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# A *SECO*-OLEAN-18-ENE TRITERPENE ACID FROM *VAHLIA CAPENSIS*

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**Key Word Index**—*Vahlia capensis*; Vahliaceae; triterpene; 3,4 *seco*-olean-4,(23),18 dien-3-oic acid.

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**Abstract**—The *n*-hexane and ethyl acetate extracts of the aerial parts of *Vahlia capensis* yielded the coumarins umbelliferone, scopoletin and scoparone, and the terpenoids sitosterol, cycloartenol, 24-methylenecycloartanol, cycloart-23-en-3$\beta$,25-diol, glutinol and a *seco* ring-A triterpene acid, 3,4-*seco*-olean-4,(23),18-dien-3-oic acid.

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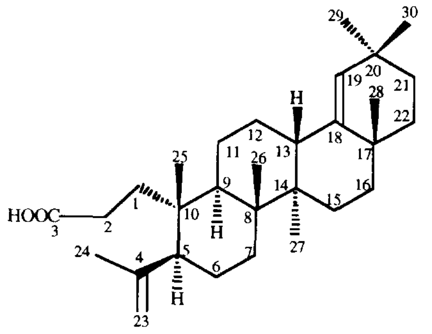
## INTRODUCTION

The small perennial shrub *Vahlia capensis* (L. f) Thunb. ssp. *vulgaris* Bridson is found mainly in the grazing areas of Botswana, Lesotho, Namibia, Zimbabwe and South Africa [1]. The genus *Vahlia* was initially placed in the family Saxifragaceae, but later moved into a family of its own, the Vahliaceae [1]. *Vahlia capensis* is a medicinal plant that has been used widely in Botswana to cure sore eyes, especially in small children [2]. To date there has been no phytochemical or pharmacological report on the plant.

## RESULTS AND DISCUSSION

The compound 3,4 *seco*-olean-4,(23), 18-dien-3-oic acid (**1**) was obtained from the *n*-hexane and ethyl acetate extracts of powdered aerial parts by a combination of column chromatography and PTLC. The $^1$H NMR spectrum (Table 1) revealed that **1** contained seven methyl singlets, resonating in the chemical shift range $\delta_H$ 0.77–1.75, while a combination of $^{13}$C NMR with $^1$H broad band decoupling, JMOD and DEPT-135 determined both the number and nature of the carbon atoms. The signal at $\delta_H$ 1.75 (3H) suggested an olefinic methyl group [3–5] [$\underline{Me}$-C = ], while signals at $\delta_H$ 4.70 (1H *br s*) and 4.90 (1H *br s*) indicated an exomethylene group, and a further broad singlet, also at $\delta_H$ 4.90, suggested an olefinic proton forming part of a trisubstituted double bond. The IR data ($\nu_{max}$ at 1750 and 3560 cm$^{-1}$) indicated a carboxylic acid, while the absorptions at $\nu_{max}$ 1360, 890 and 850 cm$^{-1}$ pointed to the presence of geminal dimethyls, an olefinic CH and an exomethylene (C$=$CH$_2$) group, respectively.



**1**

The high resolution EI mass spectrum of the compound gave a molecular ion at *m/z* 440.3654, which solved for the empirical formula $C_{30}H_{48}O_2$. The calculated double bond equivalents are seven which can be accounted for by two double bonds, one carbonyl and four rings. The observed mass spectral fragment at *m/z* 367 for loss of $C_3H_5O_2$ $[M - 73]^+$ is consistent with the presence of a -CH$_2$CH$_2$COOH moiety leading to the conclusion that the compound possesses a *seco*-oleanene skeleton. The base peak at *m/z* 177 $[C_{13}H_{21}]^+$ and other high intensity ions at *m/z* 205 $[C_{15}H_{25}]^+$, 204 $[C_{15}H_{24}]^+$ and 189 $[C_{14}H_{21}]^+$ strongly supported a $\Delta^{18}$-oleanene derivative [6]. The latter three ions have been reported in $\Delta^{18}$-oleanenes, e.g. methyl moronate, methyl morolate and germanicol acetate, and arise by a retro-Diels–Alder reaction involving the rupture of ring C followed by loss of a methyl [6]. The ion at *m/z* 177 $[C_{13}H_{21}]^+$, found in those derivatives with a methyl at C-17 ($\Delta^{18}$-oleanene and germanicol acetate), is thought to arise from a fragment at *m/z* 205 by another retro-Diels–Alder reaction involving the elimination of ethene [6].

The $^1$H and $^{13}$C NMR data were very similar to literature values for other $\Delta^{18}$-oleanene derivatives [7–10]. Application of 2D NMR methods (HMBC, HC-COBI and NOESY) allowed the resolution of structure **1** as

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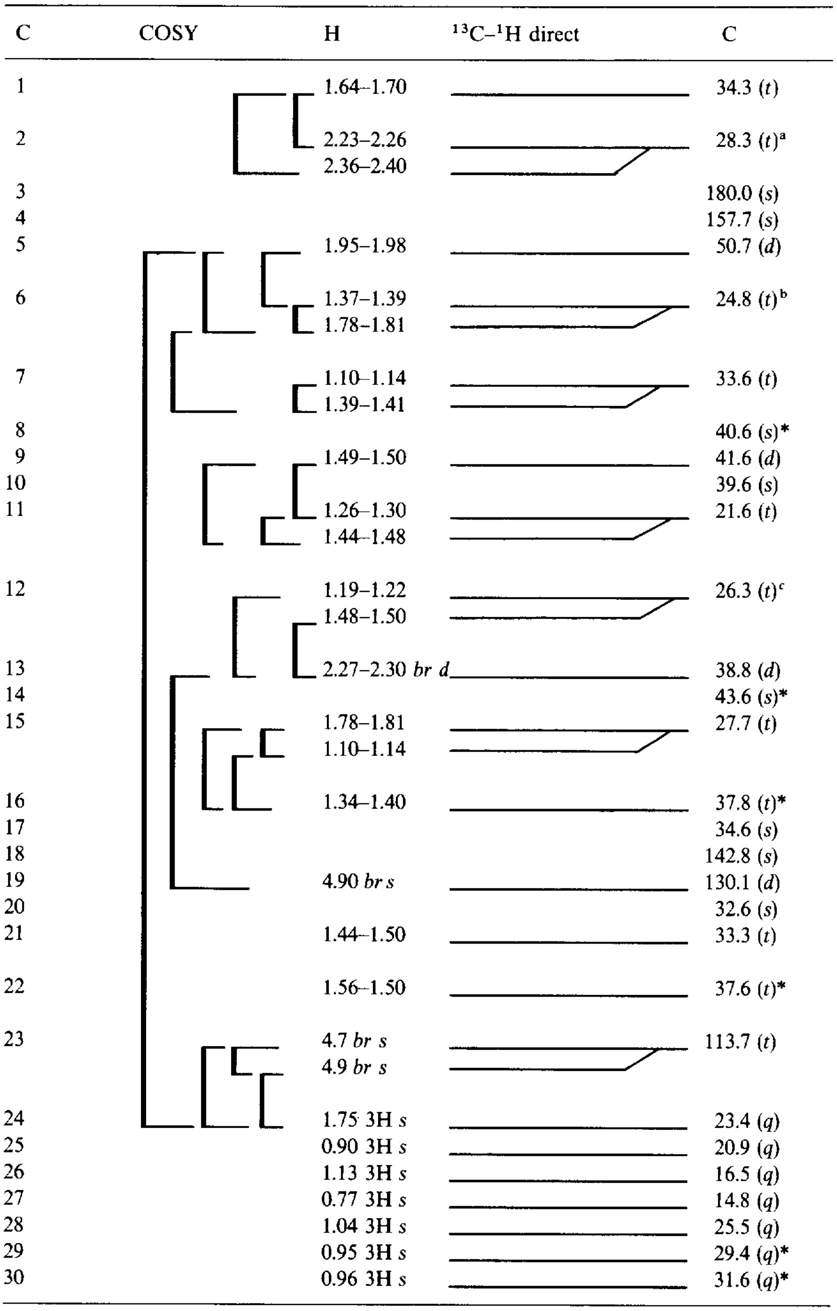
Table 1. $^{1}$H–$^{1}$H COSY and $^{13}$C–$^{1}$H direct for **1**



| C | COSY | H | $^{13}$C–$^{1}$H direct | C |
|---|---|---|---|---|
| 1 | | 1.64–1.70 | | 34.3 (*t*) |
| 2 | | 2.23–2.26<br>2.36–2.40 | | 28.3 (*t*)$^{a}$ |
| 3 | | | | 180.0 (*s*) |
| 4 | | | | 157.7 (*s*) |
| 5 | | 1.95–1.98 | | 50.7 (*d*) |
| 6 | | 1.37–1.39<br>1.78–1.81 | | 24.8 (*t*)$^{b}$ |
| 7 | | 1.10–1.14<br>1.39–1.41 | | 33.6 (*t*) |
| 8 | | | | 40.6 (*s*)* |
| 9 | | 1.49–1.50 | | 41.6 (*d*) |
| 10 | | | | 39.6 (*s*) |
| 11 | | 1.26–1.30<br>1.44–1.48 | | 21.6 (*t*) |
| 12 | | 1.19–1.22<br>1.48–1.50 | | 26.3 (*t*)$^{c}$ |
| 13 | | 2.27–2.30 *br d* | | 38.8 (*d*) |
| 14 | | | | 43.6 (*s*)* |
| 15 | | 1.78–1.81<br>1.10–1.14 | | 27.7 (*t*) |
| 16 | | 1.34–1.40 | | 37.8 (*t*)* |
| 17 | | | | 34.6 (*s*) |
| 18 | | | | 142.8 (*s*) |
| 19 | | 4.90 *br s* | | 130.1 (*d*) |
| 20 | | | | 32.6 (*s*) |
| 21 | | 1.44–1.50 | | 33.3 (*t*) |
| 22 | | 1.56–1.50 | | 37.6 (*t*)* |
| 23 | | 4.7 *br s*<br>4.9 *br s* | | 113.7 (*t*) |
| 24 | | 1.75 3H *s* | | 23.4 (*q*) |
| 25 | | 0.90 3H *s* | | 20.9 (*q*) |
| 26 | | 1.13 3H *s* | | 16.5 (*q*) |
| 27 | | 0.77 3H *s* | | 14.8 (*q*) |
| 28 | | 1.04 3H *s* | | 25.5 (*q*) |
| 29 | | 0.95 3H *s* | | 29.4 (*q*)* |
| 30 | | 0.96 3H *s* | | 31.6 (*q*)* |

* Assignments may be reversed.

$^{a-c}$Assignments which differ from those of Tanaka *et al.* [11].

3,4-*seco*-olean-4(23), 18-dien-3-oic acid which was very recently reported by Tanaka *et al.* [11] from *Euphorbia chamaesyce* (Euphorbiaceae). The NMR data reported for **1** [11] agree with our findings with the exception of the $^{13}$C assignments for C-2, C-6 and C-12. The long range heteronuclear coupling data we obtained allowed C-2, C-6 and C-12 to be assigned unambiguously and also agree with published data on related compounds [9]. The melting points also differ significantly, which may be explained by use of different solvents for recrystallization.

The $\Delta^{12}$-isomer of **1**, nyctanthic acid was first isolated from the shrub *Nyctanthis abor-tristis* by Turnbull *et al.* [12, 13]. This acid was later isolated mixed with roburic acid from oak galls formed by the insect *Cynips mayri* on common oak (*Quercus robur*) [14].

## EXPERIMENTAL

*General.* Mp: uncorr. $^1$H (250, 400 MHz) and $^{13}$C (100 MHz) NMR: $CDCl_3$ with TMS as int. standard. HR EIMS: 70 eV. CC: silica gel 60 (70–230 mesh). TLC: Merck silica gel 60 $F_{254}$ (0.25 mm). PTLC: silica gel 60 $F_{254}$ (0.50 mm). Visualization: UV radiation $\lambda$-254, 366 nm and vanillin sulphuric acid. The plant material was collected in Serowe, Central District, Botswana, in January 1991 and identified at the National Herbarium, Gaborone, Botswana, where a voucher specimen was deposited.

*Extraction and isolation.* The whole plant (1 kg) was ground and extracted at room temp. successively with *n*-hexane, EtOAc and MeOH. The *n*-hexane and the EtOAc extracts were evapd *in vacuo* to give 6 and 10 g, respectively, of dark green tar. The combined extracts were subjected to CC using *n*-hexane with increasing proportions of EtOAc. The fr. showing distinctive streaking on analyt. TLC plates, that gave a dark brown band upon spraying with vanillin sulphuric acid, was further purified (PTLC: toluene–EtOAc-HOAc 35 : 14 : 1) to give needles of **1** which were recrystallized from hexane (15 mg). Other frs yielded umbelliferone (8 mg), scopoletin (5 mg), scoparone (4 mg), sitosterol (30 mg), cycloartenol (10 mg), cycloart-23-en-3$\beta$,35-diol (15 mg), 24-methylenecycloartanol (25 mg) and glutinol (8 mg). The $^1$H and $^{13}$C NMR data for these compounds agreed with reported data [7, 15–19]. The identity of cycloart-23-en-3$\beta$,25-diol and 25-methylenecycloartanol was confirmed by detailed 2D experiments.

*Compound* **1**. $C_{30}H_{48}O_2$, needles (from hexane) mp 196–198$^0$, $[\alpha]_D + 10$ ($CHCl_3$; $c$ 0.10). IR: $\nu_{max}^{KB}$ cm$^{-1}$: 3560, 2950, 2850, 1720, 1650, 1640, 1450, 1370, 1360, 1260, 1180, 1140, 1110, 1040, 890, 880 and 850. $^1$H and $^{13}$C NMR: Table 1.

EIMS (rel. int.). 440 (71.7) $[M]^+$; 425 (30.2) $[M - Me]^+$, 367 (8.8) $[M - C_3H_5O_2]^+$, 359 (12.2), 218 (16.7), 205 (19.5), 204 (30.2), 203 (19.5), 191 (10.1), 190 (11.4), 189 (38.9), 178 (22.0), 177 (100), 176 (31.0), 175 (15.4), 163 (12.6), 161 (13.2), 149 (12.6), 157 (13.3), 135 (14.0), 133 (16.0), 123 (12.0), 121 (26.7), 119 (21.2), 109 (31.2), 105 (18.4), 95 (45.6), 93 (24.0), 91 (14.9), 83 (11.7), 81 (37.0), 79 (16.0) and 69 (34.4).

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