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A XANTHONE FROM *SENECIO MIKANIOIDES* LEAVES

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Key Word Index—*Senecio mikanioides*; Asteraceae; leaves; xanthones; 2-(2′-*O*-*p*-hydroxybenzoyl)-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone; muraxanthone.

Abstract—A new *p*-hydroxybenzoylated xanthone, [2-(2′-*O*-*p*-hydroxybenzoyl)-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone], muraxanthone, and four known xanthones have been isolated from the leaves of *Senecio mikanioides*. The structure of the new compound has been defined by means of FAB-mass spectrometry and a combination of homo- and hetero-nuclear one- and two-dimensional NMR techniques.

INTRODUCTION

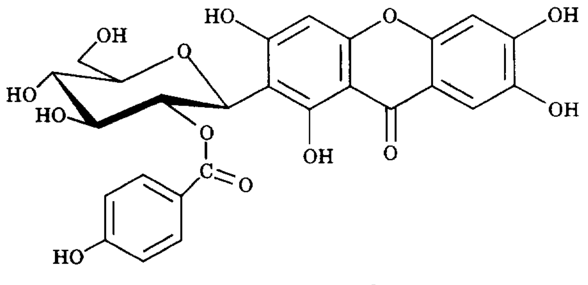
As a part of a phytochemical research on the genus *Senecio*, we have investigated *Senecio mikaniodes* Otto (ex Walpers). This species is a climbing plant typical of the African flora, but naturalized in South and West Europe, and growing wild in Italy (Liguria, Calabria, Sardegna). Previous phytochemical studies have determined only the presence of alkaloids [1]. We now report on the xanthones of this plant.

RESULTS AND DISCUSSION

We have isolated from the leaves a complex mixture of xanthones: mangiferin (**1**), isomangiferin (**2**), mangiferitin (**3**), tripteroside (**4**), in addition to a mangiferin derivative *p*-hydroxybenzoylated on the 2 position of the sugar moiety, the 2-(2′-*O*-*p*-hydroxybenzoyl)-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**5**) which we have named muraxanthone. Xanthones are relatively restricted in their natural distribution to the Guttiferae and Gentianaceae. Mangiferin is unique among the natural xanthones in having a wider occurrence (*Mangifera*, Anacardiaceae; *Heptaptera*, Umbelliferae; *Polystachya*, Orchidaceae) [2]. Among Asteraceae this xanthone has been found previously only in *Senecio tamoides* and *Dahlia australis* [3].

Mangiferin **1** was purified by crystallization from the $CHCl_3$–MeOH (9:1) extract and successive recrystallization from MeOH. Isomangiferin **2** was obtained from the MeOH extracted by chromatography on a polyamide column using MeOH–H_2O as eluents. Mangiferitin **3** and tripteroside **4** were isolated from the $CHCl_3$–MeOH (9:1) residue by Sephadex LH-20 gel filtration followed by HPLC. All the compounds were identified by comparison of their spectral data with those reported in literature [4–10]. Muraxanthone (**5**) was separated from the $CHCl_3$/MeOH (9:1) extract by mean of Sephadex LH-20 gel filtration followed by HPLC.

The FAB-mass spectrum of compound **5** shows a $[M + H]^+$ peak at *m/z* 543, consistent with the formula $C_{26}H_{22}O_{13}$, which was confirmed by ^{13}C NMR and DEPT experiments, and an adduct ion at *m/z* 565 $[M + Na]^+$. The IR spectrum revealed bands at 3500–3260 cm^{-1} for aliphatic and aromatic hydroxyl groups



5 muraxanthone

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Table 1. ^{13}C NMR data of mangiferin (**1**) and muraxanthone (**5**) (50 MHz, DMSO-d_6)

C	**1**	**5**	C	**1**	**5**
1	161.9	162.8	9 (C=O)	179.2	179.0
2	107.7	105.7	1′	73.2	70.7
3	163.9	161.6	2′	70.4	72.2
4	93.4	93.8	3′	79.1	76.5
4a	156.3	154.2	4′	70.7	70.7
4b	150.9	150.7	5′	81.7	81.9
5	102.7	102.6	6′	61.6	61.5
6	154.1	156.3	1″	—	120.8
7	143.8	143.8	2″/6″	—	131.0
8	108.1	108.0	3″/5″	—	115.0
8a	111.8	111.6	4″	—	161.6
8b	101.4	102.9	O—C=O	—	164.5

and at 1647, 1608 and 1587 cm^{-1} for a chelated carbonyl group. The presence of an aromatic carboxyl ester was also shown by the signal at 1700 cm^{-1}, in addition to that of an aromatic ring at 3270 and 1070 cm^{-1}. Moreover, the IR spectrum has a band characteristic of xanthone-*C*-glucosides at 893 cm^{-1} (C_1-H bending) [11]. The UV spectrum shows absorption maxima at 243, 265.5, 315.6 and 364.7 nm. The bathochromic shift of band IV with $AlCl_3$/HCl (35 nm) reveals the presence of a free 1-hydroxyl group and that of band III (23 nm) with NaOAc indicates unsubstituted hydroxyl groups at C-3 and C-6 [12].

The ^{1}H NMR spectrum, COSY, NOESY and HETCOR experiments confirm many of the above features and, in addition, reveal the presence of the mangiferitin nucleus and of an acylated glucopyranose (Table 1).

The *p*-hydroxybenzoyl structure of the ester moiety was first deduced from the FAB-mass spectral data, which shows fragments at 121 and 433 *m/z* owing to the loss of a *p*-hydroxybenzoyl group. This is confirmed by the two coupled doublets in the ^{1}H NMR spectrum: (2H each) at 6.71 and 7.60 δ ($J = 8.6$ Hz); these data are also supported by the ^{13}C NMR spectrum and by hydrolysis products (mangiferin and *p*-hydroxybenzoic acid). The aromatic region of the COSY spectrum reveals only the couplings of the AA′BB′ system of the *p*-hydroxybenzoyl moiety, while at higher fields the anomeric proton shows a cross peak in the COSY spectrum with the multiplet centred at 5.72 δ (H-2′); this unusual high value of chemical shift for this proton indicates that the site of benzoylation is the OH linked to C-2′. This situation is confirmed also by the typical ^{13}C NMR acylation shift (about 3 ppm downfield shift for the *ipso* carbon and about 3 ppm upfield shift for the vicinal carbons). The above indications are further confirmed by the HETCOR experiment that shows all the expected $^1J_{CH}$ correlations and permits to unambiguously assign all the resonances, particularly the protonic ones of the sugar moiety, previously evidence by the COSY spectrum. Therefore, compound **5** is 2-(2′-*O*-*p*-hydroxybenzoyl)-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone, a new compound which we named muraxanthone.

EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were recorded respectively at 200 and 50 MHz in DMSO-d_6 with a Bruker AC200 instrument; chemical shifts are given in δ values (ppm) with TMS as internal standard. FAB-MS were registered in positive-ion mode in a thioglycerol matrix using a VGZAB instrument. UV spectra were recorded in MeOH; IR spectra as nujol mulls. TLC were carried out on silica gel 60 F_{254} Merck plates. Semiprep. HPLC was carried out with a Shimadzu LC-8A pumps equipped with an UV detector SPD-6A in isocratic conditions ($CHCl_3$–MeOH–MeCN 81:14:5) using a Lichrospher 100 Diol column (250 × 10 mm).

Plant material. Senecio mikanioides cuttings collected in Cape Town (South Africa) were cultivated at Lucca Botanical Garden (Italy). The leaves were collected from 2-year-old plants on June 1993. A voucher specimen is deposited at Dipartimento di Chimica Bioorganica in Pisa (Italy).

Extraction and isolation of **5**. Dried leaves of *S. mikanioides* (720 g) were defatted with *n*-hexane and extracted in a Soxhlet apparatus with $CHCl_3$ and $CHCl_3$–MeOH (9:1). The crude $CHCl_3$–MeOH extract (10 g) was dissolved in hot MeOH, the unsoluble part was filtered and the solution chromatographed on a Sephadex LH-20 column eluting with MeOH. Twenty-two fractions (I–XXII) were collected and analysed by TLC with $CHCl_3$–MeOH–H_2O (6:4:1) as eluent. Fraction XVI was further purified with semiprep HPLC to give pure compound **5** (mg 73).

Compound **5** (muraxanthone): m.p. 203–204°; $[\alpha]_D^{22}$ $-108.6°$ (MeOH; *c* 0.163); UV λ_{max}^{MeOH} nm: 243, 256.5, 315.6, 364.7; $+AlCl_3$/HCl: 273.0 sh, 264.6, 338.8, 402.8; +NaOAc: 255.0, 278.3, 338.8, 401.9; FAB-MS (*m/z*): 543 $[M+H]^+$, 565 $[M+Na]^+$, 423 $[M+H-120]^+$, 121 $[C_7H_5O_2+H]^+$; ^{1}H NMR (200 MHz, DMSO-d_6) δ: 13.79 (1H, *s*, 1-OH), 7.60 (2H, *d*, $J = 8.6$ Hz, H2″ and H6″), 7.32 (1H, *s*, H8), 6.79 (1H, *s*, H5), 6.71 (2H, *d*, $J = 8.6$ Hz, H3″ and H5″), 6.29 (1H, *s*, H4), 5.72 (1H, *m*, H2′), 4.92 (1H, *d*, $J = 9.7$ Hz, H1′), 3.78 (1H, *m*, H4′), 3.73 (1H, *m*, H6′), 3.48 (1H, *m*, H3′), 3.29 (1H, *m*, H5′).

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