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(*R*)-PRECHRYSOPHANOL FROM *ALOE GRAMINICOLA*

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Key Word Index—*Aloe graminicola*; Liliaceae; subterranean stem; anthraquinones; pre-anthraquinones; (*R*)-prechrysophanol.

Abstract—From the subterranean stem of *Aloe graminicola*, a new pre-anthraquinone named prechrysophanol was isolated. Chrysophanol, helminthosporin, (*R*)-aloesaponol I, (*R*)-aloesaponol II, aloesaponarin I, aloesaponarin II and laccaic acid D methyl ester were also identified.

INTRODUCTION

There are more than 360 *Aloe* species distributed in tropical Africa, Madagascar and southern Arabia [1]. Because of the widespread use of the leaves of *Aloe* in medicine and cosmetics [2], most of the phytochemical studies have been on the leaves [3]. The only reports available on the roots and subterranean stem are on *A. saponaria* [4–7] and *A. berhana* [8]. We report the isolation and characterization of a new natural product (*R*)-prechrysophanol (**1**) and other known compounds from the subterranean stem of *A. graminicola*.

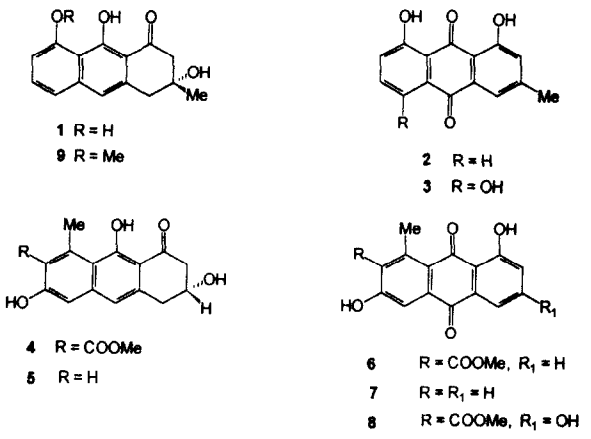
RESULTS AND DISCUSSION

The subterranean stem of *A. graminicola* was defatted with petrol and further extracted with chloroform. Chromatographic separation of the chloroform extract resulted in the isolation of eight compounds. Of these, chrysophanol (**2**), helminthosporin (**3**), (*R*)-aloesaponol I (**4**), (*R*)-aloesaponol II (**5**), aloesaponarin I (**6**), aloesaponarin II (**7**) and laccaic acid D methyl ester (**8**) were identified by comparing their spectroscopic data with those reported in the literature.

The yellow crystalline compound **1**, $C_{15}H_{14}O_4$, $[\alpha]_D$ −45° (MeOH), displayed in its UV-VIS spectrum absorption maxima at λ_{max} 268, 292, 298, 322 and 408 nm suggesting a pre-anthraquinone skeleton [5]. Treatment of **1** with 5% NaOH at room temperature gave chrysophanol (**2**). This is typical of pre-anthraquinones having a hydroxyl group at C-3 [4].

The ^{1}H NMR spectrum of **1** showed two singlets at δ9.65 and 16.10 which are attributable to the C-8 and C-9 hydroxyl protons, respectively [5]. The ABC pattern at δ7.08 (*dd*, J = 8.4, 2.0 Hz), 7.39 (*t*, J = 8.4 Hz) and 6.78 (*dd*, J = 8.4, 2.0 Hz), is due to H-5, H-6 and H-7, respectively. The broad singlet at δ6.95 is assigned to the aromatic proton at C-10. The signal due to the methyl group at C-3 appeared at δ1.33. The pair of AB quartets centred at δ2.77 and 3.00 are attributable to the methylene protons at C-2 and C-4, respectively. In agreement with structure **1**, the ^{13}C NMR spectrum displayed the presence of a carbonyl group (δ203.7), two hydroxylated (δ157.4 and 164.1), four quaternary (δ135.0, 139.3, 112.4 and 109.4) and four methine (δ110.65, 116.1, 118.5 and 132.4) aromatic carbons. In addition, the aliphatic region revealed the presence of a hydroxylated quaternary carbon (δ70.2), two methylenes (δ43.0 and 51.4) and a methyl (δ28.4) group.

The CD spectrum of **1** displayed a negative first and positive second Cotton effect and is similar to that reported for (*R*)-aloechrysone (**9**) [8]. This indicates that the absolute configuration at C-3 of **1** is *R*. Aloesaponol I (**4**) and aloesaponol II (**5**) isolated from this plant should also have (*R*)-configuration at C-3 as they gave similar



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CD curves to that reported for (*R*)-aloesaponol I isolated from *A. berhana* [8].

It is well known that atrochrysone and torosachrysone are important precursors in the biogenesis of the common, C-6 oxygenated, anthraquinones such as emodin and physcion [9]. Similarly, compound **1** appears to be an important precursor to chrysophanol (**2**) and related anthraquinones which lack oxygenation at C-6. It is worth noting that compound **1** was identified as one of the intermediates in a biomimetic synthesis of chrysophanol (**2**) [10]. However, this is the first report on the occurrence of prechrysophanol (**1**) in nature.

EXPERIMENTAL

General. IR: KBr discs; UV: MeOH; EIMS: 70 eV, direct inlet system; ^{1}H and ^{13}C NMR: 400 and 100 MHz, respectively.

Plant material. Aloe graminicola Reynolds was collected on the Nairobi–Nakuru road (140 km from Nairobi), Kenya. A voucher specimen (AY 34) is deposited at the Herbarium, University of Nairobi.

Extraction and isolation. Air-dried and powdered subterranean stem (700 g) of *A. graminicola* was successively extracted with petrol and $CHCl_3$ by percolation at room temp. The $CHCl_3$ extract (15 g) was subjected to CC on oxalic acid impregnated silica gel (300 g) eluting with petrol–CH_2Cl_2 and then with CH_2Cl_2–EtOAc mixtures of increasing polarities. A total of 16 × 200 ml frs were collected. Fraction 2 (petrol–CH_2Cl_2, 9:1) gave helminthosporin (**3**) (3 mg); fr. 3 (petrol–CH_2Cl_2, 4:1) gave chrysophanol (**2**) (15 mg); fr. 6 (petrol–CH_2Cl_2, 1:1) gave prechrysophanol (**1**) (42 mg); fr. 10 (petrol–CH_2Cl_2, 1:4) gave aloesaponarin I (**6**) (60 mg); fr. 12 (CH_2Cl_2) gave aloesaponarin II (**7**) (8 mg). Aloesaponol I (**4**) (60 mg), aloesaponol II (**5**) (5 mg) and laccaic acid D methyl ester (**8**) (6 mg) were isolated from frs 14–16 (CH_2Cl_2–EtOAc, 4:1) by repeated prep. TLC over silica gel plates using $CHCl_3$–EtOAc (1:1) as eluent.

(R)-*Prechrysophanol* (**1**). Yellow crystals, mp 199–202° (Me_2CO) (lit. [10] 203–205°); $[\alpha]_D$ −45° (MeOH; *c* 0.01); UV λ_{max}^{MeOH} (log ε) nm: 218 (4.4), 268 (4.7), 292 (3.6), 298 (3.6), 322 (3.6), 408 (3.9); UV $\lambda_{max}^{MeOH/AlCl_3}$ nm: 222, 274, 288, 446; CD λ_{max}^{MeCN}: 402.8 (Δε −0.34), 343 (+0.26), 314 (+0.83), 277.2 (+0.35), 264.8 (−0.83), 229.2 (+0.84), 214.4 (−1.29), 194.4 (+1.48); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2950, 1620 (chelated C=O), 1590, 1445, 1410; ^{1}H NMR (Me_2CO-d_6, 400 MHz): δ 16.10 (1H, *s*, OH-9), 9.65 (1H, *s*, OH-8), 7.39 (1H, *t*, *J* = 8.4 Hz, H-6), 7.08 (1H, *dd*, *J* = 8.4, 2.0 Hz, H-5), 6.95 (1H, *s*, H-10), 6.78 (1H, *dd*, *J* = 8.4, 2.0 Hz, H-7), 3.03 (1H, *d*, J_{gem} = 17.5 Hz, CH_2-4), 2.97 (1H, *d*, J_{gem} = 17.5 Hz, CH_2-4), 2.80 (1H, *d*, J_{gem} = 17.5 Hz, CH_2-2), 2.73 (1H, *d*, J_{gem} = 17.5 Hz, CH_2-2), 1.33 (3H, *s*, Me-3); ^{13}C NMR ($CDCl_3$–MeOH; 1:1, 100 MHz): δ 203.7 (C-1), 164.1 (C-8), 157.4 (C-9), 139.3 (C-10a), 135.0 (C-4a), 132.4 (C-6), 118.5 (C-5), 116.1 (C-10), 112.4 (C-8a), 109.4 (C-9a), 110.6 (C-7), 70.2 (C-3), 51.4 (C-4), 43.0 (C-2), 28.4 (C-Me); found: $[M]^+$ 258.0885; $C_{15}H_{14}O_4$ requires: 258.0892; EIMS *m/z* (rel. int.): 258 $[M]^+$ (100), 240 ($[M-H_2O]^+$, 82), 225 (8), 215 (18), 200 (41), 115 (47), 43 (75).

Conversion of (R)-*prechrysophanol* (**1**) *to chrysophanol* (**2**). Prechrysophanol (**1**) (10 mg) was dissolved in 5% methanolic KOH and the soln was stirred for 3 days. It was then acidified and extracted with CH_2Cl_2 to give chrysophanol (**2**) (6 mg). It was identified by direct comparison (UV, IR, co-TLC) with authentic sample.

Chrysophanol (**2**). Orange needles, mp 194–196° (MeOH) (lit. [5] 197°); UV and IR were identical to those reported in ref. [5]. EIMS *m/z* (rel. int.): 254 $[M]^+$ (100).

Helminthosporin (**3**). Red needles, mp 215–217° (lit. [5] 210–212°); UV, IR and ^{1}H NMR were identical to those reported in ref. [5]; EIMS *m/z* (rel. int.): 270 $[M]^+$ (100).

(R)-*Aloesaponol I* (**4**). Pale yellow crystals, mp 246–248° (lit. [4] 248–250°); UV, IR and ^{1}H NMR were identical to those reported in ref. [4]; CD λ_{max}^{MeCN}: 373.4 (Δε +0.28), 356.2 (+0.24), 342.8 (+0.39), 319.0 (+1.12), 309.6 (+1.05); EIMS *m/z* (rel. int.): 316 $[M]^+$ (31), 298 ($[M-H_2O]^+$, 6), 284 ($[M-MeOH]^+$, 100), 266 ($[M-H_2O-MeOH]^+$, 9), 256 (28), 228 (22), 210 (20), 128 (30).

(R)-*Aloesaponol II* (**5**). Pale yellow crystals, mp 240–243° (lit. [4] 242–245°); UV, IR and ^{1}H NMR were identical to those reported in ref. [4]; CD λ_{max}^{MeCN}: 397.8 (Δε +0.15), 373.4 (+0.16), 350.2 (+0.29), 329.6 (+0.89), 319.6 (+0.91), 306.6 (+0.63), 295.6 (+0.53); EIMS *m/z* (rel. int.): 258 $[M]^+$ (100), 240 ($[M-H_2O]^+$, 45).

Aloesaponarin I (**6**). Orange crystals, mp 198–200° (lit. [4] 199–203°); UV, IR and ^{1}H NMR were identical to those reported in ref. [4]; EIMS *m/z* (rel. int.): 312 $[M]^+$ (60), 297 ($[M-Me]^+$, 13), 280 ($[M-MeOH]^+$, 100), 252 (23), 224 (30), 196 (13), 168 (24), 139 (33).

Aloesaponarin II (**7**). Orange crystals, mp 256–258° (ref. [4] 250–254°); UV, IR and ^{1}H NMR were identical to those reported in ref. [4]; EIMS (rel. int.) *m/z*: 254 $[M]^+$ (100), 198 (30), 197 (45), 169 (26), 152 (29), 115 (39).

Laccaic acid D methyl ester (**8**). Orange crystals, mp 271–274° (ref. [4] 270–275°); UV, IR and ^{1}H NMR were identical to those reported in ref. [4]; EIMS *m/z* (rel. int.): 328 $[M]^+$ (58), 313 ($[M-Me]^+$, 18), 296 ($[M-MeOH]^+$, 100), 268 (23), 240 (25), 212 (16), 184 (10), 155 (8).

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