A New Mint (Variety of *Mentha aquatica* L.) Containing (-)-Isopinocampnone as a Major Constituent of Essential Oil*

Sir:

Essential oils from various mint species generally contain predominantly monocyclic terpenes. Several investigators^{1~3)} reported the presence of carvone or pulegone in the essential oils of *Mentha aquatica* in South Europe. Reitsema⁴⁾ found a menthofuran-dominant *aquatica* in America, and this furan was also detected in European *aquatica* oil by Hegnauer.⁵⁾ In the present paper we wish to report on a new chemical strain of *aquatica*, containing (-)-isopinocampnone, a bicyclic monoterpene ketone, as a major constituent. The material seeds of *M. aquatica* were imported from the following countries; Belgium, Plantentuin der Rijksuniversiteit to Gent; Belgium, Institut et Jardin de Botanique de l'Université de Liège; France, Jardin Botanique Ville de Nantes; Italy, Istituto ed Orto Botanico dell' Univ. di Rome; Portugal, Hortus Botanicus Coimbra. They were cultivated in Okayama University and Kurashiki Experimental Station for Agriculture.

By analyzing the essential oils obtained from the above mentioned *aquatica* herbs by gas chromatography (column, SAIB 20% on Gelite 545; column temp., 155°C; carrier gas, hydrogen; flow rate, 65 ml/min.), we divided *aquatica* mint into following three chemical strains.

Linalool strain seems to be very similar

to *Mentha citrata*⁶⁾ from chemical and morphological point of view. Menthofuran in the second oil was identified by infrared spectrum, thin-layer chromatography (a purple red spot by vanillin sulfuric acid reagent) and Flückiger reagent test. It will be surely identical with American *aquatica* reported by Reitsema.⁴⁾

The essential oil obtained from third strain showed strong absorption at 1700 cm⁻¹ and gave semicarbazone of m.p. 232°C in the yield of 30%. The oil regenerated from this semicarbazone by treatment with acid media showed two peaks in the gas chromatogram, the later of which was determined to coincide with the main peak of *aquatica* original oil; retention time relative to (-)-menthol was 0.88. This indicates that *aquatica* ketone is sensitive to acid and isomerizes to a stable isomer. The original ketone was isolated purely by silica column chromatography (first eluting solvent, petroleum ether, then followed by ether); b.p. 81°C/5 mm., $[\alpha]_D^{15} -7.3^\circ$. By the reduction with lithium aluminum hydride, a borneol-like smelling crystal (m.p. 40~45°C) was obtained. From the elementary analysis of its 3,5-dinitrobenzoate (Found: C, 58.70; H, 5.83; Calcd. for C₁₇H₂₀N₂O₆=dinitrobenzoate of C₁₀H₁₈O: C, 58.61; H, 5.79%), the molecular formula for original ketone was established to be C₁₀H₁₆O.

It showed no double bond in the infrared spectrum and gave pinonic acid by potassium permanganate oxidation (identified as semicarbazone of m.p. 204°C). From these results *aquatica* ketone seemed to be a bicyclic ketone such as pinocampnone or isopinocampnone.

1) Ber. Schimmel, 1889, October 55; 1913, April 70; 1932, 45.

2) T. Sacco, *Riechstoffe und Aromen*, 9, 287 (1959).

3) G. Romeo and U. Giuffrè, *Annali. Chim. Applic.*, 17, 83 (1927).

4) H. Reitsema, *J. Am. Pharm. Assoc. Sci. Ed.*, 43, 414 (1954).

5) R. Hegnauer, "Die ätherischen Öle" Ed. VII by Gilde-meister (Akademie Verlag, Berlin, 1961), p. 393.

* This report was presented at the 9th Symposium of Chemistry of Perfume, Terpene and Essential oil in Japan, on 17th, Oct., 1965 at Kumamoto University.

6) "The Essential Oil" by E. Guenther (D. Van Nostrand Co., New York, 1949) Vol. III, p. 685; According to Index Kewensis. *Mentha citrata* Ehrh. is identical with *M. aquatica* L.

chemical strain	n_D^{15}	d_4^{15}	$[\alpha]_D^{15}$	content of major constituent	origins of mints
1) Linalool strain	1.4655	0.8864	- 9.50	43% (including acetate 22.1)	France
2) Menthofuran strain	1.4760	0.9115	+31.02	49%	Belgium
3) Isopinocampnone strain	1.4750	0.8794	-24.70	49%	Italy, Belgium Portugal

NMR spectrum of this ketone in deuteriochloroform showed the presence of gem-dimethyl (singlets, 9.12 8.68 τ) and one methyl (doublet, 8.85, 8.73 τ , $J=7$ c.p.s.), which support isopinocampnone skeleton.⁷⁾

Then, (-)-isopinocampnone was prepared by hydroboration of (-)-pinene, $[\alpha]_D^{15} -35^\circ$ according to Brown's method,⁸⁾ b.p. 91~105°C/20 mm., after silica chromatography, $[\alpha]_D^{15} -8.8^\circ$. Infrared spectrum absorption and retention time of (-)-isopinocampnone were found to be completely identical with those of *aquatica* ketone.

This is the first paper which shows the presence of (-)-isopinocampnone in the essential oil of the Genus *Mentha*, while (-)-pinocampnone was found in the oil of *Hysosopus officinalis* L.⁹⁾ and ground ivy (*Glechoma hederacea* L. subsp. *grandis* (A. Gray) Hara).¹⁰⁾

7) R. L. Erskine and S. A. Knight, *Chem. & Ind.* **1960**, Sept. 1160.

8) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2350, 2951 (1961).

9) "The Essential Oil" by E. Guenther; Vol. II, p. 442 (1949).

10) Hikino, Kusano and Takemoto; Proceeding of 6th Symposium of Chem. Perfumery, Terpenes and Essential oils, 115 (1962).

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Sumio SHIMIZU
Denei KARASAWA
Nagamori IKEDA*

Laboratory of Agricultural Chemistry,
Shinshu University,
Ina, Nagano.

*Laboratory of Plant Breeding,
Okayama University,
Tsushima, Okayama.

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