

Studies on Camphor Oils, V. On the Sesquiterpenes and Sesquiterpenalcohols of the Japanese Camphor Oil.¹

By

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Since the existence of sesquiterpenes such as bisabolene² and cadinene³, in camphor oil was first noticed by the chemists of Schimmel & Co., similar researches were undertaken by many others. In 1913 Semmler and Rosenberg⁴ reported the isolation of a new bicyclic sesquiterpene and a bicyclic sesquiterpenalcohol from the so-called camphor blue oil, and named them sesquicamphene and sesquicamphenol respectively. Dr. K. Kafuku⁵, on the other hand, observed the presence of a sesquiterpenalcohol which was deemed by him to have tricyclic properties.

Crude sesquiterpenes and sesquiterpenalcohols, used in this experiment were prepared from the high boiling fraction of camphor oil by treating it with metallic sodium under a reduced pressure and these showed the following properties :

- 1 This paper was read before the Chemical Society of Japan on April 7, 1924. But as the author had to go to Formosa soon afterwards, its publication was greatly delayed, and while in press a paper on the same subject by Z. Ruzicka and M. Stoll appeared in the *Helv. chim. Acta.*, VII, 260 (1924).
- 2 Bericht von Schimmel & Co., Oktober 24 (1909).
- 3 *Ibid.*, April 9 (1889).
- 4 F. W. Semmler und I. Rosenberg: *Ber. D. chem. Ges.*, 46, 768 (1913).
- 5 K. Kafuku: *Kogyo-Kwagaku Zasshi* (*Jour. chem. Ind. (Tokyo)*), 19, 815 (1916).

	d	n_D	α_D (1 dm.)
Crude sesquiterpene	$0.9338 \left(\frac{11}{4} \right)^\circ$	1.5138(10.5°)	+22.55°(12°)
Crude sesquiterpenalcohol	$0.9637 \left(\frac{13.5}{4} \right)^\circ$	1.5078(13.5°)	+45.50°(17°)

And from these crude materials the author was able to isolate one bicyclic sesquiterpene and two bicyclic sesquiterpenalcohols having the physical properties given below :

Boiling point	Chemical composition	d	n_D	M.R.	α_D	$[\alpha]_D$	Authors
129—133° (8m.m.)	C ₁₅ H ₂₄	0.9015(20°)	1.50058(20°)	66.61	+ 3.0	—	F. W. Semmler und I. Rosenberg ¹
140—141°(15m.m.)	C ₁₅ H ₂₄	0.9025 $\left(\frac{20}{4}\right)^\circ$	1.5050(20°)	66.74	+25.30	—	K. Ono
159—162° (7m.m.)	C ₁₅ H ₂₆ O	0.9513	—	68.39	—	—	F. W. Semmler und I. Rosenberg ¹
130—133° (5m.m.)	C ₁₅ H ₂₆ O	0.9790(18°)	1.5035(18°)	66.90	—	—	K. Kafuku ²
160—163°(10m.m.)	C ₁₅ H ₂₆ O	0.9595 $\left(\frac{14}{4}\right)^\circ$	1.5075(14°)	68.239	—	+49.30°	K. Ono
170—174°(10m.m.)	C ₁₅ H ₂₆ O	0.9692 $\left(\frac{14}{4}\right)^\circ$	1.5084(14°)	68.388	—	+66.58°	K. Ono

As may be seen in the above table, the refractive index and the optical rotation of the sesquiterpene isolated by the author are greater than those found by Semmler, but the sesquiterpenalcohol boiling at 160—163° (10 m.m.) is in perfect agreement with Semmler's sesquicamphenol (B. p. 159—162° (7 m.m.)). The other sesquiterpenalcohol boiling at 170—174° (10 m.m.) may perhaps be a new compound. The author could not find such a tricyclic sesquiterpenalcohol as was reported by K. Kafuku².

Two sesquiterpenalcohols were found to have the same composition, C₁₅H₂₆O, and toward Denigès reagent and acetic anhydride behaved as tertiary alcohols. From the molecular refraction they are inferred to be bicyclic.

A sesquiterpene with the boiling point 133—136° (12 m.m.) was obtained by treating the sesquiterpenalcohol boiling at 160—163° with potassium bisulphate. Its physical properties were determined as follows :

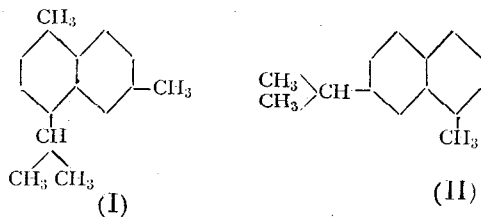
Boiling point	d	n_D	M.R.	α_D	$[\alpha]_D$	Authors
125—130° (7m.m.)	0.9138(20°)	1.50895(20°)	66.61	+50.0°	—	F. W. Semmler und I. Rosenberg
133—136°(12m.m.)	0.9138 $\left(\frac{16}{4}\right)^\circ$	1.5104 (16°)	66.581	—	+15.22°	K. Ono

1 Loc. cit.

2 Loc. cit.

These properties, except the optical rotatory power well agree with those of Semmler's sesquiterpene. It may possibly be a mixture of isomers, but not a simple compound. Another sesquiterpene boiling at 139—142° (10 m.m.) was analogously obtained from the higher boiling sesquiterpenalcohol. Its molecular refraction was determined to be 67.271 against the calculated value 66.137. It appears therefore evident that the new sesquiterpene thus formed has a conjugated double linking.

Recently Ruzicka and his collaborators¹ succeeded in dehydrogenating sesquiterpene and sesquiterpenalcohol by boiling them with sulphur and found that it always resulted in the production of either of two different naphthalene hydrocarbons. The product from cadinene, calamene, calamenol, zingiberene and farnesol was named "cadalin" (I), while that from eudesmol, eudesmene and selinene, which by the treatment lose a methyl group in the form of methyl mercaptane "eudalin" (II). Thus they classified the sesquiterpenes and sesquiterpenalcohols into two divisions, that is, the cadinene type and the eudesmol type.



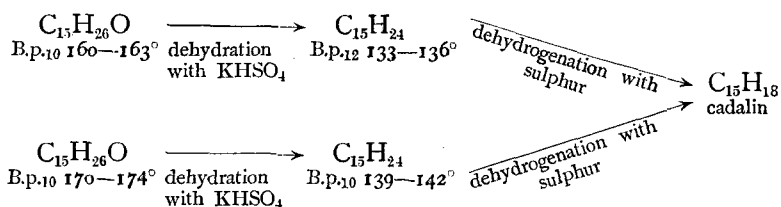
It will be very interesting to ascertain whether cadalin or eudalin is produced from the above sesquiterpene and sesquiterpenalcohol. L. Ruzicka and M. Stoll² have stated in their 7th. report on "Höhere Terpenverbindungen" as follows:

"Zum Eudesmoltypus zählen wir jetzt folgende Verbindungen: das Eudesmol, das Selinen, das α -Santalol (und α -Santalol) und einen der in Campheröl enthaltenen Sesquiterpenalkohole."

It was therefore expected that the dehydrogenation product of my sesquiterpenalcohol would be eudalin. The result of the experiment, however, turned out quite differently.

¹ L. Ruzicka u. J. Meyer: *Helv. chim. Acta.*, **4**, 505 (1921); L. Ruzicka, J. Meyer u. M. Mingazzini: *Ibid.*, **5**, 369 (1922).

² *Helv. chim. Acta.*, **5**, 930 (1922).



Sesquiterpene in camphor oil was also easily transformed into cadalin when treated with sulphur.

It is now confirmed that sesquiterpene* and sesquiterpenalcohol separated by the author have the same skeleton as the naphthalene compound. The two alcohols seem to be both tertiary sesquiterpenalcohol and isomeric with each other just as the tertiary alcohol of the composition $\text{C}_{10}\text{H}_{18}\text{O}$ exists in the form of two isomers, terpineol-1¹ and α -terpineol².

Experimental Part

1. Materials used in the Experiment.

A fraction of Japanese camphor blue oil boiling at $120-190^\circ$ (13—14 m.m.) was used in the experiment. It was a dark greenish viscous oil and had the following physical properties:

$d\left(\frac{8}{4}\right)^\circ$	n_D°	$[\alpha]_D^{19.5^\circ}$	Acid Value	Ester Value	Saponification Value ³ after acetylation
0.9635	1.5148	+49.26°	Nil.	4.534	124.559

500 grams of the above oil were heated with 35 grams of metallic sodium for several hours under 7—8 m.m. pressure at a temperature below 70° on a sand bath, and distilled under reduced pressure, whereupon about 175 grams of a crude sesquiterpene fraction were obtained. The residue of the distillation was cautiously decomposed with water and extracted with ether, and from the extract about 277 grams of a crude sesquiterpenalcohol fraction were obtained.

2. Research of Sesquiterpene.

The composition of the crude sesquiterpene fraction was determined by analysts.

- 1) 0.2161 gr. substance gave 0.6640 gr. CO_2 and 0.2164 gr. H_2O .
- 2) 0.1902 gr. substance gave 0.5820 gr. CO_2 and 0.1874 gr. H_2O .

¹ E. Gildmeister: Die ätherischen Öle, Bd. II, 482 (1913).

² Bericht von Schimmel & Co., April 9(1888); April 8(1889); Oktober 15(1903).

³ E. Gildmeister: Die ätherischen Öle, Bd. I, 597(1910).

	(I)	(II)
Carbon	83.80%	83.49%
Hydrogen	11.12	10.95
Oxygen	5.08	5.56

As the crude sesquiterpene fraction was thus found to contain about 5% of oxygen, it was again treated with metallic sodium under 5—6 m.m. pressure, and sesquiterpenes, having the following properties and composition were produced :

$d_{4}^{19^{\circ}}$	$n_{D}^{19^{\circ}}$	$\alpha_{D} [1dm.]$
0.9058	1.5041	+24.750°

0.2398 gr. substance gave 0.7745 gr. CO₂ and 0.2475 gr. H₂O.

	Found	Calc. (C ₁₅ H ₂₄)
Carbon	88.11%	88.15%
Hydrogen	11.46	11.85
Oxygen	0.43	0

60 grams of the sesquiterpene thus purified were fractionated by distilling it under 15—16 m.m. pressure on metallic sodium, and the following fractions were collected :

Fraction	Yield	$d_{4}^{20^{\circ}}$	$n_{D}^{20^{\circ}}$	M.R.
up to 128°	4.8 ^{grs.}	0.8879	1.5011	67.702
128—135°	6.7	0.8993	1.5020	66.951
135—141°	36.1	0.9023	1.5036	66.740
141—145°	4.8	0.9051	1.5054	66.895
145—150°	4.2	0.9065	1.5070	66.969
150—160°	1.4	0.9057	1.5071	67.040

Each fraction was analysed :

Fraction	Substance	CO ₂	H ₂ O	C%	H%
up to 128°	0.1213 ^{gr.}	0.3936 ^{gr.}	0.1301 ^{gr.}	88.48	11.99
128—135°	0.1536	0.4955	0.1580	87.97	11.50
135—141°	0.1810	0.5827	0.1849	87.79	11.42
141—145°	0.1047	0.3373	0.1123	87.85	11.99
145—150°	0.2008	0.6472	0.2083	87.89	11.60
150—160°	0.1332	0.4367	0.1428	88.57	11.98
Calc. for C ₁₅ H ₂₄				88.15	11.85

The fraction boiling at 135—141° was once again subjected to fractional distillation on metallic sodium under reduced pressure and a sesquiterpene having the following properties was produced:

Boiling point 140—141° (15 m.m.) $d\left(\frac{20}{4}\right) = 0.9025$ $n_D^{20} = 1.5050$

M.R. 66.740 Calc. for C₁₅H₂₄F₂ 66.153 $\alpha_D(\text{1dm.}) + 25.30^\circ$.

This substance was analysed with the following results:

Substance	CO ₂	H ₂ O	C%	H%
0.1217 ^{gr.}	0.3957 ^{gr.}	0.1244 ^{gr.}	88.62	11.42
0.1410	0.4562	0.1442	88.23	11.43
Mean			88.42	11.42
Calc. for C ₁₅ H ₂₄			88.15	11.85

10.8 grams of the sesquiterpene were heated with 5.2 grams of sulphur for 8 hours on an oil-bath at 180—230° according to L. Ruzicka's direction,¹ and then distilled under reduced pressure. About 3.5 grams of the fraction boiling at 147—162° (14 m.m.) were collected. The oil thus produced was treated with an alcoholic picric acid solution, when a dark orange-coloured precipitate separated out. It was pressed on a tile and purified by recrystallizing three times from alcohol. It forms small orange-coloured needles, melting at 114—115°, giving the following results on analysis:

¹ Loc. cit.

0.1342 gr. substance gave 0.2883 gr. CO_2 and 0.0604 gr. H_2O .

	Found	Calc. ($C_{21}H_{21}O_7N_3$)
Carbon	58.58%	59.02%
Hydrogen	5.08	4.92

The oil separated by treating the picrate with strong ammonia water, was extracted with ether and washed with a dilute sodium hydroxide solution and water successively. After distilling off the ether, a small quantity of viscous oil (B.p. 156—158° (11—12 m.m.), n_D^{16} 1.5836) was obtained.

0.0836 gr. substance gave 0.2767 gr. CO_2 and 0.0659 gr. H_2O .

	Found	Calc ($C_{15}H_{18}$)
Carbon	90.25%	90.84%
Hydrogen	8.82	9.16

The yellowish crystalline substance obtained by treating the above hydrocarbon with an alcoholic trinitroresorcine solution was recrystallized from alcohol, and small yellowish needles melting at 138—139° were obtained.

From the above results it seems evident that the hydrocarbon produced by the dehydrogenation of sesquiterpene in camphor oil with sulphur is identical with Ruzicka's cadalin.

3. Research of Sesquiterpenalcohols.

The crude sesquiterpenalcohol was analysed with the following results:

0.1507 gr. substance gave 0.4487 gr. CO_2 and 0.1484 gr. H_2O .

	Found	Calc. ($C_{15}H_{26}O$)
Carbon	81.09%	81.01%
Hydrogen	10.94	11.78

From the above analysis this crude material appears to consist mostly of sesquiterpenalcohol $C_{15}H_{26}O$. 150 grams of the substance were subjected to fractional distillation under 8—9 m.m. pressure.

1 Loc. cit.

Fraction	Yield
up to 150°	3.5 ^{gms.}
150—157°	7.0
157—167°	94.6
167—175°	23.5
175—187°	8.6

Both the fractions boiling at 157—167° and at 167—175° were repeatedly fractionated by distilling them under reduced pressure and the following two principal fractions were collected.

(a) Boiling point 160—163° (10 m.m.), a pale yellowish viscous oil, $d\left(\frac{14}{4}\right)^\circ = 0.9595$

$$n_D^{14} = 1.5075$$

M.R. 68.239

Calc. for $C_{15}H_{26}OF_1$ 68.128

Substance	Solvent	$\alpha_D(1dm.)$	$(\alpha)_D^{17^\circ}$
0.5071 gr.	absolute alcohol 10 c.c.	+2.4°	+49.30°

Substance	CO ₂	H ₂ O	C%	H%
0.1544 ^{gr.}	0.4575 ^{gr.}	0.1573 ^{gr.}	80.80	12.03
0.1337	0.4042	0.1398	81.69	11.69
0.1211	0.3589	0.1262	80.85	11.79
Mean			81.11	11.79
Calc. for $C_{15}H_{26}O$			81.01	11.78

Substance	Solvent	Δt	Mol. wt.	
			Found	Calc. ($C_{15}H_{26}O$)
0.8667 gr.	benzene 26.4536 gr.	-0.750°	219.428	222.208

(b) Boiling point 170—174° (10 m.m.), a pale greenish viscous oil,

$$d\left(\frac{14}{4}\right)^\circ = 0.9692 \quad n_D^{14} = 1.5084$$

M.R. 68.388

Calc. for $C_{15}H_{26}OF_1$ 68.128

Substance	Solvent	$\alpha_D(1dm.)$	$(\alpha)_D^{19^\circ}$
0.6694 gr.	absolute alcohol 10. c.c.	+4.32°	+66.58°

Substance	CO ₂	H ₂ O	C%	H%
0.1601 ^{gr.}	0.4801 ^{gr.}	0.1686 ^{gr.}	81.77	11.77
0.0974	0.2893	0.1014	80.25	11.77
0.1436	0.4269	0.1539	81.07	11.98
Mean			81.03	11.76
Calc. for C ₁₅ H ₂₆ O			81.01	11.78

Substance	Solvent	Δt	Mol. wt.	
			Found	Calc. (C ₁₅ H ₂₆ O)
0.7278 gr.	benzvine 26.8731 gr.	-0.612°	221.265	222.208

15 grams of the former sesquiterpenalcohol were heated with 30 grams of potassium bisulphate for 4 hours on an oil bath at 180—200°. After cooling the product was extracted with ether and dried with anhydrous sodium sulphate. On distilling off the ether, the residue was distilled on metallic sodium under reduced pressure, and the fraction boiling at 125—140° (11 m.m.) was collected. It was again distilled on metallic sodium and the following fraction (yield about 9.6 grams) was collected.

Boiling point 133—136°(12 m.m.), a colourless liquid,

$$d\left(\frac{16}{4}\right)^{\circ} = 0.9138 \quad n_{D}^{20} = 1.5104$$

M.R. 66.581 Calc. for C₁₅H₂₄F₂ 66.136.

Substance	Solvent	α _D (1 dm.)	[α] _D ²⁰
0.4363 ^{gr.}	absolute alc. 10 c.c.	+0.61°	+15.28°
0.7423	"	+1.03°	+15.17°
		Mean	+15.22°

Substance	CO ₂	H ₂ O	C%	H%
0.1123 ^{gr.}	0.3630 ^{gr.}	0.1189 ^{gr.}	88.14	12.37
0.1037	0.3358	0.1113	88.40	11.99
Mean			88.27	12.18
Calc. for C ₁₅ H ₂₄			88.15	11.85

5.4 grams of this sesquiterpene were heated with 2.6 grams of sulphur for 7 hours on an oil-bath at 180—230°, and about 1.6 grams of a substance boiling at 142—157° (12 m.m.) [$n_D^{17} = 1.5732$] were obtained. It was analysed as its picrate, orange needle crystals melting at 114—115°.

0.1209 gr. substance gave 0.2603 gr. CO_2 and 0.0520 gr. H_2O .

	Found	Calc. ($C_{21}H_{21}O_7N_3$)
Carbon	58.71%	59.02%
Hydrogen	4.80	4.92

The picrate was quite identical with cadalin picrate produced from sesquiterpene in camphor oil.

By treating the sesquiterpenalcohol with the boiling point 170—174° in an analogous manner a hydrocarbon boiling at 139—142° (10 m.m.) was obtained. Its physical properties and composition were determined as follows :

Boiling point 139—142° (10 m.m.), colourless oil,

$$d\left(\frac{17}{4}\right)^\circ = 0.9139 \quad n_D^{17} = 1.5145$$

M.R. 67.251 Calc. for $C_{15}H_{24}F_2$ 66.136 Exaltation 1.115

Substance	Solvent	$\alpha_D(1dm.)$	$(\alpha)_D^{17^\circ}$
0.6042 gr.	absolute alc. 10 c.c.	+2.09°	+37.71°

Substance	CO_2	H_2O	C%	H%
0.1375 ^{gr.}	0.4452 ^{gr.}	0.1464 ^{gr.}	88.29	11.90
0.0931	0.3008	0.0965	88.10	11.48
Mean			88.19	11.69
Calc. for $C_{15}H_{24}$			88.15	11.85

5.4 grams of this were treated with 2.6 grams of sulphur, and about 1.7 grams of the substance boiling at 150—165° (12 m.m.) were obtained. On examining it as the picrate (M. p. 114—115°) it was also found to be nothing but cadalin.

The author is indebted to Mr. Z. Takeda for his assistance in some of the experimental work.