

Studies on Camphor Series II.

By

Shigeru Komatsu.

(Received June 7, 1922.)

In the previous article¹, Komatsu and Masumoto stated that the formation of lævo-isocamphan from dextro and lævo-camphors respectively would be explained by assuming an intermediate formation of camphene, and the present investigation was undertaken in co-operation with K. Fujii, S. Yamaguchi and R. Nakai to present some evidence in support of this assumption and also to solve such an interesting and extraordinary case in stereochemistry.

As a matter of fact, dextro-borneol was generally attended by lævo-isoborneol in the course of the reduction of dextro-camphor with metallic sodium in alcohol solution, and the reduction at high temperature is favorable for the formation of the iso-compound.² It is, therefore, natural to assume that the large quantity of dextro-camphor by the catalytic hydrogenation at 180° would be transformed into lævo-isoborneol of unstable character toward dehydrating agents, and consequently such treatment facilitates the transformation of camphor into camphene.

In the transformation of dextro-camphor by the Grignard reaction into aryl derivatives of borneol, lævo-isobornyl compounds were only obtained as seen in J. Bredt's experiment.³

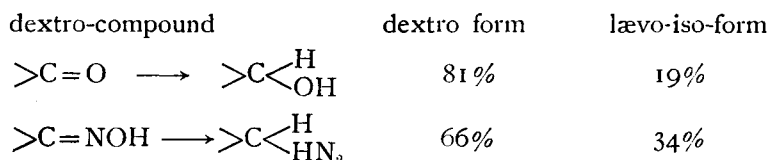
¹ First article; "Catalytic Reduction of Dextro-Camphor, I." Mem. Coll. Sci., Kyoto, **5**, 225 (1922).

² E. Beckmann, J. prak. Chem., (2). **55**, 31 (1897).

³ J. prak. Chem., (2). **98**, 96 (1918).

Fujii, applying the Reformatsky synthesis on dextro-camphor with ethyl, lævo-menthyl and dextro-bornyl esters of iodoacetic acid in absolute ether solution, using metallic magnesium as catalyser, has succeeded in isolating ethyl, menthyl and bornyl esters of bornyl acetic acid respectively. When these esters were saponified with barium hydroxide in alcohol solution, contrary to our expectation, the resulting acid was the same and identical lævo-isobornyl acetic acid.

Dextro-camphor oxime, by reduction with metallic sodium in absolute amyl alcohol solution, yielded simultaneously dextro- and lævo-iso-bornyl amines in a proportion of 65.9 : 34.1 in the reaction product as shown in Yamaguchi's experiment :



Such fruitful yield of lævo-isocompound in the case of the oxime reduction compared with that of the ketone reduction under the same conditions, might be a proper way to regard the influence of the NH_2 group of more positive character than the OH group on the asymmetric transformation of the carbonyl carbon atom in camphor molecule.

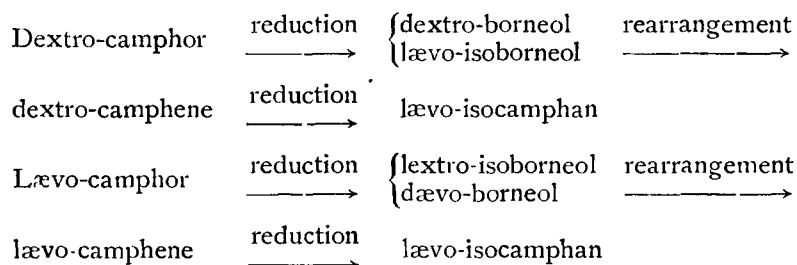
In order to prepare only dextro-bornyl amine, avoiding the formation of the iso-compound, dextro-borneol was passed with dry ammonia gas on thoria heated at 400° , Nakai's efforts, however, did not bring the expected result; a trace of an amine compound could be detected by the carbyl amine reaction of the reaction product and the major portion of the borneol used was observed to be transformed into dextro-camphene. Lævo-borneol, in the same manner, was transformed into lævo-camphene.

To prove the camphene was derived from bornyl amine formed temporarily by the interaction of borneol and ammonia, but not directly from borneol by the Wagner rearrangement, dextro-bornyl amine was passed on the heated thoria and was observed by Yamaguchi to decompose entirely into dextro-camphene and ammonia.

The striking result here is the formation of lævo-isocamphan from both dextro-camphene and lævo-camphene by the catalytic hydrogenation with reduced nickel and hydrogen.

Thus, the formation of lævo-isocamphan from both dextro- and

lævo-camphor by catalytic hydrogenation will be explained experimentally without any assumption as shown in the following scheme :



As to the existence of solid and liquid modifications in camphene and isocamphan the subject is now being studied in my laboratory and the result will be communicated in the next article.

I. SYNTHESIS OF LAEVO-ISOBORNYL ACETIC ACID AND ITS ESTERS.

BY

KITARO FUJII.

1. *Isobornyl Acetic Acid Ethylester*, $C_9H_{16}C \begin{cases} CH_2COOC_2H_5 \\ OH \end{cases}$.

It was prepared by the Reformatzky synthesis from 11 gm. metallic magnesium, 32 gm. dextro-camphor m.p. 177° , $[\alpha]_D = +44.22^\circ$ in alcohol solution, and iodo-acetic ester¹ of B.p. $83-85^\circ$ at 2.3 mm. pressure obtained from chloro-acetic acid ethyl ester² B p. $144-145^\circ$, $d_4^{25} = 1.005$ and potassium iodide. The organo-magnesium compound thus formed, was decomposed with ice-cooled dilute sulphuric acid and the generated ester was extracted with ether. The ether solution, after distilling off the solvent, was subjected to steam distillation to remove the unchanged camphor and iodo-acetic ester. The residue in the flask was extracted again with ether, and the solution, after being dried with anhydrous sodium sulphate was subjected to fractional distillation under reduced pressure. The fraction, boiling at $108-112^\circ$. 3 mm was collected, was a light yellow viscous liquid. The

¹ J. Chem. Soc., **65**, 482 (1894).

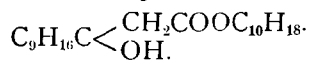
² Lieb. Ann., **188**, 218 (1877).

yield was 10.2 gm. (20.2%). The specific rotatory power in 98% alcohol solution and the chemical composition of the ester were determined:

Substance	Solvent	α_D^{25} in 2 dm. tube	$[\alpha]_D^{25}$
0.2014 gm.	25 cc.	- 23.8'	- 24.62°
0.1890 "	"	- 22.6'	- 24.91°
0.4231 "	"	- 51.8'	- 25.51°
0.4330 "	"	- 50.43'	- 24.82°
		mean	- 24.97°

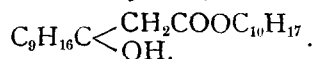
Substance	CO ₂	H ₂ O	C %	H %
0.1318	0.3471	0.1185	70.19	10.06
0.1058	0.2725	0.0937	70.24	9.91
0.0901	0.2292	0.0813	69.41	10.09
0.1672	0.4215	0.1476	68.77	9.90
		mean	69.65	9.99
		Calc. for C ₁₄ H ₂₂ O ₃	69.95	10.06

2. *Laevo-Bornyl Acetic Acid Laevo-Menthyl Ester,*



It was prepared by the interaction of 3.3 gm. dextro-camphor and 7.0 gm. iodo-acetic acid laevo-menthyl ester B.p. 110-130°, 4 mm. pressure, prepared from potassium iodide and chloro-acetic acid laevo-menthyl ester, in the presence of 1.2 gm. metallic magnesium, in 21 gm. absolute ether solution. The ester purified from menthol and iodo-acetic ester, was a syrupy substance, and was directly transformed by hydrolysis with barium hydroxide solution into free acid.

3. *Lævo-Isobornyl Acetic Acid Dextro-Bornylester,*



Keeping the principle of an asymmetric synthesis in mind, an attempt to produce a dextro-bornyl derivative was undertaken by employing iodo-acetic acid dextro-bornyl ester instead of lævo-menthyl ester. Contrary to the expectation the resulting substance was a derivative of the same lævo-isobornyl acetic acid.

The ester was prepared by the interaction of 5 gm. metallic magnesium, 14.3 gm. dextro-camphor and 30 gm. iodoacetic acid dextro bornyl ester B.p. 130–140°, 3–5 m.m. pressure, $[\alpha]_D^{17} = +34.6^\circ$ in 98% alcohol solution, obtained from 30 gm. chloroacetic dextro bornylester¹ $[\alpha]_D^{17} = +30.63^\circ$ purified by distillation under reduced pressure and 20 gm. potassium iodide.

The free ester was purified by recrystallization from the dilute alcohol solution and found to be melted at 196–197°. The yield was 7.12 gm. (22%).

Substance	CO ₂	H ₂ O	C %	H %
0.1164 gm.	0.3258 gm.	0.1075 gm.	76.22	10.34
0.1031 "	0.2879 "	0.0997 "	76.03	10.57
mean			76.13	10.46
Calc. for C ₂₂ H ₃₆ O ₃			75.80	10.45

Substance	Solvent alcohol	a_D^{18} 1 dm. tube	$[\alpha]_D^{18}$
0.1616 gm.	10 cc.	+ 16.6'	+ 17.12°
0.1322 "	10 "	+ 14.1'	+ 17.75°
mean			+ 17.44°

¹ C. R., 134, 609 (1902).

4. *Laevo-Bornyl Acetic Acid*, $C_9H_{16} < \begin{matrix} CH_2COOH. \\ OH. \end{matrix}$

1.5 gm. ethyl ester was saponified in 5 c.c. alcohol solution with 5 c.c. of 30% caustic potash solution, heating the mixture on a water bath for 4 hours, and the product was then treated with ether to remove the unchanged ester and other product. The aqueous solution acidified with ice-cooled dilute sulphuric acid, the generated free acid was extracted with ether in the Sudō-Kumagawa apparatus.

The free acid was more conveniently prepared from the ethyl ester by saponifying with saturated barium hydroxide solution; an excess of barium hydroxide was removed by means of carbon dioxide from the solution and the filtrate from the barium carbonate, was evaporated to dryness on a water bath. The barium salt, thus formed was decomposed with 10% sulphuric acid, and the free acid was extracted with ether.

To the ether solution, dry ammonia gas was passed, the ammonium salt precipitated, was separated from the solution and was transformed into silver salt which was analysed on drying in a vacuum desiccator and the results are shown with those of barium salt in the following table.

Sub-stance	CO ₂	H ₂ O	Ag	C %	H %	Ag %
0.1212 ^{gm.}	0.1994 ^{gm.}	0.0687 ^{gm.}	0.0428 ^{gm.}	44.87	6.35	35.33
0.0963 „	—	—	0.0362 „	—	—	37.5
Calc. for C ₁₂ H ₂₁ O ₂ Ag				45.14	6.00	34.82

Sub-stance	CO ₂	H ₂ O	BaSO ₄	C %	H %	Ba %
0.1303 ^{gm.}	0.1303 ^{gm.}	0.0931 ^{gm.}	—	54.17	6.66	—
0.2138 „	—	—	0.0804 ^{gm.}	—	—	22.14
Calc. for (C ₂₁ H ₂₂ O ₄) Ba				54.85	6.36	23.83

The barium salt of the same acid was also obtained from dextro-bornyl ester and laevo-menthyl ester respectively, by hydrolysing with

barium hydroxide in alcohol solution. The analytical results of the salt are shown in the following.

Sample	CO ₂	H ₂ O	BaSO ₄	C %	H %	Ba %
0.1916 ^{gm.} (salt from <i>d</i> -bornyl ester)	—	—	0.0795 ^{gm.}	—	—	24.35
0.0569 ,, (salt from <i>l</i> -menthyl ester)	0.0536 ^{gm.}	0.0333 ^{gm.}	0.0238 ,,	55.71	6.55	24.62

The specific rotatory power of the barium salt in the aqueous solution and of the free acid in 98% alcohol solution was determined:

I. Barium Salt.

Sub-stance	Remark	Solvent	α_D^{18} 2dm. tube	$[\alpha]_D^{18}$
0.2077 ^{gm.}	from ethyl ester	25 c.c. H ₂ O	— 10.21'	— 12.91°
0.0998	from <i>d</i> -bornyl ester	„	— 5'	— 10.51°
0.2138		„	— 12'	— 11.69°
0.1203	from <i>l</i> -menthyl ester	„	— 5.50'	— 9.53°

II. Free Acid.

Sub-stance	Remark	Solvent	α_D 1 dm. tube	$[\alpha]_D^{17}$
0.028 ^{gm.}	from ethyl ester	10 c.c. alcohol	— 2.4'	— 20.32°
0.2330 ,,	„ <i>d</i> -bornyl ester	25 c.c. „	— 27.6'	— 24.82°
0.1106 ,,		25 c.c. „	— 12.6'	— 25.62°
0.0399 ,,	„ <i>l</i> -menthyl ester	10 c.c. „	— 4'	— 19.85°

The free acid, soluble in water and alcohol, was observed to be decomposed, when heated with conc. sulphuric acid into an unsaturated compound.

The barium and ammonium salts were soluble in water, but its silver salt insoluble in water.

II. BORNYLAMINE AND ITS TRANSFORMATION INTO ISOCAMPHENE.

BY

SHOZO YAMAGUCHI.

For the preparation of bornylamine 16 gm. dextro camphor-oxime Mp. 118° were reduced following M. Forster's directions¹ with 20 gm. metallic sodium in 160 c.c. absolute isoamylalcohol solution. The reaction product acidified with hydrochloric acid, and isoamylalcohol was distilled off, whereas the amine hydrochloride crystallized out. By concentrating the mother liquor separated from the first crop, the amine salt was deposited. The total yield was 15 gm. The specific rotatory power of the two samples in absolute alcohol solution was determined, and the results were $[\alpha]_D^{17.5} = +16.4$ and $[\alpha]_D^{17.5} = -5.5$ respectively. The aqueous solution of an equimolecular mixture of bornylamine hydrochloride and silver dextro camphor sulphonate, filtered silver chloride off, was evaporated on a water bath to dryness and the resulting amine camphor sulphonate was recrystallized from anhydrous acetone solution to separate the dextro bornylamine salt from laevo-isobornylamine salt by the difference of their solubilities in the solvent. The purity of the isolated substance was determined by measuring the rotatory power of 10 c.c. aqueous and absolute alcohol solutions. As seen in the following table, to attain desired purity of dextro-bornylamine dextrocaphor sulphonate, the crystallization should be repeated for seven times.

No. of time	Substance	Solvent	a_D^{18}	$[\alpha]_D^{18}$
5	0.1919 gm.	water	+ 27'	+ 23.5°
6	0.2755 "	"	+ 41'	+ 24.8°
7	0.1451 "	"	+ 22.5'	+ 25.5°

¹ J. Chem. Soc., 73, 386 (1898).

No. of time	Substance	Solvent	α_D^{18}	$[\alpha]_D^{18}$
7	0.2107 gm.	absolute alcohol	+ 47.8'	+ 37.5°
8	0.1914 gm.	„	+ 43.0'	+ 37.4°

For confirmation, the contents of the sulphur and nitrogen in the compound were determined :

0.1421 gm. substance gave 0.0866 gr. BaSO_4 8.40% S

theory requires for $\text{C}_{20}\text{H}_{34}\text{SNO}_4$ 8.30% S

0.1010 gm. substance gave 4.00% N by the Kjeldahl

theory requires for $\text{C}_{20}\text{H}_{34}\text{SNO}_4$. 3.63% N.

The camphor-sulphonate with caustic potash solution, was hydrolysed, the generated free amine was extracted with ether, which was transformed into hydrochloride.

A solution of 0.1582 gm. substance in absolute alcohol and made up to 10 cc. $\alpha_D^{18} = +23.5'$ in 10 cm. tube ; whence $[\alpha]_D^{18} = +24.7^\circ$.

0.1246 gm. substance gave 0.094 gm. AgCl

found calc. for $\text{C}_{10}\text{H}_{20}\text{NCl}$

Cl 18.20 18.60

The authors' substance showed the higher specific rotatory power for 1.5° compared with Forster's, which might be considered to indicate the purity of the former.

To calculate the proportion of both dextro-bornylamine and laevo-isobornylamine formed simultaneously in the reducing product of the oxime, 1.5 gm. dextro-camphor-oxime was reduced as above mentioned, and 1.58 gm. hydrochloride of mixed amines were obtained which showed $\alpha_D = -2$. in 1 dm. tube of its 50 c.c. absolute alcohol solution ; whence $[\alpha]_D = -1.05^\circ$.

Hence the percentage was :

d-bornylamine 65.9%

l-isobornylamine 34.1%

where *d*-bornylamine hydrochloride

$[\alpha]_D = +24.7^\circ$ (Auteurs' data).

l-isobornylamine hydrochloride

$[\alpha]_D = -44.2^\circ$ (Forsters' data).

12 gm. of the bornylamine hydrochloride of $[\alpha]_D = +16.4^\circ$ dissolved in water, alkalinised with caustic soda and then subjected to steam

distillation to get the amine in free state, and 6 gm. solid and 4 gm. liquid substance were obtained. Both solid and liquid forms separated mechanically, confirmed to be a mixture of bornylamine and isobornylamine in different proportions, by the determination of the rotatory power in absolute alcohol solution and of the nitrogen contents of their hydrochlorides:

Form	Substance	Solvent	Length of tube	α_D^{18}	$[\alpha]_D^{18}$
Liquid	0.2720 gm	10 c.c. abs. alcohol	1 dm.	+ 27'	+ 16.5°
Solid	0.2377 "	10 c.c. "	"	+ 28'	+ 19.6°

0.1005 gm. gave 7.81% N (by the Kjeldahl method).

Liquid { dextro-form 88%
laevo-iso-form 12%

0.1248 gm. gave 7.57% N (by the Kjeldahl method).

Solid { dextro form 92%
laevo iso form 8%

O. Wallach¹ has observed that when bornylamine heated at 200–210° with acetic acid anhydride was decomposed into camphene and ammonia. The question will naturally be developed from the idea of reversibility that such chemical change might be realized by the catalytic action of thoria or alumina on bornylamine, 7.5 gm. bornylamine m.p. 157.5–158° $[\alpha]_D^{18} = \frac{37.5 \times 100}{0.2998 \times 60 \times 10} = +42.1^\circ$, consisting of 96.2% dextro-bornylamine 3.8% laevoisobornylamine, were passed on thoria heated at 400°, and yielded 5.5 gm. liquid product.

Dextro-camphene was separated from the reaction product, after acidifying with hydrochloric acid, by steam distillation, and extracted with ether. The ether was distilled off from the solution, and the residue was fractionated under ordinary pressure and collected, the fraction boiling at 160–167°. The yield was 2 gm. It was again distilled on metallic sodium and obtained the fraction boiling at 153–167° with a yield of 1 gm.

The specific rotatory power in absolute alcohol solution, density, index of refraction and chemical composition were determined.

¹ Lieb. Ann., 269, 349 (1892).

Substance	α_D^{18} 1 dm. tube	$[\alpha]_D^{18}$	d_4^{25}	n_D^{25}	M. R.
0.1949	+ 7'	5.9°	0.8591	1.4750	44.63

Substance	CO ₂	H ₂ O	C %	H %
0.0986 gm.	0.3132 gm.	0.1039 gm.	86.63	11.83
0.1173 „	0.3531 „	0.1173 „	86.84	11.85
		mean	86.74	11.84
	Calc. for	C ₁₀ H ₁₆	88.15	11.85

III. CATALYTIC PREPARATION OF CAMPHENE AND ISOCAMPHAN.

BY

RISABURO NAKAI.

An attempt to prepare bornylamine by the catalytic process proposed by Professor Paul Sabatier¹ from bornyl ethyl ether or bornyl acetate with ammonia was tried but to no purpose.²

To obtain the amine by the catalytic method from borneol and ammonia, 110 gr. dextro-borneol m.p. 203-204°, $[\alpha]_D^{20} = \frac{19' \times 10}{0.2093} = +15^\circ.13$ in alcohol solution (68.76% *d*-borneol 31.24% *l*-isoborneol³) prepared from dextro-camphor m.p. 177°, $[\alpha]_D^{20} = \frac{51 \times 10}{0.2033} = +41^\circ.81$, by reduction with metallic sodium, were passed with dry ammonia gas on thoria heated at 400°, and 103 gr. of the reaction product of

¹ La Catalyse en Chimie Organique, 1920, p. 287.

² Oppenheim und Precht, Ber. D. Chem. Ges., 9, 325 (1876); N. Menshutkin, Ibid., 15, 2512 (1882); J. Nef, J. Amer. Chem., 26, 1549 (1904).

³ E. Beckmann, J. prak. Chem., (2), 55, 31 (1897).

dark-yellow liquid were obtained. The product after being acidified with hydrochloric acid, was subjected to steam distillation and the acidic residue was alkalinized with caustic soda and distilled off a basic substance with steam. The basic distillate was extracted with ether and the ether solution having distilled off the ether, there remained a few milligrams of solid substance which gave the carbyl amine reaction, indicating the presence of a primary amine compound.

The first distillate, the main part of the reaction product, was distilled under ordinary pressure and collected the fraction 130–350° which amounted to 60 gr.

The fraction was fractionated under 764 mm. pressure 5 times and the following result were obtained.

Fraction	Yield	Remark
135–150°	2.5 gr.	colourless
150–158°	3.9 "	"
158–162°	9.5 "	light-yellow
162–166°	4.8 "	"
166–173°	7.3 "	"
173–180°	3.5 "	yellow
180–205°	4.7 "	yellowish-brown
above 205°	13.7 "	dark-brown. containing borneol
	49.9 "	
loss	10.1 "	

The optical rotatory power of the alcohol solution, the density the index of refraction and the elementary analysis of each fraction were determined, and the results are shown in the following table:

Fraction	Substance	α_D^{20} , 1 dm. tube	$[\alpha]_D^{20}$	d_{40}^{25}	n_D^{25}
135–150°			0	0.8736	1.4692
150–158°	0.2037 gr.	+ 11'.00	+ 9°.00	0.8825	1.4772
158–162°	0.1998 "	+ 12'.00	+ 10°.01	0.8630	1.4689

Fraction	Substance	a_D^{20} , 1 dm. tube	$[\alpha]_D^{20}$	d_{40}^{25}	n_D^{25}
162-166°	0.1957 gr.	+ 10'.00	+ 8°.52	0.8653	1.8080
166-173°	0.2064 „	+ 5'.25	+ 4°.24	0.8869	1.4747
173-180°	0.2151 „	+ 10'.25	+ 7°.94	0.8951	1.4797
180-205°	0.2075 „	+ 22'.00	+ 17°.67	0.9016	1.4807

Fraction	Substance	CO ₂	H ₂ O	C %	H %
135-150°	0.1113 gr.	0.3432 gr.	0.1151 gr.	84.10	11.57
	0.0932 „	0.2876 „	0.0956 „	84.16	11.48
	0.1012 „	0.3113 „	0.1031 „	83.89	11.40
	mean			84.05	11.48
150-158°	0.1145 „	0.3561 „	0.1186 „	84.86	11.60
	0.1030 „	0.3202 „	0.1086 „	84.78	11.80
	0.1172 „	0.3663 „	0.1208 „	85.24	11.53
	mean			84.96	11.64
158-162°	0.1082 „	0.3463 „	0.1139 „	87.33	11.79
	0.1134 „	0.3654 „	0.1204 „	87.88	11.88
	0.1266 „	0.4059 „	0.1346 „	87.43	11.90
	mean			87.55	11.85
162-166°	0.1070 „	0.3389 „	0.1123 „	86.38	11.74
	0.1196 „	0.3810 „	0.1232 „	86.88	11.53
	0.0895 „	0.2844 „	0.0924 „	86.67	11.55
	mean			86.64	11.61
166-173°	0.1069 „	0.3208 „	0.1085 „	83.68	11.36
	0.1107 „	0.3395 „	0.1109 „	83.63	11.21
	0.1068 „	0.3284 „	0.1081 „	83.86	11.33
	mean			83.72	11.30

Fraction	Substance	CO ₂	H ₂ O	C %	H %
173-280°	0.1054 gr.	0.3177 gr.	0.1043 gr.	82.25	11.08
	0.1149 „	0.3477 „	0.1123 „	82.53	10.94
	0.1131 „	0.3426 „	0.1103 „	82.65	10.92
	mean			82.48	10.98
180-205°	0.1042 „	0.3094 „	0.1012 „	81.02	10.87
	0.1077 „	0.3213 „	0.1037 „	81.36	10.78
	0.1143 „	0.3403 „	0.1104 „	81.20	10.81
	mean			81.19	10.82

As seen in the above tables, the first fraction B. p. 135-150°, consists of an aromatic hydrocarbon and the last fraction B. p. 180-205°, a mixture of borneol and a small quantity of hydrocarbon C₁₀H₁₆, which showed a higher specific rotatory power than that of the borneol used indicating that the lævo-isoborneol associated with dextro-borneol, was partially removed by the catalytic action of thoria and transforming itself into camphene. The third fraction B. p. 158-162°, consisting of pure camphene, requires C=88.15% ; H=11.85%, which was formerly obtained by M. Pelonze,¹ G. Kachler,² O. Wallach³ and N. Zelinsky & T. Zelikow² from borneol by the action of various dehydrating agents.

The liquid dextro-camphene, B. p. 158-162°, thus obtained was distilled on metallic sodium, and the fraction B. p. 158-168°, the colourless liquid, was observed to possess the chemical composition and physical properties as shown in the following table:—

Substance	CO ₂	H ₂ O	C %	H %
0.1080 gr.	0.3479 gr.	0.1139 gr.	87.86	11.80
0.1042 „	0.3366 „	0.1094 „	88.10	11.75
mean			87.98	11.78

¹ Lieb. Ann., 40, 326 (1841); C.R., 11, 365 (1840).

² Lieb. Ann., 164, 75 (1872).

³ Lieb. Ann., 230, 225 (1885).

⁴ Ber. D. Chem. Ges., 34, 3249 (1901).

Substance	α_D^{20} , 1 dm. tube	$[\alpha]_D^{20}$	d_{40}^{25}	n_D^{25}	M.R.
0.2068 gr.	+ 12'	+ 9°·96	0.8613	1.4689	43.98

In another experiment, two fractions (I) B.p. 155–157° and (II) B.p. 158–160° which were considered to consist of liquid camphene, on standing from two weeks at ordinary temperature, after being treated with metallic sodium, were observed to solidify. The crystals obtained from the first fraction, melted at 50° and showed the specific rotatory power $[\alpha]_D^{20} = +17^{\circ}\cdot61$ in ethyl alcohol solution.

The author has obtained lævo-camphene on applying the same treatment to lævo borneol as to the dextro compound; using 43 gr. lævo-borneol, m.p. 202.5–203°, $[\alpha]_D^{20} = \frac{45' \times 10}{0.2027} = -37^{\circ}\cdot01$, 41 gr. of the reaction product were obtained, and this was purified by fractional distillation 4 times under 757–758 mm. pressure :

Fraction	Yield	Remark
Below 150°	1.0 gr.	light yellow
150–157°	4.9 "	"
157–163°	9.4 "	yellow
163–166°	2.5 "	"
166–173°	1.5 "	"
	19.3 "	

Each fraction was redistilled with metallic sodium, and the following results were obtained :

Fraction	Yield	Remark
140–154°	2.1 gr.	colourless
154–158°	5.5 "	"
158–163°	7.4 "	"
163–170°	2.6 "	"
above 170°	0.7 "	yellow
	18.3 "	
loss	1.0 "	

The analytical results and physical constants of the two fractions, (I) B.p. 154–158°; (II) B.p. 158–163°, are shown in the following table:

Fraction	Substance	CO ₂	H ₂ O	C %	H %
154–158°	0.1045 gr.	0.3323 gr.	0.1087 gr.	86.72	11.64
158–163°	0.1054 „	0.3392 „	0.1097 „	87.77	11.65

Fraction	Substance	α_D^{20} , 1 dm. tube	$[\alpha]_D^{20}$	d_{40}^{25}	n_D^{25}	M.R.
154–158°	0.2040 gr.	– 8'.0	– 6°.54	0.8645	1.4674	43.73
158–163°	0.20475 „	– 4'.5	– 3°.66	0.8619	1.4684	43.94

Camphene	B.p.	$[\alpha]_D^{20}$	d_{40}^{25}	n_D^{25}	M.R.
from <i>d</i> -borneol	158–168°	+ 9°.96	0.8618	1.4689	43.98
<i>l</i> -borneol	158–163°	– 3°.66	0.8619	1.4684	43.94
<i>d</i> -bornylamine (by S. Yamaguchi)	150–167°	+ 5°.90	0.8591	1.4750	44.63

The fraction B.p. 158–163° was observed to consist of pure camphene found in the corresponding fraction obtained from dextro-borneol. The fact that camphene was derived from bornylamine as observed by S. Yamaguchi, has induced the author to consider that the formation of camphene from borneol by the catalytic action of thoria in the atmosphere of ammonia gas would be explained easily, admitting the intermediate formation of bornyl amine.

Professor P. Sabatier and Senderens¹ have obtained liquid hydrocarbon C₁₀H₁₈ B.p. 164–165°, d_{40}^{25} =0.849 by the catalytic reduction of camphene, N. Zelinsky² and Nametkine and Abakoumovskaia,³ however,

¹ C.R., **132**, 1254 (1901).

² F. W. Semmler: Die Ätherischen Öle, II., p. 70 (1906).

³ P. Sabatier: La Catalyse en Chimie Organique, p. 182, (1920).

have reported that solid camphan was obtained from camphene by the same process.

The author has transformed camphene following Professor P. Sabatier's directions into liquid isocamphan; 3 gr. dextro camphene B.p. 158-168° purified by distillation on metallic sodium, was reduced with nickel and hydrogen, and 1.5 gr. of reaction product were obtained which was purified by distillation, and of the fraction B.p. 164-167° the optical rotatory power, the density, the index of refraction and the chemical composition were determined.

Substance	CO ₂	H ₂ O	C %	H %
0.0943 gr.	0.2994 gr.	0.1154 gr.	86.59	13.69
0.1013 „	0.3220 „	0.1227 „	86.69	13.55
mean			86.64	13.62
Calc. for C ₁₀ H ₁₈			86.87	13.13

Substance	α_D^{20} , 1 dm. tube	$[\alpha]_D^{20}$	d_4^{25}	n_D^{25}	M.R.
0.20795 gr.	- 4'.5	- 3°.61	0.8386	1.4534	44.56

Both fractions (I) B.p. 154-158°; (II) B.p. 158-163° of laevo-camphene, obtained from laevo-borneol, were reduced by the catalytic process, and 1 gr. the purified substance B.p. 160-164°, 750 mm. from 2 gr. fraction (I) and 1 gr. B.p. 160-163°, 1.5 gr. isocamphan B.p. 163-165°, 750 mm. from 3 gr. fraction (II) were isolated. Of each purified substance, the physical properties and the chemical composition were determined:

Fraction	Substance	CO ₂	H ₂ O	C %	H %
160-164° (from I.)	0.10505 gr.	0.33415 gr.	0.1270 gr.	86.77	13.53
163-165° (from II.)	0.1096 „	0.34775 „	0.1317 „	86.53	13.45
Calc. for C ₁₀ H ₁₈				86.87	13.13

Fraction	Sub- stance	a_D^{20} , 1 dm. tube	$[\alpha]_D^{25}$	n_D^{20}	n_D^{25}	M.R.
160-164° (from I.)		0	0	0.8460	1.4451	43.47
163-165° (from II.)	0.2039 gr.	- 4'	- 3°.27	0.8440	1.4492	43.92

The interesting results here obtained are that the same lævo iso-camphan was derived from dextro- and lævo-camphenes respectively by catalytic hydrogenation.

May, 1922, Laboratory of Organic Chemistry.