10-Hydroxyaloin B 6′-*O*-Acetate, an Oxanthrone from *Aloe claviflora*

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Analysis of the leaf exudate of *Aloe claviflora* resulted in the isolation of a new oxanthrone, 10-hydroxyaloin B 6′-*O*-acetate (**1**), whose structure was determined on the basis of spectral evidence as well as by conversion to the known compound 10-hydroxyaloin B (**2**).

Aloe species are known to elaborate anthrones, the most common of which is aloin or barbaloin. Recently, a number of oxanthrones based on the aloin skeleton have been discovered, in particular in leaves of *Aloe* species that belong to the series *Asperifoliae*.[1−3] *Aloe claviflora* Strydenburg (Aloaceae), which also belongs to this series, is the only species of *Aloe* that occurs in Strydenburg, Free State Province, South Africa.[4] Subjecting the methanolic extract of the leaf exudate of this species to column chromatography over reversed-phase Si gel yielded the oxanthrone (**1**), which exhibited pseudomolecular ions at *m*/*z* 477 ($[M + H]^+$) and 499 ($[M + Na]^+$) in its positive ion FABMS, indicating an M_r of 476. The HRESIMS of **1** revealed a $[M + Na]^+$ peak at *m*/*z* 499.1228, which corresponded to the molecular formula $C_{23}H_{24}O_{11}$ (see Tables 1 and 2). The IR spectrum of **1** suggested the presence of hydroxyl (3385 cm^{-1}), unconjugated ester carbonyl (1718 cm^{-1}), and chelated carbonyl (1636 cm^{-1}) functional groups.

The ^{13}C-NMR spectrum of **1**, including the DEPT measurements, showed 23 carbon atoms comprising 1 methyl (δ 20.6), 2 oxymethylenes (δ 64.6, 64.9), 10 methines, and 10 quaternary carbons, of which two are carbonyls. The presence of two chelated hydroxyl groups was further confirmed from the ^1H-NMR spectrum, which showed two singlets at δ 11.67 and 11.75. Assignments of the five aromatic protons and the other ^1H-NMR signals are shown in Table 1.

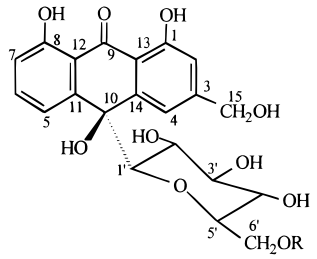
The acetate unit was placed at C-6′ of the glucose moiety due to the downfield shift of the signals of these methylene protons in **1** (δ 3.75, 4.12) relative to those in **2** (δ 3.32, 3.50). Acid hydrolysis of **1** yielded the known compound **2**, an observation that also served to prove the α orientation of the glucose group at C-10, insofar as this fact was established earlier[2] for **2** by comparing its CD spectrum with that reported by Rauwald and Lohse.[1] Thus, compound **1** was assigned as 10-hydroxyaloin B 6′-*O*-acetate.

The remaining compounds were identified as the recently described oxanthrones littoraloin and deacetyllitoraloin by comparison with authentic samples, HPLC analysis, and spectral data.[2,3] Compound **1** was reported earlier as an unknown with t_R 22.4 by HPLC, and it was also indicated that it is one of the chemotaxonomic markers for the series *Asperifoliae* of *Aloe*.[3]

Table 1. ^1H NMR Spectral Data of 10-Hydroxyaloin B 6′-*O*-acetate (**1**) and 10-Hydroxyaloin B (**2**) (300 MHz, MeOH-d_4)[a]

proton	**1**	**2**
OH-1	11.67[b](s)	11.76[b](s)
OH-8	11.75[b](s)	11.81[b](s)
2	6.99 (d, 1.1)	6.87 (d, 1.5)
4	7.56 (d, 1.1)	7.40 (d, 1.5)
5	7.45 (dd, 8.0, 0.7)	7.32 (dd, 7.8, 1.0)
6	7.67 (t, 8.0)	7.62 (t, 7.8)
7	7.02 (dd, 8.0, 0.7)	6.93 (dd, 7.8, 1.0)
H_2-15	4.58 (s)	4.60 (s)
1′	3.25 (d)	3.23 (d)
2′	3.12 (t)	3.08 (t)
3′	3.34 (t)	3.38 (t)
4′	2.81 (t)	2.92 (t)
5′	3.07 (m)	2.98 (m)
$6'_1$	4.12 (dd, 11.8, 1.9)	3.50 (dd)
$6'_2$	3.75 (dd, 11.8, 7.2)	3.32 (dd)
OAc	2.01 (s)	

[a] In parentheses are given the multiplicities of the signals and the coupling constants *J* in Hz. [b] Spectrum recorded in DMSO-d_6.



1 R = Ac
2 R = H

Experimental Section

General Experimental Procedures. The melting point was determined with Kofler apparatus and is uncorrected. The optical rotation was measured on a Perkin−Elmer 241 polarimeter. The UV spectrum was obtained on Milton Roy Spectronic 1001 Plus instrument. The IR spectrum was taken with a Perkin−Elmer 1600 series FT-IR spectrometer. The NMR spectra (MeOH-d_4, 300 MHz for ^1H and 75 MHz for ^{13}C) were recorded on a Bruker AMXR 300 NMR spectrometer with TMS as internal standard. The FABMS (positive ion mode) was conducted on a Finnigan MAT 95Q double-focusing mass spectrometer with a cesium gun: glycerin matrixes. Column chromatography was carried out over reversed-phase Si gel with PrepPAK

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Table 2. ^{13}C-nmr Spectral Data of 10-Hydroxyaloin B 6′-*O*-acetate (**1**) and 10-Hydroxyaloin B (**2**) (75 MHz, MeOH-d_4)[a]

carbon	1	2
1	162.4	162.3
2	114.9	114.5
3	152.9	152.9
4	115.4	115.4
5	118.9	118.1
6	136.3	136.1
7	118.2	117.7
8	162.8	162.5
9	194.4	194.2
10	77.3	76.7
11	146.2	146.5
12	117.7	117.2
13	116.5	115.6
14	149.8	148.8
15	64.6	64.2
1′	84.2	84.1
2′	72.8	72.7
3′	79.2	79.1
4′	71.2	71.5
5′	78.7	80.9
6′	64.9	63.0
$OCCH_3$	172.3	
$OCCH_3$	20.6	

[a] Signal assignments are based on ^{1}H−^{13}C COSY and DEPT.

500 (Waters Associates). The HRESIMS was recorded on MAT 95Q with API II interface and electrospray head.

Plant Material. A bulk sample of leaf exudate of *Aloe claviflora* was collected at Strydenburg, Free State Province, South Africa, in January 1996, and identified by B.-E.V.W. A voucher specimen has been deposited at the Botany Department, Rand Afrikaans University.

Extraction and Isolation. The MeOH-soluble portion of the leaf exudate (5 g) of *A. claviflora* was subjected to column chromatography over reversed-phase Si gel eluting with MeOH and H_2O gradients. The fourth fraction, which was eluted by MeOH−H_2O (1:1), resulted in the isolation of a pale yellow substance (**1,** 80 mg) after removal of H_2O by freeze-drying. The remaining fractions were further purified by preparative TLC ($CHCl_3$−MeOH, 4:1), which gave the yellow substances littoraloin, deacetyllitoraloin, and 10-hydroxyaloin B (**2**).

10-Hydroxyaloin B 6′-*O*-acetate (1): yellow amorphous solid; mp 296−298 °C; $[\alpha]^{23}_D$ −41° (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ϵ) 270 (3.62), 300 (4.20), 370 (4.43) nm; IR (KBr) λ_{max} 3385 (br), 2924, 1718, 1636, 1616, 1560, 1456, 1422 cm^{-1}; ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2); FABMS (positive ion mode) *m/z* 499 $[M + Na]^+$(10), 477 $[M + H]^+$ (1), 459 $[M + H - H_2O]^+$ (9), 272 $[M + H - Glc - 6'\text{-}OAc]^+$ (14); HRESIMS $[M + Na]^+$ at *m/z* 499.1228, calcd for $C_{23}H_{24}O_{11}$, 499.1216, R_f 0.6 ($CHCl_3$-MeOH, 4:1).

Hydrolysis of Compound 1 to 10-Hydroxyaloin B (2). A solution of **1** (8 mg) in 1% methanolic HCl (2 mL) was stirred for 6 h at room temperature. After removal of the solvent, the reaction mixture was neutralized with 10% $NaHCO_3$ and extracted with EtOAc to give a product (4 mg) identical with **2** (co-TLC and ^{1}H NMR).

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References and Notes

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