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EUDESMANOLIDES FROM *ARTEMISIA CANARIENSIS*

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Key Word Index—*Artemisia canariensis*; Compositae; sesquiterpene lactones; eudesmanolides; acetyltabarin; tabarin; vulgarin; 4-epivulgarin; 11,13-dihydrosantamarin; 11,13-dihydroreynosin.

Abstract—Six eudesmanolides have been isolated from the aerial parts of *Artemisia canariensis* and identified as acetyltabarin, 4-epivulgarin, 11,13-dihydrosantamarin, 11,13-dihydroreynosin, vulgarin and tabarin.

INTRODUCTION

The genus *Artemisia* is one of the largest and most widely distributed of *ca* 60 genera in the tribe Anthemideae of Asteraceae (Compositae). This genus, with nearly 300 species, is found predominantly in the northern temperate regions of the world [1].

Two eudesmanolides vulgarin (**1**) and tabarin (**2**) were previously reported [2] to occur in the aerial part of *Artemisia canariensis* Lees.

Careful chromatography of the extract of the aerial parts of *A. canariensis* has now furnished, in addition to **1** and **2**, compounds **3**–**6**.

RESULTS AND DISCUSSION

Acetyltabarin (**3**)

Mp 219–220°, with the molecular formula $C_{17}H_{22}O_6$, mass spectra, M^+ at *m/z* 322. This substance was identical (IR and ^{1}H NMR spectra superimposable) with material obtained by acetylation of tabarin by González *et al.* [2].

4-*Epivulgarin* (**4**)

Mp 192–194°; $[\alpha]_D$ + 77.5°; mass spectra, M^+ at *m/z* 264, and the molecular formula $C_{15}H_{20}O_4$; IR bands at 3540 (OH), 1765 (γ-lactone) and 1678 cm^{-1} (carbonyl). The ^{1}H NMR spectrum indicated that substance **4** was the epimer at C-4 of vulgarin. Thus, because of a 1,3-diaxial relationship between the C-4 hydroxyl and the C-10 methyl group, the signal of the latter appeared at a field δ 0.16 lower than that of the C-10 methyl group of vulgarin [3]. This substance was identical (IR and ^{1}H NMR spectra superimposable) with 4-epivulgarin synthesized by Ando *et al.* [3].

11,13-*Dihydrosantamarin* (**5**)

Mass spectra (M^+ at *m/z* 250) in agreement with the molecular formula $C_{15}H_{22}O_3$; IR bands at 3600 (OH), 1760 (γ-lactone). The ^{1}H NMR spectrum was identical with the one described for the same substance by Shafizadeh *et al.* [4].

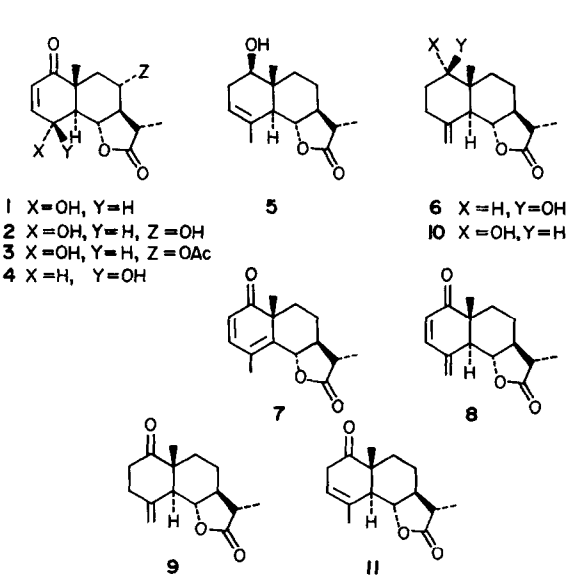
11,13-*Dihydroreynosin* (**6**)

Freed from admixture of **5** by treatment with glacial acetic acid. The IR spectrum had bands at 3600 (OH), 1760 (γ-lactone), 1645 (double bond). The ^{1}H NMR spectrum was similar to that of **5**, but differed in that the coupling constants of the C-1 proton at δ 3.50 with the two vicinal protons were 4 and 10 Hz, respectively, as would be expected for an axial proton coupling with one axial and one equatorial proton [5].

The structures of **5** and **6** were confirmed as follows. Dehydration of vulgarin with glacial acetic acid containing a trace of sulphuric acid [6] yielded **8** (15%); mp 146–147° and **7** (66%) mp 134–135°.

Reduction of **8** with zinc–hydrochloric acid gave an exomethylene ketone (**9**) (68.3%) which was reduced to give a mixture of epimeric alcohols (**6**) and (**10**) in 50% and 35% yields, respectively. Compound **6** was identical with natural dihydroreynosin [5].

Compound **1** was converted with zinc–hydrochloric acid to the β,γ-unsaturated ketone (**11**) [6] in 69% yield.



Part 46 in the series "Constituents of the Compositae". For Part 45 see A. G. González, J. Bermejo, F. Estévez and R. Velázquez (1983) *Phytochemistry* **22**, 1515.

The position of the double bond in **11** was assigned by the ^{1}H NMR spectrum, which showed a broadened singlet at δ 1.82 C-4 methyl. Sodium borohydride reduction of **11** gave **5** which was identical with the natural product.

EXPERIMENTAL

Mps are uncorr. Optical activities were measured in $CHCl_3$. ^{1}H NMR spectra were recorded at 90 MHz, using TMS as int. standard. Analytical TLC was performed on Si gel (Merck 60 $PF_{254+366}$), and CC was on Si gel (Merck 0.063–0.2).

The aerial parts of the plant (10 kg) collected in Mesa Mota (Tenerife) were finely ground and extracted, first with H_2O, the aq. residue was then completely extracted with $CHCl_3$. The resulting extract was separated by CC and eluted with hexane–EtOAc mixtures and EtOAc, giving: **1** (1 g), **3** (0.1 g), **4** (0.1 g), **5** (0.1 g), **6** (0.05 g) (hexane–EtOAc, 3:2) and **2** (3 g) (hexane–EtOAc, 1:1).

Acetyltabarin (**3**). Mp 219–220° (C_6H_6–hexane), $[\alpha]_D$ + 33.1° ($CHCl_3$; *c* 5.2), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1790 (γ-lactone), 1740 (ester), 1680 (C=O).

4-*Epivulgarin* (**4**). Mp 192–194° (C_6H_6–hexane); $[\alpha]_D$ + 77.5° ($CHCl_3$; *c* 5.7).

11,13-*Dihydrosantamarin* (**5**). Mp 132–133°; $[\alpha]_D$ + 71° ($CHCl_3$; *c* 1.0).

11,13-*Dihydroreynosin* (**6**). Mp 136–137° (hexane).

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FURTHER GUAIANOLIDES FROM *ARCTOTIS GRANDIS**

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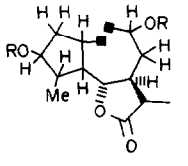
Key Word Index—*Arctotis grandis*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—Two further guaianolides were isolated from the aerial parts of *Arctotis grandis*.

In addition to widespread polyacetylenes [1], the genus *Arctotis* (Compositae, tribe Arctoteae) has afforded several sesquiterpene lactones, especially guaianolides [2–6]. For example, three guaianolides have been isolated from *Arctotis grandis* Thunb [2, 3, 5]. We have re-investigated the polar fractions of the aerial parts of this plant. In addition to the lactones isolated previously two new ones were obtained. The more polar compound, $C_{15}H_{22}O_4$, showed IR bands at 3600 and 1770 cm^{-1} indicating the presence of a γ-lactone with hydroxy groups. Acetylation afforded a diacetate as followed from the molecular formula and from the ^{1}H NMR spectral data (Table 1) which further showed that a saturated lactone was present. Accordingly, two methyl doublets were visible. Spin decoupling allowed the assignment of all signals although a few signals were overlapping multiplets both in the spectrum of the diol and the corresponding diacetate. In the spectrum of the diol, five low field signals were visible. Two broadened singlets were due to the protons of an exomethylene group. A three-fold doublet at δ 4.26, which was shifted to 5.03 in the spectrum of the diacetate,



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*Part 472 in the series "Naturally Occurring Terpene Derivatives". For Part 471 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1983) *Phytochemistry* **22**, 1288.