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BIFLAVONYLS FROM GUTTIFEREAE—*GARCINIA LIVINGSTONII**

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Abstract—Morelloflavone (BGH-II) and a new biflavonyl, BGH-III along with optically active amentoflavone and podocarpusflavone A have been isolated from the phenolic extractives of heartwood, bark and leaves of *Garcinia livingstonii*. Two members of a new series of 3,8-linked biflavones have been produced from BGH-II and BGH-III. Mass spectral and NMR studies including solvent dependent shifts of OMe resonances are used for structure elucidation. An anomaly in the method of OMe proton shifts is pointed out.

GARCINIA species are becoming a focus of attention for the investigation of biflavonyls with reduced heterocyclic systems.[1-6] The present paper describes the isolation and characterization of four biflavonyl pigments from the leaf, heartwood and bark extracts of *Garcinia livingstonii*† procured from the Horticulture Research Centre, Saharanpur, India. Morelloflavone[2] (BGH-II, Ic) and BGH-III, Ia, both with reduced heterocyclic rings were found in the heartwood and bark while the leaf extracts yielded flavone dimers, amentoflavone[7] and podocarpusflavone A.[8] The latter constitute the first example of the occurrence of biflavonyls in the leaves of Garcinia species. The observation with regard to the occurrence of biflavonyls derived from flavone-flavone units (higher oxidation level) in leaves and those derived from flavanone-flavone units (lower oxidation level) in heartwood and bark of *G. livingstonii* agrees well with the earlier suggestion that there is a tendency for the state of oxidation of flavonoids to increase as the upper extremities of the plants are reached.[9]

The phenolic extractives of the defatted heartwood on solvent fractionation and repeated preparative TLC yielded two closely spaced homogeneous components designated as BGH-II and BGH-III.

Both pigments gave a red colour in the Shinoda test[10], and a green one with alcoholic ferric chloride. The IR spectra showed broad OH bands at 3250 cm^{-1} and a chelated CO appeared at 1645 cm^{-1}. The latter resolved into two bands at 1670 and 1645 cm^{-1} in the spectra of Me ethers suggesting the presence of a 5-hydroxyflavanone and 5-hydroxyflavone units. BGH-II and BGH-III showed absorption maxima at 228, 275, 288 and 345 mμ and 227, 276 (influx), 290 and 340 mμ respectively. The

*A part from K. K. Chexal, Ph.D. thesis, Aligarh Muslim University, Aligarh, (1970).

† After the completion of our work on the biflavonyls of the leaves, heartwood and bark of Garcinia livingstonii, reports of the isolation of morelloflavone and a new biflavonyl, volkensiflavone from G. volkensii[5] and talbotaflavone from G. talboti[6] appeared. However, the methods used by ourselves tend to complement those used by previous workers[5,6] and hence are presented in this paper.

molecular formulae of BGH-II and BGH-III determined by analytical methods and mass spectrometry corresponded to $C_{30}H_{20}O_{11}$ and $C_{30}H_{20}O_{10}$ respectively.

Methylation of BGH-III mp 267–268° [lit. [5, 6] mp 250° (dec) and 300° (dec)] with methyl iodide and potassium carbonate in acetone yielded a methyl ether (Ib) mp 254–256° (lit.[6] mp 265°) *m/e* 624 (M^+, $C_{36}H_{32}O_{10}$). The mass spectrum[1, 3, 11, 13] supported the presence of a phloroglucinol nucleus derived from 5,7-dihydroxy-flavanone system with ions at *m/e* 154 and 181 consistent with fragments $[C_6H_3(OMe)_2OH]^+$ and $[C_6H_2(OMe)_2OH.CO]^+$ respectively. In addition the presence of another free aromatic ring in a flavonone unit was suggested by ions at *m/e* 121 and 108 corresponding to fragments $[C_6H_4(OMe).CH_2]^+$ and $[C_6H_5OMe]^+$ respectively. The existence of an ion at *m/e* 132 $[C_6H_4(OMe)C{\equiv}CH]^+$ indicated that ring B of a flavone unit was not involved in the interflavonyl linkage.

The NMR spectrum of the methyl ether showed OMe signals between τ 6·08 to τ 6·36 which integrated for 18 protons. The doublets at τ 4·28 and 5·18 (J_{trans} = 12 c/s) were shown to be coupled by double resonance. These were assigned to H-2 and H-3 trans protons of ring C of the flavanone unit. The aromatic protons were assigned (double resonance) as shown in Table 1.

TABLE 1*

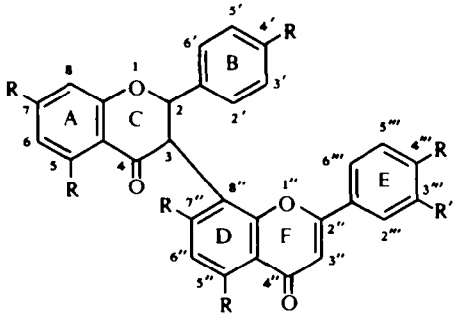
Proton	Ib	Id
2′, 6′	2·95 d J = 9	2·91 d J = 9
3′, 5′	3·44 d J = 9	3·40 d J = 9
8	3·7 d J = 2	3·81 d J = 3
6	3·9 d J = 2	3·88 d J = 3
6″	3·83 s	3·74 s
3″	3·59 s	3·54 s
2	4·28 d J = 12	4·16 d J = 12
3	5·18 d J = 12	5·08 d J = 12
2‴, 6‴	2·4 d J = 8	
3‴, 5‴	3·2 d J = 8	
6‴		2·6 q J_1 = 9, J_2 = 3
2‴		2·85 d J = 3
5‴		3·20 d J = 9
OMe	6·08–6·36 (18 protons)	6·08–6·36 (21 protons)

s = singlet, d = doublet, q = quartet.

*Spectra run in $CDCl_3$ at 100 Mc/s, TMS as an internal standard = τ 10·00. Values of J in c/s.

The two sets of aromatic protons of A_2B_2 pattern were assigned to rings B and E. Two meta coupled doublets at τ 3·7 and 3·9 were attributed to the H-8 and H-6 protons of ring A. Of the two singlets at τ 3·82 and τ 3·59, the former was assigned to H-6″ (ring D) and the latter to H-3″ (olefinic proton in ring F). The data was in full agreement with a structure in which C-3 of a flavanone is linked either to C-8 or C-6 of flavone unit. The possibility of 2–8″/2–6″ linkage i.e. isoflavanone-flavone structure

cannot be ruled out at this stage as H-2 and H-3 protons in both cases are expected to show the same chemical shifts.



I a: R = OH; R′ = H
b: R = OMe; R′ = H
c: R = R′ = OH
d: R = R′ = OMe

The mass spectrum supported the above postulates as the fragmentation of the molecular ion at *m/e* 624 could be rationalized by RDA of a flavanone at ring C to give a fragment ion at *m/e* 444 followed by loss of 28 units (CO)[11,12] to give an ion of *m/e* 416. These results can only be accommodated by a linkage from the heterocyclic ring C (flavanone unit) to the phloroglucinol ring D (flavone unit).

The problem of the linkage with C-6 or C-8 of ring D was solved by solvent induced shifts studies of OMe resonances.[14–17] On change of solvent from $CDCl_3$ to 80% C_6D_6/20% $CDCl_3$ all the OMe resonances (τ 6·08–6·36) of Ib moved upfield (τ 6·5–6·8) (Fig I) showing that each OMe group has one ortho proton. This clearly established the substituent unit as being at C-8 rather than at C-6 in the flavone half of the molecule.

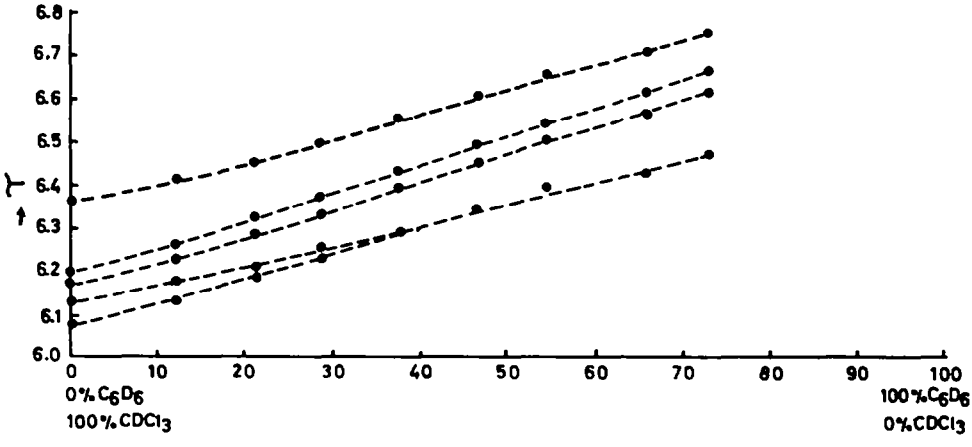


FIG. 1 Spectrum of benzene induced methoxy shifts in Ib

Acetylation of BGH-III with pyridine-acetic anhydride gave an acetate (IIa) mp 202–205° (lit.[6] mp 190–192°). The interesting observation was the complete lack of correlation between the NMR spectra of BGH-III acetate and its methyl ether. The doublets at τ 4·28 and τ 5·18 due to H-2 and H-3 respectively had disappeared and instead a downfield singlet appeared at τ 3·92. Further the signals due to acetoxy protons integrated for 21 protons instead of the expected 18 protons. It seemed as if, during acetylation, opening of the chromanone ring C had occurred transforming the flavanone to the corresponding chalcone. Although such cases of isomerization of flavanones to chalcones during acetylation with acetic anhydride-sodium acetate in monomeric flavonoids are known.[18,19] the flavanone-chalcone transformation using acetic anhydride-pyridine for acetylation is unusual as the latter conditions are claimed to be the most satisfactory for the preparation of flavanone acetates.[9] Another striking feature of the compound was its failure to isomerise during methylation using methyl sulphate/methyl iodide-potassium carbonate in acetone, as these conditions are known to induce chalcone formation.[9]

The results of NMR studies of BGH-III acetate are shown in Table 2. The singlet at τ 3·92 was assigned to H-β of the chalcone unit. The protons of one acetoxy group appeared at a considerably higher field, τ 8·08 and may either be at C-7 of ring D which is close to the unsaturated system of chalcone or possibly at C-4 of ring B.

TABLE 2

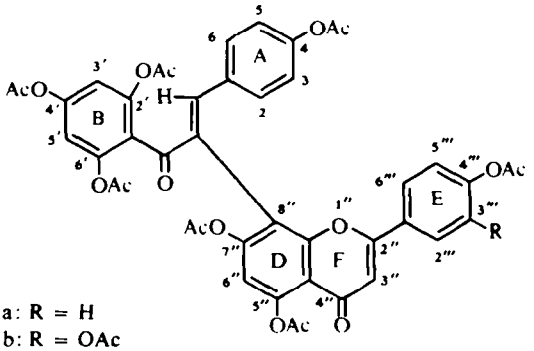
Proton	IIa	IIb
2·6	2·45 d J = 9	2·47 d J = 9
3·5	3·00 d J = 9	3·01 d J = 9
3'	3·38 d J = 2	3·40 d J = 3
5'	3·49 d J = 2	3·52 d J = 3
6''	3·22 s	3·21 s
3''	3·36 s	3·38 s
H-β	3·92 s	3·92 s
2''', 6'''	1·98 d J = 8	
3''', 5'''	2·75 d J = 8	
2'''		2·15 d J = 3
5'''		2·68 d J = 9
6'''		2·15 q J_1 = 9
		J_2 = 3
OAc	7·62–8·08 (21 protons)	7·26–8·08 (24 protons)

s = singlet, d = doublet, q = quartet.

*Spectra run in $CDCl_3$ at 100 Mc/s, TMS as an internal standard = τ 10·00. Values of J in c/s.

The possibility of a 2–8″ linkage i.e. isoflavanone-flavone structure was ruled out by ozonolysis of BGH-III acetate. The formation of ρ-acetoxy benzaldehyde (detected by TLC) clearly indicated the 3–8″ linkage.

On the basis of above considerations BGH-III was assigned the structure of 4′,4″,5,5″,7,7″-hexahydroxy-3 (8″-) flavonylflavanone (Ia) and BGH-III acetate that of 2′,4,4′,4″ ′,5″,6′,7″-hepta acetoxy-α(8″-) flavonylchalcone (IIa). BGH-II mp 300°

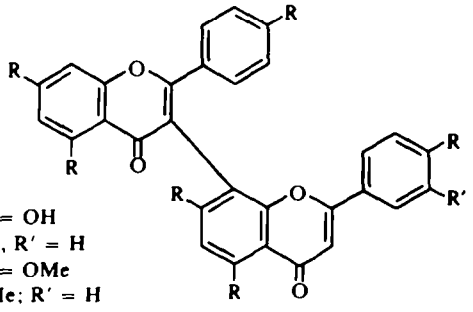


II a: R = H
b: R = OAc

(lit.[2] mp 298–299° dec) gave an acetate mp 212–215° (lit.[6] mp 203–204°) and a methyl ether mp 212–213° (lit.[2] mp 198–199°) *m/e* 654 (M^+, $C_{37}H_{34}O_{11}$). On similar grounds, BGH-II and its acetate were assigned the structures of 3″ ′,4′,4″ ′,5,5″,7,7″-heptahydroxy-3 (8″-) flavonylflavanone (Ic, morelloflavone[2]) and 2′,3″ ′,4,4′,4″ ′,5″,6′,7″-octaacetyl-α(8″-) flavonylchalcone (IIb) respectively.

The bark extracts of *G.livingstonii* by a similar isolation procedure gave two homogeneous components. They were found to be identical with BGH-II and BGH-III by comparison of mps, mmps, and R_f values. Their UV, IR, mass and NMR spectra including solvent dependent OMe shifts were also identical in all respects with those of BGH-II and BGH-III.

Further support to the structures of BGH-II and BGH-III was provided by dehomogeneous of the flavanone halves of these compounds, using iodine-sodium acetate in acetic acid,[20] to two new but expected compounds IIIa and IIIb. Methylation of IIIa and IIIb with methyl iodide-potassium carbonate in acetone gave IIIc and IIId respectively. The former was characterized as 3″ ′,4′,4″ ′,5,5″,7,7″-heptamethoxy-3,8″-biflavone and the latter as 4′,4″ ′,5,5″,7,7″-hexamethoxy-3,8″-biflavone by NMR studies (Table 3). These compounds constitute the first examples of 3-8″-



III a: R = R′ = OH
b: R = OH, R′ = H
c: R = R′ = OMe
d: R = OMe; R′ = H

TABLE 3

Proton	IIIc	IIId
2', 6'	2·68 d J = 9	2·67 d J = 9
3', 5'	3·20 d J = 9	3·32 d J = 9
6	3·44 d J = 3	3·42 d J = 3
8	3·62 d J = 3	3·60 d J = 3
6''	3·49 s	3·52 s
3''	3·61 s	3·60 s
2'''	2·94 d J = 10	
5'''	2·74 q J_1 = 10	
	J_2 = 2	
6'''	3·32 d J = 2	
2'''', 6''''		2·51 d J = 8
3'''', 5''''		3·32 d J = 8
OMe	6·00–6·56 (21 protons)	6·00–6·29 (18 protons)

s = singlet, d = doublet, q = quartet.

*Spectra run in $CDCl_3$ at 100 Mc/s. TMS as an internal standard = τ 10·00. Values of J in c/s.

linked biflavones, which may be anticipated as natural products arising from standard radical coupling of the two flavone units. We suggest the name "saharanflavone" for the parent compound IIIa.

A striking feature of the NMR spectrum of IIIc was the appearance of an aromatic OMe group at an exceptionally high position (τ 6·56) suggestive of its being already entirely solvated. Examination of the molecular model of IIIc was revealing in that there were, in fact, certain conformations in which the particular OMe group could lie above the plane of benzene ring of another flavone unit, thus rendering it unique. Further, on charge of solvent from $CDCl_3$ to 80% C_6D_6/20% $COCl_3$ all OMe groups were expected to move upfield more than 25 c/s as each OMe group had an ortho proton. The OMe group in question (at τ 6·56) however, moves hardly at all (Fig II) thus supporting the above postulate. This does mean, of course, that when we are dealing with an aromatic OMe group showing at an unusual value, the method of solvent induced shifts must be used with the greatest caution.

On going from $CDCl_3$ to 80% C_6D_6 all the OMe resonances (τ 6·00–6·29) in IIId moved as expected. (Fig III).

The phenolic extractives of dried leaves of *G. livingstonii* on solvent fractionation and column chromatography followed by preparative TLC gave two components. The component mp 255–256° (lit.[7] mp > 300°), $[\alpha]_D^{25}$ + 9 gave an hexaacetate mp 235° and a hexamethyl ether mp 225°. The second compound mp 266–268° (lit.[8] mp 320–322°), $[\alpha]_D^{25}$ − 6, gave a pentaacetate mp 235–236° and a hexamethyl ether mp 225°. They were characterized as amentoflavone and podocarpusflavone A respectively by NMR spectral studies of their acetates and methyl ethers. The NMR spectra were comparable in all respects to those of authentic samples. The solvent dependent OMe shifts, IR, UV spectra were also identical. The differences in mps of the parent compounds and those reported in literature appear to be due to the racemic nature of the earlier samples and the optical activity of the materials now isolated.

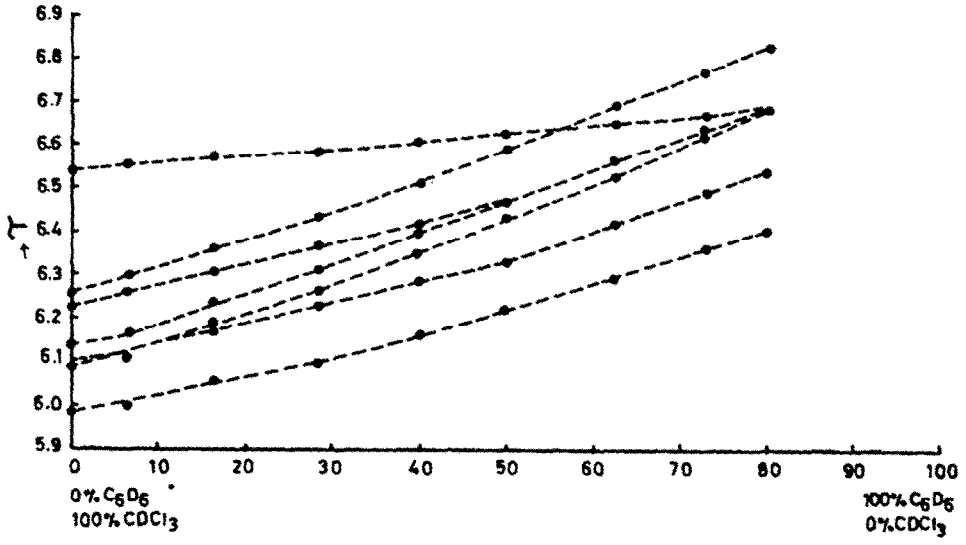


FIG. II. Spectrum of benzene induced methoxy shifts in IIIb.

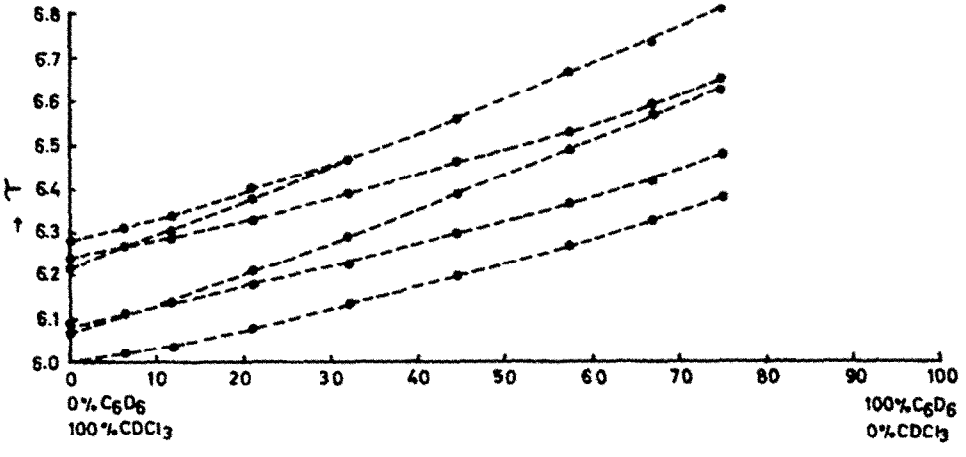


FIG. III. Spectrum of benzene induced methoxy shifts in IIId.

EXPERIMENTAL

M.ps are uncorrected. TLC and preparative TLC was carried out on silica gel (N.C.L.Poona) using benzene:pyridine:formic acid, 36:9:5 as the developing solvent system.[21, 22] Optical rotations were taken in Hilger polarimeter in pyridine-EtOH (c·1 mg/ml).

Biflavonyls from heartwood of Garcinia livingstonii

Defatted powdered heartwood (4 kg) was completely exhausted with hot acetone and the solvent was distilled off. The dark brown concenterate was successively treated with light petroleum (40–60°), benzene, chloroform and hot water to remove non-flavonoidic and resinous matters. The brownish gummy mass was then refluxed with EtOAc (1 l.) for 8 hr and filtered. The filtrate was concentrated to 50 ml and ether was added gradually till there was no more precipitation. The ppt was discarded and the filtrate evaporated to dryness to give a light brown residue (3 g) which showed the usual flavonoid colour tests. The mixture was separated into two homogeneous components by preparative TLC.

BGH-III (Ia). Slowly crystallized from MeOH as yellow plates (500 mg) m.p. 267–268°, R_f 0·21, λ_{max}^{EtOH} 227, 276, 340 mμ. [Found: C, 61·19; H, 4·26. $C_{30}H_{20}O_{10}$. $3H_2O$ requires: C, 61·20; H, 4·42%].

BGH-III acetate (IIa). BGH-III (100 mg), pyridine (1·5 ml) and Ac_2O (1·5 ml) were heated on a water bath for 2 hr. The mixture was cooled to room temp (½ hr) and poured onto crushed ice. The solid was filtered, washed with water and dried. It crystallized from $CHCl_3$-MeOH as colourless needles (78 mg) m.p. 202–205°, ν_{max}^{Nujol} 1760, 1640, 1619, 1600, 1502, 1358, 1190, 1172, 1125, 1089, 1065, 1052, 1015, 1015, 900, and 852 cm^{-1}. [Found: C, 61·19; H, 4·26. $C_{44}H_{34}O_{1}$. H_2O requires: C, 62·00; H, 4·20%].

BGH-III methyl ether (Ib). BGH-III (100 mg), MeI (2 ml) and K_2CO_3 (2 g) were refluxed in dry acetone (100 ml) for 16 hr with further addition of MeI (0·5 ml) and K_2CO_3 (1 gm) after 8 hr. The mixture was filtered and the residue washed several times with hot acetone. The filtrate and the washings were combined and evaporated to dryness. The yllow residue was taken up in chloroform (100 ml) and washed several times with water in a separatory funnel. The chloroform sol was concentrated to 20 ml and purified by preparative TLC. The white solid crystallized from $CHCl_3$-MeOH as colourless cubes (76 mg) m.p. 254–256°, R_f 0·45, λ_{max}^{EtOH} 228, 284 mμ, ν_{max}^{Nujol} 1670, 1645, 1620, 1520, 1338, 1316, 1254, 1232, 1221, 1178, 1165, 1120, 1044, 1032, 830, 815, and 725 cm^{-1}. [Found: C, 68·93; H, 5·42. $C_{36}H_{32}O_{10}$ requires: C, 69·20; H, 5·11. Mol. wt. 624 (mass)].

Ozonolysis of BGH-III acetate. A stream of ozonized O_2 was passed through a cooled (−20° to −30°) sol of BGH-III acetate (60 mg) in dry EtOAc (10 ml) until the theoretical amount of O_3 was generated. The sol was allowed to attain room temp (½ hr) and was then hydrogenated in the presence of 5% Pd-charcoal (100 mg) until the rapid intake of H_2 ceased. The catalyst was filtered off and the solvent was reduced to 2 ml. The mixture on co-chromatography (silica gel, E. Merck; benzene-dioxan-acetic acid, 90:25:4 as developing solvent system) with an authentic sample showed the presence of *p*-acetoxybenzaldehyde. The identity of the spots was further supported by using *p*-diazotized sulphanilic acid as chromogenic reagent.

BGH-II (Ic). Crystallized from MeOH as yellow plates (600 mg) m.p. 300°, R_f 0·023, $[\alpha]_D^{25}$ ±0 MeOH (1mg/ml), λ_{max}^{EtOH} 228, 275, 288, and 345 mμ [Found: C, 60·06; H, 4·17. Calc. for $C_{30}H_{20}O_{11}$. $2H_2O$: C, 60·80; H, 4·05%].

BGH-II acetate (IIb). A mixture of BGH-II (100 mg), pyridine (1 ml) and Ac_2O (1 ml) was refluxed on water bath for 2 hr. The mixture was cooled and poured onto crushed ice. The white solid was filtered off, washed with water and dried. It crystallized from $CHCl_3$-MeOH as colourless prisms (70 mg) m.p. 212–215°, ν_{max}^{KBr} 1780, 1660, 1600, 1502, 1380, 1198, 1121, 1090, 1070, 1050, 1021, 898, and 850 cm^{-1}. [Found: C, 61·76; H, 3·96. $C_{46}H_{36}O_{19}$ requires: C, 61·90; H, 4·00%].

BGH-II methyl ether (Id). The biflavonyl (100 mg), anhyd K_2CO_3 (1 g) and MeI (1 ml) were refluxed for 12 hr with further addition of MeI (0·5 ml) and K_2CO_3 (1 g) after 6 hr. The mixture on usual work up and purification by preparative TLC yielded a white solid which crystallized from EtOHc light petroleum (60–80°) as colourless plates (65 mg) m.p. 212–213°, R_f 0·95 λ_{max}^{EtOH} 228, 274 and 336 mμ, ν_{max}^{Nujol} 1670, 1645, 1620, 1578, 1532, 1360, 1320, 1221, 1180, 1150, 1120, 1070, 1050, 1030, 1020, 865, 840, 832, and 768 cm^{-1}. [Found: C, 66·40; H, 5·09. Calc. for $C_{37}H_{34}O_{11}$. EtOAc: C, 66·45; H, 5·6] (Mol. Wt. 654 (mass)).

Ozonolysis of BGH-II acetate. Ozonolysis of BGH-II acetate followed by work up as described in the case of BGH-III acetate showed the presence of *p*-acetoxybenzaldehyde (TLC).

3″,4′,4″,5,5″,7,7″-Heptamethoxy-3,8″-biflavone (IIIc). To a sol of BGH-II (200 mg) in glacial AcOH (2 ml) was added freshly fused KOAc (400 mg). I_2 (200 mg) in glacial AcOH (2 ml) was added to boiling mixture slowly during 1 hr and refluxing continued for another hr. The mixture was cooled and poured into

ice cold 5% $Na_2S_2O_3$. The yellow ppt was filtered off, washed and dried. The yellow solid (180 mg) was methylated with MeI (2 ml) and K_2CO_3 (2 g) in acetone (100 ml). The methyl ether, after purification by preparative TLC, crystallized from $CHCl_3$-MeOH as colourless needles (110 mg) m.p. 150–152°, R_f 0·34. [Found: C, 67·40; H, 5·01. $C_{37}H_{32}O_{11}$ requires: C, 67·20; H, 5·01%; Mol. wt. 652. (mass)].

4',4'',5',5'',7,7''-Hexamethoxy-3,8''-biflavone (IIId). BGH-III, on similar treatment as described, gave a methyl ether which crystallized from $CHCl_3$-MeOH as colourless needles (80 mg) m.p. 175°, R_f 0·39. [Found: C, 69·30; H, 4·80. $C_{36}H_{30}O_{10}$ requires: C, 69·45; H, 4·90%. Mol. wt. 622. (mass)].

Biflavonyls from bark of G.livingstonii. BGHIII and morelliflavone were also isolated from the bark extracts of *G.livingstonii*. The methods of isolation and purifications were similar to those used in the case of heartwood.

Biflavonyls from leaves of G. livingstonii

Defatted leaves (1·5 kg) were extracted with hot acetone and the solvent removed under reduced pressure. The green viscous mass was then treated successively with light petroleum (40–50°), benzene, chloroform and water. The gummy residue was taken in acetone and chromatographed over magnesium silicate (Woelm) using eluotropic series of organic solvents. The yellow products (1·6 g) eluted with EtOAc, acetone and EtOAc (saturated with water) were combined and separated by using preparative TLC into two homogeneous constituents.

Amentoflavone (WG-1). Crystallized from MeOH as fine yellow rods (430 mg) m.p. 255–256°, R_f 0·173 $[\alpha]_D^{25}$ +9, λ_{max}^{EtOH} 272, 335 mμ. [Found: C, 60·76; H, 4·18. Calc. for $C_{30}H_{18}O_{10}.3H_2O$: C, 60·91; H, 4·18%].

Acetylation of WG-I (100 mg) with pyridine and Ac_2O gave an acetate which crystallized from $CHCl_3$-MeOH as colourless needles (85 mg) m.p. 235°. [Found: C, 63·40; H, 3·87. Calc. for $C_{42}H_{30}O_{16}$: C, 63·80; H, 3·80%; Mol. wt. 790 (mass)]; NMR ($CDCl_3$) (τ scale): 2·92 (d, J = 9 c/s, 1H, H-3'', 5''); 2·50 (d, J = 9 c/s, 2H, H-2'', 6''); 1·99 (q, J_1 = 9 c/s and J_2 = 3 c/s, 1H, H-6'); 2·48 (d, J = 9 c/s, 1H, H-5'); 1·94 (d, J = 3 c/s, 1H, H-2'); 3·30, 3·32 (s, 2H, H-3, 3''); 2·73 (d, J = 3 c/s, 1H, H-8); 3·31 (d, J = 3 c/s, 1H, H-6); 2·97 (s, 1H, H-6''); 7·50, 7·54, 7·67, 7·72, 7·89 and 7·93 (18H, 6 OAc).

WG-I was methylated with MeI and K_2CO_3 in acetone and the product purified by preparative TLC. It crystallized from $CHCl_3$-MeOH as colourless needles, m.p. 225°, R_f 0·404, $[\alpha]_D^{25}$ +28, λ_{max}^{EtOH} 267, 368 mμ. [Found: C, 63·90; H, 4·80. Calc. for $C_{36}H_{30}O_{16}$: C, 69·45; H, 4·90%. Mol. wt. 622 (mass)]; NMR spectrum was identical with that of an authentic sample.[16]

Podocarpusflavone A (WG-II). Crystallized from MeOH-$CHCl_3$ as yellow needles (600 mg) m.p. 266–268°, R_f 0·373, $[\alpha]_D^{25}$ −6, λ_{max}^{EtOH} 273, 336 mμ. [Found: C, 64·63; H, 3·80. Calc. for $C_{31}H_{20}O_{10}.1\frac{1}{2}H_2O$: C, 64·25; H, 3·80%].

Acetylation of WG-II with pyridine-AcO gave an acetate which crystallized from $CHCl_3$-MeOH as colourless needles m.p. 235–236°. [Found: C, 64·44; H, 3·97. Calc. for $C_{41}H_{30}O_{15}$: C, 64·56; H, 3·96%, Mol. wt. 762 (mass)]; NMR ($CDCl_3$) (τ scale): 3·21 (d, J = 9 c/s, 2H, H-3'', 5''); 2·58 (d, J = 9 c/s, 2H, H-2'', 6''); 2·00 (q, J_1 = 9 c/s and J_2 = 3 c/s, 1H, H-6'); 2·94 (d, J = 9 c/s, 1H, H-5'); 1·95 (d, J = 3 c/s, 1H, H-2'); 3·40, 3·41 (s, 2H, H-3, 3''); 2·75 (d, J = 3 c/s, 1H, H-8); 3·15 (d, J = 3 c/s, 1H, H-6); 3·01 (c, 1H, H-6''); 6·25 (s, 3H, OMe-4''); 7·56, 7·51, 7·68, 7·90, 7·94 (15H, 5 OAc).

Methylation of WG-II with MeI K_2CO_3 in acetone gave amentoflavone hexamethyl ether which was characterized by its m.p., m.m.p., R_f value and spectral studies.

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