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CHROMONE AND ALOIN DERIVATIVES FROM *ALOE BROOMII*, *A. AFRICANA* AND *A. SPECIOSA*

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Key Word Index—*Aloe africana*; *A. broomii*; *A. speciosa*; Asphodelaceae; 5-methylchromone; aloin; aloesin; ferulic acid; coumaric acid; caffeic acid; cinnamic acid; electrospray mass spectrometry (ES-MS).

Abstract—Four new 5-methylchromone derivatives, namely (*E*)-2-acetonyl-8-(2′-*O*-feruloyl)-β-D-glucopyranosyl-7-methoxy-5-methylchromone from *A. africana*, (*E*)-2-acetonyl-8-(2′,6′-di-*O*,*O*-coumaroyl)-β-D-glucopyranosyl-7-hydroxy-5-methylchromone from *A. speciosa*, (*E*)-2-acetonyl-8-(2′-*O*-caffeoyl)-β-D-glucopyranosyl-7-methoxy-5-methylchromone and (*E*)-2-acetonyl-8-(2′-*O*-caffeoyl)-β-D-glucopyranosyl-7-methoxy-5-methyl-chromone along with 6′-*O*-cinnamoyl-5-hydroxyaloin A and 5-hydroxyaloin A from *A. broomii*, were isolated. The structures of the new compounds were determined on the basis of spectroscopic methods including ES-MS.

INTRODUCTION

The composition of *Aloe* leaf exudates have been investigated extensively [1]. The compounds that have been identified can generally be classified into two main groups, namely chromones and anthraquinones. In some cases both types are present, and in other cases only one. Furthermore, many of the major constituents such as aloesin (**1**), and aloin A and B (**2**) occur in chemotaxonomically distinct species. We have started a detailed screening of *Aloe* using a new approach, viz. HPLC coupled to electrospray mass spectrometry (ES-MS) with the aim of identifying unique constituents which may be used as markers with possible chemotaxonomic significance. We now report the first results from this investigation which resulted in the isolation of five new compounds (**3**, **4**, **5**, **6** and **7**) from *Aloe africana* Mill. from section *Pachydendron*, *A. broomii* Schonl. from the artificial series *Longistylae* Berger and *A. speciosa* Bak. from the monotype series *Principales* Berger [2]. We also report for the first time ES-MS spectra of these compounds and show that they provide valuable structural information.

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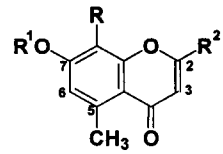
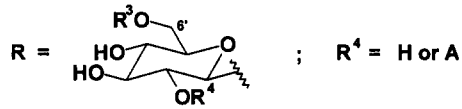
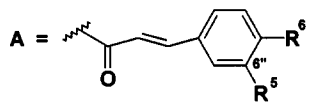
RESULTS AND DISCUSSION

HPLC analysis and TLC of the exudate of *A. africana* revealed the presence of aloesin (**1**), aloin A and B (**2**), aloinoside A and B and an unidentified compound (**3**) [1]. The purification of **3** was effected by low temperature flash chromatography over silica gel in a methanol–chloroform mixture. The compound (**3**) exhibited absorption maxima in its UV–VIS spectrum characteristic of *C*-glucosylated 5-methylchromones [3]. The ^{1}H and ^{13}C NMR (see Experimental and Table 1) spectra have characteristics similar to those of aloeresin A (**8**) [4, 5], except for (i) the simple AA′BB′ pattern for the protons of the coumaric ester were replaced by an ABX pattern for three protons, thus indicating the presence of a ferulic ester and (ii) the spectrum contains a 3-proton singlet of a methoxyl group. This compound (**3**) corresponds to the 7-methyl ether of 2″-feruloylaloesin isolated by Makino *et al.* [6]. The difference in chemical shifts observed between the aromatic carbons of **3** and aloesin (**1**) was consistent with the methylation of the 7-hydroxyl group. The ester group of **3** is attached to C-2′ of the carbohydrate moiety. The corresponding H-2′ resonates at δ_H 5.47. The assignment of all ^{1}H and ^{13}C signals of this and all other compounds described herein were confirmed using COSY [7], TOCSY [8], ROESY [9], HMQC [10] and HMBC [11].







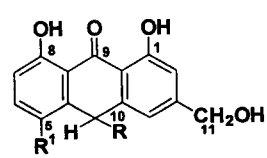
	R^1	R^2	R^3	R^4	R^5	R^6
1	H	CH_2COCH_3	H	H	-	-
3	Me	CH_2COCH_3	H	A	OMe	OH
4	H	CH_2COCH_3	coumaroyl	A	H	OH
6	Me	CH_2COCH_3	H	A	OH	OH
7	Me	CH_2COCH_3	H	A	H	H
8	H	CH_2COCH_3	H	A	H	OH
9	β-D-Glc	CH_2COCH_3	H	A	H	OH
11	Me	$CH_2CH(OH)CH_3$	H	A	OH	OH

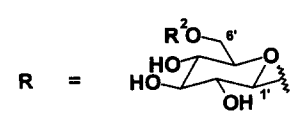
Strong peaks with *m/z* 583 $[M - 1]^-$ and *m/z* 407 $[M - 177]^-$ were observed in the negative mode ES-MS spectrum. The loss of a fragment with mass 177 could be interpreted as the loss of a $COCH{=}CHC_6H_3(OCH_3)(OH)$ fragment from a ferulic acid derivative. This fragmentation is followed by the loss of water from *m/z* 407. The spectrum showed no peaks corresponding to the subsequent loss of the carbohydrate moiety after the loss of the acyl group. In contrast, the negative ES-MS of aloesin (**1**) showed a strong $[M - 1]^-$ ion and a base peak at *m/z* 272 corresponding to the loss of the carbohydrate moiety. This information allows formulation of **3** as (*E*)-2-acetonyl-8-(2′-*O*-feruloyl)-β-D-glucopyranosyl-7-methoxy-5-methylchromone.

In addition to homonataloin [12], HPLC analysis of the leaf exudate of *A. speciosa* indicated the presence of a previously unidentified compound (**4**). This unknown **4** was isolated by low temperature flash chromatography. The UV–VIS spectrum of **4** was closely related to that of aloeresin C (**9**) while the negative mode ES-MS showed a strong $[M - 1]^-$ peak at *m/z* 685. Other strong peaks in the high mass range resulted from the consecutive loss of a fragment of mass 147 (equivalent to $COCH{=}CHC_6H_4OH$) and water.

The ^1H and ^{13}C NMR data (see Experimental and Table 1) of **4** were in close agreement with those reported for the chromones of the aloeresin series [4]. The presence of four sets of doublets in the aromatic region of the ^1H spectrum suggested the presence of two coumaric acid ester residues. The ^{13}C NMR showed the expected two sets of signals for two coumaroyl residues (see Table 1). The remaining ambiguity, i.e. the positions of attachment of the coumaroyl groups, was resolved on the basis of the low field positions of H-6′a and H-6′b at δ_H 4.52 and 4.06, respectively, and H-2′ at δ_H 5.49, and confirmed using COSY [7], TOCSY [8], ROESY [9], HMQC [10] and HMBC [11].

Preparative HPLC (reverse phase) was used to isolate the four compounds **5**–**7** and **10** from the leaf





2 $R^1 = R^2 = H$

5 $R^1 = OH$, $R^2 =$ caffeoyl

10 $R^1 = OH$, $R^2 = H$

Table 1. ^{13}C NMR (125.76 MHz) chemical shifts of **3**, **4**, **6** and **7**

C	3*	4*	6*	7†
2	160.6	160.1	160.6	159.8
3	112.5	112.5	112.5	112.9
4	178.6	178.4	178.5	178.6
4a	115.6	114.7	115.6	116.2
5	141.8	140.9	141.7	143.1
6	111.5	114.8	111.5	111.1
7	159.7	159.8	159.6	155.5
8	110.8	108.7	110.8	110.3
1a	157.4	159.8	157.4	156.0
9	47.9	48.1	47.9	48.7
10	202.1	202.3	202.1	201.8
11	29.6	29.2	29.5	29.4
5-Me	22.7	22.5	22.7	23.2
1′	70.4	70.7	70.4	71.0
2′	72.2	72.0	72.2	72.3
3′	75.8	75.6	75.7	76.5
4′	70.6	70.4	70.5	70.8
5′	81.9	78.3	81.8	80.1
6′	61.5	64.4	61.5	62.1
1″	165.4	165.4	165.3	163.9
2″	114.2	114.0	113.7	117.4
3″	144.6	144.4	144.6	144.4
4″	125.5	125.1	125.3	134.0
5″	111.1	130.1	114.6	127.7
6″	147.9	115.7	145.5	128.7
7″	149.2	158.3	148.3	130.1
8″	115.5	115.7	115.7	128.7
9″	122.9	130.1	121.1	127.7
7-OMe	55.5[a]	—	56.4	56.0
6″-OMe	56.3[a]	—	—	—
1‴	—	166.7	—	—
2‴	—	114.0	—	—
3‴	—	144.9	—	—
4‴	—	125.0	—	—
5‴ & 9‴	—	130.3	—	—
6‴ & 8‴	—	115.7	—	—
7‴	—	159.1	—	—

*Solvent: DMSO-d_6.
†Solvent: 5% DMSO-d_6 and $CDCl_3$.
[a]Signals interchangeable.

Table 2. ^{13}C NMR (125.76 MHz) chemical shifts of **5*** and **10***

C	5	10	C	5	10
1	161.3	161.3	2′	78.9	77.2
1a	116.5	116.8	3′	71.2	71.4
2	113.0	112.8	4′	71.4	70.1
3	151.3	151.0	5′	77.1	77.8
4	116.1	115.8	6′	62.6	63.6
4a	144.5	144.9	1″	—	166.9
5	145.9	145.7	2″	—	114.2
5a	124.9	124.9	3″	—	144.6
6	124.1	123.8	4″	—	126.4
7	116.4	116.2	5″	—	114.8
8	155.4	155.3	6″	—	147.7
8a	117.6	117.8	7″	—	145.1
9	193.8	193.8	8″	—	115.6
11	63.4	63.3	9″	—	121.3
1′	83.8	83.8			

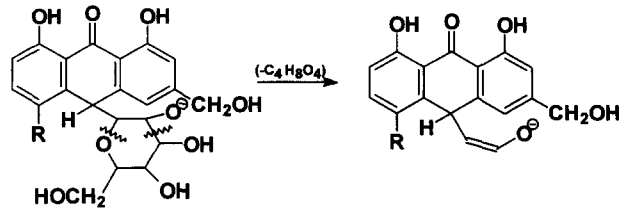
*Solvent: 5% DMSO-d_6 and $CDCl_3$.

exudate of *A. broomii*. The major component was identified as 5-hydroxyaloin A **10**, previously described as a constituent of this *Aloe* species [13]. However, the evidence for the structure was incomplete, particularly with regard to NMR data [14–17]. The structure was therefore confirmed on the basis of a complete analysis of ^1H and ^{13}C NMR data (see Experimental and Table 2) of **10**, including the use of COSY [7], HMQC [10] and HMBC [11]. It is of interest to note that the negative mode ES-MS spectrum showed a strong $[M - 1]^-$ parent ion at *m/z* 433 while the base peak at *m/z* 271 resulted from the loss of the sugar moiety, $C_6H_{11}O_5$, from the parent molecule. A moderately abundant ion at *m/z* 313 probably results from the loss of a $C_4H_8O_4$-fragment from the $[M - 1]^-$ parent ion. The loss of this fragment from the $[M - 1]^-$ parent ions of aloin A and B (**2**) and homonataloin give rise to the base peaks of the negative mode ES-MS spectra of these molecules. In the case of aloin A and B (**2**) this fragmentation is tentatively rationalized in Scheme 1. The FAB-spectrum of **10** showed the corresponding positive ions at *m/z* 435 and 272, respectively, together with a fragment with *m/z* 255, probably resulting from the loss of OH.

The other three compounds of *A. broomii* (**5**, **6** and **7**) have not been described previously. The FAB-spectrum of compound (**5**) showed a strong $[M + 1]^+$ parent ion at *m/z* 597 corresponding to the caffeoyl ester of 5-hydroxyaloin (**10**). Fragment ions at *m/z* 433 (weak) and 271 (strong) corresponded to the loss of caffeoyl and caffeoyl plus carbohydrate moieties from the parent molecule. A further fragment ion with *m/z* 314 corresponds to the loss of the ester group together with a four carbon fragment (*vida supra*) of the carbohydrate moiety. The negative ES-MS spectrum showed a strong $[M - 1]^-$ parent ion at *m/z* 595 and a significant fragment ion at *m/z* 271. The deductions on the basis of the mass spectra were confirmed by the ^1H and ^{13}C NMR (see Experimental and Table 1) spectra, e.g. the position of attachment of the ester moiety followed from the appearance of the low field positions of H-6′a and H-6′ at δ_H 4.20 and δ_H 3.78, respectively, as well as extensive decoupling experiments.

The negative ES-MS spectrum of the second new compound (**6**) from *A. broomii* showed a strong $[M - 1]^-$ parent ion at *m/z* 569 which was tentatively interpreted as that of a caffeoyl ester of aloesin (**1**). The compound was formulated as (*E*)-2-acetonyl-8-(2′-*O*-caffeoyl)-β-D-glucopyranosyl-7-methoxy-5-methylchromone (**6**) on the basis of its ^1H and ^{13}C NMR spectra (see Experimental and Table 1). The corresponding dihydro compound, rabaichromone **11** is a known constituent of *A. rabaiensis* [19].

The negative ES-MS of **7** showed a strong $[M - 1]^-$



: R = H *m/z* 417 *m/z* 297 (base)

Scheme 1.

parent ion at *m/z* 537 and fragments at *m/z* 407 and 389 corresponding to the consecutive loss of the cinnamoyl group and water. From the low field signal at δ_H 5.42 it followed that the ester group is attached to C-2 of the carbohydrate moiety.

The molecular mass of this and all other compounds described herein was confirmed by positive mode ES-MS. However, these spectra showed more extensive and complex fragmentation patterns than the corresponding negative mode ES-MS.

The types of compound isolated in this study can be regarded as typical of the genus *Aloe* and may prove to have some chemotaxonomic significance. Evidence is provided that ES-MS is a valuable tool for the identification and structural elucidation of *Aloe* exudate components.

EXPERIMENTAL

General. NMR: 500.13 MHz and 125.76 MHz for ^1H and ^{13}C, respectively, using DMSO-d_6 as solvent and TMS as int. standard unless otherwise stated. EI-MS and FAB-MS (glycerol matrix, Ar bombarding gas) were recorded on a VG-7070e spectrometer and ES-MS on a VG-QUATR spectrometer; CC: Silica gel (Merck, 230–400 mesh); TLC: (Merck, $60F_{254}$).

Plant material. Leaf exudate samples from *Aloe africana* were collected near Ann's Villa and from *A. speciosa* in the Zuurberg (both on the road between Paterson and Cookhouse in the Eastern Cape); the *A. broomii* samples came from a locality 130 km south of Bloemfontein. Since these characteristic species were identified *in situ* by the *Aloe* taxonomist Dr Ben-Erik van Wyk, no voucher specimens were collected.

Procedures. The exudate samples were pre-cleaned using C_{18} cartridges, with MeOH as solvent. They were then dissolved in a MeOH–H_2O (1 : 1) mixt. and studied by HPLC using a Phenomenex IB-Sil C_{18} reverse phase column (5 μm particle size, 250 × 4.6 mm internal diameter for analytical runs; flow rate 1 ml min^{-1}; 20 μl sample loop). The solvent system was a 30–60% linear gradient of MeOH in H_2O over 25 min, 3 min isocratic, 100% in 2 min, 4 min isocratic. A diode array detector with two channels (A set at 275 ± 70 nm; B set at 365 ± 40 nm) was used.

Extraction and isolation (A. africana). The yellow exudate was dissolved in MeOH. After filtration, the solvent was removed *in vacuo* to provide a brown residue which contained one unknown compound with R_f 0.33 (MeOH–$CHCl_3$, 2 : 8). Analysis of the sample with the analytical HPLC system revealed the presence of aloesin (**1**), aloin A and B (**2**), aloinoside A and B and **3** (R_t 21.48). A portion (1 g) of the residue was flash chromatographed on silica gel (100 g) at low temp. (−15°C) in MeOH–$CHCl_3$ (1 : 9). The sepn was monitored by TLC and analytical HPLC.

(E)-2-*Acetonyl*-8-(2′-O-*feruloyl*)-β-D-*glucopyranosyl*-7-*methoxy*-5-*methyl-chromone* (**3**). Amorphous solid (7.8%). UV λ_{Max}^{MeOH} nm: 326 sh, 298, 238 sh, 217. ^1H NMR: δ_H 2.26 (3H, *s*, 11-Me), 2.68 (3H, *s*, 5-Me), 3.36 (2H, 2 × *m*, H-4′ and H-5′), 3.42 (1H, *m*, H-6′a), 3.50 (1H, *m*, H-3′), 3.73 (1H, *m*, H-6′b), 3.77 (3H, *s*, 7-OMe), 3.80 (2H, *s*, H-9), 3.84 (3H, *s*, 6″-OMe), 4.4 (1H, *t*, *J* = 5.8 Hz, 6′-OH), 4.94 (1H, *d*, *J* = 10.1 Hz, H-1′), 5.13 (1H, *d*, *J* = 4.9 Hz, 4′-OH), 5.21 (1H, *d*, *J* = 5.4 Hz, 3′-OH), 5.47 (1H, *t*, *J* = 9.5 Hz, H-2′), 6.17 (1H, *d*, *J* = 15.9 Hz, H-2″), 6.18 (1H, *s*, H-3), 6.74 (1H, *d*, *J* = 8.2 Hz, H-8″), 6.86 (1H, *s*, H-6), 7.01 (1H, *dd*, $J_{5'',9''}$ = 1.9 Hz, $J_{8'',9''}$ = 8.2 Hz, H-9″), 7.2 (1H, *d*, *J* = 1.9 Hz, H-5″), 7.27 (1H, *d*, *J* = 15.9 Hz, H-3″), 9.52 (1H, *s*, 7″-OH). ^{13}C NMR (Table 1). ES-MS: *m/z* (rel. int.) 583 (100), 407 (31), 389 (7).

Extraction and isolation (A. speciosa). The yellow exudate was dissolved in MeOH. After filtration, the solvent was removed *in vacuo* to provide a yellow–brown residue which contained one major unknown compound with R_f 0.65 (MeOH–$CHCl_3$, 1 : 2). Analysis of the sample with the analytical HPLC system revealed the presence of homonataloin and **4** (R_t 28.75). A portion (1 g) of the residue was adsorbed onto silica gel and flash chromatographed on silica gel (100 g) at low temperature (−15°C) in MeOH–$CHCl_3$ (1 : 10). The sepn was monitored by TLC and analytical HPLC.

(E)-2-*Acetonyl*-(2′,6′-*di*-O,O-*coumaroyl*)-β-D-*glucopyranosyl*-7-*hydroxy*-5-*methylchromone* (**4**). Amorphous solid (14%). UV λ_{max}^{MeOH} nm: 255 sh, 305. ^1H NMR: δ_H 2.24 (3H, *s*, 11-Me), 2.56 (3H, *s*, 5-Me), 3.34 (1H, *m*, H-4′), 3.78 (2H, *s*, H-9), 4.06 (1H, *m*, H-6′b), 4.15 (2H, 2 × *m*, H-3′ and H-4′), 4.52 (1H, *d*, *J* = 11 Hz, H-6′a), 4.92 (1H, *d*, *J* = 10.2 Hz, H-1′), 5.32 (1H, *d*, *J* = 3.9 Hz, 3′-OH), 5.43 (1H, *br s*, 4′-OH), 5.49 (1H, *t*, *J* = 9.6 Hz, H-2′), 6.11 (1H, *d*, *J* = 16.0 Hz, H-2″), 6.15 (1H, *s*, H-3), 6.43 (1H, *d*, *J* = 16.0 Hz, H-

2‴), 6.58 (1H, *s*, H-6), 6.74 (2H, *d*, $J = 8.7$ Hz, H-6″ and H-8‴), 6.76 (2H, *d*, $J = 8.7$ Hz, H-6‴ and H-8‴), 7.25 (1H, *d*, $J = 16.0$ Hz, H-3″), 7.44 (2H, *d*, $J = 8.6$ Hz, H-5″ and H-9″), 7.52 (2H, *d*, $J = 8.6$ Hz, H-5‴ and H-9‴), 7.54 (1H, *d*, $J = 15.9$ Hz, H-3‴), ^{13}C NMR (Table 1). ES-MS: *m/z* (rel. int.) 685 (58), 539 (8), 521 (100).

Extraction and isolation (A. broomii). Chopped leaves of *A. broomii* were extracted with MeOH (1000 ml), the extract filtered and the solvent removed *in vacuo* to provide a yellow brown residue. Analysis of the sample with the analytical HPLC system revealed the presence of aloin A and B (**2**) as well as the unknown compounds **5** (R_t 30.27 min), **6** (R_t 21.56 min), **7** (R_t 31.27 min) and **10** (R_t 24.24 min). A portion (1 g) of the residue was subjected to prep. HPLC using a Phenomenex IB-Sil C_{18} reverse phase column (5 μm particle size, 250 × 10 mm internal diameter; flow rate 4.5 ml min^{-1}; 1 ml sample loop). The solvent system was a 40–60% linear gradient of MeOH in H_2O over 25 min, 100% in 2 min. A diode array detector with two channels (A set at 275 ± 70 nm; B set at 365 ± 40 nm) was used. The sepn was monitored by analytical HPLC.

(10R, 1′S)-6′-O-*Caffeoyl-5-hydroxyaloin A* (**5**). Amorphous solid (8.6%). UV λ_{Max}^{MeOH} nm: 300 sh, 330. ^{1}H NMR (5% DMSO-d_6 and $CDCl_3$): δ_H 2.85 (1H, *t*, $J = 9.2$ Hz, H-3′), 2.87 (1H, *t*, $J = 9.2$ Hz, H-4′), 3.02 (1H, *m*, H-5′), 3.24 (1H, *t*, $J = 9.2$ Hz, H-1′), 3.26 (1H, *t*, $J = 9.2$ Hz, H-2′), 3.78 (1H, *m*, H-6′b), 4.20 (1H, *m*, H-6′a), 4.52 (2H, *d*, $J_{a,b} = -14.2$ Hz, 11-Me), 4.68 (1H, *d*, $J = 2.4$ Hz, H-10), 6.03 (1H, *d*, $J = 16$ Hz, H-2″), 6.64 (1H, *d*, $J = 8.6$ Hz, H-7), 6.74 (2H, *d*, $J = 1.2$ Hz, H-2 and H-4), 6.78 (1H, *d*, $J = 8.6$ Hz, H-8″), 6.88 (1H, *dd*, $J_{8'',9''} = 8.6$ Hz, $J_{5'',9''} = 1.5$ Hz, H-9″), 7.01 (1H, *d*, $J = 1.5$ Hz, H-5″), 7.03 (1H, *d*, $J = 8.6$ Hz, H-6), 7.28 (1H, *d*, $J = 16$ Hz, H-3″), 11.37 (1H, *s*, 8-OH), 11.73 (1H, *s*, 1-OH), ^{13}C NMR (5% DMSO-d_6 and $CDCl_3$) (Table 2). ES-MS: *m/z* (rel. int.) 595 (100), 271 (60). FAB-MS: *m/z* (rel. int.) 597 (48), 433 (60), 314 (16), 271 (100).

(E)-2-*Acetonyl*-8-(2′-O-*caffeoyl*)-β-D-*glucopyranosyl*-7-*methoxy*-5-*methyl-chromone* (**6**). Amorphous solid (4.2%). UV λ_{Max}^{MeOH} nm: 302, 329 (sh). ^{1}H NMR: δ_H 2.27 (3H, *s*, 11-Me), 2.66 (3H, *s*, 5-Me), 3.21 (1H, *m*, H-4′), 3.25 (1H, *m*, H-5′), 3.38 (1H, *m*, H-6b′), 3.51 (1H, *m*, H-3′), 3.71 (1H, *m*, H-6′a), 3.79 (3H, *s*, 7-OMe), 3.82 (2H, *s*, H-9), 4.40 (1H, *br s*, 6′-OH), 4.93 (1H, *d*, $J = 10.0$ Hz, H-1′), 5.17 (1H, *br s*, 4′-OH), 5.19 (1H, *br s*, 3′-OH), 5.42 (1H, *t*, $J = 9.8$ Hz, H-2′), 5.95 (1H, *d*, $J = 15.9$ Hz, H-2″), 6.17 (1H, *s*, H-3), 6.71 (1H, *d*, $J = 8.1$ Hz, H-8″), 6.84 (1H, *s*, H-6), 6.87 (1H, *dd*, $J_{5'',9''} = 2.1$ Hz, $J_{8'',9''} = 8.1$ Hz, H-9″), 6.93 (1H, *d*, $J = 2.0$ Hz, H-5″), 7.17 (1H, *d*, $J = 15.9$ Hz, H-3″). ^{13}C NMR (Table 1). ES-MS: *m/z* (rel. int.) 569 (100), 407 (35), 389 (8).

(E)-2-*Acetonyl*-8-[(2′-O-*cinnamoyl*)-β-D-*glucopyranosyl*-7-*methoxy*-5-*methylchromone* (**7**). Amorphous solid (3.2%). UV λ_{Max}^{MeOH} nm: 251, 284. ^{1}H NMR (5% DMSO-d_6 and $CDCl_3$): δ_H 2.29 (3H, *s*, 11-Me), 2.69 (3H, *s*, 5-Me), 3.41 (1H, *m*, H-5′), 3.63 (1H, *m*, H-4′), 3.66–3.82 (3H, *m*, H-3′, H-6′a and H-6b′), 3.81 (5H, *s*, H-9 and 7-OMe), 5.09 (1H, *d*, $J = 10.1$ Hz, H-1′), 5.57 (1H, *t*, $J = 9.5$ Hz, H-1′), 6.06 (1H, *s*, H-3), 6.12 (1H, *d*, $J = 15.5$ Hz, H-2″), 6.55 (1H, *s*, H-6), 7.29 (3H, *m*, H-6″, H-7″ and H-8″), 7.36 (1H, *d*, $J = 15.4$ Hz, H-3″), 7.37 (2H, *m*, H-5″ and H-9″). ^{13}C NMR (5% DMSO-d_6 and $CDCl_3$) (Table 1). ES-MS: *m/z* (rel. int.) 537 (100), 407 (5), 389 (65).

(10R, 1′S)-5-*Hydroxyaloin A* (**10**). Amorphous solid (16%). UV λ_{Max}^{MeOH} nm: 268, 298, 365. ^{1}H NMR (5% DMSO-d_6 and $CDCl_3$): δ_H 2.84 (1H, *m*, H-5′), 2.85 (1H, *t*, $J = 9.2$ Hz, H-2′), 2.96 (1H, *t*, $J = 9.2$ Hz, H-3′), 3.28 (1H, *t*, $J = 9.2$ Hz, H-4′), 3.33 (1H, *m*, H-6′b), 3.35 (1H, *t*, $J = 9.2$ Hz, H-1′), 3.44 (1H, *m*, H-6′a), 4.56 (1H, *d*, $J_{a,b} = -14.6$ Hz, H-11), 4.69 (2H, *d*, $J = 2.4$ Hz, H-10), 6.68 (1H, *d*, $J = 8.6$ Hz, H-7), 6.78 (1H, *d*, $J = 1.5$ Hz, H-2), 6.94 (1H, *d*, $J = 1.5$ Hz, H-4), 7.04 (1H, *d*, $J = 8.6$ Hz, H-6), 11.35 (1H, *s*, 8-OH), 11.68 (1H, *s*, 1-OH). ^{13}C NMR (5% DMSO-d_6 and $CDCl_3$) (Table 2). ES-MS: *m/z* (rel. int.) 433 (55), 313 (8), 271 (100). FAB-MS: *m/z* (rel. int.) 435 (65), 418 (12), 272 (100), 255 (60).

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