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).

Acknowledgement—We thank Professor M. Ando for kindly giving us IR and ^{1}H NMR spectra of 4-epivulgarin.

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Phytochemistry, Vol. 22, No. 6, pp. 1510–1512, 1983.
Printed in Great Britain.

0031-9422/83/061510-03$03.00/0

FURTHER GUAIANOLIDES FROM *ARCTOTIS GRANDIS**

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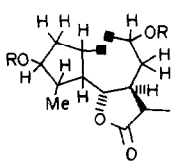
(*Received* 14 *June* 1982)

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,



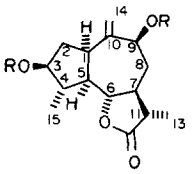
A

*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.

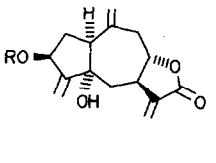
Table 1. ^{1}H NMR spectral data of compounds **1** – **3** (400 MHz, TMS as internal standard)

	1			**3**	
	$CDCl_3$	$CDCl_3$–C_6D_6	**2**($CDCl_3$)	$CDCl_3$	$CDCl_3$–C_6D_6
H-1	2.69 *br ddd*	2.28 *br ddd*	2.83 *br ddd*	2.57 *br dd*	2.41 *br dd*
H-2	2.35 *ddd*	2.10 *m*	2.20 *m*	2.45 *ddd*	2.31 *ddd*
H-2′	2.17 *ddd*			1.68 *ddd*	1.48 *ddd*
H-3	4.26 *ddd*	3.97 *ddd*	5.03 *ddd*	4.73 *br t*	4.55 *br t*
H-4	2.35 *m*	2.16 *ddq*	2.57 *ddq*	—	—
H-5	2.06 *m*	2.10 *m*	2.23 *dd*	—	—
H-6	4.05 *dd*	3.72 *dd*	4.07 *dd*	2.11 *br d*	1.98 *br d*
H-6′	—	—	—	1.80 *dd*	1.67 *dd*
H-7	1.79 *dddd*	1.37 *dddd*	1.86 *dddd*	3.05 *br dd*	2.94 *br dd*
H-8	2.38 *ddd*	2.03 *ddd*	2.34 *ddd*	4.45 *ddd*	4.01 *ddd*
H-8′	1.32 *ddd*	0.95 *ddd*	1.45 *ddd*	—	—
H-9	3.99 *br dd*	3.53 *br dd*	4.91 *br dd*	2.57 *dd*	2.47 *dd*
H-9′	—	—	—	3.13 *ddt*	3.02 *ddt*
H-11	2.28 *dq*	2.10 *m*	2.30 *dq*	—	—
H-13	1.23 *d*	1.03 *d*	1.24 *d*	6.21 *d*	6.16 *d*
H-13′	—	—	—	5.48 *d*	5.37 *d*
H-14	5.52 *br s*	5.32 *br s*	5.35 *br s*	5.06 *br s*	4.97 *br s*
H-14′	5.21 *br s*	5.01 *br s*	5.16 *br s*	5.05 *br s*	4.96 *br s*
H-15	0.95 *d*	0.82 *d*	0.94 *d*	5.33 *d*	5.37 *d*
H-15′	—	—	—	5.25 *d*	5.24 *d*
OAc	—	—	2.09 s(6H)	—	—

J (Hz): Compounds **1** and **2**: 1, 2 ~ 10; 1, 2′ = 12; 1, 5 ~ 9; 2, 2′ = 12; 2, 3 = 5; 2′, 3 = 6; 3, 4 = 4, 5 = 4, 15 = 7; 5, 6 = 10; 6, 7 = 11; 7, 8α = 3; 7, 8β = 11; 7, 11 = 12; 8α, 8β = 12.5; 8α, 9 = 4; 8β, 9 = 10.5; 11, 13 = 7; compound **3**: 1, 2 = 8; 1, 2′ = 11.5; 2, 2′ = 13.5; 2, 3 = 2′, 3 ~ 7; 3, 15 = 3′, 15 = 2; 6, 6′ = 15; 6′, 7 = 10.5; 7, 8 = 10; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 10; 8, 9′ = 7; 9, 9′ = 14; 9′, 14 = 1.



1 R = H
2 R = Ac



3 R = H
4 R = Ac

could be assigned to H-3 since irradiation at 2.57 in the spectrum of the diacetate collapsed one of the methyl doublets (0.94) to a singlet, the double doublet at 2.23 to a doublet and the low field signal at 5.03 to a double doublet. Further spin decoupling led to the sequence **A** which, after addition of the missing exomethylene group, led to structure **1**. The stereochemistry clearly followed from the couplings observed if a model was considered. The corresponding 3-keto derivative has been isolated previously from the same species [5].

The less polar lactone was also a dihydroxy lactone; this followed from the mass spectrum. The molecular formula was $C_{15}H_{18}O_4$, while a two-fold elimination of water (*m/z* 244 and 216) indicated the presence of a diol. The ^{1}H NMR spectrum (Table 1) displayed the typical signals of a methylene lactone (δ 6.21 *d* and 5.48 *d*) which were coupled with a broadened double doublet at 3.05. Irradiation of the latter signal collapsed a three-fold doublet at δ 4.45 to a double doublet, the double doublet at 1.80 to a singlet and sharpened the broadened doublet at 2.11. The latter two signals obviously were those of H-6 while that at 4.45 had to be assigned to H-8. The absence of additional couplings of H-6, except the geminal one, showed that one of the hydroxyl groups was at C-5, while the second one had to be placed at C-3. Accordingly, the corresponding H-3 signal was a broadened triplet whose chemical shift indicated an allylic position. This was established by decoupling. Irradiation at δ 4.73 collapsed the doublets at 5.33 and 5.25 to singlets. Further decoupling allowed the assignment of all signals while the stereochemistry followed from the couplings observed. The α-position of the hydroxyl at C-5 was indicated by the chemical shift of H-6α (1.80 *dd*). A β-hydroxy group should have a deshielding effect leading to a downfield shift of H-6 double doublet. The ^{1}H NMR spectral data were close to those of the corresponding acetate, **4**, which was isolated previously from the same species [3].

EXPERIMENTAL

The air-dried aerial parts (500 g) were extracted with $CHCl_3$. 1 g of the extract obtained (total 4.8 g) was separated by HPLC using Si gel and Me_2CO–petrol (**1**–**4**) (50 fractions, 30 ml each). Fractions 7–14 contain arctolide and desoxyarctolide [3], fractions 15–17 the 3-dehydro derivative of **1** [5] and fractions 19–22 revealed crude **3** which was further purified by HPLC (Si gel, $CHCl_3$–EtOAc, 1:1), yielding 12 mg **3**. Fractions 28–32 gave crude **1** which was further purified by HPLC (Al_2O_3, Me_2CO–Et_2O, 2:3), yield 18 mg.

9β-Hydroxy-4β,15,11β,13-tetrahydrozaluzanin C (**1**). Colourless crystals, mp 65°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1645 (C=CH_2); MS *m/z* (rel. int.): 248.152 [M]$^+$ (28)

($C_{15}H_{22}O_4$), 230 $[M-H_2O]^+$ (14), 215 $[230-Me]^+$ (11), 204 $[248-CO_2]^+$ (9), 175 $[204-CHO]^+$ (53), 55 $[C_4H_7]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-25 \quad -25 \quad -28 \quad -45} \text{ (}CHCl_3\text{; } c = 0.26\text{)}.$$

4 mg **1** was heated with 0.1 ml Ac_2O for 1 hr at 70°. TLC (Et_2O–petrol, 3:1) afforded 3 mg **2**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 1745, 1240 (OAc), 1645 (C=CH_2); MS *m/z* (rel. int.): 350 $[M]^+$ (0.2), 290 $[350-HOAc]^+$ (6), 230 $[290-HOAc]^+$ (100), 215 $[230-Me]^+$ (9), 202 $[230-CO]^+$ (12).

3-*Desacetyl*-10,14-*desoxoarctolide* (**3**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 262.121 $[M]^+$ (3) ($C_{15}H_{18}O_4$), 244 $[M-H_2O]^+$ (23), 226 $[244-H_2O]^+$ (11), 216 $[244-CO]^+$ (22), 201 $[216-Me]^+$ (14), 192 (31), 138 (48), 91 (72), 55 (78), 53 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365}{+40 \quad +43 \quad +49 \quad +85 \quad +141} \text{ (}CHCl_3\text{; } c \text{ 0.44)}.$$

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Phytochemistry, Vol. 22, No. 6, pp. 1512–1513, 1983.
Printed in Great Britain.

0031-9422/83/061512-02$03.00/0

A DITERPENIC ACID FROM *STEVIA LUCIDA**

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(*Revised received* 18 *October* 1982)

Key Word Index—*Stevia lucida*; Compositae; Eupatorieae; labdane-type diterpene.

Abstract—A new furan diterpenic acid was isolated from *Stevia lucida*. On the basis of IR, ^1H NMR and mass spectra, as well as chemical evidence, the acid was assigned the structure 5β,9β*H*,10α,-labda-7,13(16),14-trien-15,16-epoxy-19-oic-acid.

INTRODUCTION

In the course of a phytochemical survey of Mexican Eupatorieae [1–4], we have isolated and elucidated the structure of a new labdane diterpenic acid from the leaves of *Stevia lucida* Lag var Bipontini, a wild herb which is plentiful in the semi-arid area of Oaxaca, Mexico.

RESULTS AND DISCUSSION

The new diterpenic acid (**1**) decomposed rapidly and its purification by CC over Si gel was only accomplished with a loss of large amounts of material. The molecular formula of **1**, was determined to be $C_{20}H_{28}O_3$. The IR spectrum revealed the presence of a hydroxyl group (3300–2700 cm^{-1}), a carbonyl function (1690 cm^{-1}) and a furan ring [5] (1440, 1020 and 870 cm^{-1}). The ^1H NMR spectrum showed three multiplet signals at δ 7.30, 7.17 and 6.22 which were assigned to two α-furan protons and a β-furan proton. A vinyl proton at δ 5.35 interacting with a vinylic methyl at 1.70 was also observed establishing the presence of a trisubstituted double bond.

The IR spectrum of the methyl ester (**2**) exhibited the expected shift from 1690 to 1730 cm^{-1} in the parent carbonyl absorption band. The characteristic absorption pattern [6] for an equatorial carboxylic methyl ester with a strong band at 1245 cm^{-1} was clearly observed between 1030 and 1000 cm^{-1}. Analysis of the ^1H NMR spectrum showed a singlet δ 1.20 for an axial Me-4 on a carbon atom bearing an equatorial carboxyl group [7, 8]. The alcohol (**3**) prepared from the ester, **2**, exhibited hydroxyl group absorption in the IR at 3360, 1240 and 1050 cm^{-1} and the ^1H NMR spectrum exhibited an AB system (δ 3.2, J = 11 Hz) assigned to the new methylene formed in the reduction reaction.

The spectroscopic and chemical behaviour of the above substances including the acetate derivative (**4**), are very similar to those of bicyclic diterpenes possessing the labdane nucleus [9, 10] and related to polyalthic acid

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