Isolation of 3-Hydroxy-7,8-dehydro-β-ionone from *Lycium chinense* M.

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We have previously reported on the steam-volatile neutral components of the fruits of *Lycium chinense* M.1,2) and have clarified the existence of many ionone-related compounds. This paper deals with the isolation of a new ionone compound from the leaves of *Lycium chinense* M.

The neutral volatiles (831.2mg) separated from 2.90 kg of leaves of *Lycium chinense* M. were separated into 16 fractions by silica-gel column chromatography. The 13th fraction, eluted with Et₂O (55.4mg, 6.91% of the neutral volatiles), was further separated by preparative GLC to give a yellow viscous oil (1) (0.8ppm of the dry leaves)

![Image](https://via.placeholder.com/150)

*δ*H 0 OH

![Image](https://via.placeholder.com/150)

*δ*H 0 OH

![Image](https://via.placeholder.com/150)

*δ*H 0 OH

The level of the recognition threshold and the odor profile of (1) in comparison with the structurally related compounds 3-hydroxy-7,8-dehydro-β-ionol (2), 3-hydroxy-β-ionone (3) and 3-hydroxy-β-ionol (4) were examined. The results are shown in Table I. The reduction of the carbonyl group in the side-chain of (1) and (3) led to the lower threshold values. The ionols (2) and (4) tended to a cool odor as compared with the ionones (1) and (3). The odor of the acetylenic compounds (1) and (2) tended to sweet as compared with the corresponding ionone (3) and ionol (4).

EXPERIMENTAL

**Analysis.** Optical rotation was measured in EtOH with a JASCO DIP-181 polarimeter. 1H-NMR and 13C-NMR spectra were measured in CDCl₃ solution with TMS as an internal standard on a JEOL FX-100 spectrometer. The IR spectrum was recorded on a JASCO A-3 spectrophotometer, and the UV spectrum was taken in an EtOH solution of a Hitachi 220-A spectrophotometer. Mass spectra were measured on a Hitachi M-80 spectrometer with an ionization voltage of 20 eV.

Preparation of the neutral volatile oil. Commercially available dried leaves of *Lycium chinense* M. (2.90 kg, 10% moisture content) was extracted twice with 14 kg of CH₂Cl₂ (room temp., 24 hr). The extract (63.3 g) was steam-distilled for 24 hr with an SDE apparatus using Et₂O as an extracting solvent. The resulting ethereal solution was dried over sodium sulfate and concentrated under reduced pressure. The volatile oil (3.30 g, 0.11% of
Table I. Sensory Evaluation of 3-Hydroxy-7,8-dehydro-β-ionone and Related Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Recognition threshold</th>
<th>Odor profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$1 \times 10^{-4}$ ~ $0.5 \times 10^{-3}$</td>
<td>Sweet, refreshing, apple-like, honey-like</td>
</tr>
<tr>
<td>(2)</td>
<td>$1 \times 10^{-5}$ ~ $0.5 \times 10^{-4}$</td>
<td>Camphor-like, cool, slightly sweet</td>
</tr>
<tr>
<td>(3)</td>
<td>$1 \times 10^{-4}$</td>
<td>Oily, dry, powdery, woody</td>
</tr>
<tr>
<td>(4)</td>
<td>$0.5 \times 10^{-4}$</td>
<td>Minty, cool</td>
</tr>
</tbody>
</table>

the dried leaves) was re-dissolved in Et₂O and successively washed with 5% NaHCO₃, 1 N NaOH, 1 N HCl and brine. The remaining ethereal solution was dried (Na₂SO₄) and concentrated under reduced pressure to give 831.2 mg of a neutral volatile oil.

Fractionation of the neutral volatile oil. The neutral volatile oil (813.7 mg) was adsorbed on a column (Merck Kiesel gel 70 ~ 230 mesh, 35 g, 100 mm × 30 mm i.d.) and eluted with 100 ml portions of hexane (Fr. 1: 72 mg; Fr. 2: 11 mg), 2% Et₂O/hexane (Fr. 3: 4.2 mg; Fr. 4: 2.8 mg), 5% Et₂O/hexane (Fr. 5: 318 mg; Fr. 6: 16 mg), 10% Et₂O/hexane (Fr. 7: 28 mg; Fr. 8: 25 mg), 20% Et₂O/hexane (Fr. 9: 31 mg; Fr. 10: 62 mg), 50% Et₂O/hexane (Fr. 11: 117 mg; Fr. 12: 33 mg), Et₂O (Fr. 13: 55 mg; Fr. 14: 7.9 mg), EtOAc (Fr. 15: 8.1 mg) and MeOH (Fr. 16: 14 mg).

Isolation of (+)-3-hydroxy-7,8-dehydro-β-ionone (I) from Fr. 13. The preparative GLC was performed on a Shimadzu GC-7A gas chromatograph (1 m × 3 mm i.d. glass column; 5% FFAP on chromosorb W-AW; 100 ~ 240°C oven temp.; 5°C/min program rate; 270°C injection temp.; 270°C TCD temp.; He carr. gas 50 ml/min) and yielded a yellow viscous oil. [$\alpha$]D +92° (EtOH, c $6.5 \times 10^{-4}$); MS: m/z 207 (M+), 191 (44), 173 (74), 147 (20), 91 (26), 77 (25) and 43 (100); GC-FI-MS: m/z 207 (M+); high resolution MS: Found (206.1326), Calcd. for C₁₃H₁₈O₂ (206.1305); IR (film): 3400 cm⁻¹, 2160 cm⁻¹, 1665 cm⁻¹; UV (EtOH): 282 nm ($c$ = $1.0 \times 10^{4}$); ¹H-NMR (CDCl₃): δ 1.14 (3H, s), 1.20 (3H, s), 1.97 (3H, s), 2.39 (3H, s), 4.02 (1H, m); ¹³C-NMR (CDCl₃): δ 22.36 (q), 28.21 (q), 29.79 (q), 32.36 (q), 35.87 (s), 41.20 (t), 45.64 (t), 63.37 (d), 90.40 (s), 93.32 (s), 121.64 (s), 146.85 (s), 184.47 (s). The distinction between s, d, t and q of each singal was made by the INEPT method.

Preparation of (+)-3-hydroxy-7,8-dehydro-β-ionone (I). Synthetic (+)-3-hydroxy-7,8-dehydro-β-ionol (2) was oxidized with DDQ in dioxane (refluxed for 6 hr) to give a single product (1). The synthetic material exhibited mass, NMR and IR spectra identical with the natural (1).

Sensory evaluation. The evaluation of the odor threshold and odor profile was performed on synthetic materials by a panel of experienced judges. The odor threshold of each compound was obtained by a method of limits.

REFERENCES