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A NEW CARVOTANACETONE DERIVATIVE FROM *BLUMEA WIGHTIANA**

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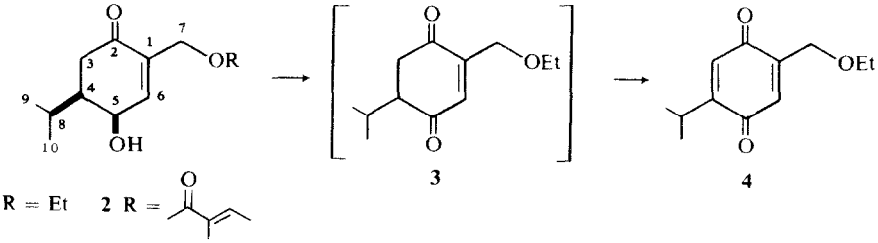
Key Word Index—*Blumea wightiana*; Compositae; Inuleae; new carvotanacetone derivatives.

So far no characteristic compounds have been isolated from *Blumea* species (tribe Inuleae). In addition to simple monoterpenes [1, 2], some flavanoids [3] and the widespread pentaynene [4], only sporadic isolations of other compounds are reported. The aerial parts of *Blumea wightiana* DC. afforded only two compounds, which were identified as the carvotanacetone derivatives **1** and **2**. The structure of **1** followed clearly from the result of the manganese dioxide oxidation, which afforded the quinone **4** as shown by ^{1}H NMR-spectroscopy (Table 1). However **1** probably was an artefact as the plant material was extracted with ethanol. The free alcohol could not be isolated. The absolute configuration probably was the same as that of D-carvotanacetone as the optical rotation of **1** also was positive.

Table 1. ^{1}H NMR data of **1**, **2** and **4** (270 MHz, $CDCl_3$, TMS as internal standard, δ values)

	1	2	4
3α-H	2.56 *dd*	2.59 *dd*	6.50 *d*
3β-H	2.47 *dd*	2.49 *dd*	
4α-H	1.67 *m*	1.68 *m*	—
5α-H	4.51 *dd*	4.52 *dd*	—
6-H	7.02 *dt*	6.93 *dt*	6.80 *t*
7-H	4.19 *ddd*	4.90 *ddd*	4.34 *d*
7′-H	4.13 *ddd*	4.83 *ddd*	
8-H	1.67 *m*	1.68 *m*	3.05 *dqq*
9-H	1.05 *d*	1.05 *d*	1.14 *d*
10-H	0.97 *d*	0.98 *d*	
OR	3.56 *q*	6.91 *qq*	3.60 *q*
	1.23 *t*	1.86 *dq*	1.26 *t*
		1.81 *dq*	

J(Hz): 3α, 3β = 16.5; 3α, 4α = 5.5; 3β, 4α = 11; 4α, 5α = 3; 5α, 6 = 5.5; 5α, 7 = 1.5; 8, 9 = 8, 10 = 7; OEt: 7; OTigl: 7 and 1.5.



1 R = Et **2** R =

3 **4**

EXPERIMENTAL

The air-dried plant material was extracted with EtOH and the resulting extract first separated by CC (Si gel, act. grade II) and further by TLC (Si gel GF 254). 1 kg of aerial parts afforded 75 mg **1** (Et_2O petrol, 1:1) and 10 mg **2** (Et_2O–petrol, 1:1).

5-Hydroxy-7-ethoxy-carvotanacetone (**1**). Colourless oil, $bp_{0.1}$ 150°. IR cm^{-1}: 3620 (OH); 1685 (C=C CO). MS *m/e* (rel. int.): 212.143 (M^+) ($C_{12}H_{20}O_3$); 195 ($M^+ - {}^{\cdot}OH$, 13); 183 ($M^+ - {}^{\cdot}C_2H_5$, 28); 169 ($M^+ - {}^{\cdot}C_3H_7$, 90); 151 (169 − H_2O, 79); 123 (151 − CO, 100); 95 (123 − C_2H_4, 93).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+59.3 \quad +61.9 \quad +70.4 \quad +113.2} (c = 4.7).$$

15 mg **1** in 3 ml Et_2O were stirred for 3 hr with 100 mg MnO_2. After TLC (Et_2O–petrol, 1:3) 10 mg **4** were obtained, yellow oil. IR cm^{-1}: 1655, 1615 (*p*-quinone). MS *m/e* (rel. int.): 210 (M^+, 33); 195 ($M^+ - {}^{\cdot}Me$, 46); 165 ($M^+ - {}^{\cdot}OEt$, 100).

5-Hydroxy-7-ethoxy-carvotanacetone (**1**). Colourless oil, $bp_{0.1}$ IR cm^{-1}: 3620 (OH); 1720, 1655 (C=C CO_2R); 1685 (C=C CO). MS *m/e* (rel. int.): 266.152 (M^+, 2) ($C_{15}H_{22}O_4$); 249 ($M^+ - {}^{\cdot}OH$, 2); 166 ($M^+ - C_4H_7CO_2H$, 24); 83 ($C_4H_7CO^+$, 100).

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REFERENCES

1. Simonsen, J. L. and Rau, G. M. (1922) *J. Chem. Soc.* 121, 876.
2. Karrer, W. (1958) *Konstitution und Vorkommen der Organischen Pflanzenstoffe*. Birkhäuser, Basel.
3. Rao, C., Rao, T. and Muralikrishna, B. (1977) *Planta Med.* 235.
4. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London and New York.

* Part 205 in the series "Naturally Occurring Terpene-Derivatives". For Part 204 see Bohlmann, F. and Dutta, L. (1979) *Phytochemistry* **18** (in press).