Chemical Investigation of Ceylonese Plants. Part 27.† Extractives of *Calophyllum cuneifolium* Thw. and *Calophyllum soulattri* Burm. f. (Guttiferae)

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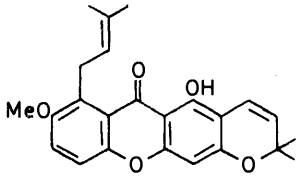
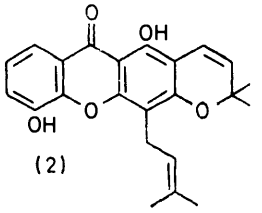
The bark and timber extractives of *C. cuneifolium* Thw. and *C. soulattri* Burm. f. have been studied. The bark extract of *C. cuneifolium* Thw. yielded calabaxanthone (1), trapezifolixanthone (2), taraxerol, simiarenol, friedelin, and a solid bark acid identified as isoapetalic acid (4a). The timber extract yielded 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone (6a), six known xanthones, and β-sitosterol. The bark extract of *C. soulattri* Burm f. gave a new coumarin alcohol, soulattrolide (13a), taraxerol, taraxerone, and β-sitosterol. The timber extract afforded four known xanthones and the trihydroxyxanthone (6a).

We have already reported studies on six endemic *Calophyllum* [1] species of the family Guttiferae. We now describe results on two other *Calophyllum* species, both now considered to be endemic to Ceylon.[2]

Calophyllum cuneifolium *Thw.—Bark extractives*. The light petroleum extract of the bark was separated into sodium carbonate-soluble and -insoluble fractions. The latter on separation on a silica gel column gave two yellow pigments, β-sitosterol, friedelin,[3] taraxerol,[4] and β-simiarenol.[5,6] The last four compounds were identical with authentic samples. β-Simiarenol was converted into its acetate and into simiarenone which were also identical with authentic samples. This is the first report of the presence of β-simiarenol in this family.[7] The two yellow pigments were identified as calabaxanthone [1a] (1) and trapezifolixanthone [1c] (2) by comparison with authentic samples.



(1)



(2)

From the sodium carbonate-soluble fraction a greenish yellow solid, m.p. 225—227°, M^+ 388, was obtained. It gave a green colouration with iron(III) chloride and showed i.r. absorption at 3 500 (OH), 1 700 (CO_2H), and 1 645 cm^{-1} (conjugated CO). The u.v. spectrum was similar to those of blancoic (3a) and apetalic acids (3b) (Table 1). It gave a crystalline methyl ester with diazomethane the n.m.r. spectrum of which was identical with that of methyl isoapetalate (4b).[8] From the above data, the compound was identified as isoapetalic acid (4a) and the structure was confirmed by comparison

TABLE 1

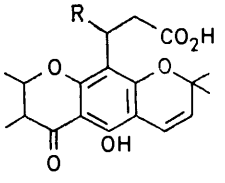
U.v. spectra [$\lambda_{max.}$ (EtOH)/nm (log ε)]

Acid m.p. 225—227°	268 (4.49)	276 (4.53)	301 (4.01)	314 (4.03)	368 (3.77)
Apetalic acid * (6b)	268 (4.49)	276 (4.53)	301 (4.40)	315 (4.03)	368 (3.37)
Blancoic acid † (6a)	267 (4.60)	275 (4.62)	300 (4.05)	312 (4.07)	365 (3.33)

* Ref. 15. † Ref. 9.

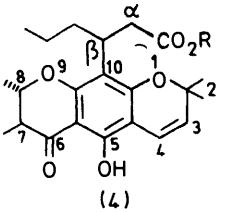
(i.r. data) of the methyl ester with authentic methyl isoapetalate [8] (4b). This ester had been reported previously as a gum,[8] the isolation of free isoapetalic acid ‡ is now reported here.

As with blancoic acid [9] (3a), oxidation of isoapetalic acid (4a) with nitric acid gave (+)-(*R*)-n-propylsuccinic acid [10] showing that the configuration at the asymmetric centre in the side chain was similar to that in blancoic acid.



(3)

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



(4)

a; R = H
b; R = Me

† Part 26, S. P. Gunasekera, M. U. S. Sultanbawa, and S. Balasubramaniam, *Phytochemistry*, 1977, in the press.

‡ This acid had been named cuneifolic acid before its structure was established (M. U. S. Sultanbawa, *J. Nat. Sci. Council of Sri Lanka*, 1973, **1**, 123]

[1] (*a*) R. Somanathan and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1972, 1935; (*b*) M. Dahanayake, I. Kitagawa, R. Somanathan, and M. U. S. Sultanbawa, *ibid.*, 1974, 2510; (*c*) R. Somanathan and M. U. S. Sultanbawa, *ibid.*, 1974, 2515; (*d*) S. P. Gunasekera and M. U. S. Sultanbawa, *ibid.*, 1975, 2215.

[2] A. J. Kostermans, personal communication.

[3] J. L. Courtney and R. M. Gascoigne, *J. Chem. Soc.*, 1956, 2115.

[4] S. Burrows and J. C. E. Simpson, *J. Chem. Soc.*, 1938, 2042.

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

[6] R. T. Alpin, H. R. Arthur, and W. H. Hui, *J. Chem. Soc.* (*C*), 1966, 1251.

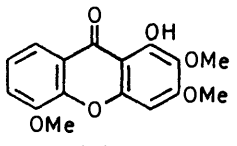
[7] S. S. Selliah, M.Sc. Thesis, University of Ceylon, 1972; S. S. Selliah and M. U. S. Sultanbawa, *Proc. Ceylon Assoc. Adv. Sci.*, 1972, **28**, 120.

[8] E. Guerreiro, G. Kunesh, and J. Polonsky, *Phytochemistry*, 1971, **10**, 2139.

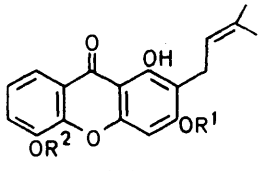
[9] G. H. Stout and K. D. Sears, *J. Org. Chem.*, 1966, **33**, 4185.

[10] (*a*) 'Dictionary of Organic Compounds,' vol. 5, Eyre and Spottiswoode, London, 1965, p. 2798; (*b*) A. Fredga, J. P. Jennings, W. Klyne, P. M. Scopes, B. Sjoberg, and S. Sjoberg, *J. Chem. Soc.*, 1965, 3928.

Timber extractives. Hot chloroform extraction of the timber gave a yellow pigment, m.p. 280—281° and a gum. The pigment gave a green colouration with iron(III) chloride and had u.v. maxima at 235 (log ε 4.49), 246 (4.42), 300 (4.26), and 359 nm (3.60) and strong i.r. absorption at 1 650 and 3 400 cm^{-1}, indicative of a xanthone structure. The n.m.r. spectrum showed signals at τ 4.69 (1 H, t), 6.61 (2 H, d), 8.20 (3 H, s), and 8.33 (3 H, s) indicating the presence of an isopentenyl side chain. The n.m.r. splitting pattern of the aromatic proton signals resembled those of 1,2,3,5-tetrasubstituted xanthone systems such as 1-hydroxy-2,3,5-trimethoxyxanthone [11] (5) or 1-hydroxy-3,5-dimethoxy-2-(3-methylbut-2-enyl)xanthone (6b), having a low field quartet at at τ 2.33 (H-8), a multiplet at τ 2.70 (H-6 and -7), and a singlet at τ 3.42. There were no methoxy-signals. Methylation of the xanthone with diazomethane gave a dimethyl ether, identical with authentic 1-hydroxy-3,5-dimethoxy-2-(3-methylbut-2-enyl)xanthone (6b); this

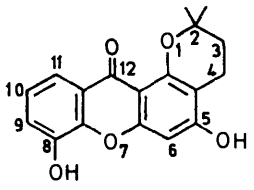


(5)



(6)

a; $R^1 = R^2 = H$
b; $R^1 = R^2 = Me$



(7)

established that the pigment was 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone (6a).

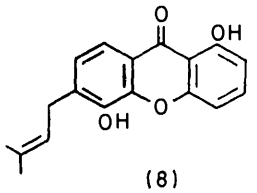
Treatment of the pigment (6a) with formic acid [12] at room temperature gave mainly the cyclised derivative (7), as shown by its n.m.r. spectrum.[13]

The benzene-soluble fraction of the chloroform extract was separated by washing with borax and sodium carbonate solutions and chromatography on silica gel into β-sitosterol, 1,5-dihydroxy-6-(3-methylbut-2-enyl)xanthone (8) (guanandin),[14] 1,7-dihydroxyxanthone (9) (euxanthone), 6-deoxyjacareubin (10a),[15] scriblitifolic acid (11),[16] and 1,6-dihydroxy-5-methoxyxanthone (12a),[17] identical with authentic samples.

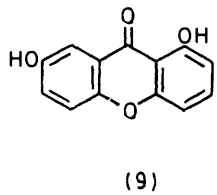
The benzene-insoluble residue on similar separation gave jacareubin [18] (10b), identical with an authentic sample.

[11] G. H. Stout and W. J. Balkenhol, *Tetrahedron*, 1969, **25**, 1947.
[12] E. D. Burling, A. Jefferson, and F. Scheinmann, *Tetrahedron*, 1965, **21**, 2653.
[13] P. J. Owen and F. Scheinmann, *J.C.S. Perkin I*, 1974, 1018; B. Jackson, H. D. Locksley, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1967, 2500.
[14] D. de Barros Correa, O. R. Gottlieb, and M. Taviera Magalhaes, *Anais Acad. brasil. Cienc.*, 1966, **38**, 296.

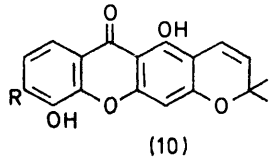
Calophyllum soulattri *Burm. f.*—*Bark extractives.* Cold light petroleum extraction gave a white solid, m.p. 201—202°, $C_{25}H_{24}O_5$, $\lambda_{max.}$ (EtOH) 233 (log ε 3.43), 287



(8)

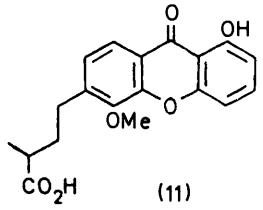


(9)

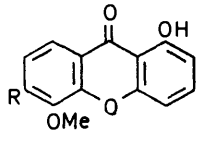


(10)

a; R = H
b; R = OH



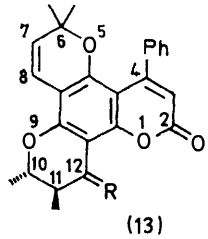
(11)



(12)

a; R = OH
b; R = H

(3.37), and 335 nm (3.08) $\nu_{max.}$ 2 479 (OH), 1 705 (αβ-unsaturated δ-lactone), and 760 and 700 cm^{-1} (monosubstituted benzene ring). These spectral data suggested that the compound was a new coumarin, and it was named soulattrolide. The mass spectrum showed the intense



(13)

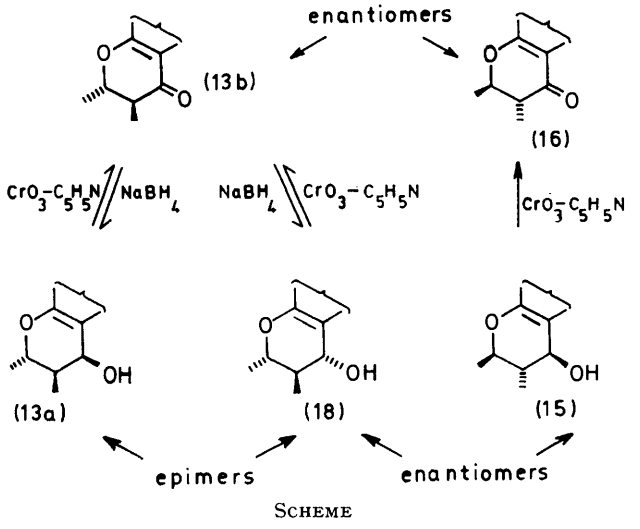
a; R = H, β = OH
b; R = O
c; R = H, β = OAc
d; R = H, β = OMe

peaks characteristic of a coumarin of the inophyllolide series: [19-21] $M - CH_3$ (*m/e* 389), $M - H_2O$ (386), $M - H_2O - CH_3$ (371), and $M - 15 - 56$ (333). These fragments suggested the presence of a secondary hy-

[15] T. R. Govindachari, D. Prakash, and N. Viswanathan, *Tetrahedron*, 1968, **24**, 6411.
[16] B. Jackson, H. D. Locklsey, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1967, 785.
[17] B. Jackson, H. D. Locksley, I. Moore, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1968, 2579.
[18] F. E. King, J. T. King, and L. C. Manning, *J. Chem. Soc.*, 1953, 3932; 1957, 563.
[19] J. Polonsky and R. Toubiana, *Compt. rend.*, 1956, **242**, 2877.
[20] S. K. Nigam, C. R. Mitra, G. Kunesch, B. C. Das, and J. Polonsky, *Tetrahedron Letters*, 1967, 2633.

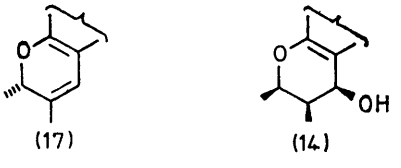
droxy-group and *gem*-dimethyl system of a chromen ring in an inophyllolide skeleton.

The n.m.r. spectrum of soulattrolide (13a) resembled



SCHEME

those of inophyllum A (14) and inophyllum B (15), two of five piscidal constituents [21,22] isolated from the leaves of *C. inophyllum* L. (Table 2). Oxidation of soulattrolide (13a) with chromic acid–pyridine gave a ketone (13b) ($\nu_{max.}$ 1 690 cm^{-1}) whose n.m.r. spectrum was identical with that of inophyllum C(16) [22] (Table 2) isolated from



the leaf of *C. inophyllum* L. Inophyllum C (16) is the (+)-form of (±)-inophyllolide isolated from the nuts of *C. inophyllum* L.[23] The i.r. spectra of the ketone (13b) and (±)-inophyllolide were identical. However the specific rotation [−45.9 ($CHCl_3$)] suggested that (13b) was the enantiomer of (+)-inophyllolide (inophyllum C), whose specific rotation has been reported to be +13° (natural product) or +54° (oxidation product of the natural alcohol, inophyllum B).[22] This discrepancy in rotation has been ascribed to the naturally occurring ketone being partially racemised.[22]

That the methyl groups at C-10 and -11 were *trans*- was evident from the values of 10.8 and 10 Hz for $J_{10.11}$ for the oxidation product (13b) and the alcohol (13a), respectively, in agreement with values recorded for such *trans*-coupling.[24,25] Therefore the ketone (13b) can be designated (−)-*trans*-inophyllolide and the alcohol soulattrolide is a diastereoisomer of inophyllum B (15) having a *cis*-configuration for the C-11 and -12 protons. This is confirmed by $J_{11.12}$ (3.2 Hz) for soulattrolide (*cf.* 7.4 Hz for inophyllum B [22,24]). (−)-*trans*-Inophyllolide (13b) on reduction with sodium borohydride gave soulattrolide (13a) (identical with natural product) and its epimer (18). The latter had the same u.v., i.r., and n.m.r. spectra as inophyllum B, with a negative specific rotation ($[\alpha]_D$ −35.3). It is therefore the enantiomer of inophyllum B (see Scheme).

Soulattrolide (13a) also gave a methyl ether (13d) without change of configuration at C-12 and a dehydration product (17) in keeping with the assignments given in the Scheme. Therefore soulattrolide is (−)-10,11-dihydro-12β-hydroxy-6,6,10α,11β-tetramethyl-4-phenyl-2*H*,6*H*,10*H*-benzo[1,2-*b*; 3,4-*b*′; 5,6-*b*″]tripyran-2-one.

The remaining gum from the light petroleum extract was separated on a column of silica gel to give taraxerone,[4] taraxerol,[4] β-sitosterol, and more soulattrolide (13a), identical with authentic samples.

Timber extractives. From the light petroleum and benzene extracts of the timber, the following compounds were isolated by silica gel chromatography: 6-deoxyjacreubin (6), 1,6-dihydroxy-5-methoxyxanthone (12a),

TABLE 2

N.m.r. data [τ values ($CDCl_3$), *J* in Hz] *

	Inophyllum C[22] (16)	Oxidation product(13b) of soulattrolide	Inophyllym A[22] (14)	Soulattrolide (13a)	Inophyllum B[22] (15)
	{(+)-*trans*-inophyllolide}	{(−)-*trans*-inophyllolide}	{(+)-*cis*-dihydroinophyllolide †}	{(−)-*trans*-dihydroinophyllolide †}	{(+)-*trans*-dihydroinophyllolide}
3-H	3.96 (1 H, s)	3.97 (1 H, s)	4.04 (1 H, s)	4.06 (1 H, s)	4.04 (1 H, s)
4-Ph	2.7 (5 H, m)	2.7 (5 H, m)	2.7 (5 H, m)	2.7 (5 H, m)	2.7 (5 H, m)
6,6-Me_2	9.02, 9.05 (6 H, s)	9.02 (6H, s)	9.06 (6 H, s)	9.07 (6 H, s)	9.07, 9.09 (6 H, s)
7-H	4.58 (1 H, d, *J* 10)	4.59 (1 H, d, *J* 10)	4.63 (1 H, d, *J* 10)	4.65 (1 H, d, *J* 10)	4.63 (1 H, d, *J* 10)
8-H	3.44 (1 H, d, *J* 10)	3.46 (1 H, d, *J* 10)	3.45 (1 H, d, *J* 10)	3.47 (1 H, d, *J* 10)	3.47 (1 H, d, *J* 10)
10-H	5.68 (1 H, m, *J* 6.6, 11.5)	5.69 (1 H, m, *J* 6.4, 10.8)	5.57 (1 H, m, *J* 7.0, 3.3)	5.69 (1 H, m, *J* 7.0, 10.0)	6.03 (1 H, m, *J* 6.8, 8.9)
11-H	7.41 (1 H, m, *J* 7.2, 11.5)	7.42 (1 H, m, *J* 7.2, 10.8)	7.73 (1 H, m)	8.22 (1 H, m, *J* 3.2, 10.0)	7.97 (1 H, m, *J* 7.0, 8.9, 7.4)
10-Me	8.44 (3 H, d, *J* 6.6)	8.46 (3 H, d, *J* 6.4)	8.57 (3 H, d, *J* 7.0)	8.56 (3 H, d, *J* 7.0)	8.53 (3 H, d, *J* 6.8)
11-Me	8.76 (3 H, d, *J* 7.2)	8.76 (3 H, d, *J* 7.2)	8.83 (3 H, d, *J* 7.2)	8.84 (3 H, d, *J* 7.2)	8.83 (3 H, d, *J* 7.0)
12-H			4.83 (1 H, d, *J* 5.4)	4.96 (1 H, d, *J* 3.2)	5.21 (1 H, d, *J* 7.4)

* (14)—(16) at 60 MHz; (13a and b) at 100 MHz. † Dihydro refers to C(12):O reduction to C(12)H(OH).

[21] K. Kawazu, H. Ohigashi, and T. Mitzui, *Tetrahedron Letters*, 1968, 2383.

[22] K. Kawazu, H. Ohigashi, M. Takanashi, and T. Mitzui, *Bull. Inst. Chem. Res. Kyoto Univ.*, 1972, **50**, 160.

[23] J. Polonsky, *Bull. Soc. chim. France*, 1957, 1079; 1958, 929.

[24] J. W. Clark-Lewis, L. M. Jackmann, and L. R. Williams, *J. Chem. Soc.*, 1962, 3858.

[25] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1969, p. 238.

1-hydroxy-5-methoxyxanthone (12b), β-sitosterol, 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone (6a), and 1,7-dihydroxyxanthone (6), identical with authentic samples. 1-Hydroxy-5-methoxyxanthone (12b) is a new natural product.

In Table 3 the metabolites isolated from these two plants are compared: products of both 1,5- and 1,7-oxygenation patterns are observed in each species. More prenylated products have been isolated from *C. cuneifolium* Thw. than from *C. soulattri* Burm f. The products differ too in the presence of a resin solid (isoapetalic acid) in the former and a coumarin (soulattrolide) in the latter.

The presence of soulattrolide in large quantities in the bark of *C. soulattri* Burm. f. is of special significance, as such 4-phenylcoumarins have been reported from the leaf and nut of *C. inophyllum* L.

Jacareubin has been isolated from 16 out of 26 *Calophyllum* species [26] that have been studied to date, and is considered to be a taxonomic marker for this genus.

TABLE 3

Amounts of compounds isolated (% based on dry weight)

	C. cuneifolium Thw.		*C. soulattri* Burm. f	
	Bark	Timber	Bark	Timber
Calabaxanthone (1)	0.08			
6-Deoxyjacareubin (10a)		0.02		0.02
1,6-Dihydroxy-5-methoxyxanthone (buchanoxanthone) (12a)		0.005		0.03
Soulattrolide (13a)			0.33	
1,7-Dihydroxyxanthone (9)		0.03		0.01
Friedelin	0.12			
Guanandin (8)		0.14		
1-Hydroxy-5-methoxyxanthone (12b)				0.05
Isoapetalic acid (4a)	0.08			
Jacareubin (10)		0.06		
1,3,5-Trihydroxy-2-(3-methylbut-2-enyl)xanthone (6a)		0.05		0.04
Scriblitifolic acid (11)		0.16		
β-Simiarenol	0.03			
β-Sitosterol	0.06	0.02	0.002	0.008
Taraxerol	0.06		0.002	
Taraxerone			0.002	
Trapezifolixanthone (2)	0.07			

The failure to isolate jacareubin from *C. soulattri* Burm. f. may be due to the presence of a powerful dehydroxylating enzyme. This view seems to be substantiated by the presence of (*a*) 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone, which could be derived from 1,3,5,6-tetrahydroxy-2-(3-methylbut-2-enyl)xanthone, the jacareubin precursor, by removal of the 6-OH; (*b*) 6-deoxyjacareubin, which could be derived from jacareubin itself or from its own precursor (6a) that has been isolated; (*c*) 1-hydroxy-5-methoxyxanthone (12b) which is reported for the first time from a plant. This may have arisen by removal of the 6-OH from 1,6-dihydroxy-5-methoxyxanthone (12a), which is present to a smaller extent in this plant than (12b).

[26] S. P. Gunsasekera, Ph.D. Thesis, University of Sri Lanka, Peradeniya Campus, 1976.

EXPERIMENTAL

U.v. spectra (solvent ethanol) were recorded with a Unicam SP 8000B spectrophotometer, and i.r. spectra with a Perkin-Elmer 257 spectrophotometer. N.m.r. and mass spectral data were obtained from the instruments at the Universities of Sheffield and Aberdeen and the Tropical Products Institute. Rotations were determined with a Bellingham and Stanley polarimeter. Analytical and preparative t.l.c. were carried out with silica gel G (Merck). Column chromatography was carried out by use of silica gel (Merck; 30—70 mesh). M.p.s were determined with a Kofler hot-stage apparatus. All R_F values refer to t.l.c. (thickness 0.25 mm). Elemental analyses were carried out at the CSIRO Microanalytical Service, Melbourne, Australia.

Calophyllum cuneifolium Thw.

Calophyllum cuneifolium Thw. was obtained from Passara (Uva Province). Bark and timber extractives were obtained separately as in earlier parts of this series.

Bark Extractives.—The bark (4.5 kg) was extracted with light petroleum (b.p. 60—80 °C) to give a brown gum (135 g, 3.0%). This gum (13 g) was dissolved in diethyl ether (1.5 l) and washed with cold 10% sodium carbonate solution. The ether layer gave a gum (A) (8.0 g, 0.18%). Acidification of the sodium carbonate solution, extraction with ether, and the usual work-up gave an acidic material (B) (4 g, 0.09%).

Friedelin and taraxerol. The gum (A) (4 g) was separated on a silica gel column (150 g). Elution with light petroleum–benzene (1 : 4) gave friedelin (0.100 g), m.p. 264° (from ethanol), $[\alpha]_D^{26}$ −21° (in $CHCl_3$) {lit.,[23] m.p. 264°, $[\alpha]_D$ −22.1° (in $CHCl_3$)}. Elution with benzene gave taraxerol (0.080 g), m.p. 279—280° (from ethanol), $[\alpha]_D^{26}$ +5° (in $CHCl_3$) (lit.,[4] m.p. 279—282°, $[\alpha]_D$ + 3°). Both compounds were identical with authentic samples (mixed m.p., i.r. spectra, and t.l.c.).

Calabaxanthone (1) *and trapezifolixanthone* (2). Further elution of the foregoing column with benzene gave calabaxanthone (0.100 g), m.p. 172° (from ethanol) (lit.,[1a] 172°); acetate, m.p. 147° (lit.,[1a] 147°). Further elution with benzene–chloroform (4 : 1) gave trapezifolixanthone (0.089 g), yellow crystals (from benzene), m.p. 171—172° (lit.,[1c] 172°). The compounds were identical with authentic samples (mixed m.p., i.r. spectra, and t.l.c.).

Isoapetalic acid (4a). The acidic gum (B) (4 g) was chromatographed on silica gel (75 g). Elution with chloroform gave *isoapetalic acid* (4a), m.p. 225—227°, $[\alpha]_D^{27}$ +18.2° ($CHCl_3$), R_F 0.5 (in $CHCl_3$) (Found: C, 68.0; H, 7.4%; M^+, 388. $C_{22}H_{28}O_6$ requires C, 68.0; H, 7.25%; M, 388); $\lambda_{max.}$ (EtOH) in Table 1; $\nu_{max.}$ (Nujol) 2 930, 1 703, 1 648, 1 623, and 1 577 cm^{-1}; τ ($CDCl_3$; 100 MHz) — 1.44 (1 H, s, 5-OH), 3.43 (1 H, d, J 10 Hz, 4-H), 4.43 (1 H, d, J 10 Hz, 3-H), 5.80 (1 H, m, 8-H), 6.28 (1 H, m, β-H), 7.25 (2 H, m, α-H), 7.32 (1 H, m, 7-H), 8.50 (3 H, d, J 7 Hz, 8-CH_3), 8.54br (4 H, CH_2·CH_2·CH_3), 8.58 (6 H, s, CMe_2), 8.82 (3 H, d, J 7 Hz, 7-CH_3), and 9.13 (3 H, t, J 7 Hz, CH_2·CH_2·CH_3); *m/e* 388, (17%), 373(100), 355(7), 345(5), 329(10), 313(10), 301(5), 299(5), 272(8), 231(3), 229(3), and 95(14).

Methylation of isoapetalic acid. Isoapetalic acid (0.100 g) in ether (5 ml) was treated with an excess of diazomethane. The usual work-up and slow evaporation of the solution gave pale yellow crystals of methyl isoapetalate (4b) (0.55 g), m.p. 82—83° (from methanol), $[\alpha]_D^{27}$ −69.1° (in $CHCl_3$)

{lit.,[8] $[\alpha]_D$ −68.3° (in $CHCl_3$)}, M^+ 402, R_F 0.80 ($CHCl_3$), $\lambda_{max.}$ (EtOH) 228 (log ε 4.01), 267 (4.42), 274 (4.63), 300 (4.02), 311 (4.07), and 362 nm (3.62); $\nu_{max.}$ (Nujol) 2 927, 1 732, 1 647, 1 627, and 1 577 cm^{-1}; τ ($CDCl_3$; 100 MHz) −2.40 (1 H, s, 5-OH), 3.40 (1 H, d, *J* 10 Hz, 4-H), 4.55 (1 H, d, *J* 10 Hz, 3-H), 5.88 (1 H, m, $J_{8,7}$ 12 Hz, 8-H), 6.27 (1 H, m, β-H), 6.45 (3 H, s, CO_2Me), 7.28 (2 H, dd, *J* 7 and 1 Hz, α-H), 7.5 (1 H, m, 7-H), 8.52 (3 H, d, *J* 6.5 Hz, 8-Me), 8.57 and 8.59 (6 H, two s, 2-Me_2), 8.81 (3 H, d, *J* 7 Hz, 7-Me), and 9.15 (3 H, t, *J* 7 Hz, $CH_2{\cdot}CH_2Me$); *m/e* 402(16%), 387(100), 371(3), 359(4), 329(10), 327(3), 299(2), 285(4), 273(3), 271(5), 257(3), 243(1), 231(2), 229(3), 189(1), 149(10), and 87(4), identical with an authentic sample (i.r. spectra).

Oxidation of isoapetalic acid. Isoapetalic acid (4.8 g) in 50% nitric acid (50 ml) was left at room temperature for 1 day and then refluxed for 5 days on a water-bath. The product was cooled, excess of sodium hydrogen sulphite was added, and the mixture was extracted with diethyl ether. The extract was dried (Na_2SO_4) and evaporated to leave an oil (0.170 g). The oil was treated with light petroleum (10 ml) and kept at 0 °C for 4 weeks to give white crystals of (+)-n-propylsuccinic acid (0.110 g), m.p. 94—95°, $[\alpha]_D^{27}$ +11.1° (in $CHCl_3$) (lit.,[10a] 93.9° $[\alpha]_D$ +9.6°) (Found: C, 52.0; H, 7.4. Calc. for $C_7H_{12}O_4$: C, 51.85; H, 7.45%).

β-*Sitosterol.* Elution of the foregoing column with chloroform afforded β-sitosterol (0.050 g), m.p. 135° (from ethanol) (lit.,[27] 136—137°), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Simiaren-3β-ol. Elution of the column with benzene–chloroform (1 : 1) gave simiaren-3β-ol (0.120 g), white cubes (from methanol), m.p. 209°, $[\alpha]_D^{26}$ +48° (in $CHCl_3$) (lit.,[6] m.p. 210°, $[\alpha]_D$ +50°), R_F 0.5 (chloroform–benzene, 1 : 4), M^+ 426; $\nu_{max.}$ (KBr) 1 650 and 3 470 cm^{-1}; acetate, m.p. 209°, $[\alpha]_D^{26}$ +68° (in $CHCl_3$) (lit.,[6] m.p. 209°, $[\alpha]_D$ +73.9°), R_F 0.5 (benzene). On oxidation with chromic acid–pyridine, it gave simiarenone, m.p. 206°, $[\alpha]_D^{26}$ +25° (lit.,[6] m.p. 207—208°, $[\alpha]_D$ +24°), R_F 0.5 (light petroleum–benzene, 1 : 3). The three compounds were identical with authentic samples.

Timber Extractives.—The timber (10.0 kg) on extraction with hot chloroform gave a yellow solid (C) (2.5 g, 0.025%) and a gum (D) (145 g, 1.45%). Hot benzene extraction of the gum (D) (50 g) left a residue (F), and removal of benzene from the solution gave a gum (E) (20 g, 0.58%). This gum (5 g) was dissolved in diethyl ether (500 ml) and washed with 10% cold aqueous borax and 10% sodium carbonate solution, successively. The ether layer gave a gum (G).

1,3,5-*Trihydroxy*-2-(3-*methylbut*-2-*enyl*)*xanthone* (6a). The yellow solid (C) (0.500 g) on repeated crystallisation from acetone gave 1,3,5-*trihydroxy*-2-(3-*methylbut*-2-*enyl*)*xanthone* (0.300 g) as a pale yellow solid, m.p. 280—281°, R_F 0.5 (chloroform–methanol, 40 : 1) (Found: C, 68.9; H, 5.15. $C_{18}H_{16}O_5$ requires C, 69.0; H, 5.15%); $\lambda_{max.}$ (EtOH) 235sh (log ε 4.49), 246 (4.42), 300 (4.26), and 359 nm (3.60); $\nu_{max.}$ (KBr) 855, 940, 1 068, 1 098, 1 125, 1 170, 1 252, 1 290, 1 310, 1 335, 1 345, 1 380, 1 405, 1 465, 1 475, 1 505, 1 580, 1 620, 1 650, and 3 400 cm^{-1}; τ [$(CD_3)_2CO$; 100 MHz] 2.33 (1 H, q, *J* 4 and 6.5 Hz, 8-H), 2.70 (2 H, m, 7- and 6-H), 3.42 (1 H, s, 4-H), 4.69 (1 H, t, *J* 7 Hz, vinyl H), 6.61 (2 H, d, *J* 9 Hz, methylene H), and 8.20 and 8.33 (6 H, two s, CMe_2).

Compound (6a) (0.100 g) in ether was treated with an excess of diazomethane; the usual work-up gave 1-hydroxy-3,5-dimethoxy-2-(3-methylbut-2-enyl)xanthone (0.075 g), m.p. 167—168° (lit.,[13] 167—170°), R_F 0.5 ($CHCl_3$), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Cyclisation of the xanthone (6a). The xanthone (0.040 g) was treated with formic acid (5 ml) at 27 °C for 15 min. The usual work-up, followed by recrystallisation from ethanol, gave 3,4-*dihydro*-5,8-*dihydroxy*-2,2-*dimethylpyrano*[3,2-a]-*xanthen*-12(2H)-*one* (7), m.p. 217—218°, R_F 0.5 (benzene–chloroform, 1 : 1) (Found: C, 69.2; H, 5.15. $C_{18}H_{16}O_5$ requires C, 69.2; H, 5.1%), $\lambda_{max.}$ (EtOH) 243 (log ε 5.48), 255(5.42), 272sh (4.24), 320 (4.20). and 350 nm (3.66); τ [$(CD_3)_2CO$; 100 MHz] 2.35 (1 H, q, *J* 3 and 6 Hz, 8-H), 2.74 (2 H, m, 7- and 6-H), 3.64 (1 H, s, 4-H), 7.30 and 8.11 (4 H, 2 t, *J* 7 Hz, chroman $CH_2{\cdot}CH_2$), and 8.52 (6 H, s, chroman CMe_2).

Guanandin (8) *and* 6-*deoxyjacareubin* (10a). The gum (G) was chromatographed on silica gel column (75 g). Elution with benzene afforded yellow plates (from benzene) of 1,5-dihydroxy-6-(3-methylbut-2-enyl)xanthone (8) (guanandin) (0.060 g), m.p. 206° (lit.,[14] 206—208°), R_F 0.83 (chloroform–methanol, 40 : 1).

Further elution of the column with benzene–chloroform (4 : 1) gave yellowish plates (from benzene) of 6-deoxyjacareubin (10a) (0.080 g), m.p. 208—210° (lit.,[13] 211—213°), R_F 0.45 (chloroform–methanol 40 : 1). Both compounds were identical with authentic samples (mixed m.p., i.r. spectra, and t.l.c.).

β-*Sitosterol.* Elution of the column with chloroform afforded β-sitosterol (0.080 g), m.p. 135—136°.

1,7-*Dihydroxyxanthone* (9). Elution of the column with chloroform–methanol (99 : 1) afforded yellow needles (from acetone) of 1,7-dihydroxyxanthone (euxanthone), m.p. 238° (lit.,[28] 238—240°), R_F 0.7 (chloroform–acetic acid, 92 : 8), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Scriblitifolic acid (11). Acidification of the borax washings and the usual work-up gave a brown solid (H) (0.400 g), which was chromatographed on silica gel (30 g). Elution with chloroform–benzene (1 : 1) afforded yellow needles (from benzene) of scriblitifolic acid (0.060 g), m.p. 164—165° (lit.,[16] 164—167°), R_F 0.25 (chloroform–methanol, 40 : 1), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

1,6-*Dihydroxy*-5-*methoxyxanthone* (*buchanoxanthone*) (12a). Acidification of the sodium carbonate washings and the usual work-up gave a gum (I) (1 g), which was chromatographed on a silica gel column. Elution with benzene afforded pale yellow needles (from acetone) of 1,6-dihydroxy-5-methoxyxanthone (12a) (buchanoxanthone) (0.030 g), m.p. 243—245° (lit.,[17] 243—246°), R_F 0.8 (chloroform–methanol, 40 : 1), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Jacareubin (10b). The residue (F) of the chloroform extract (4 g) was chromatographed on a silica gel column. Elution with chloroform–methanol (75 : 1) gave bright yellow needles (from ethanol–water) of jacareubin (10b), m.p. 253—254° (lit.,[18] 254—256°), R_F 0.5 (chloroform–acetic acid, 92 : 8), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Calophyllum soulattri Burm. f.

C. soulattri Burm. f. was obtained from Morapitiya, Kalutara District. Bark and timber extractives were obtained separately as in earlier parts of this series.

[27] Ref. 10*a*, p. 2902.

[28] T. R. Govindachari, B. R. Pai, P. S. Subramaniam, U. R. Rao, and N. Muthukumaraswamy, *Tetrahedron*, 1967, **23**, 243.

Bark Extractives.—Powdered bark (6.0 kg) was extracted with cold light petroleum to give a white solid (J) (26 g, 0.44%) and a gum (K) (110 g, 1.83%).

Soulattrolide (13a). Repeated crystallisation of the white solid (J) from methanol gave *soulattrolide*, white needles (20 g, 0.33%) m.p. 201—202°, $[\alpha]_D^{27}$ −29.6° (in $CHCl_3$), R_F 0.52 (ethyl acetate–chloroform, 1 : 9) (Found: C, 74.3; H, 6.15%; M^+, 404. $C_{25}H_{24}O_5$ requires C, 74.25; H, 6.0%; *M*, 404) (no change in u.v. pattern in the presence of $AlCl_3$, NaOAc–H_3BO_3); $\nu_{max.}$ (Nujol) 3 479, 2 930, 2 860, 1 705, 1 640, 1 590, 1 565, 1 470, 1 415, 1 372, 1 349, 1 310, 1 255, 1 230, 1 200, 1 180, 1 150, 1 140, 1 130, 1 115, 1 062, 1 022, 995, 965, 930, 880, 850, 795, 772, 760, 710, and 700 cm^{-1}; n.m.r. data in Table 2; *m/e* 404(20%), 389(62), 386(46), 371(100), 333(46), 317(3), 305(3), 202(3), 193(4), 178(16), 164(5), 115(5), 105(5), 78(6), and 42(6).

Oxidation of soulattrolide (13a). Soulattrolide (0.050 g) in pyridine (3 ml) was treated with chromium trioxide (0.020 g) and left at room temperature for 2 days. The usual work-up and removal of solvent gave a waxy solid mixture of three compounds (t.l.c.). The mixture was separated on a silica gel plate with methanol–chloroform (1 : 19) into (−)-trans-*inophyllolide* (13b) {trans-10,11-*dihydro*-6,6,10,11-*tetramethyl*-4-*phenyl*-2H,6H,12H-*benzo*[1,2-b; 3,2-b′; 5,6-b″] *tripyran*-2,12-*dione*} (0.030 g), m.p. 187—190°, $[\alpha]_D^{27}$ −45.9° (in $CHCl_3$) {lit.,[21] m.p. 188—199°, $[\alpha]_D^{20}$ +13° and +54° for enantiomer (in $CHCl_3$)} R_F 0.63 (ethyl acetate–chloroform, 1 : 9); M^+ 402; $\lambda_{max.}$ (EtOH) 257sh (log ε 4.46), 266 (4.49), and 302 nm (4.39); $\nu_{max.}$ (Nujol) 2 930, 2 860, 1 740, 1 690, 1 640, 1 600, 1 580, 1 555, 1 405, 1 380, 1 340, 1 315, 1 240, 1 195, 1 190, 1 145, 1 130, 1 089, 1 000, 955, 920, 880, 860, 835, 775, 735, and 705 cm^{-1}; n.m.r. data in Table 2; *m/e* 402(33%), 387(100), 353(2), 346(3), 331(70), 263(3), 229(2), 219(2), 189(2), 105(2), and 77(2), identical (i.r. data) with authentic (±)-*trans*-inophyllolide.

Acetylation of soulattrolide (13a). Soulattrolide (0.035 g) was acetylated with acetic anhydride–pyridine (1 : 1) (4 ml). The *acetate* (13c) (0.025 g) had m.p. 180—181° (from light petroleum), $[\alpha]_D^{27}$ −125° (in $CHCl_3$), $\nu_{max.}$ (Nujol) 1 750, 1 730, 765, and 710 cm^{-1} (Found: C, 72.35; H, 5.85. $C_{27}H_{26}O_6$ requires C, 72.65; H, 5.85%); τ ($CDCl_3$; 100 MHz) 2.7 (5 H, m, Ph), 3.46 (1 H, d, *J* 10 Hz, 8-H). 3.56 (1 H, d, *J* 4.0 Hz, 12-H), 4.04 (1 H, s, 3-H), 4.63 (1 H, d, *J* 10 Hz, 7-H), 5.84 (1 H, m, 10-H), 7.88 (3 H, s, 12-OAc), 8.04 (1 H, m, 11-H), 8.54 (3 H, d, *J* 6.2 Hz, 10-CH_3), 8.92 (3 H, d, *J* 10 Hz, 11-CH_3), and 9.04 (6 H, s, 6-Me_2).

Reduction of (−)-trans-*inophyllolide* (13b). (−)-*trans*-Inophyllolide (0.100 g) in methanol (20 ml) was treated with sodium borohydride (0.100 g) in methanol (10 ml). The mixture was stirred for 2 h, the excess of hydride was destroyed with water and the product was extracted with ether. The gum obtained on evaporation was separated on a silica gel plate with methanol–chloroform (2 : 98) into two compounds. The more polar compound on crystallisation from light petroleum yielded soulattrolide (13a) (0.016 g), m.p. 201—202°, identical with the natural compound (mixed m.p., $[\alpha]_D$, i.r., and t.l.c.). The less polar fraction was the enantiomer (18) of inophyllum B (15) [22] and was not crystallised; yield 0.032 g, $[\alpha]_D^{27}$ −35.3° (in $CHCl_3$) (lit.,[22] $[\alpha]_D$ +36° for enantiomer), R_F 0.60 (ethyl acetate–chloroform, 1 : 9), $\lambda_{max.}$ (EtOH) 233 (log ε 3.43), 278sh (3.36), 285 (3.41), and 335 nm (3.08); $\nu_{max.}$ (KBr) 865, 968, 1 058, 1 140, 1 370, 1 587, 1 645, and 1 715 cm^{-1}; τ ($CDCl_3$; 60 MHz) 2.7 (5 H, m, Ph), 3.47 (1 H, d, *J* 10 Hz, 8-H), 4.05 (1 H, s, 3-H), 4.64 (1 H, d, *J* 10 Hz, 7-H), 5.21 (1 H, d, *J* 7.4 Hz, 12-H), 6.0 (1 H, m, 10-H), 8.0 (1 H, m, 11-H), 8.53 (3 H, d, *J* 6.8 Hz, 10-CH_3), 8.83 (3 H, d, *J* 7.0 Hz, 11-CH_3), and 9.05 and 9.10 (6 H, two s, 6-Me_2); *m/e* 404 (10%), 389 (36), 371 (10), 333 (22), 317 (3), 305 (7), 178 (10), 149 (100), 115 (7), 105 (11), 85 (44), and 83 (62).

Oxidation of (−)-*Inophyllum B* (18). The product (18) (0.020 g) was oxidised with chromic oxide (0.030 g) in pyridine (5 ml) for 2 days. The usual work-up and crystallisation from light petroleum gave material (0.016 g), m.p. 188—189°, $[\alpha]_D^{27}$ −48.1° (in $CHCl_3$), identical with (−)-*trans*-inophyllolide (13b) (mixed m.p., i.r., and t.l.c.).

Dehydration of soulattrolide (13a). Soulattrolide (0.100 g) and toluene-*p*-sulphonic acid (0.010 g) in dry benzene (10 ml) were refluxed for 30 min and the product was washed with water. Removal of benzene and crystallisation from light petroleum yielded pale yellow crystals of the dehydration product (17) (0.086 g), m.p. 197—198° (lit.,[22] 198° for epimer), $[\alpha]_D$ +43.3° (in $CHCl_3$) (lit.,[22] $[\alpha]_D$ −42° for epimer), R_F 0.21 (benzene); $\lambda_{max.}$ (EtOH) 251 (log ε 4.28), 290 (4.25), 301sh (4.14), 315 (4.07), and 350 nm (3.83); $\nu_{max.}$ (Nujol) 1 650 and 1 718 cm^{-1}; τ ($CDCl_3$; 60 MHz) 2.7 (5 H, m, Ph), 3.30 (1 H, s, 12-H), 3.46 (1 H, d, *J* 10 Hz, 8-H), 4.06 (1 H, s, 3-H), 4.64 (1 H, d, *J* 10 Hz, 7-H), 5.08 (1 H, q, *J* 6.8 Hz, 10-H), 8.12 (3 H, s, 11-CH_3), 8.60 (3 H, d, *J* 6.8 Hz, 10-CH_3), and 9.07 (6 H, s, 6-Me_2); *m/e* 386 (44%), 371 (100), 357 (1), 343 (2), 193 (3), 178 (5), and 164 (3).

Methylation of soulattrolide (13a). To soulattrolide (0.100 g) in methanol (2 ml) was added one drop of 2N-hydrochloric acid and the solution was refluxed for 4 min. The product was diluted with water and extracted with ether. Removal of the solvent gave an oil which was separated on a silica gel plate with benzene–chloroform (1 : 3). The methyl ether (13d) was a gum (0.036 g), $[\alpha]_D^{27}$ −60.0° (in $CHCl_3$), R_F 0.16 (chloroform–benzene, 1 : 1), $\lambda_{max.}$ (EtOH) 233 (log ε 4.25), 278sh (4.21), 287 (4.27), and 337 nm (4.08); $\nu_{max.}$ (Nujol) 1 650 and 1 725 cm^{-1}; τ ($CDCl_3$; 60 MHz) 2.7 (5 H, m, Ph), 3.47 (1 H, d, *J* 10 Hz, 8-H), 4.05 (1 H, s, 3-H), 4.66 (1 H, d, *J* 10 Hz, 7-H), 5.39 (1 H, d, *J* 2.5 Hz, 12-H), 5.8 (1 H, m, 10-H), 6.36 (3 H, s, 12-OMe), 8.22 (1 H, m, 11-H), 8.60 (3 H, d, *J* 7 Hz, 10-CH_3), 8.84 (3 H, d, *J* 7.2 Hz, 11-CH_3), and 9.07 (6 H, s, 6-Me_2); *m/e* 418, 403, 387, 371, 348, 347, 193, 178, 149 (out of scale for intensity determination).

Taraxerone. The gum (K) (2.4 g) was chromatographed on a column of silica gel (75 g). Elution with light petroleum–benzene (4 : 6) gave taraxerone (0.025 g), m.p. 238—240° (from chloroform) (lit.,[4] 240—241°), $[\alpha]_D^{27}$ +15° (in $CHCl_3$) (lit.,[4] $[\alpha]_D$ +12.0°), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Taraxerol and β-*sitosterol*. Elution of the above column with benzene gave taraxerol (0.025 g), m.p. 276—278° (from chloroform—acetone), $[\alpha]_D^{27}$ +5°, and β-sitosterol (0.028 g), m.p. 136—137°. Elution with benzene–chloroform (3 : 1) then gave more soulattrolide (0.015 g).

Timber Extractives.—Powdered timber (8.5 kg) was extracted with cold light petroleum to give a yellow solid (L) (5.0 g, 0.05%) and a gum (M) (12.0 g, 0.14%). Similarly the benzene extract gave a yellowish brown solid (N) (12.08 g, 0.14%) and a gum (O) (10 g, 0.11%).

6-*Deoxyjacareubin* (10a) *and* 1,6-*dihydroxy*-5-*methoxyxanthone* (12a). The solid (L) (0.5 g) was chromatographed on a column of silica gel (50 g). Elution with light petroleum–benzene gave 6-deoxyjacareubin (0.05 g), m.p. 210—213°, R_F 0.85 (ethyl acetate–chloroform 1 : 9). Elution

with benzene gave 1,6-dihydroxy-5-methoxyxanthone (0.045 g), m.p. 241—242°.

1-*Hydroxy*-5-*methoxyxanthone* (12b). Fraction (M) (0.5 g) was chromatographed on a column of silica gel (50 g). Elution with light petroleum–benzene (3 : 1) gave 1-hydroxy-5-methoxyxanthone, m.p. 213—214° (from acetone) (lit.,[16] 214—215°), R_F 0.50 (ethyl acetate–light petroleum, 3 : 17), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

6-*Deoxyjacereubin* (10a), 1,6-*dihydroxy*-5-*methoxyxanthone* (12a), *and* β-*sitosterol*. Further elution of the column with benzene gave 6-deoxyjacareubin (0.050 g), m.p. 210—213°, 1,6-dihydroxy-5-methoxyxanthone (0.100 g), m.p. 241—242°; and β-sitosterol (0.020 g), m.p. 136—137°.

1,3,5-*Trihydroxy*-2-(3-*methylbut*-2-*enyl*)*xanthone* (6a). The solid (N) (0.500 g) on repeated crystallisation from methanol–chloroform (1 : 1) gave 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone (0.300 g), m.p. 280—282°. With diazomethane in ether, it gave 1-hydroxy-3,5-dimethoxy-2-(3-methylbut-2-enyl)xanthone, m.p. 166—168°. Both compounds were identical with authentic samples (mixed m.p., i.r. spectra, and t.l.c.). The mother liquor from crystallisation of (N) formed fraction (P) (0.175 g).

1,7-*Dihydroxyxanthone* (9). Fraction (P) (0.150 g) was chromatographed on a column of silica gel (25 g). Elution with benzene–chloroform (2 : 1) gave 1,7-dihydroxyxanthone (0.020 g), m.p. 239° (from toluene), R_F 0.70 (ethyl acetate–chloroform, 1 : 9). Further elution with chloroform–methanol (1 : 1) gave 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone (0.010 g), m.p. 280—284°.

6-*Deoxyjacareubin* (10a), 1,6-*dihydroxy*-5-*methoxyxanthone* (12a), β-*sitosterol, and* 1,7-*dihydroxyxanthone* (9). The gum (O) (0.500 g) was chromatographed on a solumn of silica gel (50 g). Elution with (i) light petroleum–benzene (1 : 1) gave 6-deoxyjacareubin (0.010 g); (ii) benzene gave 1,6-dihydroxy-5-methoxyxanthone (0.020 g) and β-sitosterol (0.010 g); and (iii) benzene–chloroform (2 : 1) gave 1,7-dihydroxyxanthone (0.050 g).

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