

# Isolation of Menthofuro lactone from *Mentha arvensis* and Solvent Effect of Oil Components on the Formation\*

by Masaaki ITO, Shigeru SAGAWA\*\*, Kazuo ABE  
and Toshio ONOGAKI\*\*\*

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## Synopsis

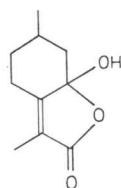
Menthofuro lactone was isolated from *Mentha arvensis* by alkali extraction. The structure was identified on the infrared and nmr spectra. The solvent effect of oil components on autoxidation of menthofuran into menthofuro lactone was measured.

Schmidt<sup>1)</sup> was the first to report on the isolation of menthofuro lactone from *Mentha piperita*. The hydroxylactone is formed from menthofuran by autoxidation or by chemical oxidation. The structure I was proposed for the hydroxylactone by R. B. Woodward and R. H. Eastman<sup>2)</sup>.

In this paper we aim to report on the presence of menthofuro lactone in *Mentha arvensis* and the spectroscopic identification of its structure on infrared and nuclear magnetic resonance spectra, and the solvent effect of oil components on autoxidation of menthofuran into menthofuro lactone.

A small quantity of hydroxylactone was isolated from natural *Mentha arvensis* by alkali extraction. The hydroxylactone recrystallized from acetic acid melted in the range of 186.0–187.5°C and was identical with the menthofuro lactone obtained by autoxidation of menthofuran in melting point and infrared spectrum. R. B. Woodward and R. H. Eastman has determined the structure on the chemical behaviors and the ultraviolet spectrum, but the infrared and nuclear magnetic resonance spectrum were obtained as following results: their spectrum showed an absorption at 3450  $\text{cm}^{-1}$  (presumably that of hydroxyl group), 1740  $\text{cm}^{-1}$  (presumably that of carbonyl group of a lactone), and 1695  $\text{cm}^{-1}$  (presumably that of conjugated double bond). The nmr spectrum in dimethyl- $d_6$  sulfoxide showed one methyl hydrogen at 46.8 Hz (3H, doublet), one methyl hydrogen conjugated with a double bond at 84.6 Hz (3H, doublet), and one hydroxyl hydrogen at 349 Hz (1H, singlet).

The acetylation of menthofuro lactone afforded acetyl menthofuro lactone under the treatment with acetic anhydride and anhydrous sodium acetate in high yield. The thin layer chromatogram of the acetate exhibited two adsorption at Rf 0.29



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\*\* Kitami Menthol Factory of Hokuren, Kitami, Hokkaido.

\*\*\* Industrial Research Institute of Hokuren, Sapporo, Hokkaido.

and Rf 0.33 under the condition used, which we presume are the two stereoisomers of the acetate. It was assumed that the component of Rf 0.29 is trans-isomer and the component of Rf 0.33 is cis-isomer, presuming from the mechanism of the acetylation. The nmr spectrum in chloroform-d showed one methyl hydrogen at 58 Hz (3H, doublet), one methyl hydrogen conjugated with a double bond at 108 Hz (3H, doublet), and one methyl hydrogen of acetyl group at 119 Hz (3H, singlet).

It goes without saying that menthofurolactone is formed from menthofuran by autoxidation<sup>2)</sup>. We report here on the solvent effect of the components of mint oil on the reaction. The decreasing order of solvent effect of the components is as follows; *l*-Menthone > *l*-menthylacetate > *l*-limonene > *l*-menthol as shown in Table 1.

Corrosive effect of menthofurolactone was also investigated for metals. It is more corrosive for tin than for zinc in acidic aqueous solution.

**Table 1.** Solvent Effect of Mint Oil Components on Autoxidation of Menthofuran

Solvent	Yield of Menthofurolactone, %
<i>l</i> -Limonene	9.6
<i>l</i> -Menthone	18.5
<i>l</i> -Menthol	3.8
<i>l</i> -Menthyl acetate	13.3

## Experimental

**Isolation of Menthofurolactone.** Natural Japanese mint oil (*Mentha arvensis*, Manyō) (20 kg) was allowed to be extracted with dilute aqueous solution of sodium carbonate. The extract was neutralized with hydrochloric acid until it was slightly acidic and the organic layer was extracted with ether. The ether solution was allowed to stand for several months. Small amounts (2.0 g) crystallized out of the isolate was filtered and recrystallized from acetic acid; mp 186.0–187.5°. The thin layer chromatogram (silica gel, n-Heptane: ethyl methyl ketone = 80:20) showed an adsorption at Rf 0.17. The isolate reduced Fehling solution, showed silver mirror reaction and positive reaction on Schiff's reagent.

The infrared spectra were recorded on a Shimadzu Model IR-27 infrared spectrophotometer as potassium bromide disc and the nmr spectrum was run on a Varian A 100 spectrophotometer. And they were described in the discussion above.

**Acetyl Menthofurolactone.** Menthofurolactone was acetylated with a mixture of 1 ml acetic anhydride and 113.0 mg sodium acetate refluxing for 2 hrs. The thin layer chromatogram (silica gel, n-Heptane: ethyl methyl ketone = 80:20) showed two adsorptions at Rf 0.29 and 0.33. The nmr spectrum was recorded on Varian A 60 spectrophotometer, and was described in the discussion above.

**Solvent Effect of Oil Components on Autoxidation of Menthofuran into Menthofurolactone.** Each 2.0 g menthofuran mixed with each 5.0 g *l*-limonene, *l*-menthone, *l*-menthol, and *l*-menthyl acetate were placed respectively on an open dish in atmospheric condition for 18 days. Menthofurolactone formed was isolated from each mixture in the same manner as mentioned above. The yield percents were shown in Table 1.

**Corrosion of Metal with Menthofurolactone.** Metals of tin and zinc were dipped into aqueous solutions of menthofurolactone acidified slightly with acetic acid. After one month, tin was more corrosive than zinc.

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#### References

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