

## CHEMICAL STUDIES ON MENTHA\*

### V. On the Odorous Substances of Mint Plants (2)\*\*

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#### I INTRODUCTION

Japanese mint oil has a good property that it contains a large quantity of *menthol*, but it has been expressed that it has the most weak point, which possesses a special disagreeable odor. For the purposes of studying the odor of Japanese mint oil, we reported<sup>1)</sup> that the volatile water of "San-Bi" (*M. arvensis*) shall be contain *ammonia*, *trimethylamine*, *dimethylamine*, and *monomethylamine* as the nitrogen compounds, by the use of paper chromatography. The same writers reported also that the bad odor of the dementholized oil of Japanese mint can be removed by the treatment with *phosphoric acid* most effectively.<sup>2)</sup>

It has not been reported that mint plants possess *amines*, but only one<sup>3)</sup> possessed *monomethylamine* in *M. aquatica*.

As the results of studying the nitrogen compounds in the volatile waters of the several mint plants, the authors confirmed that a large quantity of *ammonia* and a small quantity of *trimethylamine* exist in them.

In regard to the existence of the nitrogen compounds in the plants, it was reported already.<sup>1)</sup> For the existence of a large quantity of *ammonia* in the volatile water, it can be assumed that this *ammonia* was liberated mainly by the hydrolysis of the *amides*.

#### II PROPERTIES OF THE VOLATILE WATER

As reported previously,<sup>1)</sup> the volatile waters were gained by the steam distillation, under the same conditions, with several mint plants and then condensed by the cohobation (Fig. 1.). Their pH values were determined by the Hitachi's Glass Electrode pH Meter.

##### 1. Differences of pH with the various species of mint plants

As a result of determination of pH with each 400 g. of the fresh leaves, the coho.-water indicated considerably alkaline property with an exception of *M. pulegium* (Table 1.).

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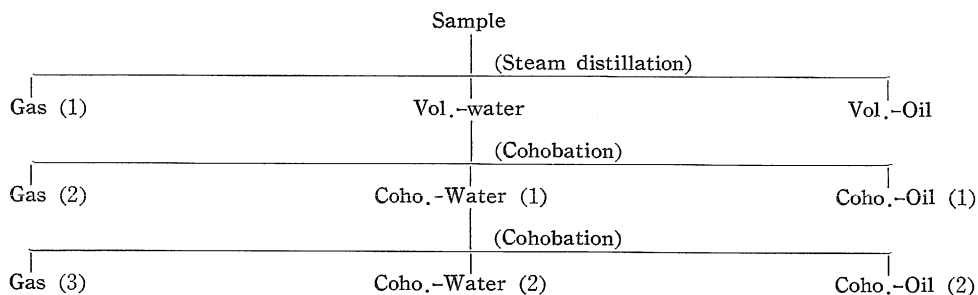


Fig. 1. Outline of Manipulation

Table 1. Differences of pH with the various species of mint plants

Species of Mints*	Time of Crop in 1961 (Month-Day)	Weights of Fresh Leaves (g.)	Time of Steam, distil. (min.)	Volume of Coho.-Water (cc.)	pH
<i>M. arvensis</i> { San-Bi	8.24	400	40	350-40	8.45
{ Brazil	"	"	"	"	8.76
<i>M. viridis</i> { Chirimen- "Red Stem"	"	"	"	"	8.00
{ Chirimen- "White Hair"	8.25	"	"	"	8.25
<i>M. rotundifolia</i>	8.24	"	"	"	8.52
<i>M. pulegium</i>	"	"	"	"	7.15

\* *M. arvensis* was distilled after dried to ca 1/4 weight of its fresh herbs. Other species were distilled with the herbs dried insufficiently. *M. pulegium* was distilled together with stems and leaves to suit its convenience.

## 2. Relation of the time of steam distillation and pH value of coho.-water

The relations of the time of the steam distillation and pH values of coho.-water were indicated in the Table 2. As a result of the distillation with 100 g. of dry leaves, it may be presumed that the nitrogen compounds were decomposed at the first time and then distilled out slowly. Their distillates have no connection with the distillation time of volatile oils.

Table 2. Relation of pH of coho.-water and time of distillation

Species	Weights of Dry Leaves (g.)	Time of Distillation (min.)	Volume of coho.-Water (cc.)	pH	Oil Yield (%)
<i>M. arvensis</i> (Brazil)	100	0-20	200-40	8.74	2.3
(1962. 8. 24)		20-40	"	8.68	0.1
		40-60	"	8.44	trace

## III NITROGEN COMPOUNDS IN COHO.-WATER

### 1. Sample

Mint herbs were used as indicated in the Table 3.

Table 3. Coho.-waters used in the Experiments

Species		Time of Crop	Weights of Fresh Plants (kg.)	Volume of Coho.-Water (cc.)	pH
<i>M. arvensis</i>	San-Bi	1957.10.22	11.0	100	8.8 *
	Brazil	"	15.0	80	8.8 *
<i>M. viridis</i>	Chirimem- "Red Stem"	1957. 8. 9	10.3	40	8.8 *
	Chirimen- "White Hair"	1959-1960	10.3	40	9.15
	Russia	1960	10.1	40	8.84
<i>M. pulegium</i>		1960. 7.22	10.6	40	8.80

\* It was determined with an aid of pH test paper.

## 2. Preparation of experimental solutions

To the coho.-water added 2N-HCl to be acidic and condensed up by evaporation under reduced pressure nearly to driness, then a few water was added to the dry mass, and condensed again until a white crystal begins to deposit. This condensed solution showed a pale brown color. These concentrated *amine hydrochloride* solutions were examined with the gas chromatograph<sup>4) 5)</sup>, the apparatus designed as the Fig. 2.

## 3. Apparatus

To separate *amines* from *amine hydrochlorides*, the writers used a new column of our own-making, its diameter and length are 6.5 mm. and 15 cm., respectively, referred to James' literature<sup>4) 5)</sup>. Fill up 2 g. of soda-lime (45-50 mesh) to the C part, and anhydrous *potassium carbonate* (45-50 mesh) to the part D, as an absorbent. Put the heating tube, which was wound around with a nickel-chrome wire, to the part C and regulated to 80-82°C at the inside of the column. Let flow hydrogen as a carrier gas from part B, and poured a sample from part A into the column with a microsyringe. To separate the regenerated *amines*, the writers used a 2 m. 5 mm.-internal diameter column, containing a 30 % of *triethanolamine* in cerite 545, using Yanagimoto Gaschromatograph Model GCG-2.

## 4. Chromatogram of ammonia and amines

The peak of water can be eliminated or decreased by use of anhydrous *potassium carbonate* as an absorbent as in the Fig. 3. If water was saturated in the

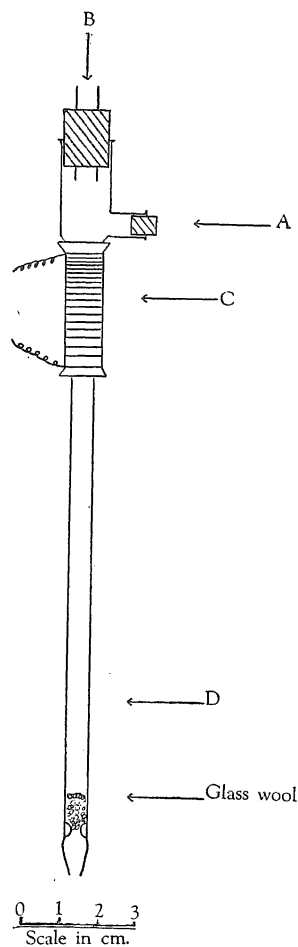


Fig. 2. The regenerative column for liberation of the amines from solutions of their salts.

soda-lime column, some peaks tend to become flat. In such a case, it is necessary to change for a new soda-lime.

The mixture of each 2.5% solution of *trimethylamine*-, *dimethylamine*-, and *monomethylamine-hydrochlorides* (each of extra pure reagent) and *ammonium chloride*, which was recrystallized with hot water, was made to investigate the separation of *ammonia* and the respective *amines*. (Fig. 4.). The *ammonia* and *amines* appeared from the column in the order of *trimethylamine* (3.5°C), *ammonia* (-33.4°C), *dimethylamine* (7.4°C), and *monomethylamine* (-6.5°C), using a commercial *triethanolamine* as a liquid phase. This order has no relation to their boiling points. Using a mixture of *hendecanol* and liquid paraffin as a liquid phase, James *et al.*<sup>4)</sup> reported to be able to separate *amines* in the order of

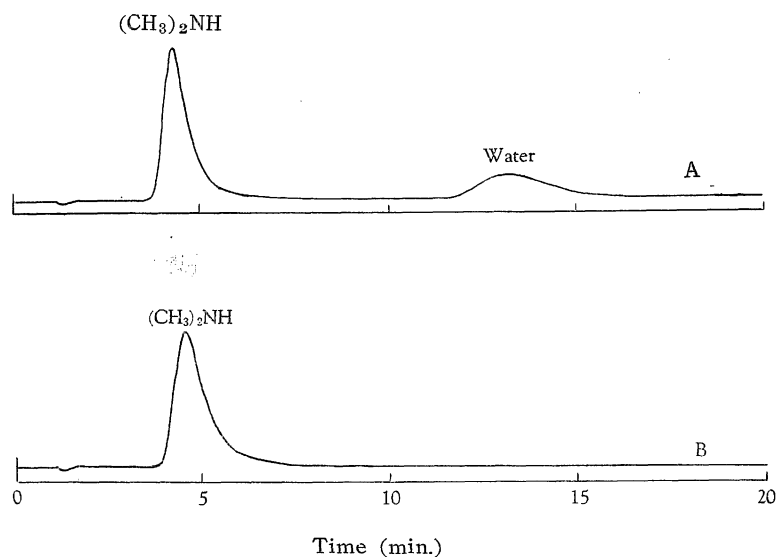


Fig. 3. The chromatogram of the solution of 2.5% dimethylamine. Column length, 2 m. ; liquid phase, triethanolamine ; temp., 78°C ; flow rate of hydrogen, 25 ml./min. ; hydrogen pressure, 0.18 kg/cm<sup>2</sup> ;  
Curve A : the generative column length, 10.3 cm. ; soda-lime, 1.9g.  
Curve B : the generative column length, 10.3 cm. ; soda-lime, 1.0g ; potassium carbonate, 0.3g.

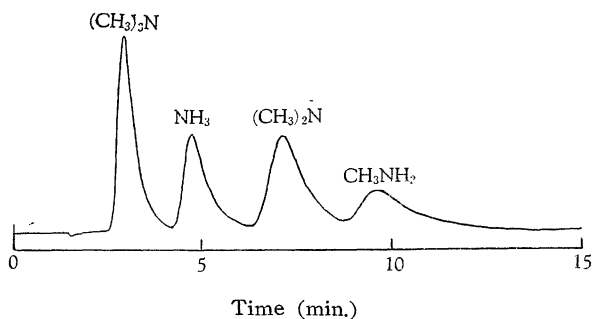


Fig. 4. The separation of ammonia, tri-, di-, and monomethylamines. Column length, 2 m. ; liquid phase, triethanolamine ; temp., 78°C ; flow rate of hydrogen, 24 ml./min. ; hydrogen pressure, 0.28 kg/cm<sup>2</sup>.



*ammonia*, *monomethylamine*, *trimethylamine*, and *dimethylamine*. Alexander *et al.*<sup>6)</sup> separated in the order of *ammonia*, *monomethylamine*, *dimethylamine*, and *trimethylamine*, with *o*-toluidine as a liquid phase. Yang *et al.*<sup>7)</sup> separated *ammonia* and *monomethylamine* by the use of 1-hexadecanol. Triethanolamine is not a good liquid phase for the separation of *ammonia* and *methylamines*; compared with those liquid phases described above, but it will be of some practical use for the separation of the *trimethylamine* as the precursor in their revelations. A small reverse peak always appeared in these experiments just after the lapse of the first one minute of the retention time. This phenomenon may be considered as due to the change of pressure by a sudden decomposition of those *aminehydrochlorides* or *ammonium chloride*.

### 5. Results and discussion

It was found in the experiments that all species of the mint used contained a large quantity of *ammonia*, and a few of *trimethylamine* (Fig. 5.). It was noticed that *trimethylamine* has a remarkable fishy odor. Other *nitrogen* compounds could not be identified. It can be supposed that the existence of a large quantity of *ammonia* in the coho.-water is mainly due to the production of *ammonia* by the hydrolysis of the *amides* and one part of free *ammonia*. Moreover, James *et al.*<sup>4)</sup> found *ammonia* and *trimethylamine* from the leaves of *Chenopodium vulvaria*, L. by the gas chromatography.

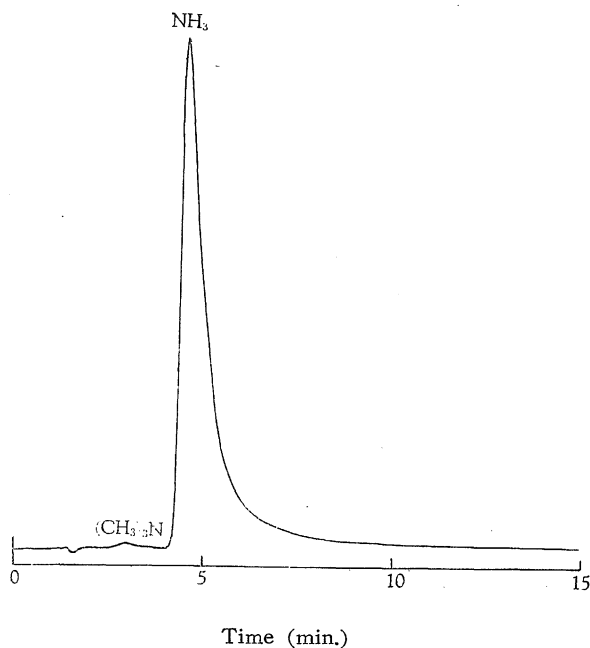


Fig. 5. Chromatogram of the amines present in the coho.-waters of the mint plants. Column length, 2 m. ; liquid phase, triethanolamine ; temp., 78°C ; flow rate of hydrogen, 24 ml./min. ; hydrogen pressure, 0.28 kg/cm<sup>2</sup>.

#### IV CONCLUSION

In the investigation on the coho.-waters of *M. arvensis* (San-Bi, and Brazil mint), *M. viridis* (Red-Stem and White Hair, Japanese spearmint), *M. pulegium*, and *M. rotundifolia*, the writers have found some *amine* compounds : -

1. The volatile waters have a basic property.
2. By the steam distillation, *nitrogen* compounds were let distilled slowly by slowly, and these distillation intervals have no connection with those of volatile oils.
3. In determinations of *amines* in coho.-waters with six species of the mint plants cultivated in the garden of Shimane University, by the use of the gas-chromatography, the writers have found a large quantity of *ammonia* and a few of *trimethylamine* in every coho.-waters.

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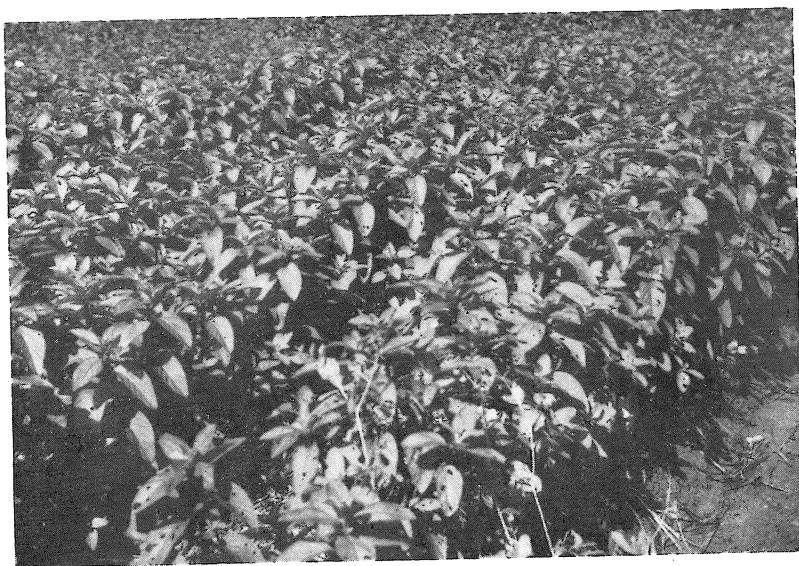
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#### APPENDIX : PHOTOGRAPHS



**Photo. 1.** Young leaves of San-Bi (*M. arvensis*)  
(May 6, 1956 at Kurashiki, by G. Ishikawa)



**Photo. 2.** First cropping period of San-Bi (*M. arvensis*)  
(June 3, 1956 at Kurashiki, by G. Ishikawa)



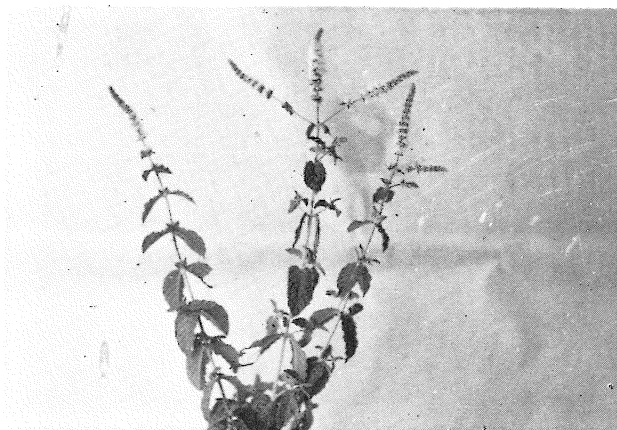
**Photo. 3.** Second cropping period of San-Bi (*M. arvensis*)  
(Aug. 12, 1956 at Kurashiki. by G. Ishikawa)



**Photo. 4.** Maruba-Chirimen (*M. rotundifolia*)  
(June 16, 1962 at Matsue,  
by T. Nagasawa)



**Photo. 5.** Chirimen-Mint of Red-Stem (*M. viridis*)  
(June 16, 1962 at Matsue,  
by T. Nagasawa)



**Photo. 6.** Chirimen-Mint of White-Hair (*M. viridis*)  
(Aug. 1, 1962 at Matsue,  
by T. Nagasawa)



**Photo. 7.** Soviet-Mint (*M. viridis*)  
(July 24, 1956 at Matsue,  
by T. Nagasawa)



**Photo. 8.** Pennyroyal (*M. pulegiurn*)  
(June 28, 1962 at Matsue,  
by T. Nagasawa)