

# Studies on Camphor Oils II. On the Reaction of Japanese Acid Clay to Camphor White Oil.

By

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At the time when this work was begun there could not be found any report of experiments made to investigate the action of Florida earth upon terpenes, except the work of Gurvitsch<sup>1</sup> who observed that pinene is thus transformed into camphene and polyterpenes.

Before the work was finished, however, valuable papers were published by C. S. Venable<sup>2</sup> and by K. Kobayashi<sup>3</sup>. Venable observed that by the action of Fuller's earth terpenes and unsaturated oxygenated terpenes are easily polymerized into dipinene and polyterpenes, while saturated oxygenated terpenes, cineol and p-cymene, do not undergo such polymerization, and that at a high temperature the dipinene so formed is slowly decomposed into low-boiling paraffin hydrocarbons and p-cymene. On distilling a mixture of turpentine oil or its main constituent, boiling at 158—161° with Japanese acid clay, K. Kobayashi and E. Yamaguchi obtained a distillate having a petroleum-like odour and a marked fluorescence similar to that of spindle oil prepared from natural petroleum. The distillate is considered by them to contain nearly equal quantities of aromatic and unsaturated hydrocarbons and

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<sup>1</sup> Jour. Russ. Phys. Chem. Soc., **47**, 827 (1915); Jour. Chem. Soc., **108**, 933 (1915).

<sup>2</sup> Jour. Am. Chem. Soc., **45**, 728 (1923).

<sup>3</sup> Kogyo-Kwagaku Zasshi (Jour. Chem. Soc. Tokyo) **26**, 463 (1923).

of naphtenic hydrocarbons.

### 1. ACTION OF JAPANESE ACID CLAY UPON CAMPHOR WHITE OIL.

The camphor white oil used in the experiment showed the following properties: Specific gravity 0.8756 (20°), refractive index 1.4698 (20°), optical rotation +20.45°, cineol content 22.30%, and from 200 c.c. of the oil it gave the following fractions when distilled:

Fraction	Distillate c.c.	$d_{17}^*$	$\alpha_D(1dm.)$	$n_D^{18}$
155—170°	10.7	0.8693	+10.50°	1.4708
170—175°	132.5	0.8752	+19.76°	1.4710
175—180°	38.2	0.8827	+26.56°	1.4705
above 180°	18.0	—	—	1.4931

General procedure:— Japanese acid clay previously dried at 110° was added to 400 grams of the camphor white oil in a copper flask (about 1 litre), and the mixture was gradually heated till the oil ceased to distill. The distillate was separated from water and dried with anhydrous sodium sulphate.

Japanese acid clay gr.	Distillate gr.	d	$n_D$
100	353.2	0.8769(10°)	1.4926(12°)
200	345.3	0.8752(10°)	1.4930(11°)
300	341.0	0.8746(10°)	1.4928(11°)
*400	273.7	0.8436(10°)	1.4772(12°)
500	308.7	0.8678(20°)	1.4950(12°)
600	303.0	0.8569(10°)	1.4844(10°)

### 2. THE REACTION PRODUCTS.

400 grams of the camphor white oil were treated with 600 grams of Japanese acid clay in a manner analogous to that described

\* This experiment was carried out in a glass flask.

in the general procedure. On repeating the same experiment 6 times 1820.3 grams of an oil (78.83% of the camphor oil) were obtained. This oil has a yellow colour with a strong greenish fluorescence and a petroleum-like odour. In order to remove terpenic and unsaturated hydrocarbons, the oil was first treated with a dilute permanganate solution and then with a concentrated sulphuric acid in cold, and finally was washed with caustic soda and water successively.

The refined oil thus obtained gave the following physical characters :  $d_{15}^{\circ}$  0.8531,  $n_D^{18.5^{\circ}}$  1.4751.

It was subjected to fractional distillation under atmospheric pressure and the following fractions were gathered.

Fraction	Distillate	Specific gravity	Refractive index
up to 100°	2.7 <sup>gr.</sup>	—	1.4015 (19°)
100—110°	3.5	—	1.4084
110—120°	6.2	0.7363( $\frac{20.5}{18}$ )°	1.4138
120—130°	2.4	—	1.4200
130—140°	3.7	—	1.4222
140—150°	8.4	0.7649( $\frac{20.5}{18}$ )°	1.4287
150—160°	20.1	0.7823( " )	1.4379
160—170°	63.7	0.8052( " )	1.4503
170—180°	323.3	0.8243( $\frac{20}{18}$ )°	1.4616
180—190°	160.2	0.8327( " )	1.4681
190—200°	61.3	0.8404( $\frac{20.5}{18}$ )°	1.4731
200—210°	6.9	0.8456( " )	1.4759
210—220°	7.2	0.8502( " )	1.4768
220—230°	10.6	0.8537( " )	1.4771
230—240°	6.7	0.8598( $\frac{18}{18}$ )°	1.4790
240—250°	6.9	0.8678( " )	1.4811
250—260°	7.3	0.8754( " )	1.4849
260—270°	11.6	0.8854( " )	1.4892
270—280°	9.8	0.8896( " )	1.4920
280—290°	15.6	0.9028( " )	1.4980
290—300°	34.0	0.9089( " )	1.5026
300—310°	56.8	0.9184( " )	1.5062
310—320°	57.0	0.9264( " )	1.5096
320—330°	38.0	0.9285( $\frac{20}{18}$ )°	1.5116
330—340°	38.5	0.9286( $\frac{14.5}{18}$ )°	1.5150
340—350°	30.8	0.9341( " )	1.5172
above 350°	6.8	—	—

## 1) Nitration of the fraction up to 100°

The fraction up to 100° was strongly nitrated, when a solid nitration product which was proved to be m-dinitrobenzene was produced.

## 2) Nitration of the fraction 110—120°

From the fraction boiling at 110—120° only a small quantity of a nitrated oil was produced, but it was not further examined. The main portion remaining inert was refined as before, and an oil having a refractive index of 1.4050 (23°), was obtained.

It was analyzed with the following results :

0.0938 gr. substance gave 0.2912 gr. CO<sub>2</sub> and 0.1145 gr. H<sub>2</sub>O.

	Found	Cal.(C <sub>8</sub> H <sub>16</sub> )
Carbon	84.68%	85.62%
Hydrogen	13.64	14.38

## 3) Nitration of the fraction 170--180°.

The well-cooled mixture of 320 grams of conc. nitric acid (sp. gr. 1.40) and 420 grams of conc. sulphuric acid (sp. gr. 1.48) was slowly added to 200 grams of the fraction 170—180° kept cooled in a flask. When the reaction was completed, the mixture was poured into a large amount of water, and the oily layers were separated.

The part unacted upon (about 95.2 grams) was washed with conc. sulphuric acid, fuming sulphuric acid, caustic soda, and water successively.

The colourless oil thus obtained gave the following physical properties :  $d_{4}^{20}$  0.8050,  $n_D^{20}$  1.4410.

In order to purify it, 60 c.c. of the oil were subjected to fractional distillation on metallic sodium 5 times under atmospheric pressure, and the following fractions were collected.

## 1st Distillation

Fraction	Distillate	$d_{4}^{20}$	$n_D^{20}$
	c.c.		
160—165°	5.9	0.7861	1.4366
165—171°	23.3	0.7969	1.4389
171—175°	16.2	0.8014	1.4400
175—180°	7.1	0.8038	1.4413
above 180°	5.7	—	1.4599

5th Distillation.

Fraction	Distillate	d( $\frac{21}{4}$ )°	n <sub>D</sub> <sup>21°</sup>	Analysis					M. R*(Found)			Determination of Mol. wt.			
				Subst.	CO <sub>2</sub>	H <sub>2</sub> O	C	H	C <sub>9</sub> H <sub>18</sub>	C <sub>10</sub> H <sub>20</sub>	C <sub>11</sub> H <sub>22</sub>	Subst.	Benzene	$\Delta t$	Mol. wt.
155-160°	c.c. 1.9	—	1.4341	— gr.	— gr.	— gr.	%	%	—	—	—	— gr.	— gr.	—	—
160-165°	6.0	0.7872	1.4360	0.1427	0.4487	0.1810	85.74	14.23	41.88	46.55	—	—	—	—	—
165-168°	5.0	0.7956	1.4384	0.0937	0.2921	0.1220	85.01	14.56	—	46.29	—	0.4075	26.5410	-0.556°	138.070
168-170°	18.6	0.8070	1.4396	0.0840	0.2620	0.1035	85.07	13.79	—	45.74	—	0.6307	26.4723	-0.861°	138.356
				0.1537	0.4806	0.1954	85.27	14.21							
				0.1419	0.4434	0.1783	85.14	14.04							
170-175°	9.6	0.8123	1.4403	0.2207	0.6892	0.3587	85.15	14.14	—	45.56	50.07	—	—	—	—
175-180°	2.1	—	1.4420	—	—	—	—	—	—	—	—	—	—	—	—
above 180°	0.4	—	1.4559	—	—	—	—	—	—	—	—	—	—	—	—

\*Lorentz-Lorenz' formula

Molecular refraction, molecular weight and percentage of hydrogen and carbon calculated for  $C_{10}H_{20}$  are as follows :

	$C_{10}H_{20}$
Carbon	85.62%
Hydrogen	14.38%
M. R ( <sup>Eisenlohr's</sup> number)	46.18
Mol. wt.	140.160

As is seen in the foregoing table, the part unacted upon by a nitration mixture seems to consist of naphthenic hydrocarbons. The 3rd. and 4th. fractions may both be regarded as a hydrocarbon of the same composition but of different constitution, that is they would be isomers brought about by thermal action.

From the fact that all terpinic compounds existing in the camphor white oil have the hexamethylene ring, it seems very probable that the hydrocarbon  $C_{10}H_{20}$  above obtained would be p-menthane. For confirmation, the substance was dehydrogenated by treating it with sulphur<sup>1</sup> and then oxidized with an alkaline potassium permanganate solution when p-oxyisopropyl benzoic acid, melting at 156°, was produced. It was analysed with the following results :

0.1374 gr. substance gave 0.3335 gr.  $CO_2$  and 0.0765 gr.  $H_2O$ .

	Found	Cal. ( $C_{10}H_{12}O_3$ )
Carbon	66.19%	66.63%
Hydrogen	6.22	6.71

The nitrated oil (about 102.6 grams) after having been washed with water was distilled with superheated-steam, and the pale yellowish distillate was purified by fractional distillation. The fraction boiling at 114—117° under 5—6 m.m. (sp. gr. 1.0772 ( $\frac{22}{4}$ )<sup>c</sup> refractive index 1.5367(22°) was collected as the main distillate.

0.1422 gr. substance gave 0.3533 gr.  $CO_2$  and 0.0894 gr.  $H_2O$ .

	Found	Cal. ( $C_{10}H_{13}NO_2$ )
Carbon	67.75%	67.00%
Hydrogen	7.03	7.31

<sup>1</sup> W. Friedmann : Jour Chem. Soc., 112, 13 (1917).

	Found	Cal. $C_{10}H_{13}NO_2\bar{3}$
Mol. refraction	51.785	51.039

Besides the above substance, a liquid of lighter specific gravity (about 10 grams) was also obtained as one of the distillation products, but its examination was omitted.

#### Oxidation of the nitro-compound.

Five grams of the nitro-compound and 100 c.c. of 25% caustic soda solution were mixed together, and to the mixture kept boiling on a sand bath a conc. potassium permanganate solution was added until the violet colour became permanent. Alcohol was then added to decolorize the violet colour, and precipitated manganese dioxide was filtered off. The alkaline filtrate thus obtained was acidified with hydrochloric acid, whereupon a small quantity of the white crystals of terephthalic acid separated out. It was filtered and the filtrate was extracted with ether. On distilling off the ether, the yellow oil which quickly crystallised into pale yellow crystals separated out. It was recrystallized with hot water when yellowish small needles, melting at 167—168° and having properties identical with *o*-nitro-*p*-oxyisopropyl benzoic acid were obtained.

It was analysed with the following results :

0.1648 gr. substance gave 0.3241 gr.  $CO_2$  and 0.0745 gr.  $H_2O$ .

	Found	Cal. ( $C_{10}H_{11}NO_5$ )
Carbon	53.62%	53.31%
Hydrogen	5.05	4.92

#### Reduction of nitro-compound.

The nitro-compound was reduced with tin and hydrochloric acid, and the amino-compound obtained was analyzed as its hydrochloride.

0.2216 gr. the hydrochloride gave 0.1692 gr.  $AgCl$

	Found	Cal. ( $C_{10}H_{13}NH_2HCl$ )
Chlorine	18.86%	19.10%

Its platinum double chloride was also analysed.

0.1238 gr. platinum double chloride gave 0.0343 gr. platinum.

	Found	Cal. [(C <sub>10</sub> H <sub>13</sub> NH <sub>2</sub> ·HCl) <sub>2</sub> PtCl <sub>4</sub> ]
Platinum	27.70%	27.53%

From the above results it is beyond doubt that the nitro-compound is p-nitro-cymene (C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>·NO<sub>2</sub>·C<sub>3</sub>H<sub>7</sub>).

### 3. ACTION OF JAPANESE ACID CLAY UPON d-LIMONENE.

d-Limonene having the following physical properties was used in the experiment :

Boiling point 175—177°, specific gravity 0.8427(22°) refractive index 1.4736(22°),  $\alpha_D^{22} + 95.22$  (1 d.m.).

300 grams of d-limonene were treated with 400 grams of Japanese acid clay in a manner analogous to that described in the general procedure. The yield of the oil was about 222 grams.

200 c.c. of the oil thus formed (sp. gr. 0.8444(25°) and  $n_D^{24}$  1.4771) were distilled under atmospheric pressure.

Fraction	Distillate c.c.	Refractive index (23°)
up to 100°	0.7	1.4047
100—110°	0.1	1.4116
110—120°	0.4	1.4250
120—130°	1.1	1.4275
130—140°	1.3	1.4291
140—150°	3.1	1.4357
150—160°	10.0	1.4440
160—170°	13.8	1.4529
170—180°	67.2	1.4640
180—190°	28.4	1.4700
190—200°	9.7	1.4759
200—210°	1.6	1.4786
210—220°	1.9	1.4809
220—230°	2.2	1.4851
230—240°	3.5	1.4882
240—250°	4.0	1.4971
250—260°	2.5	1.5010
260—270°	2.4	1.5087
270—280°	2.7	1.5120
280—290°	4.3	1.5169
290—300°	6.2	1.5197
300—310°	5.1	1.5212
310—320°	7.6	1.5221
above 320°	19.4	—



Nitration of the fraction 170—180°.

70 grams of the fraction boiling at 170—180° (sp. gr. 0.8227( $\frac{23}{4}$ )°) were treated with a dilute permanganate solution and then nitrated.

The part remaining unacted upon (about 17 grams) gave the following physical properties:

Specific gravity 0.8036( $\frac{23}{4}$ )°, refractive index 1.4447(23°).

13 c.c. of it were distilled on metallic sodium under atmospheric pressure.

1st Distillation

Fraction	Distillate	Refractive index
	c.c.	(24)°
160—165°	1.6	1.4359
165—170°	3.0	1.4372
170—175°	4.8	1.4394
175—180°	1.3	1.4410
above 180°	1.1	—

3rd Distillation

Fraction	Distillate	Refractive index
	c.c.	(24)°
159—160°	0.2	1.4344
160—165°	0.9	1.4359
165—168°	1.8	1.4376
168—170°	3.2	1.4380
170—175°	2.0	1.4400
175—180°	1.7	1.4414
above 180°	0.9	—

The fraction boiling at 168—170° [sp. gr. 0.7976( $\frac{24}{4}$ )°, mol. refraction\* 46.13] was analyzed with the following results:

0.1319 gr. substance gave 0.4152 gr. CO<sub>2</sub> and 0.1638 gr. H<sub>2</sub>O.

	Found	Cal. (C <sub>10</sub> H <sub>20</sub> )
Carbon	85.84%	85.62%
Hydrogen	13.88	14.38

The nitrated compound [b. p. 113.5—117° (4~6 m.m.) and d( $\frac{23}{4}$ )° 1.0783] was oxidized with an alkaline potassium permanganate

\* Mol. refraction calculated for C<sub>10</sub>H<sub>20</sub> is 46.18.

solution and yellowish small needles, melting at 167—168° were obtained. It was identified to be o-nitro-p-oxyisopropyl benzoic acid.

#### 4. ACTION OF JAPANESE ACID CLAY UPON CINEOL

300 grams of cineol (b. p. 175—177°, sp. gr. 0.9236(23°),  $n_D^{25}$  1.4596, and  $[\alpha]_D \pm 0$ ) were treated with 700 grams of Japanese acid clay, and about 206 grams of new oil were obtained.

200 grams of the oil (sp. gr. 0.8389(23°) and  $n_D^{25}$  1.4735) were fractionated by distilling it under atmospheric pressure.

Fraction	Distillate	Refractive index
	gr.	(24)°
up to 100°	0.6	1.3937
100—110°	0.2	1.4112
110—120°	0.6	1.4188
120—130°	1.2	1.4271
130—140°	1.5	1.4345
140—150°	3.8	1.4411
150—160°	6.1	1.4492
160—170°	10.4	1.4551
170—180°	96.8	1.4641
180—190°	32.3	1.4716
190—200°	5.7	1.4770
200—210°	3.0	1.4800
210—220°	2.4	1.4821
220—230°	1.3	1.4850
230—240°	0.9	1.4890
240—250°	1.4	1.4931
250—260°	1.5	1.4990
260—270°	2.4	1.5038
270—280°	2.3	1.5082
280—290°	2.5	1.5115
290—300°	3.0	1.5159
300—310°	4.1	1.5179
310—320°	6.4	1.5183
above 320°	8.7	1.5272

70 grams of the fraction boiling at 170—180° (sp. gr. 0.8239 ( $\frac{25}{4}$ )°) were treated with a dilute permanganate solution and conc. sulphuric acid, and then nitrated. The nitro-compound (about 27 grams) having b. p. 115—119° (7—8 m.m.) and sp. gr. 1.0782( $\frac{24}{4}$ )°, was oxidized with an alkaline potassium permanganate solution and

o-nitro-p-oxyisopropyl benzoic acid, melting at 167–168° was obtained.

The part remaining unacted upon (about 11 grams) was also fractionated on distilling it on metallic sodium under atmospheric pressure.

## 1st Distillation

Fraction	Distillate	Refractive index
	c.c.	(25)°
160–165°	1.2	1.4360
165–170°	2.8	1.4374
170–175°	4.2	1.4391
175–180°	0.9	1.4401
above 180°	0.7	—

## 3rd Distillation

Fraction	Distillate	Refractive index
	c.c.	(25)°
up to 160°	0.1	1.4342
160–165°	0.3	1.4358
165–168°	1.2	1.4361
168–170°	2.7	1.4370
170–175°	1.6	1.4389
175–180°	1.3	1.4397
above 180°	0.8	—

The fraction boiling at 168–170° (sp. gr. 0.7942( $\frac{25}{4}$ )°, mol. refraction\* 46.23) was analyzed with the following results:

0.1024 gr. substance gave 0.3197 gr. CO<sub>2</sub> and 0.1282 gr. H<sub>2</sub>O.

	Found	Cal. (C <sub>10</sub> H <sub>20</sub> )
Carbon	85.13%	85.62%
Hydrogen	13.99	14.38

From these experimental results it appears evident that the main portion of cineol changes into p-cymene and p-menthane by the action of Japanese acid clay. These changes and also those observed by Venable<sup>1</sup> may all be looked upon as the results of dehydration and

\* Mol. refraction calculated for C<sub>10</sub>H<sub>20</sub> is 46.18.

<sup>1</sup> loc. cit.

polymerization which are in high temperatures followed by decomposition, as is represented in the following scheme :

