

## Occurrence of (—)-Car-3-en-2-one in *Zieria aspalathoides* (Rutaceae)

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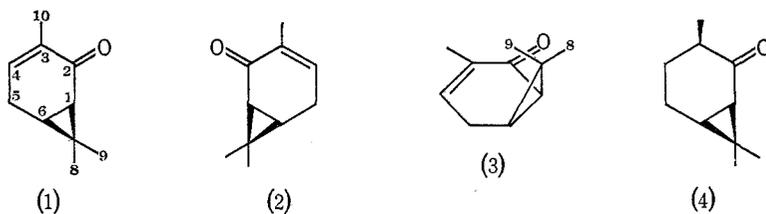
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### Abstract

The steam-volatile leaf oil of *Zieria aspalathoides* A. Cunn. ex Benth. contains (—)-car-3-en-2-one as its major component. Minor amounts of  $\alpha$ -phellandrene, car-3-ene, terpinolene, limonene, 1,8-cineole, myrtenol,  $\beta$ -trans-ocimene,  $\alpha$ -thujone and caryophyllene were tentatively identified by g.l.c. co-chromatography.

*Zieria aspalathoides* A. Cunn. ex Benth., popularly known as 'whorled zieria', is a small ericoid shrub of rocky ranges of central Victoria, western New South Wales and south-western Queensland. Steam distillation of foliage collected from the Warrumbungle National Park near Coonabarabran, N.S.W., yielded 0.7% of a volatile oil with a strong, characteristic odour. Infrared and gas-liquid chromatographic analysis indicated the presence of one major ketonic component (58%) and several minor components. Amongst the latter were tentatively identified  $\alpha$ -phellandrene (4%), car-3-ene (17%), terpinolene (9%), limonene (0.5%), 1,8-cineole (0.2%),  $\alpha$ -thujone (0.1%),  $\beta$ -trans-ocimene (1.5%), myrtenol (1%) and caryophyllene (1.5%).

The major component, a strongly laevorotatory, almost colourless liquid ( $[\alpha]_D -324^\circ$  in  $\text{CHCl}_3$ ), for which structure (1) is proposed, was shown to have the formula  $\text{C}_{10}\text{H}_{14}\text{O}$  by high resolution mass spectrometry. Its i.r. spectrum exhibited strong bands at  $1660\text{ cm}^{-1}$  ( $\alpha,\beta$ -unsaturated carbonyl) and at  $1640$  and  $900\text{ cm}^{-1}$  ( $\text{CH}=\text{C}<$ ).



The u.v. spectrum,  $\lambda_{\text{max}}$  228 nm ( $\epsilon$  6640), was indicative of a car-3-enone whilst the p.m.r. spectrum was very similar to the spectrum of synthetic (+)-car-3-en-2-one (2) ( $[\alpha]_D +243^\circ$  in  $\text{CHCl}_3$ ).<sup>1</sup>

Conclusive evidence for structure (1) was obtained from p.m.r. double irradiation, and benzene and europium complex shift experiments (Table 1). In benzene, the

<sup>1</sup> Burns, W. D. P., Carson, M. S., Cocker, W., and Shannon, P. V. R., *J. Chem. Soc. C*, 1968, 3073.

allylic methyl and the C1 cyclopropyl proton signals remained almost unchanged ( $\Delta\delta(\text{CCl}_4 - \text{C}_6\text{D}_6) -0.09$  and  $-0.06$  p.p.m. respectively) whereas the vinylic and C6 cyclopropyl proton signals experienced appreciable upfield shifts ( $\Delta\delta(\text{CCl}_4 - \text{C}_6\text{D}_6) +0.45$  p.p.m. in both cases), in agreement with the rules applying to chemical shifts induced by benzene in ketones.<sup>2,3</sup>  $\text{Eu}(\text{dpm})_3$  shifted the signals of protons closest to the carbonyl group further downfield, thus allowing the assignment of the C8 and C9 methyls as shown in (3).

Table 1. P.m.r. data for (-)-car-3-en-2-one

Chemical shifts are in p.p.m. from  $\text{Me}_4\text{Si}$ ; s singlet, m multiplet, dd doublet of doublets

Proton	Multiplicity	$\delta$ values		$\Delta\text{Eu}$ in $\text{CCl}_4$ (Hz/molar equiv.)	$J$ (Hz)
		In $\text{CCl}_4$	In $\text{C}_6\text{D}_6$		
H1	dd	1.52	1.58	2380	$J_{1,6}$ 7.8 $J_{1,5}$ 1.4
H4	m	6.28	5.83	840	$J_{4,6}$ 1.2 $J_{4,10}$ 1.4 $J_{4,5}$ 3.6 and 4.4
H5a	m	2.61	2.10	790	
H5b	m	2.44	1.99	920	$J_{5a,5b}$ 22.4
H6	m	1.35	0.90	760	$J_{6,5}$ 7.2 and 1.4
(C8)H <sub>3</sub>	s	1.17	0.84	300	
(C9)H <sub>3</sub>	s	1.04	0.84	930	
(C10)H <sub>3</sub>	m	1.68	1.77	1800	$J_{10,5}$ 2.0 and 2.4

Hydrogenation of (1) in the presence of a Pd/C catalyst yielded the dihydro derivative (4). Its spectral properties agreed well with published values for *cis*-caran-2-one.<sup>4</sup>

This is the first recorded occurrence of car-3-en-2-one in nature.

## Experimental

Infrared spectra were measured for liquid films. Gas-liquid chromatography was conducted in a Perkin-Elmer 900 gas chromatograph on 15 m by 0.5 mm i.d. S.C.O.T. columns with helium as carrier gas. Percentages of oil components were obtained with a Hewlett-Packard 3370A integrator. P.m.r. spectra were measured at 100 MHz for approximately 10% solutions with  $\text{Me}_4\text{Si}$  as internal reference; chemical shifts are in p.p.m. Mass spectrometry was conducted on a AEI MS 902 mass spectrometer operated at 70 eV. High resolution mass matching was conducted on gas-chromatographically pure samples.

### Isolation of Volatile Material

Fresh foliage and terminal branchlets (400 g) of *Zieria aspalathoides* (Voucher specimen 73-091, Museum of Applied Arts and Sciences Herbarium) were cohobated for 6 h in an all-glass apparatus to yield a pale yellow oil (2.7 ml),  $n_D^{20}$  1.4928,  $[\alpha]_D^{22} -156.4^\circ$  (neat oil),  $d_4^{20}$  0.9388.

### Identification of Known Components

$\alpha$ -Phellandrene, car-3-ene, terpinolene, limonene, 1,8-cineole,  $\beta$ -trans-ocimene,  $\alpha$ -thujone, caryophyllene and myrtenol were identified gas-chromatographically by their retention times and co-injection of pure isolates with the whole oil on two different columns (FFAP and SE-30).

<sup>2</sup> Williams, D. H., and Bhacca, N. S., *Tetrahedron*, 1965, **21**, 2021.

<sup>3</sup> Connolly, J. D., and McCrindle, R., *Chem. Ind. (London)*, 1965, 379.

<sup>4</sup> Cocker, W., Shannon, P. V. R., and Staniland, P. A., *J. Chem. Soc. C*, 1967, 485.

(-)-Car-3-en-2-one (I)

The crude oil (0.6 ml) was chromatographed on a silica column (25 g, silica BDH), light petroleum (75 ml, b.p. 60–80°), light petroleum–diethyl ether 9 : 1 (75 ml) and diethyl ether (75 ml) being used as eluents. The diethyl ether eluate was evaporated yielding (-)-car-3-en-2-one as an almost colourless liquid (300 mg),  $n_D^{20}$  1.5003,  $[\alpha]_D^{22}$   $-324^\circ$  (c, 4.6 in  $\text{CHCl}_3$ ),  $\lambda_{\text{max}}$  (EtOH) 228 nm ( $\epsilon$  6640); mass spectrum,  $m/e$  (%) (peaks of relative intensity < 7% of base peak not included): 150 (M, 100), 135 (32), 121 (7), 109 (19), 108 (34), 107 (42), 105 (8), 95 (11), 94 (7), 93 (8), 91 (26), 82 (13), 80 (15), 79 (19), 77 (11), 67 (25). Mol. wt (mass matching) found  $150.1040 \pm 0.001$ . Calc. for  $\text{C}_{10}\text{H}_{14}\text{O}$ : 150.1045.

Hydrogenation of (I)

(-)-Car-3-en-2-one (50 mg) was dissolved in 95% ethanol (10 ml) and hydrogenated at room temperature and atmospheric pressure for 20 min in the presence of a palladium/charcoal catalyst (20 mg, 10% Pd). The filtered solution yielded on evaporation of the solvent (+)-cis-caran-2-one (4) as a colourless liquid (50 mg),  $n_D^{20}$  1.4737,  $[\alpha]_D^{22}$   $+104^\circ$  (c, 2.0 in EtOH) (lit.<sup>4</sup> for enantiomer  $n_D^{20}$  1.4717,  $[\alpha]_D^{20}$   $-81^\circ$  in EtOH);  $\nu_{\text{max}}$  1695, 1452, 1378, 1330, 1219, 1179, 1073, 1026, 988, 956, 935, 887, 788  $\text{cm}^{-1}$ ; p.m.r. spectrum ( $\text{CCl}_4$ ):  $\delta$  0.95 (3H, d,  $J$  7 Hz,  $\text{CH}_3\text{CH}<$ ), 1.06 and 1.11 (6H, 2s,  $\text{Me}_2\text{C}<$ ); mass spectrum,  $m/e$  (%) (peaks of relative intensity < 5% of base peak not included): 152 (M, 36), 137 (5), 126 (22), 125 (5), 124 (10), 123 (7), 113 (5), 111 (7), 110 (31), 109 (19), 97 (8), 96 (9), 95 (50), 93 (7), 84 (7), 83 (31), 82 (100), 81 (24), 79 (8), 71 (8), 70 (12), 69 (14), 68 (11), 67 (55). Mol. wt (mass matching) found  $152.1204 \pm 0.001$ . Calc. for  $\text{C}_{10}\text{H}_{16}\text{O}$ : 152.1201.

Acknowledgments

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