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A NEW 8-HYDROXYFLAVONOL FROM *LARREA TRIDENTATA*

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INTRODUCTION

In a continuation of our investigation of the flavonoids of *Larrea* species (Zygophyllaceae), we report here the isolation and structure determination of gossypetin 3,7-dimethyl ether (**1**), the third 8-hydroxyflavonol obtained from a hexaploid population of *Larrea tridentata* Cav. from Mojave Co., Arizona, the other two 8-hydroxyflavonols previously isolated from this species being gossypetin 3,7,3′-trimethyl ether and herbacetin 3,7-dimethyl ether [1]. In addition to these 8-hydroxyflavonols, 10 other flavonoids were previously identified from this species: kaempferol, its 3-methyl and 3,7-dimethyl ethers and 3-rhamnoglucoside, isorhamnetin, and quercetin and its 3-methyl and 3,7,3′-trimethyl ethers, 3-glucoside and 3-rhamnoglucoside [2,3].

The new 8-hydroxyflavonol (**1**) was isolated as orange crystals (from MeOH); λ_{max} MeOH 264sh, 278, 300sh, 344, 378 nm., the band Ia absorption at 378 nm is typical for 8-hydroxyflavonols and a similar absorption was observed for the two other 8-hydroxyflavonols (see above) isolated from the same plant. The new compound exhibited the same bluish color on paper under UV light as these two substances, both of which contain 3,7-methoxyl and 5,8-hydroxyl substitution. The color of **1** changed to yellow–green with ammonia (under UV light) supporting the presence of a free 4′-hydroxyl group. The presence of a B-ring *o*-dihydroxyl group was supported by a hypsochromic shift (22 nm) of band Ia in the $AlCl_3$–HCl spectrum in comparison with the $AlCl_3$ spectrum, and by a bathochromic shift (9 nm) of band I in $NaOAc$–H_3BO_3 spectrum in comparison with band I in the MeOH spectrum [4a]. A large bathochromic shift (60 nm) of band Ia in the $AlCl_3$–HCl spectrum (compared with the MeOH spectrum) appears to be typical for the presence of 5,8-hydroxyl groups in 3-*O*-substituted flavonols [1]; in any case, this result eliminated the possibility of oxygenation at C-6 [4b].

The mass spectrum of **1** exhibited a molecular ion at *m/e* 346 (51% intensity relative to the base peak) corresponding to $C_{17}H_{14}O_8$, that is, for a flavone with four hydroxyl and two methoxyl groups. An M-1 peak at *m/e* 345 (29%) supported the presence of an 8-hydroxyl group since the loss of a proton from an 8-hydroxyflavonol is a major fragmentation process. An intense peak (60%) at *m/e* 303 corresponded to a fragment ion $(M\text{-}COMe)^+$ typical for either a 3-, 6-, or 8-methoxyl group [5–11]; however, on the basis of the data presented above, **1** must contain a 3- rather than a 6- or 8-methoxyl function [5–13]. A very intense peak at *m/e* 183 (75%) and a peak at *m/e* 182 (49%) suggested the presence of a methoxyl group in the A-ring; a base peak at *m/e* 137 (B-ring plus CO) suggested the presence of a dihydroxyl system in the B-ring (see Fig. 1).

The NMR spectrum of the TMS ether of **1** in CCl_4 showed a singlet at δ 3·90 for six protons supporting the presence of two methoxyl groups at the 3- and 7-positions (8-methoxyl groups appear at δ 3·75–3·8 in many flavonols); a singlet at δ 6·23 for an H-6 proton; a doublet (J=8 Hz) at δ 6·84 for the H-5′ proton; a double doublet (J=8, and 2 Hz) at δ 7·67 for H-6′, and a doublet (J=2 Hz) at δ 7·77 for H=2′, supported the presence of a 3′,4′-dioxygenated B-ring. The NMR spectrum of the TMS ether of **1** in C_6D_6 showed two singlets at δ 3·27 (Δ + 0·63 ppm shift; typical for a 7-methoxyl group) and at δ 3·83

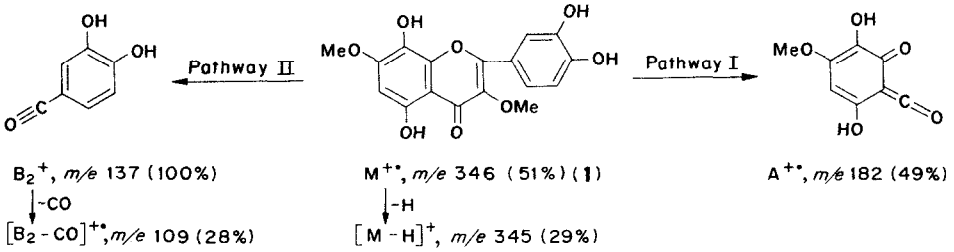

Fig. 1. MS fragmentations of gossypetin 3,7-dimethyl ether.

(Δ + 0·07 ppm; typical for a 3-methoxyl group) [14].

The above spectral findings indicated that compound **1** is a new 8-hydroxyflavonol corresponding to gossypetin 3,7-dimethyl ether.

EXPERIMENTAL

NMR spectra were measured at 60 MHz with tetramethylsilane as an internal standard.

Air-dried and ground leaf material from a hexaploid population of *Larrea tridentata* (collected in Mojave Co., Arizona, on July 1971 by Barbara Timmermann) was extracted with 85% aq MeOH; a voucher (B.T., n.s.) is deposited in the University of Texas at Austin Herbarium. The extract was filtered and evaporated down to an aq soln which was extracted with Et_2O. The ethereal extracts were combined, evaporated and taken to dryness *in vacuo*; 12 g of syrup were chromatographed over polyamide (560 g packed in Egger's solvent, $CHCl_3$–MeOH–MeCOEt–2,4-pentanedione, 20:10:5:1. Using Egger's solvent for elution, fractions of about 20 ml each were collected. Rechromatography of fractions 424–454 on a second column of polyamide with MeOH gave orange crystals of gossypetin 3,7-dimethyl ether after recrystallization from MeOH.

Gossypetin 3,7-dimethyl ether (1): MS peaks not noted in text: 317 (M-HCO; 9%), 182 (A^+; 49%), 173 (M^{2+}; 20%), 121 (48%), 109 (B^+; 28%); R_f values: 0·07 (Benzene-HOAc–H_2O; 6:7:3 upper phase) and 0·38 (25% HOAc); UV in MeOH: 264, 278, 300sh, 344, 378; NaOMe: 264, 396, 457sh (dec.); $AlCl_3$: 258sh, 284, 316, 420, 460; $AlCl_3$–HCl: 271sh, 285, 312, 361, 438; NaOAc: 263sh, 276, 301sh, 343, 395; NaOAc–H_3BO_3: 267, 301sh, 387 (Proc. II). NMR spectral data are described in the text.

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