Phytochemistry, 1978, Vol 17, pp. 759–761. Pergamon Press Printed in England

NEW NORSESQUITERPENES FROM *SENECIO DIGITALIFOLIUS**

FERDINAND BOHLMANN and CHRISTA ZDERO
Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, Germany

(*Received* 22 *November* 1977)

Key Word Index—*Senecio digitalifolius*; Compositae; bisabolene derivatives; new norsesquiterpenes.

Abstract—The South African *Senecio digitalifolius* contain besides several known furanoeremophilanes three new norsesquiterpenes all related to bisabolene. The structures are elucidated by spectroscopic methods.

In connection with our work on South African *Senecio* species [1, 2] we have now investigated *Senecio digitalifolius* DC. collected in Natal in the Cathedral Peak area. The roots contained, in addition to eremophilene (**1**) the known furanoeremophilanes **2**–**7**. Except for **2** these are benzofurans, which have been isolated only from a few *Senecio* species [1–3], but which are common in *Cacalia* species [4].

The aerial parts contained minute amounts of the pentaynene **8**, sesamine (**9**), germacrene D (**10**), γ-curcumene (**11**) and α-curcumene (**12**) but the main constituent was a ketone with the molecular formula $C_{14}H_{22}O$. The IR spectrum showed that it was an unsaturated ketone (1670, 1635 cm^{-1}) and all data were only in agreement with structure **13**. The ^1H- and ^{13}C-NMR data are summarized in Table 1. Using double resonance and shift reagent the assignment of all the signals in the ^1H-NMR spectrum were established, while those in the ^{13}C-NMR spectrum were in good agreement with those of piperitone (**14**) and the corresponding bisabolene derivative [5]. The MS showed that the ketone was a bisabolene derivative. In particular the typical fragment at *m/e* 110 (100%), formed by a McLafferty fragmentation showed that only a formula with a methyl cyclohexenone part structure was possible.

Furthermore we have isolated two C_{14}-hydrocarbons which could be separated from **10**–**12** only by $AgNO_3$-Si gel TLC. The spectral data (Table 2) clearly showed that the structures of the hydrocarbons are **15** and **16**, which are closely related to **13**. Comparison of the optical rotations with those of α-curcumene showed that the absolute configuration was most probably that given in structures **15** and **16**. We suggest the trivial name senedigitalene for compound **16**. Norsesquiterpenes of this type have not been isolated before and further work is necessary to determine whether these compounds are chemotaxonomically important.

EXPERIMENTAL

IR were measured in CCl_4; optical rotations were determined in $CHCl_3$. The air dried plant material (voucher 77/84) was extracted with Et_2O–petrol and the extracts were separated by CC (Si gel, act. grade II) and further by TLC (Si gel, GF 254) using Et_2O–petrol mixtures as eluents. 250 g roots afforded 100 mg **1**, 5 mg **2**, 60 mg **3**, 100 mg **4**, 70 mg **6**, 300 mg **5** and 180 mg **7**, while 500 g aerial parts yielded 5 mg **11**, 5 mg **15**, 5 mg **12**, 10 mg **16**, 0.1 mg **8**, 600 mg **13** (Et_1O–petrol, 1:10)

Table 1. NMR data of compound **13**. ($CDCl_3$, 270 MHz and 25 MHz respectively, δ-values, TMS as internal standard)

		+ $Eu(fod)_3$	^{13}C	**13**	**14**
1α-H	*ddd* 2.14	*ddd* 2.78	C-1	*d* 49.9	*d* 51.6
3-H	*tq* 5.86	*s*(*br*) 6.46	C-2	*s* 200.9	*s* 200.0
5α-H	*ddd* 1.93	*dd*(*br*) 2.59	C-3	*d* 127.2	*d* 126.8
5β-H	*m* 1.78	*ddd* 2.49	C-4	*s* 161.0	*s* 160.5
6-H	*m* 1.78	*m* 2.12	C-5	*t* 30.9	*t* 30.5
7α-H	*m* 2.30	*dddq* 2.89	C-6	*t* 26.9	*t* 23.2
8-H	*m* 1.42	*m* 1.52	C-7	*d* 30.5	
9-H	*m* 1.28		C-8	*t* 34.1*	
10-H	*dt* 2.05	*m* 2.12	C-9	*t* 24.1	
11-H	*ddt* 5.80	*ddt* 5.85	C-10	*t* 34.0*	
12t-H	*ddt* 5.0	*d*(*br*) 5.02	C-11	*d* 138.9	
12c-H	*ddt* 4.94	*d*(*br*) 4.96	C-12	*t* 114.4	
14-H	*d* 0.79	*d* 1.12	C-14	*q* 15.8	
15-H	*s*(*br*) 1.93	*s*(*br*) 2.04	C-15	*q* 24.1	

J(Hz): 1α, 6α = 4; 1α, 6β = 12.5; 1α, 7 = 4; 3,5 = 1.5; 3,15 = 1.5; 5α,5β = 15; 5α,6α = 4; 5α,6β = 9; 5β,6α = 4; 5β,6β = 3; 7α,8 = 7α,14 = 7; 9,10 = 7; 10,11 = 6.5; 10,12 = 1.5; 11,12(*cis*) = 10; 11,12(*trans*) = 17; 12,12 = 1.

* These signals are interchangeable.

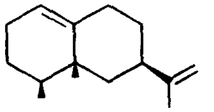
Table 2. ^1H-NMR data of compounds **15** and **16** ($CDCl_3$)

	15	**16**
2-H	*d* 5.61	*d* 7.11
3-H	*d* 5.58	*d* 7.07
5-H	*s*(*br*) 2.08	*d* 7.07
6-H		*d* 7.11
7-H	*dt* 2.14	*dt* 2.14
8-H	*m* 1.33	*m* 1.32
9-H		
10-H	*dt* 2.03	*dt* 2.02
11-H	*ddt* 5.79	*ddt* 5.76
12t-H	*d*(*br*) 4.98	*d*(*br*) 4.96
12c-H	*d*(*br*) 4.93	*d*(*br*) 4.91
14-H	*d* 1.01	*d* 1.22
15-H	*s*(*br*) 1.77	*s*(*br*) 2.32

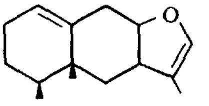
J(Hz): 7,8 = 7,14 = 7; 9,10 = 7; 10,11 = 6.5; 11,12(*trans*) = 17; 11,12(*cis*) = 10 **15**: 2,3 = 6 **16**: 2,3 = 8.

---

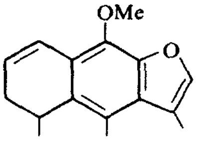
* Part. 141 in the series 'Naturally Occurring Terpene-Derivatives'; for part 140 see: Bohlmann, F. and Czerson, H. (1978) *Phytochemistry* in press.



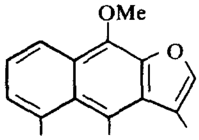
1



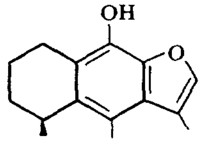
2



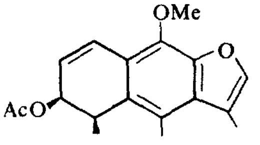
3



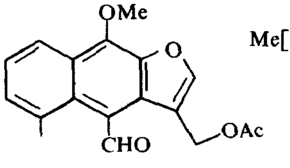
4



5



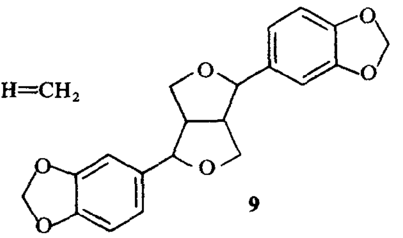
6



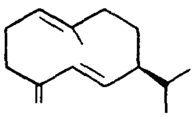
7

$Me[C{\equiv}]_5CH{=}CH_2$

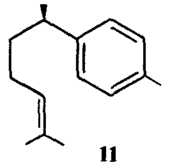
8



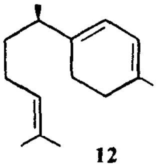
9



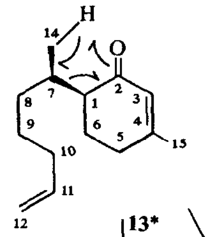
10

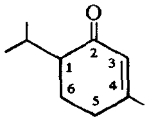


11

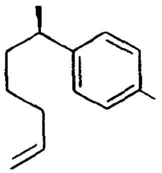


12

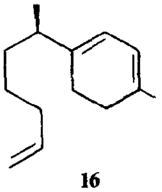




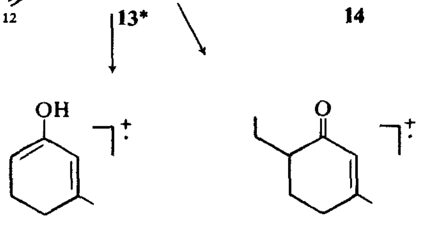
14



15



16



m/e 110 (100%)
17

m/e 137 (52)
18

*Numbering as that of bisabolene.

and 40 mg **9** (**11**, **12**, **15** and **16** were separated by TLC ($AgNO_3$-Si gel, Et_2O–petrol, 1:20).

1,2-Dihydrosenedigital-2-one (**13**). Colourless oil, $bp_{0.1\,Torr}$ 130°, IR ν_{max} cm^{-1}: $C{=}C{-}C{=}O$ 1670, 1635; $-CH{=}CH_2$ 3110, 995, 920. MS *m/e* (rel. int.): 206.167 (5) (calc. for $C_{14}H_{22}O$ 206.167); 137 (52); $-{}^{\cdot}CH_3$ 191 (3); **17**: 110 (100); 110 $-{}^{\cdot}CH_3$ 95 (53); 110 $-CO$ 82 (50)

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\text{ nm}}{-39.4 \quad -41.7 \quad -50.2 \quad -125.7^\circ} (c = 4.1)$$

5,6-Dehydrosenedigitalene (**15**). Colourless oil, not completely free from **11**, IR ν_{max} cm^{-1}: $-CH{=}CH_2$ 990, 910. MS *m/e* (rel. int.): 188.156 (9) (calc. for $C_{14}H_{20}$ 188.156); $-{}^{\cdot}CH_3$ 173 (9); $-H_2C{=}CHCH_2{}^{\cdot}$ 145 (12); $-H_2C{=}CH(CH_2)_3{}^{\cdot}$ 119 (100).

Senedigitalene (**16**). Colourless oil, $bp_{0.1\,Torr}$ 70°, IR ν_{max} cm^{-1}: $-CH{=}CH_2$ 3120, 990, 900. MS *m/e* (rel. int.): 190.172 (24) (calc. for $C_{14}H_{22}$ 190.172); $-{}^{\cdot}CH_3$ 175 (8); $-H_2C{=}CHCH_2{}^{\cdot}$ 147 (6); $-H_2C{=}CH(CH_2)_3{}^{\cdot}$ 121 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\text{ nm}}{-32.6 \quad -34.0 \quad -39.9 \quad -135.5^\circ} (c = 1.38)$$

Acknowledgements—We thank Dr O. Hilliard, Department of

Botany, University of Natal, for her help in collecting and identification of the plant material and the 'Deutsche Forschungsgemeinschaft' for financial support.

REFERENCES

1. Bohlmann, F. and Zdero, C. (1978) *Phytochemistry* in press.
2. Bohlmann, F., Knoll, K. H., Zdero, C., Mahanta, P. K., Grenz, M., Suwita, A., Ehlers, D., Le Van, N., Abraham, W. R. and Natu, A. A. (1977) *Phytochemistry* **16**, 965.
3. Bohlmann, F., Zdero, C. and Grenz, M. (1977) *Chem. Ber.* **110**, 474.
4. Naya, K., Miyoshi, Y., Mori, H., Takai, K. and Nakanishi, M. (1976) *Chem. Letters* 73.
5. Bohlmann, F., Zdero, C. and Schöneweiss, (1976) *Chem. Ber.* **109**, 3366.