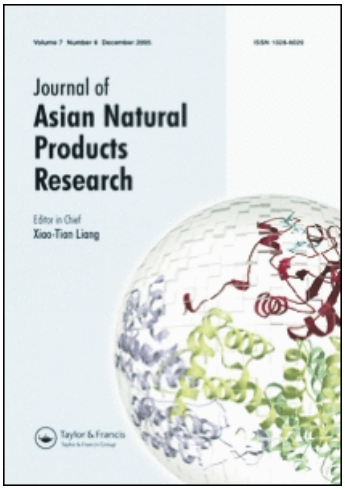

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Note: A new biologically active flavonol glycoside from *Psoralea corylifolia* (Linn.)

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Note

A new biologically active flavonol glycoside from *Psoralea corylifolia* (Linn.)

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A new biologically active flavonol glycoside (**1**) mp 264–265°C, $C_{32}H_{38}O_{20}$, $[M]^+$ 742 (EIMS) has been isolated from the methanol-soluble fraction of the defatted seeds of *Psoralea corylifolia* (Linn.). It was characterised as the new flavonol glycoside 3,5,3′,4′-tetrahydroxy-7-methoxyflavone-3′-*O*-α-L-xylopyranosyl(1 → 3)-*O*-α-L-arabinopyranosyl(1 → 4)-*O*-β-D-galactopyranoside by several colour reactions, spectral analysis and chemical degradations. Compound **1** showed anti-microbial activity against various bacteria and fungi.

Keywords: *Psoralea corylifolia* (Linn.); Leguminosae; Flavonoid; Antimicrobial activity

1. Introduction

Psoralea corylifolia (Linn.) [1–3] belongs to family Leguminosae. It is commonly known as "Babchi" or "Bukchi" in Hindi. It is found in Rajasthan and the eastern districts of Panjab and Uttar Pradesh, and its seeds are used as a laxative, aphrodisiac, anthelmintic, diuretic and diaphoretic in febrile conditions.

We report here the isolation and structural elucidation of a new biologically active flavonol glycoside, 3,5,3′,4′-tetrahydroxy-7-methoxyflavone-3′-*O*-α-L-xylopyranosyl(1 → 3)-*O*-α-L-arabinopyranosyl(1 → 4)-*O*-β-D-galactopyranoside (**1**), by various chemical degradations and spectral analysis. Compound **1** showed antimicrobial activity against several bacteria and fungi.

2. Results and discussion

A new flavonol glycoside (**1**) mp 264–265°C, $C_{32}H_{38}O_{20}$, $[M]^+$ 742 (EIMS), isolated from the methanol-soluble fraction of the defatted powdered seeds of *Psoralea corylifolia* (Linn.),

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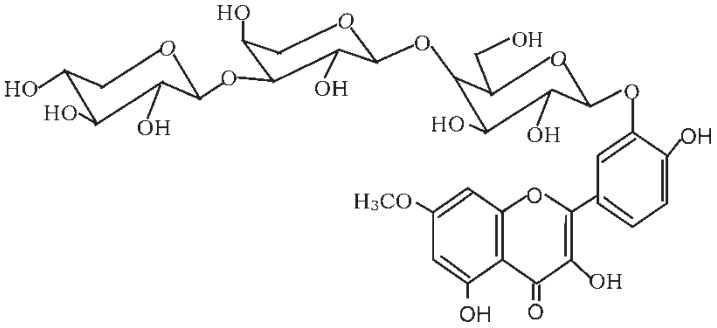
gave colour reactions characteristic of flavonoid [4]. Its IR spectrum has absorption bands at 3410, 2935, 2865, 1655, 1212, 1115, 830, cm^{-1}. The ^1H NMR spectrum of compound **1** shows doublets at, δ 6.35, 6.59 for H-6 and H-8; δ 7.70 for H-2′, δ 6.88 for H-5′; double doublet at δ 7.67 for H-6′; singlet at δ 3.87 for the $-OCH_3$ group at C-7. The anomeric protons of sugars showed doublets at 5.46, 5.06 and 5.65, which were assigned to H-1″, H-1‴ and H-1⁗ of D-galactose, L-arabinose and L-xylose, respectively.

Acid hydrolysis of **1** with 9% methanolic H_2SO_4 gave aglycone **2**, mp 225–226°C, $C_{16}H_{12}O_7$, $[M]^+$ 316, which was identified as 3,5,3′,4′-tetrahydroxy-7-methoxyflavone by comparison of its spectral data with reported literature values [5].



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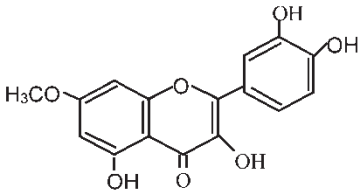

2

The aqueous hydrolysate, after the removal of the aglycone, was neutralized with $BaCO_3$ and $BaSO_4$ was filtered off. The filtrate was then concentrated and subsequent paper chromatography using nBAW (4:1:5) as solvent revealed the sugars D-galactose (R_f 0.15), L-arabinose (R_f 0.22) and L-xylose (R_f 0.28) (Co-PC and Co-TLC). Periodate oxidation [6] of **1** further confirmed that all the sugars were present in the pyranose form.

The position of sugar moiety in **1** was established by its permethylation [7] followed by acid hydrolysis. The permethylated aglycone was identified as 3′-hydroxy-3,5,7,4′-tetramethoxyflavone and the methylated sugars were identified as 2,3,6-tri-*O*-methyl-D-galactose, 2,4-di-*O*-methyl-L-arabinose and 2,3,4-tri-*O*-methyl-L-xylose [8,9], which showed that the C-1⁗ of L-xylose was linked with C-3‴ of L-arabinose, C-1‴ of L-arabinose was linked to C-4″ of D-galactose, and C-1″ of D-galactose was linked to C-3′ of the aglycone. The inter-linkages (1 → 3) and (1 → 4) between both sugars were further confirmed by ^{13}C NMR (see Experimental section).

Enzymatic hydrolysis of **1** with Takadiastase liberated L-xylose first, then L-arabinose and 3,5,3′,4′-tetrahydroxy-7-methoxyflavone-3′-*O*-β-D-galactopyranoside as proaglycone, thus

confirming the α-linkage between L-xylose and L-arabinose as well as between L-arabinose and proaglycone. Proaglycone on further hydrolysis with almond emulsin liberated D-galactose and aglycone, which confirmed the β-linkage between aglycone and D-galactose.

On the basis of above evidences, the structure of **1** was identified as 3,5,3′,4′-tetrahydroxy-7-methoxyflavone-3′-*O*-α-L-xylopyranosyl(1 → 3)-*O*-α-L-arabinopyranosyl(1 → 4)-*O*-β-D-galactopyranoside.

3. Experimental section

Melting points are uncorrected. The IR spectra were recorded in KBr discs. ^{1}H NMR spectra were run at 300 MHz using TMS as internal standard and $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded at 75 MHz using DMSO-d_6 as solvent.

3.1 Plant material

The seeds of *Psoralea corylifolia* (Linn.) were collected around the Sagar region and were taxonomically authenticated by the Department of Botany, Dr. H. S. Gour University Sagar, India. A voucher specimen has been deposited in the Natural Products Laboratory, Department of Chemistry, Dr. H. S. Gour University Sagar (MP), India.

3.2 Extraction and isolation

Air-dried and powdered seeds (3 kg) of the plant were extracted with light petroleum ether (60–80°C) in a Soxhlet apparatus for 85–90 h. The total defatted powdered seeds were successively extracted with C_6H_6, $CHCl_3$, $CH_3COOC_2H_5$, CH_3COCH_3 and MeOH. The methanol fraction of the defatted powdered seeds of the plant was concentrated at room temperature, which showed three spots on TLC examination, indicating it to be mixture of **1** and **1a** and **1b**, which were separated by TLC and purified by column chromatography over silica-gel G. Both **1a** and **1b** were found in very small quantities and therefore they could not be examined further. Compound **1** was further purified by column chromatography, and was found to be homogeneous on TLC examination. It was then crystallised from methanol (1.12 g).

3.3 Study of compound 1

Mp 264–265°C, $C_{32}H_{38}O_{20}$ (elemental analysis: found (%) C 51.74, H 5.10 calcd. for $C_{32}H_{38}O_{20}$, C 51.75, H 5.12). ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm) 6.35 (1H, d, $J = 2.0$ Hz, H-6), 6.59 (1H, d, $J = 2.0$ Hz, H-8), 7.70 (1H, d, $J = 2.1$ Hz, H-2′), 6.88 (1H, d, $J = 8.1$ Hz, H-5′), 7.67 (1H, dd, $J = 2.1$, 8.3 Hz, H-6′), 3.87 (3H, s, 7-OMe), 5.46 (1H, d, $J = 7.7$ Hz, H-1″), 4.62 (1H, dd, $J = 3.7, 9.7$ Hz, H-2″), 4.55 (1H, dd, $J = 9.7$, 3.3 1 Hz, H-3″), 4.57 (1H, d, $J = 3.1$ Hz, H-4″), 4.60 (1H, m, H-5″) 4.41 (2H, d, $J = 6.3$ Hz, H-6″), 5.06 (1H, d, $J = 7.4$ Hz, H-1‴), 4.42 (1H, m, H-2‴), 4.03 (1H, m, H-3‴), 4.15 (1H, m, H-4‴), 3.52 (2H, m, H-5‴), 5.65 (1H, d, $J = 6.2$ Hz, H-1⁗), 4.21 (1H, m, H-2⁗), 4.20 (1H, m, H-3⁗),4.19 (1H, m, H-4⁗), 4.48 (1H, dd, $J = 11.4$, 3.9,H-5⁗). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 158.6 (C-2), 135.6 (C-3), 179.3 (C-4), 162.7 (C-5), 98.9 (C-6), 167.4 (C-7), 93.2 (C-8), 158.0 (C-9), 106.5 (C-10), 56.2 (–OCH_3,C-7), 123.3 (C-1′), 117.1 (C-2′), 146.7

(C-3′), 145.8 (C-4′), 116.1 (C-5′), 123.6 (C-6′), 100.6 (C-1″), 70.6 (C-2″), 71.4 (C-3″), 71.1 (C-4″), 72.3 (C-5″), 62.5 (C-6″), 106.3 (C-1‴), 73.7 (C-2‴), 74.3 (C-3‴), 69.8 (C-4‴), 67.4 (C-5‴), 104.8 (C-1⁗), 75.2 (C-2⁗), 78.6 (C-3⁗), 70.7 (C-4⁗), 67.2 (C-5⁗).

3.4 Acid hydrolysis of compound 1

Compound **1** (200 mg) was dissolved in MeOH (25 ml) and then boiled under reflux with 9% H_2SO_4 (10 ml) on a water bath for 6–7 h. The contents were then allowed to cool and the residue was shaken with Et_2O. The resultant ethereal layer was washed with water and the residue was chromatographed over silica-gel G using a methanol–chloroform mixture (8:6) as solvent to give compound **2**, mp 225–226°C, $C_{16}H_{12}O_7$, $[M]^+$ 316 (elemental analysis: found (%) C 60.74, H 3.79; calcd. for $C_{16}H_{12}O_7$ C 60.76, H 3.80). Compound **2** was identified as 3,5,3′,4′-tetrahydroxy-7-methoxyflavone by comparing spectral data with that reported in the literature [5].

The aqueous hydrolysate was then neutralized with $BaCO_3$, and $BaSO_4$ filtered off. The filtrate was concentrated and subjected to paper chromatography examination using (BAW 4:1:5) as solvent and aniline hydrogen phthalate as spraying agent, which showed the presence of D-galactose (R_f 0.15), L-arabinose (R_f 0.22), and L-xylose (R_f 0.28) (Co-PC and Co-TLC).

3.5 Permethylation followed by acid hydrolysis of compound 1

Compound **1** (30 mg) was treated with MeI (7 ml) and Ag_2O (25 mg) in DMF (8 ml) for two days and then filtered. The filtrate was dried under vacuum and hydrolysed with 9% methanolic H_2SO_4 for 7–8 h to yield the methylated aglycone, which was identified as 3′-hydroxy-3,5,7,4′-tetramethoxyflavone, and methylated sugars, which were identified as 2,3,6-tri-*O*-methyl-D-galactose, 2,4-di-*O*-methyl-L-arabinose, and 2,3,4-tri-*O*-methyl-L-xylose (Co-PC and Co-TLC).

3.6 Enzymatic hydrolysis of compound 1

Compound **1** (50 mg) was dissolved in MeOH (40 ml) and hydrolysed with an equal volume of Takadiastase at room temperature to yield L-xylose (R_f 0.28), L-arabinose (R_f 0.22) and proaglycone, confirming the presence of the α-linkage between L-xylose and L-arabinose as well as between L-arabinose and proaglycone. Praglycone on further hydrolysis with almond emulsion liberated D-galactose (R_f 0.15) and aglycone, which confirmed the presence of the β-linkage between aglycone and D-galactose.

3.7 Antimicrobial study of compound 1

The antibacterial and antifungal activity of the methanol-soluble fraction of compound **1** was tested at various dilutions using methanol as solvent at different concentrations. The various bacterial species were first incubated at 40°C for 46 h. The zones of inhibition were recorded at 37 ± 1°C for 24 h for bacteria and 28 ± 1°C after 48 h for fungi.

The antimicrobial activity was determined by the Whatman No.1 filter paper discs (6 mm) method [10]. Paper discs were soaked with various samples tested and were dried at 50°C. The discs were then kept on soft nutrient agar (2%) Petri discs previously seeded with a suspension of bacterial species.

Table 1. Antibacterial and antifungal activity of compound **1**.

		Diameters of zone of inhibition(mm)[a]					
S.No.	*Micro-organisms*	*Methanol fraction*	*8:2*	*6:4*	*4:6*	*2:8*	*Std.*[b]
	Bacterial species						
1	*(−)Pseudomonas aerugenosa*	19.0	17.5	13.0	11.5	9.5	22.0
2	*(−) Escherichia coli*	10.5	6.5	2.5	–	–	17.0
3	*(+) Staphylococcus aureus*	16.2	13.5	9.0	7.5	6.5	19.0
4	*(+) Bacillus coagulans*	12.5	8.5	3.5	1.0	–	20.0
	Fungal species						Std.[c]
5	*Fusarium oxysporum*	17.0	15.5	12.5	10.5	8.2	21.0
6	*Aspergillus niger*	9.5	7.5	5.6	3.2	0	16.0
7	*Penicillium digitatum*	19.0	16.5	13.1	10.7	7.4	22.5
8	*Tricoderma viride*	11.5	8.4	4.5	–	–	23.2
9	*Fusarium monoliforme*	9.5	7.5	5.0	2.5	–	19.5

[a] The zone of inhibition (mm) is the average of four determinations in four different directions; Whatman No. 1 Filter paper (6 mm) was soaked with each sample to test for their activity.
[b] Streptomycin used as standard antibacterial agent.
[c] Griseofulvin used as standard antifungal agent.

For fungi, Petri discs were placed on Sabouraud's broth [11] medium (1%). The zones of inhibition were expressed as an average of the maximum diameter in four different directions. The various results are recorded in table 1.

The above results showed that the antibacterial activity of the compound **1** is fairly good against Gram positive bacteria, *e.g. Staphylococcus aureus*, and Gram negative bacteria, *e.g. Pseudomonas aerugenosa*. Greater antifungal activity for **1** was found against *Fusarium oxysporum* and *Penicillium digitatum*, even for very dilute concentrations.

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