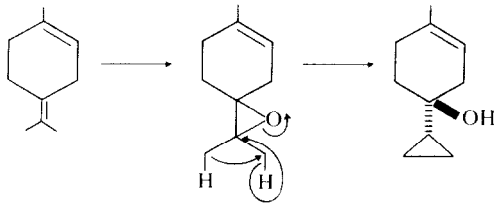
tramolecular band), ^{1}H NMR: δ 0.30 (*m*, 4H, H-9 and H-10), 0.70 (*m*, 1H, H-8), 1.27 (*s*, 3H, H-7), 1.74 (*dd*, 1H, H-3α, $J_{3\alpha,2}$ = 2.2 Hz, J_{gem} = 15 Hz), 1.95 (*d*, 1H, H-3β, J_{gem} = 15 Hz), 3.05 (*br*, 1H, H-2), 3.0 (*s*, 1H, OH proton)] was reduced with $LiAlH_4$ to racemic **2a**,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

REFERENCES

1. Caputo, R., Mangoni, L., Monaco, P., Palumbo, G., Aynehchi, Y. and Bagher, M. (1978) *Phytochemistry*, **17**, 815.
2. Ohloff, G. and Uhde, G. (1965) *Helv. Chim. Acta* **48**, 10.
3. Braude, E. and Webb, A. (1958) *J. Chem. Soc.* 328.
4. Wilson, C. W., III and Shaw, P. E. (1973) *J. Org. Chem.* **38**, 1684.

Phytochemistry, Vol. 21, No. 3, pp. 812–814, 1982.
Printed in Great Britain.

0031–9422/82/030812–03 $03.00/0

THE VOLATILE HERB OIL OF *KIPPISTIA SUAEDIFOLIA*

JOSEPH J. BROPHY, TERENCE M. FLYNN,* ERICH V. LASSAK*† and JOHN PICKARD‡§

School of Chemistry, University of New South Wales, Kensington, N.S.W., 2033, Australia; * Biological and Chemical Research Institute, N.S.W., Department of Agriculture, Rydalmere, N.S.W., 2116, Australia; ‡ National Herbarium of New South Wales, Royal Botanic Gardens, Sydney, N.S.W., 2000, Australia

(*Received* 12 *May* 1981)

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*-

† To whom correspondence should be addressed.
§ Present address: Antarctic Division, Melbourne, Victoria, 3004. Australia.

Table 1. Constituents of the oil of *K. suaedifolia*

Peak no.	Compound	%	Identification
1	α-Pinene	7.9	MS; co-GLC
2	Unknown	0.4	
3	β-Pinene	1.7	MS; co-GLC
4	Myrcene	5.6	MS; co-GLC
5	Unknown	tr*	
6	Car-3-ene	1.1	MS; co-GLC
7	Unknown	tr	
8	(+)-Limonene	12.9	MS; co-GLC; IR; α_D
9	β-*trans*-Ocimene	0.1	MS; co-GLC
10	Unknown	tr	
11	Terpinolene	0.4	MS; co-GLC
12	β-Caryophyllene	0.3	MS; co-GLC
13	Unknown	tr	
14	Sesquiterpene MW 204	0.2	MS
15	Sesquiterpene MW 204	0.1	MS
16	γ-Elemene (?)	0.2	MS
17	Unknown	tr	
18	Sesquiterpene MW 204	0.2	MS
19	*trans*-Carveol	0.4	MS; co-GLC
20	Unknown MW 146	0.5	MS
21	*cis*-Carveol	0.6	MS; co-GLC
22	(+)-Perillyl acetate	65.1	MS; co-GLC; IR; ^{1}H NMR; α_D
23	Unknown MW 178	1.0	MS
24	Unknown	0.2	
25	Unknown	0.1	

* tr, 0.1%.

carveol also appeared to be present in the oil, albeit in amounts too small to allow their isolation in sufficient quantity for a determination of optical rotation. Since perillyl alcohol is not found in freshly extracted oil, the possibility of the two carveols being artefacts of aerial oxidation of limonene, a reaction known to yield all three compounds (in addition to other oxidation products) [2], has been ruled out. All GLC data are summarized in Table 1.

Perillyl acetate is an uncommon essential oil constituent. It has been reported as a minor component of spearmint oil (*Mentha spicata*) [3], *Salvia dorisiana* herb oil [4], grapefruit oil [5] and the oil of *Citrus natsudaidai* [6]. Whilst spearmint perillyl acetate is laevorotatory (the optical rotations of the three other occurrences have not been recorded in the literature), *K. suaedifolia* appears to represent the first occurrence of the dextrorotatory enantiomer in nature.

Perillyl acetate has been reported to have some usefulness as a perfumery ingredient [7].

EXPERIMENTAL

Isolation of the volatile oil. The flowering herb of *K. suaedifolia* (1 kg) collected in an abandoned gypsum mine at Marlowe near Ivanhoe in western N.S.W. (Voucher: Pickard 2927; National Herbarium of New South Wales) was steam-distilled with cohobation in an all-glass apparatus to yield a pale yellow oil (12 ml), n_D^{20} 1.4799; α_D^{22} +72.6°; d_{20} 0.9508; IR ν_{max}^{film} cm^{-1} 1750 and 1250 cm^{-1} (acetate).

Identification of oil constituents. Analytical GLC: FFAP and Silicone DC-550-coated stainless steel SCOT columns (15 m × 0.5 mm); carrier gas He; dual FID; temp. programme 80–150° at 6°/min. Individual compounds were identified by their R_Is and by co-chromatography with authentic specimens. Compositions (%) were determined using an electronic integrator. GC/MS: FFAP-coated SCOT column (70 m × 0.77 mm) interfaced to a AEI MS-12 through an all-glass straight split; temp. programme 70–230° at 5°/min; MS 70 eV with the ion source at 150°. The spectra were recorded and processed by a VG Digispec Display data system.

Isolation of (+)-perillyl acetate. The essential oil (5 g) was chromatographed on activated Si gel (300 g) by successive elution with *n*-hexane (10 × 50 ml) and Na-dried Et_2O (5 × 50 ml). The first 50-ml aliquot of Et_2O eluate yielded on evaporation of the solvent crude (+)-perillyl acetate (2.5 g; 96% pure by GLC). Rechromatography on fresh Si gel raised the purity to 98.5% (GLC); n_D^{20} 1.4790 (*l*-enantiomer: lit. n_D^{20} 1.47897 [8], 1.4812 [9], 1.48142 [10]; α_D^{22} +75.6° (*l*-enantiomer: lit. α_D −74.67° [8], −48° [10]); MS *m/z* (rel. int.) (except $[M]^+$ only peaks ≥10% rel. int. are listed): 194 $[M]^+$ (2), 152 $[M - CH_2{=}CO]^+$ (24), 135 (12), 134 $[M - HOAc]^+$ (77), 119 (84), 109 (12), 106 (31), 105 (37), 93 (46), 92 (57), 91 (100), 84 (28), 79 (38), 78 (10), 77 (25), 68 (59), 67 (30), 65 (11), 55 (13), 53 (14), 43 (87), 41 (30). ^{1}H NMR (100 MHz, $CDCl_3$ TMS int. standard): δ 2.06 (3 H, *s*, acetate), 4.46 (2 H, *s*, H-7), 4.73 (2 H, *s* (*br*), H-9), 1.73 (3 H, *s* (*br*), H-10), 5.77 (1 H, *m*, H-2).

Alkaline hydrolysis of (+)-perillyl acetate. (+)-Perillyl acetate (1.5 g) was refluxed with methanolic KOH (5%, 50 ml) for 12 hr; after work-up in the usual way (+)-perillyl alcohol was obtained as a pale yellow liquid (1 g), n_D^{20} 1.4965 (lit. n_D^{20} 1.4957 [8], 1.4991 [2]); α_D^{22} +92° (lit. α_D +85.2° [2]); IR spectrum superimposable on a published spectrum of the compound [11]; ^{1}H NMR (100 MHz, $CDCl_3$, TMS int. standard): δ 4.00 (2 H, *s*, H-7), 4.74 (2 H, *s*, H-9), 1.74 (3 H, *s*, H-10), 5.72 (1 H, *m*, H-2), 2.43 (1 H, *s*, OH; D_2O exchangeable).

Isolation of (+)-limonene. The essential oil (20 ml) was fractionally distilled under red. pres. Fraction bp_{10} 55–65°,

shown to be slightly impure limonene by GLC and IR, had α_D^{22} +84° (lit. α_D +126° [12]).

Acknowledgements—The authors thank Dr. J. E. Nemorin, The University of Sydney, for NMR spectra and the Director, National Herbarium of New South Wales, for helpful comments on botanical matters.

REFERENCES

1. Lander, N. S. and Barry, R. (1980) *Nuytsia* **3**, 215.
2. Blumann, A., Farnow, H. and Porsch, F. (1965) *J. Chem. Soc.* 2990.
3. Elze, F. (1910) *Chem. Z.* **34**, 1175.
4. Halim, A. F. and Collins, R. P. (1975) *J. Agric. Food Chem.* **23**, 506.
5. Moshonas, M. G. (1971) *J. Agric. Food Chem.* **19**, 769.
6. Ohta, Y. and Hirose, Y. (1966) *Agric. Biol. Chem.* **30**, 1196.
7. Thomas, A. F. and Ohloff, G. (1975) Ger. Offen. 2,427,609; (1975) *Chem. Abstr.* **83**, P79412f.
8. Schmidt, H. (1950) *Chem. Ber.* **80**, 193.
9. Kergomard, A. and Philibert-Bigou, J. (1958) *Bull. Soc. Chim. Fr.* 393.
10. Semmler, F. W. and Zaar, B. (1911) *Ber. Dtsch. Chem. Ges.* **44**, 52.
11. Mitzner, B. M., Mancini, V. J., Lemberg, S. and Theimer, E. T. (1968) *Appl. Spectrosc.* **22**, 34.
12. Guenther, E. (1949) *The Essential Oils*, Vol. 2. Van Nostrand, New York.