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NOVEL ANTHRONE-ANTHRAQUINONE DIMERS FROM *ALOE ELGONICA*

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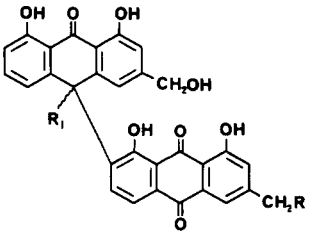
ABSTRACT.—In addition to aloe-emodin, aloenin, aloesin, and aloeresin B, the leaf exudate of *Aloe elgonica* has yielded two new dimeric compounds. These have been identified as the anthrone emodin-10-*C*-β-glucopyranoside linked through C-10 to C-7 of the anthraquinone aloe-emodin. The two dimers, named elgonica-dimers A and B, appear to differ in configuration at C-10.

Aloe elgonica Bullock (Liliaceae) is a distinctive species with a limited distribution along the southern and eastern slopes of Mount Elgon, Kenya (1). The plant is tetraploid and displays considerable variation in leaf surface anatomy, cytology, and tlc-based chemical profiles (2). However, these variations appear to be continuous and are not correlated with each other, and so do not support the establishment of sub-specific taxa.

As part of a study of a number of Kenyan *Aloe* species (3–5), we have examined the leaf exudate of *A. elgonica* grown at The Royal Botanic Gardens, Kew. Cc over Si gel eluting with $CHCl_3$ and then $CHCl_3$ containing increasing amounts of MeOH followed, in each case, by purification with circular preparative tlc gave aloe-emodin, a mixture, aloenin (3), and aloesin (4). From the mixture, aloeresin B (4) was obtained by circular preparative tlc on cellulose, and a minor band, when subjected to further circular preparative tlc on Si gel, gave small amounts of the new compounds elgonica-dimers A and B (both depicted in the general structure **1**).

The two dimers gave identical uv spectra, suggesting the presence of anthrone (355, 390 nm) and anthraquinone (435 nm) elements. This was confirmed by the eims spectra, which revealed fragments attributable to anthrone (*m/z* 256, $C_{15}H_{12}O_4$) and anthraquinone (*m/z* 270, $C_{15}H_{10}O_5$) components. Unfortunately eims failed to show a molecular ion, but fabms did give a potential $[M^+ + 1]^-$ at *m/z* 687, attributable to $C_{36}H_{30}O_{14}$. This could be rationalized as aloe emodin anthraquinone and emodin anthrone plus a *C*-linked hexose unit. Reductive cleavage of the dimers with sodium dithionite yielded only aloe-emodin.

The ^{1}H-nmr spectrum of elgonica-dimer A (Table 1) revealed signals for nine aromatic protons, four H-bonded hydroxyls, two hydroxymethyl groups, and a hexose. Coupling patterns among the aromatic protons indicated two pairs of meta-coupled protons, one pair of ortho-coupled protons, and an ABC system. The deshielded nature of the ortho-



1 R=OH, R_1=β-glucose
2 R=H, R_1=OH

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TABLE 1. ^{1}H-nmr Chemical Shift Data (δ), Multiplicities, and Coupling Constants for Elgonica-dimers A and B [**1**] and Chysalodin [**2**].

Proton	Compound		
	Elgonica-dimer[a]		**2**[b]
	A	B	
H-2	7.22 br s	7.22 br s	7.08 br s
H-4	7.68 d, 1.2	7.68 d, 1.5	7.56 br s
H-5	8.43 d, 8.1	8.44 d, 8.2	[c]7.96 d, 8
H-6	7.79 d, 8.1	7.86 t, 8.2	[c]8.79 d, 8
H-2′	6.57 br s	6.83 br s	6.92 br s
H-4′	6.72 br s	6.88 br s	7.56 br s
H-5′	[d]6.86 d, 8.1	[d]6.59 d, 7.9	[d]6.87 d, 7.5
H-6′	7.37 dd, 8.1, 8.1	7.33 dd, 8.2, 7.9	7.49 dd, 8, 7.5
H-7′	[d]6.88 d, 8.1	[d]6.75 d, 8.2	[d]6.91 d, 8
3-CH_2OH	4.60 br s	4.60 br s	2.44 br s (CH_3)
3′-CH_2OH	4.31/4.38 ABq, 13.0	4.37 br s	4.54 br s
OH	11.59, 12.15 12.40, 12.59	11.60, 12.17 12.45, 12.57	11.64, 12.10 12.26, 12.30
H-1″	4.23 d, 9.4	4.27 d, 9.2	
H-2″	2.38 dd, 9.4, 8.8[e]		
H-3″	3.05 dd, 8.8, 8.8[e]		
H-4″	2.71 dd, 8.8, 8.8[e]		

[a]Run in DMSO-d_6.
[b]In Me_2CO-d_6.
[c]Signals should be reversed.
[d]Resonance assignments interchangeable.
[e]Signals lost under a water peak.

coupled protons, which is indicative of H-5 and H-6 of an anthraquinone, and the absence of any H-10 proton in the anthrone required a C-10 to C-7 linkage. In support of this the aromatic signals showed a strong similarity (Table 1) to those reported previously for chrysalodin [**2**] from *Kniphofia foliosa* (6). The anomeric proton of the hexose was observed as a doublet at δ 4.23 indicating a *C*-glycoside, and through a series of decoupling experiments H-2 to H-4 of the sugar were also found to be axially oriented, thereby identifying the hexose as glucose. The spectrum obtained for elgonica-dimer B was similar to that for elgonica-dimer A except in the anthrone moiety where appreciable variations were observed (Table 1). These differences, which can only be attributed to a different arrangement of substituents around C-10, were much larger than those noted in the two forms of barbaloin (7). They can most probably be attributed to the 'shielding cone' (8) which occurs around the anthraquinone component of the dimer which, in elgonica-dimers A and B, affects different parts of the anthrone unit.

EXPERIMENTAL

PLANT MATERIAL.—Plant material grown at the Royal Botanic Gardens, Kew, under the codes 74-1456, 74-1458, and 74-1459 was used in this study. Voucher specimens are deposited at Kew.

EXTRACTION AND ISOLATION OF COMPOUNDS.—Leaves were cut into small sections and immediately placed in MeOH and left overnight. The MeOH extract was then concentrated and freeze-dried. A portion of the freeze-dried extract (30 g) was dissolved in H_2O (300 ml) and extracted with 5 × 250 ml EtOAc. The EtOAc-soluble material (2.8 g) was subjected to cc over acid-washed Si gel (30 g), eluting with $CHCl_3$ and then $CHCl_3$ containing increasing amounts of MeOH. Early fractions eluted with EtOAc

alone were further purified by circular preparative tlc (Chromatotron) [Si gel; toluene-EtOAc (1:1)] to give aloe-emodin (8 mg). Elution with 5% MeOH gave a mixture which was partially resolved by circular preparative tlc (microcrystalline cellulose), eluting with 50% aqueous MeOH to give aloeresin B (20 mg). Continued elution of the preparative tlc plate with H_2O gave a mixture which was resolved by further circular preparative tlc [Si gel; $CHCl_3$-EtOH (9:1)] to give elgonica-dimer A (1.5 mg) and elgonica-dimer B (2 mg). Elution with 10% MeOH followed by further cc eluting with an EtOAc/iPrOH gradient and then circular preparative tlc [Si gel; $CHCl_3$-MeOH (37:3)] yielded aloenin (15 mg). Finally, the eluate obtained with 12.5% MeOH was rechromatographed over polyamide eluting with H_2O to give aloesin (56 mg).

Aloeresin B, aloenin, and aloesin were identified as reported previously (3,4).

ALOE-EMODIN.—Amorphous; $[M]^+$ 270.0517, calcd for $C_{15}H_{10}O_5$, 270.0528; uv λ max (MeOH) 252, 285, 428 nm, (+ NaOH) 237, 285, 525; ^{1}H nmr (DMSO-d_6, 250 MHz) δ 4.62 (2H, br s, 3-CH_2), 7.28 (1H, d, J = 1.7, H-2), 7.37 (1H, dd, J = 7.8, 1.7, H-7), 7.68 (1H, d, J = 1.7, H-4), 7.70 (1H, dd, J = 7.8, 1.7, H-5), 7.79 (1H, dd, J = 7.8, 7.8, H-6), 12.02 (2H, br s, 2 × OH); eims *m/z* (rel. int.) $[M]^+$ 270 (100), 253 (3), 241 (91), 225 (5), 214 (3), 197 (3), 168 (5), 139 (11).

ELGONICA-DIMERS A AND B [**1**].—Amorphous; uv λ max (MeOH) 260, 295, 335, 390, 435 nm, (+ $AlCl_3$) 260, 292, 481; fabms (negative ion mode with glycerol matrix) *m/z* $[M^+ + 1]^-$ 687, $[M^+ + H]^-$ 453 $[M^+ - \text{hexose} + H]^-$; eims *m/z* (rel. int.) $[C_{15}H_{10}O_5]^+$ 270 (100), 268 (8), $[C_{15}H_{12}O_4]^+$ 256 (5), 239 (3), 214 (2); ^{1}H nmr of both dimers (360 MHz, DMSO-d_6) see Table 1.

Reductive cleavage of [**1**].—To a solution of **1** (2 mg as a mixture) in 5% aqueous NaOH was added $Na_2S_2O_4$ (5 mg) followed by heating to 80° for 7 h. The reaction mixture was acidified and extracted with $CHCl_3$. The organic phase was dried over Na_2SO_4 and examined by tlc [Si gel; $CHCl_3$-EtOAc (1:1); toluene-EtOAc-HOAc (80:18:1)] which revealed only one product, which was identical to authentic aloe-emodin.

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