

A Novel Flavone Glycoside From the Stems of *Dalbergia Sympathetica*

R.N. YADAVA* and ANILA ROY

Natural Products Laboratory

Department of Chemistry, Dr. H.S. Gour University,

Sagar-470 003, India

A novel flavone glycoside isolated from the stems of *Dalbergia sympathetica* and its structure was identified as 5,7-dihydroxy-4'-methoxy flavone-5-O- α -L-rhamnopyranosyl (1 \rightarrow 6)-O- β -D-galactopyranoside by various chemical reactions and spectral analysis.

INTRODUCTION

*Dalbergia Sympathetica*¹⁻³ belongs to Leguminosae family which is found almost throughout India. Its leaves are used as an alternative. A paste made from the bark is used as an application for pimples. In the present paper we report the isolation and structural elucidation of a novel flavone glycoside from the stems of this plant.

RESULTS AND DISCUSSION

The chloroform soluble fraction of the ethanolic extract of the stems of *D. sympathetica* afforded a novel compound (I). It was analysed for m.f. C₂₈H₃₁O₁₃, m.p. 264–265°C and [M]⁺ 575. It gave positive response to Molisch test for glycosidic nature and Shinoda test⁴ for its flavonoid nature. A bathochromic shift of 28 nm in bond I with NaOAc (relative to MeOH) suggests the presence of free hydroxy group at C-7 position⁵ in ring A and the absence of a bathochromic shift with AlCl₃ suggests the presence of blocked hydroxy group at C-5 position in ring A. Its IR spectrum showed absorption bands at 3443 (—OH), 2970 (—CH), 2875 (—OCH₃), 1625 (>C=O).

The compound I on acid hydrolysis with 7% ethanolic H₂SO₄ yielded an aglycone (II), m.f. C₁₆H₁₂O₅, m.p. 276°C and [M]⁺ 284 and sugars were identified as L-rhamnose (R_f 0.35) and D-galactose (R_f 0.15) (by Co-PC). The aglycone (II) was identified as 5,7-dihydroxy-4'-methoxy flavone by its spectral analysis (see experimental).

The compound I on acetylation with Ac₂O/pyridine yielded a hepta-acetyl derivative of the glycoside (III), m.f. C₄₂H₄₅O₂₀, m.p. 194–195°C and [M]⁺ 869 (EIMS). ¹H-NMR spectrum of compound III showed a three-proton singlet at δ 3.04 due to —OCH₃ group and three singlets were observed at δ 6.68, 6.82,

7.43 each one proton intensity due to H-3, H-6 and H-8 respectively. Two doublets observed at δ 5.31 and δ 4.42 each one-proton intensity were assigned for anomeric proton of galactose and rhamnose, and another doublet at δ 1.04 was due to the rhamnose methyl group.

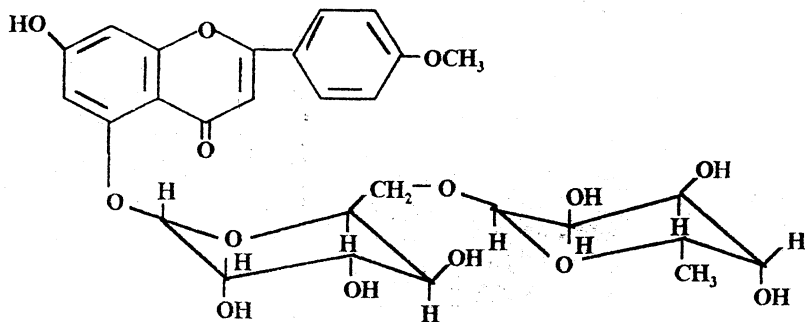
The EIMS peak at m/z 284 corresponded for aglycone fragment. A fragment at m/z 152 in the retro-Diels Alder fragmentation suggested the presence of two hydroxyl groups in ring A and another fragment at m/z 132 suggesting the presence of one methoxy group in ring B.

The position of the sugar residue in compound I was established by permethylation⁶ of I followed by acid hydrolysis yielding 5-hydroxy-7,4'-dimethoxy flavone and 2,3,4-tri-O-methyl-D-galactose, 2,3,4-tri-O-methyl-L-rhamnose according to Petek⁷, showing the C-5 position of the aglycone involved in glycosilation.

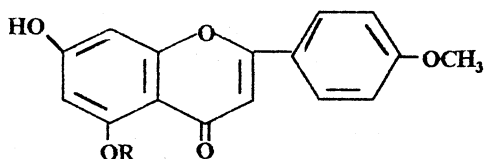
Periodate oxidation⁸ of compound I consumed 3.02 moles of periodate with the liberation of 1.18 moles of formic acid confirming that the presence of both the sugars were in pyranose form.

Quantitative estimation of sugars in the glycoside done by Somogyis procedure⁹ showed the presence of both the sugars in equimolar ratio (1 : 1).

Enzymatic hydrolysis of the compound (I) by Takadiastase liberated L-rhamnose (by Co-PC, R_f 0.35) confirming α -linkage between L-rhamnose and D-galactose and on further hydrolysis by almond emulsion, D-galactose (by



I



II

Co-PC, R_f 0.15) was observed, confirming β -linkage between D-galactose and aglycone.

On the basis of all the above evidences the structure of the compound I was identified as 5,7-dihydroxy-4'-methoxy flavone-5-O- α -L-rhamnopyranosyl (1 \rightarrow 6)-O- β -D-galactopyranoside.

EXPERIMENTAL

Plant Material: The stems of *Dalbergia sympathetica* were collected from M/s United Chemicals and Allied Products, Calcutta and taxonomically authenticated by the Department of Botany, Dr. H.S. Gour University, Sagar (M.P.).

Extraction and Isolation: The air-dried and powdered stems of *Dalbergia sympathetica* were extracted with 95% EtOH in a Soxhlet extractor. The total ethanolic extract was concentrated under reduced pressure to yield yellow viscous mass, which was successively extracted with petroleum ether (60–80°C), benzene, chloroform, ethylacetate, acetone and methanol. The concentrated chloroform soluble fraction when chromatographed on a silica-gel 'G' column eluting with EtOH-MeOH (8 : 4) gave compound I, crystallised from MeOH as yellow crystals, m.p. 264–265°C, m.f. $C_{28}H_{31}O_{13}$ and $[M]^+$ 575 (EIMS) (found: C, 58.45%; H, 5.37%; calcd. for $C_{28}H_{31}O_{13}$: C, 58.43%; H, 5.39%). IR (KBr) $_{max}$ 3443, 2970, 2875, 1625, 1524, 1210, 1145, 820 cm^{-1} . UV λ_{max} (+MeOH) 253, 274, 283, 323; (+NaOAc): 263, 277, 288, 341, 351; (+AlCl₃) 260, 271, 286, 325; (+AlCl₃/HCl) 259, 270, 286, 325 nm; EIMS $[M]^+$ 575, $[M]^+$, m/z 504, 284, 256, 341, 152, 153, 132, 124, 117. On acetylation of the glycoside with Ac₂O/pyridine yielded hepta acetyl derivative of glycoside (III) m.p. 194–195°C, m.f. $C_{42}H_{45}O_{20}$, and $[M]^+$ 869 (EIMS) (found: C, 57.96%; H, 5.19%; calcd. for $C_{42}H_{45}O_{20}$: C, 57.99%; H, 5.17%). ¹H-NMR spectrum of compound III (300 MHz, CDCl₃): δ 6.68 (1, s, H-3), δ 6.82 (1, s, H-6), δ 7.43 (1, s, H-8), δ 7.48 (1, d, J = 2.0 Hz, H-2'), δ 7.30 (1, d, J = 2.0 Hz, H-3'), δ 7.21 (1, d, J = 2.0 Hz, H-5'), δ 7.52 (1, d, J = 8.1 Hz, H-6'), δ 2.34 (3, s, 7-OAc), δ 3.04 (3, s, 4'-OCH₃), δ 5.31 (1, d, J = 8.0 Hz, H-1''), δ 4.42 (1, d, J = 8.5 Hz, H-1'''), δ 3.38–3.76 (6, m, protons of galactose), δ 4.68–4.92 (4, m, protons of rhamnose), δ 1.55–1.80 (18, m, protons of sugar acetoxy), δ 1.04 (3, d, J 6.0, Rha Me). ¹³C-NMR of compound I (400 MHz, CDCl₃): δ 163.3 (C-2), 104.2 (C-3), 182.8 (C-4), 163.2 (C-5), 97.6 (C-6), 164.7 (C-7), 96.1 (C-8), 158.2 (C-9), 106.7 (C-10), 122.5 (C-1'), 115.6 (C-2'), 146.2 (C-3'), 160.7 (C-4'), 118.1 (C-5'), 131.5 (C-6'), 57.9 (-OMe), 103.4 (C-1''), 76.6 (C-2''), 73.3 (C-3''), 84.5 (C-4''), 67.4 (C-5''), 62.1 (C-6''), 103.2 (C-1'''), 72.8 (C-2'''), 73.4 (C-4'''), 82.9 (C-4'''), 68.2 (C-5'''), 18.4 (C-6''').

Acid hydrolysis of compound I: The compound I was refluxed with 7% H₂SO₄ for 8 h. at 100°C. The contents were allowed to cool and after the removal of the solvent yielded an aglycone as precipitate, which was separated by filtration. The aglycone (II) was recrystallised from EtOH as yellow needles, m.f. $C_{16}H_{12}O_5$, m.p. 276°C and $[M]^+$ 284 (EIMS). UV, λ_{max} (+MeOH) 252, 273, 282, 323; (+NaOAc) 262, 275, 289, 341, 352; (+AlCl₃) 259, 272, 285, 364;

(+AlCl₃/HCl) 258, 272, 285, 245 nm. On acetylation of the aglycone (II) by Ac₂O/pyridine yielded diacetyl derivative (IV), m.f. C₂₀H₁₆O₇, m.p. 195°C and [M]⁺ 368 (EIMS), ¹H-NMR (300 MHz, CDCl₃) δ 6.65 (1, s, H-3), δ 6.81 (1, s, H-6), δ 7.40 (1, s, H-8), δ 7.46 (1, d, J = 1.5 Hz, H-2'), δ 7.25 (1, d, J = 1.5 Hz, H-3'), δ 7.20 (1, d, J = 1.5 Hz, H-5'), δ 7.51 (1, d, J = 8.1 Hz, H-6'), δ 2.28 (3, s, 5-OAc), δ 2.32 (3, s, 7-OAc), δ 3.02 (3, s, 4'-OCH₃). EIMS, [M]⁺ 284, m/z 256, 241, 240, 153, 152, 132, 127, 126, 124, 118.

The aqueous hydrolysate obtained after the acid hydrolysis of compound (I) was neutralised with BaCO₃ and BaSO₄ filtered off. The filtrate was concentrated and subjected to paper chromatography examination (BAW: 4 : 1 : 5) showing the presence of L-rhamnose (R_f 0.35) and D-galactose (R_f 0.15) (by Co-PC and Co-TLC).

Permethylation of compound I: Compound I was treated with CH₃I and Ag₂O in DMF at room temperature for 24 h, and then filtered. The filtrate was concentrated and hydrolysed with 10% HCl for 8 h, which after the usual work-up yielded methylated aglycone and methylated sugars. The methylated sugars were identified as 2,3,4-tri-O-methyl-L-rhamnose and 2,3,4-tri-O-methyl-D-galactose (by Co-PC and Co-TLC) according to Petek.⁷

Periodate oxidation of compound I: The compound I was dissolved in MeOH and treated with sodium metaperiodate for 48 h. The quantities of sodium metaperiodate consumed and of formic acid liberated were estimated by Jone's method.⁸

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