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LUTEOLIN 7,4′-DIMETHYL ETHER 3′-GLUCOSIDE FROM *GELONIUM MULTIFLORUM*

NAZNEEN PARVEEN and NIZAM U. KHAN

Department of Chemistry, Aligarh Muslim University, Aligarh 202001, India

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Key Word Index—*Gelonium multiflorum*; Euphorbiaceae; luteolin 7,4′-dimethyl ether 3′-glucoside.

Abstract—A new flavone glycoside has been isolated from the leaves of *Gelonium multiflorum* and characterized as luteolin 7,4′-dimethyl ether 3′-glucoside.

INTRODUCTION

Gelonium, a genus of shrubs and small trees is distributed in the tropical and sub-tropical parts of Asia and Africa. Three species of *Gelonium* from India are well known for their medicinal properties [1]. We now report the characterization of a new flavone glycoside (**1**) from leaves of *G. multiflorum*.

RESULTS AND DISCUSSION

Compound **1** analysed for $C_{23}H_{24}O_{11}$, responded to the Shinoda test [2], gave a positive Molisch test and reduced Tollen's reagent. The UV spectrum showed λ_{max} at 285 and 335 nm, and the IR spectrum exhibited absorption bands due to hydroxyl (3400 cm^{-1}), an α,β-unsaturated ketone (1650, 1601 cm^{-1}) and an aromatic ring (900, 850, 770 cm^{-1}). The characteristic colour reactions and spectral properties indicated **1** to be a flavone glycoside.

Hydrolysis of **1** with both 6% HCl and β-glucosidase yielded D-glucose and an aglycone (**2**) which was identical with an authentic sample of luteolin 7,4′-dimethyl ether (pilloin) [3, 4]. The presence of a free hydroxyl at C-5 [5] was confirmed by a bathochromic shift with aluminium chloride. The formation of a diacetate and a tetramethyl ether supported the presence of two free hydroxyls and two free methoxyl groups in **2**.

The ^{1}H NMR spectrum of **1** in DMSO-d_6 showed an AMX system due to a 3′,4′-disubstitution. An *ortho* coupled doublet of one proton at δ7.68 (J = 8 Hz), a double doublet of one proton at δ7.85 (J = 2 and 8 Hz) and a *meta* coupled doublet of one proton at δ7.63 (J = 2 Hz) are assigned to H-5′, H-6′, and H-2′, respectively. The 5,7 substitution patttern was demonstrated by the presence of two *meta* coupled doublets of one proton each at δ6.60 and δ7.03, ascribable to H-6 and H-8, respectively. A sharp singlet at δ6.90 is assigned to the H-3 proton. Two singlets at δ3.87 and δ3.90 integrating for three protons each, confirmed the presence of two aromatic methoxyls. The anomeric proton, H-1″ of the glucose appeared as a doublet at δ5.69 (J = 7 Hz). The chemical shift confirmed the direct attachment to the aglycone and the diaxial coupling (J = 7 Hz) between H-1″ and H-2″ suggested a β-configuration. These data indicated that **1** is a 5,7,3′,4′-oxygenated compound and the mass spectrum gave a base peak of [M − glucose]$^+$ at m/z 314.

The position of the linkage of glucose was established by comparing the UV and ^{1}H NMR spectra of the glycoside (**1**) and the aglycone (**2**). Since **2** has free 5 and 3′ hydroxyls the glucose in **1** must be attached to one of these positions. A bathochromic shift of 20 nm with aluminium chloride leaves only the 3′ position free for glycosylation. This was further confirmed by methylation and subsequent hydrolysis of the methylated product with 6% HCl to give a partial methyl ether characterized as 5,7,4′-trimethoxyluteolin by spectral studies. The sugar was confirmed as glucose by co-paper chromatography with an authentic sample and periodate oxidation indicated that it was in the pyranose form [6]. Compound **1** is therefore identified as luteolin 7,4′-dimethyl ether 3′-*O*-β-D-glucoside.

EXPERIMENTAL

All mps are uncorr., UV and IR spectra were recorded in MeOH and as KBr pellets, ^{1}H NMR were measured at 60 MHz in $CDCl_3$ with TMS as int. standard.

Extraction and isolation. Air dried leaves of *G. multiflorum* A. Juss. collected from FRI, Dehradun, were refluxed with MeOH. The MeOH concentrate was successively treated with petrol (60–80°), C_6H_6 and EtOAc. The EtOAc concentrate was chromatographed over silica gel. Elution with EtOAc afforded **1** mp > 300°, which crystallized from EtOAc-Me_2CO as pale yellow needles. It gave a positive colour with Mg-HCl (orange) and $FeCl_3$ (green). ^{1}H NMR (60 MHz, DMSO-d_6): δ6.60, 7.03 (1H each, *d*, J = 2 Hz, H-6 and H-8), 6.90 (1H, *s*, H-3), 7.68 (1H, *d*, J = 8 Hz, H-5′), 7.85 (1H, *dd*, J = 2 and 8 Hz, H-6′), 7.63 (1H, *d*, J = 2 Hz, H-2′), 3.87, 3.90 (3H each, OCH_3-7, 4′), 3.30–4.0 (6 glucosyl protons). UV λ_{max}^{MeOH} nm: 285, 335; + $AlCl_3$: 296, 355; + $AlCl_3$/HCl: 296, 355; + NaOAc: 288, 335; + NaOAc/H_3BO_3: 288, 335; + NaOMe: 290, 335. MS m/z: 314 [M − glucose]$^+$, 285 [M − 29]$^+$, 271 [M − 43]$^+$, 268 [M − 46]$^+$, 167 [$C_8H_7O_4$], 148 [$C_9H_8O_2$], 138 [$C_7H_6O_3$], 133 [$C_8H_5O_2$] and 123 [$C_7H_7O_2$].

Acid hydrolysis of 1 with 6% HCl at 100° for 2 hr gave yellow crystals of an aglycone (2), mp 236°. When analysed for $C_{17}H_{12}O_{16}$, $[M]^+ = 314$ it was identical with authentic luteolin 7,6'-dimethyl ether (mp, MS, UV and IR). The acetate of 2, mp 185°, was also identical (MS and NMR) with authentic sample [3]. Compound 1 was also methylated and then hydrolysed with 6% HCl to give 5,7,4'-trimethoxy luteolin, mp 220°, UV λ_{max}^{MeOH} nm: 285, 335; + $AlCl_3$: 287, 335; + $AlCl_3$/HCl 287, 335; + NaOAc 285, 335; + NaOAc/H_3BO_3 285, 335; + NaOMe 290, 335. The identity of the sugar was confirmed as glucose by Co-PC with an authentic marker in *n*-butanol–HOAc–H_2O using aniline hydrogen phthalate as detection reagent.

REFERENCES

1. Sastri, B. N. ed. (1956) *The Wealth of India*, CSIR, New Delhi. p. 122.
2. Shinoda, J. (1928) *J. Chem. Pharm. Soc. Japan* **48**, 214.
3. Nunez-Alarcon, J. (1971) *J. Org. Chem.* **36**, 2829.
4. Jain, A. C. and Sharma, B. N. (1973) *Phytochemistry* **12**, 1455.
5. Markham, K. R. and Mabry, T. J. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds), Chapman and Hall, London.
6. Sinha, K. S., Sinha, S. K. and Dewivedi, N. (1985) *J. Ind. Chem. Soc.* **LXII**, 169.

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FLAVONOID AGLYCONES FROM *XANTHOCEPHALUM GYMNOSPERMOIDES* VAR. *GYMNOSPERMOIDES*

SANGGONG YU,* NIANBAI FANG† and TOM J. MABRY

The University of Texas at Austin, Austin, TX 78713, U.S.A.

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Key Word Index—*Xanthocephalum gymnospermoides* var. *gymnospermoides*; Compositae; Astereae; 5,7,4'-trihydroxy-3,3',5'-trimethoxyflavone.

Abstract—Six known flavonoid aglycones and the newly described 5,7,4'-trihydroxy-3,3',5'-trimethoxyflavone were isolated from *Xanthocephalum gymnospermnoides* var. *gymnospermnoides*.

INTRODUCTION

In 1961, Solbrig recognised eight species for *Xanthocephalum* [1], while Lane (1980) treated the genus as having five species with other taxa being transferred to *Gutierrezia* [2]. As part of our continuing chemical systematics investigation of the '*Gutierrezia–Xanthocephalum* complex' [3–9], we report here the isolation of seven flavonoids from the aerial parts of *Xanthocephalum gymnospermoides* (Gray) B. and H. var. *gymnospermoides*.

RESULTS AND DISCUSSION

Column chromatography and preparative paper chromatography of the material from the dichloromethane and ethyl acetate extracts of a concentrated aqueous methanol extract of the aerial parts of *X. gymnospermoides* var *gymnospermoides* afforded flavonoids 1–7 including one new compound. The new substance is 5,7,4'-trihydroxy-3,3',5'-trimethoxyflavone (1) and the six known compounds are 5,3',5'-trihydroxy-3,7,4'-trimethoxyflavone (2), 5,7,4'-trihydroxy-3',5'-dimethoxyflavone (3), 5,7,4'-trihydroxy-3,3'-dimethoxyflavone (4), 5,3',4'-trihydroxy-3,7-dimethoxyflavone (5), 3,5,7,3',4'-pentahydroxyflavone (6) and 5,7,4'-trihydroxy-3-methoxyflavone (7). The flavonoid chemistry of this taxon is different from that of woody species of *Gutierrezia* [3–6] and the related monotypic *Gymnosperma glutinosum* [9]; these latter taxa produce large quantities of flavonoids with 6,8-oxygenation as well as flavonol 3-methyl ethers with rare 2'-oxygenation. In contrast, the flavonoids isolated from *Xanthocephalum gymnospermoides* var. *gymnospermoides* are similar to those of two herbaceous species of *Gutierrezia*, *G. wrightii* [8] and *G. alamanii* var. *megalocephala* [7], two taxa formerly placed in *Xanthocephalum* [2]. The species investigated here and the latter two species all yielded only a few flavonoids, which all lacked 6,8-oxygenation and 2'-oxygenation. Detailed data are presented only for compound 1.

^{1}H NMR spectrum in carbon tetrachloride of the TMSi ether of 1 showed one two-proton singlet which was assigned to protons at 2' and 6' (δ7.30 ppm) in a symmetrically substituted B-ring and two one-proton doublets at δ6.15 (J = 2.5 Hz) and 6.48 (J = 2.5 Hz) characteristic of H-6 and H-8, respectively [10]. The remaining signals in

*Permanent address: Wuhan Institute of Medical Sciences, Wuhan, China.

†Permanent address: Hubei College of Chinese Traditional Medicine, Wuhan, China.