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Note

A new isoflavone from *Dalbergia rubiginosa* (Roxb)

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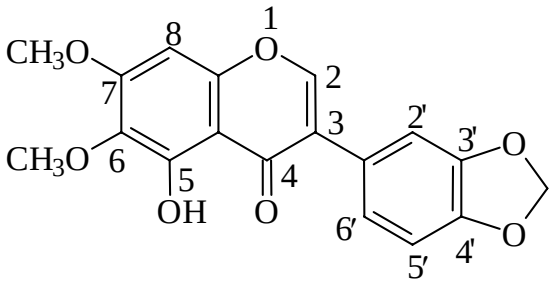
A new isoflavone, characterized as 5-hydroxy-6,7-dimethoxy-3′,4′-methylenedioxyisoflavone **1** by chemical and spectral studies, along with nitiducarpin, β-sitosterol and oleanolic acid, has been isolated from the roots of *Dalbergia rubiginosa*.

Keywords: Isoflavone, *Dalbergia rubiginosa*, Roxb, nitiducarpin, β-sitosterol, oleanolic acid

IPC: Int.Cl.[8] A 61 K

Dalbergia is a large genus (Fam: Leguminosae) and nearly 35 members of this genus are available in India[1]. Species of this genus are reported to have anti-biotic, anti-inflammatory and anti-arthritic pro-perties[2,3]. Earlier chemical investigations of new *Dalbergia* species carried out in our laboratory resulted in the isolation of new isoflavones, iso-flavone glycosides, rotenoid and dalbergiquinone[4-10]. Present work deals with the chemical investigation of *Dalbergia rubiginosa*, a new species.

Herein we report the isolation of a new isoflavone from the acetone extract of the roots of *D. rubiginosa* and its characterization as 5-hydroxy-6,7-dimethoxy-3′,4′-methylenedioxyisoflavone **1**.



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The air-dried roots of *D. rubiginosa* were exhaustively extracted with pet. ether (60-80°C) and acetone. Examination of the pet. ether (60-80°C) extract revealed the presence of nitiducarpin, a pterocarpan earlier reported from other *Dalbergia* species[11] and β-sitosterol. Acetone extract when subjected to column chromatography over silica gel resulted in the isolation of oleanolic acid and a new compound from one of the fractions collected.

Results and Discussion

The compound recrystallized from methanol as colourless crystals, m.p. 182°C, gave positive Wolfrom test for isoflavones. The compound also responded to neutral ferric chloride test and Labat test showing the presence of chelated hydroxyl and methylenedioxy groups. The UV and IR spectral data also revealed the nature of the compound as an isoflavone[12].

The ^{1}H NMR spectra displayed a prominent peak at δ 5.99 integrating for two protons indicating the presence of methylenedioxy group. The singlet at δ 12.70 integrating to one proton was due to hydroxyl group at C-5 position. The two singlets at δ 3.92 and 3.96 integrating to a total of six protons revealed the presence of two methoxy groups in the molecule.

The one proton singlet at δ 7.89 was assigned to C-2 proton and the upfield singlet at δ 6.47 was assigned to A-ring proton. The presence of only one A-ring proton suggested that the remaining three positions should be substituted.

The multiplet in the region δ 6.89-7.04 integrating for three protons, which could be due to B-ring protons, indicated that two positions in B-ring are substituted. The hydroxyl group is at C-5 position. Regarding the positions of two methoxy and one methylenedioxy group, the two methoxy groups may be in A-ring and methylenedioxy in B-ring or vice versa.

In the EIMS of the compound, the m/z value at 146 due to RDA fragmentation indicated that the methylenedioxy group is in B-ring, subsequently, the two methoxy groups in A-ring. The three proton multiplet in the region δ 6.89-7.04 appeared as ABX splitting pattern, which is characteristic of H-2',5',6' protons in the B-ring[13] and hence the methylenedioxy group was placed at 3',4' positions.

Regarding the position of methoxy groups in A-ring, they may be at C-6 and C-7 or C-7 and C-8 positions and in either case the remaining proton will give a singlet in the same region δ 6.30-6.50. In ^{13}C NMR spectrum of isoflavones[14], the unsubstituted C-8 carbon atom exhibited an upfield signal around δ 93 and the unsubstituted C-6 carbon atom showed a downfield signal around δ 104 to 108.

The presence of an upfield signal at δ 90.76 in the ^{13}C NMR spectrum of the compound corresponded to the unsubstituted C-8 carbon and hence the methoxy group was placed at C-6. Further, this was confirmed by the positive Gibbs test and the singlet at δ 6.47 was assigned to C-8 proton.

The ^{13}C NMR spectra of the compound exhibited 17 signals which corresponded to 18 carbon atoms in the molecule. It further revealed the presence of a carbonyl carbon at δ 182, one methylenedioxy carbon at δ 101.69 and two methoxy carbons at δ 61.28, 56.73. The 3' and 4' carbons of methylenedioxy group exhibited same chemical shift value at δ 145. The DEPT 45 ^{13}C NMR spectrum exhibited 8 signals accounting for the presence of two methoxy carbons, one methylenedioxy carbon and five methine carbons.

The EIMS spectrum of the compound exhibited the molecular ion peak at m/z 342 which corresponded to the molecular formula, $C_{18}H_{14}O_7$. The compound formed a monomethyl ether derivative with dimethyl sulphate. It exhibited a molecular ion peak at m/z 356 and compared with an authentic sample of dalspinin dimethyl ether[4]. All these data led to the structure of the compound as 5-hydroxy-6,7-dimethoxy-3′,4′-methylenedioxyisoflavone **1**, a new isoflavone, not reported earlier from natural source.

Experimental Section

General. Melting points were determined in sulphuric acid-bath and are uncorrected. UV spectra were recorded using Shimadzu UV 160 spectrometer; IR spectra on a Bruker IFS 66V FT-IR spectrometer; ^1H NMR spectra in $CDCl_3$ on a Jeol GSX 400 MHz spectrometer with TMS as an internal standard; ^{13}C NMR spectra in $CDCl_3$ at 300 MHz using TMS as an internal reference; and EIMS on a VG7070H instrument.

Collection of plant material

D. rubiginosa was collected during March 2001, from the dry slopes of Pachai Hills near Uppiliapuram, Tamil Nadu. The species was identified by Fr. Dr K M Matthew S.J., Herbarium Director, The Rapinat Herbarium, Trichy.

Extraction and Isolation

The roots of *D. rubiginosa* were cut into small pieces and air-dried. The air-dried chips (1.8 kg) were then extracted successively under reflux with pet. ether (60-80°C) and acetone. The acetone extract was concentrated *in vacuo* and was chromatographed over a column of silica gel (Qualigens 60-120 mesh) and eluted with pet. ether (60-80°C), benzene, chloroform and methanol in different proportions. The compound was obtained from benzene-chloroform (50:50) mixture.

5-Hydroxy-6,7-dimethoxy-3′,4′-methylenedioxy-isoflavone 1: Colourless crystalline solid, m.p 182°C; EIMS: m/z 342 (M^+), 341, 327, 146; UV (MeOH): 268, 300 nm, +NaOAc, 269, 300 nm, +$AlCl_3$, 274, 300 nm, +$AlCl_3$ and HCl, 276.2, 300 nm; IR (KBr): 1640 cm^{-1} (chromone carbonyl); ^1H NMR ($CDCl_3$): δ 5.99 (2H, s, O-CH_2-O), 7.89 (1H, s, H-2), 3.92 and 3.96 (6H, 2s, 2 × OCH_3), 6.47 (1H, s, H-8), 6.89-7.04 (3H, m, H-2′,5′,6′), 12.70 (1H, s, HO-C-5); ^{13}C NMR ($CDCl_3$): δ 182.0 (C=O, C-4), 159.36 (C-7), 153.92 (C-2), 153.23 (C-5), 148.21(C-9), 145.0 (C-3'&C-4'), 133.0 (C-6), 124.0 (C-3), 122.86 (C-6'), 121.0 (C-1'), 110.01 (C-2'), 108.93 (C-5'), 107.0 (C-10), 101.69 (O-CH_2-O), 90.76 (C-8), 61.28 (OCH_3), 56.76 (OCH_3).

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