Chemical Investigation of Ceylonese Plants. Part VII.[1] Extractives of *Calophyllum thwaitesii* Planch and Triana and *Calophyllum walkeri* Wight (Guttiferae)

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The bark and timber extractives of *C. thwaitesii* Planch and Triana and *C. walkeri* Wight have been studied. The former contained taraxerol and friedelin in the bark whilst the latter had taraxerol and β-simiarenol. In addition a new di-isoprenylated xanthone, named thwaitesixanthone, has been isolated from the former and shown to be 13-hydroxy-3,3,10,10-tetramethyl-3*H*,10*H*-dipyrano[3,2-*a*:2',3'-*i*]xanthen-14-one (IV) while calabaxanthone. 5-hydroxy-8-methoxy-2,2-dimethyl-7-(3-methylbut-2-enyl)-2*H*-pyrano[3,2-*b*]xanthen-6-one (I) was isolated from the latter. The timber extractives of both species gave 1,5-dihydroxyxanthone, 1,7-dihydroxyxanthone, jacareubin (IIa), and β-sitosterol. The latter species also contained guanandin (VIII), 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone (X), and the new metabolite 1,5-dihydroxy-2,3-dimethoxyxanthone (IX).

THIS paper describes studies on two Guttiferae species *Calophyllum thwaitesii* Planch and Triana [2] and *Calophyllum walkeri* Wight.[2,3]

Bark Extractives of C. thwaitesii *Planch and Triana.*—From the cold light petroleum extract of the bark, friedelin [4] taraxerol,[5] β-sitosterol, and a bright yellow compound were isolated by silica gel chromatography. The latter was insoluble in sodium hydroxide and failed to give an iron(III) chloride colouration. The u.v. data and i.r. absorption at 1648 cm^{-1} indicated that it was a xanthone, and it was therefore named thwaitesixanthone. Tetrahydrothwaitesixanthone had a u.v. spectrum very similar to that of tetrahydrocalabaxanthone [6] (V) and dihydro-osajaxanthone monomethyl ether [7] and related 1,3,7-trioxygenated systems as shown in Table 1, thus suggesting that thwaitesixanthone had a 1,3,7-trioxygenated xanthone nucleus.

The n.m.r. spectrum of thwaitesixanthone showed a sharp low field signal at τ — 3·53 (1H) which indicated the presence of a chelated hydroxy-group. The presence of a single hydroxy-group was evidenced by the formation of monomethyl ether with dimethyl sulphate, in which the methoxy-group n.m.r. signal was at τ 6·08. The above data fixed the chelated OH group at C-1 of a xanthone nucleus. Singlets at τ 8·52 (6H) and 8·54 (6H) and doublets at 1·98 (1H) and 4·19 (1H) (*J* 10·2 Hz) and 3·26 (1H) and 4·41 (1H) (*J* 10·2 Hz) suggested the presence of two 2,2-dimethyl-2*H*-pyrano-rings, involving the oxygen functions at C-3 and -7. Evidence for this is also available from the mass spectral fragments [5] at *m/e* 361 and 173 (see below).

The three aromatic protons appeared as singlets at τ 3·72 (1H) and 2·83 (2H). The high chemical shift of the 1H signal indicated that this proton should be located in the electron rich phloroglucinol ring of thwaitesixanthone as in the case of calabaxanthone [6] (I) where the corresponding proton appeared at τ 3·77. Additional support can be provided from osajaxanthone diacetate [7] (IIb) which had the corresponding signal at τ 3·29 comparable with τ 3·33 in thwaitesixanthone

[1] Part VI, G. Pavanasasivam and M. U. S. Sultanbawa, *Phytochemistry*, 1973, **12**, 2725.

[2] A preliminary report was presented at the 8th I.U.P.A.C. Symposium on the Chemistry of Natural Products, New Delhi, 1972, Abstracts of Proceedings, p. 80.

[3] M. Dahanayakem, R. Somanathan, and M. U. S. Sultanbawa, *Proc. Ceylon Assoc. Adv. Sci.*, 1972, **28**, 129.

[4] H. R. Arthur, C. M. Lee, and C. N. Ma, *J. Chem. Soc.*, 1956, 1461.

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

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

[7] M. Wolfrom, F. Komitsky, and J. H. Looker, *J. Org. Chem.*, 1965, **30**, 144.

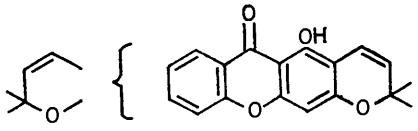
acetate. As thwaitesixanthone gave a positive Gibbs test,[8] the proton is placed *para* to the 1-hydroxy group. Hence C-2 is involved in the formation of the one of the

TABLE 1

Comparison of u.v. absorption maxima

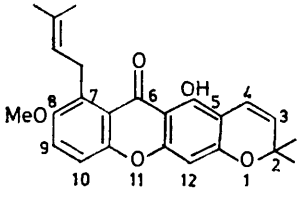
	$\lambda_{max.}$(EtOH)/nm (log ε)						
Calabaxanthone	240 (4·53)		287 (4·89)	292 (4·86)	314 (4·46)		384 (3·93)
Osajaxanthone monomethyl ether	240 (4·33)	248 (4·30)	286 (4·64)		339 (3·96)		375 (3·65)
Thwaitesixanthone	245 (4·13)	275sh (4·37)	283 (4·49)	292 (4·52)	299sh (4·45)	329 (4·13)	403 (3·64)
Tetrahydro calabaxanthone	241 (4·80)	262 (4·81)			316 (4·56)		369 (3·96)
Dihydro-osajaxanthone monomethyl ether	233 (4·50)	263 (4·55)			316 (4·22)		375 (3·79)
Tetrahydro-thwaitesixanthone	238 (4·41)	263 (4·49)			310 (4·18)		365 (3·64)

2,2-dimethyl-2*H*-pyrano-rings, giving a linear tetracyclic system. The partial structure (A) can then be written for thwaitesixanthone. Structure (A) is further

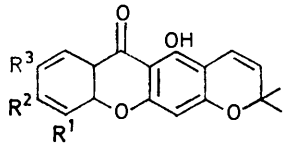


(A)

supported by the intense u.v. absorption at $\lambda_{max.}$ 283 nm (log ε 4·49) as a spectrum of this type has been reported for calabaxanthone (I) and osajaxanthone (IIb) which have linearly fused 2,2-dimethyl-2*H*-pyrano-rings. The other 2,2-dimethyl-2*H*-pyrano-ring involving the oxygen function at C-7 could be attached in



(I)

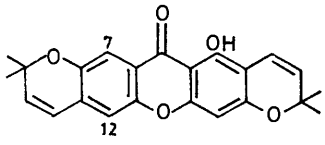


(II)

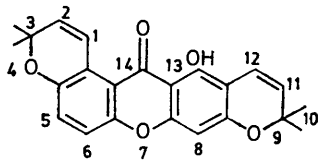
a; $R^1 = R^2 = OH$, $R^3 = H$

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

two ways to give a linearly fused structure (III) or angularly fused structure (IV). Evidence which supported an angular fusion was (*a*) the other two protons appearing as a singlet at τ 2·83 as in calabaxanthone (I) (τ 2·73). If the molecule had linear fusion as in (III), 7-H, which is *peri* to the carbonyl group, should appear much lower than τ 2·83 as in the diacetate of osajaxanthone (IIb) (τ 2·08) and in addition the chemical shifts for the protons at C-7 and -12 in (III) should be different. (*b*) The low chemical shifts [τ 1·98 (1H) and 1·83 (1H) respectively] for one of

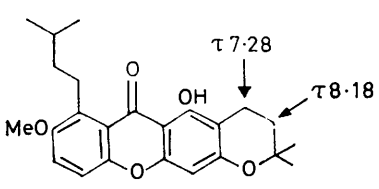


(III)

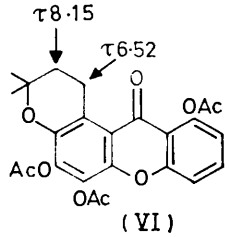


(IV)

the doublets in thwaitesixanthone and its methyl ether which would support a double bond in the deshielding region of the carbonyl group as has been shown for tovoxanthone[9] and tovophyllin A and B.[10] (*c*) The n.m.r. spectrum of tetrahydrothwaitesixanthone which contained four sets of doublets at τ 6·50 (2H), 7·28 (2H), and 8·18 (4H), two of which were coincident. One pair of values is similar to that of tetrahydrocalabaxanthone[6] (V) in which the pyrano-ring is linearly fused. The other pair was similar to that found for ring-closed celibixanthone acetate[11,12] (VI) in which the pyrano-ring is angularly fused. On this basis thwaitesixanthone was formulated as 13-hydroxy-3,3,10,10-tetramethyl-3*H*,10*H*-dipyrano-[3,2-*a*:2′,3′-*i*]xanthen-14-one (IV).



(V)



(VI)

Further confirmation of the linear arrangement of one of the 2,2-dimethyl-2*H*-pyrano-rings was obtained from the proton shifts observed for the acetate (Table 2).

TABLE 2

Chemical shift differences

	τ Values				
	H-12	H-11	H-8	H-1	H-2
Thwaitesixanthone	3·26	4·41	3·72	1·98	4·19
Thwaitesixanthone acetate	3·50	4·28	3·33	2·04	4·23
Diamagnetic Δτ/p.p.m.	+0·24			+0·06	+0·05
Paramagnetic Δτ/p.p.m.		−0·13	−0·39		
		Linear		Angular	

A positive diamagnetic shift and a negative paramagnetic shift for the protons of a linear 2,2-dimethyl-2*H*-pyrano-ring and a negative paramagnetic shift

[8] F. E. King, J. T. King, and L. C. Manning, *J. Chem. Soc.*, 1957, 563.

[9] S. J. Gabriel and O. R. Gottlieb, *Phytochemistry*, 1972, **11**, 3035.

[10] W. Goncalves De Oliveira, O. R. Gottlieb, and A. A. Lins Mesquita, *Phytochemistry*, 1972, **11**, 3323.

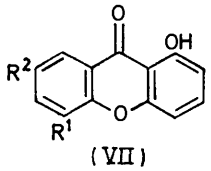
[11] G. H. Stout, V. F. Stout, and M. J. Welsh, *Tetrahedron Letters*, 1963, 667.

[12] L. M. Jackman, in ' Progress in the Chemistry of Organic Natural Products,' ed. L. Zeichmeister, vol. XXIII, Springer, Vienna, 1965, p. 354.

for C-8 aromatic protons is in agreement with the linear ring.[13] Table 2 also records the proton shifts observed for the acetate for the other 2,2-dimethyl-2*H*-pyrano-ring. The observed proton shifts may also be indicative of angular fusion although no such examples have been reported.

The mass spectrum of calabaxanthone (I) contained peaks at *m/e* 392 (M^+), 377 ($M - CH_3$, 100%), and a prominent fragment at 349 ($M - CH_3 - CO$).[14] Doubly charged ions at *m/e* 188·5 and 174·5 were also observed. However, the spectrum of thwaitesixanthone contained the molecular ion *m/e* 376 with prominent fragments at 361 [$(M - CH_3)^+$] and 173 [$(M - 2CH_3)^{2+}$], but the loss of CO from the above fragments produced ions of low intensity at *m/e* 333 and 159 respectively.[14]

Timber Extractives of C. thwaitesii *Planch and Triana.*—From the light petroleum extract of the timber 1,5-dihydroxyxanthone[15] (VIIa) and β-sitosterol were isolated. The methanolic extract of the timber on further processing gave additional amounts of 1,5-dihydroxyanthone, 1,7-dihydroxyxanthone[16] (euxanthone) (VIIb), and jacareubin[17] (IIa). The three xanthones were identified by mixed m.p., i.r., and t.l.c. comparison with authentic samples.



(VII)

a; R^1 = OH, R^2 = H

b; R^1 = H, R^2 = OH

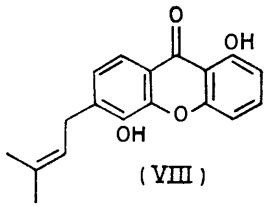
Bark Extractives of C. walkeri *Wight.*—The solid obtained from the light petroleum extract on separation on a silica gel column gave β-simiarenol and taraxerol, and a yellow pigment. The latter was characterised as calabaxanthone by comparison with an authentic sample (m.p., mixed m.p., u.v., i.r., and t.l.c.). This compound had been isolated earlier from *C. calaba* L. and *C. bracteatum* Thw. The acidic compounds in the gum were not investigated.

Timber Extractives of C. walkeri *Wight.*—The light petroleum extract of the timber gave β-sitosterol and waxes which were not further investigated.

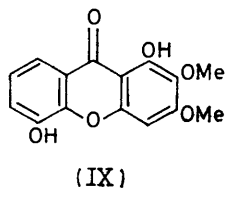
The chloroform extract of the methanolic extract of the timber on separation on a silica gel column gave guanandin[18] (VIII), 1,5-dihydroxyxanthone (VIIa), and 1,7-dihydroxyxanthone (euxanthone) (VIIb) which were identified by comparison with authentic samples (m.p., mixed m.p., u.v., i.r., and t.l.c.).

Further elution of the column gave a new pigment. The i.r. and u.v. spectra indicated that it was a tetraoxygenated xanthone. The n.m.r. spectrum showed signals at τ — 2·68 (chelated OH), 6·03 and 6·22 (2 × MeO), 3·22 (1H, s, ArH), and 2·30—2·98 (3H, m, ArH). The presence of a chelated hydroxy-group was further supported by a bathochromic shift in the u.v. spectrum on addition of aluminium chloride and the group was located at C-1. Since the substance was stable to alkali and the u.v. spectrum was not altered by the addition of $NaOAc-H_3BO_3$ the possibility of two *ortho*-hydroxy-groups was eliminated.

On methylation with dimethyl sulphate and potassium carbonate, a tetramethoxyxanthone was isolated and



(VIII)



(IX)

shown to be identical with an authentic sample of 1,2,3,5-tetramethoxyxanthone[6] (m.p., mixed m.p., u.v., i.r., and t.l.c.). This indicated the 1,2,3,5-oxygenation pattern for the compound. Hence the two methoxy-groups can only be at C-2 and -3, leaving position 5 for the other hydroxy-group. The structure of this compound is thus 1,5-dihydroxy-2,3-dimethoxyxanthone (IX).

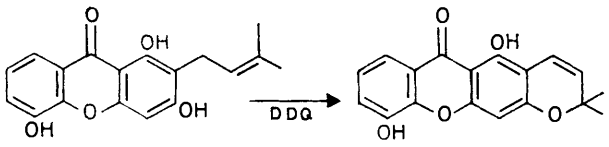
On further elution of the column with chloroform–methanol (99 : 1) jacareubin (IIa) was obtained, and identified by comparison with an authentic sample (mixed m.p., i.r., and t.l.c.). Continued elution of the column with the same solvent gave the pigment 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone[19] (X) which was identical with an authentic sample (mixed m.p., u.v., i.r., and t.l.c.).

Both plants contain 1,5- and 1,7-dihydroxyxanthone and these metabolites have been isolated from other *Calophyllum* species. Jacareubin (IIa) which had been isolated from all *Calophyllum* species that have been investigated,[20] has also been isolated from these two species. In addition, *C. walkeri* Wight contains the two monoisoprenylated xanthones, guanandin (VIII) and 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone (X). The latter is the presumed precursor of 6-deoxyjacareubin and was readily converted into 6-deoxyjacareubin (XI) by oxidation with 2,2-dichloro-5,6-dicyanobenzoquinone[21] (DDQ); compound (XI), however, was not isolated from the plant extract.

The di-isoprenylated xanthone calabaxanthone[6] has been isolated from the bark of three of the four species reported to date. Thwaitesixanthone, isolated from *C. thwaitesii* Planch and Triana, could be envisaged

[13] A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, *Tetrahedron Letters*, 1967, 4201.
[14] *Cf.* J. R. Lewis and J. B. Reary, *J. Chem. Soc.* (*C*), 1970, 1662.
[15] B. Jackson, H. D. Locksley, I. Moore, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1968, 2579.
[16] D. B. Spoelstra and N. J. Van Rayen, *Rec. Trav. chim.*, 1929, **48**, 370.
[17] F. E. King, J. T. King, and L. C. Manning, *J. Chem. Soc.*, 1953, 3932.
[18] De Barros Correa, O. R. Gottlieb, and M. Taveira Magalhaes, *Anais. Acad. brasil. Cienc.*, 1966, **38**, 296.
[19] S. Selliah, M.Sc. Thesis, University of Ceylon, 1972, p. 185.
[20] I. Carpenter, H. D. Locksley, and F. Scheinmann, *Phytochemistry*, 1969, **8**, 2013.
[21] G. Cardillo, R. Cricchio, and L. Merlini, *Tetrahedron*, 1968, **24**, 4825.

to have been formed from the precursor of calabaxanthone (I) (demethylated compound) by oxidative cyclisation, or by oxidative cyclisation of prenylated



(X) (XI)

osajaxanthone. However attempts to demethylate calabaxanthone, without affecting the pyrano-ring have so far been unsuccessful.

EXPERIMENTAL

U.v. spectra were recorded with a Unicam 8000B spectrophotometer. I.r., n.m.r., and mass spectral data were obtained from the Universities of Osaka, Sheffield, Aberdeen, and Strathclyde. Optical rotations were determined with a Bellingham and Stanley polarimeter. Analytical and preparative t.l.c. (p.l.c.) were carried out with silica gel G (Merck). Separation by column chromatography was carried out on silica gel (Koch–Light or Merck). M.p.s were determined on a Kofler hot stage apparatus. Light petroleum refers to the fraction b.p. 60—80°. Elemental analyses were carried out at the C.S.I.R.O., Microanalytical Service, Melbourne.

C. thwaitesii Planch and Triana was obtained from the Ratnapura district and *C. walkeri* Wight from Rangala area. Extractives were obtained and processed as reported in Part I.[6]

Extractives from the Bark of C. thwaitesii *Planch and Triana.*—Cold extraction of the bark (1·5 kg) with light petroleum yielded a yellow solid (0·800 g) and a brownish yellow oil (10 g). The solid (0·800 g) was separated on a silica gel column (50 g) prepared with light petroleum. The eluates were examined by t.l.c. and three main fractions were obtained on further elution with benzene.

Isolation of thwaitesixanthone. Fraction (*1*) on removal of the solvent gave a bright yellow solid (0·268 g) which gave needles of *thwaitesixanthone* (13-*hydroxy*-3,3,10,10-*tetramethyl*-3H,10H-*dipyrano*[3,2-a:2′,3′-i]*xanthen*-14-*one*) (IV), m.p. 221—224° (from 95% ethanol) (Found: C, 73·15; H, 5·3%; M^+, 376·13073. $C_{23}H_{20}O_5$ requires C, 73·4; H, 5·3%; *M*, 376·13106), $\nu_{max.}$ (KBr) 2950, 1648, 1611, 1585, 1464, 1394, 1374, 1358, 1332, 1302, 1266, 1246, 1218, 1170, 1130, 1120, 1090, 1064, 952, 914, 887, 846, 794, 724, and 714 cm^{-1}, τ ($CDCl_3$; 100 MHz) −3·53 (1H, s, 13-OH), 1·98 (1H, d, *J* 10·2 Hz, 1-H), 2·83 (2H, s, 5- and 6-H), 3·26 (1H, d, *J* 10·2 Hz, 12-H), 4·19 (1H, d, *J* 10·2 Hz, 2-H), 4·41 (1H, d, *J* 10·2 Hz, 11-H), 3·72 (1H, s, 8-H), and 8·52 and 8·54 (each 6H, s, 3- and 10-Me_2), *m/e* 376 (25%), 361 (72), 334 (13), 320 (10), 319 (46), 223 (9), 205 (7), 174 (7), 173 (30), 167 (9), 159·5 (10), 150 (12), 149 (100), 97 (7), 95 (6), 71 (10), 69 (11), 57 (22), 56 (10), and 55 (16).

Thwaitesixanthone methyl ether. Thwaitesixanthone (100 mg), calcined potassium carbonate (4 g), and dimethyl sulphate (2 ml) in dry acetone (5 ml) were refluxed for 16 h, cooled, and filtered. The filtrate on concentration yielded a brown oil which on treatment with ammonia and water precipitated the methyl ether 13-*methoxy*-3,3,10,10-*tetramethyl*-3H,10H-*dipyrano*[3,2-a:2′,3′-i]*xanthen*-14-*one* as a pale yellow solid, m.p. 160—162° (Found: C, 73·7; H, 5·85. $C_{24}H_{22}O_5$ requires C, 73·8; H, 5·7%), $\nu_{max.}$ (KBr) 2904, 1632, 1598, 1580, and 1564 cm^{-1}, τ ($CDCl_3$; 60 MHz) 1·83 (1H, d, *J* 10·2 Hz, 1-H), 2·75 (2H, s, 5- and 6-H), 3·06 (1H, d, *J* 10·2 Hz, 12-H), 3·34 (1H, s, 8-H), 4·25 (1H, d, *J* 10·2 Hz, 2-H), 4·36 (1H, d, *J* 10·2 Hz, 11-H), 6·08 (3H, s, 13-OMe), and 8·56 (12H, s, 3- and 10-Me_2).

Tetrahydrothwaitesixanthone. Thwaitesixanthone (100 mg) in absolute ethanol (100 ml) was hydrogenated over palladised charcoal at ordinary temperature and pressure. The catalyst was filtered off and the filtrate on concentration gave yellow needles of 1,2,3,10,11,12-*hexahydro*-13-*hydroxydipyrano*[3,2-a:2′,3′-i]*xanthen*-14-*one*, m.p. 200° (Found: M^+, 380. $C_{23}H_{24}O_5$ requires *M*, 380), $\nu_{max.}$ (KBr) 3430, 2930, 2935, 1647, 1606, and 1579 cm^{-1}, τ ($CDCl_3$; 100 MHz) −3·50 (1H, s, 13-OH), 2·88 (2H, s, 5- and 6-OH), 3·78 (1H, s, 8-H), 6·50 (2H, t, *J* 4 Hz, $ArCH_2$), 7·28 (2H, t, *J* 4 Hz, $ArCH_2$), 8·18 (4H, t, *J* 4 Hz, CH_2CMe_2), and 8·64 and 8·65 (each 6H, s, CMe_2), *m/e* 380 (100%), 365 (31), 351 (30), 338 (42), 337 (98), 325 (68), 324 (52), 309 (39), 295 (17), 281 (92), 269 (80), 253 (10), 241 (17), 212 (6), 211 (7), 156 (6), 128 (7), 115 (8), 93 (5), 77 (11), and 65 (6).

Thwaitesixanthone acetate. Thwaitesixanthone (0·040 g) was acetylated with acetic anhydride (1 ml) and pyridine (1 ml) for 20 h, and the usual work-up and recrystallisation from methanol gave *thwaitesixanthone acetate* (0·020 g), m.p. 219—220°, R_F 0·5 [benzene–light petroleum (1 : 1)] (Found: C, 71·7; H, 5·3%; M^+, 418. $C_{25}H_{22}O_6$ requires C, 71·8; H, 5·3%; *M*, 418), $\nu_{max.}$ ($CHCl_3$) 2965, 1760, 1642, 1617, and 1586 cm^{-1}, τ ($CDCl_3$; 60 MHz) 2·04 (1H, d, *J* 10·2 Hz, 1-H), 2·86 (2H, s, 5- and 6-H), 3·33 (1H, s, 8-H), 3·50 (1H, d, *J* 10·2 Hz, 12-H), 4·23 (1H, d, *J* 10·2 Hz, 2-H), 4·28 (1H, d, *J* 10·2 Hz, 11-H), 7·80 (3H, s, 13-OAc), and 8·18 and 8·23 (each 6H, s, CMe_2), *m/e* 418 (80%), 403 (55), 376 (100), 362 (50), 361 (35), 319 (25), 317 (15), 303 (11), 203 (5), 187 (8), 173 (60), 143 (5), 115 (7), 85 (20), and 83 (31).

Isolation of friedelin and taraxerol. Fraction (2) gave friedelin (0·20 g), m.p. 259—261°, $[\alpha]_D^{26}$ −21° (lit.,[4] m.p. 262—263°, $[\alpha]_D^{26}$ +22·1°), and fraction (3) gave taraxerol (0·010 g), m.p. 279—280°, $[\alpha]_D^{26}$ +5° (lit.,[5] m.p. 279—282°, $[\alpha]_D^{20}$ +3·1°). Both compounds were identified by comparison with authentic samples (mixed m.p., t.l.c., and i.r.).

T.l.c. examination of the oil from the bark extract showed the presence of thwaitesixanthone, friedelin, taraxerol, and β-sitosterol.

Extractives from Timber of C. thwaitesii *Planch and Triana.*—Cold extraction of the timber (14·35 kg) with light petroleum gave a yellowish white crystalline solid A (1·70 g) and a waxy solid B (3·50 g).

Isolation of 1,5-*dihydroxyxanthone*, 1,7-*dihydroxyxanthone, and jacareubin.* The solid A (1·70 g) was separated into acidic and neutral fractions by washing with 10% sodium hydroxide. The acidic fraction gave 1,5-dihydroxyxanthone, m.p. 264—265° (lit.,[15] 266—267°); dimethyl ether, m.p. 193—194° (lit.,[22] 194—196°). The compound and its derivative were identical with authentic samples (mixed m.p., t.l.c., and i.r. comparison). From the neutral fraction β-sitosterol was isolated, m.p. 136—137° (lit.,[23] 136—137°).

[22] B. Jackson, H. D. Locksley, and F. Scheinmann, *J. Chem. Soc.* (*C*), 1967, 785.

[23] Dictionary of Organic Compounds, Eyre and Spottiswoode, London, 1965, vol. V, p. 2902.

The waxy solid B was shown by t.l.c. to contain the same compounds.

The methanol extract (217 g) of the timber was further extracted with light petroleum, benzene, and chloroform. Silica gel chromatography of the benzene extract (7·5 g) gave further amounts of 1,5-dihydroxyxanthone, 1,7-dihydroxysanthone (euxanthone) (3·5 g), m.p. 237—238° (lit.,[16] 239), and jacareubin (0·100 g), m.p. 252—254° (lit.,[17] 254—256°), identical with authentic samples by mixed m.p., t.l.c., and i.r. comparison.

Extractives from the Bark of C. walkeri *Wight.*—Cold extraction of the bark (4·1 kg) with light petroleum gave a yellowish white solid L (2·97 g) and a gum (44 g).

Isolation of calabaxanthone, β-simiarenol, and taraxerol. The solid L was separated on a silica gel column and gave calabaxanthone (1·245 g), m.p. 172° (lit.,[6] 172°), R_F 0·74 (chloroform) [Found: M^+, 392. Calc. for $C_{24}H_{24}O_5$: *M*, 392), *m/e* 392 (43%), 378 (32), 377 (100), 360 (10), 349 (90), 321 (30), 307 (32), 280 (10), 188·5 (0·6), 174·5 (1), 167 (20), and 161 (12); β-simiarenol (0·005 g), m.p. 200—205°, $[\alpha]_D^{28}$ +48° (chloroform) (lit.,[24] m.p. 210°, $[\alpha]_D$ +50°); and taraxerol. These three compounds were identical with authentic samples by mixed m.p., t.l.c., and i.r. comparison.

The neutral portion of the gum was shown to contain calabaxanthone, β-simiarenol, taraxerol, and β-sitosterol by t.l.c.

Extractives from Timber of C. walkeri *Wight.*—Powdered timber (7·75 kg) on extraction with light petroleum gave a product A (15·0 g). The timber on further extraction with methanol gave a gum which on re-extraction with hot chloroform left a residue (119 g) and a chloroform-soluble fraction B (50 g).

Product A gave only β-sitosterol and a waxy solid which was not further investigated.

Isolation of guanandin, 1,5-dihydroxyxanthone, and 1,7-dihydroxyxanthone. The product B (5 g) on separation on a silica gel column gave guanandin (0·15 g), m.p. 205—208° (lit.,[18] 206—208°), 1,5-dihydroxyxanthone, and 1,7-dihydroxyxanthone, which were identical with authentic samples by mixed m.p., t.l.c., and i.r. comparison.

Isolation of 1,5-dihydroxy-2,3-dimethoxyxanthone. Further elution with $CHCl_3$–MeOH (99 : 1) gave a yellow solid which crystallised from acetone to give yellowish brown crystals of *1,5-dihydroxy-2,3-dimethoxyxanthen-9-one* (0·040 g), m.p. 254—255° (Found: M^+, 288. $C_{15}H_{12}O_6$ requires *M*, 288), $\lambda_{max.}$ (EtOH) 205 (log ε 3·91), 245 (3·92), 255 (3·91), 265sh (3·87), 275sh (3·81), 308 (3·77), and 365nm (3·56), $\lambda_{max.}$ (EtOH–$AlCl_3$) 245 (log ε 3·91), 255sh (3·92), 265sh (3·91), 275 (3·87), and 312 nm (3·81); there was no shift of $\lambda_{max.}$ with NaOAc or NaOAc–H_3BO_3, $\nu_{max.}$ (KBr) 3419, 1666, 1657, 1499, 1459, 1407, 1369, 1334, 1308, 1259, 1235, 1206, 1201, 1164, 1106, 1078, 1013, 974, 926, 857, 829, 817, 799, 782, 699, 685, and 672 cm^{-1}, τ [$(CD_3)_2SO$; 100 MHz] −2·68 (1H, s, 1-OH), 2·30—2·98 (3H, m, 6-, 7-, and 8-H), 3·22 (1H, s, 4-H), and 6·03 and 6·22 (each 3H, s, 2- and 3-OMe), *m/e* 288 (92%), 273 (100), 259 (17), 246 (60), 202 (20), 174 (9), 136 (23), 115 (8), and 108 (7).

1,2,3,5-Tetramethoxyxanthone. 1,5-Dihydroxy-2,3-dimethoxyxanthone (0·005 g), potassium carbonate (2 g), dimethyl sulphate (1 ml), and dry acetone (25 ml) were refluxed for 3 h and worked up in the usual manner to give white needles of 1,2,3,5-tetramethoxyxanthone (from ethanol), m.p. 145—146° (lit.,[25] 146—147°), identical with an authentic sample by mixed m.p., t.l.c., and i.r. comparison.

Isolation of jacareubin. Further elution of the column with $CHCl_3$–MeOH (99 : 1) gave jacareubin (0·020 g).

Isolation of 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone. Continued elution with the same solvent mixture gave a yellow solid (0·110 g) which gave the xanthone as yellow crystals (from acetone), m.p. 280—282° (lit.,[19] 280—281°), $\lambda_{max.}$ (EtOH) 235sh (log ε 4·42), 248 (4·40), 301 (4·26), and 358 nm (3·50), identical with an authentic sample by mixed, m.p., t.l.c., and i.r. comparison.

Conversion of 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)-xanthone into 6-deoxyjacareubin. 1,3,5-Trihydroxy-2-(3-methylbut-2-enyl)xanthone (0·020 g), DDQ (0·020 g), and benzene (20 ml) were refluxed for 2 h, cooled, and filtered. On removal of the benzene under reduced pressure and crystallisation of the residue from acetone, 6-deoxyjacareubin (0·012 g) was obtained, m.p. 209—210° (lit.,[18] 211—213°), identical with an authentic sample by mixed m.p., t.l.c., u.v., and i.r. comparison.

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