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TWO NEW MONOTERPENES FROM THE BLED RESIN OF *PISTACIA VERA*

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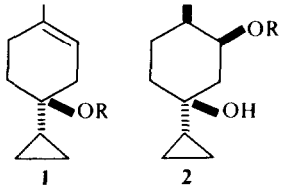
Key Word Index—*Pistacia vera*; Anacardiaceae; bled resin; *p*-menthane monoterpenes; structural determination.

Abstract—Structure determination and synthesis of two novel bicyclic *p*-menthane monoterpenes isolated from *Pistacia vera* are reported.

Two *p*-menthane monoterpenes with the unique feature of an extra C-9, C-10 linkage to give a cyclopropane ring have been found in the bled resin of *Pistacia vera* [1], a plant widely distributed in the Mediterranean area.

Compound **1a** was an optically active oil, $[\alpha]_D$ + 38° ($CHCl_3$; *c* 0.9) having a molecular formula $C_{10}H_{16}O$ (MS). The IR spectra (CCl_4) contained OH bands at 3610 and 1160 cm^{-1}, a strong olefinic band at 1650 cm^{-1} and characteristic cyclopropyl bands at 3080 and 1020 cm^{-1}. The ^1H NMR spectrum showed signals that could be assigned to a cyclopropane ring at δ 0.35 (*m*, 4H, H-9 and H-10) and 0.94 (*m*, 1H, H-8), an olefinic proton at δ 5.27 (*br*, 1H), a vinylic methyl at δ 1.6 (*s*, 3H) besides a signal at δ 2.09 (*d*, 1H, J = 17 Hz) which was assigned to the 3β-H from careful decoupling experiments. ^{13}C NMR data were consistent with structure **1a** (Table 1). A tentative configuration *S* was assigned to C-4 by analogy with the molecular rotation of terpinen-4-ol [2] $[\alpha]_D$ + 25° and 1,8-*p*-menthadien-4-ol [2] $[\alpha]_D$ + 43°. Acetylation (MeCOCl-dimethylaniline) of **1a** afforded the acetate **1b**: $[\alpha]_D$ + 49° ($CHCl_3$; *c* 1.0); $\nu_{max}^{CCl_4}$ cm^{-1} 1720 and 1250; ^1H NMR δ 0.44 (*m*, 4H, H-9 and H-10), 0.88 (*m*, 1H, H-8), 1.66 (*s*, 3H, H-7), 1.98 (*s*, 3H, CH_3CO—), 2.23 (*m*, 1H, H-5β), 2.43 (*d*, 1H, H-3β, J = 17 Hz), 5.20 (*br*, 1H, H-2).

The second compound **2a**, $[\alpha]_D$ + 21° ($CHCl_3$; *c* 1.2) had a molecular formula $C_{10}H_{18}O_2$ (MS). The IR spectra (CCl_4) showed strong bands at 3600 (sh), 3520 (sh), 3370 (*br*), 1150, 1130 and 1020 cm^{-1}. The ^1H NMR spectra (C_6D_6) contained cyclopropyl protons at δ 0.24 (*m*, 2H), 0.47 (*m*, 2H) and 0.61 (*m*, 1H), a *sec*-Me group at δ 1.01 (*d*, 3H, J = 6.6 Hz), a *gem*-OH proton at δ 5.17 (*br*, 1H) besides signals attributed through pertinent decoupling



1 **2**

a R = H **b** R = COMe

experiments to 3β-H (δ 1.89, two *dd*, J_{gem} = 14.6 Hz, $J_{3\beta\cdot2\alpha}$ = 2.94 Hz and long-range $J_{3\beta\cdot5\beta}$ = 2.21 Hz) and 3α-H (δ 1.20, *dd*, J_{gem} = 14.6 Hz, $J_{3\alpha\cdot2\alpha}$ = 2.94 Hz). The ^{13}C NMR data of **2a** are listed in Table 1.

Acetylation (Ac_2O–pyridine) slowly (3 days, 70% yield) converted **2a** into the corresponding monoacetate **2b**: $[\alpha]_D$ + 44° ($CHCl_3$; *c* 0.8), $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (sh), 1740 and 1215; ^1H NMR δ 0.88 (*d*, 3H, H-7), 1.59 (*dd*, 1H, H-3α), 1.89 (2*dd*, 1H, H-3β), 2.06 (*s*, 3H, CH_3CO—) and 5.17 (*br*, 1H, H-2). Physical features of **2a** and the slow conversion into monoacetate **2b** were consistent with the assigned structure of a *cis*-1,3-diol.

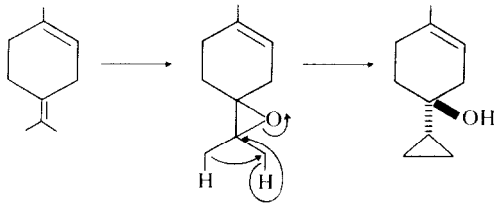
The structures of **1a** and **2a** were both confirmed by comparison with synthetic samples prepared from 1-methyl-cyclohexen-4-one [3]. Grignard reaction with cyclopropyl bromide gave a racemic alcohol identical with natural **1a**; *p*-nitroperbenzoic acid in dry Et_2O converted this compound into a mixture of *trans*- and *cis*-epoxy derivatives; the latter [$\nu_{max}^{CCl_4}$ cm^{-1} 3495 (sharp in-

Table 1. ^{13}C NMR (67.88 MHz) chemical shifts (ppm from TMS) of compounds **1a** and **2a**

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1a	133.94 *s*	118.48 *d*	37.81 *t*	68.60 *s*	31.11 *t* (27.40)	27.40 *t* (31.11)	23.31 *q*	20.59 *d*	0.21 *t* (−0.17)	−0.17 *t* (0.21)
2a	36.45 *d*	71.87 *d*	41.41 *t*	71.27 *s*	36.83 *t* (23.80)	23.80 *t* (36.83)	18.30 *q*	22.55 *d*	0.46 *t* (−0.12)	−0.12 *t* (0.46)

tramolecular band), ^{1}H NMR: δ 0.30 (*m*, 4H, H-9 and H-10), 0.70 (*m*, 1H, H-8), 1.27 (*s*, 3H, H-7), 1.74 (*dd*, 1H, H-3α, $J_{3\alpha,2}$ = 2.2 Hz, J_{gem} = 15 Hz), 1.95 (*d*, 1H, H-3β, J_{gem} = 15 Hz), 3.05 (*br*, 1H, H-2), 3.0 (*s*, 1H, OH proton)] was reduced with $LiAlH_4$ to racemic **2a**, identical with the natural compound, according to the results of Wilson and Shaw [4] with (+)-limonene oxidation.

The cooccurrence of a cyclopropane ring with an OH group at C-4 in **1a** and **2a** suggests that both could be derived from terpinolene, also identified in the oleoresin, by ring opening of a 4(8)-epoxy intermediate followed by hydride migration from one of the *gem*-dimethyl groups and loss of a proton from the other one.



EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were performed at the Centro di Metodologie Chimico Fisiche (I. Giudicianni) of the University on a Fourier transform spectrometer in $CDCl_3$ solns (if not otherwise specified) using TMS as int. standard.

Extraction and isolation. Fresh oleoresin of *P. vera* (30 g; collected from various plants by Dr. A. Castagna in Palermo) was extrd with Et_2O (1l.) to afford, after removal of the solvent, an oil (22 g) which was redissolved in Et_2O and washed with N Na_2CO_3 to eliminate acidic compounds. The neutral residue (12 g) after sequential CC and prep. TLC (Si gel) afforded **1a** (40 mg; petrol–Et_2O, 9:1) and **2a** (55 mg; petrol–Et_2O, 4:1).

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THE VOLATILE HERB OIL OF *KIPPISTIA SUAEDIFOLIA*

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Key Word Index—*Kippistia suaedifolia*; Asteraceae; volatile herb oil; (+)-perillyl acetate.

Abstract—Steam-distillation of the whole flowering plant of *Kippistia suaedifolia* yielded a volatile oil rich in (+)-perillyl acetate and (+)-limonene. Ten minor oil components were also identified by co-chromatography and capillary GC/MS.

INTRODUCTION

Kippistia suaedifolia F. Muell. (subfamily Asteroideae, tribe Astereae) is a yellow-flowered, bushy, slightly woody perennial, up to 60 cm high. It has been reported from all mainland states of Australia (except Queensland), growing on a variety of soils usually around salt lakes and often in association with gypsum deposits [1]. The species, originally described by F. von Mueller, was later reclassified by Bentham under *Minuria suaedifolia*. However, a recent taxonomic revision [1] indicated that the species should be reassigned its original name. Whereas all species of *Minuria* exhibit little if any odour, *K. suaedifolia* is strongly aromatic when crushed.

RESULTS AND DISCUSSION

An examination of the strongly scented steam-distilled herb oil by capillary GC/MS, indicated that the main component (*ca* 65% of the oil) was a monoterpenoid acetate, subsequently identified as (+)-perillyl acetate by alkaline hydrolysis and isolation of (+)-perillyl alcohol. The second most abundant constituent of the oil was (+)-limonene. Since both compounds possess the same (*R*)-configuration, it is probable that the former is formed in the plant from the latter by allylic oxidation. Two other allylic oxidation products of limonene, *cis*- and *trans*-

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