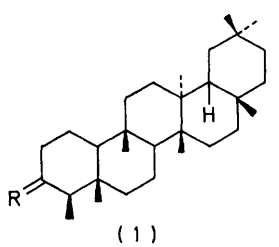
Chemical Investigation of Ceylonese Plants. Part 23.† Extractives of *Hydnocarpus octandra* Thw. (Flacourtiaceae); Isolation and Characterisation of Six New Triterpenoids ‡

By **Sarath P. Gunasekera** and **M. Uvais S. Sultanbawa,*** Department of Chemistry, University of Sri Lanka, Peradeniya Campus, Peradeniya, Sri Lanka

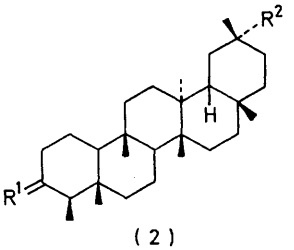
From the bark of *H. octandra* Thw., six new triterpenoids named octandrolal (3a), octandrolol (3c), octandrolic acid (3e), octandronal (3b), octandronol (3d), and octandronic acid (3f) have been isolated, interrelated, and identified. Seven other, known triterpenoids and mangostin have also been isolated and characterised. Timber and fruit pericarp gave β-sitosterol and friedelin. Molecular rotation differences of friedelane derivatives are discussed.

In Part 22, we reported the isolation of several new triterpenoids from a plant belonging to family Flacourtiaceae.[1] We have now investigated *Hydnocarpus octandra* Thw. a species endemic to Sri Lanka.[2]



(1)

a; R = H_2
b; R = O
c; R = α−OH, β−H
d; R = α−OAc, β−H
e; R = β−OH, α−H



(2)

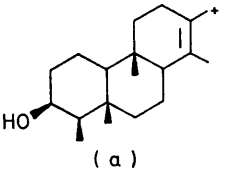
a; R^1 = O, R^2 = CO_2H

Bark Extractives.—The bark benzene extract gave a solid and a brown semisolid. The solid was first subjected to column chromatography and in fractions of increasing polarity mixtures of compounds were collected (see Experimental section). All triterpenoids reported gave a positive response to the Liebermann–Burchard test.[3]

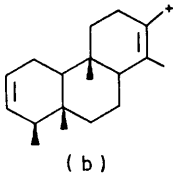
From the first three fractions, friedelan-3-one[4] (1b), friedelan-3β-ol[5] (1e), and friedelan-3α-ol[5] (1c) were separated and identified by comparison with authentic samples. The fourth fraction was purified on a column of neutral alumina to give a white crystalline compound, shown to be a new terpene aldehyde (see below), and named octandrolal, $C_{30}H_{50}O_2$. The i.r. spectrum indicated the presence of OH (3 496 cm^{-1}) and CHO (1 722 cm^{-1}). Resistance towards catalytic hydrogenation, supported by i.r. and n.m.r. data, confirmed that the molecule was saturated. The presence of a tertiary aldehyde function was confirmed by the n.m.r. spectrum, which showed a sharp singlet at τ 0.55 (1 H). In addition the presence of six tertiary methyl signals and one secondary methyl n.m.r. signal and the o.r.d. curve of the derived octandronic acid (3f) (see below), indicated a friedelane skeleton. Huang Minlon[6] reduction of the compound gave friedelan-3α-ol (1c), confirming the presence of a friedelane-type skeleton with a 3-hydroxy-group.

The mass spectrum of octandrolal showed the base peak at *m/e* 413 (*M* − CHO).[7] Intense peaks at *m/e* 275(a) and 257(b) revealed that rings A, B, and C contained only one oxygen atom[8] (the 3-OH). Therefore the point of attachment of CHO is limited to C-17 and C-20.

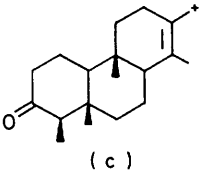
A C-17 carbaldehyde was eliminated by comparison of the product of Jones oxidation of octandrolal with



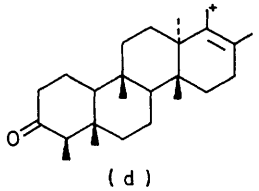
(a) *m/e* 275



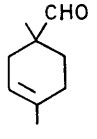
(b) *m/e* 257



(c) *m/e* 273



(d) *m/e* 355



(e) *m/e* 137

authentic 3-oxofriedelan-28-al[9] (canophyllal) (4c). Ready oxidation (alkaline $KMnO_4$–excess of KIO_4) and

† Part 22, ref. 18.
‡ Preliminary communication, S. P. Gunasekera and M. U. S. Sultanbawa, *Chem. and Ind.*, 1973, 790.

[1] B. A. Abeywickrama, *Ceylon J. Sci.*, 1959, **2**, 120.
[2] W. M. Bandaranayake and M. U. S. Sultanbawa, 'List of Endemic Plants of Ceylon,' *Proc. Ceylon Assoc. Adv. Sci.*, 1969, **25**. 90.
[3] C. Liebermann, *Ber.*, 1885, **181**. 1805; H. Burchard Inaugural Dissertation, Rostock, 1889.
[4] J. L. Courtney and R. M. Gascoigne, *J. Chem. Soc.*, 1956. 2115.
[5] C. W. Shoppee, M. E. H. Howden, and G. A. R. Johnston, *J. Chem. Soc.*, 1962. 498.
[6] Huang Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.
[7] J. S. Shannon, C. G. Macdonald, and J. L. Courtney, *Tetrahedron Letters*, 1963. 173.
[8] J. L. Courtney and J. S. Shannon, *Tetrahedron Letters*, 1963, 13.
[9] T. R. Govindachari, V. Viswanathan, B. R. Pai, U. Ramadas Rao, and M. Sirinivasan, *Tetrahedron*, 1967, **23**. 1901.

reduction (Wolff–Kishner; lithium aluminium hydride) of the CHO group suggests that it is at a non-crowded position. Since rings D and E in the friedelane skeleton are *cis*-fused,[10] the axial methyl group at C-20 is much more crowded than the equatorial methyl group at C-20, owing to the folding of the molecule and to a 1,4-diaxial interaction with the methyl group at C-17. Therefore the CHO group in octandrolal is at C-20.

The Jones oxidation product mentioned above was low melting and less polar than the starting material, and exhibited M^+ 440 ($C_{30}H_{48}O_2$). This indicated that only the hydroxy-group had been transformed (confirmed by the lack of OH i.r. absorption). The i.r. spectrum showed bands at 1 722(CHO) and 1 712 cm^{-1} (CO in a six-membered ring). The mass spectrum had an intense M — 29 peak (loss of CHO), other intense peaks at *m/e* 273 (c) and 355(d), and the base peak at *m/e* 137(e). This product was named octandronal.

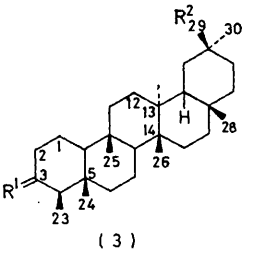
Oxidation of octandrolal with alkaline permanganate in the presence of an excess of potassium periodate gave a more polar crystalline product, $C_{30}H_{50}O_3$ (M^+ 458) (addition of one oxygen atom). The absence of CHO i.r. absorption, the presence of a new absorption at 1 690 cm^{-1}, and the polarity of the compound indicated it to be a carboxylic acid. The mass spectrum had a peak at *m/e* 412 (M — CO_2H — H). From these data the compound was identified as the acid corresponding to octandrolal, *i.e.* octandrolic acid. Oxidation of this with chromic acid–pyridine yielded a new crystalline product, $C_{30}H_{48}O_3$ (M^+ 456). The i.r. spectrum showed absorptions at 1 690 (CO_2H) and 1 714 cm^{-1} (six-membered ring C=O), indicating that the 3α-OH had undergone oxidation, and the product was named octandronic acid. Its physical data [11] and the mass spectrum showed it to be different from the known 3-oxofriedelan-30-oic acid [12] (polpunonic acid) (2a).

Therefore octandrolal is 3α-hydroxyfriedelan-29-al (3a), octandronal is 3-oxofriedelan-29-al (3b), octandrolic acid is 3α-hydroxyfriedelan-29-oic acid (3e), and octandronic acid is 3-oxofriedelan-29-oic acid (3f).

octandronic acid (3f) (above) and the identity was confirmed by direct comparison.

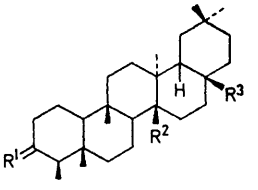
The fifth fraction on column chromatography gave β-sitosterol [13] and octandronal (3b).

Reduction of octandrolal (3a) with lithium aluminium hydride gave a single crystalline product. The i.r.



(3)

a; R^1 = α–OH, β–H, R^2 = CHO
b; R^1 = O, R^2 = CHO
c; R^1 = α–OH, β–H, R^2 = CH_2·OH
d; R^1 = O, R^2 = CH_2·OH
e; R^1 = α–OH, β–H, R^2 = CO_2H
f; R^1 = O, R^2 = CO_2H
g; R^1 = α–OAc, β–H, R^2 = CHO



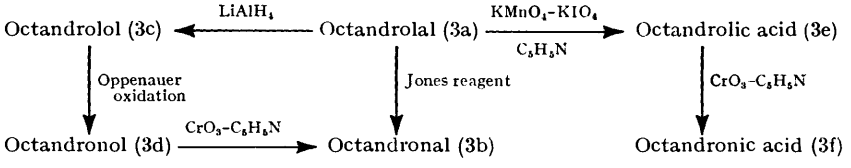
(4)

a; R^1 = α–OH, β–H, R^2 = CO_2H, R^3 = Me
b; R^1 = β–OH, α–H, R^2 = CO_2H, R^3 = Me
c; R^1 = O, R^2 = Me, R^3 = CHO
d; R^1 = β–OH, α–H, R^2 = CHO, R^3 = Me

spectrum indicated the absence of CHO. The highest mass peak in the mass spectrum was at *m/e* 413, probably due to loss of CH_2·OH. Therefore the product is friedelane-3α,29-diol (octandrolol) (3c). Oppenauer oxidation of (3c) gave a mixture from which the major component, $C_{30}H_{50}O_2$ (M^+ 442), was obtained by p.l.c. The i.r. spectrum showed absorption due to a carbonyl in a six-membered ring (1 710 cm^{-1}) and OH(3 442 cm^{-1}). The mass spectrum had a strong peak at *m/e* 411 (loss of CH_2OH) and a peak at *m/e* 273 indicating the presence of fragment (c). From these data the product is identified as 29-hydroxyfriedelan-3-one (octandronol) (3d). The inter-relationships of compounds (3a—f) are given in the Scheme.

The sixth fraction afforded β-sitosterol and octandrolol (3c), identical with the sample already obtained.

The seventh fraction on column chromatography gave



SCHEME

The second compound obtained from the fourth fraction of the benzene extract was soluble in 5% sodium hydroxide solution, indicating it to be a carboxylic acid. The physical properties agreed with those of two sub-fractions. The less polar of these on p.l.c. gave octandronic acid (3f) and trichadenic acid B [14] (4b); the more polar fraction on column chromatography gave trichadenic acid A [14] (4a) and ursolic acid.[15] All these compounds were identical with authentic samples.

The brown semisolid obtained from the hot benzene

[10] H. Dutler, O. Jeger, and L. Ruzecka, *Helv. Chim. Acta*, 1955, **38**. 1268.
[11] C. Djerassi, R. Rinker, and B. Rinker, *J. Amer. Chem. Soc.*' 1956, **78**. 6362.
[12] F. Delle Monache, J. F. De Mello, G. B. Marini Bettolo, O. Goncalves De Lima, and I. L. D. Albuquerque, *Gazzetta*, 1972, **102**. 636.
[13] 'A Dictionary of Organic Compounds,' ed. I. M. Heilbron, Oxford University Press, 1965, vol. 5, p. 2902.
[14] S. P. Gunasekera and M. U. S. Sultanbawa, *Tetrahedron Letters*, 1973, 2837.
[15] E. S. Ewens and F. S. Spring, *J. Chem. Soc.*, 1943. 523.

extract of *H. octandra* Thw. bark was also subjected to column chromatography separation. The more polar compound isolated from the least polar fraction was a white crystalline solid, shown to be octandronal (3b) by comparison with the sample already prepared. The less polar compound was identified as friedelan-3α-yl acetate [5] (1d), by comparison with an authentic sample. The second fraction on p.l.c. gave a yellow compound identified as mangostin.[16]

The light petroleum extracts of the timber and the fruit pericarp of *H. octandra* Thw. provided friedelin-3-one and β-sitosterol as the only isolated products.

The friedelane derivatives isolated from *H. octandra* Thw. and *Trichadenia zeylanica* Thw. are presumably formed by oxidation of a tertiary methyl group. In *H. Octandra* Thw. the acid, aldehyde, and alcohol were

TABLE 1

	$M_D(1)$	$M_D(2)$	$M_D(2) - M_D(1)$
Friedelane	+74		
-3-one [4]		−121	−195
-3α-ol [19]		+77	+3
-3β-ol [19]		+103	+29
-3α-yl acetate [18]		+56	−18
-3β-yl acetate [19]		+155	+81
25-al [7]		−148	−222
26-oic [18]		+19	−55

obtained and the aldehyde was the predominant component. On the other hand from *T. zeylanica* Thw. only the aldehyde and acid were obtained, the acid being the major product. The occurrence of the acetates of

TABLE 2

	$M_D(1)$	$M_D(2)$	$M_D(2) - M_D(1)$
3-Oxofriedelane [7]	−121		
-25-al [9]		−272	−151
-26-al [18]		−119	+2
-28-al [7]		−66	+55
-29-al		−23	+98
-25-ol [7]		−88	+33
-28-ol [9]		−93	+28
-29-ol		−110	+11
-26-oic acid [18]		+128	+249
-29-oic acid		+73	+194
Friedelane -2,3-dione [20]		+110	+231
-3,7-dione [21]		−144	−23
-3,21-dione [21]		+506	+627

trichadenic acid A (4a) and trichadenal (4d) may be due to the presence of a powerful acetylating enzyme in *Trichadenia zeylanica* Thw.

As several friedelane derivatives had become available it was of interest to determine molecular rotation differences (ΔM_D) for these compounds and others described in the literature.[17] Tables 1—6 give the ΔM_D values [14] for monosubstituted friedelanes with reference to friedelane and for disubstituted compounds with reference to friedelin, friedelan-3α-ol, friedelan-3β-ol, and their acetates.

[16] P. Yates and G. H. Stout, *J. Amer. Chem. Soc.*, 1958, **80**, 1691.
[17] D. H. R. Barton and W. Klyne, *Chem. and Ind.*, 1948, 755.
[18] S. P. Gunasekera and M. U. S. Sultanbawa, preceding paper.

In monosubstituted friedelane derivatives an oxo- or α-acetoxy-group at C-3, CHO at C-9, or CO_2H at C-14 gives a negative ΔM_D. In disubstituted compounds a C-14 or C-20 carboxy-group (with reference to friedelin, friedelan-3α-ol, friedelan-3β-ol, friedelan-3α-yl acetate, or friedelan-3β-yl acetate) appears to give positive ΔM_D. The positive ΔM_D decreases with respect to

TABLE 3

	$M_D(1)$	$M_D(2)$	$M_D(2) - M_D(1)$
Friedelan-3α-ol [19]	+77		
-3α,29-diol		+93	+15
3α-Hydroxyfriedelan-29-al		+102	+25
-29-oic acid		+234	+157
-26-oic acid [18]		+114	+37

TABLE 4

	$M_D(1)$	$M_D(2)$	$M_D(2) - M_D(1)$
3β-Hydroxyfriedelane [19]	+103		
-26-al [18]		+38	−65
-26-oic acid (pyridine) [20]		+179	+76
-28-oic acid [9] (pyridine)		+96	−7

TABLE 5

	$M_D(1)$	$M_D(2)$	$M_D(2) - M_D(1)$
3α-Acetoxyfriedelane [18]	+56		
-26-oic acid [18]		+140	+84

TABLE 6

	$M_D(1)$	$M_D(2)$	$M_D(2) - M_D(1)$
3β-Acetoxyfriedelane [19]	+155		
-26-oic acid [18]		+279	+124

Solvent $CHCl_3$. M_D to the nearest whole number.

friedelin or friedelin-3 α-ol as the C-20 group changes from CO_2H to CHO to $CH_2{\cdot}OH$. The same trend is shown with respect to friedelin when (a) the C-14 substituent changes from CO_2H to CHO, (b) the C-17 substituent changes from CHO to CH_2OH. However at C-9 the change of CHO to $CH_2{\cdot}OH$ produces the opposite effect. As more compounds become available it may be possible to obtain greater information about the chiral contribution of a group at various positions in the friedelane skeleton.

EXPERIMENTAL

For general procedures see Part 22.[18] *H. octandra* Thw. was collected from Kanneliya Forest Reserve.

Bark Extractives.—The powdered bark (19.6 kg) was extracted with hot benzene. The solid extracted (74.8 g, 0.38%) was dissolved in hot acetone–light petroleum (1 : 1; 600 ml) and the solution set aside for 2 days. The solid formed was filtered off, washed, and dried to give a

[19] J. McLean, G. H. Rettie, and F. S. Spring, *Chem. and Ind.*, 1958, 1515.
[20] V. V. Kane and B. Stevenson, *J. Org. Chem.*, 1960, **25**, 1394.
[21] P. Sengupta, A. H. Chakraborty, A. M. Duffield, L. J. Durham, and C. Djerassi, *Tetrahedron*, 1968, **24**, 1205.

grey powder (A) (23 g). The filtrate on concentration gave a dark brown semisolid (B) (50.9 g).

The solid A (23 g) was chromatographed on a column of silica gel (500 g) to give fractions as follows: eluant benzene–light petroleum (2 : 3), 10.3 g (A_1); benzene–light petroleum (9 : 11) 2.2 g (A_2); benzene–light petroleum (1 : 1), 2.6 g (A_3); benzene–light petroleum (3 : 1) 1.5 g (A_4); benzene, 1.2 g (A_5); chloroform–benzene (1 : 1), 1.6 g (A_6); chloroform, 0.6 g (A_7). Similarly the semisolid B (20 g) was chromatographed on a column of silica gel (500 g) and separated into fractions as follows: eluant light petroleum, 6.3 g (B_1); benzene–chloroform (1 : 1), 0.450 g (B_2); benzene, 1.0 g (B_3); benzene–chloroform (1 : 1). 0.800 g (B_4); benzene–chloroform (3 : 1), 0.550 g (B_5); chloroform, 7.2 g (B_6); methanol–chloroform (1 : 99), 1.4 g (B_7); methanol–chloroform (1 : 19), 0.500 g (B_8).

Isolation of friedelan-3-one (1b). Fraction A_1 (5.0 g) was chromatographed on a column of silica gel (250 g). Elution with benzene–light petroleum (2 : 3) gave friedelan-3-one (1b) (4.1 g, 0.02%), m.p. 264—265° [from acetone–light petroleum (1 : 1)], $[\alpha]_D^{26}$ − 21° (in $CHCl_3$) (lit.,[4] m.p. 261—264°, $[\alpha]_D$ −21°), identical with an authentic sample.

Isolation of friedelan-3α-ol (1c). Fraction A_3 (0.500 g) was chromatographed on a column of silica gel (20 g). Elution with benzene–light petroleum (9 : 11) gave friedelan-3α-ol (0.120 g, 0.007%), m.p. 300—303° (from light petroleum), $[\alpha]_D^{26}$ +16.9° (in $CHCl_3$) (lit.,[5] m.p. 292—301°, $[\alpha]_D$ +18°), identical with an authentic sample.

Isolation of friedelan-3β-ol (1e). Fraction A_2 (0.50 g) in pyridine (15 ml) was refluxed for 2 h with hydroxylamine hydrochloride (0.250 g). The product was diluted with water and extracted with diethyl ether. The solid obtained was chromatographed on a column of silica gel; elution with benzene–light petroleum (2 : 3) gave friedelan-3β-ol as white crystals, m.p. 282—283°, $[\alpha]_D^{26}$ +23.7° (in $CHCl_3$) (lit.,[5] m.p. 283—285°), $[\alpha]_D$ +24°, identical with an authentic sample.

Isolation of 3α-hydroxyfriedelan-29-al (3a). Fraction A_4 (1.5 g) was chromatographed on a column of neutral alumina (45 g). Elution with diethyl ether–light petroleum (1 : 19) gave *3α-hydroxyfriedelan-29-al* (3a) as shiny prisms (0.160 g, 0.000 8%), m.p. 318—319° (from light petroleum) $[\alpha]_D^{26}$ +23.3°; R_F 0.38 (chloroform–benzene, 2 : 1) (Found: C, 81.6; H, 11.2%; M^+, 442. $C_{30}H_{50}O_2$ requires C, 81.3; H, 11.4%; *M*, 442); $\nu_{max.}$ (KBr) 810, 862, 895, 918, 943, 1 002, 1 036, 1 121. 1 178, 1 290, 1 300, 1 365, 1 367, 1 438, 1 455, 1 722, 2 700, 2 800, 2 870, 2 940, and 3 490 cm^{-1}; τ($CDCl_3$; 100 MHz) 0.55 (1 H, s, tert. CHO), 6.26 (1 H, m, $W_{1/2}$ 9 Hz, 3-H), 8.45 (1 H, s, 3-OH, disappears on shaking with D_2O), 8.20—8.90 (CH_2), 8.97, 9.03, 9.05, 9.21, 9.24, and 9.35 (each 3 H, s, Me), and 9.11 (3 H, d, *J* 6 Hz, sec. Me); *m/e* 442(1%), 413(30), 395(60), 275(35), 257(100), 247(40), 231(33), and 175(65).

Conversion of 3α-hydroxyfriedelan-29-al (3a) *into friedelan-3α-ol* (1c). A mixture of the aldehyde (3a) (0.020 g), hydrazine hydrate (85%; 0.1 ml), and sodium ethoxide (0.060 g) was heated (sealed tube) at 180 °C for 5 h. The resulting material was diluted with water and extracted with diethyl ether. The crude product was chromatographed on a column of silica gel (2 g). Elution with benzene–light petroleum (9 : 11) gave friedelan-3α-ol (1c) (0.012 g), m.p. 300—301°, identical with an authentic sample.

Acetylation of 3α-hydroxyfriedelan-29-al (3a). Acetylation of the alcohol (3a) (0.020 g) with acetic anhydride (0.2 ml) and pyridine (3 ml) at room temperature overnight gave the *acetate* (2 g) (0.020 g), m.p. 324—325° (from light petroleum), $[\alpha]_D^{26}$ −4.4° (in $CHCl_3$), R_F 0.43 (benzene); $\nu_{max.}$ (KBr) 1 722 (CHO) and 1 740 cm^{-1} (OAc), M^+ 484; *m/e* 484(1%), 454(25), 423(5), 395(100), 317(12), 257(70), 231(24), 189(25), 175(90), 163(90), and 137(85).

Oxidation of 3α-hydroxyfriedelan-29-al (3a). A drop of Jones reagent was added to the aldehyde (3a) (0.015 g) in acetone (3.5 ml). The mixture was shaken for a few minutes and the excess of reagent was destroyed with a few drops of methanol. The product was diluted with water and taken up in diethyl ether; crystallisation from light petroleum gave *3-oxofriedelan-29-al* (3b) (0.013 g), m.p. 247—248°, $[\alpha]_D^{26}$ −4.9° (in $CHCl_3$), R_F 0.30 (benzene) M^+ 440; $\nu_{max.}$ (KBr) 1 712 cm^{-1}, identical with material isolated from the same plant.

Reduction of 3α-hydroxyfriedelan-29-al (3a). The aldehyde (3a) (0.025 g) in dry diethyl ether (10 ml) was added dropwise to a solution of lithium aluminium hydride (0.012 g) in dry diethyl ether (10 ml). The mixture was refluxed for 1 h and left overnight at room temperature. The product was diluted with water and extracted with diethyl ether. Crystallisation from light petroleum yielded *friedelane-3α,29-diol* (3c) as white crystals (0.019 g), m.p. 312—313°, $[\alpha]_D^{26}$ +21.20 (in C_5H_5N), R_F 0.73 (methanol–chloroform, 1 : 19); $\nu_{max.}$ (KBr) 3 300 cm^{-1} (OH); τ($CDCl_3$; 100 MHz) 6.09 (3 H, m, C*H*·OH and CH_2·OH), 8.02—8.82 (CH_2), and 8.87—9.17 (21 H, Me), identical with the diol isolated from the same plant.

Oxidation of 3α-hydroxyfriedelan-29-al with potassium permanganate–potassium iodate. The aldehyde (3a) (0.050 g), potassium permanganate (0.008 g), potassium iodate (0.040 g), hydrated sodium carbonate (0.010 g), water (0.5 ml), and pyridine (9.5 ml) were shaken for 5 min and left overnight at room temperature. The product was diluted with water and extracted with ether. Evaporation, and crystallisation from light petroleum yielded 3α-hydroxyfriedelan-29-oic acid (3e) (0.044 g), m.p. 293—294°, $[\alpha]_D^{26}$ +55° (in $CHCl_3$), R_F 0.21 (chloroform); $\nu_{max.}$ 3 465 cm^{-1} (OH), identical with the acid isolated from the same plant.

Oxidation of 3α-hydroxyfriedelan-29-oic acid (3e). The acid (3e) (0.015 g), chromic acid (0.075 g), and pyridine (1 ml) were kept at room temperature overnight; work-up and crystallisation from light petroleum yielded *3-oxofriedelan-29-oic acid* (3f) (0.012 6 g) as white crystals, m.p. 260—261°, $[\alpha]_D^{26}$ +15.8° (in $CHCl_3$), R_F 048 (chloroform), M^+ 456; $\nu_{max.}$ (KBr) 1 690 (CO_2H) and 1 716 cm^{-1} 1 716 (CO); o.r.d. (methanol): negative Cotton effect, peak at 265 nm (+ 6 380), trough 304 nm (−5 198), and secondary trough 315 nm (−3 556); identical with the oxo-acid isolated from the same plant.

Isolation of β-sitosterol. Fraction A_5 (1.2 g) was chromatographed on a column of silica gel (40 g). Elution with diethyl ether–light petroleum (1 : 19) gave β-sitosterol (0.675 g, 0.003 5%), m.p. 136—137° (lit.,[13] 136—137°, $[\alpha]_D$ −36°), identical with an authentic sample.

Isolation of 3-oxofriedelan-29-ol (3d). Further elution of the above column with diethyl–ether light petroleum (1 : 19) gave a white solid which on crystallisation from light petroleum yielded *3-oxofriedelan-29-al* (3d) (0.025 g, 0.000 12%) as white shiny crystals, m.p. 276—277°, $[\alpha]_D$ −24.5° (in $CHCl_3$), M^+ 442; $\nu_{max.}$ (Nujol) 981, 998, 1 030, 1 058, 1 084, 1 127, 1 168, 1 207, 1 251, 1 368, 1 380, 1 465, 1 710, and 3 542 cm^{-1}; τ($CDCl_3$; 100 MHz), 6.36

(2 H, s, CH_2OH), 7.68 (3 H, m, $CH_2{\cdot}C{\cdot}CH$), 7.91—8.09 (CH_2), 8.86, 9.01 (×2), 9.08, 9.12, and 9.28 (3 H, s, for 6 tert. Me), and 9.13 (3 H, d, J 6 Hz, sec. Me); *m/e* 442(2%), 427(1), 411(95), 301(12), 287(4), 273(100), 247(40), 233(20), 205(36), 203(25), 189(30), 137(80), 122(56), and 121(45), identical with the Oppenauer oxidation product of friedelane-3α,29-diol.

Oxidation of 3-oxofriedelan-29-ol (3d). The alcohol (3d) (0.010 g), chromic acid (0.005 g), and pyridine (2.5 ml) were left at room temperature overnight. The usual work-up and crystallisation from light petroleum gave 3-oxofriedelan-29-al (3b) as white needles (0.007 g), identical with the aldehyde isolated from the same plant.

Isolation of friedelane-3α,29-diol (3c). Fraction A_6 (1.6 g) was chromatographed on a column of neutral alumina (45 g). Elution with diethyl ether–light petroleum (1 : 19) gave β-sitosterol (0.730 g); elution with diethyl ether–light petroleum (1 : 9) gave a white solid which on crystallisation from light petroleum gave *friedelane-3α,29-diol* (3c) as white crystals (0.017 g) (0.000 09%), m.p. 312—313°, $[\alpha]_D^{26}$ −21.2° (in C_5H_5N), R_F 0.73 (methanol–chloroform, 1 : 19), *m/e* 413 ($M-31$); $\nu_{max.}$ (KBr) 880, 895, 1 009, 1 037, 1 055, 1 060, 1 121, 1 150, 1 245, 1 367, 1 380, 1 398, 1 455, 1 475, 2 870, 2 940, and 3 300 cm^{-1}; *m/e* 413(85%), 395(85), 275(48), 257(100), 247(42), 231(27), 221(15), 189(45), and 175(55), identical with the diol synthesised from the aldehyde (3a).

Oppenauer oxidation of friedelane-3α,29-diol (3c). Aluminium isopropoxide (0.005 g) in dry toluene (1 ml) was added dropwise to a boiling mixture of friedelane-3α,29-diol (0.010 g) in cyclohexane (1 ml) and dry toluene (5 ml). The mixture was refluxed for 6.5 h, steam-distilled, and the residue was extracted with ether and separated on a preparative silica gel plate with chloroform (×2). The u.v.-fluorescent band at R_F 0.61—0.63 was extracted, and the product on crystallisation from light petroleum gave 3-oxofriedelan-29-ol (3d) as white crystals (0.003 3 g), identical with the hydroxy-ketone isolated from the same plant.

Isolation of 3α-hydroxyfriedelan-29-oic acid (3e). Fraction A_7 was chromatographed on a column of silica gel (20 g). Elution with diethyl ether–light petroleum (7 : 93) gave fractions A_{7a} (0.095 g) and A_{7b} (0.580 g). Fraction A_{7a} was chromatographed on a preparative silica gel plate with chloroform (×2). The u.v.-fluorescent band at R_F 0.54 was scraped off and worked up. Crystallisation from light petroleum gave *3α-hydroxyfriedelan-29-oic acid* (3e) (0.011 g, 0.000 06%), m.p. 293—294°, $[\alpha]_D^{26}$ +55° (in $CHCl_3$), R_F 0.21 (chloroform); M^+ 458; $\nu_{max.}$ (KBr) 930, 950, 1 012, 1 028, 1 040, 1 122, 1 189, 1 200, 1 222, 1 235, 1 250, 1 290, 1 305, 1 368, 1 395, 1 460, 2 875, 2 940, and 3 465 cm^{-1}; *m/e* 458(3%), 440(72), 425(60), 412(15), 275(45), 257(66), 231(72), 191(69), 189(87), 177(72), and 162(90), identical with the hydroxy-acid prepared from the aldehyde (3a).

Isolation of 3-oxofriedelan-29-oic acid (3f). From the above preparative plate the u.v.-fluorescent band at R_F 0.76 was scraped, and the product was worked up. Crystallisation from light petroleum yielded *3-oxofriedelan-29-oic acid* (3f) as white crystals (0.007 g, 0.000 04%), m.p. 260—261°, $[\alpha]_D^{26}$ +15.8° (in $CHCl_3$), R_F 0.48 (chloroform); M^+ 456; $\nu_{max.}$ (KBr) 915, 930, 985, 1 008, 1 077, 1 122, 1 188, 1 220, 1 250, 1 370, 1 392. 1 462, 1 690, 1 716, 2 875, 2 940, and 3 420 cm^{-1}; *m/e* 456(36%), 430(24), 423(20), 410(28), 395(48), 371(45), 303(15), 273(100), 235(40), 205(60), 203(40), 189(95), 163(98), 155(20), and 121(96), identical with the oxo-acid prepared from the aldehyde (3a).

Isolation of 3β-hydroxyfriedelan-26-oic acid (4b). From the above preparative plate the u.v.-fluorescent band at R_F 0.61 was scraped and the product worked up. Crystallisation from light petroleum gave 3β-hydroxyfriedelan-26-oic acid (4b) (0.023 g, 0.000 11%), m.p. 333—334°, $[\alpha]_D^{23}$ +40.1° (in $CHCl_3$) (lit.,[18] 333—335°, $[\alpha]_D$ +39.0°); $\nu_{max.}$ (KBr) 867, 931, 950, 1 002, 1 050, 1 093, 1 148, 1 182, 1 262, 1 327, 1 397, 1 689, 2 380, 2 460, and 3 420 cm^{-1}, identical with trichadenic acid B fom the reduction of trichadonic acid isolated from *Trichadenia zeylanica* Thw.

Isolation of ursolic acid. Fraction A_{7b} (0.580 g) was chromatographed on a column of silica gel. Elution with 14% diethyl ether–light petroleum (7 : 43) gave ursolic acid (0.028 g, 0.000 14%), m.p. 283—284° (from MeOH), $[\alpha]_D^{26}$ +66.2° (in $CHCl_3$) (lit.,[15] 283—284°, $[\alpha]_D$ +65.9°), identical with an authentic sample.

Isolation of 3α-hydroxyfriedelan-26-oic acid (4a). Further elution of the above column with diethyl ether–light petroleum (1 : 4) gave a white solid which on crystallisation from light petroleum yielded 3α-hydroxyfriedelan-26-oic acid (4a) (0.018 g, 0.000 09%), m.p. 294—296°, $[\alpha]_D^{26}$ +25.1° (in $CHCl_3$) (lit.,[18] 294°, $[\alpha]_D$ +25.0°); $\nu_{max.}$ (KBr) 1 688 and 3 380 cm^{-1}, identical with authentic trichadenic acid A.

Isolation of friedelan-3α-yl acetate (1d). Fraction B_2 (0.450 g) was chromatographed on a column of silica gel (25 g). Elution with benzene–light petroleum (3 : 7) gave friedelan-3α-yl acetate (0.055 g, 0.000 27%), m.p. 313—315° (lit.,[5] 314—315°), identical with an authentic sample.

Isolation of 3-oxofriedelan-29-al (3b). Further elution of the above column with diethyl ether–light petroleum (2 : 3) gave a white solid which on crystallisation from light petroleum yielded *3-oxofriedelan-29-al* (3b) (0.028 g, 0.000 14%), m.p. 248—249°, $[\alpha]_D^{16}$ −46° (in $CHCl_3$), R_F 0.30 (benzene), M^+ 440; $\nu_{max.}$ (KBr) 788, 822, 870, 912, 968, 1 008, 1 045, 1 052, 1 072, 1 113, 1 147, 1 172, 1 188, 1 203, 1 219, 1 350, 1 365, 1 389, 1 457, 1 712, 2 675, and 2 930 cm^{-1}; τ($CDCl_3$; 100 MHz) 0.56 (1 H, s, CHO), 7.53—7.92 (3 H, m, $\cdot CH_2{\cdot}CO{\cdot}CH$), 7.89—8.85 ($CH_2$), and 8.93, 9.02, 9.04, 9.07, 9.15, 9.26, and 9.32 (21 H, 6 s and 1 d, 7 × Me); *m/e* 440(8%), 411(68), 393(6), 355(10), 301(15), 273(70), 247(27), 219(9), 205(22), 191(20), and 137(100), identical with the ketone prepared from the aldehyde (3a).

Timber Extractives.—Powdered timber (9.0 kg) was extracted with hot benzene; concentration gave an oil (16.5 g). The benzene extract (5.0 g) was chromatographed on a column of silica gel (250 g). Elution with light petroleum gave a pale brown oil (4.2 g, 0.12%), n_D^{26} 1.463, d 0.948 g cm^{-3} at 26 °C, iodine no. 189.2.

Isolation of friedelan-3-one (1b) *and β-sitosterol.* Further elution with benzene–light petroleum (9 : 11) gave friedelan-3-one (1b) (0.060 g. 0.002%). Elution with benzene gave β-sitosterol (0.095 g. 0.03%).

Fruit Pericarp Extract.—The fruit pericarp (3.5 kg) was extracted with hot light petroleum. Concentration gave an oil (4.2 g). The oil (1 g) was chromatographed on a column of silica gel. Elution with light petroleum gave an oil (0.900 g), n_D^{26} 1.479, d 0.942 g cm^{-3}, iodine no. 97.2. Further elution with benzene–light petroleum (9 : 11) and benzene gave friedelan-3-one (0.023 g, 0.027%) and β-sitosterol (0.047 g, 0.055%).

We thank Professors W. D. Ollis (University of Sheffield), R. H. Thomson (University of Aberdeen), Sir Derek Barton (Imperial College, London), and C. Ponnamperuma (University of Maryland) for n.m.r. and mass spectral data; Dr. T. R. Govindachari (C.I.B.A., Bombay) for an authentic sample of canophyllal; Dr. S. Balasubramanian for identification of plant material; Dr. A. A. L. Gunatilaka for discussions; and Mrs. S. C. Weerasekera, S. Ramachandran, and D. V. Ariyapala for technical assistance. The programme has been supported in part by grants from the National Science Council of Sri Lanka and the United States Department of Agriculture.

[6/1186 *Received*, 21*st June*, 1976]