configuration, as the other possibility, H-6 and H-8 α-orientated, did not explain the observed shifts. Consequently, the new diterpene was 7-oxo-6α-hydroxyhardwickiic acid lactone (**1**). Obviously, further species of *Pulicaria* will have to be investigated to clarify the chemotaxonomy of this genus. So far relationships to *Inula* can be stated though this genus does not appear very uniform with regard to its chemistry.

EXPERIMENTAL

The air-dried plant material (250 g), collected near Teheran (voucher A. R. 115) was extracted with Et_2O–petrol (1:2). CC (Si gel) and TLC (Si gel) of the polar fractions (Et_2O–CH_2Cl_2, 2:1) gave 30 mg colourless crystals (**1**), mp 161°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1785, 1750, 1690, 1605, 1515, 885; MS m/z (rel. int.): 328.167 $[M]^+$ (42), 313 $[M - Me]^+$ (8), 233 $[M - CH_2CH_2\ \text{furane}]^+$ (19), 205 $[233 - CO]^+$ (20), 95 $[^+CH_2CH_2\ \text{furane}]^+$ (91), 81 $[\text{pyrilium}]^+$ (100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546\,\text{nm}}{-62.3 \quad -65.0 \quad -74.9}\,(c = 2.39,\ \text{CHCl}_3).$$

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GUAIANOLIDES FROM *CENTAUREA CANARIENSIS*[*]

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Key Word Index—*Centaurea canariensis*; Compositae; sesquiterpene lactones; guaianolides; costic acid derivative.

Abstract—The aerial parts of *Centaurea canariensis* afforded four new guaianolides, all closely related to dehydrocostus lactone, and a derivative of costic acid. The structures were elucidated by spectroscopic methods.

INTRODUCTION

Many species from the large genus *Centaurea* (tribe Cynareae) have been investigated chemically. In addition to polyacetylenes [1] several sesquiterpene lactones [2] have been isolated. *C. canariensis* Brouss. var. *subexpinnata* Burch. also contains acetylenes and several sesquiterpene lactones, all closely related to dehydrocostus lactone.

RESULTS AND DISCUSSION

The roots of *C. canariensis* afforded the tetrayne **1** and aplotaxene (**2**), while the aerial parts gave capillol acetate (**3**) [1], germacrene D, bicyclogermacrene, γ- and δ-cadinene and five new compounds, the costic acid derivative **4** and four guaianolides (**7**–**10**). **4** after addition of diazomethane afforded on oxidation the ketone **6**. The ^1H NMR data of **4** and **6** (Table 1) clearly showed that **4** was a derivative of costic acid. Spin decoupling allowed the assignment of all signals. The position of the hydroxy group followed from the ^1H NMR data of the corresponding ketone **6**. The downfield shift of the broadened singlets of H-15 agreed only with a keto group at C-3. The small coupling $J_{2,3}$ required a 3β-hydroxy group. The stereochemistry at C-5 and C-7 followed from the couplings observed for H-5 and H-7. Consequently, the ^1H NMR data were in part very similar to those of costic acid. The ^1H NMR data of **7**, **9** and **10** were close to those of 8α-senecioyloxy dehydrocostus lactone [3]. (Table 1). Spin decoupling allowed the assignment of all

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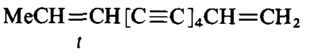
[*] Part 372 in the series 'Naturally Occurring Terpene Derivatives'. For Part 371, see Bohlmann, F. and Zdero, C. (1981) *Phytochemistry* **20** 2529.

Table 1. ^{1}H NMR spectral data of compounds **4** and **6–10** (400 MHz, $CDCl_3$, TMS as internal standard)

	4 (C_6D_6)	**6**	**7**	**8***	**9**	**10**
H-1	5.40 *dd*	6.00 *d*	2.99 *ddd*	2.93 *ddd*	2.99 *ddd*	3.00 *ddd*
H-2α H-2β	5.47 *dd*	6.85 *d*	1.83 *m*	1.91 *m* 1.85 *m*	1.84 *m*	1.83 *m*
H-3α H-3β	5.32 *s* (*br*)	—	2.44 *m* 2.51 *m*	2.48 *m* 2.54 *m*	2.45 *m* 2.54 *m*	2.45 *ddddd* 2.53 *m*
H-5	2.01 *d* (*br*)	1.88 *d* (*br*)	2.81 *dd* (*br*)	2.81 *dd* (*br*)	2.82 *dd* (*br*)	2.83 *dd* (*br*)
H-6α	1.69 *d* (*br*)	1.77 *d* (*br*)	—	—	—	—
H-6β	1.41 *dddd*	1.62 *m*	3.96 *dd*	3.89 *dd*	4.05 *dd*	4.04 *dd*
H-7	2.56 *dddd* (*br*)	2.64 *dddd* (*br*)	2.83 *ddddd*	2.48 *m*	3.21 *ddddd*	3.23 *ddddd*
H-8α	1.59 *dd* (*br*)	1.75 *m*	—	—	—	—
H-8β	1.34 *m*	1.6 *m*	3.92 *ddd*	3.71 *m*	5.07 *ddd*	5.01 *ddd*
H-9α H-9β	1.4 *m*	1.5 *m*	2.69 *dd* 2.26 *dd*	2.70 *dd* 2.14 *dd*	2.70 *dd* 2.34 *dd*	2.72 *dd* 2.35 *dd*
H-13	6.34 *s* (*br*)	6.22 *s* (*br*)	6.27 *d*	1.40 *d*	6.23 *d*	6.22 *d*
H-13′	5.36 *s* (*br*)	5.62 *s* (*br*)	6.15 *d*		5.62 *d*	5.62 *d*
H-14 H-14′	0.79 *s*	0.96 *s*	5.05 *s* (*br*) 4.93 *s* (*br*)	4.94 *s* (*br*) 4.91 *s* (*br*)	5.04 *s* (*br*) 4.92 *s* (*br*)	5.05 *s* (*br*) 4.91 *s* (*br*)
H-15	5.32 *s* (*br*)	6.08 *s* (*br*)	5.28 *s* (*br*)	5.22 *s* (*br*)	5.29 *s* (*br*)	5.28 *s* (*br*)
H-15′	4.69 *s* (*br*)	5.17 *s* (*br*)	5.07 *s* (*br*)	5.04 *s* (*br*)	5.09 *s* (*br*)	5.04 *s* (*br*)
OCOR	—	—	—	—	6.18 *s* (*br*)	6.33 *s* (*br*)
					5.67 *s* (*br*)	5.96 *s* (*br*)
					1.95 *s* (*br*)	4.38 *s* (*br*)
OMe	—	3.77 *s*	—	—	—	—

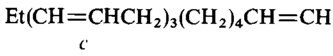
*H-11, *dq* 2.54.

J(Hz): compound **4**: 1,2 = 10; 1,3 = 1.5; 2,3 = 2.5; 5,6β = 6α,6β = 6β,7α = 12; 6α,7α = 7α,8α = 3; 7α,8β = 12; 8α,8β = 13; 8α,9α = 4; compound **6**: 1,2 = 10; 5,6β = 6α,6β = 6β,7α = 12; 6α,7α = 7α,8α = 3; compounds **7–10**: 1,2α = 1,2β = 1,5 = 8.5; 5,6 = 10; 6,7 = 9; 7,13 = 3.5; 7,13′ = 3.0; 7,8 = 10; 8,9α = 5; 8,9β = 4.5 (compound **8**: 7,8β = 8; 7,11 = 10.5; 11,13 = 7; compound **10**: 3α,3β = 17; 2α,3α = 2β,3α = 8.5; 3α,15 = 2).



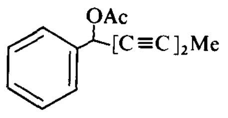
$\underset{t}{\mathrm{MeCH{=}CH}}[\mathrm{C{\equiv}C}]_4\mathrm{CH{=}CH_2}$

1

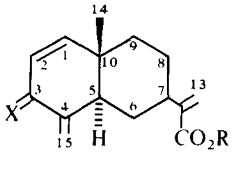


$\mathrm{Et}(\underset{c}{\mathrm{CH{=}CH}}\mathrm{CH_2})_3(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}$

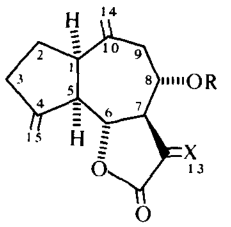
2

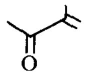
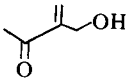


3



	4	**5**	**6**
R	H	Me	Me
X	βOH,H	βOH,H	=O



	7	**8**	**9**	**10**
R	H	H		
X	$=CH_2$	αMe, H	$=CH_2$	$=CH_2$

signals, especially those of the main constituent **10**, where only a few signals were overlapped multiplets. The stereochemistry followed from the couplings observed for H-1, H-5, H-7 and H-8, while the nature of the oxygen function at C-8 was easily deduced from the typical ^{1}H NMR signals. In the ^{1}H NMR spectrum of **8** (Table 1) only a few signals were slightly different from those of **7**. However, the missing signals of methylene protons (H-13) were replaced by a methyl doublet at δ 1.40 and a doublet quartet at δ 2.54, indicating the presence of a dihydro derivative of **7**. The stereochemistry at C-11 followed from the large coupling $J_{7,11}$. **10** is a 3-desoxy derivative of cynaropicrin, which has been reported several times from the genus *Centaurea* [4–8]. Highly oxygenated germacranolides, however, are much more widespread [2].

EXPERIMENTAL

The air-dried plant material (collected from Tenerife, voucher 80/1480, deposited in the Herbarium of the Institute of Plant systematic, Göttingen) was extracted with Et_2O–petrol (1:2) and the resulting extracts were sepd by CC (Si gel) and repeated TLC (Si gel). Known compounds were identified by comparison of their IR and ^{1}H NMR spectra with those of authentic material. The roots (10 g) afforded 2 mg **1** and 10 mg **2**, while the aerial parts (200 g) gave 50 mg germacrene-D, 50 mg bicyclogermacrene, 5 mg γ- and 20 mg δ-cadinene, 5 mg **3**, 3 mg **4** (Et_2O–petrol, 3:1), 2 mg **7** (Et_2O–petrol, 1:1), 2 mg **8** (Et_2O–petrol, 1:1), 2 mg **9** (Et_2O–petrol, 1:1) and 20 mg **10** (Et_2O–petrol, 3:1).

3-*Oxo*-1,2-*dehydrocostic acid* (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 3500–2700, 1690, 1620 ($C{=}CCO_2H$); MS m/z (rel. int.): 248.141 $[M]^+$ (81) ($C_{15}H_{20}O_3$), 230 $[M - H_2O]^+$ (24), 215 $[230 - Me]^+$ (32), 202 $[230 - CO]^+$ (30), 187 $[202 - Me]^+$ (37), 91 $[C_7H_7]^+$ (100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+18 \quad +19 \quad +22 \quad +23} (c = 0.15, \text{CHCl}_3).$$

To 3 mg **4** in 1 ml Et_2O was added excess CH_2N_2. TLC (Et_2O–petrol, 1:1) afforded 3 mg **5**, which was stirred with 50 mg MnO_2 in 2 ml Et_2O for 2 hr. TLC (Et_2O–petrol, 1:3) afforded 2 mg **6**, colourless gum; MS m/z (rel. int.): 260.141 $[M]^+$ (53) ($C_{16}H_{20}O_3$), 245 $[M - Me]^+$ (37), 228 $[M - MeOH]^+$ (56), 213 $[228 - Me]^+$ (23), 200 $[228 - CO]^+$ (51), 185 $[200 - Me]^+$ (47), 91 $[C_7H_7]^+$ (100).

8α-*Hydroxydehydrocostus lactone* (**7**). Colourless crystals, mp 106° (Et_2O–petrol), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS m/z (rel. int.): 246.126 $[M]^+$ (5) ($C_{15}H_{18}O_3$), 228 $[M - H_2O]^+$ (38), 91 (78), 69 (100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+76 \quad +84 \quad +100 \quad +156} (c = 0.1, \text{CHCl}_3).$$

8α-*Hydroxy*-11β,13H-*dehydrocostus lactone* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1790 (γ-lactone); MS m/z (rel. int.): 248.149 $[M]^+$ (18) ($C_{15}H_{20}O_3$), 230 $[M - H_2O]^+$ (21), 202 $[230 - CO]^+$ (10), 158 $[202 - CO_2]^+$ (63), 107 (100), 91 (79), 79 (85), 71 (85), 69 (63); $[\alpha]_D = +16°$($c = 0.1$, $CHCl_3$).

8α-*Methacryloyloxy dehydrocostus lactone* (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790 (γ-lactone), 1730 ($C{=}CCO_2R$); MS m/z (rel. int.): 314.152 $[M]^+$ (0.3) ($C_{19}H_{22}O_4$), 228 $[M - RCO_2H]^+$ (28), 213 $[228 - Me]^+$ (2), 200 $[228 - CO]^+$ (9), 69 $[C_3H_5CO]^+$ (100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+102 \quad +110 \quad +128 \quad +165} (c = 0.1, \text{CHCl}_3).$$

3-*Desoxycynaropicrin* (**10**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1770 (γ-lactone), 1720, 1640 ($C{=}CCO_2R$); MS m/z (rel. int.): 330 $[M]^+$ (0.1), 312 $[M - H_2O]^+$ (0.2), 228.115 $[M - RCO_2H]^+$ (100) ($C_{15}H_{16}O_2$), 213 $[228 - Me]^+$ (7), 200 $[228 - CO]^+$ (7), 85 $[HOC_3H_4CO]^+$ (20);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+112 \quad +117 \quad +133 \quad +183} (c = 2.0, \text{CHCl}_3).$$

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