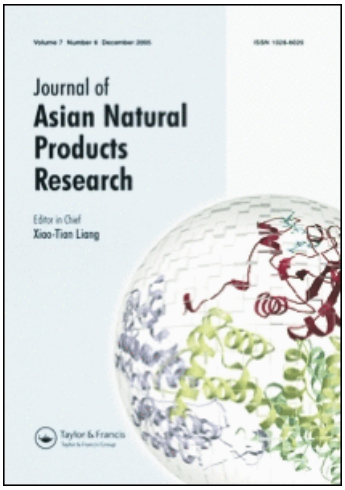

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R. N. Yadava[a]; P. K. Agrawal[a]
[a] Natural Products Laboratory, Department of Chemistry, Dr. H.S. Gour University, Sagar, MP, India

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A NEW FLAVONOID GLYCOSIDE: 5,7,4′-TRIHYDROXY-6,3′,5′-TRIMETHOXY-FLAVONE 7-*O*-α-L-ARABINOPYRANOSYL-(1 → 6)-*O*-β-D-GLUCOPYRANOSIDE FROM THE ROOTS OF *MIMOSA RUBICAULIS*

R.N. YADAVA* and P.K. AGRAWAL

Natural Products Laboratory, Department of Chemistry,
Dr. H.S. Gour University, Sagar-470003 (MP), India

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A new flavonoid glycoside (**1**) was isolated from the roots of *Mimosa rubicaulis*, its structure was elucidated as 5,7,4′-trihydroxy-6,3′,5′-trimethoxy-flavone-7-*O*-α-L-arabinopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside by chemical degradation and spectral analysis.

Keywords: *Mimosa rubicaulis*, Leguminosae, 5,7,4′-trihdroxy-6,3,5′-trimethoxy-flavone-7-*O*-α-L-arabinopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside

INTRODUCTION

Mimosa rubicaulis (Leguminosae) [1-3] commonly known as Shiahkanta in Hindi is distributed throughout India. The leaves of this plant are used for the treatment of piles. The crushed leaves are reported to be useful for burns. The powder form of its roots are useful for the treatment of vomiting. Since no systematic phytochemical investigations have been done on this plant and because of its important therapeutic values, we have taken this plant for the present investigation.

In this paper we report the isolation and characterization of a new flavonoid glycoside from the roots of *Mimosa rubicaulis*.

* Corresponding author. Tel.: 07582-26465. Fax: 07582-23236.

RESULTS AND DISCUSSION

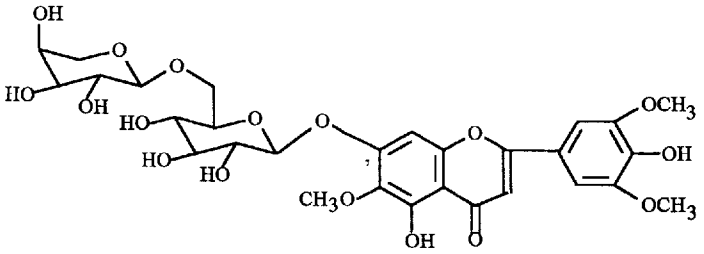
The acetone soluble fraction yielded compound **1**, which was crystallized as light yellow needles, m.p. 210 212°C. A molecular formula of $C_{29}H_{34}O_{17}$ for compound **1** was established from its EIMS ($M^+ = 654$) and elemental analysis. It was recognized as a flavonoid glycoside from positive tests with Molisch and Shinoda reagent [4]. The UV spectrum showed characteristics of flavone chromophore. A bathochromic shift of 44 nm in band I with $AlCl_3$ (in MeOH) and a bathochromic shift of 48 nm in band I with NaOMe (in MeOH) confirmed the presence of free hydroxyl groups at C-5 and C-4′ respectively [5,6]. Its IR spectrum showed absorptions at ν_{max} 3505–3485 (OH), 2950 (CH), 2868 (C=C), 1130–1015 (*O*-glycoside linkage), and 825 cm^{-1}. The ^1H NMR spectrum showed a two-proton singlet at δ 7.34 (H-2′ and H-6′) indicating the presence of a symmetrical substitution in ring B. The highfield proton singlets at δ 6.68 and 6.58 were assigned to H-8 and H-3 while the signals at δ 3.70, 3.78 and 3.86 showed the presence of three methoxyl groups at C-6, C-3′ and C-5′. A D_2O exchangeable signal at δ 13.05 indicated the presence of a hydrogen bonded hydroxyl group at C-5. A base peak at *m/z* 360 in the EIMS corresponded to the aglycone fragment, while an intense peak at *m/z* 345 (74.2) by the loss of a methyl radical confirmed the location of 6-OMe rather than 8′-OMe [7]. Acid hydrolysis of compound **1** yielded arabinose, glucose and yellow needles of the aglycone **2**, m.p. 225–226°C, [M$^+$] *m/z* 360, $C_{18}H_{16}O_8$. It was characterized as 5,7,4′-trihydroxy-6,3′,5′-trimethoxy-flavone by comparison of its spectral data with that reported in literature [8].

Enzymatic hydrolysis of compound **1** with Takadiastase yielded L-arabinose and a proaglycone 5,7,4′-trihydroxy-6,3′,5′-trimethoxy-flavone 7-*O*-β-D-glucopyranoside, $C_{27}H_{16}O_{13}$, m.p. 202–203°C. Further hydrolysis with almond emulsion yielded D-glucose and the aglycone **2**. The fact that the two anomeric proton signals, in the ^1H NMR spectra appeared at δ 4.79 ($J = 10.5$ Hz) and 4.96 ($J = 6.7$ Hz) suggested that L-arabinose was attached to D-glucose through α-linkage and D-glucose was linked with the aglycone through β-linkage. The ^{13}C NMR spectrum of compound **1** revealed the presence of 29 carbon atoms. The carbon signals of the sugar moiety were identical with those reported in the literature [9].

Permethylation of compound **1** followed by acid hydrolysis afforded compound **3**, $C_{20}H_{20}O_8$, m.p. 193°C. Its UV spectrum showed a bathochromic shift of 40 nm in band I with NaOAc indicating the presence of a C-7 OH. Based on spectral analysis it was determined as

7-hydroxy-5,6,3′,4′,5′-pentamethoxy-flavone. Thus the sugar moiety of compound **1** should be linked at C-7.

On the basis of the above evidences, compound **1** was established as 5,7,4′-trihydroxy-6,3′,5′-trimethoxy-flavone-7-*O*-α-L-arabinopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside.



EXPERIMENTAL SECTION

General experimental procedure Melting points were determined on a Richert microscope hot stage apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer (FTIR) and mass spectra on a Jeol-D-300. ^{13}C NMR and ^{1}H NMR spectra were recorded on a Bruker 300 MHz using TMS as internal reference.

Plant material The roots of *Mimosa rubicaulis* were collected locally around Sagar region and was taxonomically identified by the Department of Botany, Dr. H.S. Gour University, Sagar (MP) and the voucher specimen (No. 208) was deposited in room No. 38 of this university.

Extraction and isolation Air dried and powdered roots (3.5 kg) of *Mimosa rubicaulis* were thoroughly extracted with 95% EtOH in a Soxhlet apparatus. The extract was concentrated under reduced pressure and was successively partitioned with *n*-hexane, acetone, chloroform and ethyl acetate. The acetone fraction was subjected to column chromatography and eluted with acetone : chloroform (7 : 3) to yield compound **1**, light yellow needles (58 mg), m.p. 210–212°C [M^+] *m/z* 654; anal. C 52.23%, H 5.18%; calcd. for $C_{29}H_{34}O_{17}$, C 52.21%, H 5.19%. IR (KBr) ν_{max} 3505, 3435, 2950, 2868, 1650, 1615, 1525, 1475, 1130, 1015, and 825 cm^{-1}. UV (MeOH) λ_{max} (log ε) 241 (sh), 275, 345 nm; λ_{max} ($AlCl_3$) 282, 306 (sh), 383, 389 nm (sh); λ_{max} ($AlCl_3$ + HCl) 253 (sh), 285, 303 (sh), 374 nm; λ_{max} (NaOAc) 278, 319, 382 (sh), 406 nm; λ_{max} (NaOAc + H_3BO_3) 278, 352, 383 nm (sh); λ_{max} (NaOMe) 265, 278 (sh), 326 (sh), 383 (sh), 393 nm. ^{1}N-NMR signals (300 MHz $CDCl_3$) at δ 13.05 (br, s, 5-OH, exchanges with D_2O), δ 7.34

(2H, s, H-2′ and H-6′), δ 6.68 (1H, s, H-8), δ 6.58 (1H, s, H-3), δ 3.70 (3H, s, 6-OMe), δ 3.75 (3H, s, 3′-OMe), δ 3.86 (3H, s, 5′-OMe), δ 4.79 (d, $J = 10.5$ Hz, H-1″), δ 4.96 (d, $J = 6.7$ Hz, H-1‴) anomeric protons. ^{13}C NMR (75 MHz in DMSO-d_6) δ 164.60 (C-2), 103.20 (C-3), 181.09 (C-4), 153.04 (C-5), 130.90 (C-6), 121.40 (C-1′), 105.20 (C-2′), 147.02 (C-3′), 140.01 (C-4′), 147.90 (C-5′), 105.20 (C-6′), 101.90 (C-1″), 74.85 (C-2″), 78.25 (C-3″), 72.20 (C-4″), 77.30 (C-5″), 70.01 (C-6″); 106.01 (C-1‴), 72.00 (C-2‴), 74.50 (C-3‴), 68.90 (C-4‴), 66.20 (C-5‴).

Acid hydrolysis of compound **1**. The compound **1** was refluxed with 10% HCl for 3 h at 100°C. On cooling the aglycone **2** was crystallised from $CHCl_3$, m.p. 225–226°C; EIMS *m/z* [M^+] 360; anal. C 60.02%, H 4.43%; calcd. for $C_{18}H_{16}O_8$ C 60.00%, H 4.44%. The aglycone was identified as 5,7,4′-trihydroxy-6,3′,5′-trimethoxy-flavone by comparison of its spectral data.

The aqueous hydrolysate was neutralised with $BaCO_3$ and subjected to co-paper chromatography with authentic sugars using *n*-BuOH : HOAc : H_2O (4 : 1 : 5) as solvent. The sugars were identified by their Rf values (arabinose Rf 0.23 and glucose Rf 0.19) [10].

Enzymatic hydrolysis of compound **1**. Compound **1** on enzymatic hydrolysis with Takadiastase yielded a proaglycone and L-arabinose indicating that L-arabinose was linked to glucose through α-linkage, the proaglycone on further hydrolysis with enzyme almond emulsin yielded D-glucose and aglycone confirming the presence of β-linkage between D-glucose and aglycone [11].

Permethylation and hydrolysis of compound **1**. Compound **1** (25 mg) was treated with CH_3I (1 ml) and Ag_2O (35 mg) in DMF (5 ml) at room temperature for 48 h. The reaction mixture was concentrated *in vacuo* and hydrolysed by 20% ethanolic H_2SO_4 to give aglycone and methylated sugars 2,3,4-tri-*O*-methyl arabinose and 2,3,4-tri-*O*-methyl glucose separated by preparative TLC on silica gel (C_6H_5-CH_3 : MeOH 5 : 2).

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