Phytochemistry, 1978, Vol. 17, pp. 559–560 Pergamon Press Printed in England

β-CYCLOLAVANDULIC ACID AND SESELIN IN THE ESSENTIAL OIL OF *CARUM ROXBURGHIANUM*

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(*Received* 13 *May* 1977)

Key Word Index—*Carum roxburghianum*; Umbelliferae; β-cyclolavandulic acid; seselin.

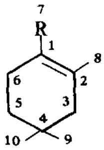
INTRODUCTION

The steam volatile oil of the seeds of *Carum roxburghianum* was reported [1] to contain a keto acid, $C_{10}H_{14}O_3$; mp 105–106° of undetermined structure and another compound, mp 114–115° which was thought to be *p*-isopropyl benzoic acid. We now present evidence for the identification of the compounds as β-cyclolavandulic acid (**1**; R = CO_2H) and seselin (**4**) respectively.

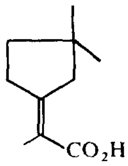
RESULTS

The essential oil obtained from the seeds of *Carum roxburghianum* was fractionally distilled at 5 mm of Hg and the fractions distilling between 82–104° on standing deposited a crystalline material. This material was dissolved in ether and extracted with dilute sodium bicarbonate solution. The aq. alkaline extract was acidified and extracted with ether. Removal of the solvent gave a solid which on recrystallisation from hexane deposited a white crystalline acid, mp 106–107°. Column chromatography of the oil over Si gel gave the acid in 15–25% yield. The acid analysed for $C_{10}H_{16}O_2$ and its UV absorption at λ_{max}^{EtOH} 223 nm (ε = 1316) and IR ($CHCl_3$) ν_{max} 3500–2500, 1680, 1640 cm^{-1} indicated an α,β-unsaturated acid. Its MS showed major peaks at *m/e* 168 (M^+), 153 (M^+-15), 140 (M^+-28), 125 (M^+-43), 123 (M^+-45) and 112 (M^+-56). On catalytic hydrogenation the acid absorbed one mole of hydrogen and gave a dihydro-derivative. *m/e* 170 (M^+), 137 (M^+-15-18), 110 (M^+-15-45) and 109 (M^+-61). The PMR ($CDCl_3$, 100 MHz) spectrum revealed the presence of two quaternary methyls at δ 0.92 (6H, *s*), one methylene at 1.37 (2H, *t*, *J* = 6 Hz), two allylic methylene at 1.94 (2H, *br.s*) and 2.34 (2H, *m*), one vinylic methyl at 2.06 (3H, *br.s*) and a carboxylic proton at 12.08 (1H, *s*). The natural abundance ^{13}C-NMR ($CDCl_3$; 25.2 MHz) spectrum in FT mode supported by off resonance decoupled experiments [2, 3] gave nine resonance lines at δ 22.6 (*q*, C-9 and C-10), 23.8 (*t*, C-5), 27.9 (*q*, C-8), 28.7 (*s*, C-4), 34.9 (*t*, C-3), 48.4 (*t*, C-6), 122 (*s*, C-1), 149.5 (*s*, C-2) and 174.3 (*s*, C-7).

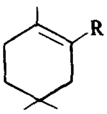
The above data pointed to structure **1** (R = CO_2H) for the acid which has already been isolated [4, 5] and synthesised [6, 7]. In the absence of a direct comparison, the methyl ester of the acid was ozonised [5] and a keto-ester, PMR ($CDCl_3$; 100 MHz) δ 1.01 (6H, *s*, Me—C—Me), 2.10 (3H, *s*, COME), 2.34 (2H, *s*), 2.81 (2H, *dd*, *J* = 8 Hz), 3.83 (3H, *s*, CO_2Me) was isolated which ruled out the possiblity of structure **2**. In order to distinguish between structure **1** (R = CO_2H) and **3** (R = CO_2H) for the acid, the diagnostic value of the lanthanide induced shift reagents was employed. Theoretically the induced shift initiated through the functional group at C-1 would give a larger shift of the resonance signal of the C-6 methylene than that of the C-3 methylene in structure **1** and it should be the opposite case in structure **3**. The induced paramagnetic shift of the resonance signals of the various protons in the alcohol **1** (R = CH_2OH) derived from the acid was observed under varying concentrations of $Eu(fod)_3$ shift reagent. With 41.4 mg of the alcohol in CCl_4 the induced downfield shifts observed for the C-3 and C-6 allylic methylene signals were Δ δ 0.12 and 0.34 at 5 mg; 0.23 and 0.74 at 10.8 mg and 0.54 and 1.80 at 25.2 mg concentration of the shift reagent. It was therefore evident that of the two allylic methylenes, the one with a multiplet (C-6), adjacent to another methylene (C-5), had a larger paramagnetic shift compared to the methylene (C-3) having a singlet resonance signal. This confirmed the structure **1** (R = CO_2H) for the acid although it might be present as the aldehyde **1** (R = CHO) in nature [5] but we could isolate only the acid.



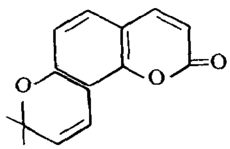
(**1**)



(**2**)



(**3**)



(**4**)

Column chromatography of the essential oil of *Carum roxburghianum* on Si gel with hexane–Et_2O (4:1) gave a fraction which was fluorescent under UV light. The fraction deposited a white crystalline compound, mp 114–115°. The water soluble portion of the essential oil consisted mainly of the same UV fluorescent compound. The total amount of this compound was 13% of the oil. It analysed for $C_{14}H_{12}O_3$; UV λ_{max}^{EtOH} nm: 330, 293, 283, 260, IR $\nu_{\max}^{CHCl_3}$ 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

REFERENCES

1. Malavya, B. K. and Dutt, S. (1942) *Proc. Ind. Acad Sci.* **16A**, 157.
2. Levy, G. C. and Nelson, G. L (1972) *Carbon-13 NMR for Organic Chemists.* Wiley Interscience, New York.
3. Strothers, J. B. (1972) *Carbon-13 NMR Spectroscopy.* Academic Press, New York.
4. Dixit, S. M., Rao, A. S. and Paknikar, S. K. (1967) *Chem. Ind. (London)* 1256.
5. Logani, M. K., Varshney, I. P., Pandey, R. C. and Dev, S (1967) *Tetrahedron Letters* 2645.
6. Brenner, A. and Schinz, H. (1952) *Helv. Chim. Acta* **35**, 1615
7. Kuhn, W. and Schinz, H. (1952) *Helv. Chim. Acta* **35**, 2008.
8. Dean, F. M. (1963) *Naturally Occurring Oxygen Ring Compounds* p 232 Butterworths, London.

Phytochemistry, 1978, Vol 17, pp 560–561 Pergamon Press Printed in England

NEW TERPENE DERIVATIVES FROM *PIQUERIA TRINERVIA**

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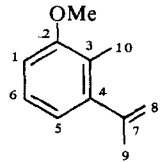
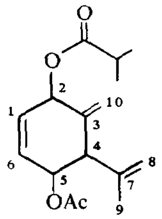
(*Received* 9 *September* 1977)

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].



1



2

Table 1. ^1H-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 *d* 1 17 *d* 1.18	2′, 3′ = 7

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 *s(br)* 4.59 *s(br)* 2.18	*tq* 6.04 *s(br)* 4.18 *s(br)* 2.15	*qq* 5.72 *d* 2,21 *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.