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SESQUITERPENE LACTONES FROM *ARTEMISIA ARGENTEA*

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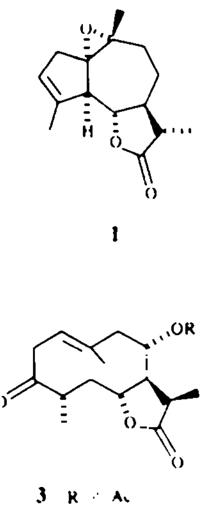
(*Received* 12 *March* 1986)

Key Word Index—*Artemisia argentea*; Compositae; sesquiterpene lactones; guaianolides; ketopelenolides.

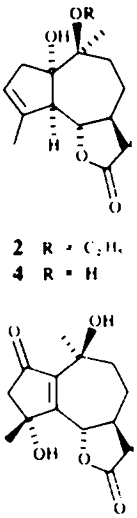
Abstract -The aerial parts of *Artemisia argentea* afforded, in addition to arborescin and argentiolides A and B, one new ketopelenolide derivative named deacetylargentiolide B and some previously unreported guaianolides.

In continuation of our studies on the sesquiterpene lactones of *Artemisia argentea* [1], we report herein the isolation and characterization of another new naturally occurring sesquiterpene lactone designated as deacetylargentiolide B (**5**), which has been prepared previously by deacetylation of the natural compound argentiolide B (**3**). In addition to known sesquiterpene lactones **1**, **3** and **6** [2], the lactones **2** and **4**, as well as considerable amounts of artemetin, sesamin and lirioresinol-C-dimethyl ether, have been isolated.

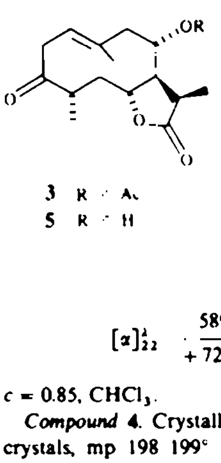
The structures of **2** and **4** followed from the ^{1}H NMR spectra (Experimental), which were similar to that of arborescin [3, 4]. In agreement with the molecular formulae the structures **2** and **4** were proposed, which, however, may be artefacts formed by hydrolysis of the epoxide moiety in **1**.



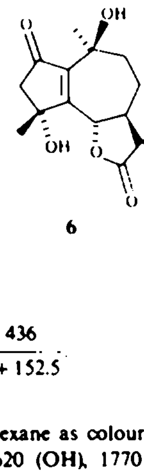
1



2 R = C_2H_5
4 R = H



3 R = Ac
5 R = H



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EXPERIMENTAL

The air-dried aerial parts were extracted with 95% EtOH at room temp. and worked up in the usual manner. Plant material (17 kg) was collected from the Medicinal Plants Experimental Station at Assiut University. A voucher has been deposited at the Department of Pharmacognosy, Faculty of Pharmacy, Assiut University.

The $CHCl_3$-soluble material (100 g from a total of 205 g) was chromatographed over a 1.6 kg silica gel column (E. Merck) (eluted with hexane and increasing percentages of EtOAc). With EtOAc–hexane (2:23), 4 g **1** (arborescin), mp 144° (lit. 145°) [34] and 100 mg **2** were obtained. The fractions with EtOAc–hexane (9:91) gave 3 g **3** (argentiolide B), mp 177 179° and the fractions with EtOAc-hexane (1:9) 5 g **4**. The fractions with EtOAc–hexane (3:22) gave 800 mg **5** (deacetylargentiolide B) and the last fraction EtOAc–hexane (7:43) gave 100 mg **6**, mp 205° (lit. 205°).

Compound **2**. Colourless crystals from Me_2CO–Et_2O mixture, mp 163–165°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 294.183 $[M]^+$ (8) (calc. for $C_{17}H_{26}O_4$: 294.182), 248 $[M - EtOH]^+$ (38), 233 $[248 - Me]^+$ (47), 205 $[233 - CO]^+$ (100). ^{1}H NMR (400 MHz, $CDCl_3$): δ2.66 and 2.01 *br d* (H-2), 5.41 *br s* (H-3), 3.27 *br d* (H-5), 4.16 *dd* (H-6), 2.10 *dq* (H-11), 1.17 *d* (H-13), 1.16 *s* (H-14), 1.87 *ddt* (H-15), OEt 3.42 and 3.40 *m*, 1.11 *t* [*J* (Hz): 2,3 = 3,5 = 5,15 ~ 1.5; 5,6 – 11; 6,7 = 9.5; 11,13 = 7].

$[\alpha]^{\lambda}_{22}$	589	578	546	436
	+ 72.1	+ 76.5	+ 87.5	+ 152.5

$c = 0.85$, $CHCl_3$.

Compound **4**. Crystallized from EtOA -hexane as colourless crystals, mp 198 199° IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 266.152 $[M]^+$ (2) (calc. for $C_{15}H_{22}O_4$: 266.152), 248 $[M - H_2O]^+$ (21), 233 $[248 - Me]^+$ (40), 205 $[233 - CO]^+$ (100). ^{1}H NMR (400 MHz, $CDCl_3$): δ2.66 and 2.08 *br d* (H-2), 5.41 *br s* (H-3), 3.21 *br d* (H-5), 4.17 *dd* (H-6), 2.14 *dq* (H-11), 1.18 *d* (H-13), 1.28 *s* (H-14), 1.87 *ddt* (H-15) [*J* (Hz): 2].

$[\alpha]^{\lambda}_{22}$	589	578	546	436
	+ 56	+ 58.4	+ 66.8	+ 113

$c = 1.36$, $CHCl_3$.

Deacetylargentiolide B (**5**). Crystallized from Et_2O as colourless needles, mp 183°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3625 (OH), 1765 (γ-lactone), 1695 (C=O); ^{1}H NMR: identical with that of the compound obtained by saponification of **3** [1]. MS *m/z* (rel. int.):

233 (12), C_3H_5 41 (100). CD (MeCN): ε_{318} + 0.92; ε_{307} + 1.3; ε_{297} + 1.0; ε_{193} + 16.6.

$$[\alpha]^{\lambda}_{22} \quad \frac{589}{+142.6} \quad \frac{578}{+149} \quad \frac{546}{+171.6} \quad \frac{436}{+318}.$$

$c = 0.82$, $CHCl_3$.

Acknowledgement—The authors would like to thank Prof. Dr. F. Bohlmann for the NMR spectral analysis, his kind help and for rewriting the full paper.

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DEACETOXYBRACHYCARPONE, A TRINORTRITERPENOID FROM *CLEOME BRACHYCARPA*

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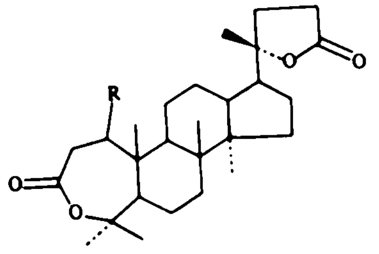
Key Word Index—*Cleome brachycarpa*; Capparidaceae; trinorterpenoid; deacetoxybrachycarpone.

Abstract—A new trinortriterpenoid dilactone, deacetoxybrachycarpone, has been isolated from *Cleome brachycarpa* and its structure determined mainly by spectroscopic studies. Cabralealactone and ursolic acid were also isolated.

INTRODUCTION

Recently we reported [1] the isolation of a new trinortriterpenoid, brachycarpone (**1**), from *Cleome brachycarpa* [L.] DC., a medicinal plant of Pakistan [2]. The structure of brachycarpone was confirmed through X-ray crystallographic studies. We have now isolated another closely related compound, deacetoxybrachycarpone (**2**), as well as the known compounds cabralealactone (**3**) and ursolic acid from the same plant.

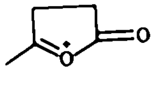


1 R = OAc
2 R = H

RESULTS AND DISCUSSION

Deacetoxybrachycarpone (**2**) analysed for $C_{27}H_{42}O_4$. Its UV spectrum showed only an end absorption at 208 nm, indicating the absence of conjugated double bonds in the compound. Its IR spectrum showed no hydroxyl absorption but strong peaks at 1765 (γ-lactone) and 1730 cm^{-1} (seven-membered lactone) were present as in brachycarpone. The peak at 1720 cm^{-1} attributed to the acetoxyl group in **1** was missing in **2**.

The ^1H NMR (300 MHz) spectrum of **2** showed the presence of six tertiary methyl singlets (δ0.88, 1.02, 1.07, 1.36, 1.40 and 1.48), each integrating for 3H. There was no signal near δ2.0 due to an acetate methyl group. A multiplet centred at δ2.59 (4H) was assigned to two methylene groups in the γ- and seven-membered lactone rings.



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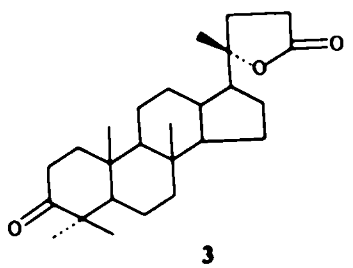

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The mass spectrum of **2** showed a weak $[M]^+$ peak at