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ANTHRACENE AND CHROMONE DERIVATIVES IN THE EXUDATE OF *ALOE RABAIENSIS*

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Key Word Index—*Aloe rabaiensis*; Liliaceae; anthraquinones; 5-methylchromones; *C*-glucosides; *C*-rhamnosides; *O*-rhamnosides.

Abstract—From the methanol-soluble exudate of the leaves of *Aloe rabaiensis* five compounds have been isolated and identified, by spectral analysis, as aloe-emodin-11-*O*-rhamnoside, the C-10 isomers of barbaloin (aloe-emodin anthrone-10-*C*-glucoside), aloe-emodin anthrone-10-*C*-rhamnoside, aloeresin D and 8-*C*-[2′-*O*-(*E*)-caffeoyl] -β-glucopyranosyl-2- [2-hydroxy] propyl-7-methoxy-5-methylchromone (trivial name rabaichromone). Rabaichromone and aloe-emodin anthrone-10-*C*-rhamnoside appear to be new while aloeresin D and aloe-emodin-11-*O*-rhamnoside are reported for the first time from a named species rather than a commercial source of Aloe resin.

INTRODUCTION

Aloe rabaiensis Rendle is a shrubby aloe locally common around Nairobi and north of Mombasa in Kenya [1]. TLC studies of the leaf exudate have revealed the presence of barbaloin and a number of other unidentified phenolic compounds [1, 2]. As part of an investigation of the phenolic components that occur in the leaf exudates of Kenyan *Aloe* species [3], we now wish to report the presence of a number of anthracene and chromone derivatives from *A. rabaiensis*.

RESULTS AND DISCUSSION

Column chromatography of the ethyl acetate soluble portion of a methanol extract of the leaf exudate over silica gel, eluting with solvent mixtures of increasing polarity, gave three pure compounds (A–C) and a mixture, eluted between B and C. Further chromatography of this mixture over a column of polyvinylpyrrolidone yielded two more compounds, D and E.

The most abundant isolate (B), obtained in a yield of 1.43% of the methanol-soluble exudate, was identical to aloeresin-D (**1**) which has previously been isolated from Kenyan Aloe [4]. The minor compound D had spectral characteristics similar to those of **1** except that the simple AA′BB′ pattern for the aromatic protons of the cinnamic ester were replaced by an ABD pattern for three protons (Table 1). This, and the mass fragment *m/z* 163 $[C_9H_7O_3]^+$, indicate that the *p*-coumaric acid ester of **1** had been replaced by a caffeic acid ester (**2**). Compound **2** (assigned the trivial name rabaichromone) appears to be the first caffeoyl ester isolated from an *Aloe* species.

The UV spectrum of E suggested an anthrone. The EIMS failed to give a molecular ion but showed a fragmentation pattern comparable to that reported for barbaloin (**3**) [5]. The ^{1}H NMR spectrum was more complex than expected and revealed two very similar series of aromatic protons (1:1 ratio) both typical of the aloe-emodin anthrone nucleus with a C-linked glucose unit at C-10 (Table 2). This agreed well with published data for the two stereoisomers of barbaloin in which the sugar (β-D-glucose) is attached α or β at C-10 [6].

Compound C was in most respects identical to **3**. The EIMS did, in this case, reveal an $[M]^+$ (*m/z* 402, $C_{21}H_{22}O_8$) and the fragmentation pattern suggested the aloe-emodin nucleus plus a hexose moiety (*m/z* 147, $[C_6H_{11}O_4]^+$). The ^{1}H NMR spectrum again revealed the substitution pattern of an aloe-emodin anthrone

Table 1. ^{1}H NMR chemical shift values for compounds **1** and **2** (run in DMSO-d_6)

H	1	2
3	6.02 *s*	6.04 *s*
6	6.83 *s*	6.84 *s*
10	4.26 *m*	4.26 *m*
1′	4.96 *d* (9.9)	4.99 *d* (9.8)
2′	5.57 *t* (9.9)	5.57 *t* (9.8)
3′-H-6′, CH_2-9	3.20–3.90 *m*	3.16–3.85 m
2″	6.06 *d* (15.9)	5.97 *d* (15.8)
3″	7.28 *d* (15.9)	7.21 *d* (15.8)
5″	7.45 *d* (8.7)	6.95 *d* (1.9)
6″	6.74 *d* (8.7)	—
8″	6.74 *d* (8.7)	6.73 *d* (8.1)
9″	7.45 *d* (8.7)	6.91 *dd* (8.1, 1.9)
Me-5	2.66 *s*	2.68 *s*
Me-11	1.20 *d* (6.1)	1.22 *d* (6.1)
OMe-7	3.83 *s*	3.85 *s*

Compound **1** run at 250 MHz, **2** at 360 MHz. *J* values (Hz) in parentheses.

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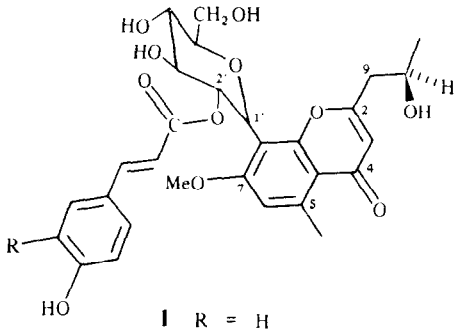
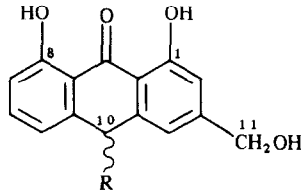
Table 2. ^{1}H NMR chemical shifts for the anthrones **3**–**5**

H	3	4	5
2	6.81 *s*	6.83 *s*	7.30 *s*
	6.84 *s*	6.84 *s*	
4	7.00 *s*	6.99 *s*	7.66 *s*
	7.02 *s*	7.04 *s*	
5	6.86 *d* (7.9)	6.87 *d* (7.9)	7.72 *d* (7.6)
	6.88 *d* (7.9)	6.88 *d* (7.6)	
6	7.53 *t* (7.9)	7.54 *t* (7.9)	7.79 *t* (7.6)
	7.53 *t* (7.9)	7.55 *t* (7.6)	
7	7.05 *d* (7.9)	7.05 *d* (7.9)	7.38 *d* (7.6)
	7.06 *d* (7.9)	7.07 *d* (7.6)	
3-CH_2	4.55 *d* (5.6)	4.77 *d* (4.8)	4.59/4.73 AX (14.5)
	4.55 *d* (5.6)	4.83 *d* (3.4)	
10	4.56 *s*	4.58 *s*	—
	4.56 *s*	4.58 *s*	
1,8-OH	11.77	11.77	11.92
	11.79	11.78	11.92
	11.83	11.79	
	11.87	11.82	
1			4.70 *s*
6′-Me		1.14 *d* (6.1)	1.15 *d* (5.4)
		1.15 *d* (6.1)	

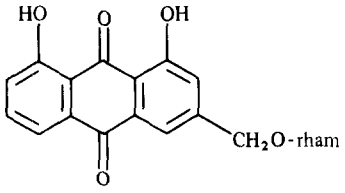
Spectra run in DMSO-d_6 at 250 MHz. *J* values (Hz) in parentheses.



1 R = H
2 R = OH



3 R = glc
4 R = rham



5

C-10 glycoside occurring as a mixture of α and β isomers (Table 2). The identity of the hexose as rhamnose was established from the ^{1}H NMR spectrum which showed doublets at δ 1.14 and 1.15 (both $J = 6.1$ Hz) for the C-6′ methyl group. C must therefore be the two isomers represented in **4**; this appears to be the first report of an anthrone C-10 rhamnoside in *Aloe*.

The remaining compound (A) analysed by HR-EIMS as $C_{21}H_{20}O_9$ and underwent facile fragmentation to give *m/z* 270 $[C_{15}H_{10}O_5]^+$ as required for the anthraquinone aloe-emodin together with *m/z* 146 $[C_6H_{10}O_4]^+$ for a hexose. The anthraquinone nature of the aglycone was further indicated by the UV spectrum. The substitution pattern of aloe-emodin and the identity of the hexose as rhamnose was confirmed by the ^{1}H NMR spectrum (Table 2). The presence of the rhamnose as an *O*-glycoside was obvious from the ease of fragmentation in the EIMS and the presence of the deshielded H-1′ proton. The *O*-rhamnoside must be placed on the C-3 hydroxymethyl substituent in view of the continued presence of the H-bonded hydroxyl protons. On this basis A is assigned structure **5**, which has previously been reported to occur in commercial Socotra Aloe (possibly *A. perryi* Baker) [7].

The types of compound isolated in this study can be regarded as typical of the genus *Aloe*, even though two appear to be new and two others are reported for the first time from a named species. The variations reflect the ability of *A. rabaiensis* to use caffeic acid as an esterifying group and to use rhamnose in the production of *C*- and *O*-glycosides. The aloe-emodin-*O*-galactoside previously reported to occur in *A. rabaiensis* [8] was not isolated.

EXPERIMENTAL

Plant material. The material used in this study was obtained from plants grown at the Royal Botanic Gardens, Kew, under the accession numbers 214-73-0211, 481-74-04483 and 084-81-00925.

Isolation of compounds. The freeze-dried MeOH-soluble exudate (30 g) was dissolved in H_2O (500 ml) and partitioned into EtOAc (1.5 l). The EtOAc extract was chromatographed over silica gel eluting with $CHCl_3$ containing increasing amounts of MeOH. Fractions eluted with 5% MeOH were bulked and on concentration yielded **5** (10 mg). Later fractions eluted with 5% MeOH gave, on similar treatment, **1** (430 mg). Further elution with 5% MeOH gave a mixture which was rechromatographed over polyvinylpyrrolidone eluting with H_2O and then H_2O containing increasing amounts of MeOH. Fractions eluted with 25% MeOH gave **2** (60 mg) and with 50% MeOH **3** (40 mg). Finally elution of the original column with 10% MeOH gave, on concn, **4** (20 mg).

Aloeresin D (**1**). Gum, UV λ_{max}^{MeOH} nm: 228, 251, 299; (+NaOH) 242, 251, 298, 360; $[\alpha]_D$ −194° (MeOH; *c* 1.01) (Lit. [4] −163°); ^{1}H NMR: see Table 1; EIMS *m/z* (rel. int.): 410 $[C_{20}H_{24}O_9]^+$ (14), 392 (11), 277 (29), 259 $[C_{15}H_{15}O_4]^+$ (100), 243 (16), 233 (68), 217 (17), 193 (80), 164 $[C_9H_8O_3]^+$ (9), 147 $[C_9H_7O_2]^+$ (12).

Rabaichromone (**2**). Amorphous, UV λ_{max}^{MeOH} nm: 234, 242, 296, 318; (+NaOH) 243, 252, 295, 375; $[\alpha]_D$ −132° (MeOH; *c* 0.84); ^{1}H NMR: see Table 1; EIMS *m/z* (rel. int.): 392 $[C_{20}H_{24}O_8]^+$ (39), 277 (1), 259 (100), 243 (33), 233 (80), 217 (24), 193 (49), 179 $[C_9H_7O_4]^+$ (1), 163 $[C_9H_7O_3]^+$ (12).

Barbaloin isomers (**3**). Brown, amorphous, UV λ_{max}^{MeOH} nm: 260, 268, 298, 358; (+NaOH) 267, 370, 389, 424, 445; ^{1}H NMR: see Table 2; EIMS *m/z* (rel. int.): 280 $[C_{17}H_{12}O_4]^+$ (79), 262 (31), 256 $[C_{15}H_{12}O_4]^+$ (100), 238 (10).

10-C-*Rhamnosyl aloe-emodin anthrone* (**4**). Amorphous. Found: M^+ 402.1313; $C_{21}H_{20}O_8$ requires 402.1315. UV λ_{max}^{MeOH} nm: 252, 260, 272, 295, 358; (+NaOH) 267, 372, 391, 423, 444; ^{1}H NMR: see Table 2; EIMS *m/z* (rel. int.): 402 $[M]^+$ (18), 298 (16), 280 (44), 262 (54), 256 (100), 238 (14), 227 (18), 210 (25), 147 $[C_6H_{11}O_4]^+$ (4).

11-O-Rhamnosyl aloe emodin (**5**). Amorphous, yellow. Found: M^+ 416.1083; $C_{21}H_{20}O_9$ requires 416.1107. UV λ_{max}^{MeOH} nm: 251, 257, 286, 428; (+NaOH) 234, 244, 250, 256, 261, 280, 508; ^{1}H NMR: see Table 2; EIMS *m/z* (rel. int.): 416 $[M]^+$ (2), 299 (49), 270 (24), 254 $[C_{15}H_{10}O_4]^+$ (100), 241 (22), 225 (25).

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LIGNANS FROM LEAVES OF *CALOCEDRUS FORMOSANA*

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Key Word Index—*Calocedrus formosana*; Cupressaceae; shonanin; 4,4′-dihydroxy-3,3′-dimethoxy-9,9′-epoxylignan; sesamin; yatein.

Abstract—Sesamin, yatein and 4,4′-dihydroxy-3,3′-dimethoxy-9,9′-epoxylignan were isolated from leaves of *Calocedrus formosana*. The structure of the epoxylignan was unambiguously determined by spectroscopic methods and X-ray diffraction.

INTRODUCTION

Calocedrus formosana [1] is an endemic conifer commonly called 'shonan'. Its heartwood is rich in terpenoid acids [2–4]. We have recently reported on the terpenoid constituents of its leaves [5]. In a continuation of this work, we have now isolated (+)-sesamin (**1**) [6], (−)-yatein (**2**) [7] and an epoxylignan (**3**) from the leaves. The lignan components of heartwood, such as hinokinin, hibalactone and calocedrin [8], were not found in leaves.

RESULTS AND DISCUSSION

The epoxylignan (**3**), namely shonanin, was obtained as colourless crystals, mp 136–137°. The structure of this optically inactive compound was determined as 4,4′-dihydroxy-3,3′-dimethoxy-9,9′-epoxylignan from its spectral data. The mass spectrum showed a parent ion at *m/z* 344 corresponding to a molecular formula $C_{20}H_{24}O_5$, while the ^{13}C NMR spectrum displayed only 10 signals, indicating that **3** is a symmetric molecule. The ^{13}C chemical shift values were similar to those of secoisolariciresinol (**4**) [9], except for C-9 (C-9′) appearing at a lower field (Table 1). A single crystal X-ray analysis of shonanin clearly showed the *trans* configuration rather than a *meso* compound.

Crystal data: $C_{20}H_{24}O_5$, orthorhombic, space group *Fdd*2, $a=21.786(5)$, $b=16.544(5)$, $c=9.92(3)$, $Z=8$; 523 reflections ($I>2.5\,\sigma$) were measured using MoK_α radiation. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to $R=0.0623$ and $R_w=0.0612$. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University