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THE ISOLATION AND STRUCTURE OF TWO BIFLAVONES FROM *GARCINIA TALBOTI**

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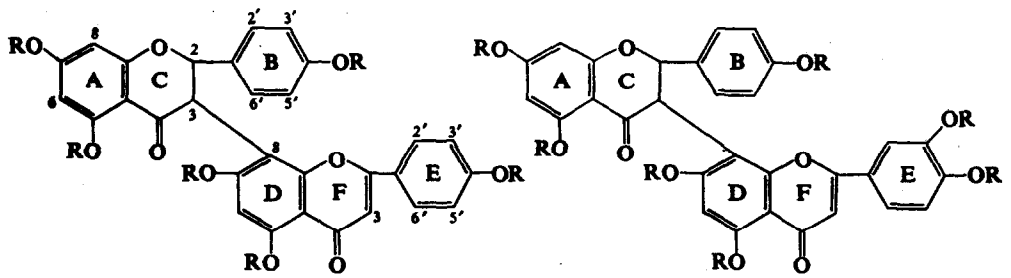
Abstract—From the roots of *Garcinia talboti* Raiz. two biflavones, talbotaflavone (Ia) and morelloflavone (IIa) have been isolated. Their structures have been derived on the basis of degradative and spectroscopic evidence.

INTRODUCTION

Garcinia talboti Raiz. (Guttiferae) is a large tree growing in the Western Ghats of India. The methanol extract of the defatted roots showed on TLC two closely related pigments having R_f 0.4 and 0·35. Chromatographic separation over silica gel yielded the pure compounds both of which were racemic as revealed by ORD measurements. One of them having the molecular formula $C_{30}H_{20}O_{10}$ is new and has been designated as talbotaflavone. The other compound, $C_{30}H_{20}O_{11}$, is identical (TLC, u.v. and i.r. spectra) with morelloflavone[1] obtained by Venkataraman and co-workers from the heartwood of *Garcinia morella* Desr. We wish to describe here spectroscopic and degradative evidence in support of structures Ia and IIa for talbotaflavone and morelloflavone respectively.



(I) (II)

(a) R = H
(b) R = Me

RESULTS

Both compounds gave a red colour in the Shinoda test[2] and a greenish ferric chloride coloration. Their i.r. spectra showed broad hydroxyl bands at 3250 cm^{-1} and the chelated carbonyls appeared at 1660 and 1630 cm^{-1}. Talbotaflavone showed absorption maxima at

* Contribution No. 164 from CIBA Research Centre.

[1] C. G. KARANJGAOKAR, P. V. RADHAKRISHNAN and K. VENKATARAMAN, *Tetrahedron Letters* 3195 (1967).

[2] K. VENKATARAMAN, in *The Chemistry of Flavonoid Compounds* (edited by T. A. GEISSMAN), p. 73, Pergamon Press, London (1962).

210, 230 (infl.), 278 (infl.), 290 and 340 nm and morelloflavone at 210, 225, 258, 279, 290 and 350 nm. The NMR spectra of both (CD_3SOCD_3) showed the absence of methoxyl and C-methyl groups.

Talbotaflavone on methylation with dimethyl sulphate and potassium carbonate provided a hexamethyl ether (Ib), m.p. 265°. The NMR spectrum ($CDCl_3$, 100 Mc) (Table 1) of Ib showed a multiplet at δ 3·6–3·9 due to the six methoxyl groups. The doublets at δ 5·75 and 4·84 ($J = 12$ c/s) were shown to be coupled by double resonance. These should be attributed to H-2 and H-3 *trans* protons of ring C. The aromatic protons are assigned as indicated in Table 1. The assignments of the protons of rings B and E are indicated by two sets of A_2B_2

TABLE 1. NMR SPECTRUM OF TALBOTAFLAVONE HEXAMETHYL ETHER (Ib)

Chemical shift (δ)	Multiplicity	Number of protons	Assignment (ring)
3·6–3·9	m	18	Six methoxyls
4·84	d (J = 12 c/s)	1	H-3 (C)
5·75	d (J = 12 c/s)	1	H-2 (C)
6·18	q (J = 1 c/s)	2	H-6, H-8 (A)
6·25	s	1	H-6 (D)
6·42	s	1	H-3 (F)
6·58	q (J = 9 c/s, 2 c/s)	2	H-3′, H-5′ (B)
6·8	q (J = 9 c/s, 2 c/s)	2	H-3′, H-5′ (E)
7·08	q (J = 9 c/s, 2 c/s)	2	H-2′, H-6′ (B)
7·6	q (J = 9 c/s, 2 c/s)	2	H-2′, H-6′ (E)

protons and analogy with morelloflavone heptamethyl ether (IIb, Table 2) and those of ring A by the presence of *meta*-splitting. Of the two singlets at δ 6·25 and 6·42, the former is assigned to H-6 (D) and the latter to H-3 (F) by analogy with 5,7-dimethoxyflavone[3] where H-8, H-6 and H-3 have δ values 6·53, 6·34 and 6·62 respectively. Of the two possible modes of linkage of C_3 (ring C) to ring D, the C_3–C_8 linkage is preferred to C_3–C_6, as in the case of the biflavone. GB_1,[4–8] because of the ease of methylation of the C_5-hydroxyl of ring D[9]. The C_3–C_8 linkage is also supported by the shift in the methoxyl frequencies in going from deuterochloroform to benzene.[10–14] All methoxyl groups moved upfield from δ 3·6–3·9 (in $CDCl_3$)

[3] J. MASSICOT, J.-P. MARTHE and S. HEITZ, *Bull. Soc. Chim. France* 2712 (1963).
[4] B. JACKSON, H. D. LOCKSLEY, F. SCHEINMANN and W. A. WOLSTENHOLME, *Tetrahedron Letters* 787 (1967).
[5] B. JACKSON, H. D. LOCKSLEY, F. SCHEINMANN and W. A. WOLSTENHOLME, *Tetrahedron Letters* 3049 (1967).
[6] B. JACKSON, H. D. LOCKSLEY and F. SCHEINMANN, *Chem. Comm.* 1125 (1968).
[7] A. PELTER, *Tetrahedron Letters* 1767 (1967).
[8] A. PELTER, *Tetrahedron Letters* 897 (1968).
[9] W. BAKER and W. D. OLLIS, in *Recent Developments in the Chemistry of Natural Phenolic Compounds* (edited by W. D. OLLIS), p. 152, Pergamon Press, London (1961).
[10] H. M. FALES and K. S. WARREN, *J. Org. Chem.* **32**, 501 (1967).
[11] R. G. WILSON, J. H. BOWIE and D. H. WILLIAMS, *Tetrahedron* **24**, 1407 (1968).
[12] M. ILYAS, J. N. USMANI, S. P. BHATNAGAR, M. ILYAS, W. RAHMAN and A. PELTER, *Tetrahedron Letters* 5515 (1968).
[13] A. PELTER, R. WARREN, M. ILYAS, J. N. USMANI, S. P. BHATNAGAR, R. H. RIZVI and W. RAHMAN, *Experientia* **25**, 350 (1969).
[14] A. PELTER, R. WARREN, J. N. USMANI, R. H. RIZVI, M. ILYAS and W. RAHMAN, *Experientia* **25**, 351 (1969).

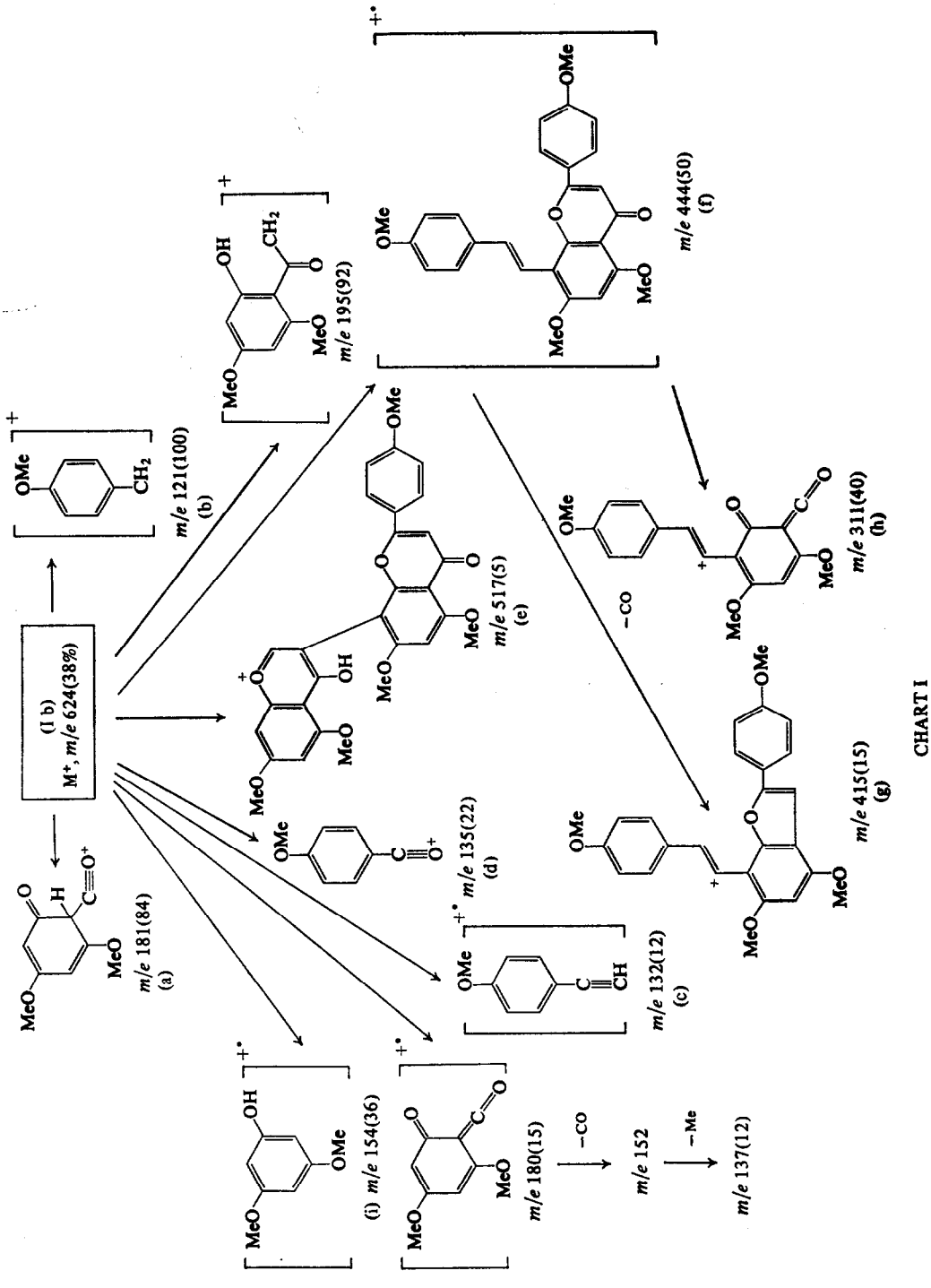

(I b)
M+, m/e 624(38%)
m/e 181(84)
(a)
m/e 121(100)
(b)
m/e 195(92)
m/e 517(5)
(e)
m/e 135(22)
(d)
m/e 132(12)
(c)
m/e 444(50)
(f)
m/e 311(40)
(h)
m/e 415(15)
(g)
(i) m/e 154(36)
m/e 180(15)
m/e 152
m/e 137(12)
-CO
-Me

CHART I

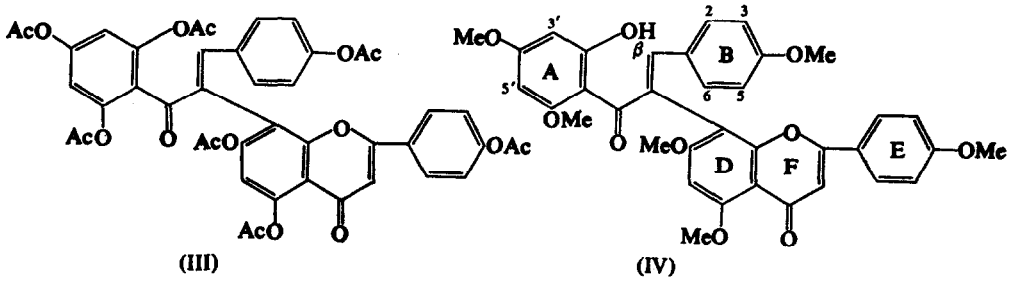
TABLE 2. NMR SPECTRUM OF MORELLOFLAVONE HEPTAMETHYL ETHER (IIb)

Chemical shift (δ)	Multiplicity	Number of protons	Assignment (ring)
3·6–3·9	m	21	Seven methoxyls
4·85	d (J = 12 c/s)	1	H-3 (C)
5·8	d (J = 12 c/s)	1	H-2 (C)
6·15	q (J = 1·2 c/s)	2	H-6, H-8 (A)
6·25	s	1	H-6 (D)
6·42	s	1	H-3 (F)
6·58	q (J = 9·5 c/s, 1 c/s)	2	H-3′, H-5′ (B)
6·75	d (J = 9 c/s)	1	H-5′ (E)
7·05	q (J = 9·5 c/s, 1 c/s)	2	H-2′, H-6′ (B)
7·15	d (J = 1·5 c/s)	1	H-2′ (E)
7·3	q (J = 9 c/s, 1·5 c/s)	1	H-6′ (E)

to δ 3·2–3·5 ppm (in C_6H_6), showing that every methoxyl group has at least one *ortho*-proton. A C_8 rather than a C_6 linkage is therefore more likely. These reasons are equally valid in the case of morelloflavone heptamethyl ether where also an upfield shift of similar magnitude is observed for all the methoxyls in going from deuterochloroform to benzene.

The mass spectrum of Ib shows fragmentations as shown in Chart 1, the patterns of fragmentation being supported by previous work on the mass spectra of flavonoids.[5,15,16]

Acetylation of talbotaflavone with acetic anhydride and sodium acetate gave a hepta-acetate, m.p. 190–192°, whose molecular weight could not be ascertained by mass spectrum. Hydroxyflavanones, on acetylation under these conditions, are known to give chalcone acetates.[17,18] Structure III can be assigned to the acetate on the basis of its NMR spectrum. The acetate methyls appear at δ 1·92 (3H), 2·22 (6H), 2·28 (6H), 2·32 (3H) and 2·40 (3H). The 2 and 3 protons of the flavanone ring C had disappeared. A complex multiplet of 13 protons could be seen in the aromatic region between δ 6·1 and 8·1.

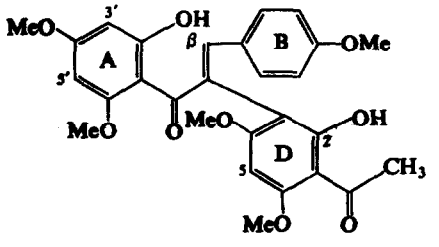


Mild cleavage of Ib with 10% ethanolic KOH for 5 min opened ring C to give an isomeric chalcone (IV), m.p. 135–140°, M^+ at *m/e* 624, which gave a positive $FeCl_3$ coloration and answered the Shinoda test for flavones. In its NMR spectrum the doublets due to the 2 and 3 protons of ring C in Ib had disappeared and instead a downfield singlet appeared at δ 7·65 due to the proton H-β in IV. The 3′ and 5′ protons of ring A appear as *meta*-split doublets (J = 2 c/s) at δ 5·65 and 6·1 and H-6 of ring D as a singlet at δ 6·3. Nine aromatic protons

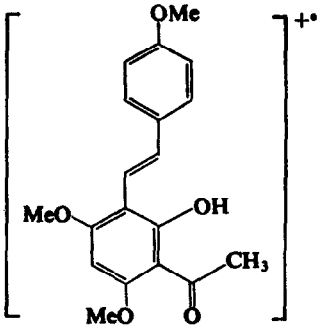
[15] A. PELTER, P. STAINTON and M. BARBER, *J. Het. Chem.* **2**, 262 (1965).
[16] C. S. BARNES and J. L. OCCOLOWITZ, *Australian J. Chem.* **17**, 975 (1964).
[17] Y. ASAHINA and M. INULRESE, *Ber. deut. chem. Ges.* **61**, 1514 (1928).
[18] D. K. BHARADWAJ, S. NEELAKANTAN and T. R. SESHADRI, *Ind. J. Chem.* **7**, 325 (1969).

appear between δ 6·4–7·6. One methoxyl appears at δ 3·2 at a considerably higher field than the other methoxyls. A shielding effect of similar magnitude has been observed by Bick *et al.*[19] in the case of bisbenzylisoquinoline alkaloids of the oxyacanthine type where a methoxyl lying above a neighbouring benzene ring appears at δ 3·02–3·2. In compound IV, the shielded methoxyl may be either the C_7-OMe of ring D which is close to the unsaturated system of the chalcone or the C_4-OMe of ring B which can be under the influence of the ring current of ring E in the flavone half of the molecule. This shielding effect is also evident in the case of the heptaacetate (III) in which the protons of one acetoxyl group appear at δ 1·92 whereas the other acetoxyls appear at δ 2·22–2·40. The chalcone (IV), on heating with ethanolic hydrogen chloride, gave the hexamethyl ether (Ib).

More drastic treatment of Ib with 12% ethanolic KOH gave anisic acid and two other crystalline compounds. One of them, $C_{28}H_{28}O_9$ (V), m.p. 215–217°, M^+ at *m/e* 508 (70%), gave a $FeCl_3$ coloration and a pink colour in the Shinoda test. The u.v. spectrum showed λ_{max} 285 and 370 nm (log ε 4·44 and 4·49) and the NMR spectrum revealed the presence of an acetyl methyl at δ 2·6 (s), five methoxyls at δ 3·9 (m), three aromatic protons at δ 6·1 (m) (H-3′ and H-5′ of ring A and H-5 of ring D), four aromatic protons at δ 6·7–7·7 (H-2′, 3′, 5′, 6′, of ring B) and a sharp peak at δ 7·8 (H-β).



(V)

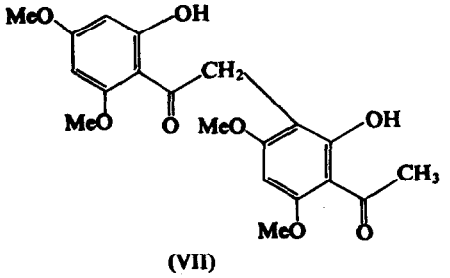


m/e 328

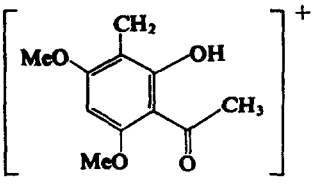
(VI)

The major mass spectral fragments were at *m/e* 328 (33%) due to the ion (VI), *m/e* 193 (63%) due to $C_8H_3O_2(OMe)_2^+$ and *m/e* 181 (100%), *m/e* 311 (2%) due to ions (a) and (h) (Chart 1).

The second compound obtained in the alkaline cleavage had the formula $C_{20}H_{22}O_8$, M^+ at *m/e* 390 (80%), m.p. 166°, and has been found to be identical with the desoxybenzoin (VII) obtained by Karanjgaokar *et al.*[1] by alkaline degradation of morelloflavone



(VII)



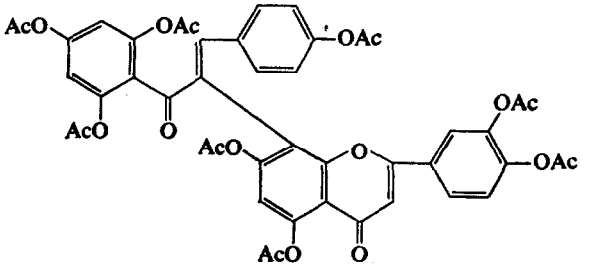
m/e 209

(VIII)

[19] I. R. C. Bick, J. Harley-Mason, N. Sheppard and M. J. Vernengo, *J. Chem. Soc.* 1896 (1961).

heptamethyl ether. Its structure is supported by its NMR and mass spectra. The base peak due to the ion (a) (see Chart 1) appears at *m/e* 181 (100%) and the other major fragment appears at *m/e* 209 (26%) due to the ion (VIII).

Acetylation of morelloflavone (IIa) with sodium acetate and acetic anhydride yielded an octaacetate (IX).

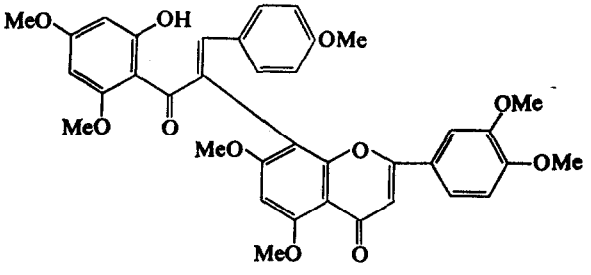


(IX)

Methylation of morelloflavone with excess diazomethane or with dimethyl sulphate and potassium carbonate yielded the heptamethyl ether (IIb), m.p. 198–199°, M^+ at *m/e* 654 (15%). The assignments of the NMR ($CDCl_3$, 100 Mc) signals of IIb are shown in Table 2.

The mass spectral fragmentations of IIb are similar to those shown for Ib except for the increase of 30 mass units in the ions (Chart 1) (c) (3%), (d) (10%), (e) (2%), (f) (46%) and (g) (22%) due to an extra methoxyl group. The intensities of the other ions are (a) (32%), (b) (32%), h (13%) and (i) (100%). This is in agreement with the fragments reported earlier.[1,20]

Morelloflavone heptamethyl ether (IIb), on treatment with 10% alkali for 5 min, gave the isomeric chalcone (X), m.p. 130° (lit.[20] m.p. 134–136°). On heating with ethanolic hydrogen chloride, X reverted to IIb.



(X)

Alkaline degradation of IIb under more drastic conditions gave veratric acid as well as the chalcone (V) and the desoxybenzoin (VII).

Besides the compounds mentioned above, alkaline degradation of both Ib and IIb yielded a hitherto unidentified phenolic product, m.p. 130°, which is under investigation.

EXPERIMENTAL

NMR spectra were taken in $CDCl_3$ solution using tetramethylsilane as an internal reference standard. M.p.s are uncorrected.

[20] M. KONOSHIMA, Y. IKESHIRO, A. NISHINAGA, T. MATSUURA, T. KUBOTA and H. SAKAMOTO, *Tetrahedron Letters* 121 (1969).

Isolation of Talbotaflavone (Ia) and Morelloflavone (IIa) From the Roots of Garcinia talboti

The powdered roots (13 kg) were percolated with hexane (3 × 30 l.). The defatted roots were then extracted with MeOH (3 × 30 l.) at room temp. and the solvent removed *in vacuo*. The viscous liquid was diluted with water, the precipitate filtered, washed with water and dried (200 g). This was suspended in a mixture of acetone–benzene (1:4; 1 l.) and the insoluble material filtered. The filtrate was found to contain (TLC) two closely moving spots with R_f 0·4 and 0·35 (silica gel; toluene–HCO_2Et–HCO_2H, 5:4:1). The filtrate was chromatographed on silica gel using acetone–benzene (1:9) as eluent. Fractions (100 ml) were collected and the progress of the chromatographic separation was followed by TLC.

Fractions	R_f
1–90	Dark-brown gum
91–181	0·4
182–190	0·4, 0·35
191–220	0·35

(a) Fractions 91–181 were combined and the solvent removed. The residue, on slow crystallization from MeOH gave yellow plates of *talbotaflavone* (Ia: 2·3 g), m.p. 300° (dec.), λ_{max}^{EtOH} 210, 230 (infl.), 278 (infl.), 290 and 340 nm (log ϵ 4·67, 4·5, 4·34, 4·44, 4·24). (Found: C, 62·6; H, 4·5. $C_{30}H_{20}O_{10}\cdot 2H_2O$ required: C, 62·5; H, 4·2%).

(b) Fractions 191–220 were evaporated and the residue was crystallized from MeOH to give morelloflavone (IIa; 1·9g), m.p. 304° (dec.), λ_{max}^{EtOH} 210, 225, 258, 279, 290 and 350 nm (logϵ 4·7, 4·6, 4·2, 4·4, 4·44 and 4·17). (Found: C, 64·8; H, 3·8. Calc. for $C_{30}H_{20}O_{11}$: C, 64·8; H, 3·6%.)

Talbotaflavone hexamethyl ether (Ib). Talbotaflavone (2·5 g), acetone (200 ml), anhydrous K_2CO_3 (40 g) and Me_2SO_4 (15 ml) were refluxed for 4 hr and the mixture filtered. Acetone was removed and the residue diluted with water. The precipitate was dissolved in benzene and chromatographed over neutral alumina. The column was eluted with benzene and then $CHCl_3$. The $CHCl_3$ eluates gave Ib as colourless *cubes* (1·8 g), m.p. 265°, which could be recrystallized from CH_2Cl_2–MeOH, λ_{max}^{EtOH} 228 and 284 nm (log ϵ 4·74 and 4·38) ν_{max} (nujol) 1680, 1660, 1620, 1600, 1520, 1340, 1315, 1255, 1230, 1220, 1180, 1165, 1120, 1045, 1030, 830, 815 and 725 cm^{-1}. (Found: C, 69·2; H, 5·4; M.wt. by mass spectrum 624. $C_{36}H_{32}O_{10}$ required: C, 69·2; H, 5·1%; M.wt. 624.)

Talbotaflavone heptaacetate (III). The biflavone (Ia; 100 mg) was heated at 100° for 4 hr with NaOAc (100 mg) and Ac_2O (16 ml), to yield after crystallization from CH_2Cl_2–MeOH, colourless prisms of the heptaacetate (47 mg), m.p. 190–192°, ν_{max} (CH_2Cl_2) 1760, 1640, 1620, 1600, 1500, 1360, 1190, 1170, 1125, 1090, 1065, 1050, 1015, 900 and 850 cm^{-1}. (Found: C, 63·2; H, 4·4. $C_{44}H_{34}O_{17}$ required: C, 63·3; H, 4·1%.)

Alkaline Hydrolysis of Ib

(a) *With 10% ethanolic KOH for 5 min to give IV.* The methyl ether (Ib; 400 mg) was refluxed with 10% ethanolic KOH (20 ml) for 5 min. The solution was diluted with water (20 ml) and acidified with 2 N HCl. It was extracted with CH_2Cl_2, washed successively with 10% $NaHCO_3$, 10% Na_2CO_3, water and dried. The CH_2Cl_2 layer on evaporation gave a yellow residue (320 mg) which, after two crystallizations from CH_2Cl_2–MeOH, gave yellow plates, m.p. 135–140° (dec.), λ_{max}^{EtOH} 215, 274 and 328 nm (log ϵ 4·44, 4·39 and 4·46). (Found: C, 66·9; H, 5·4; M.wt. by mass spectrum 624. $C_{36}H_{32}O_{10}.H_2O$ required: C, 67·3; H, 5·3%.)

(b) *With 12% ethanolic KOH to give anisic acid, and the compounds V and VII.* A suspension of the hexamethyl ether (Ib) (1·6 g) was refluxed for 2 hr with ethanolic KOH (4·0 g in 5 ml water and 30 ml EtOH). The compound gradually went into solution. The reaction mixture was cooled, diluted with water (30 ml) and acidified with 2 N HCl. It was extracted with CH_2Cl_2 (3 × 30 ml) and the CH_2Cl_2 layer extracted with 10% $NaHCO_3$. The bicarbonate layer on acidification and extraction with CH_2Cl_2 gave a crude acid (200 mg) which, on crystallization from water, gave an acid, m.p. 175°. This was shown to be identical with anisic acid by mixed m.p., TLC and superimposable i.r. spectrum. The neutral CH_2Cl_2 layer was evaporated and a preparative TLC was run on silica gel using benzene–acetone (19:1). The yellow bands with R_f 0·78 and 0·7 were extracted with MeOH. The former band gave, on crystallization from CH_2Cl_2–MeOH, orange prisms (V; 15 mg), m.p. 215–217°, λ_{max}^{EtOH} 285 and 370 nm (log ϵ 4·4 and 4·49). (Found: C, 63·9, H, 5·7; M.wt. by mass spectrum 508. $C_{28}H_{28}O_9.H_2O$ required: C, 63·9; H, 5·7%.) The latter band gave VII (18 mg), m.p. 166° (literature[1] m.p. 116°), λ_{max}^{EtOH} 214 and 288 nm (log ϵ 4·11 and 4·16). Its i.r. spectrum (nujol) was identical with that of the desoxybenzoin obtained by Karanjgaokar *et al.*[1] However, a sample was not available for comparison. (Found: C, 62·0; H, 5·8; M.wt. by mass spectrum 390. Calc. for $C_{20}H_{22}O_6$: C, 61·5; H, 4·7%.)

Conversion of the Compound IV to Ib with Ethanolic HCl

A suspension of the flavone–chalcone (IV; 50 mg) was refluxed with ethanol (10 ml) and HCl (0·5 ml) for 30 min. The compound slowly went into solution. Removal of the solvent and dilution with water afforded a

gum which slowly recrystallized from MeOH (22 mg), m.p. 262–263°. This was identical with Ib by TLC, i.r. spectrum and mixed m.p.

Morelloflavone Heptamethyl Ether (IIb)

(*a*) *With Me_2SO_4 and K_2CO_3.* A mixture of morelloflavone (1·0 g), acetone (80 ml), anhyd. K_2CO_3 (15 g) and Me_2SO_4 (15 ml) was refluxed on a water bath for 4 hr. Working up of the reaction mixture as for Ib and chromatographic separation gave morelloflavone heptamethyl ether as colourless plates from methanol (600 mg), m.p. 210°, λ_{max}^{EtOH} 208, 228, 276, and 336 nm (log ϵ 4·8, 4·76, 4·61 and 4·13). υ_{max} (nujol) 1680, 1660, 1620, 1580, 1530, 1360, 1320, 1270, 1220, 1180, 1170, 1150, 1120, 1070, 1050, 1030, 1020, 865, 840, 830 and 770 cm^{-1}. (Found: C, 67·4; H, 5·4; M.wt. by mass spectrum 654. Calc. for $C_{37}H_{34}O_{11}$: C, 67·9; H, 5·2%.)

(*b*) *With diazomethane.* To a solution of morelloflavone (150 mg) in methanol (15 ml) an ethereal solution of CH_2N_2 (prepared from 3 g of nitrosomethylurea) was added and left overnight. Excess CH_2N_2 was decomposed with a few drops of AcOH and the solvent removed. The residue gave from methanol colourless plates (50 mg), m.p. 208–210°, identical with IIb.

Morelloflavone Octaacetate (IX)

Morelloflavone (100 mg) was heated at 100° for 4 hr with Ac_2O (16 ml) and anhyd. NaOAc (100 mg). The product was crystallized from CH_2Cl_2–MeOH to give colourless prisms (62 mg), m.p. 203–204°, υ_{max} (CH_2Cl_2) 1780, 1660, 1600, 1500, 1380, 1200, 1120, 1090, 1070, 1050, 1020, 900, and 850 cm^{-1}. (Found: C, 61·8; H, 4·3. $C_{46}H_{36}O_{19}$ required: C, 61·9; H, 4·0%.)

Alkaline Hydrolysis of (IIb)

(*a*) *With 10% ethanolic KOH for 5 min to give X.* The methyl ether (IIb; 800 mg) was heated with 10% ethanolic KOH (40 ml) for about 5 min. The solution was cooled, acidified with 2 N HCl and the yellow precipitate extracted with CH_2Cl_2. This was extracted successively with 10% $NaHCO_3$, 10% Na_2CO_3 and 10% NaOH. The neutral CH_2Cl_2 layer was dried and the solvent removed to give a yellow residue (600 mg). Crystallization from MeOH gave yellow plates, m.p. 130°, λ_{max}^{EtOH} 268, 275 and 335 nm (log ϵ 4·76, 4·51 and 4·54). υ_{max} (nujol) 1660, 1600, 1520, 1360, 1330, 1260, 1220, 1180, 1150, 1110, 1050, 1030, 840, 820, 770 and 725 cm^{-1}. (Found: C, 67·4; H, 5·5; M.wt. by mass spectrum 654. Calc for $C_{37}H_{34}O_{11}$: C, 67·9; H, 5·2%.)

(*b*) *With 7% ethanolic KOH to give veratric acid.* The methyl ether (IIb; 500 mg) was refluxed for 6 hr with 7% ethanolic KOH (30 ml). The solution was cooled, acidified with dil. HCl and extracted with CH_2Cl_2. The organic layer was extracted with 10% $NaHCO_3$. Acidification of bicarbonate layer and extraction with CH_2Cl_2 gave a residue which sublimed under vacuum (100 mg), m.p. 181°. This was shown to be identical with veratric acid by mixed m.p., TLC, and i.r. spectrum.

(*c*) *With 12% ethanolic KOH to give V and VII.* The methyl ether (IIb; 1·6 g) was refluxed with ethanolic KOH (4 g in 4 ml water and 30 ml EtOH) for 2 hr. The reaction mixture was worked up as for Ib and the crude product chromatographed on silica gel. The bands having R_f 0·78 and 0·7 were extracted with MeOH and crystallized from CH_2Cl_2–MeOH. The compounds having m.p. 215–217° and 166° were shown to be identical with V and VII respectively by mixed m.p. and i.r. spectra.

Conversion of Compound X to IIb with Ethanolic HCl

A suspension of X (25 mg) in EtOH (10 ml) and conc. HCl (0·5 ml) was refluxed for 30 min. Removal of the EtOH and addition of a few drops of water gave a gummy residue which crystallized slowly from MeOH (6 mg), m.p. 197–199°. It was found to be identical with morelloflavone heptamethyl ether (IIb) in its mixed m.p., TLC and i.r. spectra.

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