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# TWO XANTHONES FROM *IXANTHUS VISCOSUS*

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**Key Word Index**—*Ixanthus viscosus*; Gentianaceae; pentaoxygenated xanthones.

**Abstract**—From the aerial parts of *Ixanthus viscosus*, 1,8-dihydroxy-2,3,6-trimethoxy xanthone and 1,3,8-trihydroxy-2,6-dimethoxy xanthone, were isolated together with the iridoid glycosides, gentiopicroside, swertiamarine and loganic acid. The structures of the two xanthones were established by chemical and spectroscopic means.

## INTRODUCTION

*Ixanthus viscosus* Grieb (Gentianaceae) is endemic to the Canary Islands. In a previous study this species was reported as an alkaloid containing plant [1]. We have found no alkaloids but we have isolated instead two new pentaoxygenated xanthones and three iridoids glucosides, from the aerial parts of this species. Compounds of these types have also been reported as constituents of other genera of the Gentianaceae family [2–8].

## RESULTS AND DISCUSSION

Chromatography of the crude acetone extract obtained from *Ixanthus viscosus* afforded compounds **1** and **2** plus gentiopicroside [9–12], swertiamarine [9–12] and loganic acid [13, 14]. The latter three compounds were identified by comparison of their physical constants and spectral data with those of authentic specimens.

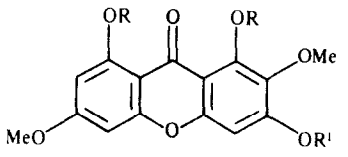
The $^1$H NMR spectrum of compound 1 showed eight signals, three singlets at $\delta$3.86 (3H), 3.88 (3H), 3.96 (3H), 3 OMe); three aromatic protons at 6.31 (1H, *d*, $J=2.5$ Hz), 6.35 (1H, *d*, $J=2.5$ Hz), 6.61 (1H, *s*) and two singlets at 11.92 (1H) and 12.19 (1H) assigned to hydrogen bridged phenolic protons. Its $^{13}$C NMR showed 16 signals; one carbonyl group ($\delta$182.5), 12 aromatic carbons (3*d* and 9*s*) and three methoxyl groups (55.9, 57.3, 60.1). The mass spectrum of **1** exhibited a molecular ion peak at *m/z* 318. These data were sufficient to consider the possibility of a pentasubstituted xanthone structure with two hydroxyl groups at C-1 and C-8, for compound 1.

Compound **1** afforded a diacetate derivative (**1a**) on treatment with acetic anhydride–pyridine the presence of two acetoxyl groups was confirmed by the $^1$H NMR spectrum of **1a**.

Compound **2** gave a mass spectrum with the highest peak at *m/z* 304, compatible with a molecular formula of $C_{15}O_7H_{12}$. The $^{13}$C NMR spectrum showed 15 signals, one carbonyl group ($\delta$182.5), 12 aromatic carbon signals (3*d* and 9*s*) and two methoxyl groups at 56.04 and 59.9. The $^1$H NMR spectrum confirmed the presence of three aromatic protons at $\delta$6.25 and 6.31 (two doublets with $J=2.5$ Hz) and 6.4 (1H, *s*); two methoxyl groups at 3.81 and 3.95 (3H each, *s*) and two associated phenol protons at 11.92 and 12.19. The analogy of this data with that obtained for compound **1**, suggested a pentasubstituted xanthone structure for **2**.

Compound **2** afforded a triacetate derivative (**2a**) on treatment with acetic anhydride–pyridine. The $^1$H NMR spectrum of **2a** confirmed the presence of three acetoxyl groups and gave an indication about their probable location. The singlet signal at $\delta$6.4 was shifted downfield by 0.6 ppm, while the two aromatic doublets at $\delta$6.25 and 6.31 were shifted by +0.2 and +0.3 ppm respectively. These observations suggested the presence of two free hydroxyl groups in *ortho*- and *para*-positions with regard to the uncoupled aromatic protons. The chemical shift of the methoxyl group on C-7 ($\delta$59.9) also confirmed the assigned position [15].

When compounds **1** and **2** were methylated with dimethyl sulphate and potassium carbonate in acetone




**1** R = H, R¹ = Me
**1a** R = Ac, R¹ = Me
**1b** R = R¹ = Me
**2** R = R¹ = H
**2a** R = R¹ = Ac

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under reflux (48 hr), they both afforded the same compound (**1b**). The $^1$H NMR spectrum and mp indicated that this compound was identical with 1,2,3,6,8-pentamethoxy xanthone [6].

## EXPERIMENTAL

Mps: uncorr. MS was determined at 70 eV, direct inlet. $^1$H and $^{13}$C NMR spectra were measured at 300 and 75 MHz, respectively, in $CDCl_3$ or DMSO soln, as indicated. Assignments were made with the aid of off-resonance and noise decoupled $^{13}$C NMR spectra. The assignments of $^{13}$C NMR spectra were based on ref. [15].

Plants of *Ixanthus viscosus* were collected in Monte de las Hiedras (Tenerife, Spain). Voucher specimens of the plants were deposited in the Herbarium of the Faculty of Pharmacy (Universidad de la Laguna).

*Extraction and isolation of the components of* Ixanthus viscosus. Dried and powdered plant material (aerial parts, 1.8 kg) were extracted with $Me_2CO$ (8 l) at room temp. for 3 days. After filtration the solvent was evapd yielding a gum (140 g). This gum was digested with EtOAc. The soluble fraction (60 g) was chromatographed on a silica gel column (Merck No. 7734, deactivated with 15% $H_2O$, 1.5 kg). Elution with *n*-hexane–EtOAc (4:1) successively yielded 1,8 dihydroxy-2,3,6-trimethoxy xanthone (**1**) and 1,3,8-trihydroxy-2,6 dimethoxy xanthone (**2**).

The insoluble residue obtained when attempting to dissolve the crude extract in EtOAc was examined by $^1$H NMR showing lack of acetoxyl signals. A portion of this residue (4 g) was treated with $Ac_2O$–pyridine. The resulting product was purified on a silica gel column using $CHCl_3$–$Me_2CO$ (4:1). The following known compounds were identified, gentiopicroside (600 mg), swertiamarine (800 mg) and loganic acid (600 mg) [mp, [α] and $^1$H NMR and $^{13}$C NMR spectra and comparison with literature data [9–14].

*Xanthone* **1**. 1,8-Dihidroxy-3,5,6-trimethoxy xanthone, yellow needles mp 177–178° ($Me_2CO$). $^1$H NMR (300 MHz, $CDCl_3$): δ11.99 (1H, *s*, OH), 11.96 (1H, *s*, OH), 6.61 (1H, *s*, H-4), 6.35 (1H, *d*, $J$=2.5 Hz) 6.31 (1H, *d*, $J$=2.5 Hz), 3-OMe at 3.96 (3H), 3.88 (3H) and 3.86 (3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ182.5 *s* (C-9), 163.8 *s* (C-6), 162.3 *s* (C-8), 160.1 *s* (C-3), 157.3 *s* (C-10a), 154.8 *s* (C-1), 152.9 *s* (C-4a), 130.2 *s* (C-2), 102.8 *s* (C-8a)[a], 102.3 *s* (C-9a)[a], 97.8 *d* (C-7), 92.1 *d* (C-5)[b] 91.2 *d* (C-4)[b], 60.1 *c* (OMe), 57.3 *c* (OMe), 55.9 *c* (OMe) ([ab]these assignments may be reversed).

*Compound* **1a**. Acetylation ($Ac_2O$–pyridine of **1** afforded **1a**. $^1$H NMR (300 MHz, $CDCl_3$): δ6.72 (1H, *s*, H-4), 6.63 (1H, *d*, $J$ =2.5 Hz), 6.47 (1H, *d*, $J$=2.5 Hz), 3-OMe at 3.91 (3H), 3.84 (3H), 3.80 (3H) and Me singlets at 2.44 (3H) and 2.38 (3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ172.5 *s* (C-9), 163.8 *s* (C-6), 158.2 *s* (C-3)[a], 158.0 *s* (10a)[a], 153.3 *s* (4a), 151.4 *s* (8), 143.7 *s* (1), 138.9 *s* (C-2), 109.3 *s* (C-9a)[b], 109.1 *s* (C-8a)[b], 107.3 *d* (C-7), 98.5 *d* (C-5), 97.6 *d* (C-4), 3-OMe at 55.9, 56.3 and 61.5. ([ab]these assignments may be reversed).

*Xanthone* **2**. 1,3,8-Trihidroxy-2,6-trimethoxy xanthone; yellow needles mp 231–233° (EtAc); $^1$H NMR (300 MHz, $CDCl_3$): δ12.19 (1H, *s*, –OH), 11.92 (1H, *s*, –OH), 6.4 (1H, *s*, H-4), 6.31 (1H, *d*, $J$=2.5 Hz), 6.25 (1H, *d*, $J$=2.5 Hz), 2-OMe at 3.95 (3H) and 3.81 (3H); $^{13}$C NMR (75 MHz, DMSO): δ182.5 *s* (C-9), 163.3 *s* (C-6), 161.9 *s* (C-8), 159.0 *s* (C-3), 156.9 *s* (C-10a), 153.4 *s* (C-1), 152.2 *s* (C-4a), 130.8 *s* (C-2), 101.0 *s* (C-9a)[a], 100.7 *s*(C-8a)[a] 97.1 *d*(C-7), 94.3 *d* (C-4), 92.7 *d* (C-5), 2-OMe at 56.04 and 59.9. ([a]these assignments may be reversed).

*Compound* **2a**. Acetylation ($Ac_2O$–pyridine) of **2** afforded **2a**. $^1$H NMR (300 MHz, $CDCl_3$): δ7.25 (1H, *s*, H-4), 6.69 (1H, *d*, $J$ =2.5 Hz), 6.48 (1H, *d*, $J$=2.5 Hz), 2-OMe at 3.84 and 3.78 and 3 acetyl Me singlets at 2.46, 2.35 and 2.28.

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