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Isolation and characterisation of sodium monocarboxylate ixoside salt from the bark of *Oxyanthus pallidus*

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Abstract

A sodium monocarboxylate ixoside salt (**1**) and four known compounds, ixoside (**2**), mannitol (**3**), uncargenine C (**4**) and oleanolic acid (**5**) have been isolated from the bark of *Oxyanthus pallidus*. Their structures were established on the basis of spectroscopic techniques.

Key words: *Oxyanthus pallidus*/ *Oxyanthus sankuruensis*/ *Oxyanthus schubotzianus*; 10-sodium monocarboxylate ixoside salt.

1. Introduction

Oxyanthus pallidus Hiern/ *Oxyanthus sankuruensis* De Wild/ *Oxyanthus schubotzianus* K. Krause is a small shrub widespread from Senegal to Nigeria, and extending from Sudan to Ethiopia (Hallé, 1970). Plants of the genus *Oxyanthus*, occupy a prominent position in traditional African medicine (Kawukpa and Angoyo, 1994; Chaaib, 2004; Bouquet, 1969; Adjonohoun et al., 1988; Iwu, 1986; Watt and Breyer-Brandwijk, 1962). Our previous contribution reported the isolation from the leaves of three new cycloartane glycosides (Tigoufack et al., 2010). In an extension of our studies, the methanol extract of the bark of *Oxyanthus pallidus* was examined in greater detail for minor concentrations of sodium monocarboxylate ixoside salt (**1**).

2. Results and Discussion

Compound **1**, C₁₆H₁₉O₁₁Na, which carbonized to a cinder without melt, was obtained as a black powder with optical rotation $[\alpha]_D^{25} +24^\circ$ (MeOH, *c*....). HR-ESI-MS in negative-ion

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mode showed a molecular ion peak at m/z 387.0927 $[M-Na]^-$ in agreement with the molecular formula $C_{16}H_{19}O_{11}$. The presence of the sodium ion in this molecular formula was deduced from the HR-ESI-MS in positive-ion mode. The study of its IR spectrum indicated the presence of hydroxyl group ($3500-3360\text{ cm}^{-1}$), carbonyl (1726 cm^{-1}), and carbon carbon double bond (1645 cm^{-1}). The ^1H NMR spectrum (table) showed characteristic signals of iridoid glycoside type of ixoside (Guarnaccia et al., 1972; Yoshio et al., 1975; Luciano et al., 2010). Indeed, two allylic protons were observed at δ 2.35 (1H, dd, $J = 1.8$ and 18.1 Hz, H-6 β), 2.87 (1H, dd, $J = 8$ and 18.1 Hz, H-6 α) and two vinylic protons at δ 6.52 (1H, dd, $J = 1.8$ and 8 Hz, H-7), 7.34 (1H, s, H-3). Signals observed at δ 3.17 (1H, m, H-9) and δ 3.32 (1H, m, H-5)] were attributed to the iridan methine groups. The signal observed at δ 5.62 (1H, d, $J = 4.7$ Hz, H-1) is attributed to the iridan acetal group due to the downfield shift. Remaining protons observed between 4.63-3.30 ppm are those of a β -glucopyranosyl moiety. Structure **1** was clarified by HMBC experiments. Indeed, the connectivity of the β -D-glucopyranosyl moiety was elucidated on the basis of HMBC correlations, observed between H-1' (δ_{H} 4.63, d, $J = 7.8$ Hz) and C-1 (δ 95.1) at the one hand H-1 (δ_{H} 5.62) and C-1' (δ 98.6) at the other, as showed on figure. The ^{13}C NMR spectrum of **1** was almost superimposable on that of ixoside (**2**) (see table), except for carbons C7 and C8 and the fact that carbon atoms of the two carbonyl groups, C-10 and C-11 appear together at the same value of δ 171.9 ppm. However, these carbon atoms were clearly observed at δ 166.7 and 169.2 for C-10 and C-11 respectively, after adding a drop of TFA in the nmr tube. The relative stereostructure of **1** was characterized by NOESY experiment; the strong NOE correlation observed between H-9 at δ_{H} 3.17 and H-5 at δ_{H} 3.32 suggested their β -orientation (Guarnaccia et al., 1972; Yoshio et al., 1975; Kanchanapoom et al., 2002; Luciano et al., 2010). The absence of NOE correlation between H-1 at δ_{H} 5.62 and H-9 at δ_{H} 3.17; H-5 at δ_{H} 3.32 confirmed the α -orientation of H-1. All these informations allowed us to suggest that, the stereostructure of compound **1** was elucidated to be a sodium monocarboxylate ixoside salt.

Structures (**2-5**) were determined by means of *Co* TLC, spectroscopic data, and by comparative analysis of physical and spectral data with those in the literature Takeda et al., 1975; Pouchet et al., 1970; Yang et al., 1995; Meicai, 2008). TLC retention time, obtained for compounds **1** and **2** in the mixture AcOEt-MeOH-H₂O (7:2:1) are 0.43 and 0.28 respectively.

Table. ^1H and ^{13}C NMR data of compounds **1** and **2** in CD_3OD .

H	1	2	C	1	2
position	$\delta^1\text{H}$ (mult., $J(\text{Hz})$)	$\delta^1\text{H}$ (mult., $J(\text{Hz})$)	position	$\delta^{13}\text{C}$	$\delta^{13}\text{C}$
1	5.62 (1H, d, 4.7)	5.70 (1H, d, 5.0)	1	95.1	94.9
3	7.34 (1H, s)	7.51 (1H, s)	3	149.4	152.1
			4	114.7	111.1
5	3.32 (1H, m)	3.33 (1H, m)	5	34.3	33.6
6 α	2.87 (1H, ddd, 17.5, 8.2, 2.5)	2.94 (1H, ddd, 17.6, 8.0, 2.3)	6	38.7	33.8
6 β	2.35 (1H, ddd, 17.5, 8.2, 2.5)	2.47 (1H, ddd, 17.6, 8.0, 2.3)			
7	6.52 (1H, brd, 1.6)	6.92 (1H, bd, 1.7)	7	138.8	146.6
9	3.17 (1H, m)	3.22 (1H, m)	8	141.0	135.0
			9	46.7	46.0
			10	171.9	166.7
			11	171.9	169.1
Glc-1'	4.63 (1H, d, 7.8)	4.65 (1H, d, 7.9)	1'	98.6	98.9
2'	3.23 (1H, dd, 8.6, 7.8)	3.22 (1H, dd, 8.5, 7.9)	2'	73.2	73.2
3'	3.38 (1H, dd, 8.9, 8.6)	3.36 (1H, dd, 8.9, 8.5)	3'	76.3	76.4
4'	3.31 (1H, dd, 8.9, 8.5)	3.32 (1H, dd, 8.9, 8.6)	4'	70.1	70.0
5'	3.30 (1H, m)	3.29 (1H, m)	5'	76.7	76.8
6' α	3.67 (1H, dd, 12.2, 2.2)	3.70 (1H, dd, 12.1, 2.1)	6'	61.3	61.2
6' β	3.85 (1H, dd, 12.2, 2.2)	3.88 (1H, dd, 12.1, 2.1)			

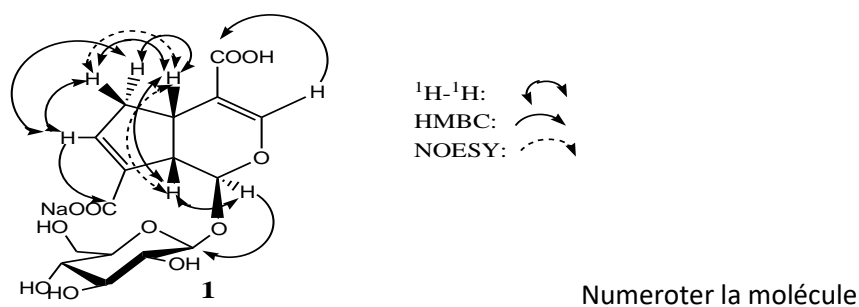
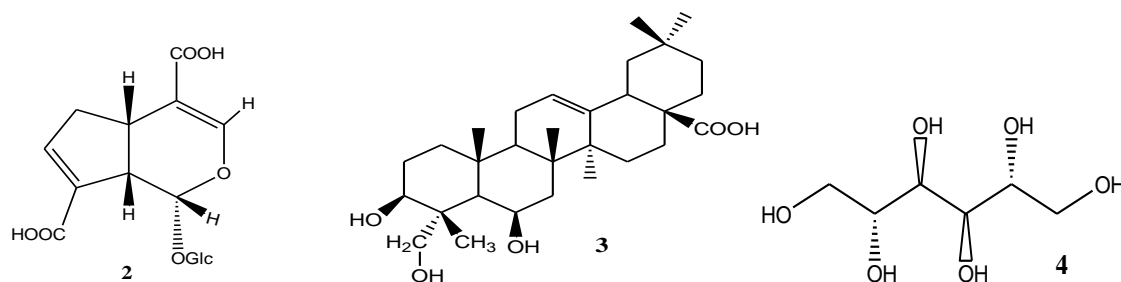
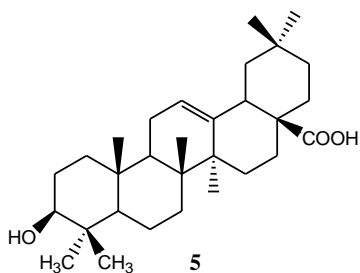


Figure: ^1H - ^1H COSY, HMBC and NOE Correlations of compound **1**





3. Experimental

3.1. General experimental procedures

All melting points were recorded with a Reichter microscope and uncorrected. I.R spectra were recorded with a Shimadzu FTIR-8400 spectrometer. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in CD_3OD on a Bruker Avance DRX-500 spectrometer. Chemical shifts (δ) are reported in parts per million with solvent signals δ_{H} 3.31 and δ_{C} 49.1 as references, while the coupling constants (J) are given in Hertz. HR-ESI-MS experiments were performed using a Micromass Q-TOF micro instrument (Manchester, UK) with an electrospray source. Column chromatography was run on Merck silica gel 60 and Sephadex LH-20 while TLC were carried out on silica gel GF₂₅₄ precoated plates with detection accomplished by spraying with 50% H_2SO_4 followed by heating à 100° C.

3.2. Plant Material

Barks fo *Oxyanthus pallidus* were collected in the city of Dschang, Cameroon, in March 2010 and identified by Mr. Nana François of the National Herbarium of Cameroon. A voucher specimen (n° 7335/ SFR/ CAM) was deposited at the National Herbarium of Cameroon, Yaounde, Cameroon (YA).

3.3. Extraction and isolation

The air-dried and finely powdered material (4.5 kg) was extracted with MeOH (10 l) in a glass tank at room temperature. After complete removal of solvent under vacuum evaporation, a dark residue (132 g) was obtained. Part of this, (52 g) was fractionated, on silica gel (40-63 μm , 98 g) column chromatography, eluted with a Ethyl acetate, followed by a mixture of EtOAc containing 10-70% amounts of MeOH, yielding five fractions (A-E). Chromatography of ethyl acetate fraction A (2g), on silica gel using hexane-EtOAc (1:1), yielded oleanolic acid. Fraction C (357.3 mg), was obtained with EtOAc-MeOH (8:2); when the mixture solvent was distilled off, a precipitate was formed in the bottom flask and recuperated with

Ethyl acetate; under vacuum filtration of crude crystal, 43.7 mg of mannitol were obtained. Fraction D (2.4 g) obtained with a mixture of Ethyl acetate and MeOH (7:3) was purified over sephadex gel using MeOH and silica gel using the mixture of EtOAc-MeOH-H₂O (8:1:1) to yield compound **2** (30.8 mg). Sub-fraction D-3 (80 mg), was purified over the silica gel column chromatography, using the mixture of EtOAc-MeOH-H₂O (8:1:1) to yield compound **1** (15 mg).

3.4. Compound 1

$[\alpha]_D^{25} +24$ (CH₃OH, c); IR ν_{\max} (NaCl) cm⁻¹: 1726 (C=O); 1271 (C-O); ¹H and ¹³C (CD₃OD) : See table; HR-ESI-MS (negative-ion mode) m/z 387.0927 [M-Na]⁻ (calculated for C₁₆H₁₆O₁₁: 387.0931).

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