

# METHOXYCOUMAROYLALOERESIN, A C-GLUCOSIDE FROM *ALOE EXCELSA*

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(Received 5 January 1987)

**Key Word Index**—*Aloe excelsa*; Liliaceae; aloesin; C-glycosides; *p*-methoxycoumaroylaloeresin.

**Abstract**—The leaves of *Aloe excelsa* afforded, aloesin, anthraquinones and a new compound 2-*p*-methoxycoumaroylaloeresin whose structure, 2-acetyl-7-hydroxy-8-*C*- $\beta$ -*D*-[2'-*O*-(*E*)-*p*-methoxycoumaroyl]-methylchromone, was established by spectral and chemical means.

## INTRODUCTION

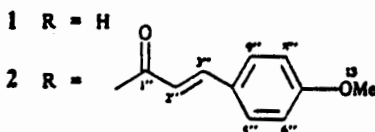
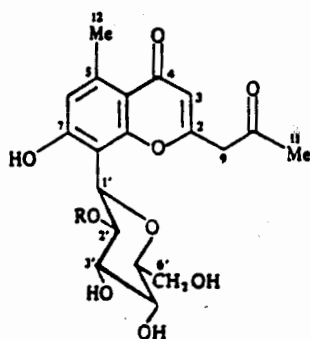
The leaves of *Aloe excelsa* A. Berger, which is widely distributed in southern Africa, are commonly used in traditional medicine to treat venereal sores, asthma and abdominal pains [1]. Many aloe species contain anthraquinones, anthrones, chromones and their C-glycosyl derivatives [2-4]. I report here a chemical investigation of the dried leaf surfaces of *Aloe excelsa* which resulted in the isolation of a new natural compound, *p*-methoxycoumaroylaloeresin (2) and known compounds, aloesin (1) [5], homonataloin [6], aloin [4] and 1,5-dihydroxy-3-hydroxymethylanthraquinone [7] from the acetone extract.

## RESULTS AND DISCUSSION

The compound 2, C<sub>29</sub>H<sub>30</sub>O<sub>11</sub>, gave a dark green colour with ferric chloride and dissolved in aqueous sodium hydroxide indicating its phenolic nature. The IR spectrum showed two carbonyl bands at 1652 and 1716 cm<sup>-1</sup> and an hydroxyl group band at 3340 cm<sup>-1</sup>. The UV spectrum had maxima at 226, 250 (sh) and 297 nm. Both spectra correspond closely with those of 1. The presence of the aloesin system is supported by the <sup>1</sup>H NMR spectrum (CD<sub>3</sub>COCD<sub>3</sub>), which showed three singlets at  $\delta$  2.36, 2.74 and 3.94 for the acetyl, aromatic and methoxyl methyl groups, respectively. The D<sub>2</sub>O exchangeable singlet at

$\delta$  10.00 was attributed to the unchelated phenolic hydroxyl group. The glucosyl protons appeared as multiplets at  $\delta$  3.40-3.90 and the methylene protons of the acetyl group appeared as a singlet at  $\delta$  3.84. The singlets at  $\delta$  6.18 and 6.85 were ascribed to the olefinic proton (H-3) and the aromatic proton (H-6), respectively. The remaining <sup>1</sup>H NMR signals at  $\delta$  3.94 (s, OMe) and a set at 6.08 (d, *J* = 16 Hz, 1H) and 7.36 (d, *J* = 16 Hz 1H) (typical AB pattern of *trans* olefinic protons) and another set at 6.88 (d, *J* = 8.6 Hz, 2H) and 7.48 (d, *J* = 8.6 Hz, 4H) (typical AA'BB' pattern of a 1,4-disubstituted aromatic compound) and the <sup>13</sup>C NMR data (Experimental) indicated the substitution of an (*E*)-*p*-methoxycoumaroyl unit in the aloesin parent structure. The position of the *p*-methoxycoumaroyl unit was deduced from the most deshielded triplet peak at  $\delta$  5.68 which was assigned to a glucosyl proton on the acylated carbon [8]. The acylation position was determined to be at C-2' by a spin decoupling experiment. Irradiation of a doublet peak at  $\delta$  5.16 (H-1'), second most deshielded, simplified only the triplet peak at  $\delta$  5.68 to a doublet. This signal was assigned to the proton H-2' of the acylated carbon.

Definitive proof of the principal structure was obtained from hydrolysis of 2 with sodium methoxide in methanol which afforded 1, identified by co-TLC and mmp with an authentic sample, and *p*-methoxycoumaric acid, identified by its <sup>1</sup>H NMR and MS data analysis. The results of the



hydrolysis further proved that the methoxyl group is attached to the coumaroyl unit (C-7") and not to the aloesin system (C-7). Further support for structure 2 was obtained from its mass spectrum which shows the molecular ion peak at  $m/z$  554, loss of the *p*-methoxycoumaric acid at  $m/z$  376 and the presence of the *p*-methoxycoumaroyl fragment ion at  $m/z$  161.

### EXPERIMENTAL

Leaves of *Aloe excelsa* collected from the University of Zimbabwe campus, Harare, Zimbabwe were skinned. The skins were air-dried, powdered and extracted with  $\text{Me}_2\text{CO}$ . After removal of the solvent, the extract was subjected to CC over silica gel when 2 was obtained with  $\text{MeOH}-\text{CHCl}_3$  (1:3). The known C-glucosides were obtained in larger quantities by CC using  $\text{H}_2\text{O}-\text{MeOH}-\text{CHCl}_3$  (1:14:10) as eluent. The red pigment; 1,5-dihydroxy-3-hydroxymethylanthraquinone [7] was obtained from prep. TLC with  $\text{MeOH}-\text{CHCl}_3$  (1:9) from the  $\text{CHCl}_3$  extract of the  $\text{Me}_2\text{CO}$  residue. All isolated known compounds were identified by direct comparison (mp, TLC, and  $^1\text{H NMR}$ ) with authentic samples.

*Z*-*p*-Methoxycoumaroylaloerisin (2). 2 was recryst. from  $\text{EtOAc}$  as light yellow crystals, mp 138–140°, soluble in  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  soln. UV  $^{\text{EtOH}}$  nm (log): 226 (4.41), 251 sh (3.90), 298 (4.14); IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3340, 1716, 1652, 1602, 1515, 1460, 1380, 1166, 916, 835, 759.  $^1\text{H NMR}$  ( $\text{Me}_2\text{CO}-d_6$ ):  $\delta$  2.35 (s, 3H, aromatic methyl), 2.74 (s, 3H, acetylonyl methyl), 3.45–4.00 (m, 8H, glucosyl protons), 3.86 (s, 2H, acetylonyl methylene), 3.94 (s, 3H, aromatic methoxyl), 5.16 (d, 1H, H-1'), 5.69 (t, 1H, H-2'), 6.08 (d, 1H, H-2"), 6.18 (s, 1H, H-3), 6.85 (s, 1H, H-6), 6.88 (d, 2H, H-6 and H-8"), 7.35 (d, 1H, H-3"), 7.48 (d, 2H, H-5") and H-9"), 9.90 [s br, 1H, phenolic

proton].  $^{13}\text{C NMR}$  ( $\text{DMSO}-d_6$ ):  $\delta$  22.7 (C-12), 29.7 (C-11), 48.3 (C-9), 55.9 (C-13), 61.5 (C-6'), 70.4 (C-1'), 70.6 (C-4'), 72.1 (C-2'), 77.8 (C-3') 81.8 (C-5'), 110.8 (C-8), 112.8 (C-3), 114.6 (C-2"), 115.6 (C-6", 8"), 115.7 (C-4a), 116.8 (C-6), 125.0 (C-4"), 130.1 (C-5", 9"), 141.8 (C-5), 144.6 (C-3"), 157.4 (C-1a), 159.7 (C-7), 160.6 (C-2), 161.3 (C-7"), 165.4 (C-1"), 178.6 (C-4), 202.1 (C-10). MS  $m/z$ : (rel. int.): 554 ( $[\text{M}]^+$ , 15), 408 (2), 376 ( $[\text{M} - \text{C}_{10}\text{H}_{10}\text{O}_3]$ , 2), 341 (7), 275 (100), 259 (14), 256 (47), 233 (61), 193 (15), 178 (4), 161 (8).

*Alkaline hydrolysis*. 2 was dissolved in 1% KOH in MeOH and soln was refluxed for 2 hr. After evap. of MeOH, the residue was diluted with  $\text{H}_2\text{O}$  and acidified with dil HCl. The soln was first extracted with  $\text{Et}_2\text{O}$  and then *n*-BuOH. The  $\text{Et}_2\text{O}$  extract, after chromatography, showed a molecular ion  $m/z$  178 in the MS and the same  $^1\text{H NMR}$  spectrum as (*E*)-*p*-methoxycoumaric acid, while the *n*-BuOH extract showed the same UV spectrum and chromatographic behaviour as 1.

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