NMR and MS spectra and comparison with authentic samples indicated **1** was brevifolin [3].

The mother liquor of **1** was concentrated to give succinic acid, the filtrate from which was diluted with Et_2O, and washed with 3% Na_2CO_3. Upon evaporation of Et_2O, a syrup was obtained and chromatographed over silicic acid, eluting with EtOAc, to give pyrogallol. The Na_2CO_3 washings were acidified (HCl), and extracted with Et_2O to give gallic acid. Both constituents were identified with authentic specimens by IR and mmp.

The aqueous layer (A) was extracted continuously with EtOAc. Evaporation of the EtOAc yielded an amorphous mixture which was positive to the colour tests of both ellagitannin ($NaNO_2$–AcOH) [4] and flavonoid (Mg–HCl). This mixture was: (i) acetylated and chromatographed over silicic acid to yield a crystalline acetate, $C_{49}H_{44}O_{29}$, mp 204°, $[\alpha]_D^{20}$ −24·5° ($CHCl_3$); (ii) methylated (CH_2N_2) and chromatographed over silicic acid to give a crystalline methyl ether, $C_{36}H_{40}O_{18}$, mp 228° (dec.), $[\alpha]_D^{16}$ −159·6° (Me_2CO). These data are identical with those of undeca-acetylcorilagin and nonamethylcorilagin, and the latter was identified by IR and mmp with the methyl ether from authentic corilagin.

Acknowledgements—We thank Professor K. Bernauer, F. Hoffman-la Roche & Co. for the samples of brevifolin and its trimethyl ether, and Dr. Y. Kamano of Taisho Pharmaceutical Co., Ltd. for the sample of corilagin.

REFERENCES

1. Asahina, Y. and Tomimura, K. (1918) *Yakugaku Zasshi* **38**, 405.
2. Tominaga, T. (1972) *Shoyakugaku Zasshi* **26**, 144.
3. Schmidt, O. T. and Bernauer, K. (1954) *Liebig's Ann.* **588**, 211.
4. Bate-Smith, E. C. (1972) *Phytochemistry* **11**, 1153.

Phytochemistry, 1975, Vol. 14, pp. 1878–1880. Pergamon Press. Printed in England.

BIFLAVONOIDS AND XANTHONES OF *GARCINIA TERPNOPHYLLA* AND *G. ECHINOCARPA**

WICKRAMASINGHE M. BANDARANAYAKE, SATHIADEVAN S. SELLIAH and M. UVAIS S. SULTANBAWA
Department of Chemistry, University of Sri Lanka, Peradeniya Campus, Peradeniya, Sri Lanka

and

W. DAVID OLLIS
Department of Chemistry, University of Sheffield, Sheffield, England

(*Received* 13 *January* 1975)

Key Word Index—*Garcinia echinocarpa*; *G. terpnophylla*; Guttiferae; biflavonoids; xanthones; sitosterol.

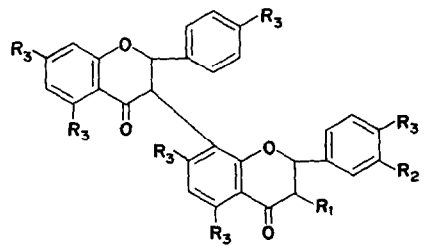
A number of species of the genus *Garcinia* (Guttiferae) have already been examined for their constituents. We now report the isolation of five biflavonoids, four xanthones and sitosterol from *Garcinia echinocarpa* Thw. (Sinhala-Madol) and *Garcinia terpnophylla* Thw. (Sinhala-Kokatiya). Both plants are found in the wet forest of Sri Lanka and the latter is endemic to Sri Lanka. They were obtained from Kanneliya forest in South Sri Lanka. The timber is used for building purposes. The oil obtained from the seeds *Garcinia echinocarpa* Thw. is used for lighting lamps.

The timber and bark of the plants were separated, dried at 60°, powdered and extracted successively with light petroleum, C_6H_6 and MeOH. The MeOH extracts were further extracted with Et_2O. The compounds were isolated from the extracts by partitioning in a counter current apparatus, by preparative TLC and by column chromatography on silica gel or polyamide.

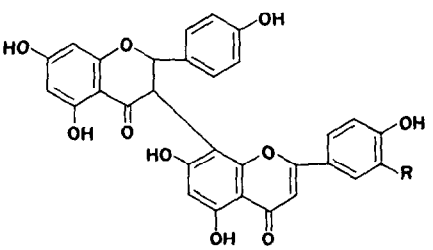
The following compounds were isolated and identified: *1,5-dihydroxyxanthone* mp 268–270° (acetone) lit. mp 268–270 [1] direct comparison and Co-TLC with authentic sample; *1,7-dihydroxyxanthone* (euxanthone), bright yellow needles mp 238–239° lit. mp 238–240° (acetone) [2] λ_{max}

* Part 18 in the series *Chemical Investigation of Ceylonese Plants.*

(EtOH) 204 (log e 4·22), 236 (4·36), 262 (4·40) and 289 nm (3·72). ν_{max} (KBr) 3400 and 1648 cm^{-1}, direct comparison and Co–TLC with authentic sample; 1,3,6,7-*tetrahydroxyxanthone* (**1c**) mp 323° (C_6H_6–Me_2CO). λ_{max} (EtOH) 239 (log e 4·53), 256 (4·40), 317 (4·48) and 363 (3·63) nm. ν_{max} (KBr) 3480, 3300, 1651, 1615 cm^{-1}. Tetramethyl ether with MeI, K_2CO_3, acetone, mp 165–166° (EtOH). Identification was confirmed by NMR and UV of the xanthone, its tetra methyl ether and its tetraacetate and mmp, Co–TLC with authentic sample of tetraacetate mp 198–199° lit. mp 197–198° [4], 1,3,6-*trihydroxy*-7-*methoxy*-2,8-*di*(3-*methylbut*-2-*enyl*) *xanthone* (mangostin) mp 182° (EtOH–H_2O) lit. mp 182–183° [3] λ_{max} (EtOH) 242 (log e 4·54), 258 (4·44), 308 (4·38) and 349 (3·86) nm., ν_{max} (KBr) 3410 and 1649 cm^{-1}. Identity was confirmed by mmp, NMR and Co-chromatography with authentic sample; *sitosterol* mp 136° (EtOH), IR, mmp Co–TLC with authentic sample. 5,7,4′,5″,7″,4‴-*hexahydroxy* [3–8″] *biflavanone* GB **1**a (**1a**) mp 240° (C_6H_6–Me_2CO) lit. mp 200° (dec.) [5] λ_{max} (EtOH) 228 (log e 4·53), 290 (4·99) and 335 nm (3·92), ν_{max} (nujol) 3300, 3200 and 1650 cm^{-1}. NMR [$(CD_3)_2CO$], 60 MHz −2·30 (*s*) and −2·31 (*s*) (2H 5-OH and 5″-OH); 2·66–2·82 (4H, 2*d*, *J* 9 Hz, 2′,6′-H and 2‴,6‴-H); 3·0–3·4 (4H, *m*, 3′,5′-H and 3‴,5‴-H); 4·04–4·07 (3H, br-S, 6, 8H and 6″-H), 4·39 and 5·39 (2H, 2,3-H), 5·17 and 6·20 (3H, 2″,3″-H). M^+ 542 (8%) significant peaks at *m/e* (%) 416 (60), 296 (100), 270 (20), 126 (82) and 107 (20). C.d (dioxan) 265 (0), 275 (2·47), 282 (0), 295 (−4·92), 320 (−1·20), 328 (0) and 342 (+0·737). 5,7,4′,3″,5″,7″,4‴-*heptahydroxy* [3–8″] *biflavanone GB I* (**1b**) mp 210° (C_6H_6–acetone) lit. m.p. 200° (dec.) [5] λ_{max} (EtOH) 225 (log e 4·53), 292 (4·44) and 335 nm (3·89), ν_{max} (KBr) 3350, 3150 and 1650 cm^{-1}. NMR [$(CD_3)_2CO$], 60 MHz 2·68 and 2·87 (4H, 2*d*, *J* 9 Hz, 2′,6′-H and 2‴,6‴-H); 3·10 and 3·26 (4H, 2*d* *J* 9 Hz, 3′,5′-H and 3‴,5‴-H); 4·0, 4·03 and 4·09 (3H, 6,8-H and 6″-H). M^+ 558 (0·2%) significant peaks at *m/e* (%) 540 (20), 432 (10) 414 (35), 296 (40), 270 (20), 126 (100) and 107 (45). 5,7,4′,3″,5″,7″,3‴,4‴-*octahydroxy* [3–8″] *biflavanone* GB 2 (**1c**) mp 230° (C_6H_6–Me_2CO) lit. mp 220° dec. [5] λ_{max} (EtOH) 225 (log e 5·56), 295 (5·45) and 335 nm (4·86), ν_{max} (nujol) 3470, 3350 and 1650 cm^{-1} NMR [$(CD_3)_2CO$], 60 MHz 2·75 (2H, *d*, *J* 9 Hz, 2′,6′-H), 3·12 (5H, 3′,5′-H and 2‴,3‴,6‴-H), 4·41 (*s*) and 5·09–6·0 (4H, 2, 2″, 3″-H). M^+ 574 (1%). Significant peaks at *m/e* (%) 448 (4), 430 (10), 296 (40), 270 (20), 242 (10), 126 (100), 123 (25), 107 (30). The identity of the biflavanones GB **1**a, GB **1** and GB **2** were confirmed by mmp, Co–TLC and IR comparison with authentic samples. Methylation of GB 2 with MeI, K_2CO_3 and dry Me_2CO gave (**1d**) and (**1e**): (**1e**), mp 135° (C_6H_6–$CHCl_3$). M^+ 672·2181 (1·2%) $C_{37}H_{36}O_{12}$ requires 672·2207. Significant peaks at *m/e* (%) 656 (27), 654 (6·9). $C_{37}H_{34}O_{11}$. 640 (100), 610 (10), 492 (10), 312 (3·5) $C_{18}H_{16}O_5$ 154 (2·4), $C_8H_{10}O_3$ and 151 (80·4) $C_9H_{11}O_2$: **1**d mp 120° (C_6H_6) M^+ 686 (0·14%). Significant peaks at *m/e* (%) 640 (100), 532 (1·4), 506 (1·5) and 3·12 (4·5).



(1a) $R_1 = R_2 = H$, $R_3 = OH$ (GB 1a)
(1b) $R_2 = H$, $R_1 = R_3 = OH$ (GB 1)
(1c) $R_1 = R_2 = R_3 = OH$ (GB 2)
(1d) $R_1 = R_2 = R_3 = OMe$ (fully methylated)
(1e) $R_1 = OH$, $R_2 = R_3 = OMe$ (partially methylated)



(2a) R = H (Volkensiflavone)
(2b) R = OH (Morelloflavone)

5,7,4′,5″,7″,4‴-*hexahydroxyflavanone* [3–8″] *flavone* (*Volkensiflavone*). (**2**a) mp 250° (C_6H_6–acetone) lit. mp 250° [6] λ_{max} (EtOH) 225 (log e 4·60), 275 (4·38), 289 (4·44) and 330 nm (4·20). ν_{max} (nujol) 3300, 1640 and 1610 cm^{-1} M^+ 540 (2%). Significant peaks at *m/e* (%) 414 (58), 296 (10), 268 (40), 167 (30), 126 (100) and 107 (10).

5,7,4′,5″,7″,4‴-*heptahydroxy flavanone* [3–8″] *flavone* (*morelloflavone*). (**2**b) mp 302–303° (MeOH) lit. mp 304° [7] λ_{max} (EtOH) 225 (log

Table 1. % Yield of xanthones and biflavonoids from *garcinia* species

Compound	*Garcinia echinocarpa* Bark	*Garcinia echinocarpa* Wood	*Garcinia terpnophylla* Bark	*Garcinia terpnophylla* Wood
1,5-Dihydroxyxanthone		0·002		0·006
1,7-Dihydroxyxanthone				0·001
1,3,6,7-Tetrahydroxy-xanthone	0·01	0·02		
Mangostin			0·004	0·001
GB I (a) (**1a**)			0·30	0·15
GB 1 (**1b**)			0·30	0·15
GB 2 (**1c**)			0·90	0·15
Volkensiflavone (**2a**)	0·03	0·08		
Morelloflavone (**2b**)	0·03	0·04		
Sitosterol		0·002	0·03	0·03

e 4·57), 275 (4·38), 288 (4·43) and 340 nm (4·25). ν_{max} (KBr) 3300, 1640 cm^{-1} NMR [$(CD_3)_2CO$] 100 MHz −4·29 and −3·89 (2H, 2*s*, 5- and 5″-OH); 2·59 (*m*), 2·87 and 3·51 (*d*, *J* 9 Hz) (3H, 2‴,5‴ and 6‴-H), 3·33 (1H, br. *s*, 3″-H), 3·75 (1H, *s*, 6″-H), 4·01 (2H, *s*, 6, 8H), 4·20 (1H, *d*, *J* 12 Hz, 2-H), 5·06 (1H, *d*, *J* 12 Hz, 3-H). M^+ 556 (10%) significant peaks at *m/e* (%) 430 (100), 402 (40), 326 (20), 296 (15), 268 (35), 126 (60), 121 (12) and 107 (20). Co-TLC and mmp proved the identity of volkensiflavone and morelloflavone. The distribution of these biflavonoids, xanthones and sitosterol is given in Table 1.

The main features of these two plants is the presence of relatively large amounts of ether extractable biflavonoids in the MeOH extract of both bark and timber. All these biflavonoids conform to types found in other *Garcinia* species. It is interesting to note that GB type biflavonoids were found only in *G. terpnophylla* Thw., while volkensiflavone and morelloflavone were found only in the extracts of *G. echinocarpa* Thw. Some of these biflavonoids have also been isolated from *Allanblackia floribunda* Oliver [8] which belong to the same sub family Clusiodeae, as *garcinia*; the presence of these biflavonoids extracts seems to be characteristic of this sub family. Mangostin was first isolated from *G. mangostana* L. [9]. It had not been isolated since from any other species of Guttiferae. Hence its presence in *G. terpnophylla* is significant, especially in the wood since di-isoprenylated xanthones are usually confined to the bark and fruit of the plants of other members of the Guttiferae [10].

Acknowledgements—The authors thank Dr. F. Scheinmann (University of Salford) for authentic samples of biflavanones GB **1**, GB **1**(a) and GB **2**, IR comparison of GB **1a** and for the new nomenclature names of the biflavonoids; Dr. K. Venkataraman (National Chemical Laboratory, Poona) for an authentic sample of morelloflavone and Dr. B. Joshi (Ciba Research Centre, Goregoan) for an authentic sample of volkensiflavone; Dr. P. Bladon (University of Strathclyde) for the high resolution mass spectra; Dr. I. Kitagawa (University of Osaka, Japan) for the NMR data; Dr. S. Balasubramaniam (Botany Department Peradeniya Campus) for the identification of plants; the University of Sri Lanka and the National Science Council of Sri Lanka for financial support.

REFERENCES

1. Jackson, B., Locksley, H. D., Moore, I. and Scheinmann, F. (1968) *J. Chem. Soc.* (c), 2579.
2. Govindachari, T. R., Pai, B. R., Subramaniam, P. S., Rao, R. S. and Muthukumaraswamy, N. (1967) *Tetrahedron* **23**, 243.
3. Yates, P. and Stout, G. H. (1958) *J. Am. Chem. Soc.* **80**, 1691.
4. Bhatia V. K., Ramanathan, J. D. and Seshadri, T. R. (1967) *Tetrahedron* **23**, 1363.
5. Jackson, B., Locksley, H. D., Scheinmann, F. and Wolstenholme, W. A. (1967) *Tetrahedron Letters* 787; (1971) *J. Chem. Soc.* (c) 3791.
6. Herbin, G. A., Jackson, B., Locksley, H. D. and Scheinmann, F. (1970) *Phytochemistry* **9**, 221.
7. Karanjgaokar, C. G., Radhakrishnan, P. V. and Venkataraman, K. (1967) *Tetrahedron Letters* 3195.
8. Locksley, H. D. and Murray, I. G. (1971) *J. Chem. Soc.* (c) 1332.
9. Schmidt, W. (1855) *Annalen* **93**, 83.
10. Sultanbawa, M. U. S. (1973) *J. Nat. Council Sri Lanka* **1**, 123.