(-)-1*R*-8-Hydroxy-4-*p*-menthen-3-one Isolated from Essential Oil of *Mentha gentilis* L.[†]

Tôru NAGASAWA, Kazuyasu UMEMOTO,
Tomoyuki TSUNEYA* and
Minoru SHIGA*

Laboratory of Chemistry, Nagoya Gakuin University,
Kamishinano-cho, Seto-shi 480-12;
*Faculty of Research of Chemistry,
Shiono Koryo Co., Ltd., Niihata,
Yodogawa-ku, Osaka-shi 532

Received June 10, 1974

In previous papers,^{1,2)} the authors determined the absolute configuration of the new terpenic compounds, (+)-(1*S*: 2*S*: 3*R*: 4*S*)-1, 2-epoxymenthylacetate, (+)-(1*S*: 2*S*: 3*R*: 4*S*)-1,2-epoxymenthol and (+)-4*S*-4-hydroxy-1-*p*-menthen-3-one in the essential oil of a wild species of *Mentha gentilis* L. grown in Tokai area of Japan.

The present paper reports the newly determined configuration of a terpenic keto-alcohol, (-)-1*R*-8-hydroxy-4-*p*-menthen-3-one [1] in the essential oil of *Mentha gentilis* L. ($2n=72$) which contains (+)-pulegone as a major component.³⁾ The essential oil was collected by steam distillation of the plants harvest-

[1]

ed at the time of blooming in August, 1972. The yield of this oil (n_D^{25} 1.4870, d_4^{25} 0.9371, $\alpha_D^{25} +21.5^\circ$) was 43.2 g (ca. 0.33%) from 13.0 kg of the fresh material. The gas chromatographic analysis of this oil showed the presence of a peak of retention time (*Rt*) 27.0 min (PEG-20M 30%, 3 mm $\times$ 2.25 m, Column Temp. 160°C, Carrier He 1.0 kg/cm²) as a minor unknown constituent (The *Rt* of 1,2-epoxymenthylacetate in the same oil is 25.5 min).

In order to identify this unknown compound, the above oil was treated with 30% sodium sulfite solution and allowed to separate into the α , β -unsaturated carbonyl part and others. The carbonyl part was

TABLE I. MS SPECTRAL DATA OF COMPOUND 1

Our MS spectra were measured by the following condition [their MS spectrum condition⁴⁾ showed in brackets]: mass spectrometer Hitachi RMU-6L [ATAS CH-4], vaporizing temperature 150°C [150°C], ionizing voltage 80 eV [70 eV] and ionizing temperature 210~220°C [250°C].

<i>m/e</i> (%)	Natural	Our Syn.	Their Syn. ⁵⁾
168 (M ⁺)	4	1	0.1
153 (M ⁺ -CH ₃)	55	23	100
150 (M ⁺ -H ₂ O)	96	63	—
135 (M ⁺ -CH ₃ -H ₂ O)	71	55	14
125	15	4	5
111	8	6	11
107	38	42	—
97	25	12	32
80	69	70	—
79	100	100	9
69	42	23	13
59 (CH ₃) ₂ C=OH ⁺	16	10	—
55	27	19	19
43	65	40	55
41	63	56	—

obtained from the original oil in ca. 76% yield. The following gas chromatographic analysis clarified that the component having to *Rt* 27.0 min and pulgone as well were both present in the carbonyl part. Then, this part was subjected to activated alumina (300 mesh) column (2.0 cm *i.d.*, 35 cm) chromatography with *n*-hexane-ether-methanol (100:0.0, 50:50:0, 0:100:0, 0:50:50 and 0:0:100 vol%). The unknown compound of a pulgone-like odor was collected from the ether-methanol fraction. The yield of this component was 1.2% from the carbonyl part.

The unknown compound purified by gas chromatographic partition (Silicone SE-30 30%, 5 mm $\times$ 1.80 m, He 0.5 kg/cm²) from the ether-methanol effluent indicated the following properties; n_D^{25} 1.4823, $[\alpha]_D^{25} -65.8^\circ$ ($c=0.534$ in CCl₄), IR $\nu_{\max}^{NaCl}$ cm⁻¹: 3450 and 1170 (alcohol O-H or C-O), 1665 (conjugated ketone C=O), NMR $\delta_{TMS}^{CCl_4}$ 1.05 (3H, doublet, $J=5.0$ Hz, CH₃-CH<), 1.31 (6H, singlet, CH₃>C(OH)-), 3.69 (1H, singlet, >C-OH), 6.75 (1H, multiplet, HC=C-C=O). Based on the above data, we estimated the unknown compound as 8-hydroxy-4-*p*-menthen-3-one.

For further confirmation, the isolated compound was compared in their properties with 8-hydroxy-4-*p*-menthen-3-one synthesized by Schulte-Elte *et al.*⁵⁾ The properties of two specimens are alike one another except MS spectral patterns as shown in Table I. To avoid this inconsistency, we also synthesized the same

[†] Studies on Wild Mints of Tokai Districts. Part III. For previous papers, see Refs. 1) and 2).

compound as Schulte-Elte's by means of photooxygenation of (+)-1*R*-pulegone and compared with the isolated compound. Thus, the MS spectra and other properties of both our synthetic and natural products coincided perfectly. Therefore, it seems that the discrepancy between the MS spectra patterns of both synthetic products is due to the condition of the measurement as shown in Table I. In our MS spectrum, the prominent peaks at *m/e* 153 (C₉H₁₃O₂) and *m/e* 150 (C₁₀H₁₄O) are derived from the molecular ion (*m/e* 168) by the loss of methyl radical or H₂O followed by the elimination of H₂O or methyl radical to give the fragment corresponding to *m/e* 135 (C₉H₁₁O), whereas in their spectrum, the base peak at *m/e* 153 (C₉H₁₃O₂) is preferentially formed by the loss of methyl radical without dehydration from the molecular ion.

As a conclusive remark, the unknown compound in the essential oil of *Mentha gentilis* L. was found to be (–)-1*R*-8-hydroxy-4-*p*-menthen-3-one [1]. We believe that this is the first report with regard to the isolation of the above compound as a natural substance.

Acknowledgement. The authors wish to thank Prof. Dr. N. Hirao of Department of Applied Chemistry, Faculty of Science and Technology, Kinki University for his worthy suggestion in connection with this research.

REFERENCES

- 1) T. Nagasawa, K. Umemoto, T. Tsuneya and M. Shiga, *Nippon Nôgeikagaku Kaishi*, **48**, 39 (1974).
- 2) T. Nagasawa, K. Umemoto, T. Tsuneya and M. Shiga, *ibid.*, **48**, 467 (1974).
- 3) T. Nagasawa, K. Umemoto, T. Tsuneya and M. Shiga, *Symposium on Chemistry of Terpenes, Essential Oils and Aromatics*, **17**, 34 (1974).
- 4) K. H. Schulte-Elte and G. Ohloff, *Helv. Chim. Acta*, **51**, 494 (1968).
- 5) K. H. Schulte-Elte, M. Gadola and B. L. Müller, *ibid.*, **54**, 1870 (1971).