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XANTHONES OF *CENTAURIUM PULCHELLUM*

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Key Word Index—*Centaurium pulchellum*; Gentianaceae; 1-hydroxy-3,7,8-trimethoxyxanthone; 1,8-dihydroxy,3,7-dimethoxyxanthone; 1,8-dihydroxy-3,5-dimethoxyxanthone.

Abstract—1-Hydroxy-3,7,8-trimethoxyxanthone, 1,8-dihydroxy-3,7-dimethoxyxanthone and 1,8-dihydroxy-3,5-dimethoxyxanthone have been isolated from the whole plant of *Centaurium pulchellum*; the compounds were characterized by UV and NMR spectroscopy.

INTRODUCTION

Plants of the Gentianaceae are a rich source of xanthones [1]; there are, however, only few reports of the isolation of xanthones from the genus *Centaurium* [2, 3]. Thus van der Sluis reported [2] the isolation of 1,8-dihydroxy-3,5-dimethoxyxanthone, 1,8-dihydroxy-3,5,6,7,8-pentamethoxyxanthone and as a minor component 1-hydroxy-3,5,8-trimethoxyxanthone from the roots of *Centaurium littorale* (Turner) Gilmour. *Centaurium scilloides* (L.f.) Druce was found to have the same xanthones as *C. littorale*, whereas *C. minus* Moench was found to contain small amounts of the above mentioned xanthones. On the other hand, 1,8-dihydroxy-3,5,6,7-tetramethoxyxanthone has been reported from *C. erythraea* [3]. A TLC chromatograph of the xanthone constituents of *C. pulchellum* was published [4], but none of the xanthones was identified. We report herein the isolation and characterization of three tetra-oxygenated xanthones from the whole plant of *C. pulchellum* (SW) Druce.

RESULTS AND DISCUSSION

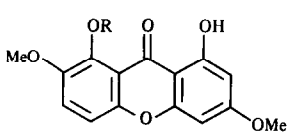
The following xanthones were obtained: 1-hydroxy-3,7,8-trimethoxyxanthone (**1**), 1,8-dihydroxy-3,7-dimethoxyxanthone (**2**) and 1,8-dihydroxy-3,5-dimethoxyxanthone (**3**).

Compound **1**, $C_{16}H_{14}O_6$, mp 160–161°, was found to be 1,3,7,8-tetraoxygenated xanthone from its UV spectrum which showed λ_{max} at 238, 258, 310 and 373 nm [5]. Its NMR spectrum showed the presence of 3 methoxyl groups at δ4.0, 3.91 and 3.85, a chelated hydroxyl group at δ13.28 and aromatic protons at δ6.35 (2H, singlet, due to completely overlapping protons in the pholoroglucinol ring) and δ6.75 (2H, quartet, J = 9.2 Hz, representing two AB pairs, arising from two *ortho* protons in the other ring). It was identified as **1** from its mp (160–161°) and the mp of its acetate (175–177°) which are very close to those reported for 1-hydroxy-3,7,8-trimethoxyxanthone (mp 159° and mp of its acetate 174.5–176.5° [6]). A comparison of the ^{1}H NMR spectrum of the acetate of **1** with that reported for 1-acetyl-decussatin [7], which are superimposable, confirmed the identity of the two.

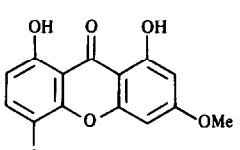
Compound **2**, $C_{15}H_{12}O_6$, mp 191° was also found to belong to the 1,3,7,8-tetraoxygenated series on the basis of the UV spectrum which showed λ_{max} at 240, 264, 312 and 374 nm [5]. The presence of two chelated hydroxyl groups at δ13.5 and 13.7 and two methoxyl groups at 3.81 and 3.57 confirmed the structure to be 1,8-dihydroxy-3,7-dimethoxyxanthone.

Compound **3**, $C_{15}H_{12}O_6$, mp 190°, on the other hand proved to be a 1,3,5,8-tetraoxygenated xanthone by its UV spectrum which showed λ_{max} at 240, 254, 315 and 337 nm [8]. The ^{1}H NMR spectrum showed the presence of two methoxyl groups at δ3.87 and 3.93, two chelated hydroxyl groups at 14.15 and 15.0 and four aromatic protons at 6.3 and 6.5 (2H, *dd*, J = 2 Hz, *meta* protons), and 6.64 and 7.18 (2H, *dd*, J = 9 Hz, *ortho* H). On this basis, **3** was identified as 1,8-dihydroxy-3,5-dimethoxyxanthone [3].

The co-occurrence of 1,3,7,8- and 1,3,5,8-tetraoxygenated xanthones in *C. pulchellum* is very interesting and may be of chemotaxonomic significance. Thus *Canscora decussata* [9–11], a plant of the same subtribe (Erythraeineae) to which *C. pulchellum* belongs, has yielded tetraoxygenated xanthones of the 1,3,5,6- and 1,3,7,8-types. It does not contain any 1,3,5,8- type of xanthones. On the other hand, both 1,3,7,8- and 1,3,5,8-types have been isolated from species of the genera *Swertia* [12–14] and *Gentiana* [15]. Thus, the xanthones of *C. pulchellum* bear a close relationship to those of *Swertia* and may indicate a close relationship between the two genera.



R
1 Me
2 H



3

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were recorded in $CDCl_3$ containing 1% TMS. Chemical shifts are expressed in ppm (δ).

Extraction of plant material. Dried, powdered plant (730 g) was extracted with MeOH (3 l.) for three days at room temp. The extract was filtered and concd under vacuum to give a semi-solid mass, which was taken up in water and extracted with C_6H_6, $CHCl_3$ and *n*-BuOH, respectively.

Isolation of xanthones. The C_6H_6 extract was concd (5.0 g) and chromatographed on a column of silica gel (150 g) and eluted with C_6H_6, C_6H_6–$CHCl_3$ (1:1) and $CHCl_3$, successively, collecting various fractions of 100 ml each. The fractions thus obtained were compared by TLC (silica gel plates using pure $CHCl_3$ as solvent) and those giving similar spots were combined.

Isolation of **1**. Fractions 1–6 eluted with C_6H_6 were concd and yielded yellowish green crystals of **1** (50 mg), which was recrystallized from $CHCl_3$, mp 160–161°, $C_{16}H_{14}O_6$. UV λ_{max}^{EtOH} nm (log ε): 238 (3.32), 258 (4.46), 310 (4.10) and 374 (4.00).

Isolation of **2**. Fractions 22–36 eluted with pure C_6H_6 were evaporated and the crystalline mass thus obtained recrystallized from $CHCl_3$ to yield yellow needles, (43 mg), $C_{15}H_{12}O_6$, mp 191°. ^1H NMR showed the presence of peaks at δ3.85, 3.87 (2 × OMe), 6.18 and 6.22 (*dd*, J = 2.0 Hz, 2 *meta* H), 6.65 and 7.10 (*dd*, J = 9.0 Hz, 2 *ortho* H).

Isolation of **3**. Fractions 37–45 eluted with C_6H_6–$CHCl_3$ (1:1) gave on evaporation yellow needles, mp 190°, $C_{15}H_{12}O_6$ (37 mg). UV λ_{max}^{EtOH} nm (ε): 240 (19 000), 254 (26 850), 315 (17 000) and 337 (11 150). The other spectral data are given in the text.

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