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ALOERESINS E AND F, TWO CHROMONE DERIVATIVES FROM *ALOE PEGLERAE*

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Key Word Index—*Aloe peglerae*; Asphodelaceae; 5-methylchromone; aloesin; cinnamoyl esters.

Abstract—The structures of two new aloesin derivatives isolated from *Aloe peglerae*, *viz.*, 2-acetonyl-8-(2-*O*-cinnamoyl-β-D-glucopyranosyl)-7-β-D-glucopyranosyloxy-5-methylchromone (aloeresin E) and 2-acetonyl-8-(2-*O*-cinnamoyl-β-D-glucopyranosyl)-7-hydroxy-5-methylchromone (aloeresin F) were determined by spectroscopic methods. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

According to Reynolds [1], *Aloe peglerae* occupies a taxonomic position in *Aloe* series *Longistylae* Berger. However, morphological and chemotaxonomic evidence has shown that *Aloe* series *Longistylae* is an unnatural group and that the three species constituting this group, *A. peglerae*, *A. longistyla* and *A. broomii*, have different leaf exudate compositions and morphological characters (B.-E. van Wyk and A. M. Viljoen, unpublished results). HPLC analysis of the methanol extract of the leaves of *A. peglerae* revealed, apart from the known metabolites, aloesin (**1**), homonataloin A and homonataloin B, the presence of two unidentified compounds that are of particular importance in the chemotaxonomic study of the genus *Aloe*. We now report the isolation and identification of these two compounds.

RESULTS AND DISCUSSION

Aloesin (**1**), homonataloin A and homonataloin B were identified by comparison with authentic samples (HPLC, retention times and UV data). The UV spectra of the two unknown compounds were closely related to that of aloesin (**1**) and these two compounds were named aloeresin E (**2**) and aloeresin F (**3**), respectively. The M_r of aloeresin F (**3**) was determined by FAB-mass spectrometry ($[M]^+$ *m/z* 524). The fragmentation pattern observed in the EI-mass spectrum suggested the presence of a cinnamoyl ester (*m/z* 147, 131 and 77). The ^1H and ^{13}C NMR data of the key structural features of aloeresin E, *viz.*, the acetonyl, γ-pyrone, 5-Me, 7-OH and 8-*C*-glucoside, were in close agreement with those reported for aloesin [2, 3], confirming the similarity between the two compounds. In addition, the NMR data also revealed the presence of a cinnamoyl ester residue (δ_H 6.37 and 7.37, $J = 16$ Hz, *trans*-α,β-unsaturated carbonyl; δ_H 7.37 and 6.60, monosubstituted phenyl; δ_C 165.1, ester carbonyl). The remaining ambiguity, i.e. the position of the cinnamoyl group, was resolved by chemical shift considerations. The triplet at δ_H 5.49 collapsed upon irradiation of the signal at δ_H 4.92 (*d*, assigned to H-1′) and was assigned to H-2′. The chemical shift of this signal is characteristic of a proton influenced by the anisotropic effect of an ester carbonyl; the cinnamoyl group was, therefore, located at C-2 of the carbohydrate moiety. On the basis of this evidence, structure **3** was assigned unequivocally to aloeresin F.

The M_r of aloeresin E (*m/z* 686) was determined by FAB-mass spectrometry. This information, with support of NMR data, suggested that the only difference between the structures of aloeresins E (**2**) and F (**3**) was the presence of an additional *O*-glucoside moiety in aloeresin E (**2**). The differences in chemical shifts observed for the aromatic carbons of aloeresin E (**2**) and of aloeresin F (**3**) indicated that the 7-hydroxyl group, and not one of the carbohydrate hydroxyl functions, had been subjected to glucosidation. Structure **2** was, therefore, assigned to aloeresin E. The close agreement of the spectroscopic data of aloeresin E (**2**) with those of aloeresin C, another 7-*O*-β-D-glucosyl derivative of aloesin [4], confirmed the assigned structure.

Although cinnamic acid derivatives are present in other *Aloe* metabolites, e.g. in the aloin series [5],

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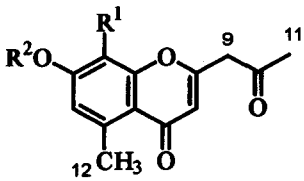
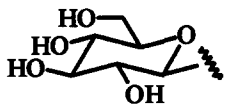


1: R^1 =



$R^2 = H$

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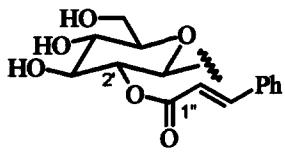

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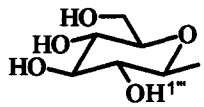

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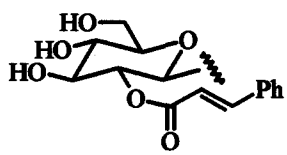

$R^2 = H$

aloeresin E (**2**) and aloeresin F (**3**) represent the first cinnamic acid derivatives in the aloeresin series of metabolites.

EXPERIMENTAL

Analytical HPLC analysis was performed on a C_{18} column (5μ, 4.5 × 250 mm, flow 1 ml min^{-1}) with the following gradient system: 30% MeOH in H_2O (1 min), 30%–60% MeOH in H_2O (25 min) and 60%–100% MeOH (2 min). Peaks were detected with a photodiode array detector. For prep. HPLC a C_{18} column (5μ, 10 × 250 mm, flow 4.5 ml min^{-1}) was used with the following gradient system: 30%–50% MeOH in H_2O (4 min), 50% MeOH in H_2O (9 min) and 50%–100% MeOH (2 min).

Isolation of metabolites. Fresh, chopped leaves (771 g) of *A. peglerae* were soaked in MeOH (24 hr, room temp.) to dissolve the exudate. After filtration and evapn, a dark brown residue (12 g) was obtained. Analysis of the sample by analytical HPLC revealed the presence of aloesin (R_t 6.9, 30%), aloeresin E (R_t 20.1, 22%), aloeresin F (R_t 25.1, 12%), homonataloin B (R_t 26.1, 7%) and homonataloin A (R_t 27.8, 10%). A portion of the extract (0.95 g) was subjected to prep. HPLC to afford aloeresins E (11 mg) and F (5 mg).

Table 1. ^{13}C NMR data of compounds **2** and **3** (50 MHz, DMSO-d_6)

C	2	3	C	2	3
2	160.7	160.7	4′	70.1	70.8
3	112.6	112.6	5′	81.5	81.9
4	178.5	179.0	6′	61.7	61.9
4a	115.1	114.7	1″	165.1	165.4
5	141.3	141.2	2″	118.1	118.0
6	116.6	116.1	3″	143.7	144.5
7	157.4	158.7	4″	134.2	134.1
8	112.1	109.1	5″,9″	128.8	129.2
8a	158.1	159.8	6″,8″	128.1	128.4
9	47.9	48.2	9″	130.2	130.7
10	202.1	202.8	1‴	101.0	—
11	29.5	29.8	2‴	73.2	—
12	22.8	22.8	3‴	76.4	—
1′	69.6	70.8	4‴	70.8	—
2′	72.4	72.8	5‴	77.1	—
3′	74.9	76.1	6‴	60.5	—

Aloeresin E. Amorphous solid. $[\alpha]_D^{20}$ −126° (MeOH, *c* 1.4). UV λ_{max}^{MeOH} (nm) 285, 250, 215. ^1H NMR (200 MHz, DMSO-d_6): δ 2.26 (3H, *s*, H-11), 2.61 (3H, *s*, H-12), 3.2–3.8 (13H, *m*, sugar-H), 3.80 (2H, *s*, H-9), 4.46 (1H, *br s*, OH), 4.58 (1H, *br s*, OH), 4.74 (1H, *d*, *J* = 7.5 Hz, H-1‴), 5.1–5.3 (3H, *m*, H-1′, 2 × OH), 5.44 (1H, *t*, *J* = 9 Hz, H-2′), 5.78 (1H, *br s*, OH), 6.21 (1H, *s*, H-3), 6.33 (1H, *d*, *J* = 16 Hz, H-2″), 6.95 (1H, H-6), 7.38 (3H, *m*, H-6″, 7″, 8″), 7.48 (1H, *d*, *J* = 16 Hz, H-3″), 7.62 (2H, *m*, H-5″, 9″). ^{13}C NMR: see Table 1. EIMS: *m/z* (rel. int.): 376 (4), 245 (5), 163 (10), 147 (21), 131 (20), 103 (24), 85 (20), 73 (53), 71 (41), 60 (47), 43 (100). FAB-MS: *m/z* 687 $[M + 1]^+$.

Aloeresin F. Amorphous solid. $[\alpha]_D^{20}$ −120° (MeOH, *c* 0.8). UV λ_{max}^{MeOH} (nm) 285, 250, 215. ^1H NMR (200 MHz, DMSO-d_6): δ 2.25 (3H, *s*, H-11), 2.55 (3H, *s*, H-12), 3.2–3.6 (6-H, *m*, sugar-H), 3.77 (2H, *s*, H-9), 4.46 (1H, *br s*, OH), 4.92 (1H, *d*, *J* = 10 Hz, H-1′), 5.20 (1H, *br s*, OH), 5.26 (1H, *br s*, OH), 5.49 (1H, *t*, *J* = 10 Hz, H-2′), 6.14 (1H, *s*, H-3), 6.37 (1H, *d*, *J* = 16 Hz, H-2″), 6.57 (1H, *s*, H-6), 7.37 (4H, *m*, H-3″, 6″, 7″, 8″), 7.60 (2H, *m*, H-5″, 9″). ^{13}C NMR: see Table 1. EIMS: *m/z* (rel. int.): 524 (8), 376 (34), 298 (10), 285 (12), 261 (33), 257 (43), 245 (28), 219 (25), 215 (24), 147 (100), 131 (78), 103 (66), 91 (27), 77 (46), 51 (27), 43 (84). FAB-MS: *m/z* 547 $[M + Na]^+$, 525 $[M + 1]^+$.

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