Chemical Investigation of Ceylonese Plants. Part 22.† Extractives of *Trichadenia zeylanica* Thw. (Flacourtiaceae); Isolation and Structures of Six New Triterpenoids containing the Friedelane Skeleton [1]

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From the bark and wood extracts of *Trichadenia zeylanica* Thw., six new triterpenoids, namely trichadenic acid A (3α-hydroxyfriedelan-26-oic acid), *O*-acetyltrichadenic acid A, *O*-acetyltrichadenic acid B (3β-acetoxyfriedelan-26-oic acid), trichadonic acid (3-oxofriedelan-26-oic acid), trichadenal (3β-hydroxyfriedelan-26-al), and *O*-acetyltrichadenal have been isolated, correlated, and identified. The extracts also contained friedelan-3α-yl acetate and β-sitosterol.

LITTLE systematic chemical work has been reported on plant species belonging to the family Flacourtiaceae.[2-4] We report here a study of the minor triterpenoid constituents of the Ceylonese species *Trichadenia zeylanica* Thw.

Bark Extractives.—The light petroleum extract of the bark was separated to give five solid mixtures, A—E (see Experimental section).

On separation on a silica gel column, solid B gave β-sitosterol. Similarly solid E gave friedelan-3α-yl acetate (1e) [5] (identified by mixed m.p., i.r. spectra ,and t.l.c.) and a new natural product, named trichadenal (2c),

† Part 21, S. P. Gunasekera, K. Sivapalan, M. U. S. Sultanbawa, and W. D. Ollis, *J.C.S. Perkin I*, 1977, 11.

[1] Preliminary report, S. P. Gunasekera and M. U. S. Sultanbawa, *Tetrahedron Letters*, 1973, 2837.

[2] R. Hegnauer, 'Chemotaxanomie de Pflanzen,' Birkhäuser Verlag, Basel und Stuttgart, 1966, vol. 4.

[3] P. C. Kiang, *China Med. J.*, 1923, **37**, 142.

[4] T. R. Govindachari, S. J. Jadhav, B. S. Joshi, V. N. Kamat, P. A. Mohamed, P. C. Patanker, D. Prakash, D. F. Rane, and N. Viswanathan, *Indian J. Chem.*, 1969, 308.

[5] C. W. Shoppee, M. E. H. Howden, and G. A. R. Johnston, *J. Chem. Soc.*, 1962, 498.

$C_{30}H_{50}O_2$, which responded to the Liebermann–Burchard test for a terpenoid. The i.r. spectrum showed a hydroxy-group (1 045 and 3 450 cm^{-1}) and an aldehyde group (1 702 cm^{-1}). In the mass spectrum, the presence of ($M^+ - 18$) and ($M^+ - 29$) peaks indicated a secondary hydroxy-group and tertiary aldehyde group, respectively.[6] The acetate was identical with another compound, *O*-acetyltrichadenal (2b), isolated from the same plant.

The solid A on separation on a silica gel column gave three solids, named trichadenic acid A (3b), *O*-acetyltrichadenal (2b), and *O*-acetyltrichadenic acid B (3e). Similarly the solid D on a neutral alumina column gave two other solids, named trichadonic acid (3a) and *O*-acetyltrichadenic acid A (3d).

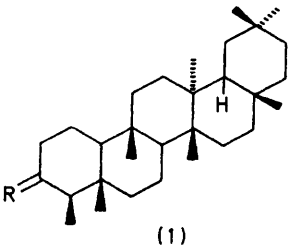
O-Acetyltrichadenal (2b), $C_{32}H_{52}O_3$, had ester (1 735 cm^{-1}) and aldehyde (1 702 cm^{-1}) i.r. absorptions. The n.m.r. spectrum showed signals at τ −0.01 (1 H, s, CHO attached to tertiary C), 5.10 (1 H, m, C*H*·OAc), 8.82 (3 H), 8.90 (3 H), 9.05 (3 H), 9.10 (3 H), and 9.12 (6 H) (six tertiary Me), and 9.22 (3 H, d, J 7 Hz, secondary Me). The absence of olefinic i.r. absorption and the lack of n.m.r. signals for olefinic protons indicated that the compound was pentacyclic and probable belonged to the friedelane series.

Trichadenal (2c) on controlled oxidation with chromic acid–pyridine gave an oxo-aldehyde, named trichadonal (2a), M^+ 440, $\nu_{max.}$ 1 703 (CHO) and 1 690 cm^{-1} (CO). Huang Minlon reduction [7] gave friedelane [8] (1a) in poor yield, identical with an authentic sample.

O-Acetyltrichadenal (2b) on modified Wolff–Kishner reduction [8] gave epifriedelinol (1c), identical with an authentic sample. Formation of this compound indicated that the acetoxy-group in (2b) is at C-3 and has a β- (axial) configuration. Reduction of *O*-acetyltrichadenal with lithium aluminium hydride gave a diol, trichadenol (2d), $\nu_{max.}$ 3 490 and 3 640 cm^{-1} (OH). The molecular ion was absent in the mass spectrum but an M^+ −31 peak at m/e 413 (100%) was prominent, owing to the ready removal of CH_2OH from the molecular ion.[6]

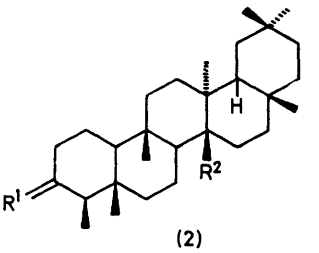
Oxidation of trichadenal (2c) with an excess of chromic oxide in pyridine for a longer period gave a mixture of two products. The less polar was identified as trichadonal (2a), obtained earlier by controlled oxidation. The more polar was identified as the naturally occurring trichadonic acid (3a) (see above). Characterisation of the above compound and assignment of the position of the CHO group in trichadenal will be dealt with in the characterisation of trichadenic acid A.

Trichadenic acid A (3b), $C_{30}H_{50}O_3$ (M^+ 458), was soluble in sodium hydroxide, giving an insoluble sodium salt, probably indicating a hindered position for the CO_2H group. The i.r. spectrum showed absorption for the carbonyl of an acid (1 689 cm^{-1}) and a hydroxy-group (3 400 cm^{-1}). The n.m.r. spectrum showed a multiplet at τ 6.78 ($W_{1/2}$ 18 Hz), appropriate for equatorial C*H*·OH, and signals for only seven methyl groups. Hence one methyl group of friedelane has become CO_2H.



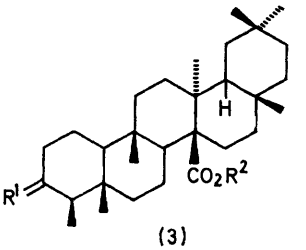
(1)

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



(2)

a; R^1 = O, R^2 = CHO
b; R^1 = β-OAc, α-H, R^2 = CHO
c; R^1 = β-OH, α-H, R^2 = CHO
d; R^1 = β-OH, α-H, R^2 = CH_2·OH



(3)

a; R^1 = O, R^2 = H
b; R^1 = α-OH, β-H, R^2 = H
c; R^1 = β-OH, α-H, R^2 = H
d; R^1 = α-OAc, β-H, R^2 = H
e; R^1 = β-OAc, α-H, R^2 = H
f; R^1 = α-O·SO_2Me, β-H, R^2 = H
g; R^1 = O, R^2 = Me
h; R^1 = O, R^2 = Et
i; R^1 = α-OH, β-H, R^2 = Me
j; R^1 = α-OAc, β-H, R^2 = Me
k; R^1 = β-OAc, α-H, R^2 = Me
l; R^1 = H_2, R^2 = H
m; R^1 = H_2, R^2 = Me
n; R^1 = $[CH_2]_2O_2$ R^2 = H

Trichadenic acid A acetate was identical with the *O*-acetyltrichadenic acid A (3d) isolated from the solid D.

The above transformations (summarised in Scheme 1) established the presence of the friedelane skeleton with an oxygen function in position 3 in all the isolated compounds.

Trichadenic acid A with diazomethane gave methyl trichadenate A (3i) (M^+ 472, $\nu_{max.}$ 1 727 cm^{-1}). The ester was resistant to normal hydrolysis but could be hydrolysed under drastic conditions, again indicating a hindered position for the CO_2H group. This view was further confirmed by the failure of attempted reduction

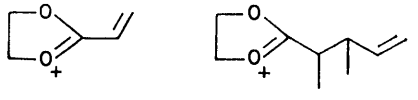
[6] J. S. Shannon, C. G. Macdonald, and J. L. Courtney, *Tetrahedron Letters*, 1963, 173.

[7] Huang Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

[8] T. R. Govindachari, N. Viswanathan, B. R. Pai, U. Ramadas Rao, and M. Srinivasan, *Tetrahedron*, 1967, **23**, 1901.

with lithium aluminium hydride in a high-boiling solvent of both trichadenic acid A and its methyl ester.

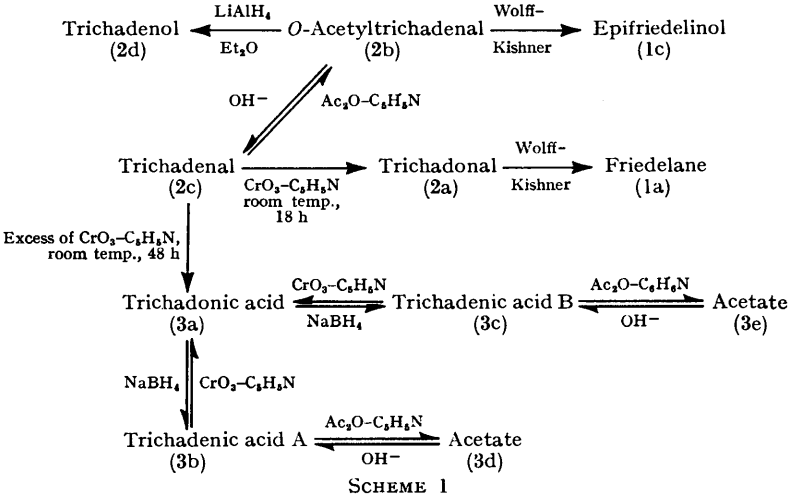
Oxidation of trichadenic acid A (3b) with chromic oxide–pyridine gave a white crystalline compound identical with the isolated trichadonic acid. The molecular formula $C_{30}H_{48}O_3$ is in keeping with the assumption that only the 3-OH group in trichadenic acid A has become an oxo-group. This agreed with the presence of a multiplet, τ 7.50—7.87 for 3 protons adjacent to a carbonyl group. The friedelan-3-one skeleton was further confirmed from the o.r.d. curve of the methyl ester (3g), in methanol, which was similar to that of friedelan-3-one,[9] showing a negative Cotton effect having a major peak at 265 (+8 460), a secondary peak at 245 (+7 805), a trough at 304 (−5 946), and a secondary trough at 315 nm (−3 948). The mass spectrum of the ethylene acetal (3n) of trichadonic acid had characteristic fragments at *m/e* 99 (a) and 153 (*b*) in keeping with a friedelan-3-one skeleton.



(a) *m/e* 99 (b) *m/e* 153

Reduction of trichadonic acid (3a) with sodium borohydride gave a mixture of two products. The less polar (17%) was identical with trichadenic acid B(3c) isolated from *Hydnocarpus octandra* Thw.[10] and also with the trichadenic acid B(3c) prepared from *O*-acetyltrichadenic acid B(3e) from this plant. The more polar compound (83%) was identical with trichadenic acid A (3b).

The n.m.r. spectrum of *O*-acetyltrichadenic acid B(3e) showed a signal at τ 5.11 (1 H, m, $W_{1/2}$ 5 Hz) for the 3-H, whereas *O*-acetyltrichadenic acid A (3d) gave a signal at τ 5.34 (1 H, m, $W_{1/2}$ 20 Hz). The low half-height width (5 Hz) [11] in the case of *O*-acetyltrichadenic acid B indicates the presence of equatorial–equatorial and axial–equatorial types of coupling, whereas in *O*-acetyltrichadenic acid A, the high half-width (20 Hz) indicates the presence of axial–axial and axial–equatorial coupling. Therefore, the oxygen function at C-3 in *O*-acetyltrichadenic acid B is axial and that of *O*-acetyltrichadenic acid A is equatorial.



SCHEME 1

Trichadonic acid (3a) on Huang Minlon reduction readily gave deoxytrichadonic acid (3l), M^+ 442, showing in the i.r. spectrum only acid carbonyl absorption at 1 690 cm^{-1}, shifted to 1 728 cm^{-1} in that of its methyl ester.

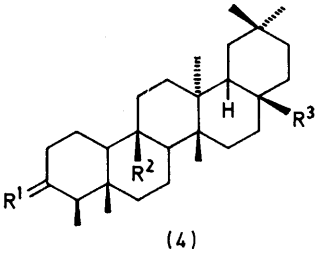
Trichadenic acid A (3b) with mesyl chloride readily gave a white crystalline mesylate ($\nu_{max.}$ 1 165 and 1 186 cm^{-1}), further supporting the presence of an equatorial hydroxy-group in the acid. Therefore, trichadenic acid A (3b) must be a 3α-hydroxyfriedelanoic acid, trichadenic acid B (3c) a 3β-hydroxyfriedelanoic acid, and trichadonic acid a 3-oxofriedelanoic acid.

The location of the carboxy-group was established by stepwise elimination of the available positions. The mass spectrum of the ethylene acetal (3n) of trichadonic acid, the stability to heat of trichadonic acid (3a), and the non-formation of a lactone from trichadenic acid B eliminated C-4 and -5. C-9, -17, and C-20 were eliminated because trichadonic acid was not identical with roxburghonic acid [12] (4a), trichadenic acid B was not identical with canophyllic acid [9] (4b), and trichadenic acid A was not identical with octandrolic acid [10] (5b) (mixed m.p.s, i.r. spectra, and t.l.c.). The possibility of trichadonic acid being polpunonic acid (6a) (20-CO_2H) was eliminated by comparison of physical data and mass spectral fragmentation patterns of the acids and their methyl esters (*cf.* ref. 13). The above

[9] C. Djerassi, R. Rinker, and B. Rinker, *J. Amer. Chem. Soc.*, 1956, **78**, 6362.
[10] S. P. Gunasekera and M. U. S. Sultanbawa, *Chem. and Ind.*, 1973, 790 and following paper.
[11] L. M. Jackman and S. Sternhell, 'Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, London, 1969.
[12] H. S. Garg and C. R. Mitra, *Phytochemistry*, 1971, **10**, 865.
[13] F. Delle Monache, J. F. de Mellow, G. B. Marini Bettolo, O. Goncalves Delima, and I. L. D'Albuquerque, *Gazzetta*, 1972, **102**, 636.

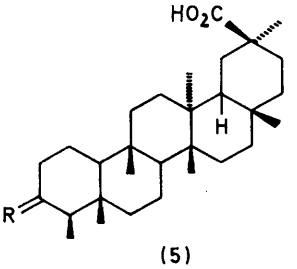
considerations limit the position of the carboxy-group to C-13 or -14.

The mass spectral fragmentation patterns were slightly different from but basically similar to those of the friedelane type.[14] This slight difference would be expected when a bulky group like CO_2H exists at a sterically crowded position in the middle of the molecule.



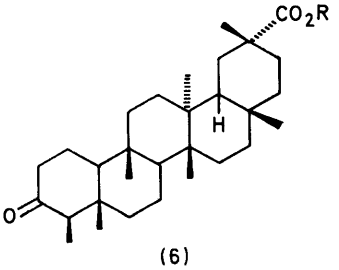
(4)

a; R^1 = O, R^2 = CO_2H, R^3 = Me
b; R^1 = β-OH, α-H, R^2 = Me, R^3 = CO_2H
c; R^1 = β-OH, α-H, R^2 = Me, R_3 = CO_2Me



(5)

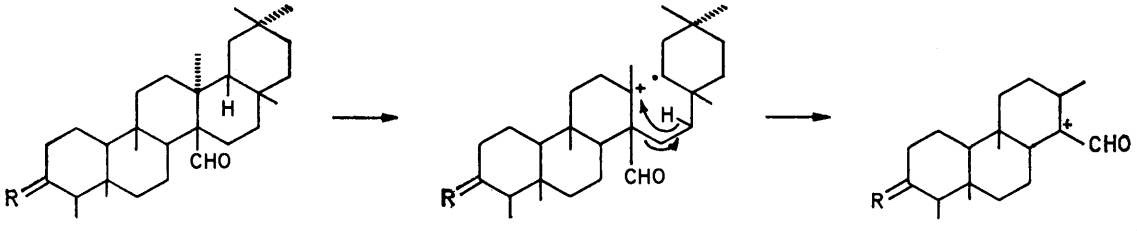
a; R = O
b; R = α-OH, β-H



(6)

a; R = H
b; R = Me

The possible mode of fragmentation given earlier[1] for the trichadenic acids has also been observed for *O*-acetyltrichadenal (2b), trichadenol (2d), and trichadonal (2a), giving the fragments (7a—c) as the base peak in two cases and as a high intensity peak in the other (Scheme 2). Although this fragmentation does not clearly distinguish C-13 and -14 as sites for the CO_2H or CHO group, it was considered to favour the presence of the functional group at C-14. This assignment was confirmed by the following considerations.



(7)

a; R = H, OAc (*m/e* 333)
b; R = OH, H (*m/e* 291)
c; R = O (*m/e* 289)

SCHEME 2

The friedelane nucleus has an all-chair sequence and rings D and E are *cis*-fused.[15] A C-14 carboxy-group is thus sterically crowded owing to a 1,3-diaxial interaction with the C-9 methyl group and also to four 1,3-diaxial interactions with hydrogen atoms at C-7, -12, -16, and -18 positions. However a carboxy-group at C-13 would be more sterically crowded owing to the folding of the molecule and the presence of a 1,4-diaxial *cis*-decalin-type interaction with the C-20 methyl group, three 1,3-diaxial interactions with hydrogen atoms at C-8, -11, and -15, and a *cis*- decalin-type 1,4-diaxial interaction with the hydrogen atom at C-22. Thus a C-13 substituent is more sterically crowded than a C-14 substituent.

A friedelane with a carboxy-group in the framework consisting of rings A, B, and C is roxburghonic acid (4a). The C-9 carboxy-group is sterically crowded owing to two 1,3-diaxial interactions with C-5 and -14 methyl groups and three 1,3-diaxial interactions with hydrogen atoms at C-1, -7, and -12.

Since A, B, C, and D are planer, a C-9 carboxy-group is seen to be less crowded than one at C-13, and to be more comparable with one at C-14. The methyl deoxyroxburghonate[12] was not reduced to the corresponding alcohol by lithium aluminium hydride. This is in keeping with the lack of reactivity of methyl trichadenate A (3i) with lithium aluminium hydride. Trichadenic acid A (3b) formed a sodium salt and a methyl and an ethyl ester, the last in 90% yield. This indicates the likelihood of the carboxy-group being at C-14 rather than C-13.

In canophyllic acid (4b) the CO_2H group is at C-17. It is equatorial and hence not as sterically crowded as a C-14 substituent. Methyl canophyllate (4c) can be reduced to the corresponding alcohol with lithium aluminium hydride. However saponification of methyl canophyllate (4c) 74% yield required drastic conditions

[14] H. Budzikiewicz, T. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3688.

[15] H. Dutler, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, 1955, **38**, 1268.

(potassium hydroxide–ethylene glycol under reflux for 18 h). Refluxing methyl trichadenate (3i) with potassium hydroxide and ethylene glycol for *ca.* 15 h gave trichadenic acid in 67% yield. Thus the rates of saponification and the yields of the products from the two esters are similar. The similarity in rate of saponification may be explained as follows. In methyl canophyllate attack at the carbonyl group by the incoming nucleophile can only occur between the C-16 and C-22 equatorial hydrogen atoms. Similarly in a C-14 carboxylate attack can only take place between the C-7 and C-16 axial hydrogen atoms, which are 1,5-diaxial to each other. However if the carboxylate group is attached to C-13 there is no way for the incoming nucleophile to attack the carbonyl group. The carboxy-group must therefore be at C-14. Therefore trichadenic acid A is 3α-hydroxyfriedelan-26-oic acid (3b), and trichadenic acid B is the 3β-isomer (3c), and trichadonic acid is the 3-oxo-analogue (3a). Thus trichadenal is 3β-hydroxyfriedelan-26-al (2c) and *O*-acetyltrichadenal is its acetate (2b).

Timber Extractives.—The hot light petroleum extract on a column of silica gel gave *O*-acetyltrichadenal (2b), β-sitosterol, and *O*-acetyltrichadenic acid B (3e).

Some general observations are given in the following paper.

EXPERIMENTAL

Analytical thin-layer plates were made with silica gel G (Merck). Preparative plates were made with Merck silica gel $PF_{254-366}$ unless otherwise stated. All R_F values apply to t.l.c. plates of thickness 0.25 mm. Column chromatography was carried out, unless otherwise stated, with Merck silica gel (30—70 mesh) or Merck neutral alumina (activity 1). M.p.s were determined with a Kofler hot-stage apparatus. Rotations were determined with a Bellingham and Stanley polarimeter. All samples for analysis were dried at 60 °C for 5 h at 20 mmHg and the microanalytical results were obtained from the CSIRO Microanalytical Service, Melbourne, Australia. N.m.r. and mass spectra and some i.r. spectra were obtained from the Universities of Aberdeen, Sheffield, Strathclyde, and London; other i.r. spectra were obtained and i.r. comparisons were made with a Perkin-Elmer 257 grating spectrophotometer, and u.v. spectra were recorded with a Unicam SP 8000B spectrophotometer in this Department. O.r.d. data were obtained from the University of Sheffield. Light petroleum used had b.p. 60—80 °C. The bark and timber material were separately dried, chipped, and powdered in a mill and extracted with solvents in a modified Soxhlet-type apparatus devised in this laboratory. All evaporations were carried out under reduced pressure on a water-bath. All room temperature reactions were carried out at 26 °C. All acetylations (acetic anhydride) and oxidations (chromic oxide) were performed in anhydrous pyridine. After the reactions, the products were diluted with water and extracted with diethyl ether. The ether layer was washed repeatedly (2N-HCl and water) to remove pyridine and dried (Na_2SO_4). Yields of the pure material isolated are expressed as % of the dry weight of the plant material used. The plant was collected from Udakarawita, Sabaragamuwa Province.

Substances stated to be identical were compared by mixed m.p. determination, i.r. spectroscopy, and t.l.c.

Bark Extractives.—The powdered bark (6.3 kg) was extracted with hot light petroleum and methanol. Evaporation gave a semisolid light petroleum extract (44.7 g, 0.70%). This extract (44.7 g) was dissolved in hot light petroleum (1.1 l) and set aside for 3 days; the solid formed (A) (2.2 g) was filtered off. The filtrate on concentration yielded a dark green semisolid (42.3 g). This (40.0 g) was dissolved in light petroleum (1.0 l) and left in a refrigerator for 7 days; the solid formed (B) (0.950 g) was filtered off. Concentration of the filtrate gave a greenish black semisolid (C) (39·0 g).

Fraction C (39.0 g) was washed with cold 10% sodium hydroxide. The organic phase on concentration gave thick oil (37.2 g). The oil was chromatographed on a column of silica gel (250 g). Elution with light petroleum gave an oil (9.5 g), n_D^{26} 1.458, *d* 0.956 g cm^{-3} at 26 °C, iodine no. 187. Further elution with benzene gave a solid (E) (0.260 g).

The aqueous phase was acidified and extracted with diethyl ether; evaporation of the ethereal layer gave a while solid (D) (1.6 g).

Isolation of β-sitosterol. Fraction B (0.950 g) was chromatographed on a column of silica gel (30 g). Elution with benzene gave β-sitosterol (0.675 g, 0.01%) as white needles (from light petroleum), m.p. 136—137° $[\alpha]_D^{26}$ −36.1° (lit.,[16] m.p. 136—137°, $[\alpha]_D$ −36°), identical with an authentic sample.

Isolation of trichadenic acid A (3b) (*3α-hydroxyfriedelan-26-oic acid*). The solid A (2.2 g) was chromatographed on a column of silica gel. Elution with benzene gave a white solid mixture A_1 (1.6 g). Further elution with chloroform–benzene (3 : 1) gave *trichadenic acid A* (0.260 g, 0.004%), white shiny needles (from light petroleum), m.p. 292—293°, $[\alpha]_D^{26}$ +25.0° (in $CHCl_3$), R_F 0.20 [methanol–chloroform (1 : 19)], red colouration in the Liebermann–Burchard test for a terpenoid (Found: C, 75.8; H, 10.9%; M^+ 458. $C_{30}H_{50}O_3$ requires C, 75.6; H, 11.0%; *M*, 458); $\nu_{max.}$ (KBr) 762, 810, 822, 865, 1 010, 1 185, 1 208, 1 260, 1 365, 1 390, 1 460, 1 689, 2 870, 2 940, and 3 400 cm^{-1}; τ ($CDCl_3$–CD_3OH; 100 MHz) 6.78 (1 H, m, $W_{1/2}$ 18 Hz, 3-H), 7.81—8.72 (CH_2), and 8.78, 8.87, 9.00, 9.05, 9.10, 9.12, and 9.22 (7 Me), *m/e* 458(9%), 440(33), 425(27), 386(12), 307(100), 290(36), 260(21), 204(27), 189(24), 175(36), 165(33), 152(78), 149(42), and 123(42).

Acetylation of trichadenic acid A (3b). Treatment of trichadenic acid A (0.050 g) with acetic anhydride (0.5 ml) and pyridine (5 ml) at room temperature overnight gave *O*-acetyltrichadenic acid A (3d) (0.043 g) as white crystals (from light petroleum), m.p. 251—252°, $[\alpha]_D^{26}$ +28.1° (in $CHCl_3$), R_F 0.77 (chloroform), M^+ 500; $\nu_{max.}$ (KBr) 1 687 (CO_2H) and 1 742 cm^{-1} (OAc), identical with *O*-acetyltrichadenic acid A isolated from the same plant. On hydrolysis it gave back the original trichadenic acid A, m.p. 292—293°.

Esterification of trichadenic acid A (3b). Trichadenic acid A (0.040 g) in diethyl ether (20 ml) was treated with an excess of diazomethane and left overnight at room temperature. Evaporation gave *methyl trichadenate A* (3i) as white crystals (0.037 g), m.p. 201—202° (from light petroleum), $[\alpha]_D^{26}$ +95.0° (in $CHCl_3$), M^+ 472; $\nu_{max.}$ (KBr) 1 727 (CO_2Me) and 3 540 cm^{-1} (OH); *m/e* 472(3%), 454(5), 440(25), 327(100), 303(10), 259(9), 257(9), 203(12), 189(15), 175(16), 123(33), and 83(70).

[16] 'A Dictionary of Organic Compounds,' ed. I. M. Heilbron, Oxford University Press, 1965.

Hydrolysis of methyl trichadenate A (3i). Methyl trichadenate A (0.015 g) was refluxed for 15 h with potassium hydroxide (0.5 g) and ethylene glycol (5 ml). The product was diluted with water, acidified with dilute hydrochloric acid, and extracted with diethyl ether. Evaporation gave trichadenic acid A (0.010 3 g), m.p. 291—293° (from light petroleum), $[\alpha]_D^{26}$ +25.3° (in $CHCl_3$).

Esterification of acetyltrichadenic acid A (3d). *O*-Acetyltrichadenic acid A (0.020 g) with an excess of diazomethane gave the *methyl ester* (3j) (0.018 g) as white crystals, m.p. 225—226° (from methanol), $[\alpha]_D^{26}$ +14.90° (in $CHCl_3$), R_F 0.62 (benzene); M^+ 514; $\nu_{max.}$ (Nujol) 1 727 (CO_2Me); *m/e* 514(10%), 499(1), 482(18), 467(4), 454(8), 439(4), 422(2), 395(4), 386(9), 363(100), 330(2), 317(6), 303(9), 259(11), 231(8), 218(9), 203(10), 189(12), 175(13), 152(22), 123(11), 119(16), 105(14), 81(46), and 69(52).

Oxidation of trichadenic acid A (3b). Oxidation of trichadenic acid A (0.050 g) with chromic acid (0.025 g) in pyridine (7.5 ml) at room temperature overnight yielded trichadonic acid (3a) (0.043 g), white crystals, m.p. 245—246° (from methanol), $[\alpha]_D^{26}$ +3.0° (m $CHCl_3$), identical with the natural trichadonic acid (mixed m.p., i.r. spectra, and t.l.c.). With diazomethane it gave methyl trichadonate (3g), m.p. 182—183°, identical with the ester prepared from the natural acid.

Reduction of trichadonic acid (3a) *with sodium borohydride*. Trichadonic acid (0.030 g) in ethanol–water (9 : 1; 10 ml) and 40% potassium hydroxide (2 ml) was refluxed for 3 h with sodium borohydride (0.050 g). The solution was cooled, diluted with water, and extracted with diethyl ether. The product was chromatographed on a column of silica gel (4 g). Elution with chloroform–benzene (1 : 3) gave trichadenic acid B (3c) (0.004 g), m.p. 333—335°, $[\alpha]_D^{26}$ +40.0° (in C_5H_5N), R_F 0.40 [methanol–light petroleum (1 : 19)]; $\nu_{max.}$ (KBr) 1 689 (CO_2H) and 3 420 cm^{-1} (OH); *m/e* 458(9%), 440(33), 425(27), 307(100), 290(36), 260(21), 204(27), 189(27), 175(36), 165(33), 148(42), and 123(42), identical with the hydrolysis product of natural *O*-acetyltrichadenic acid B and with trichadenic acid B from *Hydnocarpus octandra* Thw.[10] bark.

Further elution of the column with chloroform–benzene (3 : 1) gave trichadenic acid A (3b) (0.019 g), m.p. 292—293° $[\alpha]_D^{26}$ +25.3° (in $CHCl_3$), identical with natural trichadenic acid A.

Huang Minlon reduction of trichadonic acid (3a). Trichadonic acid (0.040 g), sodium hydroxide (0.050 g), hydrazine hydrate (99—100%) (0.5 ml), and ethylene glycol (5 ml) were refluxed at 170—180° for 2 h. The mixture was then concentrated and refluxing was continued for another 2 h, with the mixture temperature kept at 200—205 °C. The mixture was cooled, acidified with dilute hydrochloric acid, and extracted with diethyl ether. The crude product was chromatographed on a column of silica gel (2.5 g). Elution with benzene gave *deoxytrichadonic acid* (3l) (0.028 g) as white crystals (from methanol), m.p. 291—292°, $[\alpha]_D^{26}$ +4.2° (in $CHCl_3$), M^+ 442; $\nu_{max.}$ (KBr) 1 690 (CO_2H) and 3 420 cm^{-1} (OH); *m/e* 442(26%), 427(28), 397(28), 371(20), 303(24), 291(100), 253(30), 239(40), and 205(28); *methyl ester* (3m) (with diazomethane), white crystals (from methanol), m.p. 180—181°, $[\alpha]_D^{26}$ −21.9° R_F 0.78 (benzene); $\nu_{max.}$ (KBr) 1 728 cm^{-1} (CO_2Me).

Mesylation of trichadenic acid A (3b). Trichadenic acid A (0.020 g) in dry pyridine (3 ml) was treated with methanesulphonyl chloride (0.5 ml) and left overnight at room temperature. The product was diluted with water, extracted with diethyl ether, and worked up as usual to give the *O*-mesyl derivative (3f) as white crystals (0.017 g) (from light petroleum), m.p. 201—202°, R_F 0.5 ($CHCl_3$), $\nu_{max.}$ (KBr) 1 700 cm^{-1} (CO_2H).

Attempted lactonisation of trichadenic acid A (3b). Trichadenic acid A (3b) (0.020 g) in diethyl ether (5 ml) was shaken with 25% sodium hydroxide (2 ml). The insoluble sodium salt was separated and dried at room temperature. The sodium salt (0.016 g), anhydrous sodium carbonate (1.0 g), n-pentane (250 ml), and mesyl chloride (0.5 ml) were stirred for 2 days at room temperature. Sodium hydroxide (2 pellets) was then added and the mixture stirred for another 3 days. The product was diluted with water and extracted with diethyl ether. The product, m.p. 200—202°, was identical with the mesyl derivative of trichadenic acid A.

Attempted lactonisation of trichadenic acid B (3c). The sodium salt of trichadenic acid B (0.020 g) on treatment as above gave white crystals of a dehydrated trichadenic acid B (0.011 g), m.p. 135—136° (from light petroleum), $[\alpha]_D^{26}$ +45.0° (in $CHCl_3$); R_F 0.52 (chloroform); M^+ 440; $\nu_{max.}$ (KBr) 1 705 cm^{-1} (CO_2H); *m/e* 440(20%), 395(8), 375(5), 335(100), 317(15), 259(20), 205(13), 191(15), 189(14), and 175(15).

Isolation of O-*acetyltrichadenal* (2b) (3β-*acetoxyfriedelan*-26-*al*). Fraction A_1 (1.6 g) was chromatographed on a column of silica gel (75 g). Elution with diethyl ether–light petroleum (1 : 19) gave O-*acetyltrichadenal* (2b) (0.075 g, 0.001%) as white needles (from light petroleum), m.p. 246—247°, $[\alpha]_D^{26}$ +13.0° (in $CHCl_3$), R_F 0.50 (chloroform), responding to a Liebermann–Burchard test for a terpenoid (Found: C, 78.95; H, 11.2%; M^+, 484. $C_{32}H_{52}O_3$ requires C, 79.35; H, 10.9%; *M*, 484); $\nu_{max.}$ (Nujol) 882, 895, 948, 980, 1 020, 1 045, 1 146, 1 164, 1 172, 1 226, 1 248, 1 380, 1 390, 1 460, 1 702 (CHO), and 1 736 cm^{-1} (OAc); τ ($CDCl_3$; 100 MHz) −0.01 (1 H, s, tert. CHO), 5.10 (1 H, m, $W_{1/2}$ 8 Hz, C*H*·OAc), 7.95 (3 H, s, Ac), 8.04—8.79 (CH_2), 8.82 (3 H), 8.90 (3 H), 9.05 (3 H), 9.10, and 9.12 (9 H, 6 tert. Me), and 9.22 (3 H, d, *J* 7 Hz, sec. Me); *m/e* 484(8%), 469(5), 424(10), 395(32), 359(5), 333(80), 315(15), 273(100), 255(75), 205(65), 189(40), 123(80), and 121(80).

Hydrolysis of O-*acetyltrichadenal* (2b). Hydrolysis of *O*-acetyltrichadenal (0.030 g) gave trichadenal (2c) (0.025 g) as white needles (from light petroleum), m.p. 300—301°, $[\alpha]_D^{26}$ +8.7° (in $CHCl_3$), R_F 0.46 (chloroform); $\nu_{max.}$ (Nujol) 1 702 (CHO) and 3 480 and 3 625 cm^{-1} (OH), identical with natural trichadenal. Acetylation gave *O*-acetyltrichadenal, m.p. 246—247°.

Oxidation of trichadenal (2c). Oxidation of trichadenal with chromic acid (0.010 g) in pyridine (2 ml) at room temperature overnight gave *trichadonal* (2a) (3-*oxofriedelan*-26-*al*) (0.007 g) as white needles (from light petroleum), m.p. 224—225°, $[\alpha]_D^{27}$ −27.0° (in $CHCl_3$), R_F 0.61 (chloroform), M^+ 440; $\nu_{max.}$ (KBr) 1 703 (CHO) and 1 716 cm^{-1} (CO); *m/e* 440(M^+, 13%), 411(13), 315(6), 289(100), 271(28), 231(4), 221(6), 205(22), 191(16), and 179(12).

Huang Minlon reduction of trichadonal (2a). Trichadonal (0.015 g), sodium hydroxide (0.040 g), hydrazine hydrate (99—100°; 0.5 ml), and ethylene glycol (4 ml) were refluxed as above and yielded friedelane (1a) (0.008 g), m.p. 246—247° (from light petroleum) (lit.,[9] 246—247°), $[\alpha]_D^{26}$ +18.4° (in $CHCl_3$) (lit.,[9] $[\alpha]_D$ +18.7°), M^+ 412; $\nu_{max.}$ (Nujol) 915, 975, 1 000, 1 050, 1 090, 1 122, 1 153, 1 185, 1 265, 1 302, 1 365, 1 385, and 1 455 cm^{-1}, identical with an authentic sample.

Isolation of O-*acetyltrichadenic acid B* (3e) (3β-*acetoxy*-

friedelan-26-oic acid). Further elution of column containing the solid A_1 with diethyl ether–light petroleum (1 : 9) gave O-*acetyltrichadenic acid B* (3e) (0.185 g) (0.003 %) as white needles (from light petroleum), m.p. 267—268°, $[\alpha]_D^{26}$ +56.0° (in $CHCl_3$), R_F 0.55 (chloroform) (Found: C, 76.8; H, 10.35%; M^+, 500. $C_{32}H_{52}O_4$ requires C, 76.8; H, 10.4%; *M*, 500); $\nu_{max.}$ (Nujol) 828, 895, 982, 993, 1 021, 1 041, 1 090, 1 105, 1 132, 1 150, 1 168, 1 270, 1 370, 1 380, 1 460, 1 695 (CO_2H), 1 725 (OAc), and 3 340 cm^{-1}; τ($CDCl_3$; 100 MHz) 5.11 (1 H, m, $W_{1/2}$ 5 Hz, C*H*·OAc), 7.98 (3 H, s, Ac), 8.08—8.72 (CH_2), and 8.78—9.22 (21 H, 7 Me); *m/e* 500(3%), 482(10), 440(77), 425(45), 395(20), 349(100), 316(56), 289(60), 272(44), 259(32), 205(43), 203(45), 189(46), and 175(66), identical with acetylation product of trichadenic acid B isolated from *Hydnocarpus octandra* Thw. The acetate (3e) was hydrolysed to give trichadenic acid B (3c) (0.032 g), m.p. 333—335°, $[\alpha]_D^{26}$ +39.0° (pyridine), identical with trichadenic acid B isolated from *Hydnocarpus octandra* Thw. The acid (3c) gave an acetate, m.p. 266—267°, identical with isolated *O*-acetyltrichadenic acid B.

Oxidation of trichadenic acid B. Oxidation of trichadenic acid B (0.015 g) with chromic acid (0.015 g) and pyridine (1 ml) at room temperature overnight gave trichadonic acid (3a) (0.011 g), m.p. 245—246°, $[\alpha]_D^{26}$ +28° (in $CHCl_3$), identical with natural trichadonic acid.

Esterification of O-*acetyltrichadenic acid B* (3e). *O*-Acetyltrichadenic acid B (0.020 g) was converted with diazomethane into *methyl* O-*acetyltrichadenate B* (3k) (0.019 g), white needles, m.p. 209—210° (from MeOH), $[\alpha]_D^{26}$ +46.8° (in $CHCl_3$), R_F 0.75 (chloroform–benzene, 3 : 1), M^+ 514; $\nu_{max.}$ (Nujol) 1 726 (OAc) and 1 735 cm^{-1} (CO_2Me); *m/e* 514(10%), 499(1), 482(18), 467(4), 454(8), 439(4), 422(2), 395(4), 386(9), 363(100), 317(6), 303(9), 259(11), 203(10), 189(12), 175(13), 152(22), 123(11), 119(16), 81(46), and 69(52).

Isolation of friedelan-3α-yl acetate (1e). The solid E (0.250 g) on chromatography on a column of silica gel (10 g) with diethyl ether–light petroleum (2 : 98) gave the acetate (1e) (0.018 g, 0.003%), m.p. 313—314° (from light petroleum) (lit.,[5] 314—316°). It was hydrolysed to friedelan-3α-ol (1d), m.p. 300—302° (from light petroleum), $[\alpha]_D^{26}$ +17.9° ($CHCl_3$) (lit.,[5] m.p. 292—301°, $[\alpha]_D$ +18°). Each compound was identical with an authentic sample.

Isolation of trichadenal (2c) (*3β-hydroxyfriedelan-26-al*). Further elution of the above column with diethyl ether–light petroleum (8 : 92) gave *trichadenal* (2c) (0.040 g, 0.006%), shiny needles (from light petroleum), m.p. 300—301°, $[\alpha]_D^{26}$ +8.7° R_F 0.46 (chloroform) (Found: C, 81.55; H, 11.6%; M^+, 442. $C_{30}H_{50}O_2$ requires C, 81.45; H, 11.3%; *M*, 442); $\nu_{max.}$ (Nujol) 918, 947, 982, 1 000, 1 021, 1 046, 1 085, 1 127, 1 180, 1 205, 1 222, 1 235, 1 310, 1 320, 1 370, 1 391, 1 453, 1 702, 2 880, 2 950, 3 480, and 3 625 cm^{-1}; τ($CDCl_3$; 100 MHz) 7.28 (1 H, t, *J* 3.3 Hz, 3-H), 7.80—8.72 (CH_2), and 8.79—9.07 (21 H, 7 Me) (not scanned below 0.00); *m/e* 442(9%), 424(15), 413(12), 395(15), 291(100), 273(82), 255(25), 205(70), 191(55), and 162(42), identical with the hydrolysis product of *O*-acetyltrichadenal. It gave an acetate (2b), m.p. 246—247°, identical with natural *O*-acetyltrichadenal.

Reduction of O-*acetyltrichadenal* (2b) *with lithium aluminium hydride*. A mixture of *O*-acetyltrichadenal (0.015 g), lithium aluminium hydride (0.025 g), and dry ether (3 ml) was refluxed for 5 h. The usual work-up gave friedelane-3β,26-diol (2d) as white crystals (0.008 6 g), m.p. 309—310° (from light petroleum), $[\alpha]_D^{26}$ +13.5° (in $CHCl_3$), R_F 0.61 (methanol–chloroform, 4 : 96); $\nu_{max.}$ (KBr) 3 490 and 3 640 cm^{-1} (OH); *m/e* 413(100%, M^+ − 31), 395(61), 341(17), 247(24), 231(31), 219(8), 217(17), 205(60), 199(59), 189(32), 179(44), 177(25), 165(24), 163(22), 149(16), 136(16), 134(16), 123(28), 109(72), 95(62), and 81(36).

Oxidation of trichadenal with an excess of chromic acid. Oxidation of trichadenal (0.015 g) with chromic acid (0.020 g) and pyridine (2 ml) at room temperature for 2 days gave a mixture of two products, separated on a u.v.-active preparative plate of silica gel with chloroform. The less polar compound (0.006 g) was identical with trichadonal (2a). The more polar (0.002 g) was trichadonic acid (3a).

Modified Wolff–Kishner reduction of O-*acetyltrichadenal* (2b). A mixture of *O*-acetyltrichadenal (0.015 g), hydrazine hydrate (0.2 ml), sodium ethoxide [sodium (0.20 g) in ethanol (3 ml)] was heated at 180 °C for 8 h. The usual work-up gave epifriedelinol (1c) (0.008 g), m.p. 282—283° (from light petroleum), $[\alpha]_D^{26}$ +23.9° (in $CHCl_3$) (lit.,[5] 283—285°, $[\alpha]_D$ +24°), identical with an authentic sample.

Isolation of O-*acetyltrichadenic acid A* (3d). Fraction D (1.6 g) was chromatographed on a column of silica gel (50 g). Elution with benzene gave a white solid (D_1) (1.1 g). This solid was rechromatographed on a column of neutral alumina (45 g). Elution with diethyl ether–light petroleum (1 : 9) gave O-*acetyltrichadenic acid A* (0.045 g) (0.000 7%), m.p. 251—225° (from light petroleum), $[\alpha]_D^{26}$ +28.0° (in $CHCl_3$), R_F 0.77 (chloroform), M^+ 500; $\nu_{max.}$ (KBr) 810, 860, 918, 949, 975, 1 042, 1 060, 1 145, 1 187, 1 250, 1 365, 1 395, 1 465, 1 687, 1 742, 2 875, 2 950, and 3 220 cm^{-1}; τ($CDCl_3$; 100 MHz) 5.34 (1 H, m, $W_{1/2}$ 20 Hz, 3-H), 7.98 (3 H, s, OAc), 8.08—8.71 (CH_2), 8.78, 8.84, 8.99, 9.03, 9.14 and 9.16 (6 × 3 H, s, Me), and 9.23 (3 H, d, *J* 7 Hz, sec. Me); *m/e* 500(3%), 482(10), 440(77), 425(45), 395(20), 349(100), 316(56), 289(60), 272(44), 259(32), 205(43) 203(45), 189(46), and 175(60), identical with acetylated trichadenic acid A. On hydrolysis it gave trichadenic acid A (3b) (0.075 g), m.p. 292—293°, identical with an authentic sample.

Isolation of trichadonic acid (3a). Further elution of the column containing fraction D with diethyl ether–light petroleum (13 : 87) gave *trichadonic acid* (0.080 g) (0.002%), white crystals, m.p. 245—246° (from light petroleum), $[\alpha]_D^{26}$ +3.0° (in $CHCl_3$), R_F 0.24 (chloroform) (Found: C, 79.1; H, 10.6%; M^+, 456. $C_{30}H_{48}O_3$ requires C, 79.15; H, 10.55%; *M*, 456); $\nu_{max.}$ (KBr) 968, 1 077, 1 140, 1 192, 1 263, 1 270, 1 365, 1 385, 1 392, 1 455, 1 685, 1 716, 2 270, 2 450, and 3 410 cm^{-1}; τ($CDCl_3$; 100 MHz) 7.50—7.87 (3 H, m, CH_2·CO·CH), 7.87—8.72 (CH_2), 8.76, 8.84, 8.91, 9.02, and 9.26 (6 × 3 H, s,), and 9.10 (3 H, d, *J* 8 Hz, sec. Me); *m/e* 456(5%), 438(17), 423(19), 395(40), 391(27), 325(30), 305(100), 287(36), 273(27), 259(90), 205(24), 109(33), 137(67), and 123(98), identical with the oxidation product of trichadenic acids A and B. Trichadonic acid (0.030 g) with diazomethane gave *methyl trichadonate* (3g) (0.030 g) as white needles, m.p. 182—183° (from light petroleum), $[\alpha]_D^{26}$ +5.2° (in $CHCl_3$) (Found: C, 79.3; H, 10.7%; M^+, 470. $C_{31}H_{50}O_3$ requires C, 79.6; H, 11.05%; *M*, 470); $\nu_{max.}$ (Nujol) 1 707 (CO) and 1 727 cm^{-1} (CO_2Me); τ($CDCl_3$; 100 MHz) 6.32 (3 H, s, OAc), 7.94—8.76 (CH_2), 8.80, 8.87, 9.01, 9.06, 9.11, and 9.29 (6 tert. Me), and 9.15 (d, *J* 6 Hz, sec. Me); *m/e* 470(14%), 455(4), 438(12), 410(7), 386(3), 385(6), 319(100), 257(54), 205(54), 191(12), and 181(12). O.r.d. in methanol: negative Cotton effect (see main text). Trichadonic acid (0.030 g), chloroform (5 ml), ethyl iodide (0.2 ml), and silver oxide (0.200 g) gave ethyl

trichadonate (3h) (0.026 g), white needles (from methanol), m.p. 165—166°, $[\alpha]_D^{26}$ +4.9° (in $CHCl_3$), R_F 0.6 (chloroform–benzene, 1 : 1); $\nu_{max.}$ (Nujol) 1 712 (CO) and 1 727 cm^{-1} (CO_2Et). Trichadonic acid (0.015 g), dry toluene (3 ml), toluene-*p*-sulphonic acid (0.010 g), and freshly distilled ethylene glycol (0.5 ml) gave *trichadonic acid ethylene acetal* (3n) (0.010 g) as white needles (from light petroleum), m.p. 313—314°, $[\alpha]_D^{26}$ +40.9° (in $CHCl_3$), R_F 0.36 (chloroform), M^+ 500; $\nu_{max.}$ (KBr) 1 712 cm^{-1} (CO_2H); *m/e* 500(85%), 485(12), 456(8), 440(6), 153(15), 123(16), 109(20), 99(100), and 81(32).

Extractives of Timber.—Powdered timber (20.2 kg) was extracted with light petroleum in a similar manner to the bark. The extract (10.2 g, 0.06%) was chromatographed on a column of silica gel (350 g). Elution with light petroleum gave a light brown liquid (8.90 g, 0.044%), n_D^{26} 1.458, *d* 0.968 g cm^{-3} at 26 °C, iodine no. 176. Further elution with benzene gave a white solid (F) (0.760 g). The solid F (0.76 g) was chromatographed on a column of silica gel (30 g) (diethyl ether–light petroleum) to give *O*-acetyltrichadenal (0.018 g, 0.000 1%), β-sitosterol (0.560 g, 0.002%), and *O*-acetyltrichadenic acid B (0.035 g, 0.000 2%), identical with authentic samples.

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