Biflavanoids and a Flavanone-Chromone from the Leaves of *Garcinia dulcis* (Roxb.) Kurz †

By **Wajid Hussain Ansari** and **Wasiur Rahman,*** Department of Chemistry, Aligarh Muslim University, Aligarh, India
David Barraclough, Mrs. Ruth Maynard, and **Feodor Scheinmann,*** The Ramage Chemical Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

From the leaves of *Garcinia dulcis* (Roxb) Kurz a series of biflavanoids were isolated. Morelloflavone was characterised as its heptamethyl ether; it forms an octa-acetate by ring opening of ring I-C. GB-2a forms an octamethyl ether having a naringenin unit linked to a chalcone. By methylation, volkensiflavone and amentoflavone were isolated (as their hexamethyl ethers); methylation of a minor component gave the novel I-4′,I-5,II-5,I-7,II-7-pentamethoxyflavanone[I-3,II-8]chromone.

THE genus *Garcinia* (family Guttiferae, sub-family Clusiodeae) has attracted considerable interest in recent years as a result of the novel metabolites that have been isolated. Thus compounds of the morellin type have the unusual fused heterocyclic bicyclo[2.2.2]octenone system (1) incorporating a partially hydrogenated xanthone skeleton,[1] and more recently modified isoprenylbenzophenones have been isolated [*e.g.* (2)].[2] The [I-3, II-8]-linked biflavanoids (3) and (4) were first characterised in *Garcinia* species,[3,4] but more recently other genera of the Clusiodeae sub-family, *e.g. Allanblackia*[5] and *Pentaphalangium*,[6] were shown to have these metabolites. The leaf extracts of *Garcinia livingstonii* also contain flavone dimers of the amentoflavone series (5).[4a] The *Garcinia* genus consists of 180 species, mostly evergreen trees and occasionally shrubs distributed in tropical Asia, Africa, and Polynesia.[7] Ten major and twenty closely allied species occur in India, but the timbers are not of commercial value. However, gamboge resin has been used as a yellow dyestuff and in medicine.[8]

We report here the characterization of methyl ether and acetate derivatives of the biflavanoids (3) and (4) and a novel flavanone–chromone (6) from the leaf extracts of *G. dulcis* (Roxb.) Kurz. The flavanoid pigments were obtained from the dried and powdered defatted leaves by re-extracting the dark viscous acetone extract with hot ethyl acetate. The mixture of metabolites was then separated by chromatography on silica gel and the fraction which gave a positive Shinoda test[9] and green colour with ethanolic iron(III) chloride was examined further.

GB-2a (3a)[3a] and morelloflavone (4a)[3d] were separated from the other flavanoids by virtue of their solubility in 0.1M-disodium tetraborate and then separated from each other by column chromatography on silica. On methylation of GB-2a with an excess of dimethyl sulphate, ring opening of ring II-C occurred to form GDIMIII, the flavanone–chalcone octamethyl ether (7). The structure of the product follows from the mass and ^{1}H n.m.r. spectra. The mass spectral fragmentation pattern shows features characteristic of both flavanone and chalcone units (Scheme 1). Thus the molecular ion at *m/e* 670 undergoes a retro-Diels–Alder fragmentation of ring C-I to give the base peak at *m/e* 490 attributed to structure (8). The fragment ions at *m/e* 181 (9) and 121 (10) are attributed to rings A and B of the flavanone unit. The chief features of the fragmentation of the chalcone part are due to cleavage on both sides of the carbonyl group to give ions at *m/e* 191 (11) and 163 (12). Loss of the elements of a dimethoxy-aromatic unit in both cases requires the veratryl unit to be part of the chalcone system. The n.m.r. spectrum (solvent [^{2}H]chloroform –[$^2H_6$]dimethyl sulphoxide) confirms the structure of the flavanone–chalcone octamethyl ether (7); it shows peaks due to seven methoxy-groups between τ 6.18 and 6.4 and the remaining methoxy-signal appears at τ 6.6. Benzene-induced solvent-shift studies confirm that the high field

† Part XXXI in the Series (from Salford) 'Extractives from Guttiferae.' Part XXX, D. M. Holloway and F. Scheinmann, *Phytochemistry*, 1975, **14**, 2517.

[1] W. D. Ollis, M. V. J. Ramsay, I. O. Sutherland, and S. Mongkolsuk, *Tetrahedron*, 1965, **21**, 1453, and references therein; P. Yates, S. S. Karmarkar, D. Rosenthal, G. H. Stout, and V. F. Stout, *Tetrahedron Letters*, 1963, 1623; S. A. Ahmad, W. Rigby, and R. B. Taylor, *J. Chem. Soc.* (*C*), 1966, 772; B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1790; M. Amorosa and G. Giovanninetti, *Ann. Chim.* (*Italy*), 1966, **56**, 232; G. Cardillo and I. Merlini, *Tetrahedron Letters*, 1967, 2529; G. Kartha, H. N. Ramachandran, H. B. Bhat, P. M. Nair, V. K. V. Raghavan, and K. Venkataraman, *Tetrahedron Letters*, 1963, 459; C. G. Karanjganonkar, P. M. Nair, and K. Venkataraman, *Tetrahedron Letters*, 1966, 687; H. B. Bhat, P. M. Nair, and K. Venkataraman, *Indian J. Chem.*, 1964, **2**, 402, 405; A. Jefferson and F. Scheinmann, *Chem. Comm.*, 1971, 966.

[2] C. G. Karanjgoakar, A. V. Rama Rao, K. Venkataraman, S. S. Yemul, and K. J. Palmer, *Tetrahedron Letters*, 1973, 4977.

[3] (*a*) B. Jackson, H. D. Locksley, F. Scheinmann, and W. A. Wolstenholme, *J. Chem. Soc.* (*C*), 1971, 3791; *Tetrahedron Letters*, 1967, 787, 3049; *Chem. Comm.*, 1968, 1125, 1360; (*b*) G. A. Herbin, B. Jackson, H. D. Locksley, F. Scheinmann, and W. A. Wolstenholme, *Phytochemistry*, 1970, **9**, 221; (*c*) B. S. Joshi, V. N. Kamat, and N. Viswanathan, *Phytochemistry*, 1970, **9**, 881; (*d*) C. G. Karanjgaokar, P. V. Radhakrishnan, and K. Venkataraman, *Tetrahedron Letters*, 1967, 3195; (*e*) M. Konoshima, Y. Ikeshiro, and S. Miyahara, *Tetrahedron Letters*, 1970, 4203.

[4] (*a*) A. Pelter, R. Warren, K. K. Chexal, B. K. Handa, and W. Rahman, *Tetrahedron*, 1971, **27**, 1625; (*b*) K. K. Chexal, B. K. Handa, and W. Rahman, *J. Chromatog.*, 1970, **48**, 484; A. Pelter, R. Warren, J. N. Usmani, S. P. Bhatnagar, R. H. Rizvi, M. Ilyas, and W. Rahman, *Experientia*, 1969, **25**, 350; (*c*) R. Hodges, *Austral. J. Chem.*, 1965, **18**, 1491; (*d*) A. Pelter, R. Warren, N. Hameed, N. U. Khan, M. Ilyas, and W. Rahman, *Phytochemistry*, 1970, **2**, 1897; A. K. Varshney, T. Mah, N. U. Khan, W. Rahman, C. W. Hwa, M. Okigawa, and N. Kawano, *Indian J. Chem.*, 1973, **11**, 1209.

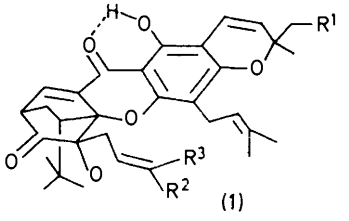
[5] H. D. Locksley and I. G. Murray, *J. Chem. Soc.* (*C*), 1971, 1332.

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

[7] 'The Wealth of India,' CSIR, New Delhi, India, 1956, vol. IV, p. 99.

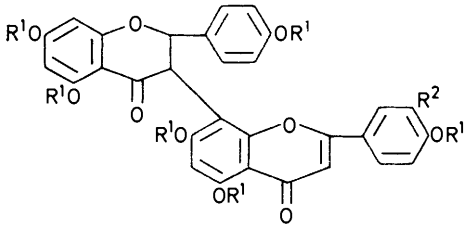
[8] 'Encyclopaedia Britannica,' 1961, vol. 9, p. 1000.

[9] J. Shinoda, *J. Pharm. Soc. Japan*, 1928, **48**, 214.



(1)

	R^1	R^2	R^3	
a;	$Me_2CH{:}CH{\cdot}CH_2$	Me	CO_2H	(gambogic acid)
b;	H	Me	CHO	(morellin)
c;	H	CHO	Me	(isomorellin)
d;	H	Me	CO_2H	(morellic acid)
e;	H	CO_2H	H	(isomorellic acid
f;	H	Me	Me	(deoxymorellin)
g;	H	CHO	Me	(dihydroisomorellin)
		[single bond at C(1'),C(2')]		

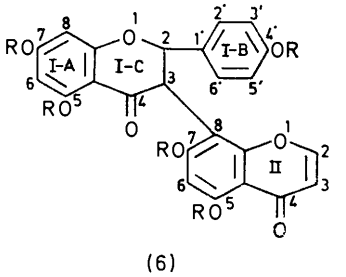


(4)

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

b ; R^1 = Me, R^2 = OMe

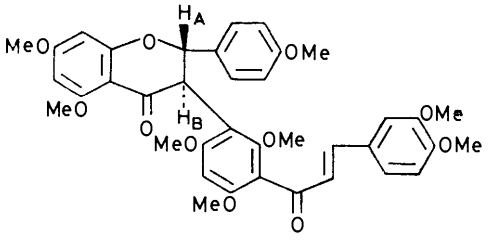
c ; R^1 = Me, R^2 = H



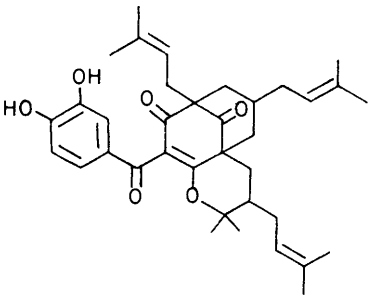
(6)

a ; R = H

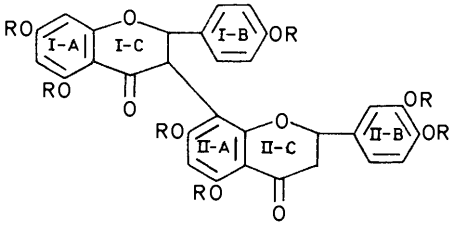
b ; R = Me



(7)

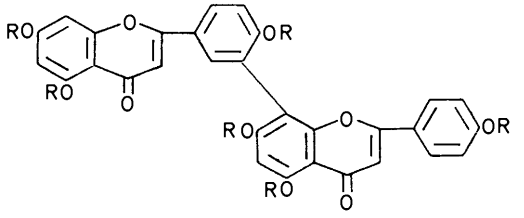


(2) (isoxanthochymol)



(3)

a; R = H



(5)

a ; R = Me

b ; R = H

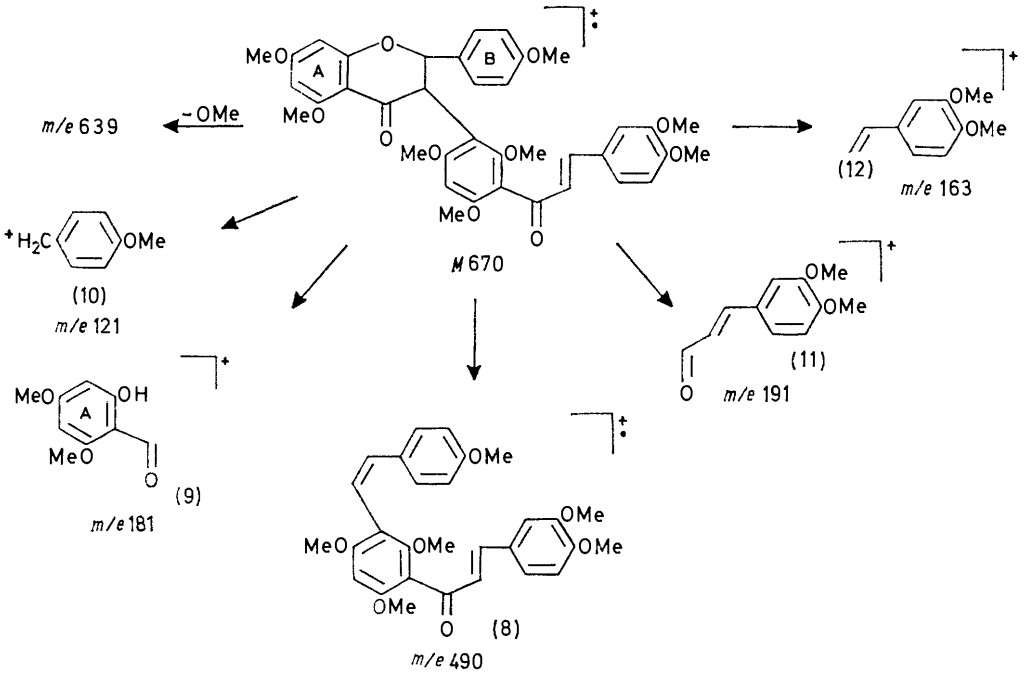
methoxy-group is the hindered one, flanked by two substituents in ring II-A: this is the only methoxy-group which does not give signals at higher field on incremental additions of [$^2H_6$]benzene. The aliphatic protons H_A and H_B in ring I-C resonate at τ 4.21 and 5.50 as doublets with J 12 Hz; a *trans*-diaxial conformation is therefore assumed. The two phloroglucinol protons of ring I-A resonate as a broad singlet (2H) at τ 3.94 whereas the signal for the one in ring II-A appears at τ 3.84. The remaining seven aromatic protons of rings I-B and II-B and the two low-field olefinic protons of the chalcone system give a complex group of signals at τ 2.6—3.44.[3a] A similar ring opening to give a flavanone–chalcone has been previously observed with GB-1a.[3a]

The structure of morelloflavone was confirmed by direct comparison with an authentic specimen, and by preparation of the heptamethyl ether (4b) and the octa-acetate (13a).[3b-d,4a]

The flavanoid residue left after extraction of GB-2a (3a) and morelloflavone (4a) was separated into two fractions, GDIII and GDIV, by chromatography. The major fraction GDIII was acetylated with acetic

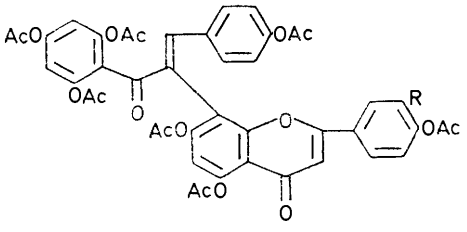
anhydride–pyridine, and volkensiflavone hepta-acetate (13b), m.p. 206—207°, was isolated after repeated recrystallization from chloroform–methanol. This hepta-acetate (13b) has been described previously as BGH-III acetate and talbotaflavone hepta-acetate, and its spectral properties are in good agreement with recorded data.[3c,4a]

The minor component GDIV was isolated as yellow crystals by preparative t.l.c. and methylated with dimethyl sulphate to give a pentamethyl ether, GDIVM. GDIVM, from its ^{1}H n.m.r. and mass spectra, has been assigned the novel flavanone–chromone structure (6b). Thus the ^{1}H n.m.r. spectrum shows five methoxy-signals



SCHEME 1 Fragmentation of GD1MIII

From methylation of fraction GDIII two biflavanoid methyl ethers (GDIIIMI and GDIIIMII) were isolated.



(13)
a; R = OAc
b; R = H

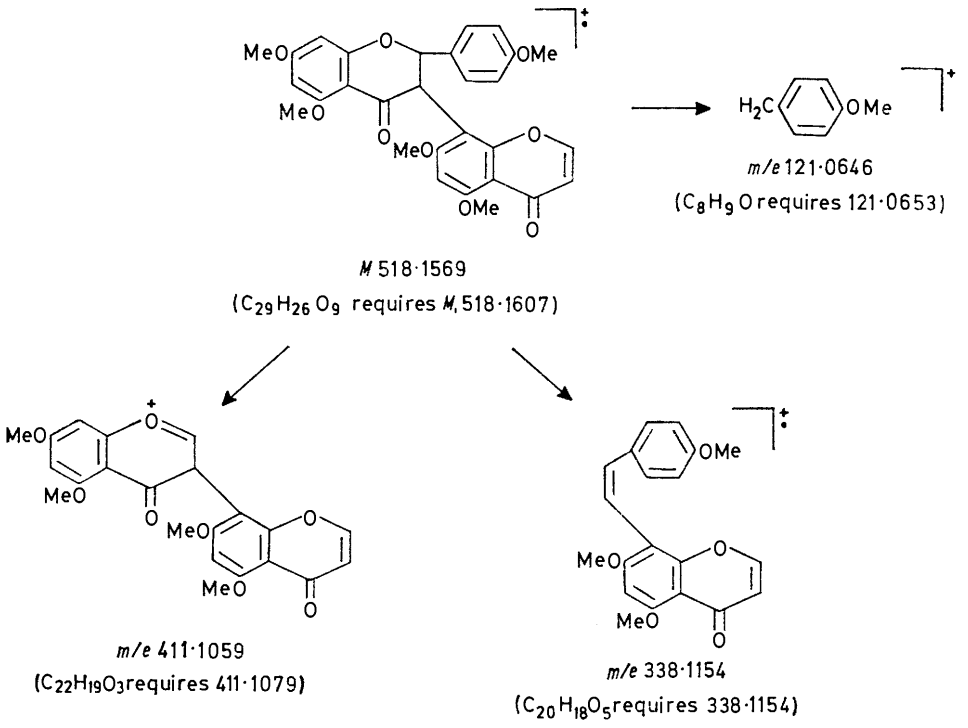
GDIIIMI was characterized as amentoflavone hexamethyl ether (5a), and GDIIIMII corresponds to volkensiflavone hexamethyl ether (4c), also described as BGH-III methyl ether [4a] and as talbotaflavone hexamethyl ether.[3c] Both these methyl ethers had previously been obtained from the metabolites of *G. livingstonii*, and direct comparison confirmed their identity.[4a]

Differences in m.p. reported for amentoflavone hexamethyl ether, *e.g.* GDIIIMI, m.p. 175°, are probably due to the isolation of either optically active, m.p. 170—171°,[4d] or racemic modifications, m.p. 217—218° and 225°.[4a-c]

in the region τ 6.1—6.4. The aliphatic protons in the heterocyclic ring of the flavanone are in *trans*-diaxial conformation as shown by the signals at τ 5.21 and 4.34 (J 12 Hz). The two aromatic protons of the phloroglucinol ring A resonate at τ 3.96 (J 2 Hz), whereas four protons of the flavanone system of ring B resonate as an AA'BB' system centred at τ 3.25. The olefinic protons of the chromone system appear as an AB system with doublets at τ 2.61 and 4.03 (J 6 Hz).[10] Irradiation at the frequency of the signal at lowest field transforms the latter doublet into a singlet. The phloroglucinol proton of the chromone system resonates at τ 3.84. The assignment of these signals necessitates that the flavanonyl–chromone linkage be either [I-3,II-8] or [I-3,II-6]. The flavanone[I-3,II-8]chromone structure was preferred since the signals of all the methoxy-groups move up-field on addition of [$^2H_6$]benzene. Furthermore, the fact that the parent metabolite underwent total methylation without undue difficulty again favoured the [I-3,II-8]-linkage, since in the alternative [I-3,II-6]-linkage the crowded hydroxy-group at II-5 may be resistant to methylation.

Examination of the effect of added [$^2H_6$]benzene on the chemical shift of the chromone protons at positions II-2

[10] T. J. Batterham, 'N.M.R. Spectra of Simple Heterocycles,' Wiley, New York, 1972, p. 395; C. T. Mathis and J. H. Goldstein, *Spectrochim. Acta*, 1964, **20**, 871.



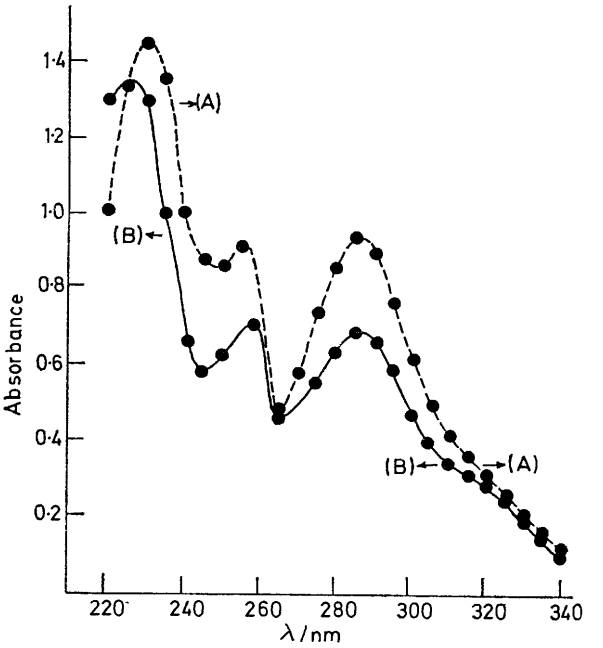
SCHEME 2 Fragmentation of GDIVM

and II-3 shows that the former undergoes a greater upfield shift than the latter. The preferential shielding of the former is explained in terms of a collision complex whereby the π-electrons of [$^2H_6$]benzene interact with the partial positive centres created by the carbonyl group of the heterocyclic ring: by conjugative electron withdrawal the proton at position II-2 is more electropositive than that at II-3 in the chromone system.

The mass spectral fragmentation of GDIVM is in agreement with the flavanone–chromone structure (5b). Thus the molecular ion (M^+ 518) undergoes a retro-Diels–Alder fragmentation to give the base peak at *m/e* 338 (Scheme 2). Other strong peaks at *m/e* 411 and 121 result from loss of the elements of a *p*-methoxyphenyl fragment from the molecular ion, and from formation of a *p*-methoxybenzyl fragment; such fragmentations have been noted previously in flavanoids.[3a,b]

The u.v. absorption spectra of GDIV and its pentamethyl ether GDIVM, with maxima in the region of 230, 260, and 290 nm, combine the features of simple flavanone and chromone chromophores, and these features are reproduced in the composite spectrum of an equimolar mixture of 5,7-dimethoxychromone and 4′,5,7-trimethoxyflavanone (see Figure).

The flavanone–chromone system assigned to GDIV is, to our knowledge, unique and the chromone unit is unusual in that there are no substituents in the heterocyclic ring.[11] Natural benzopyran-4-ones have phenolic substituents at C-2 or C-3 when the heterocyclic ring is derived from shikimic acid.[11a,c] For an acetate-derived



U.v. spectra in methanol: (A) equimolar (1 × 10^{-4}M) mixture of 5,7-dimethoxychromone [$\lambda_{max.}$ 255 (ε 11 × 10^3) and 290 nm (5.2 × 10^3)] and 4′,5,7-trimethoxyflavanone [$\lambda_{max.}$ 230 (ε 14.5 × 10^3) and 285 nm (8.3 × 10^3)]; (B), the flavanone–chromone (6b) [$\lambda_{max.}$ 225 (ε 54.0 × 10^3), 258 (28.2 × 10^3), and 285 nm (27.6 × 10^3)]

heterocyclic ring the substituent at C-2 is usually a methyl group.[11a,b] Although no information on the

[11] (*a*) F. M. Dean, 'Naturally Occurring Oxygen Ring Compounds,' Butterworths, London, 1963; (*b*) A. Mustafa, 'Furopyrans and Furopyrones,' Wiley–Interscience, London, 1967; (*c*) T. A. Geissman in 'Biogenesis of Natural Compounds,' Pergamon, Oxford, 1967.

biogenesis of GDIV is available its co-occurrence with the biflavanones in the leaves of *G. dulcis* (Roxb.) Kurz is of interest. Thus if the flavanone–chromone GDIV (6a) and the biflavanones are related in their mode of biogenesis, the unsubstituted chromone ring could be derived by elimination of a phenolic substituent from a biflavone.

EXPERIMENTAL

Analytical and preparative t.l.c. were performed on silica gel G (Merck, nach Stahl) or silica gel NCL-Poona in benzene–pyridine–formic acid (36 : 9 : 5) (BPF) or toluene–ethyl formate–formic acid (5 : 4 : 1) (TEFF). N.m.r. spectra were taken for solutions in $CDCl_3$ at 100 MHz with Me_4Si as internal standard, and mass spectra were measured on an MS12 or MS9 spectrometer. Solvent shift data for GB-2a octamethyl ether and GDIVM are available as Supplementary Publication No. SUP 21723 (7 pp.).*

Extraction.—Dried and powdered leaves (4 kg) collected at Sipore, West Bengal, India were completely extracted with light petroleum (b.p. 40—60°). The treated leaves were dried and exhausted with boiling acetone. The combined acetone extracts were concentrated at atmospheric pressure to give a dark viscous mass. This was extracted successively with light petroleum (b.p. 40—60°), benzene, and hot water to remove non-flavanoid and resinous matter. The brownish gummy mass was then refluxed with ethyl acetate for 10 h and the mixture was filtered. The filtrate was evaporated to give a dark brown residue (15 g), which responded to the usual colour test for flavanoids.

Chromatographic Separation.—The dark brown solid (15 g) was adsorbed on silica gel (20 g) and transferred to a column of silica gel (150 g) made up with light petroleum (b.p. 40—60°). Elution was performed with the following solvents successively, giving the material shown in parentheses: (i) light petroleum (green oil), (ii) benzene (gummy mass), (iii) chloroform (green oil), (iv) benzene–acetone (8 : 2) (light brown solid; 5 g), and (v) acetone (dark brown mass). Fraction (iv) gave positive colour tests for flavanoids. T.l.c. showed three closely moving spots, two major (R_F 0.12 and 0.21) and one minor (R_F 0.30) (BPF). Fraction (iv) was dissolved in ethyl acetate and extracted with 0.1M-disodium tetraborate. The organic layer gave a yellowish brown solid (1.2 g) consisting mainly of GDIII and GDIV, which were separated by preparative t.l.c. (NCL; BPF) to give pure GDIII (400 mg) and GDIV (120 mg). The borate extract was acidified with dilute hydrochloric acid and the resulting suspension was extracted with ethyl acetate. This extract yielded a yellow solid (3.0 g), which was separated into two fractions, GDI and GDII, by column chromatography (silica gel) in acetone–benzene (1 : 9) followed by preparative t.l.c. (TEFF).

Morelloflavone (4a).—Fraction GDII was crystallized from methanol to give morelloflavone (4a) as yellow plates (1.5 g), m.p. 298—300°, R_F 0.38.

Morelloflavone Heptamethyl Ether (4b).—GDII (300 mg), acetone (300 ml), anhydrous potassium carbonate (3 g), and dimethyl sulphate (1 ml) were refluxed for 12 h and the mixture was filtered. Acetone was removed and the residue purified by preparative t.l.c. to yield a white solid. Morelloflavone heptamethyl ether (4b) crystallized (from $CHCl_3$–MeOH) as plates (195 mg), m.p. 211—213°, R_F 0.57; τ ($CDCl_3$) 2.9 (2 H, d, J 9 Hz, H-I-2′,6′), 3.41 (2 H, d, J 9 Hz, H-I-3′,5′), 3.81 (1 H, d, J 3 Hz, H-I-8), 3.88 (1 H, d, J 3 Hz, H-I-6), 3.74 (1 H, s, H-II-6), 3.54 (1 H, s, H-II-3), 4.16 (1 H, d, J 12 Hz, H-I-2), 5.08 (1 H, d, J 12 Hz, H-I-3), 2.6 (1 H, q, J 9 and 3 Hz, H-II-6′), 2.85 (1 H, d, J 3 Hz, H-II-2′), 3.02 (1 H, d, J 9 Hz, H-II-5′), and 6.08—6.36 (21 H, 7 OMe).

Morelloflavone Octa-acetate (13a).—A mixture of GDII (130 mg), pyridine (1 ml), and acetic anhydride (1.5 ml) was refluxed on a water-bath for 2 h, cooled, and poured on to crushed ice. The white solid was filtered off, washed with water, and dried. It crystallized (from $CHCl_3$–MeOH) as prisms (95 mg), m.p. 213—214°, τ ($CDCl_3$) 2.47 (2 H, d, J 9 Hz, H-I-2,6), 3.01 (2 H, d, J 9 Hz, H-I-3,5), 3.40 (1 H, d, J 3 Hz, H-I-3′), 3.52 (1 H, d, J 3 Hz, H-I-5′), 3.21 (1 H, s, H-II-6), 3.38 (1 H, s, H-II-3), 3.92 (1 H, s, H-I-β), 2.15 (1 H, d, J 3 Hz, H-II-2′), 2.68 (1 H, d, J 9 Hz, H-II-5′), 2.15 (1 H, q, J 9 and 3 Hz, H-II-6′), and 7.26—8.08 (24 H, 8 OAc).

GB-2a (3a).—Fraction GDI gave an amorphous solid (1 g), m.p. 225°, R_F 0.45, identified as GB-2a.

GB-2a Octamethyl Ether (*Octa-O-methylflavanone*[I-3,II-8]-*chalcone*) (7).—The pigment GDI (250 mg) was methylated with an excess of dimethyl sulphate and anhydrous potassium carbonate in boiling acetone for 18 h. The product on preparative t.l.c. yielded GB-2a octamethyl ether (7) as a white solid, which crystallized (from $CHCl_3$–MeOH) as cubes (200 mg), m.p. 237—238°, R_F 0.79, τ [$CDCl_3$–$(CD_3)_2SO$] 2.6—3.44 (9 H, m, two olefinic and seven aromatic protons from rings I-B and II-B), 3.84 (1 H, s, H-II-A), 3.94 (2 H, s, H-I-6,8), 4.21 (1 H, d, J 12 Hz, H-I-2), 5.50 (1 H, d, J 12 Hz, H-I-3), 6.18 (6 H, s, 2 OMe), 6.22 (3 H, s, OMe), 6.28 (3 H, s, OMe), 6.30 (3 H, s, OMe), 6.36 (3 H, s, OMe), 6.40 (3 H, s, OMe), and 6.60 (3 H, s, OMe).

Volkensiflavone Hexamethyl Ether (4c) *and Amentoflavone Hexamethyl Ether* (5a).—A mixture of GDIII (250 mg), anhydrous potassium carbonate (2.5 g), and dimethyl sulphate (1 ml) in dry acetone (300 ml) was refluxed for 14 h. After the usual work-up, t.l.c. (BPF) showed the presence of hexamethyl ethers of volkensiflavone (4c) and amentoflavone (5a) (R_F value and characteristic shade in u.v. light).[4a,b] Both components were separated by preparative t.l.c. to give pure (4c) as cubes (from MeOH) (105 mg), m.p. 250—251° (lit.,[3c] 265°), R_F 0.46, τ ($CDCl_3$) 2.44 (2 H, d, J 8.5 Hz, H-II-2′,6′), 3.25 (2 H, d, J 8.5 Hz, H-II-3′,5′), 2.95 (2 H, d, J 8.5 Hz, H-I-2′6′), 3.46 (2 H, d, J 8.5 Hz, H-I-3′,5′), 3.64 (1 H, s, H-II-3), 3.80 (1 H, d, J 1.5 Hz, H-I-8), 3.90 (1 H, d, J 1.5 Hz, H-I-6), 3.88 (1 H, s, H-II-6), 4.34 (1 H, d, J 12 Hz, H-I-2), 5.22 (1 H, d, J 12 Hz, H-I-3), 6.16 (3 H, s, OMe), 6.20 (3 H, s, OMe), 6.24 (6 H, s, OMe), 6.26 (3 H, s, OMe), 6.41 (3 H, s, OMe). Direct comparison also confirmed the structures (4c) and (5a).

Amentoflavone hexamethyl ether (5a) crystallizes as needles (from $CHCl_3$–MeOH) (40 mg), m.p. 175° (lit., [4d] 170—171°), R_F 0.41, τ ($CDCl_3$) 2.10 (1 H, q, J 2.5 and 8.5 Hz, H-I-6′), 2.18 (1 H, d, J 2.5 Hz, H-I-2′), 2.92 (1 H, d, J 8.5 Hz, H-I-5′), 2.65 (2 H, d, J 8.5 Hz, H-II-2′,6′), 3.28 (2 H, d, J 8.5 Hz, H-II-3′,5′), 3.42 (1 H, s, H-II-6), 3.48 and 3.52 (1 H each s, H-I-3 and H-II-3), 3.57 (1 H, d, J 2 Hz, H-I-8), 3.70 (1 H, d, J 2 Hz, H-I-6), 5.98 (3 H, s, OMe), 6.11 (3 H, s, OMe), 6.15 (3 H, s, OMe), 6.21 (3 H, s, OMe), 6.28 (3 H, s, OMe), and 6.30 (3 H, s, OMe).

Volkensiflavone Hepta-acetate (13b).—A solution of GDIII (100 mg) in pyridine (1 ml) and acetic anhydride (1.5 ml) was refluxed on a water-bath for 2 h. Usual work-up and repeated crystallizations (from $CHCl_3$–MeOH) gave needles

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

of volkensiflavone hepta-acetate (13b) (65 mg), m.p. 206—207° (lit.,[3c] 190—192°), τ ($CDCl_3$) 2.04 (2 H, d, *J* 8.5 Hz, H-II-2′,6′), 2.84 (2 H, d, *J* 8.5 Hz, H-II-3′,5′), 2.50 (2 H, d, *J* 8.5 Hz H-I-2,6), 3.06 (2 H, d, *J* 8.5 Hz, H-I-3,5), 3.26 (1 H, s, H-II-6), 3.42 (1 H, s, H-II-3), 3.44 (1 H, d, *J* 2 Hz, H-I-3′), 3.56 (1 H, d, *J* 2 Hz, H-I-5′), 3.97 (1 H, s, H-I-β), 7.66 (3 H, s, OAc), 7.72 (3 H, s, OAc), 7.78 (6 H, s, OAc), 7.83 (6 H, s, OAc), and 8.12 (3 H, s, OAc).

I-4′,I-5,II-5,I-7,II-7-*Pentahydroxyflavanone*[I-3,II-8]-*chromone* (6a).—Band GDIV gave yellow crystals of (6a) (120 mg) (from $CHCl_3$–EtOAc), m.p. 300°, R_F 0.31 (BPF), $\lambda_{max.}$ (MeOH) 263 and 294 nm.

I-4′,I-5,II-5,I-7,II-7-*Penta*-O-*methylflavanone*[I-3,II-8]-*chromone* (6b).—A mixture of GDIV (75 mg), anhydrous potassium carbonate (1 g), and dimethyl sulphate (0.5 ml) in dry acetone (150 ml) was refluxed for 16 h. Usual work-up and preparative t.l.c. yielded a white solid (6b), which crystallized (from $CHCl_3$–MeOH) as *cubes* (58 mg), m.p. 149—151°, R_F 0.45, $\lambda_{max.}$ (MeOH) 259 and 285 nm; τ ($CDCl_3$) 3.07 (2 H, d, *J* 9 Hz, H-I-2′,6′), 3.42 (2 H, d, *J* 9 Hz, H-I-3′,5′), 3.94 (1 H, d, *J* 2.5 Hz, H-I-8), 3.98 (1 H, d, *J* 2.5 Hz, H-I-6), 3.84 (1 H, s, H-II-6), 4.34 (1 H, d, *J* 12 Hz, H-I-2), 5.21 (1 H, d, *J* 12 Hz, H-I-3), 2.61 (1 H, d, *J* 6 Hz, H-II-2), 4.03 (1 H, d, *J* 6 Hz, H-II-3), 6.16 (3 H, s, OMe), 6.18 (3 H, s, OMe), 6.23 (3 H, s, OMe), 6.26 (3 H, s, OMe), and 6.34 (3 H, s, OMe) (Found: M^+, 518.156 9. $C_{29}H_{26}O_9$ requires *M*, 518.160 7).

One of the authors (W. H. A.) thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial assistance.

[5/1630 *Received*, 18*th August*, 1975]