IR) and sulphate (ppt. with $BaCl_2$). ^{13}C NMR spectra were recorded at 50.3 MHz using DMSO-d_6 as solvent and TMS as int. standard.

Compound **1.** Yellow crystals; R_f values: BAW (0.28), H_2O (0.89); 15% HOAc (0.77); colours at 366 nm: dark brown (without any treatment), dark yellow (NH_3), fluorescent yellow ($AlCl_3$), yellow (NA); UV λ_{max}^{MeOH} nm: 268, 283 sh, 350; +NaOMe: 275, 325, 400; $+AlCl_3$: 267, 295 sh, 350, 400; $+AlCl_3+HCl$: 276, sh 295, 350, 400; +NaOAc: 275, 310, 390; $+NaOAc+H_3BO_3$: 268, 295, 352; IR ν_{max}^{KBr} cm^{-1}: 3400, 3250, 1660, 1505, 1400, 1300, 1040 and 805.

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REFERENCES

1. Harborne, J. B. (1975) *Phytochemistry* **4**, 1331.
2. Harborne, J. B. (1975) *Phytochemistry* **4**, 1147.
3. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, pp. 44–49. Springer, Berlin.
4. Harborne, J. B. and King, L. (1976) *Biochem. Syst. Ecol.* **4**, 111.
5. Markham, K. R. (1982) in *Techniques of Flavonoid Identification*. Academic Press, London.
6. Harborne, J. B. (1965) *Phytochemistry* **4**, 107.

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SEMECARPETIN, A BIFLAVANONE FROM *SEMECARPUS ANACARDIUM*[*]

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

Abstract—A new biflavanone, semecarpetin, has been recently isolated from the nut shells of *Semecarpus anacardium*. Its structure has been characterized on the basis of spectral and chemical data as 7″-hydroxy-7,3‴,4′,4‴-tetramethoxybi(8″,3′) flavanone.

From part A of the acetone soluble fraction [1] of the alcoholic extract of the defatted nut shells of *Semecarpus anacardium* L., three new compounds [1–3] besides the three known biflavanones [4] were reported. Two new dimeric flavanones designated as nallaflavanone and semecarpetin have recently been isolated from part B of the acetone soluble fraction [1]. Structure **1** has already been assigned [5] to nallaflavanone. The present report deals with the structural determination of semecarpetin.

Semecarpetin (**2**) appeared as bright yellow crystals from chloroform and methanol mixture, $C_{34}H_{30}O_9$, mp 164–65°. It afforded a pink colour with magnesium–hydrochloric acid and a red colour with sodium borohydride–hydrochloric acid characteristic of a flavanone. The UV spectrum in alcohol exhibited maxima at 298 nm which on addition of sodium acetate to the test solution underwent a bathochromic shift (298→331 nm) while with aluminium chloride no such shift was observed revealing the absence of chelated hydroxyl groups in the biflavonoid. Further, in its ^1H NMR spectrum no low field proton was noticed. The compound showed IR bands at 3430 (hydroxyl group), 2830 (methoxyl groups), 1680 (flavanone carbonyl), 1610 and 1560 (aromatic) cm^{-1}. The above observations clearly revealed that there was at least one 7-hydroxyflavanone system [6, 7] in the molecule.

The ^1H NMR spectrum (80 MHz, $CDCl_3$, TMs as internal standard) of semecarpetin (**2**) displayed signals due to two benzylic methine protons (C-2, F-2″) at δ5.24 (*m*, 2H) and four methylene protons (C-3, F-3″) at 2.86 (2H, *br*, *cis*-protons) and 3.12 (2H, *m*, *trans*-protons). The three protons corresponding to 5, 6 and 8 positions of ring A were observed respectively at δ7.66 (1H, *d*, $J = 8$ Hz), 6.24 (1H, *dd*, $J = 2,8$ Hz), and 6.34 (1H, *d*, $J = 2$ Hz). There are two unresolvable multiplets between δ6.68 and 6.92, and 7.12 and 7.34 integrating each for three protons; the former multiplet corresponded to 2‴, 5‴ and 6‴ protons of ring E while the latter to 2′, 5′ and 6′ protons of ring B. The two *ortho*-coupled protons corresponding to 5″ and 6″ positions of ring D were noticed respectively at δ7.72 (1H, *d*, $J = 8$ Hz) and 6.56 (1H, *d*, $J = 8$ Hz). Further, the ^1H NMR spectrum showed the

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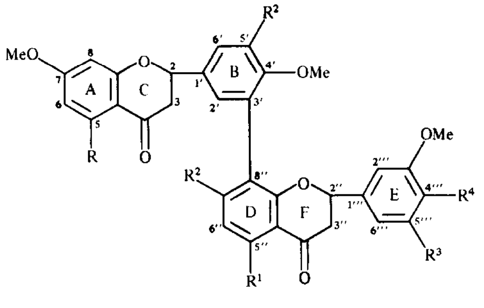
[*] Part 10 in the series 'Naturally Occurring Biflavonoid Derivatives' For part 9, see ref. [5].

presence of one non-chelated D_2O exchangeable hydroxylic proton at 8.22 (*s*) and four methoxyl groups at 3.70 (*s*, 3H) and 3.76 (*s*, 3 × 3H) and these could be ascribed respectively to D-7″, A-7, B-4′, E-3‴, 4‴ positions.

All the nine oxygen atoms in **2** are accounted for by the four pyranone oxygen atoms, one non-chelated hydroxyl group and four methoxyl groups. Hence the diaryl linkage between the two flavanone units must be through a C–C linkage only. Oxidation of semecarpetin with neutral permanganate gave only one mole of veratric acid (identified by mmp and IR) suggesting that one of the side-phenyl rings is involved in the interflavonoid linkage.

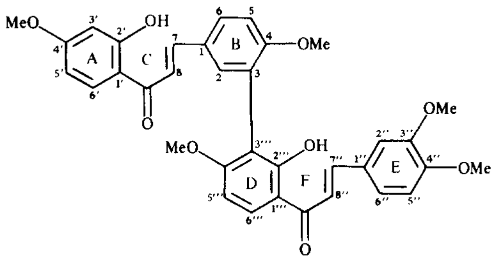
On acetylation with acetic anhydride and pyridine on a steam bath for one hour, semecarpetin afforded an acetate (**3**), $C_{36}H_{32}O_{10}$, mp 126° whose ^{1}H NMR spectrum ($CDCl_3$) showed one acetoxyl group at 2.21 corresponding to D-7″ position. Methylation of semecarpetin with diazomethane gave a monomethyl ether (**4**), $C_{35}H_{32}O_9$, mp 138° while with dimethyl sulphate and potassium carbonate in acetone under reflux, it furnished a bichalcone pentamethyl ether (**5**), $C_{35}H_{32}O_9$, mp 214–215°. The ^{1}H NMR spectrum of **4** ($CDCl_3$) indicated the presence of five methoxyl groups at 3.43 (*s*, 3H), 3.73 (*s*, 3H) and 3.79 (*s*, 3 × 3H). The upfield methoxy signal at 3.43 was assigned to the D-7″ methoxyl group by comparison with glaucine [8]. Further, **5** showed in its ^{1}H NMR spectrum ($CDCl_3$), the presence of five methoxyl groups at 3.47 (*s*, 3H), 3.77 (*s*, 3H) and 3.81 (*s*, 3 × 3H). The upfield signal at 3.47 was assigned to D-4‴ methoxyl group as in **4**. It showed the presence of two chelated hydroxylic protons at 14.26 (*s*, 1H) and 14.42 (*s*, 1H) corresponding to A-2′ and D-2‴ positions, respectively [4]. The four olefinic protons in **5** were noticed at 6.52 (2H, *d*, $J = 16$ Hz, C-8, F-8″) and 7.80 (2H, *d*, $J = 16$ Hz, C-7, F-7″).



1 R^1 = OH, R^2 = R^3 = OMe, R^4 = OH
2 R^1 = R^3 = H, R^2 = OH, R^4 = OMe
3 R^1 = R^3 = H, R^2 = OAc, R^4 = OMe
4 R^1 = R^3 = H, R^2 = R^4 = OMe

When the bichalcone pentamethyl ether (**5**) was oxidized with neutral permanganate, both veratric acid and 2-hydroxy-4-methoxy benzoic acid (identified by mmp and IR) were obtained. Hence, the two remaining methoxyl groups must be in the diaryl system which are assigned by analogy and ^{1}H NMR spectral data at the B-4 and D-4‴ positions (chalcone numbering). Consequently the biflavonoid linkage in **5** must be either at the B-3–D-3‴ position (B-3′–D-8″) or at the B-3–D-5‴ position (B-3′ – D-6″) flavonoid numbering in the parenthesis). Since semecarpetin contains no chelated hydroxyl groups, the positions at A-5 and D-5″ are free. Further the ^{1}H NMR spectra of the parent compound **2** and its three derivatives (**3**–**5**) clearly indicate the presence of two *ortho*-coupled protons which must correspond to ring D. On the basis of this observation, the C–C linkage at the B-3′–D-6″ position can be eliminated and hence semecarpetin must have the biflavonoid linkage at the B-3′–D-8″ position. This is also in good agreement with the biflavanones already reported from this plant [1–5].

Semecarpetin (**2**) in its mass spectrum displayed the molecular ion (M$^+$) at *m/z* 582 (12%). The peak at *m/z* 163 [3,4-(OMe)$_2$-C$_6$H$_3$-CH=C$^+$H; 71%] not only revealed that the rings E and F do not carry the biflavonoid linkage but also indicated that the 3‴ and 4‴ positions of ring E were occupied by the two methoxyl groups. The central fragment at *m/z* 267 (19%) corresponding to the ion **6** was formed after two RDA fragmentations. Compound **4** in its mass spectrum showed a peak at *m/z* 550 (6%) which is formed by the loss of 46 mass units. This fragment can be formulated as **7** in which the *ortho*-methoxyl groups to the biphenyl linkage cyclize to a furan ring [9]. Perhaps the most significant feature is the formation of the two fragments **6** and **7** which could be diagnostic of the biphenyl linkage. It may be mentioned here that similar fragments have been reported in morelloflavone heptamethyl ether [10]. Overall the mass spectral fragmentation pattern of semecarpetin exhibits a close similarity with that of GB-2 [11]. Thus semecarpetin has structure **2**.



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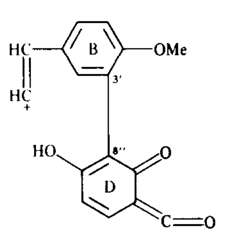

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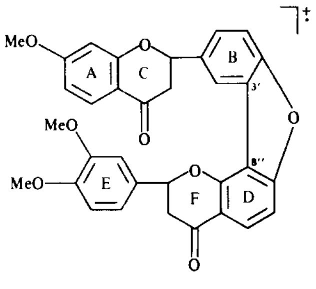

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REFERENCES

1. Murthy, S. S. N. (1985) *Phytochemistry* **24**, 1065.
2. Murthy, S. S. N. (1983) *Phytochemistry* **22**, 1518.
3. Murthy, S. S. N. (1985) *Indian J. Chem.* **24B**, 398.
4. Prakasa Rao, N. S., Ramachandra Row, L. and Brown, R. T. (1973) *Phytochemistry* **12**, 671.
5. Murthy, S. S. N. (1987) *Proc. Indian Natl. Sci. Acad.* **53A**, 632.
6. Horowitz, R. M. and Jurd, L. (1961) *J. Org. Chem.* **26**, 2446.
7. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, pp. 165–171. Springer, New York.
8. Bick, I. R. C., Harley-Mason, J, Sheppord, N. and Vernengo, M. J. (1961) *J. Chem. Soc.*, **1896**.
9. Natarajan, S., Murti, V. V. S. and Seshadri, T. R. (1969) *Indian J. Chem.* **7**, 751.
10. Karanjgaokar, C. G., Radhakrishnan, P. V. and Venkataraman, K. (1967) *Tetrahedron Letters* 3195.
11. Jackson, B., Locksley, H. D., Scheinmann, F. and Wolstenholme, W. A. (1971) *J. Chem. Soc.* (*C*) 3791.

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EMEHETERONE, A PYRAZINONE DERIVATIVE FROM *EMERICELLA HETEROTHALLICA**

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Key Word Index—*Emericella hetrothallica*; Eurotiaceae; 2(1*H*)-Pyrazinone; emeheterone; stellatin.

Abstract—Emeheterone, a novel pyrazinone derivative, has been isolated from the culture filtrate of the fungus *Emericella heterothallica*, along with stellatin. Its molecular structure has been investigated by spectroscopic means.

INTRODUCTION

Recently the antifungal epidithiodioxopiperazines, emestrin [2] and dithiosilvatin [3], were isolated from *Emericella striata* (Rai, Tewari & Mukerji) Malloch & Cain and *Aspergillus silvaticus* Fennell & Raper, respectively. In the course of screening for dioxopiperazine derivatives from *Emericella* spp., a novel pyrazinone derivative designated emeheterone (1) was isolated from the dichloromethane extract of the culture filtrate of *Emericella heterothallica* (Kwon, Fennell & Raper) Malloch & Cain (anamorph: *Aspergillus heterothallicus* Kwon, Fennell & Raper) (mating type a), strain ATCC 16824, along with a dihydroisocoumarin, stellatin (**2**).

RESULTS AND DISCUSSION

Emeheterone (**1**), mp 215–217°, gave molecular ions at *m/z* 322 in EIMS and at *m/z* 323 in CIMS, and elemental analysis confirmed the molecular formula as $C_{19}H_{18}N_2O_3$. The strong ion at *m/z* 91 $[C_6H_5CH_2]^+$ in the EIMS suggested the presence of benzyl groups in the molecule of **1**. The ^1H NMR signals at δ 7.20–7.40 (10H), 3.93 (2H), and 4.20 (2H), the 10 ^{13}C NMR signals at δ 126–137 and the two ^{13}C NMR signals at δ 30.39 and 34.01 were assigned to two benzyl groups. The other ^1H NMR signals at δ 3.92 (3H) and 3.73 (1H) in **1** were assigned to a methoxy group, which appeared at δ 61.73 in the ^{13}C NMR spectrum, and a hydroxyl group, respectively.

The IR absorption maximum at 1650 cm^{-1} and the ^{13}C NMR signal at δ158.14 (St) in emeheterone (**1**) suggested the presence of a conjugated carbonyl, probably an amide. Compound **1** gave a positive coloration (greenish brown) with 0.5% aq. copper chloride [4], which suggested the presence of an oxime-like structure. The UV absorption maxima at 228, 276, 334 (sh), and 352 nm of **1** were closely similar to those at 225, 265, 279 (sh), 347 (sh), and 364 nm for deferriastechrome **3** [5], which also has a maximum at 291 nm due to the indole moiety. The above results are consistent with structure **1** for emeheterone, but do not suggest the orientation of the methoxy and hydroxyl groups located at N-1 and C-5.

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* Part 20 in the series 'Studies on Fungal Products'. For Part 19 see ref. [1].