Chemical Investigation of Ceylonese Plants. Part XVI.† Extractives of *Calophyllum cordato-oblongum* Thw. (Guttiferae)

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From the bark of *Calophyllum cordato-oblongum* Thw. the new resin acid, cordato-oblongic acid (Ia) was isolated and identified as 3-(6,7-dihydro-5-hydroxy-2,2,*trans*-7,8-tetramethyl-6-oxo-2*H*,8*H*-benzo[1,2-*b*:5,4-*b*']-dipyran-10-yl)butyric acid. The timber extract contained the known xanthones 2-hydroxyxanthone (VIII), scriblitifolic acid (X), 1,5,6-trihydroxyxanthone (VIIb), 1,6-dihydroxy-5-methoxyxanthone (VIIa), and jacareubin (XV), and the two new xanthones 3-hydroxy-4-methoxyxanthone (IXa) and cordato-oblonguxanthone (XIII) {identified as 1,2-dihydro-6-hydroxy-3,3-dimethylpyrano[2,3-*a*]xanthen-12(3*H*)-one}. Friedelin and β-sitosterol were isolated from both extracts.

RESULTS of the investigation of four indigenous *Calophyllum* species have been reported in two earlier Parts of this series;[1,2] the present paper reports our results on the rare species *Calophyllum cordato-oblongum* Thw. (Guttiferae).

Bark Extractives.—The cold extract of the bark was first separated into acidic and neutral fractions by washing with sodium carbonate solution. From the neutral fraction friedelin[3] and β-sitosterol were separated on a silica gel column. Separation of the acidic fraction in a similar manner gave a yellow solid (3.4%), $[\alpha]_D^{27}$ −148.8° ($CHCl_3$), $C_{20}H_{24}O_6$. The i.r. spectrum showed absorption at 1 645 cm^{-1} for a chromanone type of carbonyl group[4] and at 1 710 cm^{-1} for a carboxy-group, and the substance was readily converted into a methyl ester ($\nu_{max.}$ 1 740 cm^{-1}) with diazomethane. It was similar to resin acids obtained from other *Calophyllum* species, and was named cordato-oblongic acid (Ia). Its u.v. data were very similar to those of blancoic acid[5] (Ie) and apetalic acid[6] (II) (Table 1). The n.m.r. spectrum showed no aromatic proton signals. A signal at τ −2.36 indicated the presence of a chelated OH. Two doublets at τ 3.41 and 4.55 (*J* 10 Hz) suggested the presence of a chromen system. Signals at τ 5.91 (m) and at 7.50 (m)

† Part XV, S. P. Gunasekera, S. S. Selliah, and M.U.S. Sultanbawa, *J.C.S. Perkin I*, 1975, 1539.

[1] R. Somanathan and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1972, 1935.

[2] M. Dahanayake, I. Kitagawa, R. Somanathan, and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1974, 2510.

[3] S. P. Gunasekera and M. U. S. Sultanbawa, *Proc. Ceylon Assoc. Adv. Sci.*, 1973, **29**, 132.

[4] E. Guerreiro, G. Kunesch, and J. Polonsky, *Phytochemistry*, (*a*) 1971, **10**, 2139; (*b*) 1973, **12**, 185.

[5] G. H. Stout and K. D. Sears, *J. Org. Chem.*, 1968, **33**, 4185.

[6] T. R. Govindachari, D. Prakash, and Viswanathan, *Tetrahedron*, 1968, **24**, 6411.

were attributed to 8-H and 7-H of a dimethylchromanone system as in (Ia) (Table 2).

Comparison of the 8-H and 8-Me signals and the $J_{7,8}$ value (10 Hz) for cordato-oblongic acid with those reported for other resin acids (see Table 3) showed that

TABLE 1

U.v. data [$\lambda_{max.}$/nm (log ε)]

Blancoic acid (Ie) (95% EtOH)	Apetalic acid (II) (EtOH)	Cordato-oblongic acid (Ia) (EtOH)
	227 (4.03)	227 (4.03)
255sh		
267 (4.60)	268 (4.52)	268 (4.52)
275 (4.62)	276 (4.53)	276 (4.56)
300 (4.05)	301 (4.00)	302 (4.02)
312 (4.07)	315 (4.03)	314 (4.06)
365 (3.33)	368 (3.37)	364 (3.32)

8-H and 7-H were *trans*-coupled as in methyl isoapetalate [4a] (Id), papuanic acid [7] (Va), and methyl chaplierate [4a] (If). The multiplet at τ 6.22 indicated the presence of a benzylic proton (β-H) coupled by the adjacent protons of the methylene group and of the β-methyl group. The signal for the two α-protons appeared as a multiplet (two prominent doublets) centred at τ 7.27 (2H) owing to the presence of an asymmetric centre at the adjacent β-position. The 7-H signal appeared at τ 7.50 as a multiplet due to coupling with 7-Me and 8-H. Absence of signals for any other aliphatic protons showed the absence of any aliphatic side chain, as in the case of blancoic acid [5] (Ie) or isoapetalic acid [4a] (Ic). The signals at τ 8.58 and 8.62 (two singlets) were assigned to chromen *gem*-methyl groups by comparison with isoapetalic acid (Ic). The two chromanone methyl signals appeared as two doublets at τ 8.51 (J 6.5 Hz, 8-Me) and 8.73 (J 7 Hz, 7-Me). The only other doublet present, at τ 8.82 (J 7 Hz), was attributed to the methyl group attached to the β-carbon atom.

The n.m.r. data discussed do not distinguish between the structure (Ia) in which the chromen system is linearly fused and any other angularly fused isomer such as (IIIb). Therefore the acetate of cordato-oblongic acid was prepared and the shifts [1] of the 4-H and 3-H n.m.r. signals on acetylation were observed (Table 4). The diamagnetic shift observed in the acetate of (Ia) for 4-H and the paramagnetic shift for 3-H indicated the linear fusion of the chromen system. This was further proved by the fact that all attempts to cyclise compound (Ia) with (*a*) acetic anhydride–pyridine or (*b*) dicyclohexylcarbodi-imide [7] in methylene chloride were unsuccessful. Hence cordato-oblongic acid was the structure (Ia). The o.r.d. curve of the acid in methanol (see Figure) was complex, and no definite conclusion could be drawn about the absolute configuration at C-7 and -8.

TABLE 2

N.m.r. data (τ values; J in Hz)

	Cordato-oblongic acid (100 MHz; $CDCl_3$)	Apetalic acid (100 MHz; $CDCl_3$)	Methyl cordato-oblongate (100 MHz; $CDCl_3$)	Methyl isoapetalate (60 MHz; $CDCl_3$)
8-H	5.91 (1 H, m, $J_{8,7}$ 10, $J_{8,8\text{-Me}}$ 6.5)	5.52 (1 H, m, J 3, $J_{8,8\text{-Me}}$ 3.2)	5.91 (1 H, m, $J_{8,8}$ 10, $J_{8,8\text{-Me}}$ 6.5)	5.87 (1 H, m, $J_{8,7}$ 12)
7-H	*ca.* 7.5 (1 H, m, $J_{8,7}$ 10, $J_{7,7\text{-Me}}$ 7)	*ca.* 7.52 (1 H, m)	*ca.* 7.5 (1 H, m)	*ca.* 7.5 (1 H, m)
5-OH	−2.36 (1 H, s)	−2.34 (1 H, s)	−2.45 (1 H, s)	−2.50 (1 H, s)
4-H	3.41 (1 H, d, J 10)	3.43 (1 H, d, J 10)	3.41 (1 H, d, J 10)	3.40 (1 H, d, J 10)
3-H	4.55 (1 H, d, J 10)	4.59 (1 H, d, J 10)	4.55 (1 H, d, J 10)	4.56 (1 H, d, J 10)
β-H	6.22 (1 H, m)	6.39 (1 H, m)	6.22 (1 H, m)	6.25 (1 H, m)
α-H	7.27 (2 H, m)	7.27 (2 H, m)	7.27 (2 H, m) α, β	7.30 (2 H, dd)
γ-H	8.82 (3 H, d, J 7)	8.30 (2 H, m)	8.82 (3 H, d, J 7)	
8-Me	8.51 (3 H, d, J 6.5)	8.69 (3 H, d, J 7)	8.51 (3 H, d, J 6.5)	8.52 (3 H, d, J 6.5)
7-Me	8.73 (3 H, d, J 7)	8.88 (3 H, d, J 7)	8.74 (3 H, d, J 7)	8.81 (3 H, d, J 7)
2-Me_2	8.58, 8.62 (2 × s)	8.59, 8.63 (2 × s)	8.58 (6 H, s)	8.57 (6 H, s)
CO_2Me			6.42 (3 H, s)	

TABLE 3

Comparison of n.m.r. signals (τ values; J in Hz) for H or Me at C-7 and C-8

	8-H	7-H	8-Me	7-Me
(Va) (*trans*) [7]	5.89	7.50	8.51	8.84
(VI) (*cis*) [7]	5.44	7.40	8.63	8.82
(II) (*cis*) [4a]	5.52 (m, $J_{7,8}$ 3.2)	7.52 (m)	8.67 (d, J 6.5)	8.88 (d, J 7)
(Id) (*trans*) [4a]	5.87 (m, $J_{7,8}$ 10)	7.5 (m)	8.52 (d, J 6.5)	8.81 (d, J 7)
(IV) (*cis*) [4b]	5.44 (m, $J_{7,8}$ 3.2)	7.5 (m)	8.62 (d, J 6.5)	8.82 (d, J 7)
(If) (*trans*) [4a]	5.96 (m, $J_{7,8}$ 12)	7.47 (m)	8.53 (d, J 6.5)	8.82 (d, J 7)
(Vb) (*trans*) [4b]	5.83 (m)	7.5 (m)	8.52 (d, J 6.0)	8.82 (d, J 7)

TABLE 4

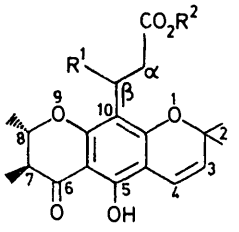
Chemical shift differences

	4-H	3-H
Cordato-oblongic acid	τ 3.41	τ 4.55
acetate	τ 3.69	τ 4.44
Diamagnetic (Δτ)	+0.28	
Paramagnetic (Δτ)		−0.11

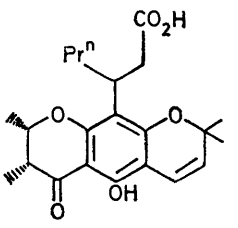
Oxidation of cordato-oblongic acid by heating with 50% nitric acid gave succinic acid. However blancoic acid (Ie) and isoapetalic acid (Ic) on oxidation in a similar manner gave (+)-pentylsuccinic acid and (+)-n-propylsuccinic acid, respectively, providing evidence of the absolute configuration at the β-carbon atom. In this case the 2β-methyl group is lost as carbon dioxide. Attempts to carry out the oxidation at room temperature

[7] G. H. Stout, G. K. Hickernell, and K. D. Sears, *J. Org. Chem.*, 1968, **33**, 4191.

over a period of weeks failed to give an identifiable product.

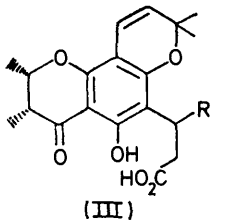


(I)



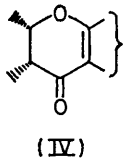
(II)

a ; R^1 = Me , R^2 = H
b ; R^1 = R^2 = Me
c ; R^1 = Pr^n, R^2 = H
d ; R^1 = Pr^n, R^2 = Me
e ; R^1 = Me$[CH_2]_4$, R^2 = H
f ; R^1 = Ph , R^2 = Me



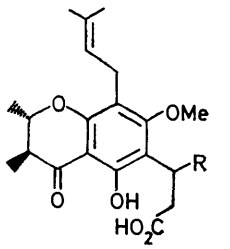
(III)

a ; R = Pr^n
b ; R = Me



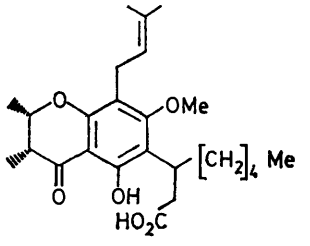
(IV)

R = Pr^n



(V)

a ; R = Me$[CH_2]_4$
b ; R = Pr^n

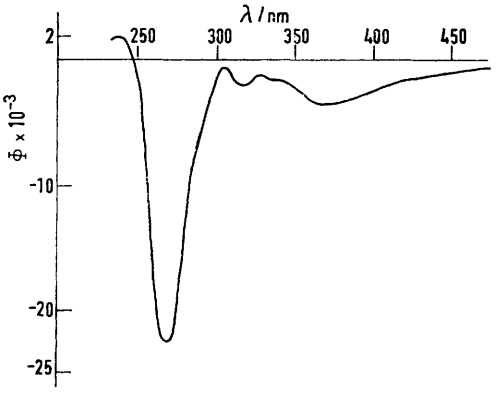


(VI)

Timber Extractives.—Material extracted into hot light petroleum was separated into acidic, phenolic, and neutral fractions by washing with sodium carbonate and sodium hydroxide solutions. The acidic fraction was separated on a column of silica gel and four yellow pigments were isolated. The least polar showed $\nu_{max.}$ 1 648 (chelated C=O) and 3 380 cm^{-1} (OH). The u.v. data were similar to those of 1,5,6-trioxygenated xanthones. The compound was identified as 1,6-dihydroxy-5-methoxyxanthone [1] (VIIa) (buchanaxanthone) by comparison with an authentic sample. The second pigment was identical with authentic 4-hydroxyxanthone [8,9] (VIII).

[8] M. O. de S. Pereira, O. R. Gottlieb, and M. Taveira Magalhaes, *Anais Acad. brasil. Cienc.*, 1966, **38**, 426.
[9] R. A. Finnigan and J. K. Patel, *J.C.S. Perkin I*, 1972, 1896.

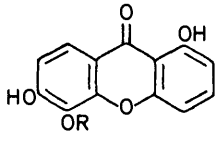
The third pigment was a new natural product (IXa). N.m.r. and i.r. spectra indicated that it was a xanthone, and the molecular weight (242) suggested that it was a monomethoxy-monohydroxy derivative. The absence of an aluminium chloride-induced shift [10] in the u.v. and



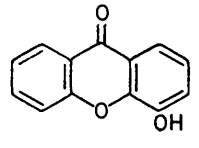
O.r.d. of cordato-oblongic acid in methanol

of a low-field signal in the n.m.r. spectrum indicated the absence of chelated OH. A sodium acetate-induced shift [11] in the higher wavelength u.v. region indicated the presence of a 3- or a 6-hydroxy-group. The n.m.r. spectrum showed two doublets with *meta*-coupling at τ 1.86 (1H) and 2.35 (1H) (*J* 8 Hz) and two triplets with *meta*-coupling at τ 2.19 (1H) and 2.57 (1H) (*J* 8 Hz), indicating that one of the xanthone rings was unsubstituted. In addition the n.m.r. spectrum showed two doublets at τ 2.21 (1H) and 3.01 (1H) (*J* 8 Hz), the former at a position appropriate for a proton *peri* to a carbonyl group. Hence these signals are assigned to H-1 and -2. A signal at τ 6.08 (3H) indicated the presence of a methoxy-group. A negative Gibbs test [12] indicated the absence of a 4-OH; hence the methoxy-group must be at position 4. Methylation with diazomethane gave the dimethoxyxanthone (IXb), m.p. 158—159°, which differed from 1,4-dimethoxyxanthone [13] (m.p. 168—169°).

The possibility of a 2,3-oxygenated system was eliminated by the absence of two singlets corresponding to H-1 and H-4 in the n.m.r. spectrum of the dimethoxyxanthone (IXb). The n.m.r. spectrum of the acetate (IXc)



(VII)



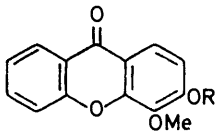
(VIII)

a ; R = Me
b ; R = H

showed paramagnetic shifts [14] of −0.14 for H-1 and −0.25 p.p.m. for H-2, indicating that the OH group is

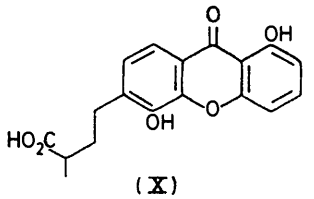
[10] J. B. Harborne, *Chem. and Ind.*, 1954, 1142.
[11] O. R. Gottlieb, M. Taveira Magalhaes, M. O. de S. Pereira, A. Lins Mesquita, D. de Barros Correa, and G. G. de Oliveira, *Tetrahedron*, 1968, **24**, 1601.
[12] F. E. King, J. T. King, and L. C. Manning, *J. Chem. Soc.*, 1957, 563.
[13] P. Arends and P. Helboe, *Dansk. Tidsskr. Farm.*, 1972, 133.

situated *ortho* to H-2. From the above data this pigment is identified as 3-hydroxy-4-methoxyxanthone (IXa).



(IX)

a ; R = H
b ; R = Me
c ; R = Ac



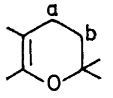
(X)

The fourth pigment was identical with authentic scriblitifolic acid [1] (X).

The neutral fraction was separated on a column of silica gel into friedelin, β-sitosterol, and a white compound, $C_{18}H_{16}O_4$. I.r. and n.m.r. data indicated that this was a xanthone and we will refer to it as cordato-oblonguxanthone (XIII). The u.v. spectrum in ethanol showed no shifts with $AlCl_3$, NaOAc, or NaOAc–H_3BO_3 indicating the absence of chelated OH, a 3- or 6-OH group, and an *ortho*-dihydroxy-system, respectively. The n.m.r. spectrum showed in the aromatic region two doublets showing *meta*-coupling at τ 1.85 (1H, *J* 8 and 1 Hz) and 2.87 (1H, *J* 8 and 1 Hz), two triplets at τ 2.31 (1H, *J* 8 and 8 Hz) and 2.46 (1 H, *J* 8 and 8 Hz), and a singlet at τ 2.32 (1H). The above data indicated that one of the rings in the xanthone nucleus is unsubstituted. In addition the n.m.r. spectrum showed a triplet at τ 6.24 (2H, *J* 7 and 7 Hz), another signal at τ 8.0 (2H), and signals at τ 8.60 and 8.67 (2 × 3H) for a *gem*-dimethyl system. The CMe_2 chemical shifts agree with a 2,2-dimethylchroman system [11,15] and not a 2,2-dimethylchromen system (Table 5). This was further supported by the absence in

TABLE 5

Comparison of n.m.r. signals (τ values) of chroman ring



	a	b	CMe_2
(XI) * ($CDCl_3$)	6.52	8.14	8.63
(XII) † ($CDCl_3$)	6.50	8.18	8.64, 8.67
(XIII) [$(CD_3)_2SO$]	6.24	8.0	8.60, 8.67
(XIVb) [$(CD_3)_2CO$]	7.30	8.11	8.62

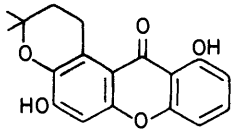
* Ref. 17. † Ref. 2.

the mass spectrum of a peak at $M - 15$ (base peak of a chromen-containing xanthone).[15,16]

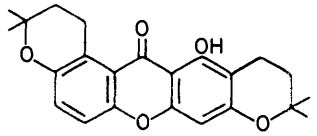
The chemical shift of the singlet at τ 2.32 indicated that it is not due to a proton at position 1 of the xanthone nucleus.[1] A negative Gibbs test [12] indicated the absence of hydrogen *para* to a hydroxy-group. From the above data cordato-oblonguxanthone must be a monohydroxy-chroman-containing xanthone, for which two structures, (XIII) and (XIVa), are possible. In structure (XIII) the benzylic CH_2 is in the deshielding region of the C=O group, whereas in structure (XIV) this is not the case. To distinguish between structures (XIII) and (XIVa), chemical shifts of the benzylic chroman ring protons in our compounds and (XIVb) were compared (Table 5). A marked difference was observed but the shift values for our material were similar to those for dihydrotovoxanthone [17] (XI) and tetrahydrothwaitesixanthone [2] (XII) (Table 5). Hence cordato-oblonguxanthone has structure (XIII).

On separation of the chloroform extract, scriblitifolic acid (X) was isolated.

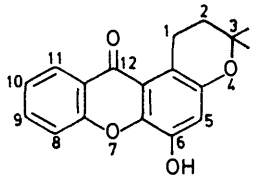
The methanol extract of the timber was re-extracted with ethyl acetate and the ethyl acetate extract was



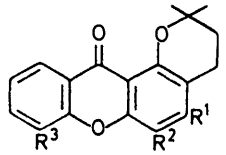
(XI)



(XII)



(XIII)

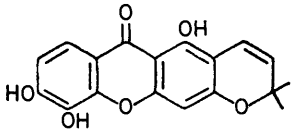


(XIV)

a ; $R^1 = R^3 = H$, $R^2 = OH$
b ; $R^2 = H$, $R^1 = R^3 = OH$

separated on a silica gel column. More scriblitifolic acid (X), jacareubin (XV), and 1,5,6-trihydroxyxanthone [1] (VIIb) were isolated, and identified by comparison with authentic samples.

4-Hydroxyxanthone (VIII) has been isolated from *C. brasilliense* Camb; [8,9] this is thus the second instance where a monohydroxyxanthone has been reported from a *Calophyllum* species. However, naturally occurring 2,4- and 3,4-dioxygenated xanthones have not been isolated



(XV)

previously from this family. The presence in this genus of two xanthones (VIII) and (IXa) without a hydroxy-group in position 1 is also significant. The xanthones isolated from this plant can be divided into the 4-oxygenated xanthone derivatives (VIII), (IXa), and (XIII) and the 1,5-dioxygenated derivatives (X), jacareubin (XV), buchanaxanthone (VIIa), and 1,5,6-trihydroxyxanthone

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(VIIb). Prenylation at positions 2 and 6 is common in this family but monoprenylation at position 1 is found only in celibixanthone [18] (XVI).

Naturally occurring xanthones with a chroman ring system are rare in this family; the only other reported is cycloguanandin [11] from *Calophyllum brasilliense* Camb.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. and i.r. spectra were obtained with a Unicam SP 8000B. and a Perkin-Elmer 257 spectrophotometer, respectively. Spectral data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 21464 (10 pp.).* Merck silica gel G was used for t.l.c. and Merck silica gel (30—70 mesh) for column chromatography. Microanalyses were carried out at the CSIRO Microanalytical Service, Melbourne. Light petroleum refers to the fraction of b.p. 60—80°.

Calophyllum cordato-oblongum Thw. was collected from Kanneliya forest near Hiniduma. The bark and timber were separated, dried, and powdered in a mill.

Bark Extractives.—The powdered bark (3.5 kg) was extracted successively with cold chloroform, hot light petroleum, and hot methanol. Evaporation gave 190 g (5.4%) of material from the chloroform, 82 g (2.3%) from the light petroleum, and 260 g (7.4%) from the methanol. The chloroform and light petroleum extracts were shown to contain the same set of compounds by t.l.c. The chloroform extract (5.0 g) was steam distilled. Work-up of the distillate gave a colourless liquid (1.30 g) (26% of the cold chloroform extract).

Alkali washing. The chloroform extract (15 g) in diethyl ether (1.5 l) was washed with cold 10% sodium carbonate solution. The sodium carbonate-soluble fraction was acidified with dilute hydrochloric acid and extracted with diethyl ether. The extracts were washed, dried ($MgSO_4$), and evaporated to give a pale yellow solid (10.2 g, 3.7%).

The sodium carbonate-insoluble fraction was washed with cold 5% sodium hydroxide solution. The sodium hydroxide-soluble fraction was worked up similarly to give a yellow solid (0.450 g), shown to be the same as the acidic fraction by t.l.c.

The neutral fraction was washed, dried ($MgSO_4$), and evaporated to give a pale yellow solid (4.3 g, 1.5%).

Isolation of friedelin and β-sitosterol. The neutral fraction (1.0 g) was separated on a column of silica gel (40 g). Elution with diethyl ether–light petroleum (3 : 97) gave a white solid, which on crystallisation from light petroleum gave white needles of friedelin (0.110 g, 0.17%), m.p. 264—265°, $[\alpha]_D^{27}$ −24.1° ($CHCl_3$) (lit.,[19] m.p. 265°, $[\alpha]_D$ −22.1°), identical with an authentic sample (mixed m.p., i.r., and t.l.c. comparison).

Further elution with diethyl ether–light petroleum (1 : 19) gave another solid which afforded white crystals of β-sitosterol (0.160 g, 0.24%), m.p. 136—137° (from light petroleum), $[\alpha]_D^{27}$ −36.5° ($CHCl_3$), identical with an authentic sample (mixed m.p., i.r., and t.l.c. comparison).

Isolation of cordato-oblongic acid. The acidic fraction (1.0 g) was separated on a column of silica gel (45 g). Elution with benzene gave 3-(6,7-*dihydro*-5-*hydroxy*-2,2-*trans*-7,8-*tetramethyl*-6-*oxo*-2H,8H-*benzo*[1,2-b:5,4-b′]*dipyran*-10-*yl*)*butyric acid* (*cordato-oblongic acid*) (Ia) (0.940 g, 3.4%) as a yellow solid, m.p. 117—118°, $[\alpha]_D^{27}$ −148.8° ($CHCl_3$), R_F 0.63 (methanol–chloroform, 2 : 98) (Found: C, 66.45; H, 6.7%; M^+, 360. $C_{20}H_{24}O_6$ requires C, 66.7; H, 6.7%; M, 360); $\lambda_{max.}$ (EtOH–$AlCl_3$) 237 (log ε 3.91), 268 (4.25), 276 (4.28), 302 (3.85), 313 (3.88), and 364 nm (3.01); $\nu_{max.}$ (Nujol) 738, 763, 792, 822, 897, 930, 960, 973, 1 011, 1 062, 1 085, 1 128, 1 150, 1 162, 1 218, 1 242, 1 245, 1 355, 1 365, 1 405, 1 465, 1 582, 1 630, 1 645, and 1 710 cm^{-1}; *m/e* 360 (100%), 345 (60), 327 (4), 319 (5), 302 (34), 284 (12), 267 (8), 260 (6), 258 (5), 244 (18), 230 (5), 224 (5), 150 (7), 149 (7), 134 (8), and 115 (12).

Acetylation of the acid (0.100 g) with acetic anhydride (1 ml) and pyridine (5 ml) at room temperature overnight and the usual work-up gave a crude product (0.10 g) which was separated on a column of silica gel (10 g). Elution with chloroform–benzene (1:9) gave the 5-*acetate** as pale yellow needles (from light petroleum) (0.085 g), m.p. 79—80°, $[\alpha]_D^{27}$ −138.0° (chloroform), R_F 0.45 (methanol–chloroform 2:98) (Found: M^+, 402.1669. $C_{22}H_{26}O_7$ requires M, 402.1678).

The acid (Ia) (0.200 g) in diethyl ether was treated with excess of diazomethane. The usual work-up gave a crude product which was separated on a column of silica gel (15 g). Elution with benzene–light petroleum (1:3) gave the *methyl ester* (Ib)* as a yellow semi-solid, $[\alpha]_D^{27}$ −141.2° (chloroform), R_F 0.90 (methanol–chloroform, 2 : 98) (Found: M^+, 374.1722. $C_{21}H_{26}O_6$ requires M, 374.1729).

The bark methanol extract on a plate of silica gel showed no characteristic compounds other than the basal brown spot.

Oxidation of Cordato-oblongic Acid (Ia).—(a) *Under reflux conditions.* Cordato-oblongic acid (5g) in 50% nitric acid (75 ml) was left at room temperature for 12 h and then heated gently on a water-bath for 2 days. The mixture was cooled and treated with sodium hydrogen sulphite to remove the excess of oxidant, and the product was extracted with ether. The extracts were washed, dried ($MgSO_4$), and evaporated to give a yellow gum (0.165 g). Crystallisation from chloroform–light petroleum (1 : 9) afforded white crystals of succinic acid (0.010 g), m.p. 183—184° (lit.,[20] 185°), identical with an authentic sample (mixed m.p., i.r., and t.l.c. comparison).

(b) *At room temperature.* Cordato-oblongic acid (5 g) in 50% nitric acid (75 ml) was shaken for 24 days. The residue (*ca.* 0.5 g) was filtered off and the filtrate was left for another 5 days at room temperature. Work-up as above gave a yellow gum (0.225 g), which was not crystallised, $[\alpha]_D^{27}$ −8.9° (EtOH). The ammonium salt of the gum was subjected to t.l.c. comparison with authentic succinic acid in 95% ethanol–water–25% ammonia (100 : 12 : 16). The plate was sprayed with Bromocresol Green indicator,[21] and warmed, and the presence of succinic acid was confirmed.

Timber Extractives.—The powdered timber (4.25 kg) was extracted successively with hot light petroleum, hot chloroform, and hot methanol. Concentration of the extracts gave a light petroleum-soluble fraction (20.0 g, 0.47%), a chloroform-soluble fraction (25.0 g, 0.6%), and a methanol-soluble fraction (60.1 g, 1.41%).

Alkali washing. The light petroleum extract (20 g) was

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

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washed with cold aqueous sodium carbonate (5%) and then with cold aqueous sodium hydroxide (5%). The neutral fraction was washed with water, dried ($MgSO_4$), and evaporated to give a pale yellow liquid (17.8 g, 0.41%). The acidic and phenolic fractions were acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the dried extracts gave the acidic fraction, a yellow solid (1.7 g, 0.04%), and the phenolic fraction (0.2 g, 4.7×10^{-3}%).

Isolation of 1,6-*dihydroxy*-5-*methoxyxanthone* (*buchanaxanthone*) (VIIa). The acidic fraction (1.7 g) was chromatographed on a column of silica gel (75 g). Elution with benzene–light petroleum (1:1) gave buchanaxanthone (0.080 g, 1.8×10^{-3}%), m.p. 244—245° (from light petroleum) (lit.,[1] 242°), R_F 0.53 (chloroform–methanol 40 : 1), M^+ 258, identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

Isolation of 4-*hydroxyxanthone* [8] (VIII). Further elution with benzene–light petroleum (17:3) gave 4-hydroxyxanthone* (VIII) (0.010 g, 2.2×10^{-4}%), m.p. 245—246° (from light petroleum) (lit.,[9] 245—246°), R_F 0.44 (chloroform—methanol, 40:1), identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

Isolation of 3-*hydroxy*-4-*methoxyxanthone* (IXa). Further elution with benzene gave 3-*hydroxy*-4-*methoxyxanthone* (IXa), pale yellow crystals (0.110 g, 2.4×10^{-3}%), m.p. 220—221° (from light petroleum), R_F 0.42 (chloroform–methanol, 40:1) (Found: C, 69.2; H, 4.25%; M^+, 242. $C_{14}H_{20}O_4$ requires C, 69.5; H, 4.15%; M, 242); $\lambda_{max.}$ (EtOH) 235 (log ε 4.47), 282 (3.97), 327 (4.19), and 370 nm (4.11); $\lambda_{max.}$ (EtOH–NaOAc) 235 (log ε 4.48), 292 (3.98), 335 (4.19), and 370 nm (3.71); $\nu_{max.}$ (Nujol) 694, 748, 793, 827, 896, 960, 1 018, 1 036, 1 068, 1 110, 1 135, 1 200, 1 230, 1 330, 1 380, 1 440, 1 596, 1 645, 2 970, and 3 200 cm^{-1}; τ [$(CD_3)_2SO$; 100 MHz] 1.86 (1H, q, J 8 and 1 Hz, 8-H), 2.19 (1H, t, J 8 and 8 Hz, 6-H), 2.21 (1H, d, J 8 Hz, 1-H), 2.35 (1H, q, J 8 and 1 Hz, 5-H), 2.57 (1H, t, J 8 and 8 Hz, 7-H), 3.01 (1H, d, J 8 Hz, 2-H), and 6.08 (3H, s, 4-OMe); Gibbs test negative; *m/e* 242 (100%), 227 (98), 213 (8), 199 (54), 171 (30), 121 (6), 115 (32), 85 (6), and 83 (10).

3,4-*Dimethoxyxanthone* (IXb). 3-Hydroxy-4-methoxyxanthone (0.025 g) in diethyl ether (20 ml) was treated with excess of diazomethane in ether. The usual work-up gave 3,4-dimethoxyxanthone* (0.023 g white crystals, m.p. 158—159° (from light petroleum), R_F 0.36 (chloroform), M^+ 256.

3-*Acetoxy*-4-*methoxyxanthone* (IXc) 3-Hydroxy-4-methoxyxanthone (0.020 g) was refluxed with acetic anhydride (0.5 ml) and pyridine (3 ml) for 0.5 h. The usual work-up gave 3-acetoxy-4-methoxyxanthone* (0.018 g), white crystals, m.p. 189—190° (from light petroleum), R_F 0.40 (chloroform), M^+ 284.

Isolation of scriblitifolic acid (X). Further elution of the column with benzene–chloroform (1 : 1) gave scriblitifolic acid [20] (1.105 g, 2.6×10^{-2}%), m.p. 165—166° (from light petroleum) (lit.,[1] 164—167°), R_F 0.25 (chloroform-methanol, 40:1), identical with an authentic sample (mixed m.p., i.r. u.v., and t.l.c. comparison).

Isolation of friedelin (1) *and* β-*sitosterol*. The neutral fraction (2.0 g) was chromatographed on a column of silica gel (60 g). Elution with light petroleum–benzene (11 : 9) gave friedelin (0.012 g, 2.5×10^{-3}%), m.p. 264—265°, and β-sitosterol (0.120 g, 2.5×10^{-2}%), m.p. 136—137°.

Isolation of cordato-oblonguxanthone {1,2-*dihydro*-6-*hydroxy*-3,3-*dimethylpyrano*[2,3-a]*xanthen*-12(3H)-*one*} (XIII). Further elution of the column with methanol–chloroform (1 : 40) gave a solid which on crystallisation from light petroleum gave white crystals of *cordato-oblonguxanthone* (0.025 g, 5.2×10^{-3}%), m.p. 244—245°, R_F 0.40 (chloroform–methanol, 40:1); $\lambda_{max.}$ (EtOH) 238 (log ε 4.48), 254 (4.63), 2.85 (3.96), 293 (3.93), and 344 nm (3.77) (no change with addition of $AlCl_3$, NaOAc, or NaOAc–H_3BO_3); $\nu_{max.}$ (Nujol) 760, 835, 910, 998, 1 058, 1 070, 1 090, 1 140, 1 158, 1 196, 1 228, 1 266, 1 347, 1 376, 1 566, 1 610, 1 648, 1 660, 2 848, 2 910, and 3 360 cm^{-1}; negative to Gibbs test; M^+ 296 ($C_{18}H_{16}O_4$); τ [$(CD_3)_2SO$; 60 MHz] 1.85 (1H, q, J 8 and 1 Hz, 8-H), 2.31 (1H, t, J 8 and 8 Hz, 6-H), 2.32 (1H, s, 3-H), 2.46 (1H, t, J 8 and 8 Hz, 7-H), 2.87 (1H, q, J 8 and 1 Hz, 5-H), 6.24 (2H, t, J 7 and 7 Hz, benzylic CH_2 of 2,2-dimethylchroman), 8.00 (2H, not clear due to solvent impurity, CH_2 of 2,2-dimethylchroman), and 8.60 and 8.67 (each 3H, s, CMe_2 of chroman); *m/e* 296 (60%), 263 (7), 238 (10), 237 (8), 227 (16), 226 (100), 225 (40), 197 (6), 139 (2), 76 (6), and 42 (12).

Chloroform extract. The chloroform extract (10 g) was washed with 10% sodium carbonate solution. The sodium carbonate soluble-fraction was acidified with dilute hydrochloric acid and extracted with ethyl acetate. Evaporation gave a dark brown solid (9.6 g, 0.56%). This (2 g) was chromatographed on silica gel (60 g). Elution with chloroform gave scriblitifolic acid, m.p. 165—166°.

Methanol extract. The methanol extract (360 g) was extracted with ethyl acetate (Soxhlet). Concentration of the extract gave a brown solid (3.5 g, 8.2×10^{-2}%). The residue on a plate of silica gel showed no characteristic compounds. The ethyl acetate extract (3 g) was chromatographed on a column of silica gel (110 g). Elution with chloroform gave scriblitifolic acid (1.6 g, 3.7×10^{-2}%) and a mixture of scriblitifolic acid and jacareubin (1.31 g). Elution with methanol–chloroform (1 : 99) gave a mixture of scriblitifolic acid and 1,5,6-trihydroxyxanthone (0.150 g).

Isolation of jacareubin (XV). The above mixture (0.200 g) was separated on a plate of silica gel [methanol–chloroform (5 : 95) × 2]. The band at R_F 0.37 was scraped off and and extracted with hot ethyl acetate; crystallisation from ethyl acetate–benzene (1:1) gave jacareubin (0.018 g, 4.2×10^{-4}%), m.p. 253—254° (lit.,[21] 254—256°), identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

Isolation of 1,5,6-*trihydroxyxanthone*[1] (VIIb). The latter mixture (0.150 g) was separated on a plate of silica gel (5%) [methanol–chloroform (1 : 19) × 2]. The band of R_F 0.35 was scraped off and extracted with methanol; concentration gave 1,5,6-trihydroxyxanthone as a brown solid (0.14 g, 3.3×10^{-4}%), m.p. 286—287° (lit.,[1] 285—286°), R_F 0.65 (chloroform–acetic acid, 5 : 1), identical with an authentic sample (mixed m.p., i.r., u.v., and t.l.c. comparison).

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