

# Studies on Camphor Oils, III. Action of Oxalic Acid upon Terpinhydrate.

By

Kashichi Ono.

(Received June 3, 1924)

---

## ABSTRACT.

$\alpha$ -Terpineol mixed with a small quantity of the  $\beta$ -variety was observed to be produced from terpinhydrate by the action of a dilute oxalic acid solution, the best yield was obtained when 2 volumes of an about 0.5% oxalic acid solution were used for every one volume of terpinhydrate and the mixture was heated on an oil-bath for 5 hours.

According to O. Aschan<sup>1</sup> the conversion of terpinhydrate into terpineol was readily effected by the action of a dilute oxalic acid solution. As the details of this experiment were, however, not at hand, the present work was undertaken with the object of ascertaining the condition which is necessary for securing the best yield of terpineol.

## EXPERIMENTAL PART.

General procedure. Terpinhydrate prepared from the camphor red oil melting at 116–117° was mixed with an oxalic acid solution in a flask provided with a warm condenser, an airtight stirrer, and a thermometer and heated on an oil-bath with constant stirring. When the reaction was over the oily part separated from the aqueous solution, was subjected to steam distillation, and the distillate, after having been dried with anhydrous sodium sulphate, was analysed.

---

<sup>1</sup> Jour. Chem. Soc., 116, i, 336 (1919).

## (i) Influence of concentration of oxalic acid.

Terpinhydrate 150 grams, oxalic acid solution 300 c.c., time of reaction 4 hours, temperature about 100°C.

Table I.

Concentration of oxalic acid	Undecomposed terpinhydrate	Oil formed			
		Yield	$d_{15}^4$	$n_D$	Terpineol <sup>1</sup>
0.479 %	grs. 4.9	grs. 91.0	0.9333	1.4818(18°)	84.82 %
1.000	1.7	106.3	0.9294	1.4830(13°)	81.34
1.960	1.1	110.0	0.9198	1.4821(145°)	62.52
2.960	0.7	120.0	0.9158	1.4832(165°)	62.40

## (ii) Influence of time of reaction.

Terpinhydrate 150 grams, oxalic acid solution 300 c.c., temperature about 100°C.

Table II.

Time of reaction	Concentration of oxalic acid	Undecomposed terpinhydrate	Oil formed			
			Yield	$d_{15}^4$	$n_D$	Terpineol
hrs. 4	% 0.479	grs. 4.9	grs. 91.0	0.9333	1.4818(81°)	84.82 %
5	0.430	0.4	114.2	0.9273	1.4839(11°)	82.33
6	0.500	0.9	102.7	0.9316	1.4860(7.5°)	80.20

## (iii) Influence of amount of oxalic acid solution.

Terpinhydrate 150 grams, time of reaction 5 hours, temperature about 100°C.

Table III.

Amount of oxalic acid solution	Concentration of oxalic acid	Undecomposed terpinhydrate	Oil formed			
			Yield	$d_{15}^4$	$n_D$	Terpineol
c.c. 300	% 0.430	grs. 0.4	grs. 114.2	0.9273	1.4839(11°)	82.33 %
200	0.500	1.7	101.9	0.9373	1.4857(11.5°)	80.51
100	0.500	49.0	62.9	0.9380	1.4835(16°)	74.16

<sup>1</sup> Ber. von Schimmel & Co., April Nr. 121 (1907).

Reaction products. 500 grams of terpinhydarte were mixed with 1000 c.c. of a 0.5% oxalic acid solution, the mixture was heated for 5 hours at about 100°C with constant stirring. The product was treated in the same manner as in the general procedure. About 368.3 grams of an oil having the following properties were obtained.

$d_{15}^*$	$n_D^{19}$	$[\alpha]_D^{18}$	Terpineol
0.9355	1.4806	$\pm 0$	87.56 %

50 c.c. of the oil were subjected to distillation in an atmosphere of carbon dioxide under 18—20 m.m. pressure, and the following fractions were collected :

Fraction	Yield	$n_D$	$d_{18}^{19}$
1. 55—80°	0.3 <sup>c.c.</sup>	1.4701(21°)	—
2. 80—90°	1.0	1.4710(21.5°)	—
3. 90—100°	4.9	1.4735(22°)	—
4. 100—110°	9.8	1.4795(22°)	0.9181
5. 110—112°	26.0	1.4795(22°)	0.9316
6. 112—114°	4.6	1.4840(22°)	—
7. above 114°	2.3	—	—

The fraction (4) was once again distilled in an atmosphere of carbon dioxide under a pressure of 12—13 m.m., and the following fractions were collected :

Fraction	Yield	$n_D^{21}$
a. 62—90°	0.6 <sup>c.c.</sup>	1.4633
b. 90—100°	0.1	1.4658
c. 100—105°	0.9	1.4746
d. 105—108°	3.7	1.4812
e. 108—110°	3.0	1.4831

The fraction (c) and (d) were analysed, and the melting-point of their phenylurethane compounds was determined.

Fraction	Substance	CO <sub>2</sub>	H <sub>2</sub> O	C%	H%	M. P. of phenylurethane
(12-13 m.m.) c. 100-105°	gr. 0-1138	gr. 0-3241	gr. 0-1171	77-66	11-50	84.5-85°
d. 105-108°	0-1223	0-3488	0-1247	77-77	11-39	109-110° <sup>1</sup>

C<sub>10</sub>H<sub>18</sub>O requires C. 77.92% H. 11.78%.

The fraction (d) appears to be a mixture of  $\alpha$ - and  $\beta$ -terpineol, while the fraction (c) mainly to consist of  $\beta$ -terpineol (*L*<sup>8(9)</sup>-*p*-menthenol (1)).

The fraction (5) was redistilled in an atmosphere of carbon dioxide under a pressure of 20-21 m.m. and the following fractions were collected :

Fraction	Yield	$n_D^{18.5}$	$d_{18}^{18}$	$[\alpha]_D^{18}$
104-110°	c.c. 1.8	1.4797	—	—
110-111°	13.8	1.4815	0.9347	±0
111-114°	3.6	1.4828	—	—
above 114°	2.8	—	—	—

The fraction boiling at 110-111° was analysed with the following results :

Substance	CO <sub>2</sub>	H <sub>2</sub> O	C%	H%
0-1264 gr.	gr. 0-3545	gr. 0-1285	76-56	11-37
0-0898	0-2560	0-0938	77-74	11-56
Mean			77-15	11-46
Calc. for C <sub>10</sub> H <sub>18</sub> O			77-92	11-78

	Found	Required for C <sub>10</sub> H <sub>18</sub> O
Mol. refraction	46.938	47.238

From its chemical and physical properties so far studied, this fraction seems to consist of pure  $\alpha$ -terpineol (*L*<sup>8</sup>-*p*-menthenol (8)). For confirmation, nitrosochloride, nitropiperidine, and phenylurethane were

<sup>1</sup> Melting-point of  $\alpha$ -terpinyl-phenylurethane given by O. Wallach and Kerkhoff (Lieb. Ann., 275, 104 (1893)) is 113°.

prepared following O. Wallach's<sup>1</sup> directions and those substances were all proved to be the derivatives of  $\alpha$ -terpineol.

Substance	M. P.
nitrosochloride	103°
nitrolpiperidine	159.5°
phenylurethane	112°

The author wishes to take this opportunity of expressing his thanks to Mr. Z. Takéda for valuable aid rendered in connection with the experimental part of this work.

---

<sup>1</sup> Lieb. Ann., **277**, 120 (1893).  
Ibid., **281**, 140 (1894).  
Ibid., **275**, 104 (1893).