STUDIES ON THE UTILIZATION OF THE CONSTITUENTS OF PEPPERMINT OILS

I. On the Synthesis of Carvone. *

Toru NAGASAWA

I. INTRODUCTION

An excellence and the most remarkable characters of the Japanese peppermint (*Mentha arvensis*, L.)[1] exist in the *l-menthol* (as crystal menthol) which contained about 80～90% at the most of essential oils of Mentha. So we could separate the menthol crystals of 50～60% of the crude oil by merely cooling it. Hence the Japanese peppermint has been considered chiefly the most important materials as manufacturing Menthol Crystals ("Hakka-Nō") for long before (downward from half age of Meiji), and the greater part of the world production of it depended upon the Japanese peppermint.

We Japanese, however, were surprized to see a sudden appearance of the large quantities of peppermint products of Japanese Mentha[2] [3] [4] in Brazil after the II War. Hence the state of the world production of the menthol crystals has been divided for three parts with China[5] [6], and Brazil, besides Japan. The Japanese peppermint industry, therefore, has arrived at the point not to be seeked the fantacy before the War.

The necessities of the establishment of the Japanese peppermint industry[7] [8] [9] [10] [11] has been exclaimed by many engineers, but remained to the present. What is the reason? The author has long been studied the Japanese Mentha[12] [13] [14] [15] and its essential oils, and exerted himself for the peppermint industry, but to the regret that it is not in route.

As the very life of the Japanese peppermint exists in *l-menthol*, most of the makers has endevoured to obtain the good quality and much quantities of menthol crystals only, but they take no attention for the application of the constituents of the oils. Peppermint oil belongs to the costly goods in general essential oils, and as the dementholized oil contains yet about 40% of menthol, it has been traded in commerce with a comparable worth.

The writer, however, has thought and pointed out[2] [3] [6] [10] the ideas that there are many problems to comment when we see world-wide the Japanese peppermint products. We must come to our senses that the Japanese mentha has rather many defects than with foreign

---

* The outlines of this research have been announced at the 17th meeting of the Chugoku-Shikoku Branch of the Chemical Society of Japan on the 8th July, 1955 (Matsue-City).

ones except for merit of the highest content of *l-menthol* in the essential oils. Because the dementholized oil, which has already removed a fragrant and refreshing menthol crystals, accompanies with a characteristic disagreable odor[2][16] and bitter taste of Japanese mentha.

To establish the Japanese peppermint industry, therefore, besides the advance of manufacturing technique, the study on the utilization of the dementholized oils is a matter of importance. So to carry, we must know first of all the constituents of the dementholized oils. We can see them in many reports[12][13][17] already had been published. In comparison the Japanese dementholized oils with foreign peppermint oils, although both contain *l-menthol*, *menthone*, and *menthyl acetate*, there exists disagreable odor and bitter substances both in the low-boiling and high-boiling portions in the former. It was reported abroad recently[18], on the contrary, that the small quantities of *menthofuran* and *jasmone*, which supposed to be the substances of the principal aroma, were found in the latter[19][20]. Hence it appears that the superiority of fragrance of the foreign peppermint to that of Japan seems to us clearly somewhat.

For the improvement of the quality of Japanese dementholized peppermint oils, which devoid of fine fragrance compared with foreign ones, we must study the application of the components of both low- and high-boiling portions of the oil. The author have once studied the high-boiling portions having unpleasant odor, and isolated *β, γ-hexenol*[21] by saponification, and appreciated the strong fresh leaf odor of this alcohol ("Leaf Alcohol") and emergence of fine laver odor of *hexenyl acetate*. Thus we have acknowledged greatly the worth of the utilization[13] of *β, γ-hexenol*. In the foreign countries before this, the syntheses of *jasmone*[22][23] and *nonadienal*[24][25][26], one of useful perfume, had been succeeded by using this alcohol.

The noticeable substances in the low-boiling portion are *l-limonene* and *ethylamyl carbinol*. With the former, *α-terpineol*, after changing to *monohydrochloride*, was synthetized completely by late Dr. Hayashi[27]. The latter oxidised to *ethlamyl ketone* easily, and used for the preparation of artificial lavender oil. *Limonene* exists in several essential oils but undesirable, like other terpene hydrocarbons, for perfumery articles. It should be eliminated better for the sake of the lower solubility upon *ethyl alcohol*. It is desirable for this substance, which is contained about 10% in the dementholized oil[2][13][17], to be transformed as an useful matter.

It is remarkable[29][31] that *l-carvone*, the important flavors for chewing gum and main constituent of the spearmint oils, has been synthetized simultaneously by both chemists Bordenca et al.[28] and Royals et al.[30] (1951), separately, using *d-limonene* of abundant byproducts of citrus industry in U. S. A., recently.

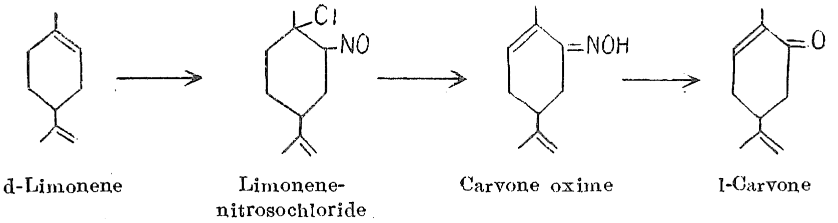
The formation of *carvone*[32] from *limonene* by air-oxidation has been known through experiments of Blumann and Zeitschel (1914)[33], but researches thereafter developed scarcely. Commencing, however, with the invention of Tilden (1877)[34] to introduce a crystalline *nitrosochloride* from *limonene*, Wallach (1888-1892)[35] [36] [37], Baeyer (1896)[38], Deussen, and Hahn (1910)[39] obtained *carvoxime* by dehydrochlorination of it with alkali reagents. Perhaps, based on the merits of the terpene chemistry[40] done before half a century, two new synthetic researches were made by Bordenca and Royals (loc. cit.) to meet with the requirements of the present time. Soon after these reports in U. S. A., Waida et al.[41][42] have announced the results of their synthesis of *carvone*.

The author has researched previously the essential oils[43] of "Oranda-Hakka" (*Mentha viridis*, L. var. *crispa*, Benth.) and found *l-carvone*[44], which contained 50~60% of the oil, should be used for important perfume materials. Now, as we synthetized *d-carvone* after Bordenca[28], and Royals[30], using mint-limonene for one case on the application of the constituents of dementholized oil, we would represent here the results of our researches.

II. GENERAL REMARKS ON THE RESEARCHES

The synthetic *l-carvone* was prepared, for the first time, from *d-limonene* in the oil of American orange by Bordenca et al. and Royals et al. * in the year 1951 separately. Their methods are cited in the TABLE 1.

TABLE 1. Synthesis of l-Carvone from d-Limonene



(a) Bordenca et al.[28]	Passing NOCl-gas into -60° -liquid -SO_2 solution	Dehydro-chlorination with Urea	Hydrolysis with H_2SO_4	Total yield 40%
(b) Royals et al.[30]	Passing ethyl nitrite into Alcohol solution at-10°, then passed moist HCl gas	Dehydrochlorination with Pyridine	Hydrolysis with Oxalic acid	56~60%

---

* loc.cit.

** Peel oil of Japanese "Natsu-Mikan", pale yellowish clear oil with a fragrant odor of orange.

*** Shiono-Koryo Co.

\# Low boiling portion of the dementholized oil, namely mint-terpene oil.

\#\#Oriental Menthol Industry Co.

On the standpoint of the progress of Japanese peppermint industry, we took their special good points of both methods for the syntheses of *carvone*, namely, (1) nitrosochlorination by (b), (2) dehydrochlorination by (a), (3) hydrolysis of *oxime* by (b).

Sources : - As sources of *limonenes* we took (A) ″Orange Oil-W″ ** of S.-Co. *** for *d-limonene*, and (B) ″First-Runing of Peppermint Oil″ # of O. M. -Co. ##

Ⅲ. SYNTHESIS OF L-CARVONE FROM D-LIMONENE (A)

1. d-Limonene.

″Orange Oil-W″ (d_4^{25} 0.8487, n_D^{25} 1.4703, η_{25} 1.23) was redistilled to obtain the main fraction (ca. 90% of the distillates) (b. p. 173～174°, d_4^{25} 0.8443, n_D^{25} 1.4695, η^{25} 1.05, $[\alpha]_D^{25}$ +110.2°, MR 44.80 ($C_{10}H_{16}F_{\overline{2}}$ 45.24), *tetrabromide* m. p. [103～104°], absorption of Br : 93 %) and this fraction was used as *d-limonene* for the preliminary synthesis of *carvone*.

2. Preparation of Limonenenitrosochloride.

In regard to the preparation of *limonenenitrosochloride* for the first step of synthetizing *carvone*, reported by Tilden [34] and Wallach formerly, we took the Wallach's method [35] to react the nascent *nitrosyl chloride* (NOCl) when formed gradually in the reaction vessel. The apparatus is shown in the FIGURE 1.

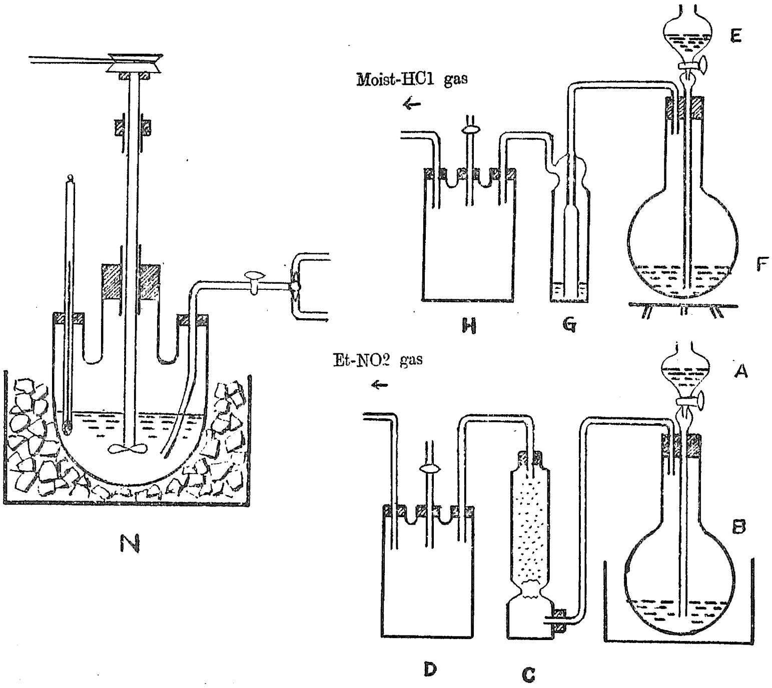


FIGURE 1. Apparatus for Nitrosochlorination.

To the mixed solution of *limonene* and *ethanol* in three-necked flask (N) with a stirrer, thermometer, and inlet tube keeping at 0~-17°C. with ice and common salt, passed *ethyl nitrite* gas produced in B till saturation, then derived moist-*HCl* gas from F. When the stirring, under cooling, was continued 30 minutes more, white crystals were deposited in the greenish solution. These crystals are filtered by suction and washed with cold *ethanol*.

We worked hard at the manipulation of reacting the moist-*HCl* gas to keep constant temperature at -5°C. as proposed by Royals et al., with sudden rise of reaction temperature. We regulated, therefore, the passing of *HCl* gas slowly and cooling strongly, when it happened to become hot. We recognized the convenience to judge the state of reaction by the color of reacting solution. That is to say, that there are some relation between the yield of products and solution color.

When the reaction temperature is under 0°C. the color of the solution becomes bluish green, but changes to brown, with emergence of NO_2 gas, as soon as the temperature goes upwards, resulting almost no yield. The results are shown as in the TABLE 2.

TABLE 2. Eormation of Limonene nitrosochloride

Experiment (No.)	Limonene (mole)	Nitrosochloride yield(%)	Reaction temp. (°C)	Solution color
1	0.5	25	Upward	Brown
2	0.5	0	Upward	Red-brown
3	0.25	41	-5~-17	Blue-green
4	0.25	36	0~-17	Green

The *nitrosochloride* washed with cold *ethanol* and dried on the tone plate has m. p. [70~80°], which is not even pure, was used for the next procedure without delay in care of unstable substances.

[**Experimental**] —— Into the 500cc. three-necked flask, with a solution of 34g. of *limonene* and 40 ml. of *ethanol*, introduced *ethylnitrite* at 0~-17°C. with a cooling mixture of ice-*NaCl*.

The *ethylnitrite* was prepared by dropping the solution of 16g. of *ethanol*, 20 ml. of concentrated *sulfuric acid*, and water to 200 ml., to the solution of 42g. of *sodiumnitrite*, 16g. of *ethanol* and water to 200 ml.

Then *hydrogen chloride* gas, which formed by dropping 55 ml. of concentrated *hydrochloric acid* to 110 ml. of concentrated *sulfuric acid*, passed through concentrated *hydrochloric acid*. After the reaction of the moist *HCl*-gas was over, the solution was agitated half an hour more, soon deposited white flocculent crystals. They are filtered by suction and washed with cold *ethanol*, then dried over tone plate, melting at [70~80°].

3. Preparation of l-Carvoxime.

Though *sodium methylate*, alcoholic-*KOH*, *pyridine*, or *urea* have been used generally for the dehydrochlorination of *limonenenitrosochloride*, we adopted *urea* as a probable scheme to obtain the *carvoxime* followed by the manual of Bordenca et al. *

Isopropyl alcohol solution of *nitrosochloride* and *urea* is refluxed on water-bath to dehydrochlorinate for 1 hour. The *carvoxime* thus obtained yielded 90% and has m.p. 〔72°〕, after recrystallization from *ethanol*, which coincided with literature.

〔**Experimental**〕— Twenty gs. of *limonenenitrosochloride*, 8g. of *urea*, and 100 ml. of *isopropyl alcohol* in the 300cc.-flask are refluxed on water bath for 1 hour. After the reaction, about 80% of the solvent was removed by distillation, and the residue was poured into a large quantity of water in which the crystals of *carvoxime* were deposited. The yields of crystals thus obtained after filtration, washing, and drying are as follows : -

No. of experiments	Limonene-nitrosochloride	l-Carvoxime	Yield
1.	20g.	15.2g.	89%
2.	19 〃	14.5 〃	90 〃

The crystals after recrystallization with *ethanol* have m.p. 〔72°〕.

4. Formation of l-Carvone.

As we have learned the tendency of racemization and isomerization according to the pH value in the formation of *l-carvone* by hydrolysis of *l-carvoxime*, it is necessary to keep them minimum.

It has been reported that Bordenca et al. * recognized *p-aminothymol* besides racemization in presence of acid, and Royals et al. * obtained *carvacrol* as a main product by 5N-mineral acid. Both of them adapted pH≒0.7 for good conditions and each used 6N-H_2SO_4 and 5% *oxalic acid* solution, respectively.

We have hydrolysed *l-carvoxime* with 5% solution of *oxalic acid*, and obtained *l-carvone* with yielding about 60%. This *carvone* was rectified by the vacuum distillation, and the physical constants compared with the recent literatures indicate good agreement as in the TABLE 3.

TABLE 3. Characters of Synthetic Carvones

Authors	B.P.(°C/mm)	d_4	n_D	$[\alpha]_D$	η^{25}**
T.Nagasawa	86～87 /7	0.9580 (25°)	1.4958 (25°)	-52.8° (25°)	2.60
C.Bordenca et al.	91～92 /10	0.9555 (27°)	1.4973 (27°)	-60° (27°)	—
E.E.Royals et al.	88～90 /4	0.9673 (25°)	1.4989 (25°)	-54.2° (25°)	—

** See Nagasawa's previous report [44) :
The relative viscosities of the essential oils were measured with Ostwald-viscometer.

---

* loc.cit.

It was derived also with *hydroxylamine hydrochloride* to the *oxime*, m. p. [72°], which coincided better with literature. This *oxime* was mixed with that *limonenenitrosochloride* and melted at 72°C. We have recognized thus the last synthetic product be *l-carvone*.

[**Experimental**] —— The mixture of 14.5g. of *l-carvoxime* and 150 ml. of 5%-*oxalic acid* solution was refluxed on the water bath for 2 hours, we obtained 8.5g. of *carvone* at 59% yield after steam distillation of the reaction products. This crude *carvone*, after dried over anhydrous *sodium sulfate*, has the following physical properties : -

d_4^{25} 0.9763, n_D^{25} 1.4961, η^{25} 4.61.

By rectification *, we obtained *l-carvone* as the main fraction having the following characteristics : -

B.P./7mm.	86~87°C,
d_4^{25}	0.9580,
n_D^{25}	1.4958,
η^{25}	2.60,
$[\alpha]_D^{25}$	-52.8°,
MR	found, 45.72 ;
	calcd. as $C_{10}H_{14}O\ |\overline{2}$, 45.26.

Oxime : -Using each 0.5g. of synthetized *carvone* and *hydroxylamine hydrochloride* as a usual manner, we obtained the *oxime* which melted at [72~73°] after recrystallization with *acetic ether*. It coincides with that of *carvoxime*. We observed also that the melting point, [72~73°], does not lowered by the mixed melting with that of dehydrochlorinated from *limonenenitrosochloride*.

Ⅳ. SYNTHESIS OF D-CARVONE FROM L-LIMONENE (B)

1. Separation of l-Limonene from the "First Running" of Peppermint Oils.

The "First-Running" ** of peppermint oils (d_4^{25} 0.8619, n_D^{25} 1.4637, η^{25} 1.39), which contains *l-limonene* mainly as a terpene hydrocarbon, is so colored intensely that 742g. of it were steam distilled and obtained 662g. of the "First-Running White Oil" (d_4^{25} 0.8527, n_D^{25} 1.4610, η^{25} 1.14).

The *menthol* % of the oil was calculated[45] from the ester value ($EV_1=27.65$) and that of after acetylation ($EV_2=59.08$). The results obtained are as the following : -

ester *menthol* 7.69%,
free *menthol* 0.06%,

The First-Running white oil, 500g., was treated with 50%-*sodium salicylate* solution[46]

---

* The distillation residue was soon congealed which proved to be unchanged *oxime* melting at [72°].

** Lower boiling fractions of the dementholized oil should be excluded when the "White Oil" to be manufactured.

to remove any oxygen compounds (*menthone* and others) and we obtained 482g. of non-reacted oil. The oil extracted ※ *in Na-salicylate* solution was only 18g., which corresponds 3.6% to the low-boiling fraction. The unreacted oil after dried has the following characters : -

d_4^{25}0.8526, n_D^{25}1.4643, η^{25}1.16.

Judging from these data, the three main constituents of *pinene*, *limonene*, and *menthone* should be separated by several fractionations.

On the first fractionation, each 235g. and 215g. of the oil was distilled under 25~15mm-Hg to four fractions and excluded 12% as each residue. The properties of each fraction are indicated in the FIGURE 2.

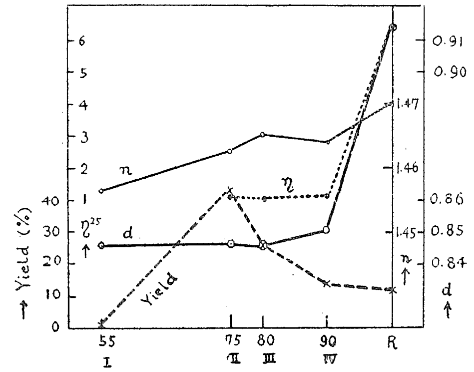


FIGURE 2. Mint-Terpene Fractions.

Each fraction is combined and redistilled five times and separated three parts as *pinene* (28%), *limonene* (37%), and *menthone* parts (30%) from their physical constants.

As a *limonene* fraction, we obtained the following characteristics : -

B. P. /20mm.	66~68°C.,
d_4^{25}	0.8431,
n_D^{25}	1.4659,
η^{25}	0.99,
$[\alpha]_D^{25}$	-65.9°,
MR	44.53 (calcd. as $C_{10}H_{16}{\vDash}_2$, 45.24).

By bromination in *ether-acetic acid* solution, we obtained fine needle crystals, m.p. [103~104°] (recrystallized from *acetic ether* solution), which coincides with *limonenetetrabromide*. The absorption of *bromine* was 81.1% as $C_{10}H_{16}Br_4$.

In this work, we took the above *limonene* as the sample for the synthesis of *carvone*.

[**Experimental**] —— **Fractionation** ((1) ~ (3)) : - Each terpene fraction was fractionated with

---

※ The author is now in research about these soluble substances, and would be reported later.

Claisen-flask under reduced pressure using rotary-oil-pump (TABLE 4~6).

TABLE 4. Fractionation (1) — Sample : Fraction II of the first distillation, 195g.

Fraction	B.P. (°C/mm.)	yield (%)	d_4^{25}	n_D^{25}	$\eta 25$
I	52~62 /19	58.5	0.8487	1.4646	1.10
II	62~65 /19	13.3	0.8481	1.4659	1.05
III	65~66 /19	6.9	0.8448	1.4658	1.02

N.B. The residue (1), 41.5g., is added to the next Fractionation.

TABLE 5. Fractionation (2) — Samples : Fraction III of the first distillation (114.5g.) and the residue (1) (41.5g.)

Fraction	B.P. (°C/mm.)	yield (%)	d_4^{25}	n_D^{25}	$\eta 25$
I	55~65 /19	56.8	0.8479	1.4658	1.06
II	65~67 /17	13.2	0.8448	1.4657	1.04

N.B. The residue (2), 47g., is added to the next Fractionation.

TABLE 6. Fractionation (3) — Samples: Fraction IV of the first distillation (64.5g.) and the residue (2) (47g.)

Fraction	B.P. (°C/mm.)	yield (%)	d_4^{25}	n_D^{25}	$\eta 25$
I	58~65 /18	34.9	0.8456	1.4658	1.06
II	65~70 /18	37.2	0.8448	1.4659	1.02
* III	70~90 /18	13.0	0.8683	1.4598	1.46
** Residue	—	43.0	0.9355	1.4715	—

* Rich in *menthone* from its physical constants.

** Red brown, viscous oil, which contains *menthone*, *menthol*, ester and higher boiling substances.

Rectification ((4) ~ (5)) : -We used a three-necked flask with Widmer' s column, filled short cuttings of glass tubes, for the rectifications. Each corresponding fraction of the former distillation (1~3) was combined and rectified in vacuum. (TABLE 7~8)

TABLE 7. Fractionation (4) — Samples : {(1) I + (2) I} 202g.

Fraction	B.P. (°C/mm.)	yield (%)	d_4^{25}	n_D^{25}	$\eta 25$
I	49~59 /15	60.4	0.8472	1.4688	1.11
* II	59~63 /15	30.0	0.8456	1.4656	1.06
** III	63~66 /15	4.5	0.8448	1.4660	1.02

N.B. The residue (4), 10g., is added to the next fractionation.

* Rich in *limonene*.

** Very rich in *limonene*.

TABLE 8. Fractionation (5) — Samples : {(1) II, III + (2) II + (3) I, II}
106g. + residue (4), 10g.

Fraction	B.P. (°C/mm.)	yield (%)	d_4^{25}	n_D^{25}	η^{25}	$[\alpha]_D^{25}$
* I	56~66 /20	7.8	0.8463	1.4652	1.06	—
** II	66~68 /20	75.0	0.8431	1.4659	0.99	-65.9°
Residue	—	12.1	0.8636	1.4647	1.30	—

* Rich in *limonene*.
** Very rich in *limonene*, MR=44.53 (theory, 45.24)

Tetrabromide : -Each 1 g. of the fraction (4) III ahd (5) II dissolved in the mixed solution of *ether* and *acetic acid*, respectively, and cooled. Adding *bromine* to each solution, we obtained crystals of *tetrabromide*, a little in the former but large quantity in the latter, which recrystallized from *acetic ether* to flat crystals melting [103~104°].

Absorption of bromine : - *Bromine* was dropped to the cold solution of each fraction (4) II and (5) II in the mixture of *ether* and *acetic ether*, respectively, and determined the absorbity of *Br* as $C_{10}H_{16}Br_4$.

Samples	Br absorbed	Absorbity of Br as $C_{10}H_{16}Br_4$
(4) II 1.6905g.	2.9745g.	74.8%
(5) II 1.6680g.	3.1835g.	81.1%.

2. Preparation of Limonenenitrosochloride.

Applying the procedure as in the part A, we obtained 18g. (22.5% *) of *limonenenitrosochloride* from 68g. of the fraction (5) II.

[**Experimental**] —— 34g. (about 0.25 mole) of the sample *limonene* (B.p. 66~68°/20mm., d_4^{25} 0.8431, n_D^{25} 1.4659, η^{25} 0.99, $[\alpha]_D^{25}$ -65.9°) and 40ml. of *ethanol* are taken in 300cc. -three-necked flask, cooled to about -10°C. with ice and salt, then introduced *ethylnitrite* gas which prepared in the other vessel. Add 5ml. of water after the reaction, then passed wet *HCl* gas at 0~-10°C. (mainly at -4~-7°C.) of the bath temperatures. When the passing of *HCl* gas was over, stirred the reaction liquid at -10°C. more 30 minutes, then white crystals deposit in the green solution. The crystals are filtered by suction, washed with cold *ethanol*, and dried on tone plate, cropped 9g. We have obtained the similar results after repeating.

Formation of ethylnitrite : - The solution, 16g. of *ethanol* and 20 ml. of concentrated *sulfuric acid* diluted to 200 ml. with water, in dropping funnel, are dropped in to the water solution consisted from 42g. of *Na-nitrite* and 16g. of *ethanol* and diluted to 200ml. with water. The *ethyl nitrite* gas, thus formed, was introduced to the reaction liquid through the *soda lime* tower.

Formation of moist HCl gas :-The moist *HCl* gas was prepared by dropping 110 ml. of concd. H_2SO_4 to 55 ml. of concd. *HCl*, and it was passed through concd. *HCl*.

3. Preparation of d-Carvoxime.

Using 15g. of *limonenenitrosochloride* prepared in the preceeding method, we obtained

---

* Calculated from the purity of *limonene* in the fraction (5) II as 80%.

7g. of *carvoxime* by dehydrochlorination with *urea*, yielding 53%. The reason of the lowering of the yield is seemed to depend on both bad quality and spontaneous decomposition of the sample after few days' standing.

〔**Experimental**〕 —— Both 15g. of crude *limonenenitrosochloride* and 6g. of *urea* are dissolved in 80 ml. of *isopropyl alcohol*,* and refluxed on the water bath for 1 hour. After distilled off 80% of the solvent, the residual matters in the reaction flask wete poured into a large quantity of cold water. Soon the oily substances were crystallized, which gave 7g. of crude *carvoxime* after filtration, washing, and drying.

4. Preparation of d-Carvone.

Hydrolysing 6g. of *carvoxime*, formed in the previous method (3), with *5%-oxalic acid*, we obtained 4g. of *d-carvone*, yielding 74%. Its specific rotation indicates +52°. Through the m. p. 〔72°〕 of its *oxime*, we recognized it to be *d-carvone*.

〔**Experimental**〕 —— After refluxing 6g. of *d-carvoxime* with 60 ml. of *5%-oxalic acid* solution on water bath for 2 hours, we obtained 4g. of crude *carvone* by steam distillation, and rectified by vacuum distillation, yielding 3g. of *d-carvone*.

Characters of synthetic d-carvone :- The physical constants of the *carvone* are as follows ——

d_4^{25} 0.9587,
n_D^{25} 1.4989,
$[\alpha]_D^{25}$ +52.8°,
MR 45.98 (calcd. as $C_{10}H_{14}O\ |\overline{2}$ 45.26).

Oxime :- Together with 1g. of the above oil and 1g. of *hydroxylaminehydrochloride* as usual, we obtained *oxime* which indicated the m. p. 〔71~72°〕 after recrystallization from *ethanol*.

V. CONCLUSION

l-Limonene is contained nearly 10% in the dementholized oil of Japanese peppermint (*Mentha arvensis*, L.). We have undertaken to utilize this worthless mint-limonene, and studied the synthesis of *carvone* from this *limonene*.

Mint-terpenes, the "First-Running" of the dementholized oil, were distilled several times to separate the "limonene-rich" fractions ($[\alpha]_D$-66°), which were determined by physical constants (specific gravity : d_4^{25}, refractive index : n_D^{25}, relative viscosity : η^{25}, specific rotation : $[\alpha]_D$). In comparison, we used Orange-limonene ($[\alpha]_D$+110°) for preliminary experiment.

Thus we synthetized each *l-*, and *d-carvone* from Orange-limonene and Mint-limonene, respectively. Both the synthetic *carvones* have the similar fragrant flavor as a natural *l-carvone* from the essential oil of Oranda-Hakka (*Mentha viridis*, L.).

Our synthetic data are summerized here : -

---

[*] We purified commercial *isopropyl alcohol* by redistillation after drying with CaO.

(A) *d-limonene* → *nitrosochloride* → *carvoxime* → *l-carvone*
41% 90% 60%
(*Et-nitrite*, *HCl*) (*urea*) (*oxalic acid*)
(B) *l-limonene* → *nitrosochloride* → *carvoxime* → *d-carvone*
23% 53% 74%

Synthetic *Carvones* from	d_4^{25}	n_D^{25}	η^{25}	$[\alpha]_D^{25}$	MR
d-limonene	0.9580	1.4958	2.60	−52.8°	45.72
l-limonene	0.9587	1.4989	—	+52.8°	45.98

(Theory, 45.26).

Acknowledgment —— The experimental assistance of S. Kamita, the graduate of science, is gratefully acknowledged. (7.Ⅶ.1955).

* * *

REFERENCES

1) T. Nagasawa : "Knowledge of Mentha" (1949).

2) T. Nagasawa : "Science of Mentha" (1950).

3) T. Nagasawa : World State of recent Japanese Peppermint (*Nogyo-Okayama*, **22**, No. 11 (1951)).

4) T. Nagasawa : Peppermint in Brazil (1) … On the Cultivation of Mentha and Production of Crude Oil (*Times of Okayama Agr. Expt. Sta.*, No. **401** (1953)).

5) Ji-Ji Correspondence : Production and Export of China Peppermint (*WorldWeekly*, **31**, No. 41, 21 (1950)).

6) T. Nagasawa : Look over the World of the Peppermint (*Koryo*, No. **20** (1952)).

7) K. Hayashi : Peppermint of Hokkaido … Utilization of Byproducts to the Chemical Industry (*Times of Hokkaido Ind. Expt. Sta.*, **12**, 1-11 (1933)).

8) E. Shinosaki : Peppermint Industry in Japan (*Org.-Biochem. Lecture*, **8**, 35-70 (1937)).

9) S. Kimura : Chemistry of Peppermint (*Koryo*, No. **7**, 30-32 (1949)).

10) T. Nagasawa : Consideration on the Development of Japanese Peppermint (*Nogyo-Okayama*, **22**, No. 3 (1951)).

11) M. Ito : On the recent Peppermint Industry (*Times of Hokkaido Ind. Expt. Sta.*, **1**, 1~25 (1954)).

12) E. Shinosaki, T. Nagasawa, A. Makino : Researches on the Japanese Peppermint Oils (II) (*Rept. Osaka Imp. Ind. Research Inst.*, **7** (15) 1~26 (1927)).

13) E. Shinosaki, T. Nagasawa : Researches on the Japanese Peppermint Oils (III～VI) (*Rept. Osaka Imp. Ind. Research Inst.*, **10** (4) 1～100 (1929) ; 10 (5) 1～60 (1929) ; **11** (9) 1～50 (1930) ; **11** (9) 51～76 (1930) ; *J. Soc. Chem. Ind. Japan* **32**, 577～82, 582～87 (1929) ; **33**, 1214～21, 1221～26 (1930)).

14) E. Shinosaki, T. Nagasawa : Increasing Method of Menthol Crystals from Japanese Peppermint Oils (*Japan. Pat.*, 69441 (1926)).

15) E. Shinosaki, T. Nagasawa : Method of the Separation of the new Perfume from Distillation Residues of Peppermint Oils (*Japan. Pat.*, 1872 (1929)).

16) T. Nagasawa : Transformation of Mentha and Chemical Characteristics (*Koryo*, No. **14**, 29～31 (1951)).

17) S. Tanaka : Constituents of the Japanese Dementholized Peppermint Oils (*Chem. Soc. Japan*, **50**, 546～52 (1929)).

18) T. Nagasawa : Studies on the Progress of Japanese Genus Mentha (V) (*Special Bull. Okayama Agr. Expt. Sta.*, No. **50**, 1～34 (1954)).

19) H. Schmidt : Peppermint Oil. I. The Occurrence of Jasmone in the Ethereal Oil of Mentha Piperita, L. (*Ber.*, **80**, 538～46 (1947) ; *C. A.*, **42**, 8788h (1948)).

20) P. Z. Bedoukian : Occurrence of Menthofuran in Oil of Peppermint (*Mentha piperita*) (*J. Am. Chem. Soc.*, **70**, 621～2 (1948) ; *C. A.*, **42**, 3140 f (1948)).

21) H. Walbaum : *J. pr. Chem.*, [2], **96**, 245 (1918)).

22) Treff, Werner : *Ber.*, **68**, 640 (1935).

23) Hunsdiecker, Wirth : *Ber.*, **75**, 460 (1942).

24) Ruzicka, Schinz : *Helv. Chim. Acta*, **27**, 1561 (1944).

25) Hunsdiecker : *Ber.*, **80**, 137 (1947).

26) S. Takei et al., *J. Soc. Agr. Chem. Japan*, **17**, 1902 (1934).

27) K. Hayashi : On the Crude Peppermint Oils. II. (*Rept. Hokkaido Ind. Expt. Sta.*, **87**, 1 (1943)).

28) Bordenca, Allison, Dirstine : *Ind. Eng. Chem.*, **43**, 1196 (1951).

29) T. Naito : Recent Progress of Terpene Chemistry (*Koryo*, No. **18**, 12 (1951)).

30) Royals, Horne : *J. Am. Chem. Soc.*, **73**, 5856 (1951).

31) H. Katsuragi : Synthetic Perfume Chemistry with Raw Materials (VI) (*Koryo*, No. **24**, 16 (1953)).

32) J. L. Simonsen : "The Terpenes", Vol. I, (1931), p. 127.

33) Blumann, Zeitschel : *Ber.*, **47**, 2623 (1914).

34) Tilden : *J. C. S.*, **31**, 554 (1877).

35) Wallach : *Ann.*, **245**, 255 (1888).

36) Wallach, Conrady : *Ann.*, **252**, 145 (1889).

37) Wallach : *Ann.*, **246**, 227 ; **270**, 175 (1892); **279**, 356 (1894).

38) Baeyer : *Ber.*, **29**, 8 (1896).

39) Deussen, Hahn : *Ber.*, **43**, 519 (1910).

40) J. L. Simonsen : "The Terpenes", Vol. I, (1931), p. 360.

41) T. Waida : Manufacture of Carvone by Synthesis (*Japan. Pat.*, 3979 (1952)).

42) T. Waida, K. Terauchi, M. Terauchi, T. Itani : On the Manufacture of Carvone (II〜III) (*Camphor Eng. Assoc. Lecture*, **16**, 70〜76, 79〜81 (1952)).

43) E. Shinosaki, T. Nagasawa : Researches on the Essential Oils of Japanese Oranda-Hakka (*Mentha crispa*) (I) (*Rept. Osaka Imp. Ind. Research Inst.*, **13** (9). 1〜53 (1932); *Rept. Assoc. Sci. Japan*, **7**, 638〜46 (1932)).

44) T. Nagasawa : Researches on the Essential Oils of Japanese Oranda-Hakka (II). On Carvone (*Rept. Osaka Imp. Ind. Research Inst.*, **19** (4), 1〜104 (1938); *J. Soc. Chem. Ind. Japan*, **41**, 499〜502 (1938)).

45) T. Nagasawa : Studies on the Progress of Japanese Genus Mentha (Ⅳ) (*Special Bull. Okayama Agr. Expt. Sta.*, No. **48**, 1〜26 (1953)).

46) E. Charabot : "Les principes odorants végétaux", (1912), p. 9, 83.