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trans-Shisool (*trans*-8-*p*-Menthen-7-ol) Isolated from the Essential Oils of *Perilla acuta* Nakai and *P. acuta* f. *viridis* Nakai*[1]

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We have examined the essential oils of *Perilla acuta* (Thunb.) Nakai[1] (=*P. frutescens* Brit. var. *acuta* Kudo[2]) (Japanese name "Shiso") and *P. acuta* f. *viridis* (Makino) Nakai[1] (=*P. frutescens* var. *acuta* Kudo f. *viridis* Kudo[2]) (Japanese name "Aojiso") of the mint family, and have isolated a new monoterpene alcohol, amounting to 2.2—8.2% of the oil.

This alcohol was purified by preparative gas-liquid chromatography and was identified as *trans*-8-*p*-menthen-7-ol (I) by a comparison of its IR spectrum and of the retention time of its gas-liquid chromatography with those of the synthesized compound. The content of the *cis*-isomer (II) in the oils was very small.

We propose the name "Shisool" for these alcohols.

Ito[3] has reported the isolation of dihydroperillyl alcohol from *P. frutescens* Brit. var. *crispa* Decaisne f. *viridis* Makino (Japanese name "Chirimen-aojiso"); he showed the structure to be 8-*p*-menthen-7-ol, but did not mention anything about its configuration.

In a more recent report, Kayahara *et al.*[4] obtained these alcohols by the reduction of *l*-perillaldehyde (III) with sodium in aqueous ammonia; they proved the conformations of I and II clearly by means of NMR and IR spectra.

Many years ago, Semmler and Zaar[5] synthesized dihydroperillyl alcohol in the course of the determination of the structure of III; they showed its physical properties to be: bp 114—115°C/10 mmHg, d^{19} 0.9284, n_D 1.4819.

*1 Presented at the 13th Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics of the Chem. Soc. of Japan (Kagoshima, October, 1969).

1) T. Nakai, *Bot. Mag. Tokyo*, **42**, 474 (1928).

2) Y. Kudo, *Mem. Fac. Sci. Agri., Taihoku Imp. Univ.*, **2**, 74 (1929).

3) H. Ito, *Shōyakugaku Zasshi*, **18**, 24 (1964).

4) H. Kayahara, H. Ueda, K. Takeo and C. Tatsumi, *Agr. Biol. Chem.*, **33**, 86 (1969).

5) F. W. Semmler and B. Zaar, *Ber.*, **44**, 56 (1911).

Experimental

Isolation. The essential oils were obtained by the steam distillation of fresh materials, while the monoterpene alcohols were separated from the bp 111—115 °C/20 mmHg fraction of the oil, by the following procedures.

The perillaldehyde of this fraction (90 g) was eliminated by shaking it with a saturated sodium sulfite solution; the residual oil (8.5 g) was then heated with phthalic anhydride at 80°C in a pyridine solution for one hour, and the esterified part was extracted by means of a sodium bicarbonate solution. The sodium salt of the phthalic acid ester was saponified by potassium hydroxide, and the regenerated alcohol was distilled with steam. The oil thus obtained (1.2 g) contained 85.5% of I.

The alcohol (I) was purified by preparative gas-liquid chromatography. This alcohol is a colorless oil: bp 225°C/760 mmHg (uncorrected), d_4^{30} 0.9212, n_D^{30} 1.4796, $\alpha_D \pm 0.00°$, and shows bands at 3350(s), 3080 (w), 2930(s), 2860(s), 1640(m), 1445(s), 1375(m), 1185 (w), 1090(m), 1035(s), 965(m), 885(s), and 530(w) cm^{-1} in its IR spectrum.

Synthesized I and II. These compounds were prepared by the method of Kayahara *et al.*[4] Namely, to a stirred mixture of III (0.5 g), benzene (2.5 m*l*), and 28% aqueous ammonia (2.0 m*l*), metallic sodium (0.2 g) was gradually added with cooling by ice water. The product was extracted with ether, the ether extract was washed with a dilute hydrochloric acid solution and water successively, and dried over anhydrous sodium sulfate, and the ether was distilled off. The oil thus obtained (0.3 g) consisted of 28.0% I and 57.5% II, besides other compounds.

The specific retention times of the gas-liquid chromatography relative to perillyl alcohol (PEG 6000, 175°C) are 0.70 and 0.78 for I and II respectively.