Chemical Investigation of Ceylonese Plants. Part XV.† Extractives of *Kayea stylosa* Thw. (Guttiferae)

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From the bark extract of *Kayea stylosa* Thw., taraxerol (Ia), simiaren-3β-ol (IIa), betulinic acid (III), β-sitosterol, and the new xanthones 10-*O*-methylmacluraxanthone {12-(1,1-dimethylprop-2-enyl)-5,9-dihydroxy-10-methoxy-2,2-dimethyl-2*H*-pyrano[3,2-*b*]xanthen-6-one} (IVa) and kayeaxanthone {11-(1,1-dimethylprop-2-enyl)-9-hydroxy-8,10-dimethoxy-2,2-dimethyl-2*H*-pyrano[2,3-*d*]xanthen-7-one} (VIIIa) have been isolated and their structures established. The timber extract contained only 1,3,5-trihydroxy-2-methoxyxanthone (VIa) and β-sitosterol.

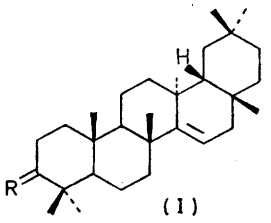
THE genus *Kayea* Wall belongs to the sub family Calophylloideae of the family Guttiferae.[1a] *Kayea stylosa* Thw. is the only species of this genus found in Ceylon and it is endemic to Ceylon.[1b] The chemistry of this genus has not been studied previously.

† Part XIV, G. Pavanasasivam and M. U. S. Sultanbawa, *Phytochemistry*, 1975, **14**, 1127.

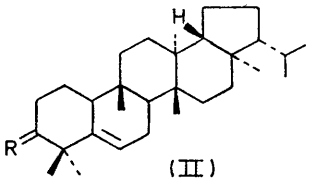
Extractives of the Bark.—The light petroleum extract of the bark gave a dark yellow resin from which a pale

1 (*a*) Appendix to J. C. Willis, 'A Dictionary of Flowering Plants and Ferns,' 7th edn., Cambridge University Press, 1966; J. Hutchinson, 'The Families of Flowering Plants,' 2nd edn., Oxford University Press, London, 1959; (*b*) W. M. Bandaranayake and M. U. S. Sultanbawa, 'List of Endemic Plants of Ceylon,' *Proc. Ceylon Assoc. Adv. Sci.*, 1969, **25**, 90.

yellow solid separated out. Chromatographic separation of the resin on a column of silica gel gave β-sitosterol, three triterpenoids, and two yellow pigments.[2] The triterpenoids have been characterised as taraxerol[3] (Ia), simiaren-3β-ol[4] (IIa), and betulinic acid[5] (III) from their m.p.s, specific rotations, and i.r., n.m.r., and mass spectra. The structures were confirmed by comparison with authentic samples (mixed m.p.s, i.r. spectra, and t.l.c.). The identity of compounds (Ia) and (IIa) was further confirmed by oxidation to the respective ketones (Ib) and (IIb) and by the preparation of acetates and comparison with authentic samples (mixed m.p.s, i.r. spectra, and t.l.c.).



a; R = H, β-OH
b; R = O



a; R = H, β-OH
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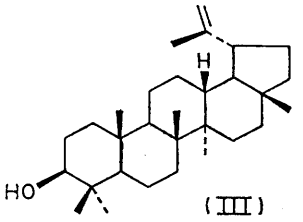


The less polar pigment of the two was purified on a silica gel plate and on crystallisation from light petroleum gave yellow needles. The C,H analysis and molecular weight (M^+ 408) agreed with the molecular formula $C_{24}H_{24}O_6$. It showed characteristic xanthone i.r. carbonyl absorption at 1 652 cm^{-1} and strong hydroxy-absorption at 3 520 cm^{-1}. The presence of a chelated carbonyl group was indicated by a bathochromic shift in the u.v. maxima on addition of aluminium chloride.[6] The u.v. data (Table 1) indicated that the pigment was a tetraoxygenated xanthone, stable to alkali, and very similar to macluraxanthone derivatives[7,8] (1,3,5,6-oxygenated).

The n.m.r. spectrum showed a signal at τ −3.58 for a chelated OH group, and two doublets at τ 2.10 and 3.04 (*J* 9.2 Hz) for two *ortho*-coupled aromatic protons. The chemical shift of the low-field doublet indicated that it could only arise from a proton *peri* to a xanthone carbonyl group, *i.e.* the 8-proton as position 1 is oxygenated. In the xanthone nucleus the adjacent position 7 must bear the other aromatic proton to account for the magnitude of the coupling constant.[9] The n.m.r. spectrum further showed two doublets (2H) at τ 2.36 (*J* 10 Hz) and 4.43 (*J* 10 Hz) and a sharp six-proton signal (two methyl groups). These signals and the characteristic coupling constant[9] indicated the presence of a 2,2-dimethylpyran system attached to the xanthone nucleus. This was confirmed by an intense $M - 15$ peak in the mass spectrum. An n.m.r. signal at τ 6.06 indicated a methoxy-group. The presence of a 1,1-dimethylprop-2-enyl side chain as in globuxanthone[10] (V) and macluraxanthone[7] (IVd) was indicated by olefinic proton signals appearing as an ABX system at τ 3.68, 5.11, and 5.16 and a CMe_2 signal at τ 8.25. The change in u.v. pattern on hydrogenation indicated that the double bond in the 2,2-dimethylpyran ring is conjugated with the xanthone system. The presence of a linearly fused dimethylpyran ring was shown by diamagnetic and paramagnetic shift differences[11] in chemical shift values of the pyran ring protons of the acetate (Table 2).

TABLE 1

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

Yellow pigment (IVa)	235 (4.22)	281 (4.57)	293 (4.49)	342 (4.15)	360 (4.27)
9,10-Di-*O*-methyl macluraxanthone (IVb)	247 (4.22)		289 (4.57)	333 (4.26)	365 (3.66)
5.9,10-Tri-*O*-methyl macluraxanthone (IVc)	245 (4.13)	275 (4.52)		321 (4.05)	350 (3.75)
Macluraxanthone (IVd)	242 (4.31)	283 (4.64)		328 (4.25)	

TABLE 2

Chemical shift differences (τ values)

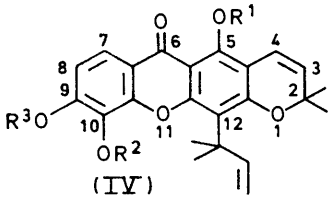
	4-H	3-H
10-*O*-Methylmacluraxanthone (IVa)	3.26	4.43
10-*O*-Methylmacluraxanthone acetate (IVe)	3.50	4.27
Diamagnetic (Δτ)	+0.24	
Paramagnetic (Δτ)		−0.16

The mass spectrum of the acetylated product showed a molecular ion at *m/e* 492 indicating a diacetate. This was supported by the presence of two acetoxy-signals at τ 7.52 and 7.63 in its n.m.r. spectrum. Thus the presence of two hydroxy-groups in the compound was confirmed.

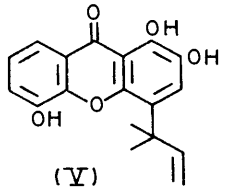
If the chelated hydroxy-group occupied position 1 of the xanthone nucleus, the linearly fused dimethylpyran must be at positions 2 and 3. A Gibbs test[12] which was

[2] S. Selliah and M. U. S. Sultanbawa, *Proc. Ceylon Assoc. Adv. Sci.*, 1971, **27**, 81.
[3] S. Burrows and J. C. E. Simpson, *J. Chem. Soc.*, 1938, 2042.
[4] R. T. Alpin, H. R. Arthur, and W. H. Hui, *J. Chem. Soc.* (*C*), 1966, 1251.
[5] A. Robertson, G. Soliman, and E. C. Owen, *J. Chem. Soc.*, 1939, 1267.
[6] J. B. Harborne, *Chem. and Ind.*, 1954, 1142.
[7] M. L. Wolfrom, F. Komitzky, G. Fraenkel, J. H. Looker, E. E. Dickey, P. McWain, and A. Thompson, *J. Org. Chem.*, 1964, **29**, 692.
[8] B. Jackson, H. D. Locklsey, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1966, 178.
[9] W. D. Ollis and I. O. Sutherland, ' Recent Developments in the Chemistry of Phenolic Compounds,' ed. W. D. Ollis, Pergamon, London, 1961, p. 74.
[10] H. D. Locksley, I. Moore, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1966, 2186.
[11] A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, *Tetrahedron Letters*, 1967, 4201.
[12] F. E. King, J. T. King, and L. C. Manning, *J. Chem. Soc.*, 1957, 563.

carried out spectrophotometrically [13] showed the absence of an absorption maximum between 500 and 700 nm, indicating that position 4 is not occupied by a hydroxy-group. That the 1,1-dimethylprop-2-enyl group was not *ortho* to the 5-hydroxy-group was shown by the resistance of the compound to cyclisation by formic acid and by dichlorodicyanobenzoquinone. On the basis of the above data, the structure (IVa) was established

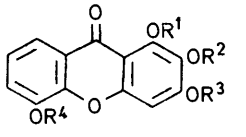


(IV)



(V)

a; $R^1 = R^3 = H, R^2 = Me$
b; $R^1 = H, R^2 = R^3 = Me$
c; $R^1 = R^2 = R^3 = Me$
d; $R^1 = R^2 = R^3 = H$
e; $R^1 = R^3 = Ac, R^2 = Me$



(VI)

a; $R^1 = R^3 = R^4 = H$, $R^2 = Me$
b; $R^1 = H$, $R^2 = R^3 = R^4 = Me$
c; $R^1 = R^2 = R^3 = R^4 = Me$

(10-*O*-methylmacluraxanthone). This was confirmed by methylation with dimethyl sulphate to give 5,9,10-tri-*O*-methylmacluraxanthone [7] (IVc), identified by mixed m.p., i.r., and t.l.c. comparison with an authentic sample.

The second yellow pigment, which we have named kayeaxanthone, was purified by preparative t.l.c. on silica gel. The molecular ion (M^+ 422) agreed with the molecular formula $C_{25}H_{26}O_6$. The compound showed i.r. absorption at 1 644 (xanthone C=O) and 3 250 cm^{-1} (phenolic OH). The u.v. spectrum of the tetrahydro-derivative was similar to those of 1,2,3,5-tetraoxygenated xanthone systems [14,15] (Table 3). The n.m.r. spectrum

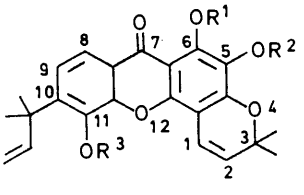
TABLE 3

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

Tetrahydrokayea-xanthone	217 (3.89)	244 (3.92)	262sh (3.82)	301 (3.83)	353 (3.53)	
1,3,5-Trihydroxy-2-methoxyxanthone [14] (VIa)	222 (31.9)	244 (3.93)	262sh (3.87)	314 (3.57)	365 (3.56)	
1-Hydroxy-2,3,5-tri-methoxyxanthone [15] (VIb)	221 (2.95)	243 (4.10)	253 (4.08)	263sh (3.88)	305 (3.81)	365 (3.43)

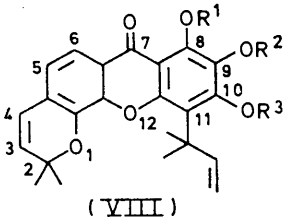
showed the absence of a chelated OH group. This was supported by absence of shifts in the u.v. maxima on addition of aluminium chloride.[6] The absence of u.v. shifts on addition of sodium acetate indicated the absence of a 3- or 6-OH group.[16] The n.m.r. spectrum showed only two aromatic doublets, at τ 2.05 and 2.90 (*J* 9 Hz). The chemical shift of the former shows that it could only arise from a proton *peri* to a xanthone carbonyl, *i.e.* the 8-proton as position 1 is oxygenated. The adjacent position 7 must bear the other aromatic proton to account for the magnitude of the coupling constant.[9] The n.m.r. spectrum also shows two characteristic doublets at τ 3.46 and 4.32 (*J* 10 Hz), and a six-proton singlet at τ 8.41 (two methyl groups), indicating the presence of a 2,2-dimethylpyran system attached to the xanthone nucleus. The fact that the dimethylpyran double bond is conjugated with the xanthone nucleus was shown by the change in the u.v. pattern of kayeaxanthone on complete hydrogenation.[9] The presence of the 2,2-dimethylpyran system was confirmed by the presence of an intense $M - 15$ peak in the mass spectrum due to the formation of a stable benzopyrylium ion.[17] Further, the n.m.r. spectrum showed the presence of a 1,1-dimethylprop-2-enyl side chain, as in the case of macluraxanthone [7] (IVd) and globuxanthone [10] (V), with the olefinic proton signals appearing as an ABX system at τ 3.51, 5.01, and 5.15 and the signals for the *gem*-dimethyl group at τ 8.25.

The n.m.r. spectrum of *O*-methylkayeaxanthone showed signals for three methoxy-groups whereas that of kayeaxanthone showed only two. This indicated the presence of two methoxy- and one hydroxy-group. A negative Gibbs test (spectrophotometric) [13] indicated the absence of H *para* to a hydroxy-group. All attempts to cyclise kayeaxanthone with formic acid and dichlorodicyanobenzoquinone failed, indicating the absence of a 1,1-dimethylprop-2-enyl side chain *ortho* to a hydroxy-group. From the above arguments only two structures, (VIIa) and (VIIIa), are probable for kayeaxanthone.



(VII)

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



(VIII)

a; $R^1 = R^3 = Me, R^2 = H$
b; $R^1 = R^2 = R^3 = Me$
c; $R^1 = R^3 = Me, R^2 = Ac$

The shift [11] of the pyran proton n.m.r. signals on acylation [to (VIIb)] would not provide any information as the OH group is *para*/*meta*-oriented and is further removed from the pyran protons. Similarly in structure (VIII) pyran protons are far from the hydroxy-group, and there cannot be significant acetate shifts. A choice between structures (VIIa) and (VIIIa) could not be made by application of benzene-induced solvent shifts, as there are no isolated methoxy-groups [18] in either

[13] E. D. Burling, A. Jefferson, and F. Scheinmann, *Tetrahedron*, 1965, 2653.
[14] R. Somanathan and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1972, 1935.
[15] G. H. Stout, E. N. Christensen, W. J. Balkenhol, and K. L. Stevens, *Tetrahedron*, 1969, **25**, 1947.
[16] O. R. Gottlieb, M. Taveira Magalhaes, M. Ottoni de Silva Pereira, A. Lins Mesquita, D. de Barros Correa, and G. G. de Oliveira, *Tetrahedron*, 1968, **24**, 1601.
[17] C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.*, 1964, **17**, 975.
[18] D. L. Dreyer, *Tetrahedron*, 1969, **25**, 4415.

structure. Also the nuclear Overhauser effect could not be used to distinguish the positions owing to the closeness of the signals.[19] As the amount of kayeaxanthone available was limited, the structure was established by comparing the chemical shifts with those for compounds with similar substituents (Table 4).

TABLE 4

Comparison of n.m.r. data (τ values)

	3-H	4-H	5-H	6-H
(VIIIa) ($CDCl_3$)	4.32	3.46	2.90	2.05
(VIIIb) [$(CD_3)_2CO$]	4.25	3.44	2.89	2.17
(IXa) [$(CD_3)_2CO$]	4.17	3.56	3.00	2.24
(IXb) [$(CD_3)_2CO$]	4.06	3.47	2.90	2.37

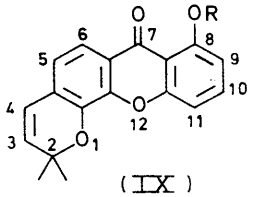
The chemical shifts of the protons at positions 3, 4, 5, and 6 of structure (VIIIb) are closely parallel to those of the 3-, 4-, 5-, and 6-protons in structures (IXa and b). Structure (IXb) is more closely related to (VIIIa) and (VIIIb) than (IXa), and the chemical shifts of the 4- and 5-protons of structure (IXb) are almost identical with those of the 4- and 5-protons of structures (VIIIa) and (VIIIb) (Table 4).

On the other hand, the chemical shifts of the 1-proton of structures (Xa),[20] (Xb),[20] and (Xc)[21] differ markedly from that of the 1-proton of the alternative structure (VIIa) (Table 5). Hence it is concluded that kayeaxanthone has structure (VIIIa).

TABLE 5

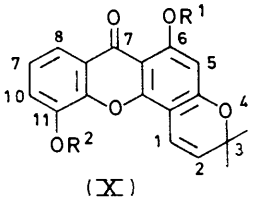
Comparison of n.m.r. signals (τ values)

Compound	2-H	1-H
(VIIa) ($CDCl_3$)	4.32	3.46
(Xa) ($CDCl_3$)	4.33	2.97
(Xb) ($CDCl_3$)	4.38	3.05
(Xc) [$(CD_3)_2CO$]	4.35	3.06



(IX)

a; R = H
b; R = Me



(X)

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

Timber Extractives.—The methanol extract of the timber was further extracted with chloroform. The chloroform extract on column chromatography gave β-sitosterol and a bright yellow pigment of molecular weight 274 (mass spectrometry). This pigment gave a green colouration with neutral iron(III) chloride and showed strong i.r. absorption at 1 652 (chelated C=O) and 2 275 cm^{-1} (OH). The u.v. and i.r. spectra suggested that the pigment was a xanthone; it was identified as 1,3,5-trihydroxy-2-methoxyxanthone[14] (VIa) from n.m.r. and mass spectral data, and the structure was confirmed by preparation of the tri- (VIb) and tetra-*O*-methyl (VIc) derivatives and comparison with authentic samples (mixed m.p.s, i.r. spectra, and t.l.c.).

The genus *Kayea* Wall is included in the tribe Calophylleae of the sub-family Calophylloideae. The presence of two di-isoprenylated xanthones in the bark shows its relationship to the genus *Calophyllum* L. of this tribe, from which several such compounds have been recently reported, rather than to the genus *Mesua* L. To date no such bark xanthones have been isolated from the latter. Kostermans [22] has recently included the members of the Malaysian *Kayea* species in the genus *Mesua* on the basis of morphological considerations. One such species [23] (*M. myrtifolia*) has been investigated by us; the only xanthone isolated was jacareubin which has not been reported from a *Mesua* species before. It appears that interesting taxonomic data would become available from the study of more of these Malaysian species.

EXPERIMENTAL

U.v. and i.r. spectral data were recorded with a Unicam SP 8000B and a Perkin-Elmer 257 spectrophotometer respectively. Mass spectral data were obtained from the University of Sheffield. N.m.r. data were obtained from the University of Aberdeen, and the Tropical Products Institute, London. Optical rotations were determined by using a Bellingham and Stanley polarimeter. Microanalyses were obtained from the CSIRO, Microanalytical Service, Melbourne. M.p.s were determined on a Kofler hot-stage apparatus. All R_F values refer to t.l.c. on silica gel G (thickness 0.25 mm). Merck silica gel (30—70 mesh) was used for column chromatography. Light petroleum refers to the fraction of b.p. 60—80°.

Plant material was obtained from the Royal Botanical Gardens, Peradeniya. The timber and bark were separated, chipped, and powdered in a mill, and extractives were obtained successively with hot light petroleum, hot benzene, and hot methanol.

Light Petroleum Extract.—Extraction of the bark (5 kg) with hot light petroleum (Soxhlet) gave, on concentration and filtration, a yellow solid (A) (1.5 g, 0.03%); removal of the solvent from the filtrate gave a gum (B) (1.6 g, 0.32%).

Isolation of Taraxerol [3] (Ia) *and β-Sitosterol.*—The gum (B) (1.6 g) was chromatographed on a silica gel column (200 g). Elution with light petroleum gave taraxerol (Ia) (100 mg), hexagonal crystals, m.p. 279—280° (from chloroform–acetone, 1 : 1), $[\alpha]_D^{28}$ +5° (in $CHCl_3$) {lit.,[3] m.p. 279—282°, $[\alpha]_D$ +3°}; $\nu_{max.}$ (KBr) 1 641, 2 970, and 3 740 cm^{-1}, identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.). Taraxerol acetate and taraxerone (Ib) prepared in the usual way were also identical with authentic samples.

Further elution of the column with benzene gave β-sitosterol (100 mg), m.p. 136° (from ethanol) (lit.,[24] 136—

[19] F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 1965, **87**, 5250; R. J. J. Ch. Lousberg, L. Paolillo, H. Kon, U. Weiss, and C. A. Salemink, *J. Chem. Soc.* (*C*), 1970, 2154.

[20] H. D. Locksley, A. J. Quillinan, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1971, 3804.

[21] P. J. Owen and F. Scheinmann, *J.C.S. Perkin I*, 1974, 1018.

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

[23] S. P. Gunasekera and M. U. S. Sultanbawa, unpublished results.

[24] 'Dictionary of Organic Compounds,' ed. I. M. Heilbron, Oxford University Press, Oxford, 1965, p. 2902.

137°), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Isolation of Simiaren-3β-ol (IIa).—Further elution of the column with benzene–chloroform (1 : 1) gave simiaren-3β-ol (120 mg), m.p. 209° (from methanol), $[\alpha]_D^{28}$ +48° (in $CHCl_3$), {lit.,[4] m.p. 210°, $[\alpha]_D$ +50°}; $\nu_{max.}$ (KBr) 1 650, 2 940, and 3 470 cm^{-1}, τ ($CDCl_3$; 60 MHz) 4.40 (1H, m, 6-H), 6.56 (1H, m, $W_{1/2}$ 10 Hz, 3-H), 8.2—8.7 (CH_2), and 9.00—9.42 (24H, 8 × Me), *m/e* 426 (M^+, $C_{30}H_{50}O$, 23%), 274 (100), 259 (65), 231 (8), 152 (16), and 134 (41), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Acetylation of simiaren-3β-ol (30 mg) with acetic anhydride (1 ml) and pyridine (1 ml) at room temperature and usual work up gave the acetate, m.p. 209° (from ethanol), $[\alpha]_D^{28}$ +68° (in $CHCl_3$) {lit.,[4] m.p. 209°, $[\alpha]_D$ +73.9°}, $\nu_{max.}$ (Nujol) 1 242, 1 650, and 1 738 cm^{-1}, identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.). Simiaren-3β-ol (25 mg) and chromic oxide (10 mg) in pyridine (2 ml) were left overnight at room temperature. The usual work-up gave simiarenone [4] (IIb), m.p. 206° (from methanol), $[\alpha]_D^{28}$ +25° {lit.,[4] m.p. 207—208°, $[\alpha]_D$ +24°}, also identical with an authentic sample.

Isolation of Betulinic Acid [5] (III).—Further elution with chloroform gave betulinic acid (500 mg), m.p. 294° (lit.,[5] 316—317°) (from methanol), $[\alpha]_D^{28}$ +13.3° (in $CHCl_3$) (lit.,[5] $[\alpha]_D$ +12°), M^+ 456 ($C_{30}H_{48}O_3$), $\nu_{max.}$ (KBr) 1 240, 1 690, 2 940, and 3 477 cm^{-1}, identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.). The acetate had m.p. 271°, $[\alpha]_D^{28}$ +28.2° (in $CHCl_3$) {lit.,[5] m.p. 289—291°, $[\alpha]_D$ +20.1°}, $\nu_{max.}$ (Nujol) 1 689 and 1 732 cm^{-1}, and was also identical with an authentic sample.

Isolation of Kayeaxanthone {11-(1,1-*Dimethylprop*-2-*enyl*)-9-*hydroxy*-8,10-*dimethoxy*-2,2-*dimethyl*-2H-*pyrano*[2,3-d]-*xanthen*-7-*one*} (VIIIa).—The solid (A) (1.5 g) was chromatographed on silica gel (75 g). Elution with benzene gave taraxerol (50 mg), and then with chloroform gave β-sitosterol (20 mg) and betulinic acid (520 mg). Further elution with chloroform gave a pale yellow solid which on preparative t.l.c. (chloroform–methanol, 30 : 1) and crystallisation from acetone gave *kayeaxanthone* (80 mg), m.p. 250—252°, R_F 0.6 (chloroform–methanol, 30 : 1) (Found: M^+, 422.1726. $C_{25}H_{26}O_6$ requires *M*, 422.1729), $\lambda_{max.}$ (EtOH) 260sh (log ε 4.29), 269 (4.31), 292 (4.63), and 368 nm (3.42) (no change on addition of $AlCl_3$, NaOAc, or NaOAc–H_3BO_3; negative Gibbs test), $\nu_{max.}$ ($CHCl_3$) 905, 970, 1 000, 1 060, 1 120, 1 125, 1 160, 1 190, 1 265, 1 300, 1 361, 1 424m 1 505, 1 564, 1 610, 1 644, and 3 250 cm^{-1}, τ ($CDCl_3$; 60 MHz) 2.05 (1H, d, *J* 9 Hz, 6-H), 2.90 (1H, d, *J* 9 Hz, 5-H), 3.46 (1H, d, *J* 10 Hz, 4-H), 3.51 (1H, q, *J* 20 and 12 Hz, X of ABX system, CH_2·CH), 4.32 (1H, d, *J* 10 Hz, 3-H), 5.01 (1H, q, *J* 20 and 1.2 Hz) and 5.15 (1H, q, *J* 12 and 1.2 Hz, AB of ABX system), 6.00 and 6.33 (6H, two s, 8- and 10-OCH_3), 8.25 (6H, s, CMe_2 of side chain), and 8.41 (6H, s, 2-CMe_2); *m/e* 422 (22%), 407 (100), 392 (6), 377 (5), 361 (6), 353 (8), 334 (3), 196 (2), 162 (3), 85 (16), and 83 (24).

Methylation of kayeaxanthone. Kayeaxanthone (30 mg) in methanol (20 ml) was treated with an excess of diazomethane for 6 h. Removal of solvent gave O-*methyl-kayeaxanthone* (VIIIb) as yellow crystals, m.p. 152—154°, R_F 0.59 (chloroform), M^+ 436 ($C_{26}H_{28}O_6$), $\lambda_{max.}$ (EtOH) 249 (log ε 4.41), 261 (4.36), 270 (4.39), 290 (4.51), 350sh (4.42), and 357 nm (3.75); $\nu_{max.}$ (KBr) 1 260 and 1 653 cm^{-1}, τ ($CDCl_3$; 100 MHz) 2.17 (1H, d, *J* 9 Hz, 6-H), 2.89 (1H, d, *J* 9 Hz, 5-H), 3.43 (1H, d, *J* 10 Hz, 4-H), 3.53 (1H, q, *J* 19 and 12 Hz, X of ABX system, CH_2·CH), 4.25 (1H, d, *J* 10 Hz, 3-H), 5.12 (1H, q, *J* 19 and 1.5 Hz) and 5.20 (1H, q, *J* 12 and 1.5 Hz, AB of ABX system), 6.00, 6.08, and 6.36 (9H, three s, 8-, 9-, and 10-OCH_3), 8.28 (6H, s, CMe_2 of side chain), and 8.50 (6H, s, 2-CMe_2).

Hydrogenation of kayeaxanthone. Kayeaxanthone (25 mg) in absolute ethanol (50 ml) was hydrogenated over pre-reduced palladised charcoal at atmospheric pressure and room temperature to give tetrahydrokayeaxanthone (15 mg), m.p. 200—202°, R_F 0.16 (chloroform), $\nu_{max.}$ (KBr) 1 645 and 3 490 cm^{-1}.

Cyclisation of Guanandin.—Guanandin (70 mg) in dry benzene (20 ml) was refluxed for 3 h with dichlorodicyanobenzoquinone (60 mg). The product was separated on a silica gel plate with benzene–chloroform (1 : 1). Crystallisation from light petroleum gave yellow crystals of dehydrocycloguanandin [16] (Ia) (0.014 g), m.p. 167—168° (lit.,[16] 167—169°), R_F 0.48 (benzene), $\lambda_{max.}$ (EtOH) 235 (log ε 4.37), 263 (4.34), 305sh (3.68), and 343 nm (4.19); $\lambda_{max.}$ (EtOH–$AlCl_3$) 235 (log ε 4.34), 275 (4.30), 298sh (3.92), and 343 nm (4.19); $\nu_{max.}$ (KBr) 1 645 and 3 400 cm^{-1}.

Methylation of dehydrocycloguanandin (IXa). Dehydrocycloguanandin (13 mg) in dry acetone (10 ml) was refluxed with anhydrous potassium carbonate (500 mg) and dimethyl sulphate (one drop) for 8 h and left at room temperature for 7 days. The usual work-up and crystallisation from methylene chloride–light petroleum (1 : 9) gave O-*methyldehydrocycloguanandin* (Xb) (12.1 mg), m.p. 163—164°, R_F 0.40 (chloroform) (Found: M^+, 308.1049. $C_{19}H_{16}O_4$ requires *M*, 308.1048), $\lambda_{max.}$ (EtOH) 235 (log ε 4.18), 248 (4.16), 259 (4.12), 317sh (3.95), and 330 nm (4.03); $\nu_{max.}$ (KBr) 1 660 cm^{-1}, τ [$(CD_3)_2CO$; 100 MHz] 2.32 (1H, t, *J* 8.2 Hz, 10-H), 2.37 (1H, d, *J* 8 Hz, 6-H), 2.90 (1H, d, *J* 8 Hz, 5-H), 2.94 (1H, d, *J* 8 Hz, 11-H), 3.06 (1H, d, *J* 8 Hz, 9-H), 3.47 (1H, d, *J* 10 Hz, 4-H), 4.06 (1H, d, *J* 10 Hz, 3-H), 6.06 (3H, s, 8-OCH_3), and 8.45 (6H, s, 2-CMe_2), *m/e* 308 (38%), 279 (12), 264 (9), 250 (11), 221 (8), 133 (12), 115 (7), and 57 (13).

Isolation of 10-O-*Methylmacluraxanthone* {12-(1,1-*Dimethylprop*-2-*enyl*)-5,9-*dihydroxy*-10-*methoxy*-2,2-*dimethyl*-2H-*pyrano*[3,2-b]*xanthen*-6-*one*} (IVa).—Fresh powdered bark (9.1 kg) was extracted with (*a*) hot light petroleum, (*b*) hot benzene, and (*c*) hot chloroform. Evaporation of solvent under reduced pressure gave materials (*a*) (63.5 g, 0.070%), (*b*) (205 g, 2.2%), and (*c*) (55 g, 0.61%).

Material (*a*) (53.5 g) in diethyl ether (1.5 l) was washed with cold sodium carbonate (5%) and cold sodium hydroxide (5%) solution. The neutral fraction on concentration gave a pale yellow solid (49.3 g, 0.65%). The phenolic and acidic fractions on acidification and extraction with ether gave brown solids (2.1 g, 0.027% and 1.7 g, 0.022% respectively).

The phenolic fraction (2.19 g) was chromatographed on a column of silica gel (80 g). Elution with benzene–light petroleum (1 : 1) gave a yellow solid (C) (140 mg), which was separated on a silica gel plate (25 g; Merck G) with chloroform (twice). The u.v.-fluorescent major band (R_F 0.23) was scraped off and the compound was extracted with warm acetone. Crystallisation from light petroleum gave 10-O-*methylmacluraxanthone* (IVa) as yellow needles (110 mg), m.p. 157—158°, R_F 0.55 (methanol–chloroform, 2 : 98) (Found: C, 70.6; H, 6.1. $C_{24}H_{24}O_6$ requires C, 70.6; H, 5.95%), $\lambda_{max.}$ (EtOH–$AlCl_3$) 242 (log ε 4.31), 281 (4.55), 290 (4.57), and 334 nm (4.27) (no change on addition of NaOAc

or NaOAc–H_3BO_3; negative to Gibbs test), $\nu_{max.}$ (Nujol) 1 652 and 3 520 cm^{-1}, τ ($CDCl_3$; 100 MHz) −3.58 (1H, s, 5-OH), 2.10 (1H, d, *J* 9 Hz, 7-H), 3.04 (1H, d, *J* 9 Hz, 8-H), 3.26 (1H, d, *J* 10 Hz, 4-H), 3.68 (1H, q, *J* 18 and 10 Hz, X of ABX system, CH_2:CH), 4.43 (1H, d, *J* 10 Hz, 3-H), 5.11 and 5.16 (2H, two doublets, *J* 18 and 10 Hz, AB of ABX system), 6.06 (3H, s, 10-OMe), 8.28 (6H, s, CMe_2 of side chain), and 8.54 (6H, s, 2-CMe_2), *m/e* 408 (M^+, 100%), 393 (76), 379 (16), 365 (14), 352 (11), 350 (5), 339 (4), 337 (4), 335 (6), 323 (14), 310 (25), 204 (15), 189 (8), 169 (6), 151 (4), 115 (24), and 83 (47).

Methylation of 10-O-*methylmacluraxanthone* (IVa). (a) *With diazomethane.* 10-*O*-Methylmacluraxanthone (20 mg) in diethyl ether (10 ml) was methylated with diazomethane to give 9,10-di-*O*-methylmacluraxanthone (IVb) (18 mg), yellow needles, m.p. 165—166° (from light petroleum), R_F 0.45 (chloroform), $\lambda_{max.}$ (EtOH) 225 (log ε 4.29), 245 (4.30), 287 (4.60), 334 (4.28), and 364 nm (3.67), $\nu_{max.}$ (Nujol) 1 270 and 1 650 cm^{-1}; *m/e* 422 (M^+, 81%), 408 (100), 393 (10), 381 (13), 379 (4), 367 (8), 196 (8), 182 (4), 176 (6), 85 (9), and 83 (13).

(b) *With dimethyl sulphate.* 10-*O*-Methylmacluraxanthone (15 mg) in dry acetone (10 ml) was refluxed with potassium carbonate (1 g) and dimethyl sulphate (0.5 ml) on a water-bath for 8 h. The usual work-up gave a mixture of two products, separated on a silica gel plate with chloroform. The major product on crystallisation from methanol gave 5,9,10-tri-*O*-methylmacluraxanthone [7] (IVc) (6 mg), white crystals, m.p. 97—98° (lit.,[7] 98°), R_F 0.79 (methanol–chloroform, 4 : 96), $\nu_{max.}$ (KBr) 1 269 and 1 650 cm^{-1}, identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Acetylation of 10-O-*methylmacluraxanthone* (IVa). 10-*O*-Methylmacluraxanthone (20 mg) in pyridine (2 ml) and acetic anhydride (0.5 ml) was maintained at 45 °C for 7 h. The usual work-up gave 5,9-*di*-O-*acetyl*-10-O-*methylmacluraxanthone* (IVe) (18 mg), white crystals, m.p. 185—186° (from light petroleum), R_F 0.14 (chloroform), $\lambda_{max.}$ (EtOH) 241 (log ε 4.41), 272 (4.74), 323 (4.11), and 352 nm (4.02), $\nu_{max.}$ (KBr) 1 260, 1 651, and 1 760 cm^{-1}, τ ($CDCl_3$; 100 MHz) 2.06 (1H, d, *J* 9 Hz, 7-H), 2.96 (1H, d, *J* 9 Hz, 8-H), 3.50 (1H, d, *J* 10 Hz, 4-H), 3.63 (1H, d, *J* 18 and 10 Hz, X of ABX system, CH_2:CH), 4.27 (1H, d, *J* 10 Hz, 3-H), 5.08 and 5.13 (2H, two d, *J* 18 and 10 Hz, AB of ABX system), 6.09 (3H, s, 10-OMe), 7.52, 7.63 (6H, two s, 5- and 9-OAc), 8.26 (6H, s, CMe_2 of side chain), and 8.52 (6H, s, 2-CMe_2); *m/e* 492 (M^+, 12%), 478 (3), 450 (80), 435 (100), 407 (15), 393 (50), 378 (7), 367 (8), 365 (9), 363 (6), 353 (7), 351 (5), 349 (4), 339 (4), and 335 (5).

Hydrogenation of 10-O-*methylmacluraxanthone* (IVa). 10-*O*-Methylmacluraxanthone (10 mg) in absolute ethanol (30 ml) was hydrogenated over Adams catalyst at atmospheric pressure and room temperature to give *tetrahydro*-10-O-*methylmacluraxanthone* {12-(1,1-*dimethylpropyl*)-3,4-*dihydro*-5,9-*dihydroxy*-10-*methoxy*-2H-*pyrano*[3,2-b]*xanthen*-6-*one*} (10 mg), yellow crystals, m.p. 184—185° (from light petroleum), R_F 0.16 (chloroform), $\lambda_{max.}$ (EtOH) 248 (log ε 4.51), 260 (4.30), 284 (4.06), 325 (4.26), and 360 nm (3.92); $\nu_{max.}$ (KBr) 1 645 and 3 380 cm^{-1}; *m/e* 412 (M^+, 70%), 397 (8), 385 (16), 384 (45), 383 (100), 369 (7), 335 (11), 342 (12), 341 (51), 329 (14), 328 (67), 327 (96), 326 (8), 325 (9), 308 (15), 307 (16), 306 (24), 297 (21), and 284 (5).

Isolation of kayeaxanthone (VIIIa). Further elution of the column with chloroform–benzene (1 : 9) gave a pale yellow solid (D) (0.900 g), separated on a silica gel G (Merck) plate (25 × 3 mm) with methanol–chloroform (3 : 97) to give kayeaxanthone (12 mg), m.p. 250—252°, identical with the earlier sample (mixed m.p., i.r. spectra, and t.l.c.).

Timber Extractives.—Powdered timber (15 kg) was extracted with (d) hot light petroleum, (e) hot benzene, and (f) hot methanol. Removal of solvents gave materials (d) (1 g, 0.006%), (e) (2 g, 0.012%), and (f) (700 g, 4.2%). Material (f) (700 g) was re-extracted with hot chloroform (Soxhlet). Removal of solvent gave a gum (4 g, 0.02%).

Isolation of β-*Sitosterol.*—The above gum (2 g) was chromatographed on acid-washed silica gel. Elution with benzene–chloroform (1 : 1) gave β-sitosterol (200 mg), m.p. 136°, identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

Isolation of 1,3,5-*Trihydroxy*-2-*methoxyxanthone* [14] (VIa). —Further elution of the column with chloroform–methanol (25 : 1) gave 1,3,5-trihydroxy-2-methoxyxanthone (100 mg), m.p. 278° (lit.,[25] 278°), R_F 0.5 (chloroform–acetic acid, 92 : 8), M^+ 274 ($C_{14}H_{10}O_6$), identical with an authentic sample (mixed m.p., u.v., i.r., n.m.r., and mass spectra). [The m.p. (252°) reported in ref. 25 should be corrected to 278°.]

Methylation of 1,3,5-*trihydroxy*-2-*methoxyxanthone* (VIa). (*a*) The xanthone (40 mg), potassium carbonate, and dimethyl sulphate (1 ml) were refluxed for 12 h; the usual work-up gave 1,2,3,5-tetramethoxyxanthone (VIc) (25 mg), m.p. 146—148° (lit.,[15] 148·5—149·5°), $\nu_{max.}$ (Nujol) 1 650 cm^{-1}, identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

(*b*) The xanthone (40 mg) was treated with an excess of diazomethane; the usual work-up gave 1-hydroxy-2,3,5-trimethoxyxanthone (VIb) (35 mg), m.p. 187—188° (lit.,[15] 189—190°) (from acetone), identical with an authentic sample (mixed m.p., i.r. spectra, and t.l.c.).

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