The Structure of the "GB" Biflavanones from *Garcinia buchananii* Baker and *G. eugeniifolia* Wall

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Pelter, on the basis of some mass spectral results[1b] and earlier biogenetic speculations,[1a] has recently reasserted[1b] his view that the four "GB" biflavanones isolated by us from the heartwoods of *Garcinia buchananii* Baker and *G. eugeniifolia* Wall may have the structures (IIa—d) rather than those earlier proposed by us (Ia—d).[2] We present preliminary details of experiments which show unambiguously that structures (Ia—d) are the correct ones for the "GB" biflavanones.†

Considerable experimental work has established that all four biflavanones have the same carbon skeleton.[2,3] Thus, choosing GB-1a (Ib) as representative of the group, we converted it with methyl iodide and silver oxide in dimethylformamide into the heptamethyl ether derivative (III) in which ring

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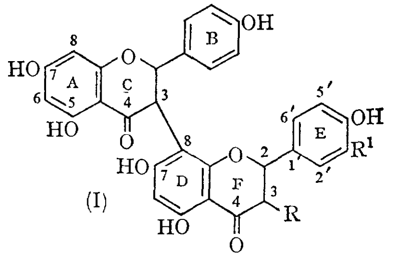
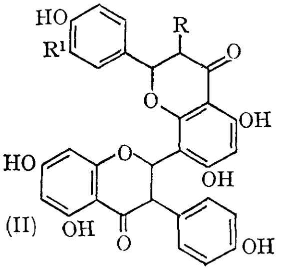
† These structures are presented with the reservation that the flavanone units may, alternatively, be 3,6-linked between rings C and D. Details of GB-2a and of the extractives of *G. eugeniifolia* Wall were first presented at The Chemical Society Autumn Meeting, University of Durham, September, 1967, Abstract H2.



(I)

	R	R¹
a;	OH	H
b;	H	H
c;	OH	OH
d;	H	OH



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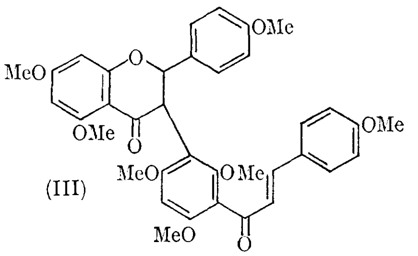
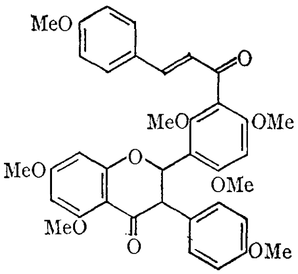
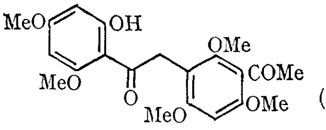


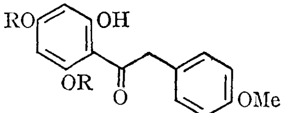
(III)



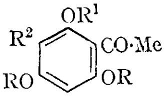
(VI)



(IV)

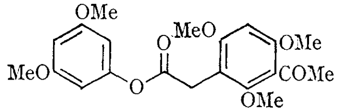


(Va) R=H
(Vb) R=Me

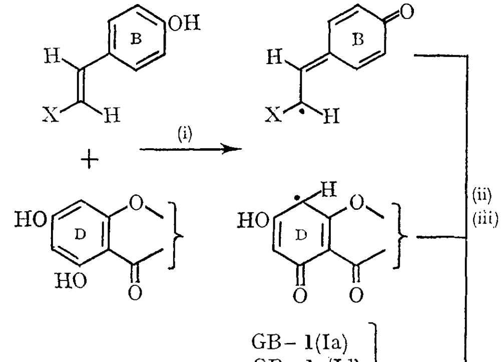


(VII)

	R	R¹	R²
a;	H	H	H
b;	Me	H	H
c;	Me	CH_2·CH:CH_2	H
d;	Me	H	CH_2·CH:CH_2
e;	Me	Me	CH_2·CH:CH_2
f;	Me	Me	CH_2·CO_2H
g;	Me	Me	CH_2·CO·Cl



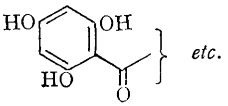
(VIII)



SCHEME

(i) hydrogen abstraction;
(ii) radical pairing;
(iii) enolisation.

X = Possible ligands in flavanone biogenesis, *e.g.* CO_2H,



etc.

F had opened to give the corresponding chalcone: ring C, on the other hand, carries two aryl substituents and does not have typical flavanone properties. The structure of the ether (III) is conclusively proven by its i.r., u.v., n.m.r., and mass spectra. Treatment with ethanolic potassium hydroxide (20% w/v), followed by acidification, degraded the ether (III) into a mixture of products, from which the deoxybenzoin (IV) was isolated. In anticipation of this result, we had earlier synthesised the same deoxybenzoin (IV) by the unambiguous route described below and, on direct comparison, the two compounds were identical. We also prepared the deoxybenzoin (Vb) which should reasonably be expected to appear in the alkali degradation mixture from the heptamethyl ether if it possessed the constitution (VI) derived from the Pelter structure (IIb). Careful t.l.c. comparison of the reference deoxybenzoins (III) and (Vb) with the alkali degradation mixture confirmed the presence of (III) but showed a complete absence of (Vb).‡ Thus, the correct constitution for the "GB" biflavanones remains (Ia—d), as originally suggested by us.[2]

The synthesis of the deoxybenzoin (IV) was

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‡ The deoxybenzoins (IV) and (Vb) have widely different R_F values on silica gel.

achieved as follows. Phloracetophenone (VIIa) on methylation yielded the dimethyl ether (VIIb), which, after reaction with allyl chloride, potassium iodide, and potassium carbonate in acetone, gave the allyl ether (VIIc). Claisen rearrangement of the ether (VIIc) in boiling *NN*-dimethylaniline yielded the *C*-allyl derivative (VIId), which on treatment with dimethyl sulphate, gave the methyl ether (VIIe). Oxidation of the olefinic bond in the ether (VIIe) with the Lemieux–von Rudloff reagent[4] gave the acid (VIIf) which was converted[5] into the acid chloride (VIIg). With phloroglucinol dimethyl ether, the acid chlorine (VIIg) gave the ester (VIII), which then underwent a Fries rearrangement at room temperature in the presence of titanium tetrachloride in nitrobenzene[6] to the required deoxybenzoin (IV).

The deoxybenzoin (Vb), synthesised by a Hoesch reaction between *p*-methoxybenzyl cyanide and phloroglucinol, gave the phenol (Va), which was isolated and then methylated with diazomethane to give the ether (Vb).§

To account for the biogenesis of the biflavanones on the basis of structures (IIa—d), Pelter proposed[1] a modified flavanonol–isoflavanone transformation, which has already been criticised.[7] With our biflavanones correctly assigned as (Ia—d), the biogenetic proposals of Pelter are untenable and it is necessary to reassert[2a] that the dimerisation stage in the biogenesis of biflavones,[8] and biflavanones,[2a] and now morelloflavone,[9] can be adequately explained by the mechanism for oxidative coupling of phenols.[10] In the case of biflavanone formation (Ia—d), *C–C* coupling may occur between a quinone methide radical and an aromatic ring (see Scheme), a process which has already been demonstrated to occur in lignification.[11]

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§ Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

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[2] B. Jackson, H. D. Locksley, F. Scheinmann, and W. A. Wolstenholme, *Tetrahedron Letters*, 1967, (a) p. 787; (b) p. 3049.

[3] B. Jackson, H. D. Locksley, F. Scheinmann, and W. A. Wolstenholme, unpublished results.

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[8] *E.g.* W. Baker and W. D. Ollis in "Chemistry of Natural Phenolic Compounds", ed. W. D. Ollis, Pergamon, Oxford, 1962, p. 152; W. Rahman and S. P. Bhatnagar, *Tetrahedron Letters*, 1968, 675; H. Miura, T. Kihara and N. Kawano, *ibid.*, p. 2339, and references therein.

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[11] For recent reviews see (a) J. M. Harkin in Ref. 10(b) p. 243; (b) F. F. Nord and W. J. Schubert in "Biogenesis of Natural Compounds" ed., P. Bernfeld, Pergamon, Oxford, 1963, p. 693; (c) F. M. Dean, "Naturally Occurring Oxygen Ring Compounds", Butterworths, London, 1963, p. 49.; (d) I. A. Pearl, "The Chemistry of Lignin", Marcel Dekker, New York, 1967, p. 136.