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A NEW ISOFLAVONE GLYCOSIDE FROM THE AERIAL PARTS OF *Retama sphaerocarpa*

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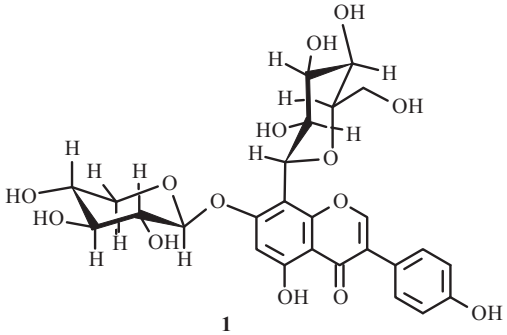
UDC 547.972

*A new isoflavone glycoside, genistein 7-*O*-xylosyl 8-C-glucoside (**1**), was isolated from the leaves of* Retama sphaerocarpa. *Its structure was elucidated by spectroscopic methods.*

Keywords: *Retama sphaerocarpa,* isoflavone glycoside, spectroscopic methods.

The genus *Retama* is located in the Atlas regions and the Sahara [1] (Arabic common name R′tem) and represented by three species in the flora of Algeria: *Retama monosperma*, *Retama retam*, and *Retama sphaerocarpa.* The last one is used to cure rabies in folk medicinal traditions in the east of Algeria. Investigations of *Retama sphaerocarpa* have led to the isolation of alkaloids [2–4], isoflavonoids [5–7], and flavonoids [8–11]. Previous studies showed that isoflavonoid glucosides are common in this genus. We now report the results of chemical examination of the methanolic extract of the flowering stems of *R. sphaerocarpa* Boissier (Fabaceae).

The powdered aerial parts (950 g) of *R. sphaerocarpa* were extracted with 70% MeOH. The MeOH extract was evaporated to dryness. The residue was dissolved in boiling water and extracted with ethyl acetate and *n*-BuOH successively. Solvents were evaporated and the residue of the ethyl acetate and *n*-BuOH extracts was dissolved in small volumes of MeOH. Two-dimensional paper chromatography using 15% AcOH and BAW (*n*-BuOH–AcOH–H_2O, 4:1:5 upper phase) as solvents had shown that the ethyl acetate and *n*-BuOH extracts contain almost the same compounds representing flavonoids. The *n*-BuOH extract was applied to a column of polyamide MN SC6 and eluted with a gradient of toluene–MeOH with increasing polarity. Compound **1** was isolated by preparative PC on Whatman 3MM paper using 15% AcOH, then by preparative TLC on polyamid DC6 eluting with H_2O–MeOH–methyl ethyl acetone–acetylacetone 13:3:3:1).



1

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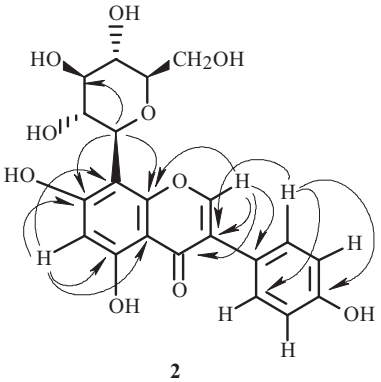

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Fig. 1. Important HMBC correlations for the structure elucidation of compound **2.**

Absorption bands at 257, 263 sh, and 324 sh nm in the UV spectrum of compound **1** in methanol and the singlet at 8.2 ppm in the ^{1}H NMR spectrum suggested that this compound was an isoflavone. Upon addition of NaOAc, the spectrum was unaffected (relative to the spectrum in methanol), suggesting that the C-7 hydroxyl group was substituted, and the presence of the 5-hydroxyl group is highlighted by the band II bathocromic shift δ λII = 10 nm after addition of $AlCl_3$ + HCl [12]. The ^{1}H NMR spectrum of compound **1** was obtained in CD_3OD, and the AA'BB' system consists of two proton doublets (J = 8.6 Hz) at δ 7.40 and 6.85 typical of a *para*-substituted B ring of the flavonoid.

We observed the presence of two anomeric sugar protons at 4.9 (1H, d, J = 9.9 Hz, anomeric proton of glucose H-1″) and 4.2 (1H, d, J = 6.6 Hz, anomeric proton of xylose H-1‴). Acid hydrolysis of **1** produced genistein 8-C-glucoside (**2**) and *D*-xylose. The identification of *D*-xylose in the water layer was carried out by comparison with an authentic sample (R_f 0.66) on TLC plates of silica gel eluted with acetone–H_2O (9:1) and was confirmed by the ^{1}H NMR coupling pattern. On the other hand, the resistance of the second sugar to acid hydrolysis confirmed the *C*-glycosyl structure. The ^{1}H and ^{13}C NMR spectral data of compound **2** were in agreement with published data [13, 14]. The positive electrospray MS exhibited a quasi-molecular ion $[M + H]^+$ at *m/z* 565, suggestive of the empirical formula $C_{26}H_{28}O_{14}$. Other important peaks appeared at *m/z* 433 $[M – 133(xylose) + H]^+$ corresponding to the loss of the xylosyl moiety from the protonated molecule. Then compound **1** was identified as genistein 7-*O*-xylosyl 8-C-glucoside.

EXPERIMENTAL

Compound **1**, $C_{26}H_{28}O_{14}$. UV (MeOH, λ_{max}, nm): 257, 263, 324; NaOAc: 263, 327; $AlCl_3$: 273, 307; $AlCl_3$/HCl: 274, 307, 364 nm. ES-MS positive ion mode *m/z*: 565 $[M + H]^+$, 587 $[M + Na]^+$, 433 $[M – 133(xylose) + H]^+$. ^{1}H NMR (CD_3OD, δ, ppm, J/Hz): 8.6 (1H, s, H-2), 7.4 (2H, d, J = 8.64, H-2′, H-6′), 6.85 (2H, d, J = 8.64, H-3′, H-5′), 6.28 (1H, s, H-6), 4.9 (1H, d, J = 9.9, anomeric proton of glucose H-1″), 4.2 (1H, d, J = 6.6, anomeric proton of xylose H-1‴).

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REFERENCES

1. P. Quezel and S. Santa, *Nouvelle Flore de l'Algerie et des Regions Desertiques et Meridionales*, Edition CNRS, Paris, 1963.
2. F. Martin-Cordero, A. M. Gil-Serrano, and M. J. Ayuso Gonzalez, *Plant Med. Phytother*., **25**, 157 (1991).
3. A. El-Shazly, A. M. Ateya, L. Witte, and M. Wink, *Z. Naturforsch., C: Biosci.*, **51**, 301 (1996).

4. D. Vazquez Maria, G. Gonzalez, J. Calvino, and Ribas-Marques Ignacio, *An. Real Soc. Espan. Fis. Quim., Ser. B: Quim.*, **62** (7–8), 837 (1966).
5. S. Louaar, S. Akkal, H. Laouer, and D. Gillet, *Chem. Nat. Comp*., **43**, 616 (2007).
6. M. Lopez Lazaro, C. Martin Cordero, F. Iglesias-Guerra, and J. Ayuso Gonzalez, *Phytochemistry*, **48**, 401 (1998).
7. C. Martin-Cordero, M. Lopez-Lazaro, J. Pinero, T. Ortiz, F. Cortes, and M. J. Ayuso, *J. Enzyme Inhib*., **15**, 455 (2000).
8. S. Louaar, S. Akkal, A. Bousetla, K. Medjroubi, L. Djarri, and E. Seguin, *Chem. Nat. Comp*., **41**, 107 (2005).
9. F. Martin-Cordero, M. Lopez Lazaro, A. Gil-Serrano, M. A. Rodriguez Carvajal, and J. Ayuso Gonzalez, *Phytochemistry*, **51**, 1129 (1999).
10. M. J. Ayuso, J. L. Espartero, M. Lopez-Lazaro, and C. Martin-Cordero, *J. Nat. Prod*., **63**, 248 (2000).
11. M. Lopez-Lazaro, C. Martin-Cordero, and M. J. Ayuso Gonzalez, *Z. Naturforsch*, **55**, 898 (2000).
12. T. J. Mabry, K. R. Markham, and M. B. Thomas, *The Systematic Identification of Flavonoids*, Springer, New York, 1970.
13. A. P. Rauter, A. Martins, C. Borges, J. Ferreira, J. Justino, M. R. Bronze, H. Ana, V. Coelho, H. Young Choi, and R. Verpoorte, *J. Chromatogr. A*, **1089**, **59** (2005).
14. R. Mekkiou, H. Touahar, M. G. Dijoux-Franca, A. M. Mariotte, S. Benayache, and F. Benayache, *Biochem. Syst. Ecol*., **33**, 635 (2005).