

THE ISOLATION OF
A NEW SERIES OF BIFLAVANONES
FROM THE HEARTWOOD OF GARCINIA BUCHANANII

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Three new biflavanones have been isolated from the heartwood of Garcinia buchananii (Guttiferae) by extraction with chloroform. The metabolites GB - 1, GB - 1a and GB - 2 were separated by extracting an ethyl acetate solution with 0.1 M sodium tetraborate which removed GB - 2. The organic phase then contained largely GB - 1 and GB - 1a which were separated by preparative thin-layer chromatography. The molecular formulae for the three amorphous extractives, determined by high resolution mass spectrometry using an A. E. I. M S 9 instrument, are $C_{30}H_{22}O_{11}$ for GB - 1, $C_{30}H_{22}O_{10}$ for GB - 1a, and $C_{30}H_{22}O_{12}$ for GB - 2:¹ the ultraviolet spectrum in each case shows maxima at 292 m μ and 329 m μ , which, on addition of sodium acetate, underwent the characteristic bathochromic shift of 5,7 - dihydroxyflavanone systems.²

GB - 1 on methylation with dimethyl sulphate yields a hexamethyl ether containing one alcoholic group, and with Purdie methylation conditions a heptamethyl ether is obtained. From an examination of the n. m. r. spectrum (Fig. 1) and the mass spectrum (Fig. 2) of the heptamethyl ether of GB - 1 the structure of GB - 1 was elucidated. The mass spectrum supported the

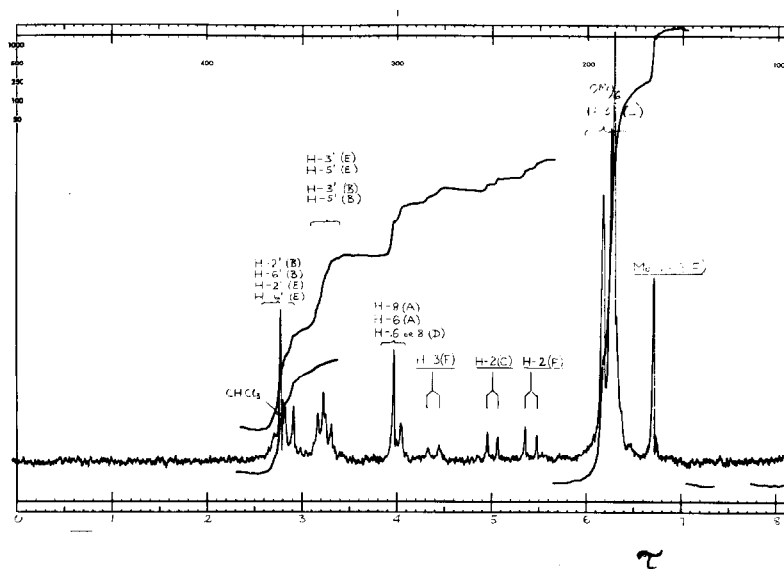


Figure 1

Benzenoid, heterocyclic and methoxyl proton resonances of the heptamethyl ether of GB-1 in deuteriochloroform obtained on a Varian HA-100 spectrometer.

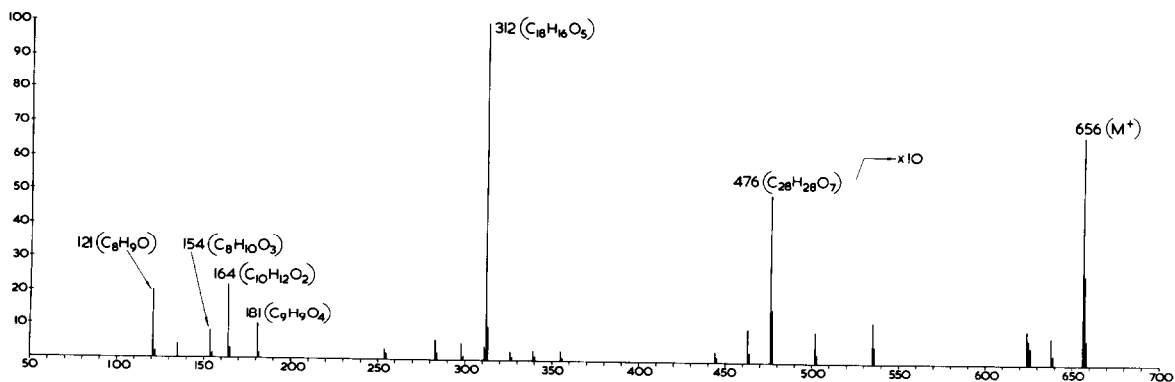


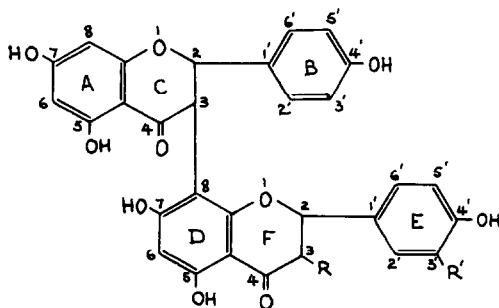
Figure 2

The mass spectrum of the heptamethyl ether of GB-1 obtained on an A.E.I. MS 9 double focussing mass spectrometer.

presence of a phloroglucinol ring system derived from a 5,7 - dihydroxyflavanone system with ions at m/e 154 and 181 consistent with the fragments $(C_6 H_3 \cdot (O Me)_2 \cdot OH)^+$ and $(C_6 H_2 \cdot (O Me)_2 \cdot OH \cdot CO)^+$. In addition the presence of another aromatic ring was suggested by an ion at m/e 121 consistent with a $(MeO \cdot C_6 H_2 \cdot CH_2)^+$ fragment. The n. m. r. spectrum (Fig. 1) in the aromatic region has three groups of protons: four protons at 2.6 - 2.9 τ are coupled to four protons at 3.1 - 3.4 τ . The third group at 3.95 - 4.05 τ , equivalent to three protons, is attributable to the aromatic protons of a phloroglucinol ring. Thus of eleven aromatic protons, eight belong to two p-methoxybenzyl moieties and three are from two phloroglucinol rings.³ The aliphatic and methoxyl region of the n. m. r. spectrum provide further evidence that GB - 1 is a biflavanone derived from two naringenin units. Thus double resonance experiments showed that the doublet at 4.38 τ ($J > 10$ c. p. s.) is coupled to the doublet at 5.4 τ . Of the other two protons only one doublet is shown at 5.0 τ ($J > 10$ c. p. s.) while the other doublet must be at 6.2 τ (from double irradiation experiments) but is obscured by the methoxyl groups. Six methoxyls appear in the region 6.1 - 6.3 τ while one in the oxygen heterocyclic ring is at 6.7 τ . This data is consistent with two flavanone units with one linked to the other from C-3 of ring C to either C-6 or C-8 of phloroglucinol ring D. The mass spectrum supported the nature of the linkage since the fragmentation of the molecular ion at 656 can be rationalised by a reverse Diels-Alder reaction of a flavanone,⁴ first at ring C to give a fragment ion at m/e 476, followed by a similar fragmentation at ring F to give an ion at m/e 312. These results can only be accommodated by a linkage from the oxygen heterocyclic ring C to the phloroglucinol ring D. While the present data does not allow us to distinguish whether the linkage is at C-6 or C-8 of ring D the fact that the hydroxyl at C-5 of that ring is not exceptionally difficult to methylate may suggest that the bulky substituent is not at C-6 but at C-8.⁵

The large coupling constants ($J > 10$ c. p. s.) of the heterocyclic

protons in rings C and F indicates that in each ring the hydrogens have a trans diaxial arrangement. Thus structure (I; R = OH, R¹ = H) is given for GB - 1 with the reservation that the flavanones may be alternatively 3,6 linked.¹ The conclusions were supported by n. m. r. and mass spectra on O-hexamethyl GB - 1, and GB - 1 itself.



I

The structures of GB - 1a and GB - 2 were readily elucidated by comparing the spectral data with that of GB - 1. Thus for GB - 1a, which contains one oxygen atom less than GB - 1, the n. m. r. spectrum is identical in the aromatic region but has five aliphatic protons. Two of these protons are at 7.3 τ consistent with the presence of a methylene group at C-3 in ring F in accord with structure (I; R = R¹ = H) for GB - 1a. This was confirmed by formation of the biflavonyl (I; R = R¹ = H; double bond between C-2 and C-3 in rings C and F) on oxidation with iodine and potassium acetate in acetic acid.⁶ In accord with the proposed structures for GB - 1 and GB - 1a alkaline degradation of the metabolites gives phloroglucinol and p-hydroxybenzoic acid.

GB - 2 which contains one more oxygen atom than GB - 1 was similar in aliphatic region of the n. m. r. spectrum but differed in the aromatic region. GB - 2 has only ten aromatic protons of which three could still be associated with two phloroglucinol rings. Thus GB - 2 differed from GB - 1 by the presence of an additional hydroxyl group in either ring B or E located next to a 4' - hydroxyl group to account for the solubility of

GB - 2 in sodium tetraborate.⁷ The mass spectrum suggests that the hydroxyl group is in ring F since fragmentation occurred to lose phloroglucinol ($M - 126$) followed by loss of water ($M - (126 + 18)$) and a reverse Diels-Alder reaction to eliminate an ethynyl catechol fragment ($M - (126 + 18 + 134)$). This data is thus consistent with structure (I; $R = R^1 = OH$) for GB - 2.

The structures of GB - 1, GB - 1a and GB - 2 represent a new class of reduced biflavonyl derivatives since two flavanone units are 3, 8 (or 3,6) linked.⁸ If it is assumed that flavanone formation occurs from a polyacetate and a $C_5 C_3$ unit then the 3, 8 (or 3, 6) linkage may occur by oxidative coupling. By analogy with formation of lignans,⁹ a hydroxycinnamic acid moiety (either as a cinnamic acid or a chalcone or a flavone derivative) from one potential flavanone unit may couple with the phloroglucinol residue of another flavanone unit or its precursor. The heartwood of Garcinia buchananii also contains xanthone derivatives¹⁰ and thus shows some resemblance to the extractives from other Garcinia species which have been studied recently.¹¹

References

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