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

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V. The Dehydration of Borneol and Isoborneol. (1) *The dehydration of borneol and isoborneol with* $H_2SO_4.3H_2O$. Borneol (m.p. 205°C., $[a]_D+18.62$) and isoborneol (m.p. 209–210°C. in a sealed tube $[a]_D$ -15.72) 10 g. of each was taken in a distilling flask, to which 0.4 c.c. of $H_2SO_4.3H_2O$ (in volume 4%) was added; and being heated at 140–145°C. for a definite time the water formed by the reaction accompanying a small quantity of camphene was distilled out. The reaction product was put into some water to be extracted with ether; and the ether solution was washed with a dilute solution of sodium carbonate and was dried to distil off the ether, and then it was fractionally distilled.

No.	Sample	Heat. hours	Yield %	Main fraction (camphene)				Fraction of higher boiling point			
				Yield %	B.p. °C.	M.p. °C.	$[\alpha]_D$	Yield %	B.p.	d_4^{20}	n_D^{20}
1	borneol	5	90	62	155–161	42–45	+3.3	13	150–167^{10} mm		
2	,,	10	93	63	155–166	43–45	+1.8	12	147–173^{11} ,,		
3	,,	15	87	58	155–161	42–44	0	10	148–168^{11} ,,		
4	iso-borneol	2	95	47	152–160	48–52	+4.4	20	120–147^{5} ,,		
5	,,	10	89	56	154–163	47–48	+0.5	18	120–153^{5} ,,	0.955	1.493
6	,,	15	91	50	152–161	42–45	0	11	120–148^{5} ,,	0.956	1.493

The mixture of fractions (1), (2), (3) of higher boiling points was fractionally distilled, and a colourless viscous compound to be considered as di-*d*-bornyl ether was obtained:—

B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D^{27°}$ (in alcohol)	M.R.	
				obs.	calc. for $C_{20}H_{34}O$
134—137^{2} mm	0.9564	1.4927	+41.68	88.15	87.40

Found: C, 82.93, H, 11.73. Calculated for $C_{20}H_{34}O$: C, 82.67; H, 11.81%.

This fraction was treated with hydrogen iodide (b.p. 125–127°C.) at 130°C. for an hour; and from the reaction product, crystal of borneol (its phenylurethane m.p. 135–137°C.) was obtained.

On the other hand, this fraction manifested no colour reaction when conc. nitric acid was added to it; and when it was heated, a yellow precipitation of camphor-like odour issued.

Next, fractions (4), (5), (6) of higher boiling points were collected and fractionally distilled, and compounds to be considered as di-*d,l*-isobornylether were obtained:—

B.p.	d_4^{20}	n_D^{20}	M.R.
$136-145^{2.5\,mm}$	0.9672	1.5010	90.29

Found: C, 82.22, H, 11.37. Calculated for $C_{20}H_{34}O$: C, 82.67, H, 11.81%.

By treating this with hydrogen iodide, alcohol was obtained, from which phenylurethane (m.p. 139–139.5°C.) was obtained.

By treating with conc. nitric acid, it changed to a green colour, which grew reddish brown when heated. Again, when it was diluted, a yellow precipitation of camphor-like odour was obtained.

(2) *The Dehydration of Borneol with Alumina.* Borneol (m.p. 205°C., $[\alpha]_D+18.62$) was passed over alumina (Merk) heated at 350°C. at the rate of about 5 g. per hour; and the reaction product, accompanying a trace of water, was fractionally distilled. The result was as follows:—

Fraction	B.p. °C.	Yield (g.)	d_4^2	n_D	M.R.	$[\alpha]_D^{12}$ in alcohol
1	33—100	2.4	—	—	—	—
2	100—145	7.1	0.8356^{20}	1.4690^{20}	45.37	0
3	145—155	38.8	0.8312^{40}	1.4596^{40}	44.82	+0.23
4	155—155.5	36.6	0.8286^{40}	1.4627^{40}	45.22	+0.58
5	155.5—161	6.4	0.8459^{20}	1.4730^{20}	45.14	+2.31
6	161—	5.5	—	—	—	—

From the main fractions (3) and (4), solid camphene (m.p. 52–53°C., $[\alpha]_D+0$) was obtained.

(3) *The action of* $H_2SO_4.3H_2O$ *on bornyl acetate.* When borneol (m.p. 204°C., $[\alpha]_D+38.44$) was heated with glacial acetic acid and potassium acetate, the following acetic ester(38) was obtained:

B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D^{11}$
$98^{11\,mm}$	0.9864	1.4655	+42.75

To 20 g. of this ester, 0.8 c.c. of $H_2SO_4.3H_2O$ was added; and, after a reaction of 10 hours at 140–145°C., the reaction product was fractionally distilled to separate it into camphene and the ester as completely as possible:

Fraction	B.p.	Yield %	d_4^{20}	n_D^{20}	$[\alpha]_D^{12}$ in alcohol
1	$30-82^{5\,mm}$	8 8	0.9511	1.4727	—
2	82—84	77.0	0.9813	1.4657	+39.13
3	residue	12.1	—	—	—

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(33) Bertram, *Ann.*, **231**, 304.

Of the reaction products, to the estimation of camphene, the bromine absorption was adopted, and to that of borneol and isoborneol, the phthalic anhydride method; and it was found that the reaction products were 96.5 moles% bornylester, 0.5 mole% isobornylester, and 3 moles% camphene.

(4) *Conversion of isobornylacetate to camphene by the action of* $H_2SO_4 \cdot 3H_2O$. Inactive isobornylacetate (b.p. $79.5–81.5^{3.5mm}$, d_4^{20} 0.9848, n_D^{20} 1.4640, saponification value (obs.) 285.8, (calc.) 286) was reacted with $H_2SO_4 \cdot 3H_2O$. From the saponification value 103.2 of the reaction product, it was calculated out that the proportions of the ester and camphene were 22 moles% and 78 moles%.

(5) *The Conversion of camphene to isoborneol by the action of* $H_2SO_4 \cdot 3H_2O$. Camphene (5 g.) was dissolved in glacial acetic acid (2.5 g.), and the solution was treated with $H_2SO_4.3H_2O$ (0.2 c.c.). From the saponification value 168.2 of the reaction product, the proportions of isobornylester and camphene were calculated out to be 50 moles% and 50 moles%.

(6) *The dehydration of isoborneol with phthalic anhydride.* Isoborneol (m.p. 209–210°C., in a sealed tube, $[\alpha]_D^{18}$–15.72 in alcohol) 20 g. and phthalic anhydride (2 moles) were reacted under the following conditions:

No.	React. temp. °C.	React. hours h	Reaction product		Camphene obtained from the dehydrated oil		
			Ester (g.)	Dehydrated oil (g.)	B.p. °C.	M.p. °C.	$[\alpha]_D$
1	140–145	11	19	6.5	153–163	48–52	$+1.34^{13}$
2	110–115	13	29.5	3.5	150–157	45–47	$+25.25^{18}$
3	80–85	46	35.2	1.3			

The ester No. 1 was separated into 10 g. of acid ester (m.p. 164°C., $[\alpha]_D^{25}$ +43.10, C=0.99 in alcohol), 10 g. of borneol and 6.3 g. of neutral ester (m.p. 100–101°C., $[\alpha]_D^{24}$ + 27.93 C = 0.806 in alcohol). By the saponification of the ester, borneol (m.p. 205–206°C) was isolated; and when the mixture of it and other borneol was put to a mixed fusion, no depression of the melting point was seen. The ester No. 2 was separated into 10 g. of acid ester (m.p. 152°C., $[\alpha]_D$–20) and 3 g. of neutral ester (m.p. 92°C., $[\alpha]_D$–22). These esters were saponified, and isoborneol of m.p. 207°C., in a sealed tube and $[\alpha]_D$–2 was obtained from the former ester, and isoborneol of m.p. 203°C. in a sealed tube and $[\alpha]_D$–7 from the latter. Moreover, to isoborneol (m.p. 212–213°C. in a sealed tube $[\alpha]_D$–34.42) 2 moles of phthalic anhydride was added; and after a reaction at 110–115°C., camphene $[\alpha]_D^{1.5}$+49.33) was obtained.

(7) *Hydration of camphene.* From bornyl chloride (m.p. 131°C., $[\alpha]_D$ +31.29), by means of the following method, diverse camphenes were obtained.

(i) By the reaction of aniline⁽³⁹⁾ for over 10 hours, the camphene produced was of m.p. 49–52°C. and $[\alpha]_D^{19}0$.

(ii) Yellow lead oxide⁽⁴⁰⁾ was heated at about 250°C., and bornyl chloride was acted on it. The camphene thus produced was of m.p. 49.5°C. and $[\alpha]_D^{19}+12.86$.

(iii) Camphene produced by the reaction of phenol⁽⁴¹⁾ was of m.p. 48–50°C. and $[\alpha]_D^{13.5}+72.69$.

The specific rotation of the isoborneols obtained by the hydration of the 3 kinds of camphenes shown above is as follows:

(i) The isoborneol obtained from the camphene $[\alpha]_D^{19}0$: m.p. 209 (in a sealed tube), $[\alpha]_D^{19}0$.

(ii) The isoborneol obtained from the camphene $[\alpha]_D^{19}+12.86$: m.p. 210°C. (in a sealed tube): $[\alpha]_D^{19}-0.54$.

(iii) The isoborneol obtained from the camphene $[\alpha]_D^{13.5}+72.69$: m.p. 208°C. (in a sealed tube), $[\alpha]_D^{19}-5.13$.

The content of borneol in the isoborneol, obtained as above, estimated by means of the phthalic anhydride method, was 10%.

Further, the influence of the time to the hydration of camphene $[\alpha]$ + 72.69 was investigated to be as follows:

No.	React. hours	Isoborneol ester				Isoborneol	
		B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D$ °C.	M.p.* °C.	$[\alpha]_D$ in alc. °C.
1	1/3	$74-77^{3.5\,mm}$	—	—	-11.47^{20}	207—208	-10.56^{19}
2	4 1/3	86^{7}	0.9825	1.4656	-7.83^{9}	208.3	-5.13^{9}
3	27 1/2	88^{6}	0.9825	1.4652	-4.14^{9}	—	—
4	118	85^{4}	0.9813	1.4650	-0.78^{9}	206	$\pm 0^{9}$

* Measured in a sealed tube.

From No. 1 unreacted camphene (m.p. 51–53°C., $[\alpha]_D^{22}+14.01$ was separated.

(i) By the reaction between bornyl chloride and phenol, a camphene $[\alpha]_D+72.69$ was obtained, which was colourless even after hydration, and there was no change of colouration.

(ii) By the reaction between bornyl chloride and yellow lead oxide or aniline, a camphene $[\alpha]+12.86$ was obtained, which became yellow when hydrated.

(iii) By the dehydration of borneol with alumina, a camphene $[\alpha]_D0$ was obtained, which, when hydrated, became faintly brown at first and changed to blackish green afterwards. Further, it became crimson red when thrown into water. This colour reaction is a phenomenon also seen in the case of hydrocarbons formed when dimethylborneol is dehydrated with $H_2SO_4 \cdot 3H_2O$.

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(39) Ullmann and Schmidt, *Ber.*, **43** (1910), 3202.

(40) Tetsusaku Ikeda, *Proc. Sci. Inst.* Japan, **4** (1925), 503.

(41) A. Reychler, *Ber.*, **29** (1896), 696.

(iv) When borneol is dehydrated with $H_2SO_4.3H_2O$, a camphene $[\alpha]_D0$ is obtained, which, in the course of hydration, becomes to a faint purple red colour at first and then changes to a faint reddish brown colour afterwards. When thrown into water, it becomes to a faint yellowish brown colour. As has been described above, according as the preparation differs, camphenes behave differently in the colour reaction by hydration. This is to be considered due to the accompanying impurities.

(8) *Racemisation of camphene by* $H_2SO_4{\cdot}3H_2O$. By the reaction between bornyl chloride and yellow lead oxide, a camphene (m.p. 52.2–52.9°C. $[\alpha]_D^{2}+8.28$) was obtained, to 10 g. of which, 0.4 c.c. of $H_2SO_4.3H_2O$ (0.05 mol) was added and it was heated at 140–145°C. Afterwards the camphene was collected and its rotatory power was examined.

No.	React. hours h	Reaci. product			Camphene			Oily part			
		B.p. °C.	Yield %	$[\alpha]_D$ °C.	M.p. °C.	Yield %	$[\alpha]_D$	Yield %	d_4^{25}	n_D^{25}	$[\alpha]_D$
1	12	154-158	72	—	52-52.4	58	0	14	0.843	1.470	+0.6
2	1	153-158	72	$+1.76^{23}$	53-54	25	+0.3	23	0.853	1.469	+1.6
3	1/6	153-155	71	+5.8	53-54	51	+5.2	2	—	1.470	—

To investigate the influence upon the racemisation of camphene at the temperature of 10–20°C., 13 g. (2.3 moles) $H_2SO_4.3H_2O$ was added to 5 g. camphene, and, after an elapse of 400 hours, it was recognised that racemisation had occurred.

No.	React. hours	React. product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	20	154—157	50	52—54	+4.8
2	412	155—170	40	48—50	+1.6

(9) *The racemisation of camphene with 50% sulphuric acid.* 5 g. camphene was treated with 0.5 g. of 50% (0.05 moles) sulphuric acid at 50–60°C.

No.	React. hours	Reaction product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	3	153—155	98	49—50	+5.2
2	24	155—159	80	52	+3.8

(10) *The recemisation of camphene with hydrochloric acid.* 10 g. camphene was treated with 0.4 c.c. $HCl{\cdot}3H_2O$ at 140–145°C. Although the rate of reaction was rather slow, it was found that racemisation had occurred to some extent.

No.	React. hours	Reaction product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	1	155—162	58	51—53	+8.5
2	12	155—162	70	43—53	+5.4

(11) *The racemisation of camphene with acetic acid.* 5 g. camphene was treated with 12.5 g. (5 moles) glacial acetic acid at 50–60°C., and some evidence of racemisation was recognised.

No.	React. hours	Reaction product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	3	155—156	50	49—53	+6.2
2	12	155 - 156	60	49—53	+6.0

(12) *The racemisation of camphene with phthalic anhydride.* To 10 g. camphene (m.p. 47–50°C., $[\alpha]_D^{13.5}+49.33$), a well dried 19 g. (2 moles) phthalic anhydride was added, and the mixture was heated at 140–145°C. for 11 hours. To separate out camphene from the reaction product, the extraction by petroleum ether was adopted instead of steam distillation, and the yield of camphene (b.p. 153–160°C., m.p. 46.5–47.5°C., $[\alpha]_D^{22}+1.9$) was 50%. Although great precautions were taken not to admit the entrance of any drop of water during the reaction, there was seen at the end of the reaction neutral and acid esters of isoborneol, both insoluble in petroleum ether. When the neutral ester $C_{28}H_{34}O_4$ was recrystallised from its solution in methyl alcohol, the following substance was obtained:

Neutral ester, m.p. 99–100.5°C., $[\alpha]_D^{27}-3.32$ (C=1.8 in alcohol). Found: C, 76.65; H, 8.62. Calculated for $C_{28}H_{38}O_4$: C, 76.66; H, 8.73%.

When the acid ester $C_{18}H_{22}O_4$ was recrystallised from its solution in methyl alcohol, the following substance was obtained: Acid ester, m.p. 169–170.5°C., $[\alpha]_D^{25}-1.57$ (C=1.91 in alcohol). Found: C, 71.47; H, 7.66; Calculated for $C_{18}H_{22}O_4$: C, 71.48; H, 7.34%.

(13) *The racemisation of camphene with alumina.* 12 g. camphene (m.p. 42–45°C., $[\alpha]_D^{18}+9.28$) together with a small quantity of steam was passed over alumina heated to 350°C. for 7 hours, and 49% camphene (b.p. 145–156°C., m.p. 46–51°C., $[\alpha]_D^{19}+1.8$) was obtained.

(14) *The racemisation of camphene by the application of heat.* The above camphene was passed alone through a glass tube heated to 350°C., and the camphene thus obtained was of b.p. 154–158.5°C., m.p. 45.5–46.5°C., $[\alpha]_D^{16}+9.9$. Therefore, no change was seen.

(15) *The racemisation of isobornyl acetate by the Bertram Walbaum's method of hydration.* The writer, dissolving camphene $[\alpha]_D^{13.5}+64.40$ in

absolute alcohol after Kachler and Spitzer's method⁽⁴²⁾ and passing hydrogen chloride through the solution cooled with ice, obtained isobornyl chloride (m.p. 146–148°C., $[\alpha]^{8.5}_{D}$ −27.08 (C=3.46 in alcohol) in yield of 85%. It was heated to 70°C. with silver acetate in a sealed tube and there was obtained, in addition to a great quantity of camphene ($[\alpha]$+58.29), an extremely small quantity of ester ($[\alpha]^{8}_{D}$−5.71). On the other hand, isoborneol (m.p. 212–213°C., in a sealed tube) was treated both with acetic anhydride and potassium acetate for indefinite hours, and the following ester of isoborneol was obtained:

No.	React. hours	Ester of isoborneol				
		Yield (g.)	B.p.	$[\alpha]_D$	d^{20}_D	n^{20}_D
1	3	11	97—$99^{11\,mm}$	−46.73^{18} C = 4.46 in alcohol	0.9882	1.4649
2	2	11	80—82^{4}	−50.29^{18} C = 4.23 ,,	0.9867	1.4659
3	1	10.5	76—77^{3}	−51.98^{18} C = 5.05 ,,	0.9867	1.4623

By saponifying the esters 2 and 3, isoborneols $[\alpha]_D$−33.18 and $[\alpha]_D$ −34.10 were obtained respectively.

To isobornyl acetate (b.p. 76–77°C.^{3mm}, d^{20}_4 0,9876, n^{20}_D 1.4649, $[\alpha]^{20}_D$ −47.81), each of the 50% sulphuric acid, acetic acid, and the mixture of the two was added separately, and the reaction was excited at 50–60°C. As to the specific rotation of the ester, there was no change whatever in the former two cases, while a decrement was observed in the case of the acid mixture, the detail being as follows:

No.	Sample (g.)	Catalyser (g.)	React. hours	Reaction product				
				Yield (g.)	d^{20}_4	n^{20}_4	$[\alpha]^{23}_D$	Br_2 test
1	4	acetic acid 10	3	4	0.9884	1.4644	−47.80	—
2	4	50% H_2SO_4 0.4	3	4	0.9840	1.4644	−47.51	—
3	4	acetic acid 10 50% H_2SO_4 0.4	1/3	4	0.9833	1.4649	−45.62	+
4	15	acetic acid 38 50% H_2SO_4 1.5	4	15	0.9813	1.4631	−17.08	+

No.	Isobornyl acetate				
	Yield (g.)	B.p.	d^{20}_4	n^{20}_D	$[\alpha]_D$
1	3.5	71—$72^{2.5mm}$	0.9856	1.4648	−47.89
2	3.2	70—$71^{2.5}$	0.9856	1.4648	−47.43
3	3.2	71—$73^{2.5}$	0.9852	1.4648	−45.58
4	11.5	115—116^{3}	0.9813	1.4651	−19.01

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(42) *Ann.*, **200**, 345.

Of the reaction products of sample No. 4, camphene was estimated by the bromine absorption to be 1.3%.

Accordingly, the reaction products were distilled, and, using the earlier distillate after Balbiano's method,⁽⁴³⁾ formed a needle-shaped addition product (m.p. 185.5–186°C.) composed of mercuric acetate and camphene, and thus the presence of camphene was confirmed. When the reaction product was once more distilled after the elapse of a whole day, a distillate b.p. 80–91°C.^{3mm}, d_4^{20} 0.9832, n_D^{20} 1.4653 was obtained; while when the distillation was tried after the elapse of 20 days, the distillate was of b.p. 81–83.5°C.$^{3.5mm}$, d_4^{20} 0.9863, n_D^{20} 1.4651. Thus an extraordinary variation⁽⁴⁴⁾ in the boiling point was shown. The ester, which was distilled out in the rear, was saponified; and it was found that the isoborneol thus obtained had the following properties and had accompanied neither camphenehydrate nor camphene and others.

M.p.	$[\alpha]_D^{25}$ in alcohol	$[\alpha]_D^{25}$ in toluene	M.p. of *p*-Nitrobenzoate	Methoxy value of what was methylated with HCl and CH_3OH
211–212°C. (in a sealed tube)	−16.74	−8.79	129C.°	10.9

No trace of water was generated even when isoborneol was heated to 220°C. for half an hour, and no decolourisation of bromine water was observed.

VI. The Dehydration of Dimethylborneol. (1) *The dehydration of dimethylborneol with* $H_2SO_4 \cdot 3H_2O$. Dimethylcamphor was reduced with metallic sodium and alcohol and then treated with phthalic anhydride at 110–115°C. To 50 g. of the dimethylborneol (m.p. 45–50.8°C., $[\alpha]_D^{26}$ + 49.05) thus obtained, 2.5 c.c. of $H_2SO_4 \cdot 3H_2O$ was added, and the mixture was heated at 140–145°C. for 15 hours. The reaction product obtained was 43.4 g. It was fractionally distilled under reduced pressure and separated into the 1.5 g. unchanged alcohol (b.p. 82–95°C.^{5mm}) and 32 g. hydrocarbons (b.p. 48–82°C.^{5mm}). The hydrocarbons were again fractionally distilled under the normal pressure over metallic sodium 8 times repeatedly.

No.	B.P. °C.	yield %	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.		
						obs.	calc. $C_{12}H_{20}\vDash_1$	Δ
1	177–182	1	0.8510	1.4681	+14.17	53.51	52.75	0.76
2	182–185	5	0.8557	1.4702	+15.45	53.49	,,	0.74
3	185–186	11	0.8570	1.4715	+17.51	53.53	,,	0.78
4	186–187	17	0.8567	1.4721	+15.51	53.61	,,	0.86
5	187–188	24	0.8557	1.4731	+15.03	53.77	,,	1.02
6	188–190	6	0.8553	1.4744	+14.01	53.93	,,	1.18
7	190–191	8	0.8543	1.4760	+12.74	54.16	,,	1.41

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(43) Balbiano and Paolini, *Ber.*, **35** (1902), 2994; **36** (1903), 3575; **48** (1915), 394.

(44) Tetsusaku Ikeda, *Proc. Sci. Inst. Japan*, **7** (1928), 269; Yasuzí Fujita, *ibid.*, **7**, 1.

No.	Sample B.p. °C.	Wt. g.	Volatile neutral substance
1	177–187	29	21
2	188–191	35	25

Hydrocarbons were put to ozone oxidation in a chloroform solution.

The volatile neutral substances were separated from each other by fractional distillation.

No.	B. p. °C.	yield g.	d_4^{25}	n_D^{25}	Remarks
1	55– 87 $^{7\text{mm}}$	3.3	0.9320	1.4690	colourless
	87– 96	1.8	0.9614	1.4710	faint yellowish green
	96–120	9.0	0.9951	1.4736	faint yellowish green, viscous
2	48– 86	7.0	0.9026	1.4699	colourless
	86– 96	0.5	—	1.4714	faint yellowish green
	96–130	10.6	0.9881	1.4723	faint yellowish green, viscous

Fractions of similar properties were collected together and the mixture was fractionally distilled three times more.

Fraction	B. p. °C.	yield g.	d_4^{25}	n_D^{25}	M. R.		Appearance	Analyses obs.	
					obs.	calc.		C %	H %
1	51 – 56 $^{7\text{mm}}$	2.0	0.8803	1.4677	51.75	$C_{12}H_{20}F_1$ 52.75	colourless	84.77	11.67
2	56– 74	0.9	—	—	—	—	,,	—	—
3	74– 79	4.5	0.9290	1.4706	49.90	$C_{11}H_{18}O$ 48.61	,,	82.25	11.11
4	79– 90	3.3	0.9525	1.4727	48.85		,,	78.18	11.51
5	90–120	2.9	0.9772	1.4756			yellowish green	75.67	10.24
6	120–126	9.2	1.0124	1.4749	54.52	$C_{12}H_{20}O_2$ 55.41	,,	73.65	10.31
7	126–129	1.6	1.0124	1.4740	54.18		,,	71.55	10.66

Calc. for $C_{12}H_{20}$: C, 87.80; H, 12.20%.
$C_{11}H_{18}O$: C, 79.52; H, 10.84%.
$C_{12}H_{20}O_2$: C, 73.47; H, 10.21%.

Each of the fractions 5–7 decomposed by every distillation and an abundant quantity of acid remained every time. About these acids, some references will be made later. It is considered that fraction 1 is mainly composed of hydrocarbons, fraction 3 contains about 60% of the compound $C_{11}H_{18}O$, fraction 4 is mainly composed of the compound $C_{11}H_{18}O$, fraction 5 contains about 50% of the compound $C_{12}H_{20}O_2$ and the fraction 6 and 7 are both mainly composed of the compound $C_{12}H_{20}O_2$. $C_{12}H_{20}O_2$.

Fractions 3 and 4 were mixed together, and the mixture was fractionally distilled repeatedly to separate out a principal component as follows:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{9}$	M. R.	
				obs.	Calc. for $C_{11}H_{18}O$
72–73°C.$^{6\ mm}$	0.9473	1.4712	+27.06	48.87	48.61
			(C=2.62 in alcohol)		

Found: C, 79.94; H, 11.26. Calculated for $C_{11}H_{18}O$; C, 79.52; H; 10.84%.

Semicarbazone is formed with a great difficulty and it decomposes at 243.6–243.9°C. 2. g. of the oxygen compound described above was reduced with metallic sodium and alcohol, and a reaction product having the following properties was obtained.

B.g.	d_4^{25}	n_D^{25}	$[\alpha]_D^{25}$	M. R.	
				obs.	Calc. for $C_{11}H_{20}O$
82–86°C$^{6\ mm}$	0.9581	1.4831	+1.5	50.07	50 12
			(C=1.373 in alcohol)		

Found: C, 78.25; H, 12.05. Calculated for $C_{11}H_{20}O$; 78.57; H, 11.90%.

The phenylurethane of this substance is a white needle which melts at 147.6–148.7°C.

Fraction 6 was purified by carefully distilling it, and a yellowish green viscous liquid was obtained.

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{10}$	M.R.		
				obs.	Calc. for $C_{12}H_{20}O_2$	Δ
120–123°C$^{6\ mm}$	1.0087	1.4746	−6.87	54.60	55.44	−0.84
			(C=1.455 in alcohol)			

Found: C, 73.39; H, 10.41. Calculated for $C_{12}H_{20}O_2$: C, 73.47; H, 10.21%.

Moreover, the hydrocarbons described above was put to ozone oxidation in its solution in benzene, and the oxidation product thus obtained was distilled under reduced pressure. There was obtained a yellowish green and viscous compound $C_{12}H_{20}O_2$, whose rotatory power was of opposite sign as follows:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.		
				obs.	Calc. for $C_{12}H_{20}O_2$	Δ
112–114°C.$^{4\ mm}$	1.0166	1.4749	+38.91	54.27	55.44	−1.17

To 2 g. of the compound $C_{12}H_{20}O_2$, 20 c.c. of nitric acid of 1.29 specific gravity was added. The mixture was heated for 15 hours over a hot water bath and 0.8 g. of an acidic substance was obtained. When it was left alone for a long time, crystals of camphoric acid (m.p. 183°C.) was obtained; and after an analysis made on its silver salt, the following results were obtained: Found: Ag, 52.84. Calculated for $C_{10}H_{14}O_4Ag_2$: Ag, 52.15%.

A reaction product was obtained by reducing 10 g. of the compound $C_{12}H_{20}O_2$ with metallic sodium and alcohol. The reaction product was separated by steam distillation into a 3.7 g. volatile substance and a 3.4 g. unvolatile substance; and, by fractionally distilling the former, there was obtained a principal component of the following properties:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{15}$	M.R.		appearance
				obs.	Calc. for $C_{12}H_{24}O_2$	
140–143°C.$^{6\ mm}$	0.9907	1.4833	−13.31 (C=1.578 in alcohol)	57.71	58.47	faint yellow, viscous

Found: C, 72.18; H, 11.58. Calculated for $C_{12}H_{24}O_2$: C, 72.00; H, 12.00%.

As crystals precipitated out from the latter, they were recrystallised from ether and petroleum ether, and two different compounds were obtained. One of them, a colourless needle crystal (m.p. 82–83°C.), was insoluble in petroleum ether but soluble in both ether and alcohol. The other, a colourless needle (m.p. 114–115°C.) assembled in an asterisk form, was insoluble in petroleum ether and less soluble in ether than the former crystal. Crystal (I) (m.p. 82–83°C.). Found: C, 66.38; H, 11.62. Crystal (II) (m.p. 114–115°C.) C, 65.82; H, 11.63. Calculated for $C_{12}H_{24}O_2 \cdot H_2O$: C, 66.06; H, 11.93%.

These two kinds of crystals were dried at 80°C. under a reduced pressure and put anew to elementary analysis.

	Decrement of wt. by drying	Theoretical number	M.P. after drying
Crystal I (M.P. 82–83°C.)	7.95 %	8.26 %	83–84°C.
Crystal II (M.P. 114–115°C.)	8.41 %	,,	115,8–116.8°C

Crystal (I) Found: C, 71.95; H, 11.99. Crystal (II) C, 71.63; H, 12.41. Calc. for $C_{12}H_{24}O_2$ C, 72.00; H, 12.00%.

To the hydrocarbons (b.p. 185–190.5°C., d_4^{25} 0.8562, n_D^{25} 1.4726, $[\alpha]_D^{11}$ +12.66) described above, some 50% sulphuric acid and glacial acetic acid were added and the mixture was heated at 70–80°C. for 25 hours. A great majority was recovered as unreacted hydrocarbons, and, in addition to these, a small quantity of a polymerisation product was obtained as follows:

B.p.	n_D^{25}	$[\alpha]_D^{24}$	M. R.			
			obs.	Calc. for $C_{12}H_{20}\digamma_1$	obs.	Calc. for $C_{24}H_{38}\digamma_2$
161–162°C$^{5\ mm}$	1.4966	+14.83	106.6	105.5	106.1	103.3

Found: C, 87.95; H, 12.56. Calc. for $(C_{12}H_{20})_2$: C, 87.80; H, 12.20. Calc. for $C_{24}H_{38}$ C, 88.34; H, 11.66%.

The determination of molecular weight (by Rast's method)

obs.	$(C_{12}H_{20})_2$	$C_{24}H_{38}$
329.5	328	326

(2) *The dehydration of dimethylborneol with phosphorus pentoxide.* 10 g. dimethylborneol was taken drop by drop into a flask, which had

already contained 13 g. phosphorus pentoxide and 30 c.c. petroleum ether. When the generation of hydrogen chloride ceased, the content was left alone for several hours. Then it was thrown into ice water and the reaction product was extracted by the aid of ether. The ether was distilled off and the reaction product was fractionally distilled for several times, and there was obtained the following hydrocarbon.

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{25}$	M. R.	
				obs.	Calc. for $C_{12}H_{20}\vDash_1$
192—193°C.$^{2\,mm}$	0.8754	1.4765	-5.76	52.38	52.75

Found: C, 87.66; H, 12.13. Calculated for $C_{12}H_{20}$; C, 87.80; H, 12.20%.

When this hydrocarbon was put to ozone oxidation, a single oxidation compound $C_{12}H_{20}O_2$ was obtained as follows:

B.p.	d_4^{25}	n_4^{25}	$[\alpha]_D^{25}$	M. R.	
				obs.	Calc. for $C_{12}H_{20}O_2$
100—105°C.$^{2\,mm}$	1.0026	1.4765	-17.78	55.20	55.44

Found: C, 73.34; H, 10.49. Calculated for $C_{12}H_{20}O_2$: C, 73.47; H, 10.21%.

This compound, to be considered as a diketone, has decomposed during distillation, forming an acidic substance, which gave trans-camphoric acid (m.p. 174°C.) when recrystallised by the aid of ether and petroleum ether. Found: C, 29.29 H, 3.39 Ag, 52.96. Calculated for $C_{10}H_{14}O_4Ag_2$: C, 29.00; H, 3.38; Ag, 52.15%.

(3) *The dehydration of dimethylborneol with phthalic anhydride.* Dimethylborneol was dehydrated, heating it with phthalic anhydride, and the following hydrocarbon was obtained.

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{18}$	M. R.	
				obs.	Calc. for $C_{10}H_{20}\vDash_1$
179—196°C.$^{3\,mm}$	0.8556	1.4710	$+7.13$	53.44	52.75

Found: C, 87.69; H, 12.50. Calculated for $C_{12}H_{20}$: C, 87.80; H, 12.20%.

To our regret, the quantity of the sample being very small, we could not continue the research further.

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