283, 260, IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1720, 1640, 1600, 1495, 1410, 1300, 1185, 1130, 1025, 855, PMR ($CDCl_3$, 100 MHz) δ 1.46 (6H, *s*), 5.67 (1H, *d*, J = 10 Hz), 6.17 (1H, *d*, J = 9 Hz), 6.66 (1H, *d*, J = 8 Hz), 6.85 (1H, *d*, J = 10 Hz), 7.18 (1H, *d*, J = 8 Hz), 7.57 (1H, *d*, J = 9 Hz), identical with seselin (**4**). ^{13}C-NMR ($CDCl_3$; 25.2 MHz) gave only eight resonance lines at δ 28.2 (*q*), 77.3 (*d*), 112.8 (*d*), 113.5 (*d*), 115.3 (*d*), 127.8 (*d*), 130 (*d*), 143.9 (*d*) which could not be resolved completely. Treatment with sulphuric acid gave umbelliferone [8] which confirmed the structure.

Acknowledgements—We thank Dr. R. Ramage, Robert Robinson Laboratories, University of Liverpool for his helpful discussion and PL-480 authorities for a supporting grant

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NEW TERPENE DERIVATIVES FROM *PIQUERIA TRINERVIA**

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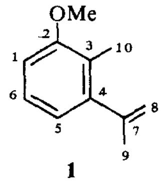
Key Word Index—*Piqueria trinervia*; Eupatorieae; Compositae; new terpene derivatives.

Piqueria trinervia Cav. has been investigated before. Besides the widespread pentaynene, santalal and santalol [1] as well as several carquejol derivatives [2] have been reported. A new investigation of the roots yields several new terpenes, all with an unusual carbon skeleton. The ^{1}H-NMR-data (Tables 1 and 2) lead to the structures **1**–**4**. From the aerial parts, besides **6** also **3** and **4** together with **5** have been isolated. While **1** and **2** are of the same skeleton as carquejol, aldehydes of the isoferulol type like **3**–**5** up to now only have been isolated from the Umbelliferae [3]. A compound very similar to **2** has been found in the roots of a *Baccharis* species [4].

Table 1. ^{1}*H*-NMR-data of **1** and **2** (270 MHz, δ-values, $CDCl_3$)

	1	J (Hz)	**2**	J (Hz)
1-H	*d*(*br*) 6.74	1,6 = 8	*ddd* 6.02	1,2 = 2.5
2-H	—	—	*s*(*br*) 5 78	1,6 = 11
4-H	—		*d*(*br*) 3.37	1,5 = 2.5
5-H	*d*(*br*) 6.83	5,6 = 8	*ddd* 5.43	4,5 = 5
6-H	*dd* 7.12		*d*(*br*) 5.80	5,6 = 3
8-H	*dq* 5.28	8,8′ = 2 3	*dq* 4.96	5.6 = 3
8′-H	*dq* 4.79	8,9 = 1.2	*s*(*br*) 4.91	
9-H	*dd* 1.99		*s*(*br*) 1.74	
10-H	*s* 2.66		*s*(*br*) 5.30	
10′-H			*s*(*br*) 5.21	
OMe	*s* 3 80		—	
OAc	—		*s* 2.05	
OCOR′	—		*qq* 2.57	2′, 3′ = 7
			d 1 17	
			d 1.18	



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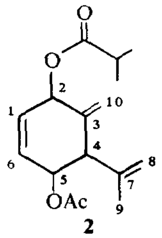

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Table 2. ^{1}H-NMR-data of **3**–**5** (270 MHz, δ-values, $CDCl_3$)

	3	**4**	**5**
2-H	*d*(*br*) 5.83	*d*(*br*) 5.82	*d*(*br*) 5.81
3-H	*dd* 5.62	*dd* 5.63	*dd* 5.61
4-H	*d*(*br*) 5.76	*d*(*br*) 5.74	*d*(*br*) 5.74
7-H	*s* 1.31	*s* 1.31	*s* 1.31
8-H	*s* 1.26	*s* 1.26	*s* 1.25
9-H	*dd* 1.17	*dd* 2 13	*s* 2.15
10-H	*s* 10.25	*s* 10.25	*s* 10.24
OCOR′	*tq* 5.90	*tq* 6.04	*qq* 5.72
	s(*br*) 4.59	*s*(*br*) 4.18	*d* 2,21
	s(*br*) 2.18	*s*(*br*) 2.15	*d* 1.92
OAc	*s* 2.13	—	—

J (Hz): 2, 3 = 3, 5; 2, 9 = 1; 3, 4 = 10.5; 9, 10 = 1; 2′, 4′ = 2′, 5′ = 1.5.

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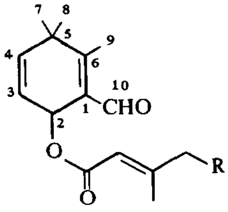
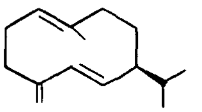
* Part 126 in the series 'Naturally Occurring Terpene Derivatives'; Part 125: Bohlmann, F. and Czerson, H. (1978) *Phytochemistry* **17**, 568.



3: R = OAc
4: R = OH
5: R = H



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EXPERIMENTAL

IR in CCl_4; ^{1}H-NMR in $CDCl_3$, δ-values; MS at 70 eV. The air dried plant material (collected in Guatemala by Dr. R. King, voucher RMK 7295) was extracted with Et_2O–petrol (1:2) and the extracts first separated by column chromatography (Si gel, act. grade II) and further by TLC (Si gel GF 254) using Et_2O–petrol mixtures. 30 g roots afford 8 mg **1** (Et_2O–petrol, 1:20), 20 mg **2** (Et_2O–petrol, 1:3), 15 mg **3** and 5 mg **4**, while 110 g aerial parts yielded 10 mg **6**, 4 mg **5** (Et_2O–petrol, 1:3), 25 mg **3** (Et_2O–petrol, 1:3) and 10 mg **4** (Et_2O–petrol, 1:1).

Tetradehydrocarquejol methyl ether (**1**). Colourless oil, IR: C=C 1650, 950; aromatic ring 1580, 1470, 1260 cm^{-1}. MS: $M^+ m/e$ 162.105 (100%) (calc. for $C_{11}H_{14}O$ 162.105); —$^{\bullet}CH_3$ 147 (65): 147 —CO 119 (54).

2-Isobutyryloxy-2H-1,6-dehydrocarquejol acetate (**2**). Colourless oil. IR: CO_2R 1740; OAc 1740, 1240; $C{=}CH_2$ 1645, 900 cm^{-1}. MS: M^+ m/e 278 (0.1%); —AcOH 218.131 (2) (calc. for $C_{14}H_{18}O_2$ 218.131), —Me_2 C=C=O 148 (100); $C_3H_7CO^+$ 71 (73); $MeCO^+$ 43 (92).

Isoferulol-(4-acetoxysenecioate) (**3**). Colourless oil, IR: OAc 1755, 1220; C=C CO_2R 1720, 1660; CHO 2760, 1685 cm^{-1}. MS: M^+ m/e 306.147 (3%) (calc. for $C_{17}H_{22}O_5$ 306.147); —$^{\bullet}CH_3$ 291 (0.5); 291 —AcOH 231 (17); —O=C=C(Me) CH_2OAc 166 (44); $HOCH_2C(Me){=}CHCO^+$ 99 (100).

Isoferulol-(4-hydroxysenecioate) (**4**). Colourless oil, IR: OH 3620; C=C CO_2R 1720, 1660; CHO 2760, 1685 cm^{-1}. MS: M^+ m/e 264 (1%); —$^{\bullet}$ Me 249.113 (10) (calc. for $C_{14}H_{17}O_4$ 249.113); —O=C=C (Me)CH_2OAc 166 (65); $HOCH_2C(Me)$ $={CHCO}^+$ 99 (100).

Isoferulol senecioate (**5**). Colourless oil, IR: C=C CO_2R 1720, 1650; CHO 1690 cm^{-1}. MS: M^+ m/e 248.141 (1%) (calc. for $C_{15}H_{20}O_3$ 248.141); —$^{\bullet}$ Me 233 (1.5); —O=C=CMe_2 166 (22); $C_4H_7CO^+$ 83 (100).

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AHD-VALTRATE, A NEW VALEPOTRIATE FROM *CENTRANTHUS RUBER*

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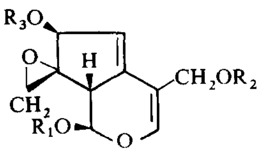
Key Word Index—*Centranthus ruber*; Valerianaceae; valepotriates; AHD-valtrate; IVHD-valtrate.

INTRODUCTION

Work conducted in recent years has shown that *Centranthus ruber* DC contains several valepotriates found earlier in *Valeriana* i.e. valtrate (**1**), didrovaltrate (**2**), acevaltrate (**3**) and IVHD-valtrate (**4**) [1, 2]. The structure of **4** was elucidated by Stahl and Schild [3], the sites of the acyloxy groups remaining, however, unspecified. These authors also mention another valepotriate of unindentified structure and with R_f value close to that of IVHD-valtrate. Studies conducted on *C. ruber* led to the isolation of two compounds with R_f values similar to that of IVHD-valtrate, which we supposed to be the latter compound and the unknown one reported by Stahl and Schild. We now report the results from our investigations on the structure of these compounds, designated here as CV_1 and CV_2.

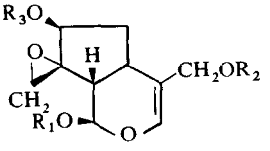
RESULTS AND DISCUSSION

Compound CV_1 is a colourless, crystalline substance, mp 107–108° (pentane). The chromatographic spot of this substance turns blue when treated with ben-



$R_1 = R_3 = Me_2CHCH_2CO$
$R_2 = MeCO$

1



$R_1 = R_2 = Me_2CHCH_2CO$
$R_3 = MeCO$

2