Chemical Studies on Mentha*
II. On the Odorous Components of the Japanese Peppermint Oils (I)**

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長沢　徹：薄荷属植物の化学的研究

第２報　日本産薄荷油の臭気成分研究（その１）

1. Introduction

Peppermint plants3), cultivated in Japan, belong to *Mentha arvensis*, L.1)2)3) and it is the most excellent species3)4) in the world, that its essential oils contained the highest yield, 80～90 %, of *l-menthol.* Having long studied the Japanese peppermint oils, the writer perceived much inferiority4) of the smell and taste of the Japanese menthol crystals to that of the foreign trade. General menthol manufacturers in Japan, however, seem to care only of appearance, that is color and a crystalline form, of the *menthol* by their experience. The progress of menthol products was prevented probably because that they did not criticise the goods in view of the chemical points.

The writer has been studying, especially, the aroma and taste of the Japanese menthol crystals.4)13)17)18)36)37)38) The menthol crystals of Japan are recrystallized with dementholized oils, therefore it is obvious that the menthol crystals are accompanied by an aroma and a taste of the solvent. Hence, we must decide to improve the aroma and taste of the peppermint oils prior to menthol crystals. The ordinary refined Japanese peppermint oils have a bitter taste4)5)10)17)18) together with a proper disagreeable odor,4)17)25)26)28)37)39)41)43)45)46) besides they are colorized13) on keeping which decreases severely the value of the articles.

The writer has commenced the research, for the purpose of the contribution to promote the Japanese peppermint industry, in view of manufacturing the superior peppermint oil after investigating the bad constituents.40)42)

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**The outlines of this report were announced at the 9th annual meeting of the Chemical Society of Japan on the 2d April, 1956 (at Kyoto University).

2. Outlines of the Research

The writer used two samples of both the forerun-oil A* and B (each yield being 0.1 and 1.0% to dementholized oils, respectively) of the lower boiling fraction of dementholized oil, which was made by a certain Menthol Factory. A and B are both mobile liquids and have the following properties:

	Boiling range	Color	Odor
A	75~160°C	Dark red	Anaesthetic and pungent
B	160~180°C	Yellowish-orange	Minty

Their physical and chemical constants are shown in the Table 1.

Table 1. Physical and Chemical Properties of Sample (A and B)

	d_4^{25}	n_D^{25}	$[\alpha]_D^{14}$	η^{25}	A.V.	E.V$_1$	E. V$_2$
A	0.8454	1.4409	−19.1°	1.00	8.02	22.6	122.0
B	0.8557	1.4631	−29.7°	1.53	1.60	15.5	80.7

N. B. A.V.=Acid Value,
EV$_1$=Ester Value,
EV$_2$=Ester Value after acetylation.

A has a strong anaesthetic pungent odor of *aldehyde* and colored intensely. A contains 0.86% of *acetic acid*, which calculated from its acid value. On the other hand, B contained 4.3% of *ester-menthol* and 19.3% of *free-menthol* estimating from its ester values.

The writer expressed his research61)62)63)64) on the *aldehydes* and *ketones* (carbonyl compounds) existing in the low-boiling portion of dementholized oils. It is remarkable that A contained, specially, more 43% of the compounds acting with *sodium sulfite*.65)66) Hence, the writer extracted the carbonyl compounds by *sodium sulfite*67)68)69) or *sodium salicylate*,70)71)72) and investigated

Photo 1. Japanese Mint (*Mentha arvensis*, L.) in bloom at August.

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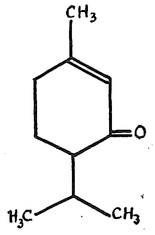
*These oils were prepared on November, 1955.

them by color reaction[73] and derivatives.

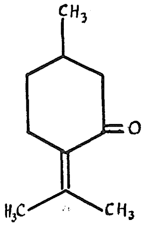
In summarizing, the writer has confirmed some *aldehydes* as *acetaldehyde*,[47] *isovaleraldehyde*,[49] *furfural*,[46,78,79] and newly found such *methyl ketones* as *acetone*,[53,74] *methylethyl ketone*,[75] *methyl-n-amyl ketone*,[74,76,77] *methyl heptenone*,[83,84,85,86,87,88] and 1-*methyl-3-cyclohexanone*.[80,81,82] It seems, therefore, that the cause of an evil odor of the Japanese peppermint oils depends mainly on the existence of these *aldehydes* and *methyl ketones* of lower boiling point. In the same time, the coloring of the oil is caused chiefly by the presence of the *furfural*.

3. Offensive Odors of Peppermint

The presence of the *piperitone*,[1,2] which has a bitter taste, and known as one of the inferior constituents of Japanese peppermint oils,[4] was detected first by Schimmel & Co.[5] of Germany in the year 1910. The writer isolated already this bitter substance[10,57] from the oil and acknowledged its queer odor. The writer also recognized,[10,13,16] that *piperitone*, unsaturated *ketone*, has a tendency to coloring under spontaneous chemical change in the period of keeping. Baker and Smith (1897)[6] have found the *piperitone* in the essential oil of one of the eucalyptus grown in Australia. They named it "Sydney-Peppermint" (*Eucalyptus piperita*) owing to its minty odor. Since that time *piperitones* were found in many eucalyptus oils.[9,12,14,15] Among them, the studies on the eucalyptus oils by Penfold et al.[9,11,12] are a splendid work. It is noticeable that *piperitone* is an important resources for the synthetic menthol. Simonsen (1921)[7] found a large quantity of *piperitone* in the essential oil of Indian *Andropogon iwarancusa*, and Morani (1923)[8] found it in the oil of *Mentha pulegium* grown in Sicily.



Piperitone



Pulegone

Here appears *pulegone*,[1,2,4] another unsaturated *ketone*, as a bad component like *piperitone* in the Japanese mint oils. It has a peculiar unpleasant odor.[4,36] It must be noticed[37,38,39] that the *piperitone* contained much in the lower species[40] of the Japanese mint (*Mentha arvensis*, L.). The writer (1929)[28] has found *d-pulegone* (over 20% yield) as a characteristic constituent in the essential oil of the Wild-mint, "Kusahakka" (grass-mint) (*M. arvensis*) grown in Hokkaido. The writer, furthermore, found it (over 30% yield)[56,57] in the oil of "Inu-hakka" (Dog-mint) (*M. arvensis*)[37] in Okayama Prefecture. *Pulegone* is widely distributed in the essential oils of mentha grasses. It was found by Kremers (1887)[20] in the oil of American pennyroyal (*Hedeoma pulegioides*), and followed by Beckmann et al. (1891)[19] in the European pennyroyal (*Mentha pulegium*). Kremers, then, found this *ketone*[25] in the oil of the Japanese mint,[26] and detected it also in the oil of americanized mint, which was trannsplanted from Japan. The writer[3,4] supposed with regret, that the cause, which reduced the fame of the Japanese mint oil, is due to the intermix of a Dog-mint.

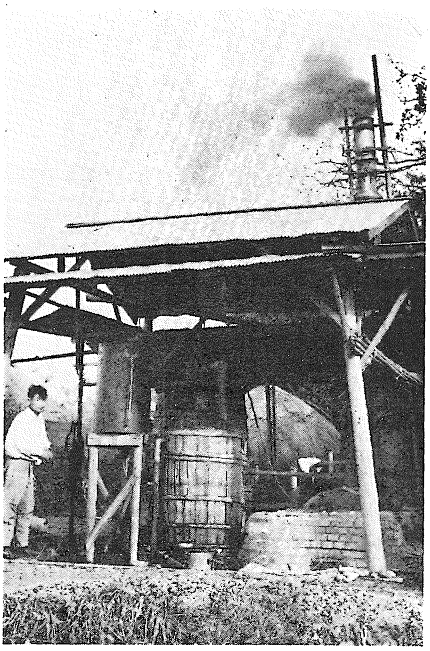


Photo 2. A scene of distilling Mint-grass in the farm-yard.

Pulegone is contained in many essential oils, thus in oil of *Pycnanthemum miticans* (60~75%),[21] *Mentha silvestris* (40%),[22] pennyroyal (75%)[27] grown in Russia. Guenther (1929)[20,35] obtained that of 90% yield from Spanish products. Further, it will be seen in Sicilian pennyroyal oil (57~88%)[30] and in *Calaminta nepeta* (69%).[31] Pinel (1941),[32] however, found the highest yield of *pulegone*, 89~97%, in the oil of Moroccan *Mentha pulegium*. Researches of Barrowcliff (1907)[23] and Bennett (1918)[24] on the American pennyroyal oils, and those of Naves (1942)[33,34] on the Iberian pennyroyal oils are remarkable.

For the odorous substances in the Japanese mint oils we should search for the lower *aldehydes* and *ketones*, besides known unsaturated cyclic *ketones*. Having been found *acetaldehyde* together with *isovaleraldehyde*, in the American peppermint oil by Power and Kleber (1894),[44] it was detected in distillation waters.[47,48] *Isovaleraldehyde*, which keeps a strong evil odor, was found in these peppermint oils of America,[44,49,50] France [49,51,52] and that of Japan.[45]

The writer confirmed the presence of *acetaldehyde* and *isovaleraldehyde* in this research. According to Guenther,[53,54] *acetone* and *furfural* exist in the distillation waters of the American peppermint oils. Garratt (1935)[46] found a small quantity of *furfural* in the lower-boiling oil of the Japanese mint. The writer confirmed, also, this one as a substance to produce a bad smell and coloring. Kremers (1921),[55] on the other hand, found 1-*methyl*-3-*cyclohexanone*, which was recognized by the writer in this paper, in the cohobated oil of American peppermint.

During the researches on the odorous substances of the Japanese mint, the writer has found[58,59] a new species of Mentha, which called "San-Bi" (Beni-hakka) (*M. arvensis*), of the highest content of *menthol*. As their chemical components were studied by the same author,(60) a subject for odors has come again as a current item.

4. Experimental Part

1. Distillation and Color Reaction.

(1) Distillation of A :- The sample A (b. 75～160°C), 100 g., were distilled with a 250-ml-Claisen flask under ordinary pressure. These results of physical constants and coloring reactions of the each fraction are shown in the Table 2 and 3.

Table 2. Fractionation of A (d_4^{25} 0.8454, n_D^{25} 1.4409, $[\alpha]_D^{14}$ −19.1°, η^{25} 1.00)

Fraction	B.P. (°C)	Yield (%)	Color	d_4^{25}	n_D^{25}	$[\alpha]_D^{12}$	η^{25}
I	61～80	6.7	pale yellow green	0.8271	1.3984	−7.5°	0.713
*II	80～100	20.2	〃	0.8277	1.4079	−13.6	0.752
*III	100～110	9.2	〃	0.8319	1.4134	−13.6	0.795
*IV	110～125	6.0	〃	0.8411	1.4247	−15.8	0.962
*V	125～140	3.8	〃	0.8500	1.4421	−19.8	—
*VI	140～150	2.9	colorless	0.8489	1.4489	−18.9	—
VII	150～160	17.0	〃	0.8508	1.4604	−30.2	1.21
VIII	160～165	12.5	〃	0.8516	1.4641	−32.5	1.24
IX	165～170	6.2	〃	0.8533	1.4645	−28.8	1.28
X	170～173	4.0	〃	0.8547	1.4642	−36.6	—
XI	173～	9.0	dark red	0.9027	—	—	—

N.B. I～V...Aliphatic series,
VI～X...Terpene series.

*The colors of the fractions I to VI changed to dark voilet on the following day, and colored deep when stood one week.

Table 3. Coloring Reaction to Each Fraction of A

Fraction	B.P.(°C)	Schiff's reagent	Aniline acetate	Fehling's solution	Bromine	Potassium permanganate
*I	61～80	+++	nil	red-brown	nil	decolorize
II	80～100	+++	faint	ppt.	decolor.	brown ppt.
III	100～110	++	+	〃	〃	〃
IV	110～125	++	+	〃	〃	〃
V	125～140	++	++	〃	〃	〃
VI	140～150	++	+++	〃	〃	〃
VII	150～160	+	++	〃	〃	〃
VIII	160～165	+	+	brown	〃	〃
IX	165～170	nil	+	nil	〃	〃
X	170～173	nil	faint	nil	〃	〃
XI	173～	—	—	—	—	—

N.B. *Fraction I has a strong anaesthetic odor of acetaldehyde.

The colors of the fractions II～IV were changed to dark-violet on the next morning. Each fraction gave no reaction of *ferric chloride*. Fraction I has an intense anaesthetic odor of *acetaldehyde*. The Schiff's reaction is remarkable in the fractions I～IV, that means an existence of *acetaldehyde*. The coloration with *aniline acetate* is deepest in VI (b. 140～150°C), that shows the presence of *furfural* clearly.

(2) Distillation of B :- The sample B (b. 160～180°C), 100 g., were distilled as above. The results are shown in the Table 4.

Table 4. Fractionation of B (d_4^{25} 0.8557, n_D^{25} 1.4631, $[\alpha]_D^{14}$ −29.7°, η^{25} 1.53)

Fraction	B.P.(°C)	Yield (%)	d_4^{25}	n_D^{25}	$[\alpha]_D^{13}$	η^{25}	Schiff test	Aniline acetate	Fehling sol.	$KMnO_4$
*I	82～120	1.5	0.8472	1.4555	−20.0°	—	+++	++	red-brown	decol. ppt.
*II	120～140	1.0	0.8479	1.4545	−28.7	—	+++	++	〃	〃
*III	140～150	2.5	0.8488	1.4590	−25.0	—	++	+++	〃	〃
IV	150～155	7.4	0.8493	1.4636	−27.0	1.21	++	+++	〃	〃
V	155～160	19.0	0.8481	1.4639		1.21	+	+	〃	〃
VI	160～163	17.7	0.8435	1.4643		1.20	faint	+	〃	〃
VII	163～165	9.9	0.8508	1.4645	−34.8	1.22	faint	faint	〃	〃
VIII	165～170	12.2	0.8514	1.4650	−33.6	1.26	faint	faint	〃	〃
IX	170～175	6.2	0.8549	1.4642	−35.6	1.29	faint	faint	〃	〃
**X	175～180	5.2	0.8586	1.4650	−28.1	1.41	+	faint	〃	〃
XI	180～	14.3	0.8952	1.4685	—	5.08	—	—	—	—

N.B. *The color of fractions I～III changed to violet on standing over night, and to intense dark violet after a time of a week.
**Carbonyl compounds existing.

Schiff's reactions appeared as good from fore-run to the boiling fraction at 160°C, but intense at the boiling range of 175～180°C, which supposed us a presence of any carbonyl compounds. The colorations with *aniline acetate* were severe in the fractions below 155～160°C, that is, perhaps, due to a strong volatility of *furfural*. Lower fractions, I～III, were changed to dark violet in the following day. No reactions of *ferric chloride* were perceived in the whole fractions.

2. Determination of Carbonyl Compounds.[57]

We have determined the carbonyl compounds in the samples by extracting with three reagents as (1) 40% neutral *sodium sulfite* solution, (2) 30% *sodium bisulfite* solution, and (3) 50% *sodium salicylate* solution, respectively. Thus the content of the carbonyl compounds showed such results from 43 to 32% by volume. From these data, we could seen the presence of *aldehydes*, *methyl ketones*, or unsaturated *ketones*.

[Experimental]—(1) : **Sodium Sulfite Determination**—Each 5 ml. of the Sample (A, B) was taken, separately, to 100-ml-Cassia flask, then introduced any quantity of 40% *sodium sulfite* solution, and shaken on the boiling water-bath, using *phenolphthalein* (1% *ethanol* solution) as an indicator. The *alkali* liberated in the reaction was neutralized with a dilute *acetic acid* (1 : 5) from time to time. The results are the following :—

The extracted oil (vol. %), A : 43.0% ; B : 5.8%

[Experimental]—(2) : **Sodium Bisulfite Determination**—Take 5 ml. of the sample A into 100-ml-Cassia flask, and shake with any quantity of 30% *sodium bisulfite* solution.

The extracted oil (vol. %), A : 33.6%

[Experimental]—(3) : **Sodium Salicylate Determination**—Each one ml. of the sample (A, B) was taken, separately, to 10-ml-shaking-mess-cylinder, and was shaken with 4 ml. of 50% *sodium salicylate* solution. (N. B. Similar results were obtained by 2 ml. of the reagent.) :—

The extracted oil (vol. %), A : 32% ; B : 11%

3. Isolation and Identification of Carbonyl Compounds.

The sample A was treated stepwise with *sodium bicarbonate*, *sodium sulfite*, and *sodium salicylate* solution. The carbonyl compounds were isolated by distillation from both the *sulfite* and the *salicylate* extracts, and then identified forming their derivatives.

[Experimental]—(4) ; **Separation of Carbonyl Compounds**—Sample A, 203.5 g., were washed (a) twice with two times of its volume of 10% *sodium bicarbonate* solution, then (b) the neutral oils were extracted twice with 4 times of its volume of 40% *sodium sulfite* solution on the boiling water-bath, at last (c) the residual oils were extracted twice with two times of the volume of 50% *Salso** at ordinary temperature. Those results are represented in the Table 5.

Table 5. Treatment of A with three Reagents (a–c) (Sample A, 203.5g.)

Reagents	Non-reacted residual Oil (g.)	Absorbed Oil (g.)	Absorbity upon Sample A (%)
(a) Sodium bicarbonate sol. (10%)	189.0	14.5	7.2
(b) Sodium sulfite sol. (40%)	(i) 145.5 (ii) 122.7	43.5 22.8	21.3 11.2
*(c) Salso sol. (50%)	98.2	24.5	12.3

N.B. *"Salso" is the abbreviate name of Sodium salicylate.
(a) for Carboxylic acids, (b) for Aldehydes and Methylketones, (c) for Ketones and Alcohols.

[Experimental]—(5) : **Liberation of Carbonyl Compounds**—The sulfite combined liquor (b), 500 ml., were treated with 30 ml. of 20% *sodium hydroxide* solution. The liberated carbonyl compounds were, then, distilled with steam. Salso-combined liquor (c) were decomposed merely with water, then steam distilled to obtain carbonyl compounds. For the reason that the sulfite-addition compound liberated much quantity of water-soluble *aldehydes* and *ketones*, the recovery of the carbonyl oil was very poor as shown below :—

		Liberated oil
(b) *Sodium Sulfite* Compounds	(i)	9.4 g. (21.6% of the theory)
	(ii)	4.2 (18.4% of the theory)
(c) *Salso* Compounds	(i)	10.1 (57.5% of the theory)
	(ii)	4.0

[Experimental]—(6) : **Physical Properties of the Carbonyl Oil**—Carbonyl oils obtained in the above procedures (b and c) were dried over anhydrous *sodium sulfate*, and measured their physical constants by usual manner. Color tests of (1) *aniline acetate,* (2) Schiff's reagent, (3) *Iodoform* reaction, (4) Fehling solution, (5) *potassium permanganate,* (6) *bromine,* and (7) *sodium nitroprusside* were made, almost as a positive result. These results are as the Table 6 and Table 7.

Table 6. Physical Constants of the Carbonyl Oil*

Treatment	Color	Odor	d_4^{25}	n_D^{25}	$[\alpha]_D^{13}$	η^{25}
(b) Extacted with Sodium sulfite (i)+(ii)	pale green	anaesthetic	0.8210	1.4104	−3.36°	0.849
(c) Extracted with Salso (i)	pale green	anaesthetic, pungent	0.8539	1.4290	−11.50	1.92
(ii)	//	//	0.8577	1.4356	− 7.40	—

N.B. *Obtained from the Sample A.

Table 7. Color Reactions of the Carbonyl Oil

Treatment	Aniline acetate (1)	Schiff's reagent (2)	Iodoform test (3)	Fehling's sol. (4)	Potassium perman-ganate (5)	Bromine (6)	Sodium nitro-prusside (7)
(b) Sodium sulfite	sharp	sharp, strong	odor, ppt.	red-brown ppt.	decolor., ppt.	slightly decolor.	orange
(c) Salso (i)	evident	//	//	//	//	—	rubyred
(ii)	//	//	//	//	//	—	//

N.B. (1) Indicates furfural,
(2) // aldehydes,
(3) // methylketones and acetaldehyde,
(4) // aldehydes,
(5)(6) // unsaturated compounds,
(7) // acetone.

[Experimental]—(7): Identification of the Carbonyl Compounds from Sulfite-treatment.—Fractionation:—8 g. of the carbonyl oil from *sulfite* compound were fractionated with a small Claisen-flask under ordinary pressure:

	B.P.(°C)	yield (g.)	odor
I	~75	0.5	strong pungent
II	75~80	1.2	//
III	80~100	2.6	//
IV	100~150	2.0	pungent
V	150~165	1.0	//

Identifications: Using 0.1−0.5 g. of each fraction and a corresponding reagent as an usual manner, we obtained some crystalline derivatives for identifying the following compounds:—

Acetone CH_3COCH_3: From fraction I (~75°):—(i) Prepared *2, 4-Dinitrophenylhydrazone,* m. [124-125°], recrystallized in *acetic ether.*

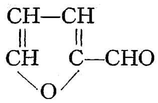
(ii) Coloration:—To the mixture of oil and a few drops of 10%-*sodium nitroprusside* solution added 3 drops of *sodium hydroxide* solution. And again, added ten drops of *acetic acid,* soon appeared ruby-red color.

Methylethyl ketone $CH_3CO \cdot C_2H_5$: From II (75~80°):—(i) *2, 4-Dintrophenylhydrazone,* m. [111

-112°]; (ii) *Semicarbazone*, m. [145-146°] (crystallization in *ethanol*).

Isovaleraldehyde C_4H_9. CHO: From III (80∼100°) :—(i) *2, 4-Dinitrophenylhydrazone*, m. [122-123°]; (ii) *Semicarbazone*, m. [106-107°].

Methyl-n-amyl ketone $CH_3CO\cdot(CH_2)_4CH_3$: From IV (100∼150°) :—(i) *2, 4-Dinitrophenylhydrazone*, m. [88-89°]; (ii) *Semicarbazone*, m. [121-123°].

Furfural  : From V (150∼165°) :—(i) *2, 4-Dinitrophenylhydrazone*, m. [228-229°]; (ii) *Oxime*, m. [88-89°], no depression of mixed melting with a commercial article. (iii) Coloration: —Intense red color, when mixed 5 ml. of a 2% solution of *aniline acetate* (freshly made) to 0.1 ml. of the oil.

[**Experimental**]—(8): **Carbonyl Water**—The volatile water, which distilled on obtaining carbonyl oil from *sulfite* compound, was condensed by cohobation and treated with several coloring reagents. The results are shown in the Table 8.

Table 8. Color Reactions of Carbonyl Water*

Reagents	Reaction
Aniline acetate	nil
Schiff's reagent	deep purple-red
Iodoform reaction	distinguishing odor and yellow-white ppt.
Fehling's solution	red color
Bromine	—

N.B. *The condensed water smells strong anaesthetic odor.

In the cohobated water, we identified *acetaldehyde* as:—

Acetaldehyde $CH_3.CHO$: (i) The odor is very strong anaesthetic and pungent, resembling this compond.

(ii) *2, 4-Dinitrophenylhydrazone*:—To 20 ml. of the cohobated water add 10 ml. of 0.4% of *2, 4-dinitrophenylhydrazine* (in *HCl*) solution. Soon, deposited much quantity of yellowish orange precipitate of the *2, 4-dinitrophenylhydrazone*, m. [145-146°].

(iii) Coloration:—As in the Table 8, the positive reactions of the Schiff's test, *iodoform* reaction, and reducing Fehling's solution, indicate the presence of *acetaldehyde*.

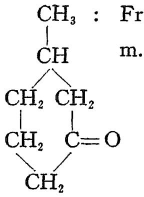
[**Experimental**]—(9): **Identification of the Carbonyl Compounds from Salso-treatment**—Fractionation:—8 g. of the carbonyl oil from *Salso* compound were fractionated with a small Claisen-flask under reduced pressure at 40 mmHg.:—

	B.P. (°C/40 mm)	yield (g.)
I	∼45	1.0
II	45∼60	1.0
III	60∼80	1.2
IV	80∼100	2.2
V	100∼	2.0

Identifications: We identified the following compounds by the crystalline derivatives, using 0.1∼0.5 g. of each fraction as an usual manner:—

Methyl-n-amyl ketone: Fraction II $(45\sim60°)_{40}$—(i) *2, 4-Dinitrophenylhydrazone*, m. [88-89°]; (ii) *Semicarbazone*, m. [121-123°].

1-Methyl-3-cyclohexanone



: Fraction III $(60\sim80°)_{40}$—(i) *2, 4-Dinitrophenylhydrazone*, m. [154-155°]; (ii) *Semicarbazone*, m. [178-180°].

Methylheptenone $(CH_3)_2C=CHCH_2CH_2\cdot COCH_3$: Fraction IV $(80\sim100°)_{40}$—(i) *2, 4-Dinitrophenylhydrazone*, m. [80-81°]; (ii) *Semicarbazone*, m. [136-138°], no depression in mixed melting. (iii) Color test:— *Bromine* or *potassium permanganate* were deprived of their color as soon as combined. *Iodoform* was easily formed with *iodine* solution in *sodium hydroxide* medium as an ordinary process. Pine shavings moistened with concentrated *hydrochloric acid* were colored to purple red.

[Experimental]—(10): **Carbonyl Water**—The volatile water obtained from the decomposition of the *salso* compound, was condensed by cohobation. We found *Methylcthyl ketone* in the volatile water as:—

Methylethyl ketone: (i) The odor is severe anaesthetic and pungent reminding this ketone.

(ii) *2, 4-Dinitrophenylhydrozone*:—To 15 ml. of the cohobated water add 10 ml. of *2, 4-dinitrophenylhydrazine* (0.4% in *HCl*) solution. We obtained much quantity of crystals of the *hydrazone*, which melted at [111-112°] after recrystallization in *acetic ether*. It does not lowered by the mixed melting with that of the above-mentioned Experimental (7).

5. Conclusion

In the foreruns of the low-boiling oil (corresponding to 0.1% of the dementholized oil) of the Japanese peppermint oils, the writer found about 43% of carbonyl compounds, which are considered as the odorous and coloring substances in them. That is to say, the Japanese dementholized oil contains 0.043% of *aldehydes* and *ketones*.

In this research, the writer found newly some *methyl ketones* as (1) *Acetone*, (2) *Methylethyl ketone*, (3) *Methyl.n-amyl ketone*, (4) *Methylheptenone*, and (5) 1-*Methyl*-3-*cyclohexanone*. In the same time, the existence of lower *aldehydes* as (1) *Acetaldehyde*, (2) *Isovaleraldehyde*, and (3) *Furfural* are recognized by the same author.

Each content of these *aldehydes* and *ketones*, estimating from the boiling yield, are as the following:—

Acetaldehyde (21°) *Acetone* (56°) *Methylethyl ketone* (80°)	.... 4.3% (0.004%)*
Isovaleraldehyde (92°)	............................12.3% (0.012%)
Methyl-n-amyl ketone (150°)	.... 1.8% (0.002%)
Furfural (161°)	............................18.4% (0.018%)
1-*Methyl*-3-*cyclohexanone* (169°)	.... 3.7% (0.004%)
Methyl heptenone (173°)	.... 2.5% (0.003%)

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*Figures of per cent in the parentheses were estimated at each content of the carbonyl compounds existed in the original dementholized oil.

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