

a HOM two-dimensional  $J$  spectrum and by analysis of the two overlapped ABX spin systems in the 1D spectrum, which resolved all the 16 lines of both AB portions in the severely crowded range  $\delta$  2.18-2.69. Moreover, since the stereochemistry of the protons at C-1 and C-4 is axial (4), it was possible to relate unequivocally the chemical shift of each proton at C-2 and at C-5, respectively, to their axial or equatorial position from the magnitude of the coupling constants.

To rule out the possibility that pacifenol is an artifact formed by rearrangement from prepacifenol through the silica gel chromatography (5), hexane extraction of *L. majuscula* gave a residue that, after washing with cold pentane and slow evaporation, gave crystalline pacifenol which is thus present as a natural product.

Details of the isolation procedure and the spectral data are available on request to the senior author.

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#### VOLATILE CONSTITUENTS OF *BORONIA LATIPINNA* LEAF

JOSEPH J. BROPHY,

*School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033, Australia*

IAN A. SOUTHWELL,\* and IAN A. STIFF

*Agricultural Research Centre, Wollongbar, N.S.W. 2480, Australia*

*Boronia latipinna* J.H. Willis or Grampians boronia (tribe Boronieae, family Rutaceae) (1), formerly grouped with *B. pinnata* (2), is endemic to the Grampian mountain regions of southwestern Victoria, Australia. This shrub, which prefers rocky situations often near mountain peaks, grows erect as a small-to-medium bush reaching from 1-4 m with pinnate leaves and bearing bright pink flowers. Although, as with other boronias, the pleasant aroma of crushed leaves indicates perfumery value, this species has hitherto escaped chemical investigation.

Other members of the genus *Boronia* are rich in citronellol (*B. citriodora*) (3), cyclocolorenone (*B. ledifolia*) (4), elemicin (*B. muelleri*) (5), ocimene (*B. anemonifolia*) (6),  $\beta$ -ionone (*B. megastigma*) (7,8), safrole (*B. safrolifera*) (9) and thujone (*B. thujona*) (10). Of these, the concentrated floral extract of *B. megastigma* is highly regarded commercially in perfumes and flavors (7,8).

## RESULTS AND DISCUSSION

Steam distillation of the leaf and terminal branchlets of *B. latipinna* from two collections in the Grampians, Victoria, gave 0.9% and 1.4% of a strongly scented, colorless volatile oil. Capillary gc/ms indicated 21 components at levels greater than 0.1% of the oil. The major component (60.6%) was shown, after lc purification, to be (+)-bornyl acetate. Gc, co-gc and gc/ms alone were insufficient to distinguish this ester from isobornyl acetate. This C2 epimer was eliminated as a possible structure by discreet ir absorption differences, <sup>1</sup>H-nmr chemical shift and coupling differences for the methyl and acetoxy methine protons and hydrolysis to (+)-borneol. Of the remaining components, 17 were identified by capillary gc/ms and co-gc (Table 1). The co-occurrence of these components in *B. latipinna* lends support to biogenetic pathways (11, 12) illustrating the relationship between bornyl acetate, borneol, camphor, tricyclene, camphene,  $\alpha$ -pinene, terpinolene, limonene, linalool, and myrcene. These transformations are also known in vitro (13, 14).

TABLE 1. Constituents of the Volatile Oil of *Boronia latipinna*

Retention Index (R <sub>I</sub> ) (FFAP)	Components	Percentage Composition	Identification
1017	tricyclene	0.6	a,b,c
1030	$\alpha$ -pinene	5.8	a,b,c
1076	camphene	9.5	a,b,c
1117	$\beta$ -pinene	0.2	a,b,c
1125	sabinene	0.1	c
1160	myrcene	2.7	a,b,c
1168	$\alpha$ -phellandrene	1.1	a,b,c
1205	limonene	5.0	a,b,c
1214	$\beta$ -phellandrene	1.8	a,b,c
1271	<i>p</i> -cymene	0.1	a,b,c
1285	terpinolene	1.5	a,b,c
1507	camphor	6.7	a,b,c
1536	linalool	1.1	a,b,c
1576	bornyl acetate	60.6	a,b,c,d,e
1592	caryophyllene	1.4	a,b,c
1665	humulene	0.1	a,b,c
1682	borneol	0.3	a,b,c
1723	C <sub>15</sub> H <sub>24</sub>	0.3	c
1960	unknown	0.5	c
2012	safrole	0.6	a,b,c
2036	unknown	0.3	c

<sup>a</sup>Retention index.

<sup>b</sup>Co-injection with authentic material.

<sup>c</sup>gc/ms.

<sup>d</sup><sup>1</sup>H nmr.

<sup>e</sup>Ir.

Bornyl acetate, available in lower yield from many plant sources (15, 16) is attracting increasing scientific interest as a perfumery and flavoring constituent (15, 16), insect antifeedant (17-19) and repellent (20), and, in the case of the (-)-isomer, a cockroach sex pheromone mimic (21).

## EXPERIMENTAL

ISOLATION OF VOLATILE OIL.—Leaf and terminal branchlets of *B. latipinna* (voucher no. CBG 8410929 lodged with the Australian National Botanic Gardens, Canberra, and MEL 668792 lodged with the National Herbarium of Victoria, South Yarra) were collected in the Mushroom Rocks region of the Grampians about 4 km south of Hall's Gap in southwestern Victoria, Australia. Steam distillation with cohobation in all glass apparatus gave a colorless oil (0.9% v/w) n<sub>D</sub><sup>20</sup> 1.4671, [ $\alpha$ ]<sub>D</sub><sup>23</sup> +43.7°. A second collection from the same population 6 months later gave an identical oil in 1.4% yield.

IDENTIFICATION OF CONSTITUENTS.—Analytical gc:FFAP and BPL fused silica WCOT columns (50 m  $\times$  0.2 mm); carrier gas N<sub>2</sub>, dual fid; temperature program: 3° per min from 70° to 200°. Individual components were identified by R<sub>I</sub> comparison and co-gc with authentic samples to confirm ms assignment. Composition (%) was determined using an electronic integrator. Gc/ms:FFAP-coated SCOT column (90

m × 0.5 mm) with the carrier gas interfaced to an AEI MS-12 through an all glass straight split; temperature program 80-225° at 3° per min; ionizing voltage 70 eV with ion source at 150°. Spectra were recorded every 6 sec and processed by a VG Digispec Display Data system.

**ISOLATION OF (+)-BORNYL ACETATE.**—The volatile oil (1.0 ml) was eluted from a deactivated alumina column (13.5 g) by flash elution with 5-ml portions of petroleum ether (40-60°). The third portion eluted substantially pure (+)-bornyl acetate (0.24 g),  $[\alpha]^{20}_D +43.3^\circ$  (CHCl<sub>3</sub>, c 12), lit. (15) +44.7°; ir, <sup>1</sup>H nmr, and ms comparable with literature values (22,23).

**HYDROLYSIS OF (+)-BORNYL ACETATE.**—The oil (1.0 ml) in MeOH (5.0 ml) was stirred at 20° with NaOH (0.2 g) in MeOH (10 ml). After 1 h, the solution was diluted with H<sub>2</sub>O (20 ml) and extracted with Et<sub>2</sub>O (3 × 20 ml). The combined organic extracts were washed with 10% H<sub>2</sub>SO<sub>4</sub> (20 ml), 5% NaHCO<sub>3</sub> solution (20 ml), brine (20 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated, and chromatographed over alumina (10.0 g). Flash elution with petroleum ether followed by petroleum ether: Et<sub>2</sub>O (50:1) gave (+) borneol  $[\alpha]^{30}_D +37$ . (CHCl<sub>3</sub>, c 6), lit. (15) +38°. Coinjection with authentic sample showed peak enhancement (R<sub>f</sub> 1687).

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