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MYRICETIN METHYL ETHERS FROM *SOLANUM PUBESCENS*

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Abstract—3,7,3',5'-Tetramethoxy-5,4'-dihydroxyflavone and a novel flavonol 3,7,3'-trimethoxy-5,4',5'-trihydroxy flavone were isolated from the leaves of *Solanum pubescens* and characterized by both physical and chemical methods

INTRODUCTION

Angiosperm families often have characteristic flavonoid patterns [1] and in the Solanaceae the pattern is based mainly on kaempferol and quercetin [2] Flavonoids with B-ring trihydroxylation such as myricetin were thought to be absent from leaves, although myricetin appeared occasionally as a by product of delphinidin synthesis in flowers [2] However, myricetin 3-methyl ether and several methylated 8-hydroxy myricetin derivatives have since been reported from *Solanum* section *androceras* [3, 4] and myricetin glycosides have been found in some tuber bearing *Solanum* species [5] We now report the isolation of two myricetin methyl ethers 3,7,3',5'-tetramethyl ether (**1**) and 3,7,3'-trimethyl ether (**2**), from the leaves of *Solanum pubescens* Willd Compound **1** was first reported from *Ledum palustre* L (Ericaceae) [6] and this is the second report of this compound from nature Compound **2** is a new compound

RESULTS AND DISCUSSION

From the methanol extract of leaves of *Solanum pubescens* **1** and **2** were isolated by chromatographic methods Compound **1** ($C_{19}H_{18}O_8$, mp 185–187°, permethyl ether, mp 154°) was identified as 3,7,3',5'-tetra-*O*-methyl myricetin by ^{1}H NMR and mass spectral data Compound **2** ($C_{18}H_{16}O_8$, mp 197°) gave a positive Shinoda test for a flavonoid and a green ferric reaction Permethylation with dimethyl sulphate yielded a hexamethoxy flavone identical with myricetin hexamethyl ether ^{1}H NMR (in acetone-d_6) of **2** showed the presence of three methoxyl groups at δ3 94 (*s*, 6H) and 3 92 (*s*, 3H) and its acetate gave three acetyl signals at δ2 35 (*s*, 6H) and 2 48 (*s*, 3H) indicating **2** to be a trimethyl ether of myricetin The signal at δ12 74 is due to the chelated 5-hydroxyl The protons at the 6 and 8 positions appeared at δ6 26 (*d*, J = 2 5 Hz) and 6 63 (*d*, J = 2 5 Hz), respectively The only other signal in the aromatic region is the singlet at δ7 4 (2H) assigned to the 2',6'-protons in the B-ring

A bathochromic shift of $+\Delta\lambda$58 nm in band I (360–418 nm) on addition of sodium methoxide without decrease in intensity suggested the presence of a free 4'-hydroxyl The lack of degeneration in the spectrum ruled out the possibility of a free 3-hydroxyl and thus one methoxyl must be at the 3-position The shift in band I (360–405 nm) on the addition of aluminium chloride–hydrochloric acid and the larger bathochromic shift (360–437 nm) with aluminium chloride indicated the presence of a free 5-hydroxyl and an *ortho*-dihydroxy system in ring-B [7] A larger shift of band I with sodium acetate ($\Delta\lambda$69 nm) than with sodium methoxide ($\Delta\lambda$58 nm) indicated the presence of a free 4'-hydroxyl and the absence of a free 7-hydroxyl (also supported by the absence of a shift with sodium acetate in band II) [7]

Table 1 ^{13}C NMR data for **2**, **3** and myricetin 3-galactoside

C	Myricetin 3-*O*-galactoside	Myricetin 3,7,3'-trimethyl ether (**2**)†	Myricetin 3,7,3'-trimethyl ether acetate‡
2	156 2	155 8	152 2
3	133 9	138 0	141 7
4	177 4	177 9	172 9
5	161 2	160 9	150 4
6	98 6	97 6	108 3
7	164 0	165 1	163 4
8	93 3	92 2	98 5
9	156 2	156 2	157 6
10	104 0	104 5	111 2
1'	120 2	119 6	128 6
2'	108 8	105 1	109 8
3'	145 3	148 1	152 1
4'	136 6	138 1	133 7
5'	145 3	145 6	143 3
6'	108 8	109 8	115 3
		59 6	60 2
OMe		56 2	56 4
		56 0	56 0
			169 4
OAc		$\underline{C}OCH_3$	168 0
			167 3
			21 1
		$CO\underline{C}H_3$	20 6
			20 2

*Ref [8]
†In DMSO-d_6
‡In $CDCl_3$

The molecular ion at $[M]^+$ 360 confirmed the trimethoxy trihydroxy flavone system In support of the above observation, a fragment ion at *m/z* 167 (65) for a dihydroxy monomethoxy substituted B-ring was observed The other methoxyl was placed at position 3′ Hence, **2** is assigned the structure 3,7,3′-tri-*O*-methyl myricetin The ^{13}C NMR of **2** and its acetate (Table 1) are consistent with the proposed structure

Myricetin derivatives are rare in the Solanaceae, there being only two previous reports [3–5] The present discovery of myricetin methyl ethers in *S pubescens* is also taxonomically significant in that this species is in the same subgenus of *Solanum*, i e *heptostemonum*, in which they were previously found [3, 4]

EXPERIMENTAL

Plant material of *Solanum pubescens* Willd was collected near Nagarjuna Sagar (Andhra Pradesh) India, in 1983 Vouchers are deposited in Nagarjuna University Herbarium (No NUH NSP001) The powdered air dried leaves were successively extracted with *n*-hexane and MeOH The concd MeOH extract was chromatographed over silica gel eluting with C_6H_6 and C_6H_6–Me_2CO mixtures Compound **1** was obtained in the C_6H_6–Me_2CO (19 1) fraction and **2** in the C_6H_6–Me_2CO (17 3) fraction

Myricetin 3,7,3′-trimethyl ether (**2**) The chromatographic fractions containing **2** were purified by prep TLC over silica gel (C_6H_6–Me_2CO, 7 3) and cryst from Me_2CO–*n*-hexane, [PC R_f 0 28 (15% HOAc), with solvent front (BAW 4 + 1 + 5),] mp 197°, UV λ_{max}^{MeOH} nm 360, 300 sh, 268, 253, NaOMe 418, 301 sh, 262, $AlCl_3$ 437, 312 sh, 274, 235 sh, $AlCl_3$ + HCl 405, 365, 310 sh, 273, NaOAc 429, 300 sh, 266, 253, NaOAc + H_3BO_3 383, 300 sh, 258 MS *m/z* (rel int) $[M]^+$ 360 (83%), 359 (43), 345 (92), 342 (10), 331 (13), 329 (23), 317 (100), 167 (65), 151 (30), 164 (9), 149 (23), 167 (65), 152 (9) Compound **2** was acetylated with Ac_2O in pyridine The acetate was cryst from $CHCl_3$–*n*-hexane to give white needles mp 195° ^1H NMR ($CDCl_3$) δ2 35 (*s*, 6H), 2 48 (*s*, 3H), 3 84 (*s*, 3H), 3 92 (*s*, 6H), 6 60 (*d*, *J* = 2 5 Hz, 1H), 6 80 (*d*, *J* = 2 5 Hz, 1H), 7 5 (*d*, *J* = 2 5 Hz, 1H), 7 68 (*d*, *J* = 2 5 Hz, 1H) Methylation of **2** (Me_2SO_4, Me_2CO, K_2CO_3) yielded 3,5,7,3′,4′,5′-hexamethoxy flavone, mp 154° ^1H NMR (Me_2CO-d_6) 3 84 (*s*, 3H), 3 88 (*s*, 3H), 3 93 (*s*, 12H), 6 50 (*d*, *J* = 2 5 Hz, 1H), 6 75 (*d*, *J* = 2 5 Hz, 1H), 7 45 (*s*, 2H)

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