

graphed on a Dowex 50w \times 2 resin column (pyridine form, 3 cm \times 100 cm). Elution was performed with a linear gradient system made by 1.5 l of pyridine-HOAc buffer (pH 3.1, 0.2 M pyridine) and 1.5 l of the same buffer (pH 5.0, 2.0 M pyridine). The fractions containing **1** were combined and concd to a small vol. The concentrate was then chromatographed on an Avicel cellulose column (4 cm \times 43 cm) with solvent 1. As compound **1** fraction thus obtained was contaminated with various substances, including proline, further purification was conducted by chromatography using a silica gel column (Wako C-200, 4 \times 40 cm) with solvent 2 and by recrystallization from H_2O - Me_2CO (\times 3). The yield of pure **1** was ca 1.2 g, mp 196–197°; $[\alpha]_D^{23} +4.0$ (H_2O ; c 1.6), $+13.0$ (6 M HCl; c 0.8); (Found: C, 44.92; H, 8.44; N, 10.42. Calc. for $\text{C}_3\text{H}_{11}\text{NO}_3$: C, 45.10; H, 8.33; N, 10.52%); ^1H NMR (90 MHz, D_2O , TSP): δ 1.26 and 1.47 (3H, s and 3 H, s, respectively, *gem*-dimethyl group), 3.65 (1H, s, H-2); IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3410, 3075, 1635, 1576, 1492, 1400, 1327, 1167, 1107, 972, 902, 740; SIMS m/z : 134 $[\text{M}+1]^+$.

HI-red P reduction. A small amount of **1** (10 mg) was heated with 1 ml of HI (57%) and 10 mg of red P in a sealed tube at 153° for 5 hr. After purification according to ref. [3], the reaction mixture was analysed by TLC (silica gel and Avicel cellulose; solvent 2 and 3) and an amino acid analyser. Valine was detected as the reaction product.

Degradation by $\text{Ba}(\text{OH})_2$. A small amount of **1** was heated with satd $\text{Ba}(\text{OH})_2$ soln at 120° for 20 hr. The reaction mixture was

adjusted to pH 3 by 1M H_2SO_4 and then filtered. The filtrate was evapd to dryness, dissolved in H_2O and then analysed by TLC and an amino acid analyser. Glycine was detected together with unreacted **1**.

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ACETYLENIC COMPOUNDS AND OTHER CONSTITUENTS FROM *CINERARIA* SPECIES

L. LEHMANN, J. JAKUPOVIC, F. BOHLMANN and L. VINCENT*

Institute of Organic Chemistry, Technical University of Berlin, D-1000 Berlin, 12, F.R.G.; *Department of Plant Sciences, Rhodes University, Grahamstown 6140, R.S.A.

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Key Word Index—*Cineraria britteniae*, *C. geifolia*; Compositae; acetylenic compounds; sesquiterpenes; myrcene derivatives.

Abstract—From two *Cineraria* species three new diacetylenes and two myrcene derivatives were isolated in addition to known compounds.

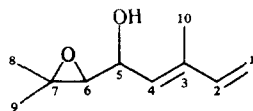
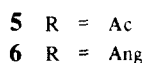
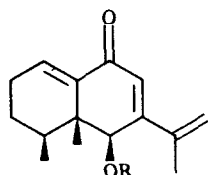
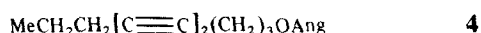
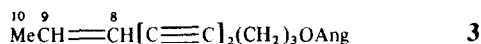
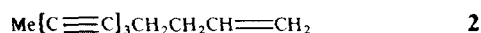
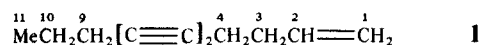
INTRODUCTION

From the South African genus *Cineraria* some species have been studied chemically [1–4]. Most characteristic are the unusual C_{11} -acetylenes and special eremophilanes. We have studied a further species and reinvestigated another one and the results are reported in this paper.

RESULTS AND DISCUSSION

The aerial parts of *Cineraria britteniae* Hutch. et R. A. Dyer afforded large amounts of the triene **2** [1]. Further-

more, the eremophilanes **5** [1] and **6** [1], spathulenol, the *E/Z*-isomers **7a/b** and the diyne **1** were present. The structure of the latter followed from the molecular formula ($\text{C}_{11}\text{H}_{14}$) and from the NMR spectral data. In the ^1H NMR spectrum characteristic signals of a vinyl end group were visible (δ 5.03 *dd*, 5.08 *dd* and 5.83 *ddt*). Spin decoupling showed that two methylene groups were attached to the vinyl group (δ 2.26 *dt* and 2.22 *tt*). The last signal showed a long range coupling with a broadened triplet at δ 2.34 which is typical for diynes. The remaining signals required a *n*-propyl group. In agreement with the fragmentation pattern in the mass spectrometer therefore



undec-1-en-5,7-diyne was present. The ^{13}C NMR spectrum further supported this structure.

The ^1H NMR of **7a** and **7b**, which could not be separated, showed the characteristic signals of *E*- and *Z*-configured prenyl groups. Furthermore, double doublets at δ 4.34 and 4.43 and doublets at δ 2.85 and 2.83, respectively, indicated the presence of α -hydroxy epoxides with two methyl substituents (δ 1.33 and 1.31 s). Thus isomeric 5-hydroxy-ocimene-6,7-epoxides were present. The configuration of the Δ^3 -bond was indicated by the chemical shifts of H-2 which is usually more down field in the *Z*-configuration dienes. Clear NOE's between H-10 and H-5 and between H-10 and H-4, respectively, established the stereochemistry. The relative configurations at C-5 and C-6 could not be determined.

The roots gave in addition to **5** the diyne **4**. The structure also followed from the ^1H NMR data which clearly indicated the presence of a primary angelate of a C_{10} -diyne. All signals could be assigned by spin decoupling.

The reinvestigation of the roots of *C. geifolia* L. gave the angelate **3** in addition to two compounds isolated previously [1]. The UV spectrum of **3** indicated the presence of a diynene (λ_{max} 280, 264, 250, 238 nm) and the ^1H NMR spectrum showed, by spin decoupling, sequences which required the structure **3** with an *E*-configuration for the double bond.

This investigation shows again that the genus *Cineraria* is very uniform chemically. The unique C_{11} -acetylenes and sesquiterpenes like **5** and derived compounds are isolated only from representatives of this genus. C_{10} acetylenes like **3** and **4** seem not to be present in other genera of the tribe Senecioneae.

EXPERIMENTAL

The air-dried plant material was collected in September 1986 in South Africa (*C. britteniae*, voucher 86/46, deposited in the

Herbarium of Rhodes University, collected at the Ecce Pass, and *C. geifolia*, voucher 86/132, deposited in the Herbarium of Rhodes University, collected on strand of Scarborough) and extracted and worked-up as reported previously [5].

The extract of 20 g roots of *C. britteniae* gave by TLC (silica gel, Et_2O -petrol, 1:9) 3 mg **4** (R_f 0.70) and 17 mg **5**. The extract of 315 g aerial parts gave by CC (silica gel) and TLC (silica gel, petrol) 650 mg **2**, 200 mg **1** (two developments, R_f 0.90), still containing **2**. The CC fraction obtained with Et_2O -petrol (1:3) gave by TLC 7 mg **5** and 40 mg **6**. The polar CC fraction (Et_2O -petrol, 1:1) afforded by TLC (Et_2O -petrol, 1:1, three developments) 100 mg spathulenol and a mixture of 7 mg **7a** and 3 mg **7b** (R_f 0.50).

The extract of 7 g roots of *C. geifolia* gave by CC and TLC (Et_2O -petrol, 1:9) 2 mg **3** (R_f 0.60). The more polar fractions afforded by TLC (Et_2O -petrol, 1:3) 4 mg **5** and 11 mg **6**. Known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material.

Undec-1-ene-5,7-diyne (1). Colourless oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 2230 ($\text{C}\equiv\text{C}$), 3080, 930 ($\text{CH}=\text{CH}_2$); MS m/z (rel. int.): 146.110 [M] $^+$ (5) (calc. for $\text{C}_{11}\text{H}_{14}$: 146.110), 145 [$\text{M}-\text{H}$] $^+$ (10), 131 [$\text{M}-\text{Me}$] $^+$ (38), 117 [$\text{M}-\text{C}_2\text{H}_5$] $^+$ (44), 103 [$\text{M}-\text{C}_3\text{H}_7$] $^+$ (36), 91 [$\text{M}-\text{C}_4\text{H}_7$] $^+$ (89), 77 [C_6H_5] $^+$ (100); ^1H NMR (CDCl_3): δ 5.03 (*dd*, H-1c), 5.08 (*dd*, H-1t), 5.83 (*ddt*, H-2), 2.26 (*dt*, H-3), 2.22 (*tt*, H-4), 2.34 (*br t*, H-9), 1.54 (*tq*, H-10), 0.98 (*t*, H-11); (J [Hz]: 1c, 2 = 11; 1c, 1t = 1.5; 1t, 2 = 17; 2, 3 = 6.5; 3, 4 = 7; 4, 9 = 1; 9, 10 = 10, 11 = 7.5), ^{13}C NMR (CDCl_3 , C-1-C-11): δ 115.9, 136.5, 32.6, 21.2, 77.7 \dagger , 65.7*, 65.3*, 76.5 \dagger , 19.1, 21.9, 13.5 (assigned by 2D $^{13}\text{C}/^1\text{H}$ -correlated spectrum, * \dagger signal may be interchangeable).

Dec-8E-ene-4,6-diyne-1-ol angelate (3). Colourless oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 2240 ($\text{C}\equiv\text{C}$), 1710 ($\text{C}=\text{CCO}_2\text{R}$); MS m/z (rel. int.): 230.131 [M] $^+$ (16) (calc. for $\text{C}_{15}\text{H}_{18}\text{O}_2$: 230.131), 215 [$\text{M}-\text{Me}$] $^+$ (22), 130 [$\text{M}-\text{RCO}_2\text{H}$] $^+$ (100), 83 [RCO] $^+$ (96); ^1H NMR (CDCl_3): δ 4.23 (*t*, H-1), 1.92 (*tt*, H-2), 2.45 (*br t*, H-3), 5.50 (*br dq*, H-8), 6.29 (*dq*, H-9), 1.80 (*dd*, H-10); OAng: 6.07 (*qq*, H-3'), 1.98 (*dq*, H-4'), 1.88 (*dq*, H-5'); (J [Hz]: 1, 2 = 6; 2, 3 = 9, 10 = 7; 8, 9 = 16; 8, 10 = 2).

Deca-4,6-diyne-1-ol angelate (4). Colourless oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 2150 ($\text{C}\equiv\text{C}$), 1720 ($\text{C}=\text{CCO}_2\text{R}$); CIMS m/z (rel. int.): 233 [$\text{M}+1$] $^+$ (41), 203 (23), 133 (5), 83 (100); ^1H NMR (CDCl_3): δ 4.23 (*t*, H-1), 1.90 (*tt*, H-2), 2.39 (*br t*, H-3), 2.23 (*br t*, H-8), 1.55 (*tq*, H-9), 0.98 (*t*, H-10); (J [Hz]: 1, 2 = 6.5; 2, 3 = 7; 8, 9 = 9, 10 = 7.5).

5-Hydroxy-6,7-epoxy-3E- and 3Z-ocimene (7a/b). Colourless oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm^{-1} : 3580 (OH), CIMS m/z (rel. int.): 169 [$\text{M}+1$] $^+$ (2.4), 151 [$169-\text{H}_2\text{O}$] $^+$ (100); ^1H NMR (CDCl_3 , in parenthesis 3Z-isomer): δ 5.13 (5.22) (*d*, H-1c), 5.27 (5.35) (*d*, H-1t), 6.40 (6.71) (*dd*, H-2), 5.55 (5.46) (*br d*, H-4), 4.34 (4.43) (*dd*, H-5), 2.85 (2.83) (*d*, H-6), 1.33 (1.31) (s, H-8, H-9), 1.83 (1.90) (*d*, H-10); (J [Hz]: 1c, 2 = 11; 1t, 2 = 17.5; 4, 5 = 9; 4, 10 = 1.5; 5, 6 = 8).

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