Murakami, Natl. Inst. of Agricultural Science, Japan, for the gift of dwarf rice seeds.

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CONFIRMATION OF THE STRUCTURE OF JEEDIFLAVANONE: A BIFLAVANONE FROM *SEMECARPUS ANACARDIUM**

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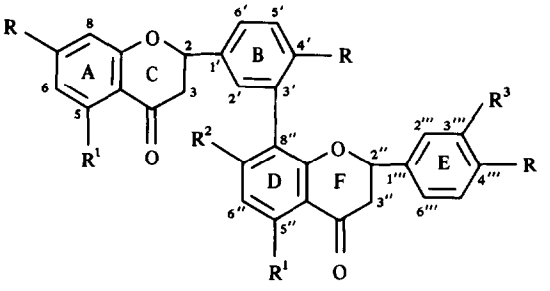
Key Word Index—*Semecarpus anacardium*; Anacardiaceae; jeediflavanone; biflavone SA5; ^{1}H NMR and mass spectra; solvent induced methoxy shifts.

Abstract—Jeediflavanone was dehydrogenated with I_2–KOAc in HOAc to the corresponding, relatively more stable biflavone designated SA5. The solvent induced methoxy shift data of SA5 heptamethyl ether confirmed the structure as well as the interflavonoid linkage of jeediflavanone.

The acetone soluble fraction of an alcoholic extract of the defatted nut shells of *Semecarpus anacardium* L. afforded a new compound jeediflavanone (**1**) [1] besides the known three biflavanones **2**–**4** [2]. The structure of jeediflavanone was elucidated mainly on the basis of ^{1}H NMR and mass spectral data and also its biflavonoid linkage at the B-3′-D-8″ position was assumed by analogy. Hence further chemical and spectral evidence is necessary to establish its structure. The present study deals with the confirmation of the structure of jeediflavanone.

Jeediflavanone (**1**) was dehydrogenated [3–5] with iodine and potassium acetate in glacial acetic acid for three hours at reflux temperature to give the corresponding stable biflavone designated SA5. It did not crystallize from common organic solvents and hence on drying in a vacuum oven at 70°, the compound appeared as a pale yellow powder from acetone, $C_{30}H_{18}O_{11}$, mp > 300°, IR (nujol): 3510–3440 (*br*, OH), 1625 (chelated flavone carbonyl), 1600 and 1590 cm^{-1} (aromatic). Compound SA5 gave a greenish-violet ferric reaction, a pink colour with magnesium–hydrochloric acid characteristic of a flavone.

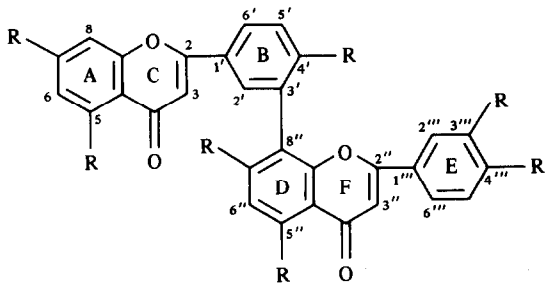
The ^{1}H NMR spectrum (80 MHz, acetone-d_6, TMS as internal standard) of SA5 showed a singlet signal† at 6.50 due to two olefinic protons at C-3 and F-3″ positions. The two signals at 6.14 (*d*, J = 2.0 Hz) and 6.20 (*d*, J = 2.0 Hz) integrating each for one proton corresponded respectively to the two *meta*-coupled protons at the 6 and 8 positions of ring A. There are two low field signals at 14.24 (*s*, 1H) and 14.35 (*s*, 1H) corresponding to the two chelated hydroxylic protons at A-5 and D-5″ positions respectively [2]. Further the ^{1}H NMR spectrum indicated the presence of five non-chelated hydroxylic protons at 7.32 (*s*, 1H), 7.48 (*s*, 2H) and 7.59 (*s*, 2H) which are exchanged with D_2O and these should correspond to A-7, B-4′, D-7″ and



1 R = R¹ = R² = R³ = OH
2 R = R¹ = R³ = OH, R² = H
3 R = R¹ = R² = OH, R³ = H
4 R = R² = OH, R¹ = R³ = H

*Part 5 in the series "Partial Conversions in Biflavonoids". For Part 4 see Murthy, S. S. N., *Curr. Sci.* (communicated).

†Chemical shifts throughout this article are in δ values.



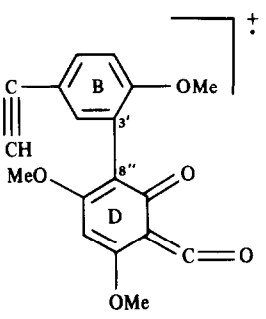
R	
5	OH
6	OAc
7	OMe

E-3‴, 4‴ positions. There are two large unresolvable multiplets between 6.90–7.13 and 7.26–7.48 integrating each for three protons; the former multiplet corresponded to 2‴, 5‴, 6‴ protons of ring E while the latter to 2′, 5′, 6′ protons of ring B. There is another singlet signal at 6.56 (1H) corresponding to either 6″ or 8″ proton of ring D.

Compound SA5 (**5**) on acetylation with NaOAc–Ac_2O gave a heptaacetate (**6**), $C_{44}H_{32}O_{18}$, mp 158–160° while with DMS–K_2CO_3 it furnished a heptamethyl ether (**7**), $C_{37}H_{32}O_{11}$, mp 172–174°. The ^1H NMR spectra (80 MHz, $CDCl_3$, TMS as internal standard) of both revealed the presence of seven acetoxyl groups (2.22–2.32) in **6** while in **7** seven methoxyl groups at 3.71 (*s*, 2 × 3H), 3.76 (*s*, 2 × 3H), 3.82 (*s*, 2 × 3H) and 3.90 (*s*, 3H) are present. Further, oxidation of SA5 heptamethyl ether (**7**) with neutral permanganate afforded only one mole of veratric acid suggesting that one of the side-phenyls is involved in the interflavonoid linkage. From the foregoing spectral and chemical data, the biflavonoid linkage in SA5 must be either at the B-3′-D-8″ position or at the B-3′-D-6″ position.

Compound SA5 heptamethyl ether (**7**) in its mass spectrum showed the molecular ion at $[M]^+$ 652 (60.4%). The peaks at *m/z* 162 (75.5%), $[3,4\text{-}(OCH_3)_2\text{-}C_6H_3\text{-}C{\equiv}CH]^+$ and *m/z* 165 [(68.6%), $3,4\text{-}(OCH_3)_2\text{-}C_6H_3\text{-}C{\equiv}O^+$] indicated that the rings E and F are not involved in the biphenyl linkage. The ion at *m/z* 310 (30.5%) corresponding to the crucial fragment **8** is formed after two RDA fragmentations. The heptamethyl ether (**7**) showed a peak at *m/z* 606 (8.5%) which is formed by the loss of 46 mass units. This fragment can be formulated as **9** in which the *ortho*-methoxyl groups to the diaryl linkage cyclize to a furan ring [6]. Perhaps the most characteristic feature is the formation of the two fragments **8** and **9** which could be sufficiently indicative or diagnostic of a C–C linkage. There are two more peaks at *m/z* 472 (11.25%) and *m/z* 490 (12.0%) corresponding to the fragments **10** and **11** respectively. It may be mentioned here that similar fragments have been reported in amentoflavone hexamethyl ether [7].

The solvent induced methoxy shift technique can be used in biflavonoids for determining the position of the methoxyl groups and the interflavonoid linkage. In order to distinguish between the two positional isomers of SA5, this technique has been profitably utilised. Solvent induced shifts for the seven methoxy groups of SA5



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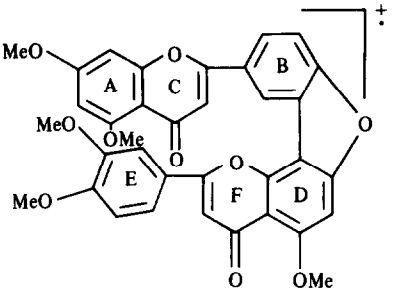

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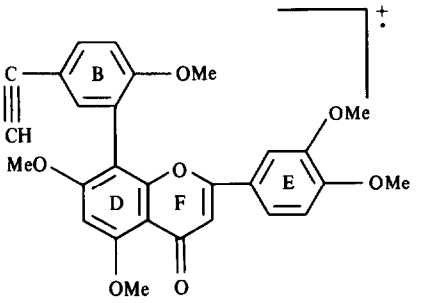

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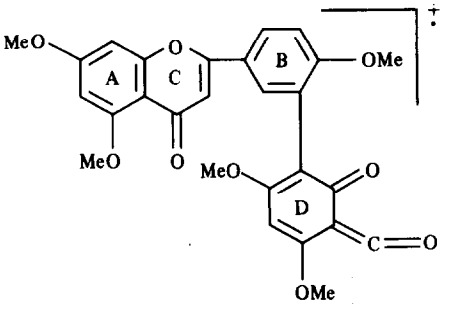

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heptamethyl ether (7) were studied for solutions containing increasing concentrations of perdeuteriobenzene in deuteriochloroform. All the seven methoxy signals were moved upfield (44, 49, 54, 55, 58, 61 and 68 Hz) as with cupressuflavone hexamethyl ether [8] and amentoflavone hexamethyl ether [9] indicating that each methoxyl group has at least one free *ortho*-position. Hence SA5 heptamethyl ether must have a C–C linkage at the B-3′-D-8″ position. For a B-3′-D-6″ linkage, the D-5″ methoxy group, with two adjacent substituents, should not undergo any solvent induced shift on addition of perdeuteriobenzene [10–12].

The above observation of SA5 heptamethyl ether with regard to the biphenyl linkage has thus given an unambiguous proof that the interflavonoid linkage in the parent compound, jeediflavanone, must be at the B-3′-D-8″ position as originally postulated [1] and not at the B-3′-D-6″ position.

From the foregoing chemical and spectral studies, the assignment of structure **5** for the biflavone SA5 is taken as confirmative evidence for the structure of jeediflavanone (**1**).

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FLEMIPHYLLIN, AN ISOFLAVONE FROM STEMS OF *FLEMINGIA MACROPHYLLA*

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Key Word Index—*Flemingia macrophylla*; Leguminosae; stems; isoflavone; 5,7,4′-trihydroxy-3′,5′,8-tri(3-methylbut-2-enyl) isoflavone; flemiphyllin.

Abstract—A new isoflavone, designated flemiphyllin, was isolated from a petrol extract of the stems of *Flemingia macrophylla*. Its structure was established as 5,7,4′-trihydroxy-3′,5′,8-tri(3-methylbut-2-enyl) isoflavone on the basis of physical and chemical evidence.

INTRODUCTION

Earlier we have communicated the isolation and structural elucidation of fleminone a new flavanone from the petrol extract of the stems of *Flemingia macrophylla* [1]. The petrol–benzene (1 : 1) elutions (fractions 34–60) from the main column chromatography [1] on purification furnished a product, designated as flemiphyllin. The present paper deals with the structure determination of this compound.

RESULTS AND DISCUSSION

Flemiphyllin (**1**), mp 172°, $C_{30}H_{34}O_5$, $[M]^+$ 474 gave a green colour with alcoholic ferric chloride solution indicating the presence of a chelated hydroxyl group. It is also soluble in alkali indicating its phenolic nature. It did not give a Shinoda test [2] indicating that it is not a flavone or a flavanone. The IR spectrum [ν_{KBr}^{max} 1625 cm^{-1} (C=O) and ν_{KBr}^{max} 3300 cm^{-1} (OH)] and a low field singlet at δ 7.72 in ^{1}H NMR spectrum (100 MHz, recorded in