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JEEDIFLAVANONE—A BIFLAVONOID FROM *SEMECARPUS ANACARDIUM**

S S N MURTHY

Organic Chemistry Laboratories, School of Chemistry, Andhra University, Waltair 530003, India

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Key Word Index—*Semecarpus anacardium*, Anacardiaceae, sitosterol, biflavanones, jeediflavanone, biflavone SA5

Abstract—A new biflavonoid, jeediflavanone, has been isolated recently from the alcoholic extract of the nut shells of *Semecarpus anacardium* It was dehydrogenated with iodine and potassium acetate in acetic acid to the corresponding, relatively more stable biflavone SA5 The solvent induced methoxy shift studies of SA5 heptamethyl ether confirmed the interflavonoid linkage as well as the structure of jeediflavanone Chemical, ^{1}H NMR and mass spectroscopic evidence are presented in support of the structures of both jeediflavanone and SA5

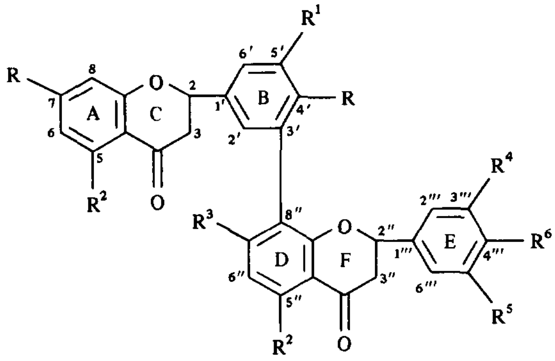
INTRODUCTION

From the ether soluble fraction of an alcoholic extract of the defatted nut shells of *Semecarpus anacardium* L, three biflavanones (**1–3**) were isolated [1] while tetrahydrorobustaflavone(B-3′-D-6″-binaringenin) and tetrahydroamentoflavone (**2**) were reported [2] from the defatted nut shells of the same plant The need to isolate the three compounds (**1–3**) for certain chemical transformations in our laboratories and particularly the isolation of tetrahydrorobustaflavone [2] which belongs totally to a different series have prompted the author to pursue the investigation again on this plant Hence in the process of isolation of the chemical constituents, the acetone soluble fraction (part A) furnished three more new compounds, semecarpuflavanone (**4**) [3], galluflavanone (**5**) [4] and jeediflavanone (**6**) besides the three known biflavanones (**1–3**) while from the *n*-hexane fraction only sitosterol was isolated The present study deals with the isolation and structure determination of jeediflavanone (**6**)

RESULTS AND DISCUSSION

The deep red viscous liquid of alcohol extract of the defatted nut shells was worked up as described in Experimental

Jeediflavanone (**6**) appeared as a fine micro-crystalline pale yellow powder from acetone, $C_{30}H_{22}O_{11}$, mp 285–287° and exhibited UV maxima in ethanol at 286 nm which underwent the bathochromic shifts on addition of sodium acetate (286 → 320 nm) and aluminium chloride (286 → 318 nm) This observation clearly indicated that there was at least one 5,7-dihydroxyflavanone system [5–7] in the molecule The ^{1}H NMR spectrum of jeediflavanone in acetone-d_6 indicated the presence of five non-chelated D_2O-exchangeable hydroxylic protons and two chelated hydroxyl protons Hence, the two flavanone units must be linked by a C–C linkage only since all the eleven oxygen atoms in jeediflavanone (**6**) are accounted for by the two chelated hydroxyl groups, five non-chelated hydroxyl groups and four pyranone oxygen atoms Oxidation of jeediflavanone with neutral permanganate furnished only one mole of protocatechuic acid (identified by mmp and IR) suggesting that one of the side-phenyls is involved in the interflavonoid linkage



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^3 = R^4 = R^5 = R^6 = OH, R^1 = R^2 = H
5 R = R^1 = R^3 = R^4 = R^5 = R^6 = OH, R^2 = H
6 R = R^2 = R^3 = R^4 = R^6 = OH, R^1 = R^5 = H
7 R = R^3 = R^6 = OMe, R^2 = R^4 = OH, R^1 = R^5 = H
8 R = R^3 = R^4 = R^6 = OMe, R^2 = OH, R^1 = R^5 = H
9 R = R^3 = R^6 = OMe, R^2 = R^4 = OAc, R^1 = R^5 = H
10 R = R^2 = R^3 = R^4 = R^6 = OAc, R^1 = R^5 = H

On methylation with excess diazomethane, jeediflavanone afforded a tetramethyl ether (**7**), $C_{34}H_{30}O_{11}$, mp 213–214° and a pentamethyl ether (**8**), $C_{35}H_{32}O_{11}$, mp 195–196° The ^{1}H NMR spectra of these two methyl ethers bear very close resemblance Each methyl ether showed the presence of two chelated hydroxyl groups as

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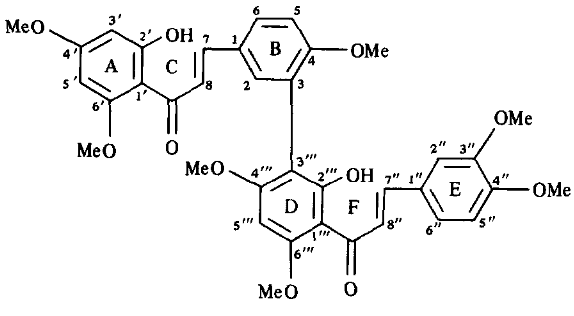
*Part 6 in the series "Naturally Occurring Biflavonoid Derivatives" For Part 5 see ref [4] in **6** In addition, compound **7** indicated the presence of one non-chelated hydroxyl proton at the E-3‴ position since the methyl ether (**7**) on oxidation with neutral permanganate gave only isovanillic acid (identified by mmp and IR) Further, the tetramethyl ether on acetylation with acetic anhydride and pyridine at room temperature afforded a triacetate (**9**), $C_{40}H_{36}O_{14}$ mp 168° which revealed in its ^{1}H NMR spectrum ($CDCl_3$) the presence of four methoxyl groups at δ3 82 (*s*) as in **7** and three acetoxyl groups between δ2 24 and δ2 30 Jeediflavanone on acetylation with acetic anhydride and pyridine on a steam-bath for 4 hr afforded a heptaacetate (**10**), $C_{44}H_{36}O_{18}$, mp 154–156° while with dimethyl sulphate and potassium carbonate in acetone for several hours under reflux it gave a bichalcone heptamethyl ether (**11**), $C_{37}H_{36}O_{11}$, mp 242–244° Both the derivatives clearly indicated the presence of seven hydroxyl groups in the parent compound

The bichalcone heptamethyl ether (**11**), on oxidation with neutral permanganate, gave both veratric acid and 2-hydroxy-4,6-dimethoxybenzoic acid (identified by mmp and IR) indicating the presence of two methoxyl groups in ring E and two such in ring A Hence, the diaryl system must contain the remaining three methoxyl groups which are placed by analogy and ^{1}H NMR spectral data at the B-4, D-4‴ and D-6‴ positions (chalcone numbering) Consequently, the interflavonoid linkage 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 parenthesis]

Jeediflavanone was dehydrogenated [8–10] with iodine and potassium acetate in acetic acid to the corresponding, relatively more stable biflavone It has been designated SA5 and appeared as a bright yellow powder from acetone, $C_{30}H_{18}O_{11}$, mp > 300° The ^{1}H NMR spectrum of SA5 (**12**) in acetone-d_6 revealed the presence of two low field protons as well as five non-chelated D_2O exchangeable hydroxylic protons as in **6** On acetylation with sodium acetate and acetic anhydride, compound SA5 afforded a heptaacetate (**13**), $C_{44}H_{32}O_{18}$, mp 158–160° while with dimethyl sulphate and potassium carbonate in acetone it gave a heptamethyl ether (**14**), $C_{37}H_{32}O_{11}$, mp 172–174° Oxidation of SA5 heptamethyl ether with neutral permanganate gave only one mole of veratric acid (identified by mmp and IR) suggesting that one of the side-phenyls is involved in the biphenyl linkage

The chemical shift and multiplicity of the protons in the respective ^{1}H NMR spectra of jeediflavanone, its derivatives and compound SA5, its derivatives are as expected for the proposed structure of jeediflavanone (**6**) [see Experimental]



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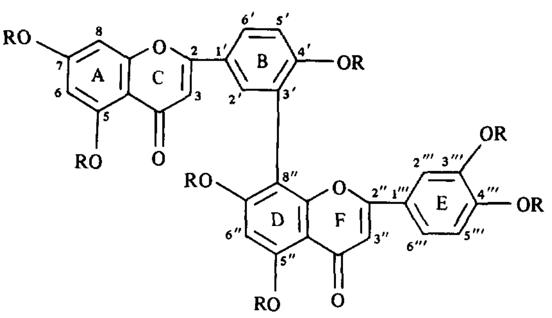
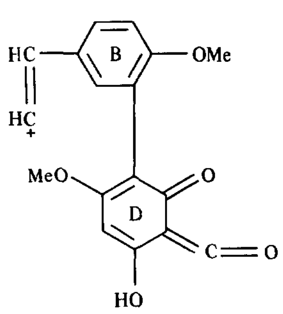


12 R = H
13 R = Ac
14 R = Me

Jeediflavanone pentamethyl ether (**8**) and SA5 heptamethyl ether (**14**) in their mass spectra displayed the molecular ions (M^+) at *m/z* 628 and 652 respectively The peak at *m/z* 163 [3,4-$(MeO)_2$–C_6H_3–CH=CH] arising from rings E and F in the pentamethyl ether (**8**) not only indicated that these rings do not carry the diaryl linkage but also revealed that the hydroxyl groups at the positions 3‴ and 4‴ in ring E are methylated Similarly in the heptamethyl ether **14**, two peaks at *m/z* 162 [3,4-$(MeO)_2$–C_6H_3–C=CH]$^+$ and *m/z* 165 [3,4-$(MeO)_2$–C_6H_3–C≡O^+] are present The peak at *m/z* 297 corresponding to the fragment **15** in the pentamethyl ether could arise after two retro-Diels–Alder fragmentations and this ion formed by the above path is important in suggesting the interflavonoid linkage There is another peak at *m/z* 298 corresponding to either of the ions **16** and **17** and these two are closely related to the fragment **15** Similarly in the heptamethyl ether, the two central fragments at *m/z* 310 and *m/z* 311 corresponding to the ions **18** and **19** are obtained Similar crucial fragments were already reported in morelloflavone heptamethyl ether [11] and (−)-succedaneaflavanone tetramethyl ether [12] Jeediflavanone pentamethyl ether and SA5 heptamethyl ether displayed the peaks at *m/z* 582 and *m/z* 606 respectively which are formed by the loss of 46 mass units These fragments can be formulated respectively as **20** and **21** in which the *ortho*-methoxyl groups to the diaryl linkage cyclise to a furan ring [13, 14] Perhaps the most significant feature is the formation of the two fragments **15** and **20** in the pentamethyl ether **8** and the two ions **18** and **21** in the heptamethyl ether **14** which clearly indicated that the interflavonoid linkage in the two compounds **8** and **14** is between rings B and D Similar fragments have already been reported in rhusflavanone [15, 16] and (±)-fukugetin heptamethyl ether [17] Overall, the mass spectral fragmentation of jeediflavanone pentamethyl ether exhibits a close similarity to that of 2,3-dihydroamentoflavone hexamethyl ether [18] and GB-2 [19, 20] Further, the MS fragmentation of SA5 heptamethyl ether showed a very close resemblance to that of amentoflavone hexamethyl ether [13]

In order to distinguish between the two positional isomers (B-3′-D-8″ or B-3′-D-6″) of SA5, the solvent-induced methoxy shift technique has been utilised Solvent induced shifts for the seven methoxyl groups of SA5 heptamethyl ether were studied for solutions con-



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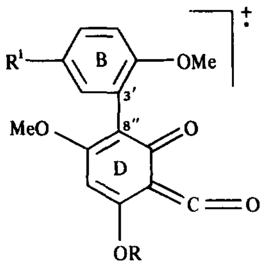
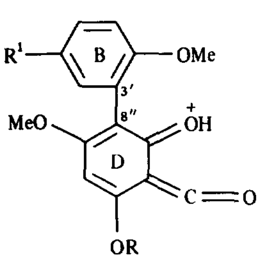


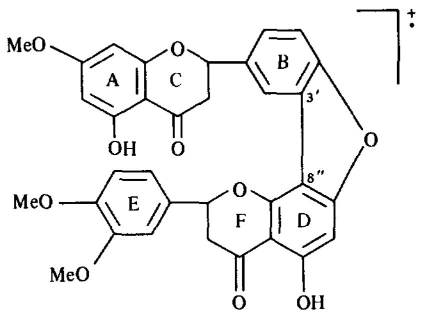
16 $R = H$, $R^1 = CH{=}CH_2$

18 $R = Me$, $R^1 = C{\equiv}CH$



17 $R = H$, $R^1 = CH{=}\overset{+}{C}H$

19 $R = Me$, $R^1 = C{\equiv}CH$



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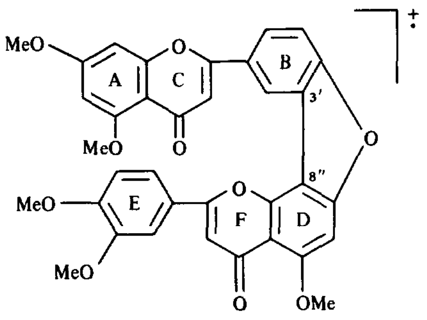

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taining increasing concentrations of perdeuteriobenzene in deuteriochloroform All the seven methoxy-signals were moved upfield (44, 49, 54, 55, 58, 61 and 68 Hz) as with cupressuflavone hexamethyl ether [21], amentoflavone hexamethyl ether [22] and GB-1 heptamethyl ether [20] indicating that every methoxyl group has at least one *ortho*-proton On the basis of this observation, the biphenyl linkage at the B-3′-D-8″ position was assigned to the SA5 heptamethyl ether (**14**) For a B-3′-D-6″ linkage, the D-5″ methoxy-group, with two well-defined *ortho*-substituents (ring B on one side and the carbonyl group on the other), should not undergo any appreciable solvent induced shift on addition of perdeuteriobenzene [23–32]

The above confirmation of the structure of SA5 (**12**) with regard to the diaryl linkage has thus given an unambiguous proof that the biflavonoid linkage in the parent compound, jeediflavanone, must be at the B-3′-D-8″ position and not at the B-3′-D-6″ position This is also in concurrence with the biflavanones already reported from this plant [1, 3, 4] From the foregoing chemical and spectroscopic evidence, structure **6** has been assigned for jeediflavanone with the interflavonoid linkage at the B-3′-D-8″ position

EXPERIMENTAL

General Mps are uncorr All the compounds were dried for carbon and hydrogen analysis at room temp or at 100°/0 2 mm for 6 hr as found suitable UV spectra were recorded in aldehyde-free EtOH All the IR spectra were taken in nujol ^1H NMR spectra were recorded with TMS as int standard Chemical shifts are expressed in δ values Silica gel-C (Acme synthetic chemicals, Bombay) was used for both analytical TLC (50 × 80 mm) as well as prep TLC (200 × 200 × 1 mm, 75 mg/chromatoplate) while silica gel (100–200 mesh) was utilised for CC TLC plates were visualised by exposing to iodine vapour and UV light

Extraction and isolation The raw nuts (5 kg) of *Semecarpus anacardium* L were secured from the Forest Department, Elamanchili, Andhra Pradesh, India. After removing the phenolic oil by percolation with hot *n*-hexane (10 syphonings), the defatted nut shells were dried under shade, powdered and were extracted with hot EtOH in a Soxhlet apparatus The reddish-brown EtOH extract was concd under red pres to a deep red viscous liquid (~ 200 ml) to which two litres of *n*-hexane were added when a red coloured gum separated out The *n*-hexane layer was decanted and the red gum was thoroughly washed with *n*-hexane (200 ml × 3) The residual gummy substance was adsorbed on small pieces of filter paper and dried under shade This material was successively fractionated, in a small Soxhlet into *n*-hexane, C_6H_6, Me_2CO and MeOH solubles The hexane fraction yielded a dark coloured residue and showed one spot on TLC (*n*-hexane–C_6H_6, 5 2). On fractional crystallization from MeOH, the residue gave sitosterol as colourless flakes, mp 134–135°, yield 200 mg. It afforded an acetate, mp 126–127° and a benzoate, mp 144–145° The residues from both benzene and methanol fractions did not show any clear spots on TLC chromatogram nor gave positive test for flavonoids. Hence further examination was not attempted

Acetone fraction The brown coloured fraction was concd under red pres to a reddish-brown viscous liquid (~ 160 ml) A satd soln of basic lead acetate in MeOH was added to the viscous liquid until no more ppt formed The pptd lead salt was filtered and decomposed with H_2S The filtrate was concd under red pres. when a dark coloured viscous liquid (~ 100 ml, Part A) was obtained The filtrate from the lead salt was also decomposed with H_2S and the filtrate after concn under vacuum gave a deep reddish-brown gum (~ 80 g, part B) which is under investigation The dark viscous liquid (Part A) showed four close running spots on TLC ($CHCl_3$–Me_2CO, 5 2) The brown residue was adsorbed on silica gel (250 g) and transferred over to a column of silica gel (500 g, 100–200 mesh) set with $CHCl_3$ The column was eluted successively with (A) $CHCl_3$, (B) $CHCl_3$–Me_2CO (7 2), Fraction FI, (C) $CHCl_3$–Me_2CO (3 1), Fraction FII, (D) $CHCl_3$–Me_2CO (5 2), (E) $CHCl_3$–Me_2CO (2 1) and finally Me_2CO When the column was run with the eluent D, a deep yellow compound was obtained It showed one major spot on TLC ($CHCl_3$–MeOH, 5 1) besides a large streak Hence the compound was separated by prep TLC using $CHCl_3$–MeOH (5 1) The compound so obtained still showed a minor impurity and hence it was filtered through a small column of silica gel with $CHCl_3$–Me_2CO (1 1) as the eluent On removal of solvent under vacuum, the column fractions, yielded a pale yellow compound, jeediflavanone, which was found to be pure on TLC Eluent E afforded an yellow compound upon concn under vacuum which showed a small tailing on TLC chromatoplate ($CHCl_3$–Me_2CO, 1 1) Hence it was removed through prep TLC using $CHCl_3$–Me_2CO (1 1) as the solvent for development It has been designated as compound X The experimental details of fractions FI and FII will be published elsewhere Since eluent A and the last eluent, Me_2CO, did not respond to the Mg–HCl test, further investigation was discontinued

Compound X It was a mixture of three compounds (**1**–**3**) which sintered at 146° and melted at 241°, yield 5 0 g TLC tests showed that the mixture was extremely complex and a direct separation seemed to be impossible Hence compound X (500 mg) in Me_2CO (20 ml) was methylated with excess CH_2N_2 (100 ml) Removal of the solvent left a residue which showed three spots R_f 0 65, 0 43 and 0 27, on TLC chromatogram in $CHCl_3$ and these were separated in pure form by prep TLC using $CHCl_3$ as the solvent for development These three biflavanone methyl ethers were found to be identical in all respects (mmp, TLC, UV, IR and ^1H NMR) with the methyl ethers of the three biflavanones (**1**–**3**) [1]

Jeediflavanone (**6**) It appeared as a pale yellow powder from Me_2CO, $C_{30}H_{22}O_{11}$, mp 285–287°, yield 850 mg It furnished a deep green ferric reaction, a pink colour with Mg–HCl and an orange colour with $NaBH_4$–HCl The compound is readily soluble in aq NaOH giving a deep orange–yellow soln UV λ_{max} nm 221, 286, 330; + NaOAc 221, 320, 336, + $AlCl_3$ 221, 318, 335, IR ν_{max} cm^{-1} 3500 (broad, OH), 3200 (OH), 1645, 1640 (chelated flavanone carbonyls), 1605, 1595 (aromatic), Found C, 64 28, H, 3 91, $C_{30}H_{22}O_{11}$ requires C, 64 52, H, 3 94%, ^1H NMR (270 MHz, acetone-d_6): δ2 74 [2H, *dd*, J = 4, 16 Hz, *cis*-protons, C-3, F-3″], 3 04 [2H, *m*, *trans*-protons, C-3, F-3″], 5 37 [2H, *dd*, J = 4, 12 Hz, C-2, F-2″], 6 12 [1H, *d*, J = 2 Hz, A-6], 6 18 [1H, *d*, J = 2 Hz, A-8], 6 79–7 05 [4H, *m*, E-2‴,5‴,6‴, D-6″ or 8″], 7 16–7 38 [3H, *m*, B-2′,5′,6′], 7 11 (1H, *s*), 7 42 (2H, *s*), 7 47 (2H, *s*) [non-chelated D_2O exchangeable hydroxylic protons A-7, B-4′, D-7″, E-3‴,4‴], 14 18 [1H, *s*, chelated hydroxylic proton, A-5], 14 27 [1H, *s*, chelated hydroxylic proton, D-5″]

Methylation of jeediflavanone (**6**) *with diazomethane* Jeediflavanone (250 mg) in Me_2CO (10 ml) was added to an ethereal soln of CH_2N_2 (70 ml) The solvent was evaporated and the residue was separated into tetra- and pentamethyl ethers by prep TLC using $CHCl_3$–Me_2CO (11 4)

Jeediflavanone tetramethyl ether (**7**) Yellow crystals from $CHCl_3$–MeOH, $C_{34}H_{30}O_{11}$, mp 213–214°, yield 140 mg, UV λ_{max} nm 220, 284, 323, + NaOAc 220, 284, 322, + $AlCl_3$ 220, 315, 328, IR ν_{max} cm^{-1} 3500 (broad, OH), 3150 (OH), 2830 (OMe), 1650, 1640 (chelated flavanone carbonyls), 1600, 1590 (aromatic), Found C, 66 24, H, 4 85, OMe, 19 62, $C_{34}H_{30}O_{11}$ requires C, 66 45, H, 4 88, OMe, 19 71%, ^1H NMR (80 MHz, $CDCl_3$): δ2 76 [2H, *dd*, J = 4, 16 Hz, *cis*-protons, C-3, F-3″], 3 12 [2H, *m*, *trans*-protons, C-3, F-3″], 5 44 [2H, *br d*, J = 11 Hz, C-2, F-2″], 6 16 [1H, *d*, J = 2 Hz, A-6], 6 22 [1H, *d*, J = 2 Hz, A-8], 6 55 [1H, *s*, D-6″ or D-8″], 6 88–7 09 [3H, *m*, E-2‴,5‴,6‴], 7 17–7 34 [3H, *m*, B-2′,5′,6′], 3 79 [(3H × 4), *s*, methoxyl groups, A-7, B-4′, D-7″, E-4‴], 7 45 [1H, *s*, non-chelated D_2O exchangeable hydroxylic proton, E-3‴], 14 14 [1H, *s*, chelated hydroxylic proton, A-5], 14 22 [1H, *s*, chelated hydroxylic proton, D-5″]

Jeediflavanone pentamethyl ether (**8**) Bright yellow crystals from $CHCl_3$–MeOH, $C_{35}H_{32}O_{11}$, mp 195–196°, yield 30 mg, UV λ_{max} nm 220, 283, 322, + NaOAc 220, 283, 320, + $AlCl_3$ 220, 316, 327, IR ν_{max} cm^{-1} 3500 (broad OH), 3150 (OH), 2830 (OCH_3), 1650, 1640 (chelated flavanone carbonyls), 1600, 1585 (aromatic), Found C, 66 52, H, 5 06, OMe, 23 98, $C_{35}H_{32}O_{11}$ requires C, 66 86, H, 5 09, OMe, 24 19%, ^1H NMR (80 MHz, $CDCl_3$): δ2 73 [2H, *dd*, J = 3, 17 Hz, *cis*-protons, C-3, F-3″], 3 10 [2H, *m*, *trans*-protons, C-3, F-3″], 5 46 [2H, *br d*, J = 10 Hz, C-2, F-2″], 6 14 [1H, *d*, J = 2 Hz, A-6], 6 20 [1H, *d*, J = 2 Hz, A-8], 6 57 [1H, *s*, D-6″ or D-8″], 6 86–7 10 [3H, *m*, E-2‴,5‴,6‴], 7 18–7 37 [3H, *m*, B-2′,5′,6′], 3 71 (3H, *s*), 3 75 (3H × 4, *s*) [methoxyl groups, A-7, B-4′, D-7″, E-3‴,4‴], 14 20 [1H, *s*, chelated hydroxylic proton, A-5], 14 30 [1H, *s*, chelated hydroxylic proton, D-5″], MS *m/z* (rel int) 628 [M]$^+$ (43 5), 613 [M – Me]$^+$ (32), 598 [M – 2 × Me]$^+$ (8 5), 582 [M – 46]$^+$ (7 5), 464 (10 5), 461 (11), 329 (11), 314 (6), 299 (5), 298 (10), 297 (27 5), 284 (4), 282 (11 5), 167 (80), 166 (30 5), 163 (100), 153 (10), 152 (7 5), 148 (6 5), 126 (5 4)

Jeediflavanone tetramethyl ether triacetate (**9**) Compound **7** (30 mg) was heated with Ac_2O (1 ml) and pyridine (1 ml) on a steam-bath for 4 hr The product was as a pale yellow powder, $C_{40}H_{36}O_{14}$, mp 168°, yield 20 mg, UV λ_{max} nm 221, 284, 325, IR ν_{max} cm^{-1} 2830 (OMe), 1740 (OAc), 1680, 1670 (flavanone carbonyls), 1600, 1585 (aromatic), Found C, 64 60, H, 4 82, OMe, 16 21, $C_{40}H_{36}O_{14}$ requires C, 64 86, H, 4 87, OMe, 16 36%, ^1H NMR (80 MHz, $CDCl_3$) δ2 72 [2H, *dd*, J = 4, 16 Hz, *cis*-protons, C-3, F-3″], 3 10 [2H, *m*, *trans*-protons, C-3, F-3″], 5 42 [2H, *dd*, J = 4, 12 Hz, C-2, F-2″], 6 14 [1H, *d*, J = 2 Hz, A-6], 6 20 [1H, *d*, J = 2 Hz, A-8], 6 58 [1H, *s*, D-6″ or D-8″], 6 90–7 09 [3H, *m*, E-2‴,5‴,6‴], 7 17–7 36 [3H, *m*, B-2′,5′,6′], 3 82 [(3H × 4), *s*, methoxyl groups, A-7, B-4′, D-7″, E-4‴], 2 24 (3H, *s*), 2 27 (3H, *s*), 2 29 (3H, *s*) [acetoxyl groups, A-5, D-5″, E-3‴]

Jeediflavanone heptaacetate (**10**) Light yellow crystals from $CHCl_3$ and Me_2CO mixture, $C_{44}H_{36}O_{18}$ mp 154–156°, yield 25 mg, UV λ_{max} nm 220, 282, 324, IR ν_{max} cm^{-1} 1750, 1740 (OAc), 1685, 1675 (flavanone carbonyls), 1595, 1585 (aromatic), Found C, 61 64, H, 4 25, $C_{44}H_{36}O_{18}$ requires C, 61 97, H, 4 23%, ^1H NMR (80 MHz, $CDCl_3$) δ2 77 [2H, *dd*, J = 4, 16 Hz, *cis*-protons, C-3, F-3″], 3 13 [2H, *m*, *trans*-protons, C-3, F-3″], 5 40 [2H, *dd*, J = 4, 12 Hz, C-2, F-2″], 6 14 [1H, *d*, J = 2 Hz, A-6], 6 20 [1H, *d*, J = 2 Hz, A-8], 6 61 [1H, *s*, D-6″ or D-8″], 6 88–7 07 [3H, *m*, E-2‴,5‴,6‴], 7 19–7 38 [3H, *m*, B-2′,5′,6′], 2 22 (3H × 2, *s*), 2 24 (3H, *s*), 2 25 (3H, *s*), 2 26 (3H × 2, *s*), 2 28 (3H, *s*) [acetoxyl groups, A-5,7, B-4′, D-5″,7″, E-3‴,4‴]

Bichalcone heptamethyl ether (**11**) A mixture consisting of jeediflavanone (180 mg), freshly ignited K_2CO_3 (2 0 g) and Me_2SO_4 (1 5 ml) was refluxed in dry acetone (50 ml) on a water bath for about 20 hr and worked up as usual Compound **11** appeared as a bright yellow powder from $CHCl_3$, $C_{37}H_{36}O_{11}$, mp 242–244°, yield 130 mg It gave a brown ferric reaction, a red ppt with $SbCl_3$ in CCl_4 and is readily soluble in aq NaOH giving an orange solution, UV λ_{max} nm 224, 376, + $AlCl_3$ 223, 428, + NaOAc 224, 378, IR ν_{max} cm^{-1} 3450 (broad, OH), 2830 (OMe), 1630, 1625 (chalcone carbonyls), 1595, 1585 (aromatic), Found C, 67 60, H, 5 45, OCH_3, 32 76, $C_{37}H_{36}O_{11}$ requires C, 67 69, H, 5 49, OMe, 33 09 %, ^{1}H NMR (80 MHz, $CDCl_3$) δ6 24 [1H, *d*, J = 2 Hz, A-5′], 6 32 [1H, *d*, J = 2 Hz, A-3′], 6 52 [2H, *d*, J = 16 Hz, C-8, F-8″], 6 63 [1H, *s*, D-5‴ or D-3‴], 6 81–7 02 [3H, *m*, E-2″,5″,6″], 7 16–7 35 [3H, *m*, B-2,5,6], 7 76 [2H, *d*, J = 16 Hz, C-7, F-7″], 3 75 (3H, *s*), 3 80 (3H × 2, *s*), 3 84 (3H × 4, *s*) [methoxyl groups, A-4′,6′, B-4, D-4‴,6‴, E-3″,4″], 14 19 [1H, *s*, chelated hydroxylic proton, A-2′], 14 32 [1H, *s*, chelated hydroxylic proton, D-2‴], MS *m/z* (rel int) 656 $[M]^+$ (45), 641 $[M-Me]^+$ (12), 626 $[M-2\times Me]^+$ (22), 610 $[M-46]^+$ (14), 493 (11 5), 475 (11), 343 (10 5), 313 (8), 312 (31), 311 (5 5), 191 (68 2), 181 (100), 180 (44 5), 165 (51 6), 163 (7 3), 162 (8 7), 153 (10 6), 152 (9 2), 151 (6 4), 134 (15 2), 126 (7 5), 124 (4 5), 120 (12), 107 (6 4)

Compound SA5 (**12**) A pale yellow powder from Me_2CO, $C_{30}H_{18}O_{11}$, mp > 300°, yield 175 mg The compound gave a greenish-violet ferric reaction a pinkish red colour with Mg–HCl, and is soluble in aq NaOH giving an orange–yellow soln UV λ_{max} nm 256, 298, 376, + $AlCl_3$ 271, 322, 433, + NaOAc 258, 274, 324, 426, IR ν_{max} cm^{-1} 3500 (broad, OH), 3200 (OH), 1635, 1630 (chelated flavone carbonyls), 1600, 1590 (aromatic), Found C, 64 82, H, 3 22, $C_{30}H_{18}O_{11}$ requires C, 64 98, 3 25 %, ^{1}H NMR (80 MHz, Me_2CO-d_6) δ6 12 [1H, *d*, J = 2 Hz, A-6], 6 18 [1H, *d*, J = 2 Hz, A-8], 6 50 [2H, *s*, C-3, F-3″], 6 56 [1H, *s*, D-6″ or D-8″], 6 90–7 13 [3H, *m*, E-2‴,5‴,6‴], 7 26–7 48 [3H, *m*, B-2′,5′,6′], 7 32 (1H, *s*), 7 52 (2H, *s*), 7 59 (2H, *s*) [non-chelated D_2O exchangeable hydroxylic protons, A-7, B-4′, D-7″, E-3‴,4‴], 14 24 [1H, *s*, chelated hydroxylic proton, A-5], 14 35 [1H, *s*, chelated hydroxylic proton, D-5″]

SA5 heptaacetate (**13**) Bright yellow crystals from $CHCl_3$ and MeOH mixture, $C_{44}H_{32}O_{18}$, mp 158–160°, yield 20 mg, UV λ_{max} nm 252, 293, 369, IR ν_{max} cm^{-1} 1750, 1735 (OAc), 1680, 1670 (flavone carbonyls), 1600, 1585 (aromatic) Found C, 61 84, H, 3 75, $C_{44}H_{32}O_{18}$ requires C, 62 26, H, 3 77 %, ^{1}H NMR (80 MHz, $CDCl_3$) δ6 14 [1H, *d*, J = 2 Hz, A-6], 6 22 [1H, *d*, J = 2 Hz, A-8], 6 49 [2H, *s*, C-3, F-3″], 6 54 [1H, *s*, D-6″ or D-8″], 6 91–7 16 [3H, *m*, E-2‴,5‴,6‴], 7 31–7 50 [3H, *m*, B-2′,5′,6′], 2 22 (3H, *s*), 2 24 (3H × 2, *s*), 2 28 (3H × 2, *s*), 2 32 (3H × 2, *s*) [acetoxyl groups, A-5,7, B-4′, D-5″,7″, E-3‴,4‴]

SA5 heptamethyl ether (**14**) Yellow crystals from $CHCl_3$–MeOH, $C_{37}H_{32}O_{11}$, mp 172–174°, yield 80 mg, UV λ_{max} nm 249, 295, 371, IR ν_{max} cm^{-1} 2830 (OMe), 1680, 1675 (flavone carbonyls), 1600, 1590 (aromatic), Found C, 67 94, H, 4 86, OMe, 32 96, $C_{37}H_{32}O_{11}$ requires C, 68 11, H, 4 91, OMe, 33 29 %, ^{1}H NMR (80 MHz, $CDCl_3$): δ6 16 [1H, *d*, J = 2 Hz, A-6], 6 22 [1H, *d*, J = 2 Hz, A-8], 6 52 [2H, *s*, C-3, F-3″], 6 57 [1H, *s*, D-6″ or D-8″], 6 82–7 08 [3H, *m*, E-2‴,5‴,6‴], 7 21–7 44 [3H, *m*, B-2′,5′,6′], 3 71 (3H × 2, *s*), 3 76 (3H × 2, *s*), 3 82 (3H × 2, *s*), 3 90 (3H, *s*), [methoxyl groups, A-5,7, B-4′, D-5″,7″, E-3‴,4‴], MS *m/z* (rel int) 652 $[M]^+$ (60 4), 637 $[M-Me]^+$ (28), 622 $[M-2\times Me]^+$ (9), 606 $[M-46]^+$ (8 5), 576 (5 6), 490 (12), 472 (11 25), 341 (8), 311 (6), 310 (30 5), 181 (100), 180 (42 5), 165 (68 6), 162 (75 5), 135 (8), 134 (49), 132 (7 5), 126 (7)

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