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TERPENOIDS FROM THE FRENCH LIVERWORT *TARGIONIA HYPOPHYLLA*

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Key Word Index—*Targionia hypophylla*; Targioniaceae; Hepaticae; *cis*- and *trans*-pinocarveyl acetates; mono-, sesqui- and diterpenoids.

Abstract—Two monoterpene acetates, *cis*- and *trans*-pinocarveyl acetates, which make up the characteristic aroma of the thalloid liverwort *Targionia hypophylla* were isolated, together with the previously known sesquiterpene alcohol, drimenol.

INTRODUCTION

Some liverworts emit monoterpenoids or simple aromatic compounds which are responsible for intense turpentine, mushroomy or fungal-like odours [1]. A very small thalloid liverwort, *Targionia hypophylla* L., belonging to the Targioniaceae emits an intense fragrance when it is crushed. In this paper, we report the isolation of two monoterpene acetates which comprise the characteristic fragrance of *T. hypophylla*.

RESULTS AND DISCUSSION

The ether-soluble portion of a methanol extract of dried and ground *T. hypophylla* was examined directly by TLC, GC and GC/MS; four monoterpene hydrocarbons, α-pinene, β-pinene, limonene and β-phellandrene, a sesquiterpene hydrocarbon, cuparene (**6**), a sesquiterpene alcohol, drimenol (**7**), and a diterpene alcohol, labda-7,13-dien-15-ol (**8**), were detected. The remaining extract was chromatographed on a silica gel–Lobar column using chloroform to give two monoterpene acetates, *cis*- and *trans*-pinocarveyl acetates (**1** and **2**) which showed the characteristic aroma of *T. hypophylla*, together with drimenol (**7**).

The presence of the acetyl groups in **1** and **2** was confirmed by their mass spectra (*m/z* 43) and ^{1}H NMR spectra [δ2.14 (*s*) for **1** and 2.06 (*s*) for **2**]. The ^{1}H NMR spectra of **1** and **2** were quite similar to those of β-pinene, indicating the presence of a pinane skeleton. The identification of the acetates (**1** and **2**) was carried out as follows: Commercially available *trans*-pinocarveol (**4**) was oxidized by pyridinium chlorochromate (PCC) to give pinocarvone (**5**), followed by lithium aluminium hydride reduction to afford a mixture of *cis*- and *trans*-pinocarveols (**3** and **4**). Both alcohols, after being isolated by a silica gel–Lobar column, were acetylated with acetic anhydride–pyridine to furnish *cis*- and *trans*-pinocarveyl acetates (**1** and **2**), whose spectral data (^{1}H NMR and MS) were identical to those of the natural monoterpene acetates. The absolute configurations of **1**, **2**, **6**, **7** and **8** remain to be established.

The occurrence of monoterpenoids in the Marchantiales is rare and pinane-, camphane-, bornane-, sabinane-, *p*-menthane- and 2,6-dimethyloctane-type monoterpenoids have been found in *Conocephalum* and *Wiesnerella* (Conocephalaceae), and *Asterella* species (Grimaldiaceae) [1]. As far as we are aware, this report is the first example of the isolation of *cis*- and *trans*-pinocarveyl acetates in plants. Drimenol (**7**) is often found in leafy liverworts [1]. The presence of labda-7,13-dien-15-ol (**8**) is known in the thalloid liverwort *Marchantia polymorpha* [2].

EXPERIMENTAL

TLC, GC and GC/MS were carried out as previously reported [3]. ^{1}H NMR spectra (400 MHz) were measured in $CDCl_3$ with TMS as internal standard.

Plant material. Targionia hypophylla L., identified by Y.A., has been deposited at the Herbarium of the Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. Dried *T. hypophylla*, collected in Le Collet de Deze, France, in August 1985, was ground and the ground material (11.5 g) was extracted with MeOH for 6 weeks. The crude extract, after removal of solvent, was partitioned between Et_2O and H_2O. On removal of the solvent, a viscous oil having a very strong characteristic aroma (206 mg) was obtained from the Et_2O layer. A small amount of the Et_2O extract was analysed directly by TLC, GC and GC/MS. The components obtained by GC/MS were identified by direct comparison of their MS with those of authentic samples. The presence of α-pinene, β-pinene, limonene, β-phellandrene, cuparene (**6**), drimenol (**7**) [1] and labda-7,13-dien-15-ol (**8**) [2] was thus identified. The remaining oil (200 mg) was chromatographed on a silica gel–Lobar column using $CHCl_3$ as solvent and divided into 3 fractions. The first fraction (10 mg) contained a mixture of mono- and sesquiterpene hydrocarbons in which α-pinene, β-pinene, limonene and β-phellandrene, and a sesquiterpene, cuparene (**6**), were detected by GC/MS. Five unidentified sesquiterpenoids, [*m/z* 204 $[M]^+$ (base 108), 204 (119), 218 (147), 218 (147) and 218 (136)] were also detected in the first fraction. Fraction 2 (30 mg) contained the intense fragrant oil, which was rechromatographed

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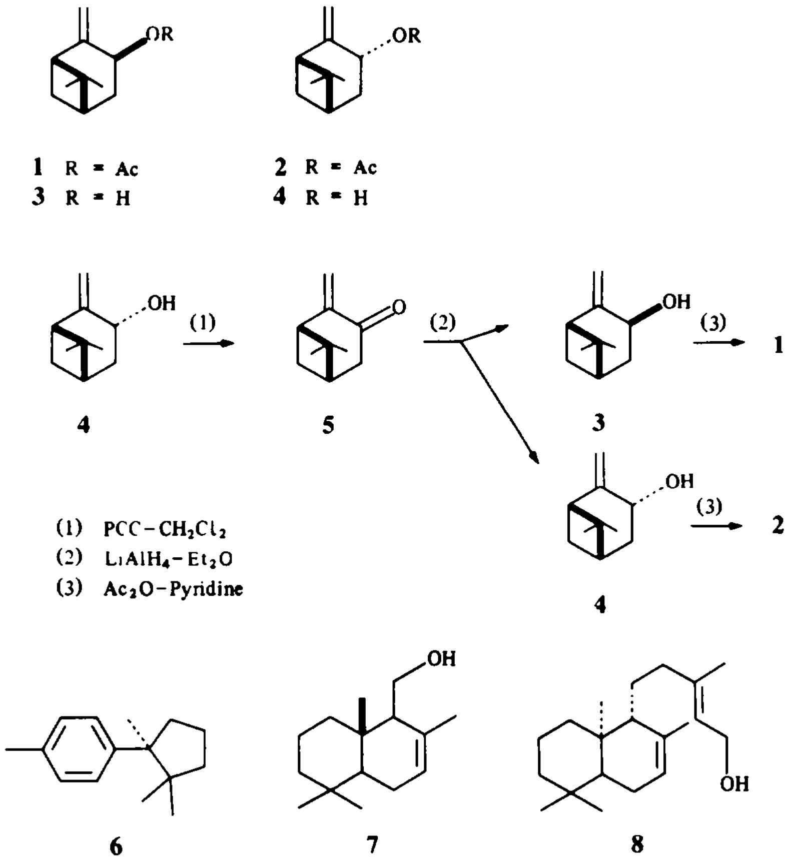

Scheme 1.

on a silica gel–Lobar column using CHCl$_3$ to give *cis*-pinocarveyl acetate (**1**) and *trans*-pinocarveyl acetate (**2**), respectively, whose spectral data were in good agreement with those of the synthetic materials.

1: ^{1}H NMR: δ0.78, 1.26 (each 3H, *s*, Me), 2.14 (3H, *s*, OAc), 4.77, 4.84 (each 1H, *br s*) and 5.69 (1H, *m*); MS *m/z* (rel. int.): 152 ([M − CH$_2$=C=O]$^+$ 5), 134 (32), 119 (31), 108 (12), 92 (48), 91 (65) and 43 (100). **2**: ^{1}H NMR: δ0.69, 1.28 (each, 3H, *s*, Me), 2.06 (3H, *s*, OAc), 4.89, 5.05 (each 1H, *br s*) and 5.56 (1H, *br d*, *J* = 8.3 Hz); MS (rel. int.): 152 ([M − CH$_2$=C=O]$^+$ 2), 134 (39), 119 (30), 108 (14), 92 (49), 91 (70), 43 (100). The third fraction (20 mg) was rechromatographed on a silica gel–Lobar column using the same solvent described above to afford drimenol (**7**) (10 mg), whose spectral data were identical to those of an authentic sample.

Preparation of cis- *and* trans-*pinocarveyl acetates* (**1** *and* **2**). Commercial *trans*-pinocarveol (**4**) (100 mg) was treated with pyridinium chlorochromate (200 mg) in CH$_2$Cl$_2$ to give pinocarvone (**5**) (80 mg). Reduction of **5** (80 mg) by LiAlH$_4$ (50 mg) in Et$_2$O gave *cis*- and *trans*-pinocarveols (**3** and **4**). *Cis*-pinocarveol (**3**) (20 mg), after being isolated by a silica gel–Lobar column, was acetylated with Ac$_2$O–pyridine for 24 hr. Work-up as usual gave *cis*-pinocarveyl acetate (**1**) (15 mg). The same treatment of **2** (15 mg) afforded *trans*-pinocarveyl acetate (10 mg).

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