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QUERCETAGETIN 6-*O*-β-D-GLUCOPYRANOSIDE FROM *TAGETES MANDONII*

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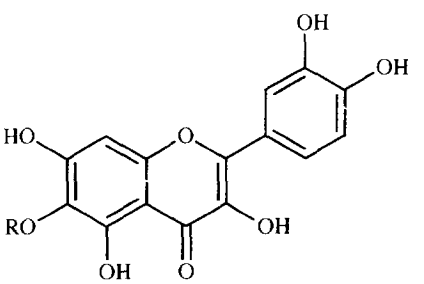
Key Word Index—*Tagetes mandonii*; Compositae; flavonol glycosides; quercetagetin 6-glycoside; ^{1}H and ^{13}C NMR.

Abstract—A new natural glycoside, quercetagetin 6-*O*-β-D-glucopyranoside, has been isolated from the methanol extract of the aerial parts of *Tagetes mandonii* and identified on the basis of ^{1}H and ^{13}C NMR and UV spectral data.

INTRODUCTION

Continuing our studies on the *Tagetes* genus (Compositae) [1], we have undertaken an investigation of the aerial parts of *Tagetes mandonii* Sch. Bip., a herbaceous plant widespread in the Peruvian Sierra where it is used for the treatment of gastrointestinal diseases and for its antidiarrhoic properties [2].

The present paper deals with the isolation of flavonol compounds, identified by NMR and UV spectral data as quercetagetin 6-glucoside (**1**), quercetin 3-glucoside (**2**), quercetin 3-rhamnoside (**3**), myricetin 3-glucoside (**4**) and rhamnetin (**5**). While the 7-*O*-glucoside [3–5] and the 3-*O*-glucoside [6] of quercetagetin are already known, **1** is a new natural product.



1 R = β-D-Glucopyranosyl

6 R = H

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of **1** showed the pattern of a quercetagetin *O*-glucoside. Thus, the signal located at δ 6.92 (1H, *s*) was ascribable to H-8, the only one proton of the ring A, while the 3H ABX system at δ 6.91 (*d*, J = 8.5 Hz), 7.77 (*d*, J = 2 Hz) and 7.68 (*dd*, J = 2 and 8.5 Hz) was consistent with the signals of a 3′,4′-disubstituted ring B of a flavonol [7]. Further features were signals corresponding to the anomeric proton (δ 5.10, *d*, J = 7.5 Hz) and to H_2-6 (δ 3.68, *dd*, J = 5 and 12 Hz; δ 3.88, *dd*, J = 3.5 and 12 Hz;) of a β-D-glucopyranosyl unit. The identity of the sugar was confirmed by ^{13}C NMR (Table 1) [8].

In the ^{13}C NMR spectrum the C-6, C-5 and C-7 signals of **1**, compared with the corresponding peaks for a sample of quercetagetin (**6**) obtained by acidic hydrolysis of **1** (Table 1) showed an upfield shift of 3.6 ppm and downfield shifts of 2.2 and 3.0 ppm, respectively. This, together with the presence of the peak at δ 137.0, characteristic of a free 3-hydroxyl [9], indicated that the glycosylation site was C-6. This hypothesis was further confirmed by UV bathochromic shifts of band I by adding powdered sodium acetate (7-hydroxyl free) and band III by adding aluminium chloride (5-hydroxyl free) (see Experimental) [10].

On the basis of these data **1** was identified as quercetagetin 6-*O*-β-D-glucopyranoside. The identification of known compounds quercetin 3-*O*-β-D-glucopyranoside (**2**), quercetin 3-*O*-β-D-rhamnoside (**3**), myricetin 3-*O*-β-D-glucopyranoside (**4**) and rhamnetin (**5**) was based on comparison with literature data [1, 8–9].

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Table 1. ^{13}C NMR data for **1** and **6** in CD_3OD (δ).

C	1	6
Aglycon		
2	146.7	146.7
3	137.0	137.0
4	177.4	177.2
5	150.2	148.0
6	130.7	134.3
7	148.8	145.8
8	95.2	95.3
9	152.7	151.0
10	106.5	104.6
1′	124.0	124.0
2′	116.0	115.9
3′	146.0	146.1
4′	148.8	148.8
5′	116.1	116.1
6′	121.8	121.6
Sugar		
1	102.5	
2	74.5	
3	77.3	
4	71.2	
5	78.3	
6	62.3	

EXPERIMENTAL

The NMR spectra were performed in CD_3OD at 500 MHz using the solvent shift as reference (δ 3.34 for ^1H and δ 49.0 for ^{13}C).

Plant material. Tagetes mandonii Sch. Bip. was collected in the region of Cusco (3800 mt above the sea level), Perù and identified by Dr Vincenzo De Feo, Facoltà di Farmacia, Università degli Studi di Salerno, Italy. A voucher specimen is deposited in the Herbarium of Cattedra di Botanica Farmaceutica (Dipartimento di Chimica delle Sostanze naturali, Università "Federico II", Napoli).

Extraction and isolation. The air-dried aerial parts (750 g) of *T. mandonii*, defatted with light petroleum and $CHCl_3$, were extracted with MeOH at room temp. The crude extract (40 g) was chromatographed on a Sephadex LH-20 column (80 × 4 cm) with MeOH in 2 g lots. Frs of 20 ml were collected and analysed by TLC (SiO_2) in BuOH–HOAcH–H_2O, 12:3:5. Frs 24–29 (1.9 g), further fractionated by HPLC on a C-18 μ-Bondapak column (30 cm × 7.8 mm i.d., flow rate 2.5 ml min^{-1}) using MeOH–H_2O, 2:3 as eluent, yielded **1** (25 mg, R_t 16 min), **4** (27 mg, R_t 19 min), **2** (40 mg, R_t 28 min), **3** (33 mg, R_t 50 min) and **5** (10 mg, R_t 52 min).

Acid hydrolysis. Compound **1** (6 mg) was refluxed for 2 hr in 6% HCl (3 ml). The hydrolysate was extracted with BuOH and the BuOH extract concd to dryness to give quercetagetin (**6**), identified by ^1H and ^{13}C NMR and UV analysis.

Compound **1**. ^1H NMR: δ 7.77 (1H, *d*, J = 2 Hz, H-2′), δ 7.68 (1H, *dd*, J = 2 and 8.5 Hz, H-6′), δ 6.92 (1H, *s*, H-8), δ 6.91 (1H, *d*, J = 8.5 Hz, H-5′); UV λ_{max}^{MeOH}: 259, 273 sh, 361; + $AlCl_3$ 278, 370 sh, 434; + $AlCl_3$ + HCl 264, 376, 416 sh; + NaOMe 284, 409; + NaOAc 282, 431; + NaOAc + H_3BO_3 252, 275 sh, 403 nm.

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