Researches on Camphor, Borneol and Their Allied Substances (*Continued*).

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I. Catalytic Oxidation of Borneol and Isoborneol. Borneol (m.p. 204.2°C, $[\alpha]_D^{16°}$ +21.34 in alcoholic solution) was prepared by the reduction of camphor.

Isoborneol (m.p. 208°C in a sealed tube, $[\alpha]_D^{16°}$ −1.3 in alcoholic solution) was synthesised by the hydration of camphene, and recrystallised for several times from its solution in petroleum ether. Reduced copper which was used as catalyser was prepared by the method described by Mr. Masumoto,(28) and reduced nickel was prepared by Sabatier's method by first igniting nickel nitrate and then reducing the nickel oxide thus obtained at 300°C.

As the experimental apparatus, combustion furnace of common type was used, and camphor of the reaction product was estimated by the semicarbazone process,(29) and borneol and isoborneol by ester value after acetylation under the following conditions. During the acetylation, as the camphene itself is esterified by 13%, the content of borneol and isoborneol underwent some adjustments accordingly.

(1) borneol

Number	Weight (g.)	Saponification hours	Ester value after acetylation	isoberneol
1	2	2	266.4	93.3 %
2	1	4	283	99.1

(2) isoborneol

Number	Weight (g.)	Saponification hours	Ester value after acetylation	isoborneol
1	1	5	283	99.1 %

(1) Catalytic oxidation of borneol by reduced copper.

Catalyser	Borneol (g.)	Reaction temp. °C	Reaction time	Reaction products		
				Yield (g.)	M.p.	$[\alpha]_D^{14}$
Cu (1)	11.9	400	2 h. 07 min.	11.7	177.8–178.1	+41.8
Cu (2)	11.9	400	1 55	11.6	161–163.5	+40.8
Cu (3)	11.5	400	1 55	11.1	178.8–182	+40.3

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(28) Loc. cit.

(29) Yamada, *J. Chem. Soc. Japan*, **48** (1927), 341.

(1)—*Concluded.*

Catalyser	Reaction products				
	Camphor (%)	Borneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
Cu (1)	96.3	3.5	0.2	99.8	0.2
Cu (2)	57	29	14	80	20
Cu (3)	58	33	9	87	13

(2) Catalytic oxidation of isoborneol by reduced copper.

Catalyser	Isoborneol (g.)	Reaction temp. °C	Reaction time	Reaction products		
				Yield (g.)	M.p.	$[\alpha]_D^{12}$
Cu (1)	11.2	150	h. min. 2 05	10.7	166–171.8	±0
Cu (1)	9.3	300	2 00	8.2	165.5–169.1	±0
Cu (2)	10.5	150	2 15	9.6	204.4–207.9	±0
Cu (2)	10.1	300	1 55	8.1	72.5– 84.0	±0

Catalyser	Reaction products				
	Camphor (%)	Isoborneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
Cu (1)	56	37	7	89	11
Cu (1)	86	10	4	96	4
Cu (2)	0	96	4	0	100
Cu (2)	22	9	69	24	76

(3) Catalytic oxidation of borneol by reduced nickel.

No.	Borneol (g.)	React. temp. °C	React. time (hr.)	Reaction products							
				Yield (g.)	M.p.	$[\alpha]_D^{16}$	Camphor (%)	Borneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
1	10.6	200	h. min. 3 25	10.1	177–178.3	+43.1	86	8	6	94	6
2	8.7	300	2 20	8.0	174.2–175.9	+42.5	90	7	3	97	3
3	11.9	400	1 30	11.6	176.5–178.8	+41.3	82	13	5	95	5

(4) Catalytic oxidation of isoborneol by reduced nickel.

No.	Isoborneol (g.)	React. temp. °C	React. time (hr.)	Reaction products							
				Yield (g.)	M.p.	$[\alpha]_D^{13}$	Camphor (%)	Isoborneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
1	11.8	200	h. min. 3 40	11.1	173.5–175.3	±0	81	19	0	100	0
2	12.1	300	2 40	11.1	167–168.8	±0	89	7	4	96	4
3	10.7	400	1 50	10.2	168.5–171.3	±0	75	16	9	89	11

II. Catalytic Reduction and Rearrangement of Camphor, Borneol and Isoborneol under High Pressures and High Temperatures.

Camphor—Refined camphor manufactured by the Nippon Camphor Company; m.p. 176.4°C, $[\alpha]^{24}_{D}+44.13$.

Borneol—By reducing the purified camphor with metallic sodium and alcohol, some borneol was obtained, which, according to the writer's own method,(30) was treated with 2 moles of phthalic anhydride under 140–145°C for 20 hours and then immediately by steam distillation volatile substances were distilled off and the residue was treated with some warm water to remove the excess of phthalic acid. The ester was purified by recrystallisation; m.p. 158–159°C, $[\alpha]^{11}_{D}+52.41$ (C=4 in alcohol).(31) The ester was saponified and the borneol thus obtained was recrystallised from its solution in petroleum ether; m.p. 204–204.5°C (in sealed tube), $[\alpha]^{15}_{D}+38.44$ (C=3.92 in toluene).

Isoborneol—Some camphor was dissolved in absolute alcohol and then was reduced by the catalytic reaction of reduced nickel under high temperature and pressure. To the isoborneol thus obtained, 2 moles of phthalic anhydride and some toluene were added, esterified by heating at 110°C for 5 hours, distilled out the volatile matter with steam, and to the residue warm water was added to remove the excess of phthalic acid. Borneol ester which contaminated the product was, as it is easily saponifiable, taken away by hydrolysis,(32) and the ester was recrystallised from its alcoholic solution, m.p. 168–168.2°C, $[\alpha]^{13}_{D}$ -83.07 (C=3.7 in alcohol),(33) isoborneol obtained by saponifying the ester was recrystallised from petroleum ether, m.p. 212–213°C., $[\alpha]_{D}-34.42$ (C=3.35 in alcohol) $[\alpha]^{15}_{D}-19.59$ (C=5.17 in toluene).

Nickel—Nickel nitrate was ignited to produce nickel oxide, which was reduced with hydrogen at 300°C.

The reaction product was separated from nickel, camphor was quantitatively estimated by the semicarbazone process, and borneol and isoborneol were calculated from the specific rotation of their respective solutions in alcohol and toluene, the mean number being adopted.

In cases of samples 5–9, among the reaction products some water was present, which clearly indicated that dehydration had occurred. Therefore, after the estimation of camphor, the sample was distilled over sodium and isocamphane(34) (b.p. 164.5–165°C, m.p. 66–67°C, $[\alpha]_{D}\pm0$) was obtained. Found: C, 86.60; H, 13.22. Calculated for $C_{10}H_{18}$: C, 86.86; H, 13.14%.

With regard to sample 17 and 18, to prove the presence of borneol 2 moles of phthalic anhydride were added in each case and the mixture was heated to 140~145°C. for 20 hours. Thus all of the isoborneol was converted to camphene, and borneol was separated in the form of phthalic ester.

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(30) *J. Chem. Soc. Japan*, **53** (1932), 807.

(31) Pickard and Littlebury, *J. Chem. Soc.*, **91**, 1978.

(32) Vavon and Peignier, *Bull. soc. chim.*, **39** (1926), 924.

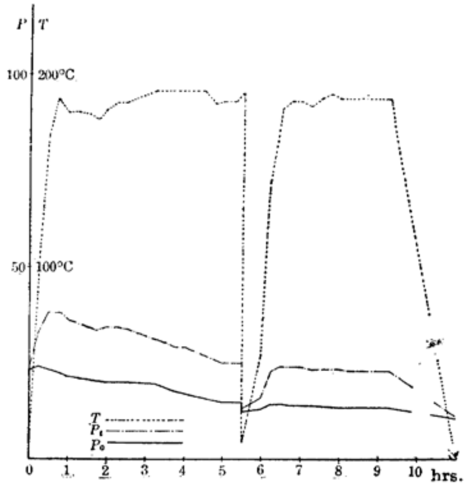
(33) Kenyon and Picard, *J. Chem. Soc.*, **107**, 59.

(34) P. Lipp, *Ann.*, **382** (1911), 279; Komatsu and Masumoto, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **5** (1922), 225.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. °C.	Temp. at the beginning of absorp. °C.	React. time (hr.)	H_2 absorbed (mol.)
1	camphor	50	23.3	170~190	170	$7^1/_2$	1.1
2	camphor	50	49.4	170~200	150	$6^1/_3$	1.0
3	camphor	50	84.5	170~190	140	$5^5/_6$	1.0
4	camphor	50	79.5	140~160	150	$20^1/_2$	0.7
5	camphor	50	91.6	200~280	—	$8^5/_6$	2.0
6	camphor	50	51	190~220	160	3	1.5
7	borneol	25	49.5	130~250	210	$7^1/_2$	1.0
8	isoborneol	15	67	170~190	—	15	0.7
9	borneol isoborneol	25 25	50.5	120~256	150 220	16	1.1
10	camphor	50	55.5	170~190	150	21	1.0
11	camphor cyclohexane	50 60	78.2	140~170	—	$7^1/_2$	1.4
12	camphor abs. alcohol	50 60	90.7	140~160	130	$5^1/_2$	1.4
13	camphor acetic acid	50 0.5	61.8	170~200	—	8	1.0
14	camphor pyridine	50 0.5	85.4	180~200	—	$8^1/_2$	0.7
15	camphor cyclohexane metallic Na	50 60 1	58.2	160~170	150	$9^1/_2$	1.2

No.	Reaction product					
	Yield (g.)	M.p. °C.	$[\alpha]_D$* at °C	Camphor %	Borneol %	Isoborneol %
1	49.0	195—196	$+11.2^{20}$	20.0	51	49
2	48.0	190—194	$+10.6^{24}$	20.0	50	50
3	49.3	187—191	$+4.8^{32}$	12.0	47	53
4	48.5	194—195	$+12.1^{32}$	21.5	51	49
5	40.5 H_2O 1.6	80—103	± 0	7.0	—	—
6	48.0 H_2O	119—125	$+8.3^{13}$	5.0	—	—
7	12.0 H_2O	100—110	$+3\ 7^{20}$	—	—	—
8	7.0 H_2O	78—79	-0.7^{10}	—	—	—
9	25.0 H_2O	78—81	± 0	—	—	—
10	49.0	197—198	$+11.8^{26}$	23.0	50	50
11	48.0	203—204	-8.2^{11}	21.0	23	77
12	47.2	208—210	-24.7^{14}	2.5	12	88
13	48.5	196—198	$+1.6^{23}$	21.5	37	63
14	49.0	199—200	$+5.5^{14}$	32.0	36	64
15	49.0	206	-7.4^{22}	8.0	33	67

* determined in alcohol.



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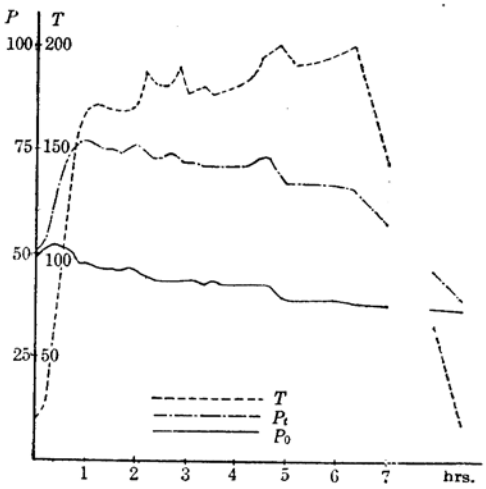
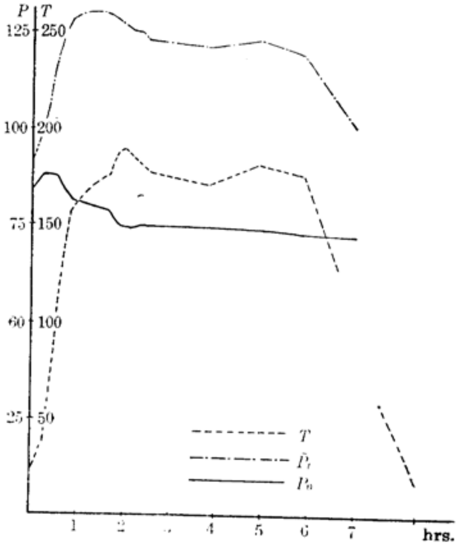


Fig. 2.



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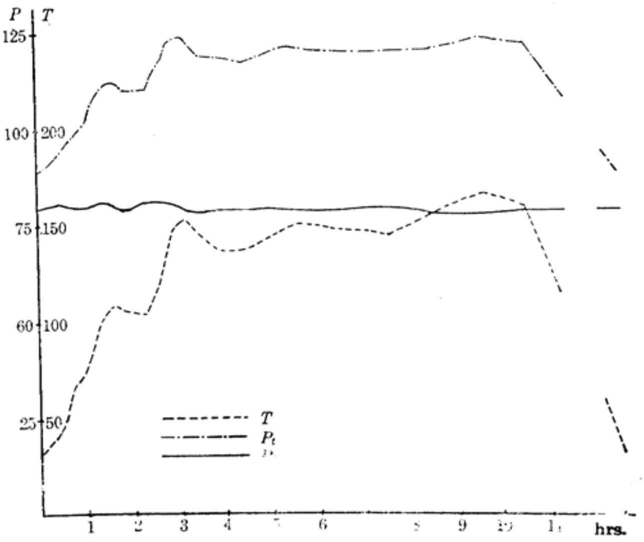

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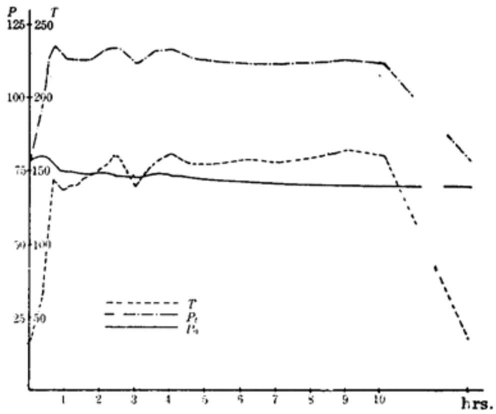
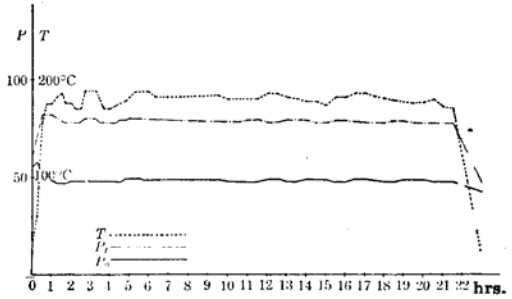


Fig. 4. (2)



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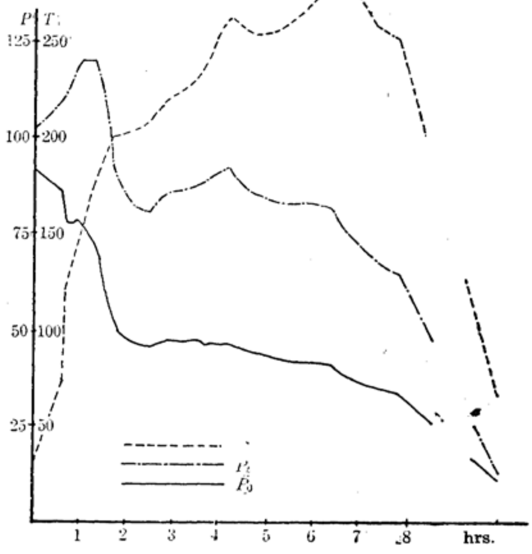

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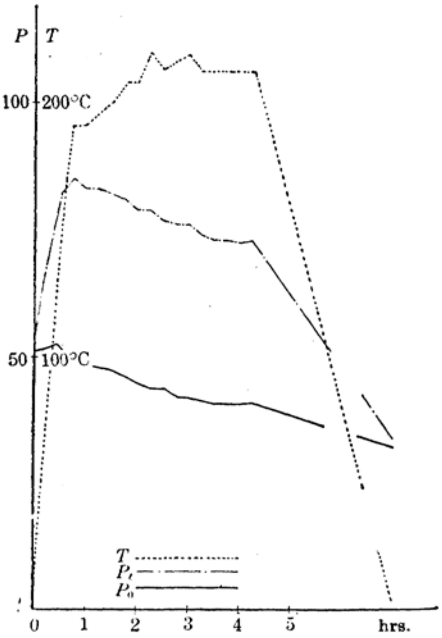

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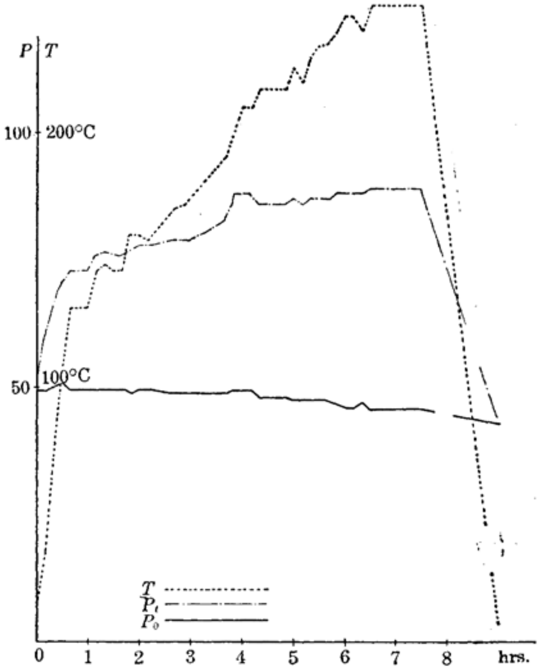

Fig. 8. Dehydration of Borneol.

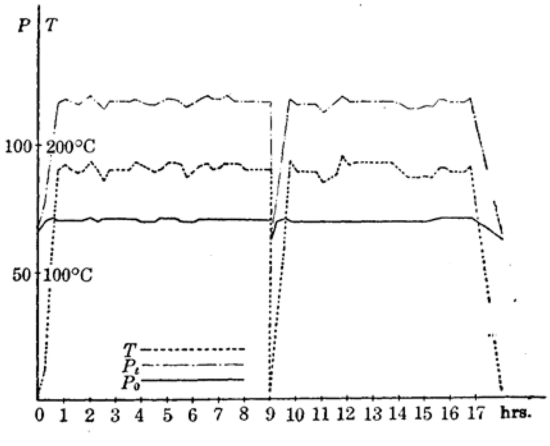

Fig. 9. Dehydration of Isoborneol.

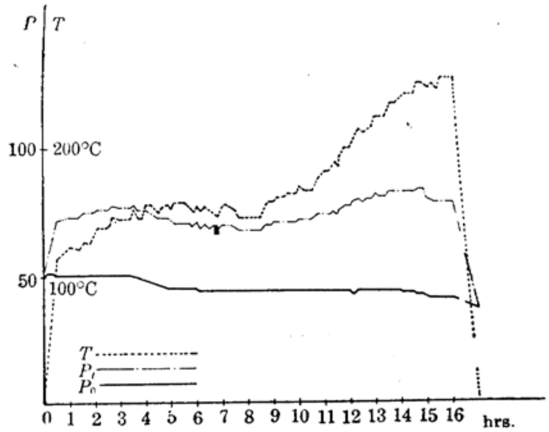

Fig. 10. Dehydration of Mixture of Borneol and Isoborneol.

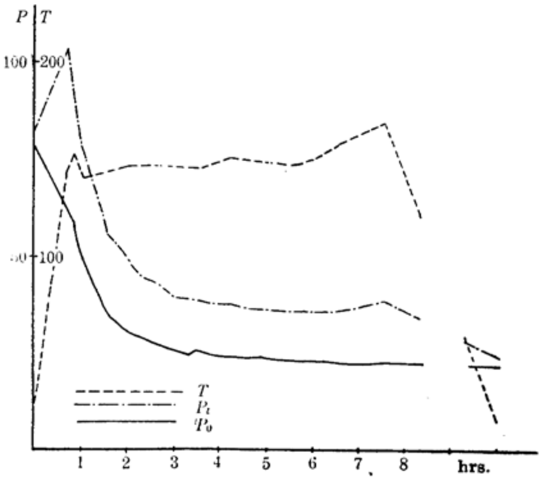

Fig. 11. Camphor+Cyclohexane.

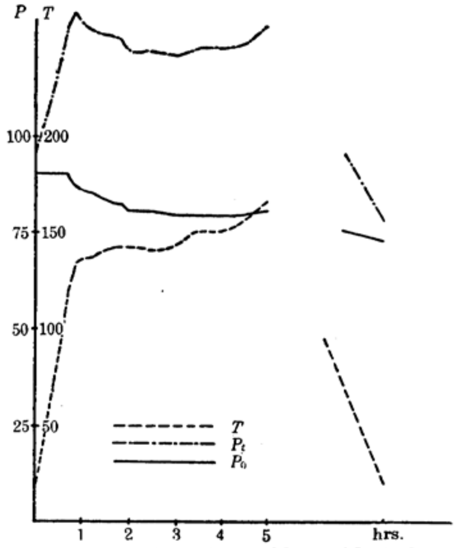

Fig. 12. Camphor+Abso. Alcohol.

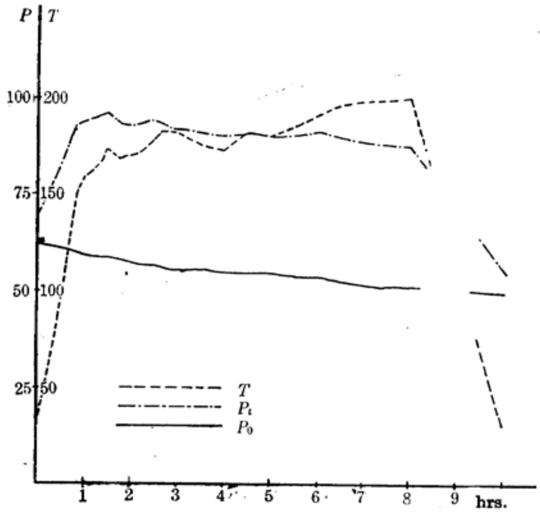

Fig. 13. Camphor+Acetic acid.

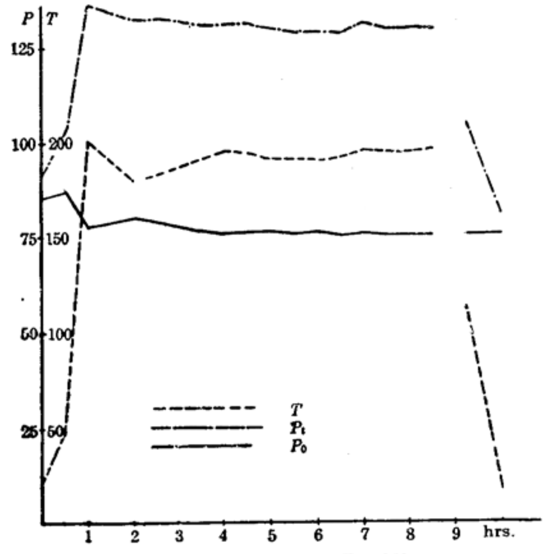

Fig. 14. Camphor+Pyridine.

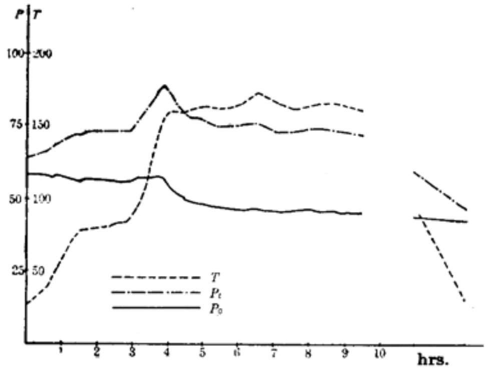

Fig. 15. Camphor+Cyclohexane+Na.

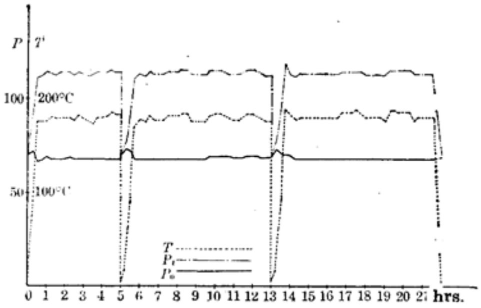

Fig. 16. Borneol.

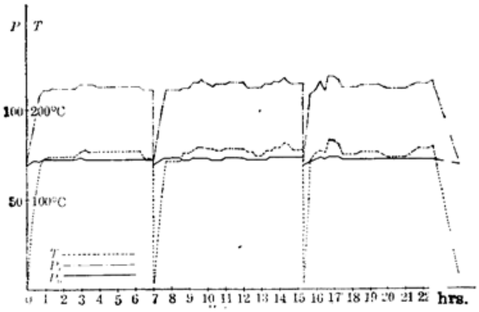

Fig. 17. Borneol-Abs. alcohol.

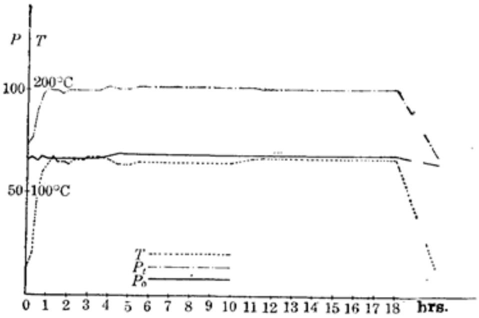

Fig. 18. Isoborneol-Abs. alcohol.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. (°C)	React. time (hrs.)	H_2 absorbed (mol)
16	borneol	15	71	170—190	19.5	0.3
17	isoborneol	25	53	130—150	4	0
18	isoborneol	35	47	140—165	4	0
19	borneol alcohol	15 20	70	150—160	20.5	0
20	isoborneol alcohol	15 20	66	130—140	16.3	0.3

No.	Reaction product							
	Yield (g.)	M.p. °C	$[\alpha]_D$ alc. °C	$[\alpha]_D$ toluene °C	Methoxy value after ether. by $HCl+CH_3OH$	Camphor %	Borneol %	Isoborneol %
16	13	201—202	$+37.1^{10}$	$+38.0^{13}$	0.5	0.6	99	1
17	23	193—202	-22.2^{16}	-10.3^{16}	10.1	0.6	16	84
18	30	199—200	$+6.1^{33}$	$+10.1^{33}$		0.5	51	49
19	13	199—199.5	$+31.2^{20}$	$+33.7^{13}$	1.5	0.2	90	10
20	13.5	209—210	-25.9^{31}	-12.6^{31}	10.3	0.6	11	89

Esters	M.p. °C	$[\alpha]_D$	Borneol obtained by saponification	
			M.p. °C	$[\alpha]_D$
Acidic ester	158.5—159	+33.89	203—204	+29.68
Neutral ester	99—100	+25.05	201—202	+11.94

The esters and borneol were confirmed to be pure by the mixed fusion method. In one half of sample 19, for the purpose of proving the presence of isoborneol, it was tried to separate it as a Mg salt of phthalic acid ester, but due to the scarcity of sample, the experiment was not successful. The other half was dehydrated with phthalic anhydride and successfully confirmed as camphene. In sample 20, borneol was separated in the form of acidic ester of phthalic acid (m.p. 158–159°C.), as before. The borneol obtained by saponification; m.p. 201–202°C., $[\alpha]_D+14.52$.

III. Reduction of Dimethylcamphor with Metallic Sodium and Alcohol.

(1) *a,a′-Dimethylcamphor*. According to the method of Haller,(35) by treating camphor with $NaNH_2$ and ICH_3 monomethylcamphor was obtained quantitatively. Moreover, this monomethylcamphor was repeatedly methylated; to remove the remaining camphor and monomethylcamphor, they were changed into oximes by heating at 100°C for 49 hours with 2 moles of $NH_2OH.ZnCl_2$ and after fractionally distilling 8 times, pure dimethylcamphor [b.p. 85–85.5°/8 mm, d_4^{25} 0.9460, n_D^{25} 1.4725, $[\alpha]_D^{25}$ +91.27, M.R. (obs.) 53.25, (calc.) 53.23] was obtained in a yield of 63%. Found: C, 79.86; H, 11.31. Calculated for $C_{12}H_{20}O$: C, 80.00; H, 11.11%.

(2) *Dimethylborneol*. Dimethylcamphor was reduced with metallic sodium and alcohol, and a crystalline matter (d_4^{25} 0.954, n_D^{25} 1.481, $[\alpha]_D^{25}+46$ in alcohol) mixed with oily substance was obtained 96.5%.

This reaction product was separated into 75% crystal and 25% oil; by recrystallising the crystal with petroleum ether for several times, a white needle crystal of borneol-like odour was obtained, b.p. 90.5–93°/5 mm., m.p. 57°C, $[\alpha]_D^{26}+50.72$ (C=2.11 in alcohol), $[\alpha]_D^{26}+53.76$ (C=1.71 in toluene). Found: C, 78.83; H, 12.15. Calculated for $C_{12}H_{22}O$; C, 79.12; H, 12.09%.

This substance makes a beautiful white short needle crystal of phenylurethane (m.p. 112–113°C.), and, by reacting with p-nitrobenzoic acid, forms a needle crystal of silky lustre and of faintly greenish white colour. This crystal (m.p. 115–115.8C. $[\alpha]_D^{25}+50.94$ (C=0.53 in alcohol) or +70.78 (C=0.367 in chloroform) is soluble in ether, petroleum ether, or warm alcohol, but sparingly soluble in cold alcohol. Further, it reacts with phthalic anhydride and forms monoester quantitatively.

Sample (g.)	Phthalic anhydride (moles)	React. temp. °C	React. time (hrs)	Monoester	
				Yield (g.)	%
4	2	110—115	10	7.2	99.4
5	2	140—145	20	9.1	99.6

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(35) *Compt. rend.*, **148** (1909), 1645.

The monoester crystallises in beautiful white needles (m.p. 177–178°C., $[\alpha]_D^{27}+16.32$ (C=0.42 in alcohol), $[\alpha]_D^{19}+19.12$ (C=0.471 in chloroform)), and is soluble in ether, alcohol, or chloroform, but insoluble in petroleum ether and water.

The Mg salt of phthalic acid ester is white lustrous crystals of scale shape, the m.p. being 175–176.2°C. The solution of dimethylborneol in benzene was boiled with zinc chloride for 3 hours, and yet no change occurred.(36)

(3) *Dimethylisoborneol.* The oily matter (d_4^{25} 0.953, n_D^{25} 1.485, $[\alpha]_D^{29}$ +38 in alcohol) separated from the crystal already mentioned was fractionally distilled under a reduced pressure, and the following three fractions were obtained.

Fraction	**B.p. 5mm**	**Yield (%)**	d_4^{25}	n_D^{25}	$[\alpha]_D^{27}$ **in alc.**
1	81–87	10.6	0.9422	1.4780	+48.5
2	87–95	13.4	0.9483	1.4809	+52.3
3	95–103	71.2	0.9522	1.4831	+52.4

Each fraction was cooled with common salt and ice; from fractions (1) and (2) no crystal was obtained, and fraction (3) solidified entirely. Further, when the fraction (2) was treated with phthalic anhydride at 140–145°C. for 10 hours, unsaturated hydrocarbon was obtained as well as ester. From this experimental fact, the presence of an isomer to be easily dehydrated was suspected. Then it was tried in vain to obtain this isomer as *p*-nitrobenzoic ester by fractional crystallization. The isomer was treated with phthalic anhydride at 110–115°C. for 10 hours, the monoester thus obtained being changed to a Mg salt. Utilising the difference in the solubility in alcohol, an easily soluble crystalline powder (m.p. 180–182°C.) was obtained abundantly. This was further changed to an acidic ester, and recrystallising it from its solution in acetic acid, a lustrous beautiful crystal of scale shape (m.p. 173–174°C.) was obtained. By saponifying it, a compound $C_{12}H_{22}O$ to be considered as dimethylisoborneol was obtained, b.p. 82–84°/3 mm, m.p. 47–49°C, $d_4^{49.5}$ 0.9406, $n_D^{49.5}$ 1.4748, M.R. (obs.) 54.5, (calc.) 54.8, $[\alpha]_D^{15}+36.47$ (C=1.70 in alcohol), $[\alpha]_D^{15}$ +42.71 (C=1.43 in toluene). Found: C, 78.79; H, 12.06. Calculated for $C_{12}H_{22}O$: C, 79.12; H, 12.09%.

Phenylurethane is a lustrous, colourless needle crystal (m.p. 116–117°C.), and *p*-nitrobenzoic ester is also a lustrous, colourless needle crystal, but its m.p. is 114.5–115°C and $[\alpha]_D^{19}+24.90$ (C=0.321 in alcohol), $[\alpha]_D^{19}+44.11$ (C=0.317 in chloroform). When heated with 2 moles of phthalic anhydride at 110–115°C. for 10 hours, monoester is obtained in yield of 90%, and when the temperature was raised to 140–145°C. and

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(36) Piccard and Littlebury, *J. Chem. Soc.*, **91**, 1977; Tetsusaku-Ikeda, *Proc. Sci. Inst. Japan*, **7**, 257.

the reaction was continued for about 10 hours, dehydration was complete and no ester was formed at all. And by the reaction with zinc chloride dehydration occurs.

Further, to find out the proportion of dimethylborneol and dimethylisoborneol in the reduction product which was obtained by reducing dimethylcamphor with metallic sodium and alcohol, 2 moles of phthalic anhydride was added, and, after the reaction at 110–115°C. for 10 hours, there were obtained 93% ester and 4% unesterified oil. The alcoholic part separated from the ester was again treated with phthalic anhydride at 140–145°C., and the product was separated into a substance (90%) to be considered as dimethylborneol and another (10%) to be considered as dimethylisoborneol. Unesterified oil, as it forms no phenylurethane by all means, was assumed to be a mixture of unsaturated hydrocarbons formed by dehydrating dimethylisoborneol and dimethylcamphor, and, from the bromine absorption,(37) the content of unsaturated hydrocarbons in the unesterified oil was found to be 34%.

Sample (g.)	1/5 N Br_2 sol. (c.c.)	React. time (hors)	$Na_2S_2O_3$ c.c.			Unsatur. hydrocarbon (%)
			Total Br absorbed	Br substituted	Br added	
0.2050	15	8	9.5	4.2	5.3	34.2
0.1649	15	8	7.7	3.4	4.3	34.8

As a result, the proportion of dimethylborneol and dimethylisoborneol formed was calculated to be 88:12.

IV. Catalytic Reduction of Dimethylcamphor at High Temperatures and under High Pressures. By catalytically reducing dimethylcamphor at 220–230°C. in hydrogen of 60 atmospheres pressure in the presence of reduced nickel, the following results were obtained.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. °C	React. time (hrs)	H_2 absorbed (mol)
1	dimethylcamphor	30	57	220—230	27½	1.1
2	dimethylcamphor abs. alcohol	30 40	60	200	20	1.1
3	dimethylcamphor acetic acid	30 0.3	60	220—230	25	1.1
4	dimethylcampbor	30	49	280	10	2.1

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(37) H. Meyer, Org. Chem. Method., Bd., I, 1126, 4. Aufl.

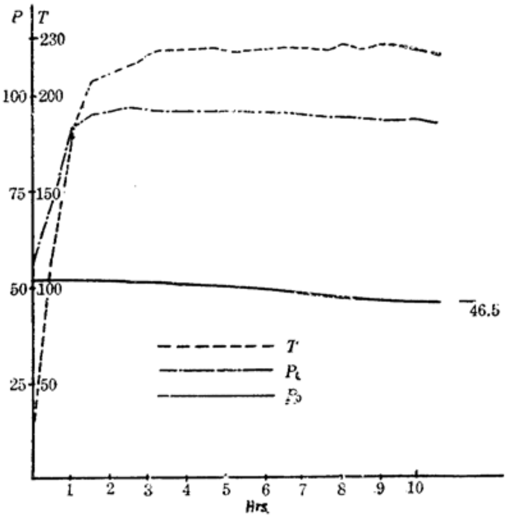

Fig. 19. (1). Dimethylcamphor.

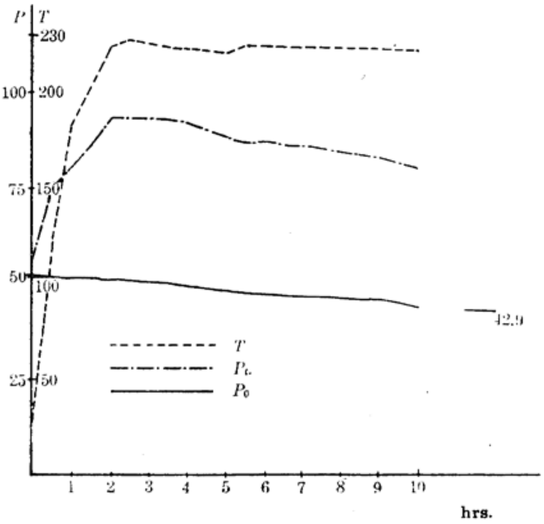

Fig. 19. (2).

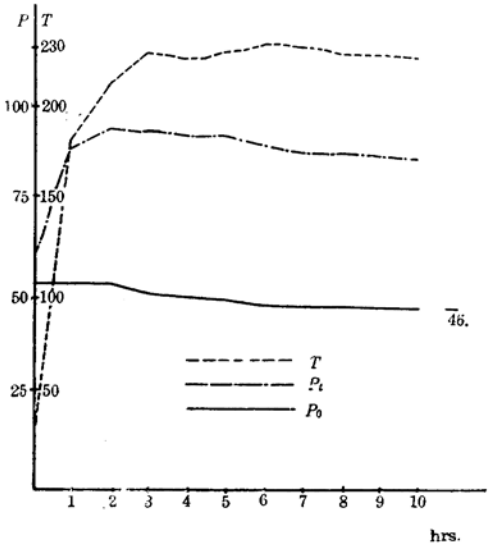

Fig. 20. (1). Dimethylcamphor + Acetic acid.

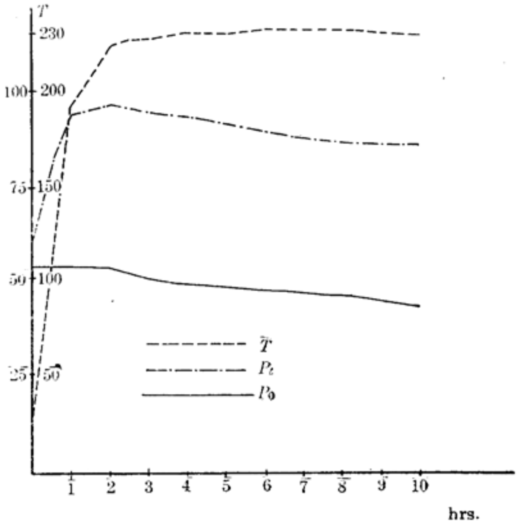

Fig. 20. (2)

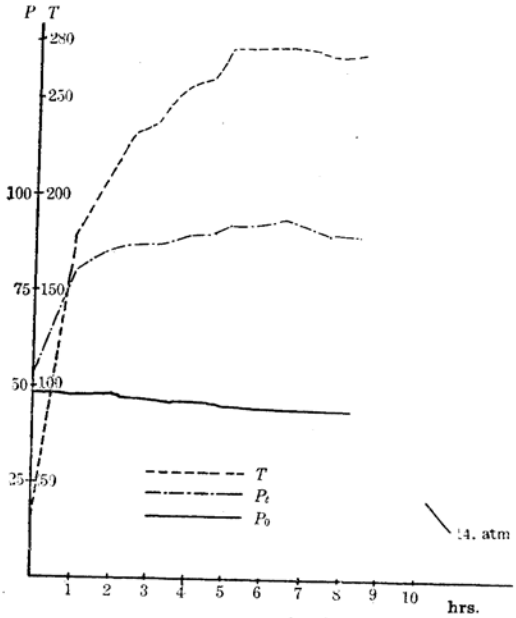

Fig. 21. Dehydration of Dimethylcamphor.

No.	Reaction product						
	Yield (g.)	d_4^{25}	n_D^{25}	$[\alpha]_D$ in alcohol	Dimethyl-camphor (%)	Dimethyl-borneol (%)	Dimethyl-isoborneol (%)
1	26	0.927	1.474	+48	80	85	15
2	24	0.948	1.475	+77	63	66	34
3	26	0.949	1.479	+59	51	86	14
4	26	0.876	1.470	−26			

In the case of sample (4), some water being mixed in the reaction product, dehydration had occurred undoubtedly. After distilling several times at ordinary pressure, the following two fractions were separated.

Fraction	B.p. °C	Yield (g.)	d_4^{25}	n_D^{25}	$[\alpha]_D$ (in alcohol)	M. R.	
						obs.	calc. for $C_{12}H_{22}$
(1)	197–200	1.9	—	—	—	—	—
(2)	200–203	20.6	0.8706	1.4695	−28.07	53.17	53.22

The elementary analysis of fraction (2) is; Found: C, 86.39; H, 13.51. Calculated for $C_{12}H_{22}$: C, 86.75; H, 13.25%.

(To be continued.)