cleavage of the C-9, 11 bond as shown in Scheme 1. In elaeodendradiol the base peak also appeared at *m/e* 177 (18%) similar to elaeodendrol. The fragments *m/e* 289 (17%) and 259 formed by the loss of HCHO indicated the presence of —CH_2OH in rings A, B or C.

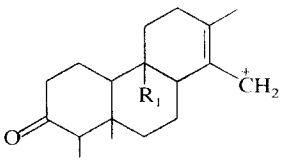
The biogenetic formation of nor-compounds has



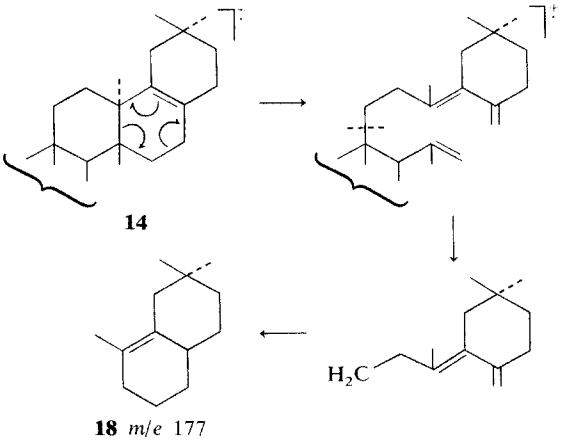
1 $R_1 = R_2 = Me$
2 $R_1 = Me$; $R_2 = CHO$
3 $R_1 = Me$; $R_2 = CH_2OH$
4 $R_1 = Me$; $R_2 = CH_2OAc$
5 $R_1 = Me$; $R_2 = OAc$
6 $R_1 = CHO$; $R_2 = Me$
7 $R_1 = CH_2OH$; $R_2 = Me$
8 $R_1 = CH_2OAc$; $R_2 = Me$
9 $R_1 = Me$; $R_2 = OH$
10 $R_1 = Me$; $R_2 = OAc$
11 $R_1 = CH_2OH$; $R_2 = OH$
12 $R_1 = CH_2OAc$; $R_2 = OAc$
13 $R_1 = CHO$; $R_2 = OH$



14 $R_1 = Me$
15 $R_1 = CH_2OAc$



16 $R_1 = Me$, *m/e* 273
17 $R_1 = CH_2OH$, *m/e* 289



14

18 *m/e* 177

Scheme 1.

been well recognized as a biological transformation of a methyl group to —COOH (—Me→—CH_2OH→—CHO→—COOH) which looses HCOOH to give the ene. The co-occurrence of roxburghonic acid [21], a 25-acid, and putrone and putrol [22] the corresponding 25-nor-9(11)-enes, is significant in this respect. The 16-ene formed from the appropiate C-28 carboxylic acid precursors in elaeodendrol and elaeodendradiol might perhaps yield an epoxide, ring opening of which could give the 28-nor-17-hydroxy compounds.

EXPERIMENTAL

The dry powder (25 kg) of the bark of *E. glaucum* (Celastraceae) collected from the Simhachalam hills, situated near Visakhapatnam, was extracted with EtOH. The residue (3 kg) was fractionated into *n*-hexane, $CHCl_3$, EtOAc and MeOH, respectively.

n-hexane extract. The green–yellow extract (5 l.) was concd and chromatographed on Si gel (100–200 mesh, 200 g) in *n*-hexane. The column was eluted successively with *n*-hexane and *n*-hexane–C_6H_6 mixtures, collecting 500 ml fractions. The fractions collected and the compounds isolated from the them are listed in Table 3.

EGB-2: friedelin (**1**). Crystallized from $CHCl_3$–MeOH as

Table 3. Isolation of triterpenes and steroids from the *n*-hexane extract of *Elaeodendron glaucum*

Fractions (500 ml)	Eluant*	Compound	R_f value†	Yield (g)
1–6	H	Oil		0.30
7–10	H	EGB-1	0.14 (H)	0.10
11–24	H:B(95:5)	EGB-2	0.69 (B)	1.20
25–46	H:B(90:10)	EGB-3	0.57 (B)	3.40
47–56	H:B(90:10)	EGB-4	0.38 (B)	0.25
57–63	H:B(90:10)	EGB-5	0.29 (B)	0.40
64–72	H:B(80:20)	EGB-6	0.27 (B)	0.20
73–88	H:B(70:30)	EGB-7	0.26 (B)	1.10
89–112	H:B(60:40)	EGB-8	0.28 (B)	0.50

*H = *n*-hexane; B = C_6H_6.
†On Si gel. Solvent in parentheses.

colourless shining needles, mp 258–259°, undepressed with an authentic sample [5], $[\alpha]_D$ −23.5° (*c* 1.0, $CHCl_3$). It gave an oxime, mp 292–294°.

EGB-3: *canophyllal* (**2**). Crystallized from $CHCl_3$–MeOH as colourless needles, mp 268–270°, $[\alpha]_D$ −18.1° (*c* 1.0, $CHCl_3$) (lit. [6] mp 263–265°, $[\alpha]_D$ −16.02°). (Found: C, 81.42; H, 10.72. Calc. for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2820, 2700, 1715 (—CHO), 1700 (>C=O). ^1H NMR (100 MHz, $CDCl_3$): Table 2, δ 2.38 (3H, *m*, 4α-H, 2-CH_2) 9.48 (1H, *s*, 28-CHO). MS *m/e* (rel. int.): 440 (M^+, 8), 425 (40), 395 (100), 301 (20), 287 (11), 273 (68), 259 (55), 219 (50), 189 (90). It gave a dioxime, mp 260–262° and a keto acid ($KMnO_4$–Me_2CO), mp 278–280°. The acid gave a keto ester, mp 242–244°, $[\alpha]_D$ −28.1° (C, 1.0, $CHCl_3$) (lit. [6] mp 247–248°). IR ν_{max}^{nujol} cm^{-1}: 1725 (—OAc), 1750 (>C=O); ^1H NMR (90 MHz, $CDCl_3$): δ 0.72, 0.84, 0.93, 1.04 (18H, all *s*, 6 tert. Me), 0.87 (3H, *d*, *J* = 6 Hz, sec. Me), 2.35 (3H, *m*, 4α-H, 2-CH_2), 3.65 (3H, *s*, 28-COOMe). MS *m/e* (rel. int.): 470 (M^+, 9), 455 (10), 439 (65), 425 (100), 411 (35), 395 (22), 378 (70), 301 (11), 287 (5), 273 (65), 249 (10), 205 (18), 189 (40).

EGB-4: *friedelan*-3-*one*-25-*al* (**6**). Crystallized from $CHCl_3$–MeOH as needles, mp 286–288°, $[\alpha]_D$ −59.8° (*c*, 1.1, $CHCl_3$) (lit. [7] mp 305–309°). (Found: C, 81.82; H, 11.21. Calc. for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2750, 1710 (—CHO), 1700 (>C=O). ^1H NMR (100 MHz, $CDCl_3$): Table 2, 2.30 (3H, *m*, 4α-H, 2-CH_2), 10.16 (1H, *s*, 25-CHO). MS *m/e* (rel. int.): 440 (M^+, 14), 425 (5), 411 (18), 395 (3), 315 (22), 301 (4), 287 (22), 259 (100), 205 (23), 189 (8). It gave a dioxime, mp 270–272° and resisted oxidation with $KMnO_4$–Me_2CO.

EGB-5: *friedelan*-3β-ol. Crystallized from $CHCl_3$–MeOH as colourless needles, mp 283–284°, undepressed with an authentic sample [5], $[\alpha]_D$ +14.6° (*c* 0.9, $CHCl_3$).

EGB-6: *elaeodendrol* (**9**). Crystallized from $CHCl_3$–MeOH as colourless shining needles, mp 229–230°, $[\alpha]_D$ −26.2° (*c* 0.6, $CHCl_3$), R_f = 0.27 (C_6H_6). [Found; C, 81.08; H, 11.42. $C_{29}H_{48}O_2$ requires: C, 81.25; H, 11.29%]. It gave pink colour in the Liebermann–Burchard test for triterpenes and violet colour in the Zimmermann colour reaction. IR ν_{max}^{KBr} cm^{-1}: 3410 (—OH), 1700 (>C=O), 1450, 1385, 1353, 1160, 1140, 1110, 1080, 1000. ^1H NMR (100 MHz, $CDCl_3$): Table 2, δ 1.51 (1H, *S*, −OH, exchanged with D_2O), 2.31 (3H, *m*, 4α-H, 2-CH_2). MS *m/e* (rel. int.): 428 (M^+, 12), 413 (6), 410 (21), 397 (8), 395 (22), 355 (27), 301 (2), 287 (2), 273 (13), 189 (22), 177 (100), 163 (60).

Acetylation of elaeodendrol: formation of anhydroelaeodendrol (**14**) *and elaeodendrol acetate* (**10**). To elaeodendrol (120 mg) in Py (6 ml) was added Ac_2O (2 ml) and then heated on a steam bath for 3 hr. The reaction product showed a mixture of two compounds with R_f values 0.64 and 0.36 on TLC (Si gel, C_6H_6). The product was absorbed on Si gel (100–200 mesh. lg) which was placed onto a Si gel (4 g) column and chromatographed using hexane–C_6H_6 mixture as eluant to give two pure compounds, anhydroelaeodendrol 40 mg, (**14**), and elaeodendrol acetate 50 mg, (**10**).

Anhydroelaeodendrol (**14**). Crystallized from $CHCl_3$–MeOH as colourless needles, mp 210–212°, $[\alpha]_D$ −32.2° (*c*, 0.4, $CHCl_3$), R_f = 0.64 (C_6H_6). (Found: C, 84.92; H, 11.42. $C_{29}H_{46}O$ requires: C, 84.81; H, 11.29%). IR ν_{max}^{nujol} cm^{-1}: 1715 (>C=O), 1460, 1385, 1375, 1260, 1155, 1100, 1075, 1015, 1005, 810, 795. ^1H NMR (100 MHz, $CDCl_3$): Table 2, 2.30 (3H, *m*, 4α-H, 2-CH_2). MS *m/e* (rel. int.): 410 (M^+, 23), 395 29.9), 371 (25.9), 273 (20.2), 231 (33.4), 205 (17.1), 189 (26.1), 177 (16.8), 163 (100.0).

Elaeodendrol acetate (**10**). Crystallized from $CHCl_3$–MeOH as colourless needles, mp 204–206°, $[\alpha]_D$ −27.8° (*c* 0.5, $CHCl_3$), R_f = 0.36 (C_6H_6). (Found: C, 78.96; H, 10.52. $C_{31}H_{50}O_3$ requires: C, 79.10; H, 10.71%). IR ν_{max}^{nujol} cm^{-1}: 1740 (−Ac), 1705(>C=O), 1460, 1385, 1375, 1270, 1228, 1210, 1150, 1079, 1068, 1005. ^1H NMR (100 MHz, $CDCl_3$): Table 2, δ 2.02 (3H, *s*, −OAc), 2.34 (3H, *m*, 4α-H, 2-CH_2), 3.40 (1H, *dd*, *J* = 10, 2 Hz, 18β-H). MS *M/e* (rel. int.): 410 (M-60, 8), 273 (24.7), 191 (21.2), 177 (100.0), 163 (35.8).

Action of $POCl_3$–Py *on elaeodendrol: anhydroelaeodendrol* (**14**). Elaeodendrol (40 mg) was discovered in dry Py (4 ml) and freshly distilled $POCl_3$ (1 ml) was added slowly in the cold. The mixture was heated on a H_2O bath for 2 hr and then refluxed for 2 hr on an oil bath. It was then poured into ice H_2O and extracted with Et_2O. The Et_2O soln was washed with dil HCl and H_2O, dried ($MgSO_4$) and evapd. The product crystallized from $CHCl_3$–MeOH to give anhydroelaeodendrol (**14**), mp 280–210°, identical with the one formed during acetylation (mmp; IR and ^1H NMR).

EGB-7: *sitosterol*. Crystallized from $CHCl_3$–MeOH as needles, mp 136–137°, undepressed with an authentic sample, $[\alpha]_D$ −360(*c* 1.1, $CHCl_3$).

EGB-8: *canophyllol* (**3**). Crystallized from $CHCl_3$–MeOH as colourless needles, mp 278–80°, $[\alpha]_D$ −22.3° (*c*, 1.0, $CHCl_3$) [Lit. [6] mp 278–80°, $[\alpha]_D$ −22.3°]. [Found: C, 81.52; H, 11.65. Calc. for $C_{30}H_{50}O_2$. C, 81.39; H, 11.38%]. IR ν_{max}^{nujol} cm^{-1}: 3548 (—OH), 1705 (>C=O); ^1H NMR (100 MHz, $CDCl_3$): Table 2, 2.34 (3H, *m*, 4α-H, 2-CH_2), 3.62 (2 H, *s*, 28-CH_2OH). The acetate (Py–Ac_2O at 100° for 3 hr) of canophyllol (**4**) crystallized from MeOH as colourless needles, mp 168–170°, $[\alpha]_D$ −32.1° (*c* 0.8, $CHCl_3$). IR ν_{max}^{nujol} cm^{-1}: 1740 (−OAc), 1750 (>C=O), ^1H NMR (90 MHz, $CDCl_3$): Table 2, δ 2.30 (3H, 4α-H, 2-CH_2), 2.04 (3H, *s*, −OAc), 4.13 (2H, AB*q*, *J* = 11 Hz, 28-CH_2OAc).

The $CHCl_3$ *extract*. Removal of the solvent left a dark green mass (90 g) which was adsorbed on Si gel (140 g) and chromatographed on Si gel column (120×8 cm, 280 g), eluted with *n*-hexane, C_6H_6, and C_6H_6–EtOAc successively and 500 ml fractions were collected. The compounds isolated are given in Table 4.

EGB-10: 25 *hydroxy-friedelan*-3-*one* (**7**). Crystallized from $CHCl_3$–MeOH as prisms, mp 300–302°, $[\alpha]_D$ −19.2° (*c* 1.0, $CHCl_3$) (lit. [8] mp 350–308°, $[\alpha]_D$ −20.0°). [Found: C, 81.18; H, 11.61. Calc. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38%]. IR ν_{max}^{nujol} cm^{-1}: 3520 (−OH), 1700 (>C=O); ^1H NMR (100 MHz, $CDCl_3$): Table 2, δ 2.20 (3H, *m*, 4α-H, 2-CH_2), 3.92 (2H, AB*q*, *J* = 2 Hz, 25-CH_2OH). MS *m/e* (rel. int.): 442 (M^+, 18), 427 (11), 424 (34), 411 (45), 397 (7), 317 (14), 302 (12), 289 (100), 273 (8), 259 (19), 205 (96), 189 (11), 123 (49). It gave an oxime, crystallized from $CHCl_3$–MeOH as needles, mp 281–283°. The 25-acetoxy-friedlan-3-one (**8**) (Py–Ac_2O at 100° for 3 hr) crystallized from MeOH as needles, mp 171–173°, $[\alpha]_D$ −23.4° (*c* 0.9, $CHCl_3$). IR ν_{max}^{nujol} cm^{-1}: 1740 (−OAc), 1710 (>C=O), ^1H NMR (100 MHz, $CDCl_3$): Table 2, δ 2.30 (3H, *m*, 4α-H, 2-CH_2), 4.36 (2H, AB*q*, *J* = 13 Hz, 25-CH_2OAc), 2.00 (3H, *s*, OAc). MS *m/e* (rel. int.): 484 (M^+, 5), 469 (4), 424 (25), 411 (48), 359 (13), 331 (6), 307 (22), 287 (21), 273 (21), 259 (24), 205 (100), 189 (25).

EGB-11: *elaeodendradiol* (**11**). Crystallized from $CHCl_3$–MeOH as colourless shining needles, mp 220–222°, $[\alpha]_D$ −24.8° (*c*, 0.8, $CHCl_3$), R_f = 0.50 (C_6H_6–EtOAc, 9:1). (Found: C, 78.12; H, 10.61. $C_{29}H_{48}O_3$ requires C, 78.33; H, 10.88%). It gave a pink colour in the Liebermann–Burchard test for triterpenes and a violet colour in the Zimmermann colour reaction. IR ν_{max}^{nujol} cm^{-1}: 3510 (−OH), 3400 (−OH),

Table 4. Isolation of triterpenes and steroids from the chloroform extract of *Elaeodendron glaucum*

Fractions (500 ml)	Eluant	Compounds	R_f Value	Yield (g)
35–39	C_6H_6	EGB-9	0.19*	0.10
40–48	C_6H_6	EGB-10	0.57†	4.80
49–56	C_6H_6–EtOAc (95:5)	EGB-11	0.50†	0.30
57–61	C_6H_6–EtOAc (95:5)	EGB-12	0.50†	0.10
62–66	C_6H_6–EtOAc (90:10)	EGB-13	0.18†	0.10
67–72	C_6H_6–EtOAc (70:30)	EGB-14	0.45‡	0.20
73–94	EtOAc	EGB-15	0.17§	3.20

*C_6H_6
†C_6H_6–EtOAc (9:1).
‡C_6H_6–EtOAc (2:3).
§EtOAc.

1700 (≥C=O), 1460, 1380, 1188, 1032, 1023; ^{1}H NMR (60 MHz, $CDCl_3$): Table 2, δ 2.20 (3H, *m*, 4α-H, 2-CH_2), 3.87 (2H, *brs*, 25-CH_2OH). MS *m/e* (rel. int.) 444 (M^+, 7), 426 (10), 413 (17), 411 (27), 395 (26), 371 (12), 340 (8), 289 (10), 259 (12), 189 (18), 177 (100), 163 (46).

Acetylation of elaeodendradiol: formation of anhydroelaeodendradiol monoacetate (**15**) *and elaeodendradiol diacetate* (**12**). To elaeodendradiol (140 mg) in Py (6 ml) Ac_2O (2 ml) was added and heated on a stream bath for 3 hr. The reaction product showed two spots on TLC. The product was adsorbed on Si gel (1 g) which was placed on a Si gel (4 g) column and eluted with C_6H_6 to give the compounds anhydroelaeodendradiol monoacetate (**15**) (50 mg), mp 196–198° and elaeodendradiol diacetate (**12**) (60 mg), mp 214–216°.

Anhydroelaeodendradiol monoacetate (**15**). Crystallized from $CHCl_3$–MeOH as needles, mp 196–198°, $[\alpha]_D$ −28.6° (*c* 0.48, $CHCl_3$). R_f = 0.64 (C_6H_6–EtOAc, 9:1). (Found: C, 79.68; H, 10.63. $C_{31}H_{48}O_3$ requires: C, 79.44; H, 10.32%). IR ν_{max}^{nujol} cm^{-1}: 1740, 1230 (—OAc), 1700 (≥C=O), 1460, 1380, 1100, 1070, 1010. ^{1}H NMR (60 MHz, $CDCl_3$): Table 2, δ 2.26 (3H, *m*, 4α-H, 2-CH_2), 4.16–4.80 (2H, *m*, 25-CH_2OAc), 2.02 (3H, *s*, −OAc). MS *m/e* (rel. int.): 425 (33.2), 289 (36.8), 259 (30.3), 177 (39.1), 163 (39.1), 137 (100.0).

Elaeodendradiol diacetate (**12**). Crystallized from $CHCl_3$–MeOH as shining flowers, mp 214–216°, $[\alpha]_D$ −31.2° (*c* 0.52, $CHCl_3$). R_f = 0.49 (C_6H_6–EtOAc, 9:1). (Found: C, 74.72; H, 10.11. $C_{33}H_{52}O_5$ requires: C, 74.96; H, 9.91%). IR ν_{max}^{nujol} cm^{-1}: 1740, 1230 (—OAc), 1700 (≥C=O), 1460, 1385, 1375, 1210, 1150, 1080, 1060; ^{1}H NMR (60 MHz, $CDCl_3$): Table 2, δ 2.26 (3H, 4α-H, 2-CH_2), 2.05 (6H, *s*, 2× −OAc), 3.40 (1H, *dd*, *J* = 10, 2 Hz, 18β-H), 4.33 (2H, *br. d*, *J* = 4 Hz, 25-CH_2OAc). MS *m/e* (rel. int.): 485 (3.3), 469 (2.5), 426 (1.7), 177 (89.7), 137 (24.6), 55 (100.0).

Oxidation of elaeodendradiol with CrO_3–Py: *17β-hydroxy-28-norfriedelan-3-one-25-al* (**13**). To elaeodendradiol (60 mg) in dry Py (4 ml) was added CrO_3 in Py (80 mg in 3 ml) at room temp. and kept aside for 2 hr. MeOH (3 ml) was added to the reaction mixture which was poured into H_2O and extracted with Et_2O. The Et_2O layer was washed with dil HCl, H_2O and dried ($MgSO_4$) and evapd. 17β-Hydroxy-28-norfriedelan-3-one-25-al (**13**) crystallized from $CHCl_3$–MeOH as needles, mp 248–250°. [Found: C, 78.54, H, 10.61 $C_{29}H_{46}O_3$ requires: C, 78.68; H, 10.47%]. IR ν_{max}^{nujol} cm^{-1}: 3410 (—OH), 2760, 1710 (—CHO), 1700 (≥C=O). ^{1}H NMR (90 MHz, $CDCl_3$): Table 2, δ 2.24 (3H, *m*, 4α-H, 2-CH_2), 10.16 (1H, *s*, 25-CHO).

EGB-14: (new steroid). Crystallized from $CHCl_3$–MeOH as tiny prisms, mp 268–270°, $[\alpha]_D$ + 130.8° (*c* 0.54, EtOH), R_f = 0.45 (C_6H_6–EtOAc, 4:6). [Found: C, 66.21; H, 7.26 $C_{30}H_{38}O_9$ requires: C, 66.40; H, 7.06%]. IR ν_{max}^{KBR} cm^{-1}: 3440 (—OH), 1740 (butenolide), 1620 (C=C). UV λ_{max}^{EtOH} nm: 270 (log ε 4.28). The acetate (Py–Ac_2O, at 100° for 3 hr) crystallized from MeOH as needles, mp 276–278°, $[\alpha]_D$ + 118.2° (*c* 0.5, $CHCl_3$). [Found: C, 65.58; H, 7.12. $C_{32}H_{40}O_{10}$ requires: C, 65.74; H, 6.90%].

EGB-15: sitosterol-β-D-glucoside. Crystallized from $CHCl_3$–MeOH as tiny prisms, mp 282–284°, undepressed with an authentic sample, $[\alpha]_D$ −40.0° (*c* 0.6, Py) (lit. [9] mp 280–282°, $[\alpha]_D$ −40.8°). It gave a tetraacetate (Py–Ac_2O at room temp. for 12 hr), mp 168–170°, $[\alpha]_D$ −30.5° (*c* 0.6, EtOH).

The EtOAc concentrate (100 g) contained several spots on TLC. Part of the extract (30 g) was adsorbed on Si gel (45 g) and fractionated over a column of Si gel (120 g, 120×6 cm) prepared in C_6H_6, and 500 ml fractions were collected. Fractions 20–28, eluted with C_6H_6–EtOAc (7:3), yielded a red gummy compound (5.25 g), EGB-16, which crystallized from H_2O as needles, mp 143–145°, $[\alpha]_D$ −39.8° (*c* 1.0, EtOH), R_f = 0.23 (C_6H_6–EtOAc, 4:6). It was identified as (−)-4′-methoxyepigallocatechin by comparison with an authentic sample already reported from its heart-wood [2].

The MeOH *extract* (800 g) was a red-brown viscous syrupy liquid. Part of the extract (50 g) was taken and dissolved in MeOH and left on a deep freezer for a few days. A white crystalline mass (3.80 g), EGB-17, separated out as needles, mp 184–185°, R_f = 0.23 (*n*-BuOH–HOAc–H_2O, 4:1:5). It gave a hexaacetate, mp 162–164° and hexabenzoate, mp 187–188° which was identified as ducitol [4].

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