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J. Nat. Prod., **1991**, 54 (4), 1092-1093• DOI: 10.1021/np50076a027 • Publication Date (Web): 01 July 2004

Journal of Natural Products
Vol. 54, No. 4, pp. 1092-1093, Jul-Aug 1991

FLAVONOIDS OF *ASTERISCUS GRAVEOLENS*

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ABSTRACT.—The aerial parts of *Asteriscus graveolens* afforded a new flavonol glycoside, as well as ten known flavonoids. The structures were established by spectroscopic and chemical methods.

From the small genus *Asteriscus* (syn. *Odontospermum*, Tribe Inuleae, Asteraceae), mainly sesquiterpenes have been reported. *Asteriscus graveolens* (Forsck.) Less (syn. *Odontospermum graveolens* (Forssk.) Schultz and Bib. gave humulene derivatives (1), while *Asteriscus sericeus* afforded, in addition to humulenes, nerolidol derivatives (2). On the other hand, only farnesol glucosides have been detected in *A. pygmaeus*.[1] Since nothing has been reported on the flavonoids of the genus, we investigated *A. graveolens*.

From the aerial parts of *A. graveolens*, we isolated 11 flavonoids: namely, the previously unreported tamarixtin 3-*O*-β-D-robinobioside; the 3-*O*-β-D-glucosides, 3-*O*-β-D-galactosides, and 7-*O*-β-D-glucosides of both kaempferol and quercetin; the 7-*O*-β-D-glucoside of luteolin, and the three free aglycones, quercetin, quercetin 3,4′-dimethyl ether, and quercetagetin 3,6,3′-trimethyl ether.

The new compound appeared purple on paper under uv light changing to brownish-green with NH_3, indicating 4′-*O* substitution (6). The lack of color change with the reagent Naturstoff-reagenz-A (Carl Roth, Germany) suggested that the compound lacks a free 3′,4′-dihydroxy system. This was confirmed by the $AlCl_3$/HCl and NaOAc/H_3BO_3 uv spectra.

On the other hand, the uv spectral data in NaOAc, NaOMe, and $AlCl_3$ suggested a 3,4′-*O* disubstitution and a free 5,7,3′-trihydroxy system (6). The ^{1}H-nmr spectrum of the TMSi ether of the new compound in $CDCl_3$ was similar to that of the quercetin skeleton: one proton double doublet at δ 7.78 (J = 9 and 2.5 Hz, H-6′), one proton doublet at δ 7.33 (J = 2.5 Hz, H-2′), an ortho-coupled doublet at δ 6.85 (J = 9 Hz, H-5′), narrow meta-coupled doublets at δ 6.48 (J = 2.5 Hz, H-8) and 6.23 (J = 2.5 Hz, H-6), and a three-proton singlet at δ 3.73 for a methoxyl group. The presence of the H-6′ signal downfield from that of H-2′ confirmed that the methoxyl group was on the 4′-hydroxyl with a free 3′-hydroxyl group (3).

The sugar moiety exhibited a signal at δ 5.67 with a coupling constant of 7.5 Hz, which was typical for the anomeric proton of the β-D-galactopyranosyl moiety, while a narrow-coupled doublet at δ 4.2 (J = 2.5 Hz) and three-proton doublet (J = 7 Hz) at δ 1.14 were assigned for the anomeric and the methyl group, respectively, of the α-L-rhamnosyl moiety. The chemical shifts of the anomeric proton and the methyl group of the rhamnosyl moiety supported a 1↦6 linkage (4,5). Moreover, the structure was confirmed by positive fabms, which showed the molecular ion at *m/z* 625 followed by elimination of the rhamnosyl and galactosyl moieties at *m/z* 461 and 317, respectively. Positive fabms with a Na_2CO_3 matrix gave $[M + Na]^+$ at *m/z* 647.

[1]Based on unpublished data.

EXPERIMENTAL

PLANT MATERIAL.—*A. graveolens* was collected from Wadi Houf, near Cairo, Egypt. Voucher specimens (no. A. 125) are deposited at the Department of Botany, El-Minia University and the Herbarium of the National Research Centre (CAIRC).

EXTRACTION, ISOLATION, AND IDENTIFICATION OF FLAVONOIDS.—Air-dired aerial parts of *A. graveolens* (500 g) were extracted with 80% and 50% EtOH. The combined extracts were concentrated and chromatographed over polyamide (6S, Riedel-De-Haen-AG, Seelze, Hannover) eluted first with H_2O and then with increasing amounts of EtOH. The isolated compounds were purified over Sephadex LH-20 prior to analysis by uv, ^{1}H-nmr and ms techniques (6). Acid hydrolysis of the glycosides (2N HCl, 1h) yielded the sugar residues and the aglycones, all of which were co-chromatographed with authentic samples.

All uv data were recorded using the standard procedures (6). ^{1}H-nmr spectra of the TMSi ethers of all flavonoids were recorded in $CDCl_3$ at 90 MHz and reported as δ values (ppm) relative to TMS as internal standard. Known compounds were identified by comparison of their uv, ^{1}H nmr, ms, and R_f with those of authentic samples.

TAMARIXETIN-3-*O*-β-ROBINOSIDE.—R_f (Whatman no. 1) [*t*-BuOH–HOAcH_2O (3:1:1)] 0.21, (15% HOAc) 0.70. Color on paper under uv, purple; uv/NH_3, brownish-green; uv λ max (MeOH) 269, 275 sh, 334; (NaOMe) 278, 283 sh, 379; ($AlCl_3$) 273, 342; ($AlCl_3$/HCl) 276, 347; (NaOAc) 270, 385; (NaOAc/H_3BO_3) 267, 335; ^{1}H nmr (as the TMSi ether in $CDCl_3$, 90 MHz) δ 7.78 (1H, dd, J = 9 and 2.5 Hz, H-6′), 7.33 (1H, d, J = 2.5 Hz, H-2′), 6.85 (1H, d, J = 9 Hz, H-5′), 6.48 (1H, J = 2.5 Hz, H-8), 6.23 (1H, J = 2.5 Hz, H-6), 5.67 (1H, d, J = 7.5 Hz, H-1″), 4.2 (1H, d, J = 2.5 Hz, H-1‴), 3.73 (3H, s, OMe), 1.14 (3H, d, J = 7 Hz, H-6‴); fabms *m/z* (rel. int.) $[M + H]^+$ 625 (1.1), $[M - 164]^+$ 461 (1.4), $[aglycone + H]^+$ 317 (1.8); (with Na_2CO_3 as a matrix) *m/z* $[M + Na]^+$ 647 (85).

ACKNOWLEDGMENTS

The author thanks the Alexander von Humboldt-Stiftung for a fellowship.

LITERATURE CITED

1. S. El-Dahmy, J. Jakupovic, F. Bohlmann, and T.M. Sarg, *Tetrahedron*, **41**, 309 (1985).
2. J. Jakupovic, L. Lehmann, F. Bohlmann, and A.A. Hogdson, *Phytochemistry*, **26**, 2854 (1987).
3. A.A. Ahmed, A.A. Ashraf, and T.J. Mabry, *Phytochemistry*, **28**, 665 (1989).
4. A.A. Ahmed, T.J. Mabry, and S.A. Matlin, *Phytochemistry*, **28**, 1751 (1989).
5. H. Röser, T.J. Mabry, M.F. Cranmer, and J. Kagan, *J. Org. Chem.*, **30**, 4346 (1965).
6. T.J. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, New York, 1970, p. 270.

Received 6 March 1990