and 17 mg $LiAlH_4$ was stirred in dry Et_2O for 2 hr. Wet Et_2O was added to the mixture and it was acidified with 5% HCl. The Et_2O phase was washed with H_2O and after evaporation of Et_2O, 35 mg of α-himachalene [5] was obtained.

β-Torosol (**2**). $[\alpha]_D^{25}$ − 175° ($CHCl_3$; *c* 2.5). MS *m/z* (rel. int.): 220 $[M]^+$ (48), 205 (18), 189 (35), 161 (30), 133 (70), 91 (100) and 79 (70). (Observed *m/z* 220.1825, calc. for $C_{15}H_{24}O$, 220.1827). Compound **2** (87 mg) was tosylated as explained above and 114 mg **2b** was obtained.

Reduction of **2b** *to γ-himachalene.* As explained above, 81 mg of **2b** was reduced with $LiAlH_4$ and 21 mg of γ-himachalene [8] was obtained.

Andirolactone (**3**). After isolation from the silica gel column, **3** was purified by prep. TLC with $CHCl_3$–EtOAc (9:1) and 85 mg of pure **3** was obtained. $[\alpha]_D^{25}$ 3.2° ($CHCl_3$; *c* 2.1). MS *m/z* (rel. int.): 178 $[M]^+$ (48), 163 (10), 145 (8), 111 (46) and 68 (100). (Observed *m/z* 178.100, calc. for $C_{11}H_{14}O_2$, 178.099).

trans-*Atlanton-6-ol* (**4**). After isolation from the silica gel column, **4** was purified by prep. TLC with $CHCl_3$–Et_2O (8:2) and 79 mg of pure **4** was obtained. $[\alpha]_D^{25}$ 0.15° ($CHCl_3$; *c* 1.2). MS *m/z* (rel. int.): 234 $[M]^+$ (34), 216 (11), 151 (100), 123 (86), 83 (90), 55 (57) and 43 (70). (Observed *m/z* 234.1625, calculated for $C_{15}H_{22}O_2$, 234.1620).

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NEROLIDOL DERIVATIVES FROM *ASTERISCUS SERICEUS*

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Key Word Index—*Asteriscus sericeus*; Compositae; sesquiterpenes; nerolidol derivatives; asteriscunolide A–D.

Abstract—The aerial parts of *Asteriscus sericeus* afforded, as other species of this genus, the humulene derivatives asteriscunolide A–D and two new types of nerolidol derivative, their structures being elucidated by high field NMR techniques.

From the genus *Asteriscus* (Compositae, Inuleae, Inulinae) so far two of the three species have been studied chemically [1–3]. Typical constituents are humulene derivatives such as asteriscunolide A–D (**1–4**) [1–3]. The investigation of a further species, *A. sericeus* (L.f.) DC., afforded in addition to widespread compounds (see Experimental) also **1–4**. Furthermore two nerolidol derivatives (**5** and **6**) were present. Though in the mass spectra no molecular ions could be detected, the molecular formulae followed indirectly from the ^{13}C NMR spectra (Table 1) and the ^1H NMR spectral data (Table 2). The ^{13}C NMR signals of **5** indicated two olefinic double bonds, two oxygen bearing carbons and one carbonyl carbon which was replaced by a secondary hydroxyl in the case of **6** (71.4 *d*). Inspection of the ^1H NMR spectra clearly showed that a vinyl and a prenyl end group was present in both compounds. Furthermore, two singlets for tertiary methyls could be detected. The chemical shifts of the latter required methyl groups at oxygen bearing carbons. Thus the presence of nerolidol derivatives with a 3,7-ether linkage were likely. Spin decoupling in the case of **6** allowed the assignment of most signals and led to the sequences H-8 through H-12(13) and $-CH_2CH_2CH(OH)-$. The latter three carbons must be C-4 – C-6. The relative position of the oxygen function could be assigned by the observed NOE's between H-15, H-2 (2%), H-lt (2%) and H-4 (4%). The position of the keto group also followed from the observed McLafferty fragmentation in the mass spectrum of **5**. Similarly, the ketone **5** showed NOE's between H-15, H-2 (10%) and H-

Table 1. ^{13}C NMR signals of **5** and **6** ($CDCl_3$, 67.9 MHz, δ-values)

C	**5**	**6**
1	112.5 *t*	110.1 *t*
2	144.7 *d*	147.3 *d*
3	73.7 *s*	73.0 *s*
4	33.9 *t*	31.7 *t*
5	40.0 *t*	40.9 *t*
6	214.8 *s*	71.4 *d*
7	82.4 *s*	77.0 *s*
8	31.7 *t*	25.0 *t*
9	22.3 *t*	22.0 *t*
10	123.9 *d*	125.6 *d*
11	131.9 *s*	130.8 *s*
12	25.6 *q*	25.9 *q*
13	17.6 *q*	17.7 *q*
14	26.1 *q*	22.0 *q*
15	28.9 *q*	28.6 *q*

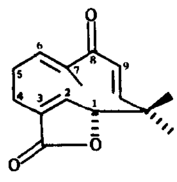
Table 2. ^{1}H NMR spectral data of **5** and **6** ($CDCl_3$, 400 MHz, δ-values)

H	**5**	**6**
1t	5.31 *dd*	5.08 *dd*
1c	5.10 *dd*	4.94 *dd*
2	5.90 *dd*	5.92 *dd*
4α	2.01 *ddd*	1.70 *m*
4β	2.14 *ddd*	
5α	2.41 *ddd*	1.74 *m*
5β	2.48 *ddd*	1.91 *m*
6	—	3.51 *m*
8	1.59 *m* 1.76 *m*	1.65 *m*
9	1.92 *m* 2.10 *m*	2.05 *m*
10	5.05 *br t*	5.08 *br t*
12	1.66 *br s*	1.68 *br s*
13	1.59 *br s*	1.62 *br s*
14	1.34 *s*	1.26 *s*
15	1.38 *s*	1.21 *s*

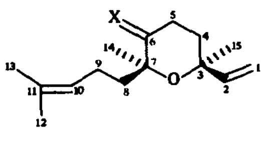
J[Hz]: 1c,1t = 1.5; 1c, 2 = 10.5; 1t, 2 = 17; 9,10 = 7; compound **5**: 4α,4β = 14; 4α,5β = 10; 4β,5β = 4β,5α ~ 5; 5α,5β = 16.

4α (10 %), between H-14, H-4α (6 %) and H-8 (4 %) as well as between H-4α, H-14 (5 %) and H-15 (5 %). Accordingly, the methyls were *cis*-orientated and the absence of NOE's of H-14 or H-15 with H-6 in compound **6** required a 6α-hydroxyl group. Inspection of models indicated that the data of **5** most likely required a rapid equilibrium of two boat conformers. As **5** and **6** are derivatives of nerolidol, the absolute configuration most likely is the same. This is supported by the positive Cotton effect of **5** as the corresponding linalol derivative, which is antipodal to nerolidol, showed a negative Cotton effect [4] due to the axial methyl at C-7. However, in the ketone **5** the equatorial methyl at C-7 is replaced by a large substituent which may lead to the opposite sign of the Cotton effect. Most likely **6** is formed via 6,7-epoxynerolidol. The desoxy derivative of **6** we have named cyclonerolidol.

The isolation of **1**–**4** from an *Asteriscus* species clearly shows that this type of humulene derivative is characteristic for this genus. So far the investigation of related genera gave always other types of natural products.



	1	**2**	**3**	**4**
Δ^6	*Z*	*E*	*Z*	*E*
Δ^9	*Z*	*Z*	*E*	*E*



5 X = O
6 X = αOH,H

EXPERIMENTAL

The air dried aerial parts (200 g, voucher 86/1925, grown in the Botanical Garden of Orotava, seeds collected in the Valle Guerra) was extracted with Et_2O–MeOH–petrol (1:1:1). After treatment of the extract with MeOH the soluble part was first separated by CC (Si gel and further by TLC (Si gel, PF 254). The less polar fractions (petrol and Et_2O–petrol, 1:9) gave 20 mg γ- and 20 mg δ-cadinene, 40 mg α-humulene, 40 mg γ-curcumene and 30 mg ar-curcumene. The fractions obtained with Et_2O–petrol (1:3) afforded 210 mg *cis*-chrysanthemyl acetate, 100 mg 1-hydroxy-ar-curcumene, 30 mg desoxyperezone and 60 mg **5** (TLC, Et_2O–petrol, 3:17, R_f 0.75). The CC fractions obtained with Et_2O gave 50 mg **6** (TLC, Et_2O–petrol, 1:1, R_f 0.80), 500 mg **1**, 350 mg **2**, 300 mg **3**, 500 mg **4** and 200 mg cadinol-T. The most polar CC fractions (MeOH) gave 10 mg sitosteryl- and 10 mg stigmasteryl-β-D-glucopyranoside. Known compounds were identified by comparison of the 400 MHz ^{1}H NMR spectra with those of authentic material.

6-*Oxo-cyclonerolidol* (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1735 (C=O); GC/MS *m/z* (rel. int.): 221 $[M-Me]^+$ (1), 154 $[M-C_6H_{10}$, McLafferty$]^+$ (26), 111 (42), 93 (23), 82 (21), 68 (100); CD (MeOH): $\Delta\varepsilon_{300} + 1.3$.

6α-*Hydroxycyclonerolidol* (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3620 (OH); CIMS *m/z* (rel. int.): 239 $[M+1]^+$ (9), 221 $[239-H_2O]^+$ (100), 203 $[221-H_2O]^+$ (23); $[\alpha]_D + 16.5$ ($CHCl_3$; *c* 0.27).

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