

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 -Me₂CO (\times 3). The yield of pure **1** was ca 1.2 g, mp 196–197°; $[\alpha]_{D}^{23} +4.0$ (H₂O; c 1.6), +13.0 (6 M HCl; c 0.8); (Found: C, 44.92; H, 8.44; N, 10.42. Calc. for C₅H₁₁NO₃: C, 45.10; H, 8.33; N, 10.52%); ¹H NMR (90 MHz, D₂O, TSP): δ 1.26 and 1.47 (3H, s and 3H, 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 [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 Ba(OH)₂. A small amount of **1** was heated with satd Ba(OH)₂ soln at 120° for 20 hr. The reaction mixture was

adjusted to pH 3 by 1M H₂SO₄ and then filtered. The filtrate was evapd to dryness, dissolved in H₂O 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.

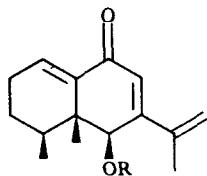
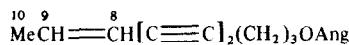
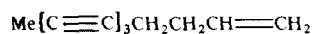
INTRODUCTION

From the South African genus *Cineraria* some species have been studied chemically [1–4]. Most characteristic are the unusual C₁₁-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

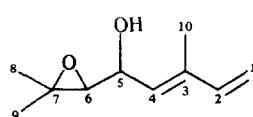
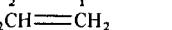
The aerial parts of *Cineraria britteniae* Hutch. et R. A. Dyer afforded large amounts of the triyne **2** [1]. Further-

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 (C₁₁H₁₄) 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



5 R = Ac

6 R = Ang



7a E

7b Z

undec-1-en-5,7-diyne was present. The ¹³C 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 C₁₀-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 C₁₁-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. britanniae*, voucher 86/46, deposited in the

Herbarium of Rhodes University, collected at the Ecca 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. britanniae* gave by TLC (silica gel, Et₂O-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 Et₂O-petrol (1:3) gave by TLC 7 mg 5 and 40 mg 6. The polar CC fraction (Et₂O-petrol, 1:1) afforded by TLC (Et₂O-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 (Et₂O-petrol, 1:9) 2 mg 3 (R_f 0.60). The more polar fractions afforded by TLC (Et₂O-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 (C≡C), 3080, 930 (CH=CH₂); MS m/z (rel. int.): 146.110 [M]⁺ (5) (calc. for C₁₁H₁₄: 146.110), 145 [M-H]⁺ (10), 131 [M-Me]⁺ (38), 117 [M-C₂H₅]⁺ (44), 103 [M-C₃H₇]⁺ (36), 91 [M-C₄H₇]⁺ (89), 77 [C₆H₅]⁺ (100); ¹H NMR (CDCl₃): 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), ¹³C NMR (CDCl₃, C-1-C-11): δ 115.9, 136.5, 32.6, 21.2, 77.7^t, 65.7^t, 65.3^t, 76.5^t, 19.1, 21.9, 13.5 (assigned by 2D ¹³C/¹H-correlated spectrum, *^tsignal 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 (C≡C), 1710 (C=CCO₂R); MS m/z (rel. int.): 230.131 [M]⁺ (16) (calc. for C₁₅H₁₈O₂: 230.131), 215 [M-Me]⁺ (22), 130 [M-RCO₂H]⁺ (100), 83 [RCO]⁺ (96); ¹H NMR (CDCl₃): 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 (C≡C), 1720 (C=CCO₂R); CIMS m/z (rel. int.): 233 [M+1]⁺ (41), 203 (23), 133 (5), 83 (100); ¹H NMR (CDCl₃): 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=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 [M+1]⁺ (2.4), 151 [169-H₂O]⁺ (100); ¹H NMR (CDCl₃, 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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