Phytochemistry, Vol. 22, No. 11, pp. 2636–2638, 1983.
Printed in Great Britain.

0031-9422/83 \$3.00+0.00
Pergamon Press Ltd.

A BIFLAVANONE FROM *SEMECARPUS ANACARDIUM**

S. S. N. MURTHY

Department of Chemistry, Andhra University, Waltair 530003, India

(*Received* 3 *May* 1983)

Key Word Index—*Semecarpus anacardium*; Anacardiaceae; biflavanones; ^{1}H NMR and mass spectra; galluflavanone.

Abstract—A new biflavanone, galluflavanone, has been isolated from the alcoholic extract of the nut shells of *Semecarpus anacardium*. It has been characterized through chemical and spectral data.

From the acetone-soluble fraction of an ethanolic extract of the defatted nut shells of *Semecarpus anacardium* L., two new compounds [1, 2] jeediflavanone (**4**) and semecarpuflavanone (**5**) besides the three known biflavanones [3] (**1**–**3**) have been recently reported. The mother liquors of the same fraction furnished another new compound (**6**) in low yield whose structural elucidation forms the subject of this communication.

Compound **6** appeared as a fine micro-crystalline, light yellow powder from acetone, $C_{30}H_{22}O_{11}$, mp 278–280° and has been designated galluflavanone. It afforded a deep brown ferric reaction, a pink colour with Mg–HCl and an orange-red colour with $NaBH_4$–HCl, characteristic of a flavanone. The biflavonoid exhibited UV maxima in ethanol at 297 nm which underwent a bathochromic shift on addition of NaOAc (297 → 324 nm) while with $AlCl_3$ no such shift was noticed, indicating the absence of chelated hydroxyl groups in the molecule. Further, in its ^{1}H NMR spectrum no low-field proton was observed. The compound showed the presence of hydroxyl groups at 3560–3450 (broad), a flavanone carbonyl at 1685 and benzene rings at 1600 and 1590 cm^{-1}. The above observations clearly indicated that there was at least one 7-hydroxyflavanone system [4, 5] in the molecule.

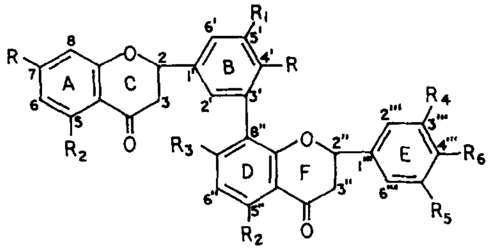
The ^{1}H NMR spectrum (270 MHz, acetone-d_6, TMS as internal standard) of galluflavanone (**6**) showed signals due to four methylene protons (C-3, F-3″) at δ 2.72 (2H, *dd*, J = 4.0, 17.0 Hz, *cis*) and 3.10 (2H, *m*, *trans*) and two benzylic methine protons (C-2, F-2″) at δ 5.40 (2H, *dd*, J = 4.0, 12.0 Hz). Four protons comprising two sets of *meta*-coupled protons of the side-phenyl rings appeared at δ 6.88 (1 H, *d*, J = 2.0 Hz), 6.98 (1 H, *d*, J = 2.0 Hz), 7.44 (1 H, *d*, J = 2.0 Hz) and 7.52 (1 H, *d*, J = 2.0 Hz). The former pair of signals corresponded to the 2‴ and 6‴ protons of ring E, the latter to the 2′ and 6′ protons of ring B. The three signals at δ 7.62 (1H, *d*, J = 8.0 Hz), 6.16 (1H, *dd*, J = 2.0, 8.0 Hz) and 6.26 (1H, *d*, J = 2.0 Hz) corresponded, respectively, to the protons at the 5, 6 and 8 positions of ring A. Further, the ^{1}H NMR spectrum of **6** showed the presence of seven non-chelated hydroxyl groups which were exchanged with D_2O at δ 7.84 (*s*, 3H), 8.02 (*s*, 2H) and 8.36 (*s*, 2H), and these were assigned to the A-7, B-4′, 5′, D-7″ and E-3‴, 4‴, 5‴ positions. There were two more doublet signals at δ 6.56 (1H, J = 8.5 Hz) and 7.72 (1H, J = 8.5 Hz) corresponding to the two *ortho*-coupled protons at the 6″ and 5″ positions of ring D, respectively.

All eleven oxygens in the biflavanone (**6**) are accounted for by the seven non-chelated hydroxyl groups and four pyranone oxygens. Consequently the two flavanone units must be linked by a C–C linkage only. Oxidation of galluflavanone (**6**) with neutral permanganate afforded only 1 mol of gallic acid suggesting that one of the side-phenyls is involved in the biphenyl linkage.

On methylation with excess diazomethane, galluflavanone gave a hexamethyl ether (**7**), $C_{36}H_{34}O_{11}$, mp 180–181° whose ^{1}H NMR spectrum (80 MHz, $CDCl_3$, TMS as internal standard) showed signals due to six methoxyl groups at δ 3.50 (*s*, 3H), 3.72 (*s*, 3 × 3H) and 3.80 (*s*, 2 × 3H). The upfield signal for the methoxyl group at δ 3.50 was assigned to the D-7″ methoxyl (compare 4,5-dimethyl-3-phenylveratrole [6], 3-(4-cinnolinyl)-veratrole [7], glaucine [8] and isocorydine methochloride [9]). There was another signal at δ 8.10 (*s*, 1 H, exchanged with D_2O) which corresponded to the non-chelated hydroxyl group at the E-4‴ position. In order to secure a complete methyl ether, the biflavanone (**6**) was refluxed with DMS–K_2CO_3 in dry acetone for several hours whereby a bichalcone heptamethyl ether (**8**), $C_{37}H_{36}O_{11}$, mp 212–213° was obtained. The ^{1}H NMR spectrum of the heptamethyl ether (80 MHz, $CDCl_3$, TMS as internal standard) showed the presence of seven methoxyl groups at δ 3.45 (*s*, 3H), 3.75 (*s*, 3 × 3H) and 3.82 (*s*, 3 × 3H) and two chelated hydroxyl groups at δ 14.40 (*s*, 1H) and 14.50 (*s*, 1H) corresponding to the A-2′ and D-2‴ positions, respectively [3]. The upfield methoxyl signal at δ 3.45 was assigned [6–9] to the D-4‴ methoxyl group. Further, the four olefinic protons (C-7, 8; F-7″, 8″) appeared as a singlet signal at δ 7.72, as was noticed by Batterham *et al.* in 4,2′,4′-trihydroxychalcone and its trimethyl ether [10], and Prakasa Rao *et al.* in bichalcones A, B1 and B2 [3].

---

*Part 5 in the series "Naturally Occurring Biflavonoid Derivatives". For Part 4 see ref. [2].



1 $R = R_2 = R_4 = R_6 = OH$, $R_1 = R_3 = R_5 = H$

2 $R = R_2 = R_3 = R_6 = OH$, $R_1 = R_4 = R_5 = H$

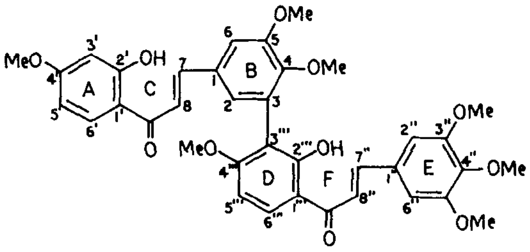
3 $R = R_3 = R_6 = OH$, $R_1 = R_2 = R_4 = R_5 = H$

4 $R = R_2 = R_3 = R_4 = R_6 = OH$, $R_1 = R_5 = H$

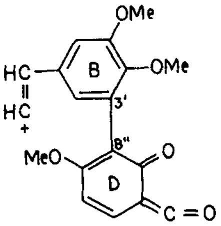
5 $R = R_3 = R_4 = R_5 = R_6 = OH$, $R_1 = R_2 = H$

6 $R = R_1 = R_3 = R_4 = R_5 = R_6 = OH$, $R_2 = H$

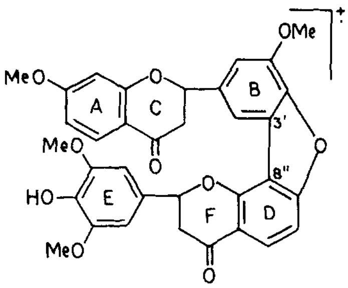
7 $R = R_1 = R_3 = R_4 = R_5 = OMe$, $R_2 = H$, $R_6 = OH$



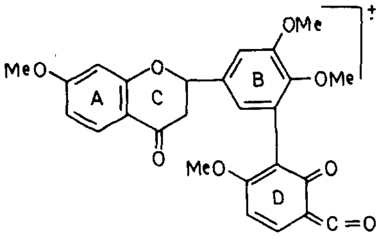
8



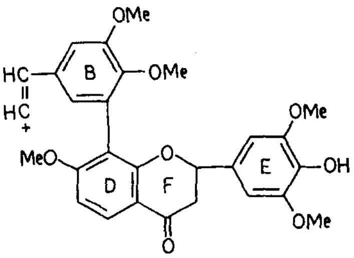
9



10



11



12

Oxidation of galluflavanone hexamethyl ether (**7**) with neutral permanganate afforded both syringic acid and 2-hydroxy-4-methoxybenzoic acid (mmp and IR). Hence the diaryl system must contain the remaining three methoxyl groups, which are placed by analogy and ^{1}H NMR at the B-4′, B-5′ and D-7″ positions. Consequently the interflavonoid linkage must be either at the B-3′–D-8″ position or at the B-3′–D-6″ position. Since the parent compound contains no chelated hydroxyl groups, the positions at A-5 and D-5″ are free. Further, the ^{1}H NMR spectra of galluflavanone and its two derivatives (**7** and **8**) clearly pointed to the presence of two *ortho*-coupled protons which must correspond to ring D. On this basis the biflavonoid linkage at the B-3′–D-6″ position can be eliminated and hence galluflavanone must possess the C–C linkage at the B-3′–D-8″ position. This is also in good agreement with the biflavanones already reported from this plant [1–3].

The galluflavanone hexamethyl ether (**7**) in its mass spectrum showed the molecular ion at M^+ 642 (45 %). The ion at m/z 179 [(67.4 %), 3,5-$(MeO)_2$-4-OH-C_6H_2-CH$=\overset{+}{C}$H] indicated that rings E and F do not carry the interflavonoid linkage. The peak at m/z 311 (28 %) corresponding to the central fragment (**9**) was formed after two retro-Diels–Alder fragmentations. The methyl ether (**7**) showed a peak at m/z 596 (7.5 %) which was formed by the loss of 46 amu. This fragment can be formulated as **10**, in which the *ortho*-methoxyl groups to the diaryl linkage cyclize to a furan ring [11]. Perhaps the most significant feature is the formation of the two fragments **9** and **10** which indicated that the biflavonoid linkage is between rings B and D. There were two more peaks at m/z 462 (9 %) and m/z 491 (10.5 %) corresponding to fragments **11** and **12**, respectively. It may be mentioned here that similar fragments have been reported in rhusflavanone [12, 13] and tetrahydroamentoflavone [14]. Overall, the mass spectral fragmentation pattern exhibits a close similarity to that of 2,3-dihydroamentoflavone hexamethyl ether [15] and GB-2 [16, 17].

From the foregoing chemical and spectroscopic evidence, structure **6** has been assigned for galluflavanone, with the biphenyl linkage at the B-3′–D-8″ position.

Acknowledgements—I am grateful to Professor L. R. Row for encouragement. I also thank Drs. P. A. Ramaiah and M. Bapuji for the ^{1}H NMR and mass spectra recorded.

REFERENCES

1. Murthy, S. S. N. *Indian J. Chem. Sect. B* (in press).
2. Murthy, S. S. N. (1983) *Phytochemistry* **22**, 1518.
3. Prakasa Rao, N. S., Ramachandra Row, L. and Brown, R. T. (1973) *Phytochemistry* **12**, 671.
4. Horowitz, R. M. and Jurd, L. (1961) *J. Org. Chem.* **26**, 2446.
5. Jurd, L. (1962) in *The Chemistry of the Flavonoid Compounds* (Geissman, T. A., ed.), p. 151. Pergamon Press, London.
6. Allen, G. and Bruce, J. M. (1963) *J. Chem. Soc.* 1757.
7. Bruce, J. M. (1959) *J. Chem. Soc.* 2366.
8. Bick, I. R. C., Harley-Mason, J., Sheppard, N. and Vernengo, M. J. (1961) *J. Chem. Soc.* 1896.
9. Katritzky, A. R., Jones, R. A. Y. and Bhatnagar, S. S. (1960) *J. Chem. Soc.* 1950.
10. Batterham, T. J. and Highet, R. J. (1964) *Aust. J. Chem.* **17**, 428.
11. Natarajan, S., Murti, V. V. S. and Seshadri, T. R. (1969) *Indian J. Chem.* **7**, 751.
12. Lin, Y. M. and Chen, F. C. (1973) *Tetrahedron Letters* 4747.
13. Chen, F. C. and Lin, Y. M. (1976) *J. Chem. Soc. Perkin Trans.* 1, 98.
14. Ishratullah, K. H., Ansari, W. H., Rahman, W., Okigawa, M. and Kawano, N. (1977) *Indian J. Chem. Sect. B* **15**, 615.
15. Varshney, A. K., Talat, M., Khan, N. U., Rahman, W., Hwa, C. W., Okigawa, M. and Kawano, N. (1973) *Indian J. Chem.* **11**, 1209.
16. Jackson, B., Locksley, H. D., Scheinmann, F. and Wolstenholme, W. A. (1967) *Tetrahedron Letters* 787.
17. Jackson, B., Locksley, H. D., Scheinmann, F. and Wolstenholme, W. A. (1971) *J. Chem. Soc. C* 3791.