Study on Sesquiterpenes. I
Sesquiterpene and Sesquiterpene Alcohol from Japanese Camphor Oil *

By

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(Received June 19, 1931)

A high boiling fraction of Japanese camphor oil, named camphor blue oil, has been reported to contain cadinene[1] and bisabolene[2].

Semmler and his co-workers have reported that the sesquiterpene and sesquiterpene alcohol in camphor oil are similar in their chemical nature to camphene. Studying the camphor oil from Formosa, Dr. Kafuku has isolated a sesquiterpene alcohol of tricyclic nature, as ascertained from its physical constants. According to Ono both the sesquiterpene and the sesquiterpene alcohol occurring in Japanese camphor oil gave cadaline when they were oxidized with sulphur. Three sesquiterpene alcohols, primary, secondary and tertiary, of cadaline type are reported to have been isolated from camphor oil by Ruzicka and his pupils.

Sesquiterpene

Researcher	B. p.	d	n_D	$(\alpha)_D$	M. R.
Semmler[3]	$(129°-133°)_8$	0.9015(20/4)	1.5006(20)	+3.0°	66.61
K. Ono[4]	$(140°-141°)_{15}$	0.9025(15/4)	1.5050(15)	+25.3	66.74
Ruzicka[5]	$(127°-128°)_{12}$	0.8876(15/4)	1.4955(15)	—	67.14
„	$(131°-134°)_{12}$	0.8943(14/4)	1.4974(14)	—	66.86
Writers	$(121°-124°)_8$	0.9100(25/4)	1.5046(25)	+17.7	66.45
			M. R. for $C_{15}H_{24}F_2$		66.14

1. Ber. Schimmel Co., 1889, April, 9.
2. Ibid., 1909, October, 24.
3. Ber., **46**, 769.
4. Mem. Coll. Sci., Kyoto Imp. Univ., **8**, 1.
5. Helv., **7**, 264.

* This paper was read before the meeting of the Government Monopoly Bureau, Camphor Department, Taiwan, on June 1929.

Sesquiterpene alcohol

Researcher	B. p.	d	n_D	$(\alpha)_D$	M. R.
Semmler[1]	$(150°-155°)_{16}$	0.9662(20/4)	1.5071(20)	+50.2°	68.39
K. Kafuku[2]	$(130°-133°)_5$	0.9790(18/4)	1.5035(18)	—	66.90
K. Ono[3]	$(160°-163°)_{10}$	0.9595(14/4)	1.5075(14)	+47.3	68.24
„	$(170°-174°)_{10}$	0.9692(„)	1.5084(„)	+64.5	68.39
Ruzicka[4] I	$(156°-158°)_{12}$	0.9568(18/4)	1.5045(18)	+2.2	68.81
„ II	$(160°-162°)_{12}$	0.9720(20/4)	1.5066(20)	−5.2	67.98
„ III	$(156°)_{12}$	0.9665(„)	1.5050(„)	—	68.21
T. Koike[5]	$(156°-159°)_{18}$	0.9654(21/4)	1.5011(21)	+40.9	68.27
„	$(165°-169°)_{18}$	0.9590(21/4)	1.5017(21)	+61.7	68.02
Writers	$(157°-160°)_{12}$	0.9501(25/4)	1.5040(25)	+35.5	68.24
			M. R. for $C_{15}H_{26}OF_1$		68.15

Although these sesquiterpenes and sesquiterpene alcohols isolated by many chemists from camphor oil show similar physical constants, their chemical structures are entirely different according to the investigators, and such difference may be attributed to the difference in the external and internal conditions of the camphor trees from which the oil has been isolated, the geographical conditions in which the trees grow or the age of the tree. It may be more appropriate, however, to attribute it to the difference in the chemical treatment of the oil, by which the structure of the sesquiterpenes will be altered owing to their instability towards chemicals and heat, as we find in the case of a compound having double bonds in the molecule.

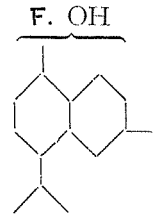
The camphor blue oil which was used in the present study was isolated by distillation from the camphor oil prepared from camphor trees grown in Formosa, and showed the following physical constants: $d_4^{25}=0.937$, $n_D^{25}=1.503$, $(\alpha)_D=+3.7°$ (in alcohol solution). The fraction boiling at $(140°\text{-}180°)_{12}$ was treated with metallic sodium to separate sesquiterpene alcohols as sodium-alcoholate. The sesquiterpene alcohol thus separated from sesquiterpene shows the following physical constants:—

B. p. $(157°\text{-}160°)_{12}$; $d_4^{25}=0.9501$; $n_D^{25}=1.5040$; $(\alpha)_D=+35.5°$;
M. R.=68.24 (M. R. for $C_{15}H_{26}OF_1=68.15$)

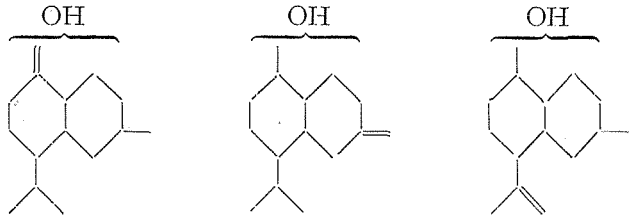
1. Ber., **46**, 770, **47**, 2074.
2. J. Jap. Ind. Chem., **19**, 815.
3. Mem. Coll. Sci. Kyoto Imp. Univ., **8**, 1.
4. Helv., **7**, 264.
5. J. Jap. Ind. Chem., **29**, 215.

When this alcohol was heated with sulphur according to the directions given by Vesterberg, hydrogen sulphide gas was generated, with a hydrocarbon which gave cadaline picrate[1], (M. p. (113°)).

The alcohol, on being treated with phenylisocyanate and acetic anhydride, decomposed into hydrocarbons of the molecular formula $C_{15}H_{24}$, and on reduction with colloidal palladium and hydrogen, with absorption of one mole of hydrogen, yielded a saturated alcohol. The same substance was also obtained by the catalytic reduction of the unsaturated alcohol under high pressure and at high temperature, and thus these facts give rise to the idea that the sesquiterpene alcohol was an unsaturated tertiary alcohol:

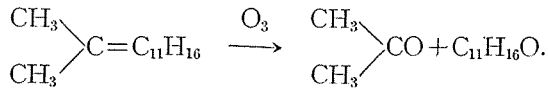


To decide the position of the double bond in the molecule, the alcohol was oxidized with ozone, and it was confirmed that formaldehyde, formic acid and keto-alcohol, $C_{14}H_{24}O_2$, occurred in the reaction product. The structure of the alcohol molecule was assigned one of the following three formulae:



I II III

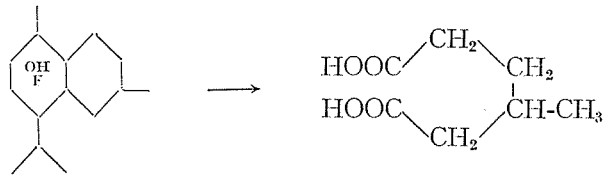
On reduction with metallic sodium and ethyl alcohol, the keto-alcohol yielded an alcohol which gave on dehydration with Japanese acid clay, a hydrocarbon, $C_{14}H_{22}$, and the latter gave acetone as one of products of oxidation with ozone, as was expected from its structure:



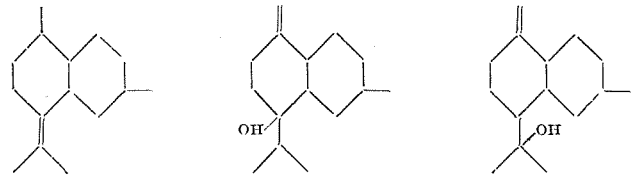
1. Ruzicka u. Mayer: Helv., **4**, 505.

This fact disposes of formula III for the sesquiterpene alcohol.

When the sesquiterpene alcohol was oxidized with alkaline potassium-permanganate solution, oxalic and methyl adipic acids were obtained. The same oxidation products resulted from the hydrocarbon derived from the alcohol by dehydration, and these results are in favour of the view that the double bond and the hydroxyl group of this alcohol should occur in the same ring :—



In order to decide the position of the hydroxyl group in the molecule, the hydrocarbon $C_{15}H_{26}$, which was obtained by the dehydration of the saturated alcohol as mentioned above, was oxidized with ozone, and acetone and ketone $C_{12}H_{20}O$, were obtained in the reaction-products, and formula V or VI (shown below) was assigned to the sesquiterpene alcohol molecule since the hydrocarbon $C_{15}H_{26}$ harmonizes in its chemical behavior with structure IV.



IV V VI

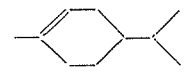
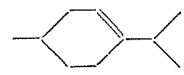
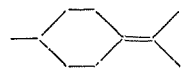
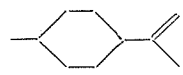
It is a noteworthy fact that the sesquiterpene alcohol yields the following hydrocarbons when various dehydrating agents are used;

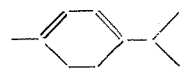
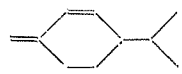
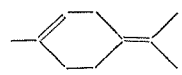
	Dehydrating agent	Molecular formula	B. p.	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.
I	Phenylisocyanate	$C_{15}H_{24}$	$(134°-139°)_{18}$	0.9026	1.4993	+46.6°	66.46
II	Acetic anhydride	$C_{15}H_{24}$	$(136°-142°)_{16}$	0.9058	1.4999	+51.4	66.29
III	Acid clay	$C_{15}H_{24}$	$(131°-134°)_{14}$	0.9060	1.5011	+22.1	66.41
IV	Acid clay	$C_{15}H_{24}$	$(137°-140°)_{14}$	0.9162	1.5066	−23.7	66.29
					M. R. for $C_{15}H_{24}F_2$		66.14

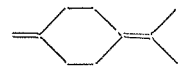
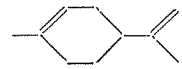
and that these hydrocarbons show different behavior towards hydrochloric gas and mercuric acetate solution, as may be seen from the following table :

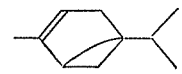
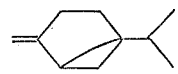
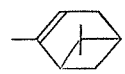
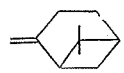
	Dehydrating agent	Hydrochloride	Addition product with mercuric acetate
I	Phenylisocyanate	+	+
II	Acetic anhydride	−	+
III	Acid clay I	−	−
IV	Acid clay II	−	−

Referring to the literature, we noticed that monoterpene hydrocarbons $C_{10}H_{18}$ and $C_{10}H_{16}$ show a close connection between the position of the double bonds in their molecules and their physical constants, as may be seen from the following table.

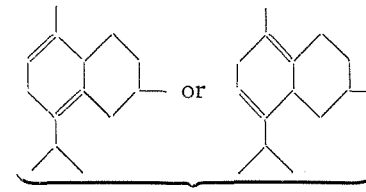
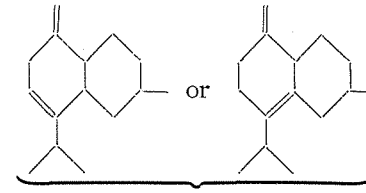
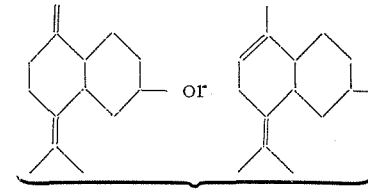
	Structure	B. p.	d_4^{20}	n_D^{20}
Carvomenthene		175°	0.8184	1.4566
Menthene Δ_3		168°	0.8122	1.4524
„ Δ_4		173°	0.8310	1.4647
„ Δ_8		170°	0.8104	1.4566

Monocyclic terpenes	Structure	B. p.	d_4^{20}	n_D^{20}
α-Terpinene		175°	0.8453	1.4858
α-Phellandrene		175°	0.8440	1.4732
β-Phellandrene		172°	0.8520	1.4788
Terpinolene		184°	0.8540	1.4840

Monocyclic terpenes	Structure	B. p.	d_4^{20}	n_D^{20}
Crithmene		179°	0.8658	1.4806
Limonene		175°	0.8426	1.4699
Isolimonene		172°	0.8370	1.4704
Menthadien 3,8		184°	0.8574	1.4943

Bicyclic terpenes	Structure	B. p.	d_4^{20}	n_D^{20}
Thujene		152°	0.8275	1.4504
Sabinene		163°	0.8481	1.4673
Pinene		155°	0.8542	1.4634
Nopinene		162°	0.8660	1.4724

Hydrocarbons which have a double bond in the side chain, especially between carbons 4 and 8, show much higher values for their physical constants than the calculated value; a similar fact was noticed in the case of the hydrocarbons having a conjugate double bond. If the rule as to the connection between the position of the double bond and the physical constants of monoterpenes is taken into consideration, the following structures for the sesquiterpenes produced from sesquiterpene alcohol by dehydration may be suggested from the study of their physical constants :—

	Dehydrating agent	Structure
I	Phenylisocyanate	 VII
II	Acetic anhydride	 VIII
III & IV	Acid clay	 IX

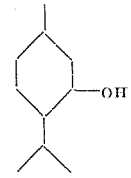
And the fact that four hydrocarbons when oxidized with ozone, yield the reaction products indicated in the following table, gives strong support to the structures of the hydrocarbons shown above.

	Dehydrating agent	Reaction Product	
		Volatile matter	Nonvolatile matter
I	Phenylisocyanate	nul	—
II	Acetic anhydride	HCHO, HCOOH	$C_{14}H_{22}O_4$
III	Acid clay I	$(CH_3)_2CO$	$C_{12}H_{18}O_4$
IV	Acid clay II	$(CH_3)_2CO$	$C_{11}H_{18}O_3$

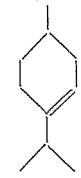
All these reactions are in favour of structure (V) for the alcohol so far studied.

It was noticed that the chemical structure of terpene hydrocarbons

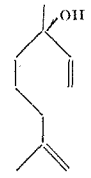
shows a close relationship to that of the terpene alcohols which occur side by side in the same essential oil, such as menthene and menthol in peppermint oil, limonene and linalool in citrus oils and cadinene and cadinol in galbaum oil.



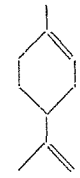
Menthol



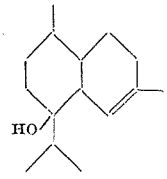
Menthene



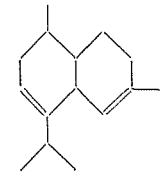
Linalool



Limonene



α-Cadinol



α-Cadinene

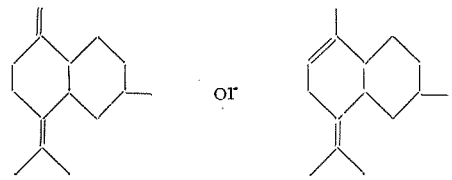
Such a structural relationship as holds between terpenes and terpene alcohols was assumed to exist between the sesquiterpenes and sesquiterpene alcohol in Japanese camphor blue oil, and the writers started on the study of the structure of the sesquiterpene in camphor oil from this assumption.

The hydrocarbons which were separated from the sesquiterpene alcohol, contained 16 % of the blue oil and were divided by fractional distillation into the following three parts :—

Fraction	B. p.	Molecular formula	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.
1	$(119°-121°)_8$	$C_{15}H_{24}$	0.9128	1.5046	+16.2°	66.25
2	$(121°-124°)_8$	$C_{15}H_{24}$	0.9100	1.5046	+17.7	66.45
3	$(124°-127°)_8$	$C_{15}H_{24}$	0.9162	1.5055	+17.3	66.71
				M. R. for $C_{15}H_{24}F_2$		66.14

The three fractions gave neither solid hydrochloride, nitrosate nor nitrosochloride and were therefore supposed to be composed of isomeric hydrocarbons of formula I or II; this assumption was partly supported by the fact that the hydrocarbons produced from the sesquiterpene alcohol by dehydration with acid clay showed similar physical and chemical properties to those of the sesquiterpenes.

	$C_{15}H_{24}$ (natural)	$C_{15}H_{24}$ (from $C_{15}H_{26}O$)
B. p.	$(121°-124°)_8$	$(131°-134°)_{14}$
d_4^{25}	0.9100	0.9060
n_D^{25}	1.5047	1.5011
$(\alpha)_D$	$+17.7°$	$+22.1°$
M. R.	66.45	66.41
Hydrochloride	—	—



(I) (II)

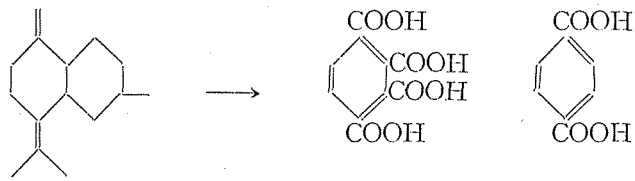
This view of the structure of the sesquiterpenes is favoured by the fact that they give the same tetrabromide,[1] and also cadaline results from oxidation with sulphur.

Fraction	Br_2 added	Br_2 % for $C_{15}H_{24}Br_4$
1	57.25	
2	57.89	61.05
3	58.28	

The double bonds in the molecule of the sesquiterpene being unreducible by means of metallic sodium and amyl alcohol[2], were regarded as not existing in a conjugate system but rather, from reference to the abnormality of their physical constants as being situated in side chains as shown in (III). The oxidation of the hydrocarbon with potassium permanganate or with manganese dioxide[3] and sulphuric

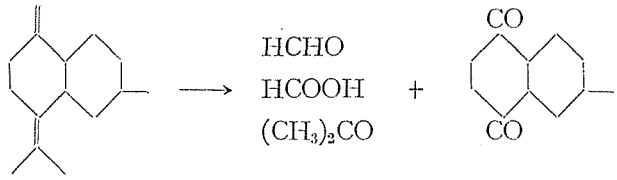
1. Allen: Analyst, **6**, 177; Levallois: C. R., **99**, 977.
2. Semmler: Ber., **36**, 1033.
3. Ruzicka u. Stoll: Helv., **7**, 84.

acid proves that the writers' assumption as to the structure is accurate, isophthalic acid being obtained in the former case and prehnitic acid in the latter.

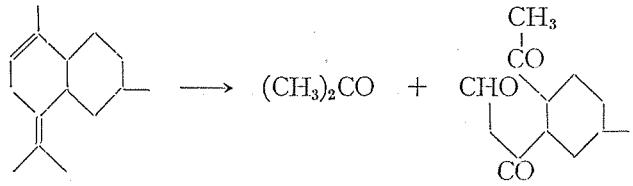


III

The fact that formaldehyde, formic acid, acetone and acetic acid were obtained as volatile reaction products from the sesquiterpene by oxidation with ozone on the one hand, and on the other, diketone $C_{11}H_{14}O_2$ and an aldehyde in a nonvolatile reaction product, is in favour

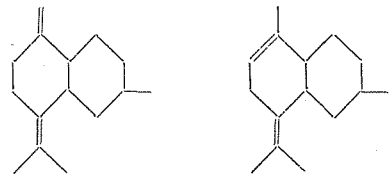


XIII



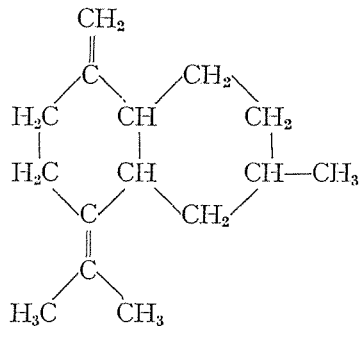
XIV

of the view that the sesquiterpene obtained from the camphor blue oil must be a mixture of two hydrocarbons represented by the following structures, IV and V.

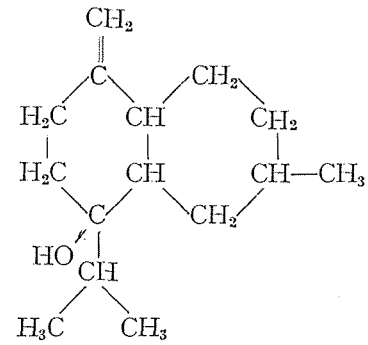


IV V

The compound which corresponds to formula V was supposed to be derived from the other (IV) by an intermolecular change during the treatment of the oil, and this assumption was proved to be partly true, as the sesquiterpene no longer gives volatile reaction products such as acetone on ozone-oxidation after repeated distillation with metallic sodium, owing to the dislocation of the double bond in the molecule. The sesquiterpene and sesquiterpene alcohol isolated by the writers from Japanese camphor oil were thus assertained to have the following chemical constitutions :—



Sesquiterpene



Sesquiterpene alcohol

EXPERIMENTAL PART

(A) Sesquiterpene Alcohol

I. Separation of sesquiterpene alcohol

The camphor blue oil obtained from camphor trees grown in Formosa was fractionated into the following 3 parts :

Fraction	B. p.	Yield
1	($-140°)_{12}$	40%
2	(140°–180°) „	50%
3	(180°–) „	10%

500 gms. of fraction (2) were heated at 50°-60° under a pressure of 12-15 m.m. for 50 hours with 35 gms. of metallic sodium, and the

hydrocarbons occurring in the oil distilled off. The residue which consisted mostly of the sodium-salt of sesquiterpene alcohol was decomposed with ether containing water to get the alcohol in a free state and the yield of the alcohol and the hydrocarbon was as follows :

	Yield	
	gms.	%
Hydrocarbon	210	23
Alcohol	200	22
Resinous matter	60	5

The alcohol separated from the hydrocarbon was distilled under reduced pressure and 5 fractions with the following properties were obtained :—

Fraction	B. p.	Yield	d_4^{25}	n_D^{25}	$(\alpha)_D$
1	($-157°)_{12}$	2.2%	—	1.5030	+20.6°
2	$(157°-160°)_{12}$	6.2	0.9501	1.5040	+35.5
3	$(160°-166°)_{12}$	0.9	—	1.5048	+32.4
4	$(166°-170°)_{12}$	2.1	0.9450	1.5044	+29.2
5	$(170°-175°)_{12}$	2.2	—	1.5044	+25.6

Fraction (2) was found to consist of sesquiterpene alcohol from its physical constants and also from elementary analysis :

B. p. $(157°-160°)_{12}$; $d_4^{25}=0.9501$; $n_D^{25}=1.5040$; $(\alpha)_D=+35.5°$;

M. R. 68.24 (M. R. for $C_{15}H_{25}OF_1=68.15$)

	Calc. for $C_{15}H_{26}O$	Found
Carbon	81.08	80.8
Hydrogen	11.71	12.0

II. Oxidation of sesquiterpene alcohol with sulphur

25 gms. of the sesquiterpene alcohol were heated with 35 gms. of sulphur at 180°-230° for 12 hours and the reaction product was distilled on metallic sodium. The hydrocarbon thus obtained showed the following physical constants :

B. p. $(145^{\circ}\text{-}160^{\circ})_{22}$; $d_4^{25}=0.9561$; $n_D^{25}=1.5408$;
M. R. 65.10 (M. R. for $C_{15}H_{18}F_5$ 64.72)
This substance yields orange coloured needles of cadaline picrate (M. p. 113°).

III. Reduction of sesquiterpene alcohol

(*a*) *Reduction of the Alcohol with Colloidal Palladium and Hydrogen*

10 gms. of the sesquiterpene alcohol were treated in 50 gms. of glacial acetic acid solution with palladium colloid (which contained 0.025 gm. of Pd) and hydrogen at 40-50° under 2 atmospheric pressures for 16 hours and the amount of hydrogen absorbed indicated that it contained one double bond in the molecule. The reaction product was distilled under reduced pressure and a saturated alcohol having the following constants was obtained:—
B. p. $(145^{\circ}\text{-}150^{\circ})_{12}$; $d_4^{25}=0.9388$; $n_D^{25}=1.4901$; $(\alpha)_D=+7.5^{\circ}$;
M. R. = 69.10 (M. R. for $C_{15}H_{23}O=68.60$)

	Calc. for $C_{15}H_{28}O$	Found
Carbon	80.29	80.2
Hydrogen	12.58	12.4

(*b*) *Reduction of the Alcohol with Reduced Nickel and Hydrogen under High Pressure and at High Temperature*

50 gms. of the sesquiterpene alcohol were heated in an autoclave with 5 gms. of reduced nickel and hydrogen at 150°-160° under 80 atmospheric pressures and the fall in the hydrogen pressure was 35 atmospheric pressures. The product was fractionated into the following two parts:

Fraction	B. p.	Yield	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.
1	$(160^{\circ}-164^{\circ})_{19}$	16 gms.	0.9303	1.4897	+16.6°	69.64
2	$(164^{\circ}-168^{\circ})_{19}$	16 „	0.9414	1.4943	+20.7	69.23
				M. R. for $C_{15}H_{28}O$		68.60

The saturated alcohols produced by two reducing methods were dehydrated separately by heating with acid clay, and the hydrocarbons (A & B) generated were found to be the same by reference to their physical constants :—

	Molecular formula	B. p.	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.
A	$C_{15}H_{26}$	$(123°-125°)_{12}$	0.8877	1.4887	−12.2°	67.06
B	$C_{15}H_{26}$	$(138°-140°)_{20}$	0.8898	1.4870	−11.2	67.29
				M. R. for $C_{15}H_{26}F_1$		66.60

IV. Oxidation of the sesquiterpene alcohol with ozone

Ozonized air was passed into a 20 % carbon tetrachloride solution of the sesquiterpene alcohol and the solvent distilled off under diminished pressure, and an ozonide remaining in the flask was decomposed with water. The aqueous solution separated from an oily reaction product showed (1) Lieben's reaction[1] for iodoform, (2) red colouration of a fuchsin solution decoloured by SO_2, (3) reduction of a silver ammoniacal solution, (4) red colouration of a solution containing a few drops of 1 % phenol solution with conc. sulphuric acid.

These reactions indicate the presence of formaldehyde and formic acid in the aqueous solution.

The oily reaction product was washed with dilute caustic soda solution and analysed after being dried in a vacuum desiccator.

	Calc. for $C_{14}H_{24}O_2$	Found		
		I	II	III
Carbon	74.93	74.6	74.3	74.7
Hydrogen	10.79	10.5	10.6	10.3

It was reduced with metallic sodium and ethyl alcohol to an alcohol which was then subjected to steam distillation. The alcohol after being purified showed the following properties :—

B. p. $(137°\text{-}140°)_5$; $d_4^{25}=0.9735$; $n_D^{25}=1.5029$; M. R. $=63.82$;

(M. R. for $C_{14}H_{26}O$ 63.98).

1. Rosenthaler: Der Nachweis organischer Verbindungen. S. 161.

	Calc. for $C_{14}H_{26}O$	Found		
		I	II	III
Carbon	79.92	79.7	79.7	79.8
Hydrogen	11.46	11.5	11.5	11.5

When acted upon by phenylisocyanate or Japanese acid clay, the alcohol gives a hydrocarbon, and on being heated with phthalic anhydride at 120°, an acidphthalate.

The hydrocarbon $C_{14}H_{24}$ generated from the alcohol by treatment with the acid clay showed the following physical constants :—

B. p. $(143°\text{-}145°)_{30}$; $d_4^{25}=0.9321$; $n_D^{25}=1.5058$; M. R.$=61.24$;
(M. R. for $C_{14}H_{24}F_1=61.99$).

The analytical results were :—

	Calc. for $C_{14}H_{24}$	Found
Carbon	87.43	87.1
Hydrogen	12.57	12.4

Oxidation of the hydrocarbon with ozone was tried and the reaction product consisted of acetone and a carbonyl compound which gave on analysis the following results, and also a semicarbazone, M. p. (162°-170°).

	Calc. for $C_{14}H_{24}O_3$	Found
Carbon	69.94	70.7
Hydrogen	10.08	10.0

V. Oxidation of sesquiterpene alcohol with potassium permanganate

β-Methyl Adipic Acid

To a mixture of 1 part of the sesquiterpene alcohol and 10 parts of 10 % caustic soda solution, powdered potassium permanganate was added slowly at 60°. The solution, separated from manganese-dioxide by filtration, was acidified with dilute hydrochloric acid, evaporated to dryness and treated with absolute alcohol to extract an acid formed by the oxidation. This was isolated in a syrupy form which

was changed to white crystals on standing in a vacuum desiccator, melting at about 80° with decomposition. Into an etherial solution of this acidic compound dry ammonia gas was passed, and the ammonium salt was converted into a silver salt which was analysed after drying in a vacuum desiccator.

	Calc. for $C_7H_{10}O_4Ag_2$	Found	
		I	II
Carbon	22.49	20.9	19.9
Hydrogen	2.67	2.4	2.5
Silver	57.73	58.4	57.1

The physical and chemical properties of the acid, and also the analytical results agree with those of β-methyl adipic acid.

VI. Oxidation of the hydrocarbon $C_{15}H_{26}$ derived from the saturated alcohol $C_{15}H_{28}O$

The hydrocarbon $C_{15}H_{26}$, which was produced by dehydration of the saturated alcohol as mentioned above, was oxidized with ozone in carbon tetrachloride solution, and an ozonized substance was decomposed with hot water. The aqueous solution of this was proved to contain acetone by ;

(1) Lieben's iodoform reaction, (2) the reaction to Fehling's solution, (3) the colouration of fuchsin solution decoloured by SO_2, (4) giving a ruby-red colour with an alkaline solution of sodium nitroprusside, (5) Frommer-Emilowicz's reaction[1], (6) giving dibenzalacetone, M. p. (110°).

The other reaction product, which was insoluble in water, was reduced with metallic sodium and ethyl alcohol, and the reduced substance gave the following constants, corresponding to alcohol $C_{12}H_{22}O$.

B. p. $(120°\text{-}130°)_4$; $d_4^{25}=0.9163$; $n_D^{25}=1.4789$; $(\alpha)_D=-7.2°$;

M. R. = 56.38 (M. R. for $C_{12}H_{22}O=54.74$) :

	Calc. for $C_{12}H_{22}O$	Found	
		I	II
Carbon	79.04	79.0	79.3
Hydrogen	12.17	12.3	12.0

1. Rosenthaler: Der Nachweis organischer Verbindungen. S. 161.

The alcohol thus formed gave a phenyl urethane derivative and also an acid phthalate when heated with phthalic anhydride at 180° for 8 hours, and these reactions agree with those of a secondary alcohol. On distillation with acid clay, it yielded a hydrocarbon with the constants.

B. p. $(145°\text{-}155°)_{25}$; $d_4^{25}=0.8934$; $n_D^{25}=1.4894$; M. R.$=53.67$;
(M. R. for $C_{12}H_{20}F_1=52.75$)

VII. Dehydration of sesquiterpene alcohol

(*a*) *Dehydration of Sesquiterpene Alcohol with Phenylisocyanate*

When the sesquiterpene alcohol was heated in a sand bath with an equal quantity of phenylisocyanate, the reaction took place with the evolution of carbon dioxide, and the chief product was a hydrocarbon which was distilled with metallic sodium under reduced pressure. The main fraction was found to consist of hydrocarbon $C_{15}H_{24}$, by the determination of its density and index of refraction and also by the analysis :—

B. p. $(134°\text{-}139°)_{18}$; $d_4^{25}=0.9026$; $n_D^{25}=1.4993$; $(\alpha)_D=+46.6°$;
M. R.$=66.46$ (M. R. for $C_{15}H_{24}F_2=66.14$).

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	87.8
Hydrogen	11.85	12.1

It yields dihydrochloride, (M. p. 191°) when treated by the usual method, and also an amorphous white mercury compound on shaking with a mercury acetate solution. By the oxidation of this hydrocarbon with ozone, an oily substance containing a carbonyl group in the molecule was isolated, which gave a semicarbazone, (M. p. 90°-93°).

(*b*) *Dehydration of Sesquiterpene Alcohol with Acetic Anhydride*

When a mixture of the alcohol and acetic anhydride was heated in a sealed tube at 150°-160° for 6 hours, a hydrocarbon of the following nature was obtained :—

B. p. $(136°\text{-}142°)_{15}$; $d_4^{25}=0.9058$; $n_D^{25}=1.4999$; $(\alpha)_D=+51.4°$;
M. R.$=66.29$ (M. R. for $C_{15}H_{24}F_2=66.14$)

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	87.9
Hydrogen	11.85	12.1

This substance gave a white mercury compound when acted on by mercury acetate solution but not any solid hydrochloride. On oxidation with ozone, it yielded formaldehyde, formic acid and a carbonyl compound, and the latter substance gave a semicarbazone showing M. p. 63°-65° and the following analytical results :—

	Calc. for $C_{14}H_{22}O_4$	Found		
		I	II	III
Carbon	66.10	65.7	66.1	66.5
Hydrogen	8.60	8.9	9.1	9.1

(*c*) *Dehydration of Sesquiterpene Alcohol with Japanese Acid Clay.*

The sesquiterpene alcohol was distilled with the acid clay and the product was divided into two portions after being purified by distilling on metallic sodium.

Fraction 1.

B. p. $(131°\text{-}134°)_{14}$; $d_4^{25}=0.9060$; $n_D^{25}=1.5011$; $(\alpha)_D=+22.1°$;
M. R.=66.41 (M. R. for $C_{15}H_{24}F_2=66.14$)

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	88.0
Hydrogen	11.85	12.0

Fraction 2.

B. p. $(137°\text{-}140°)_{14}$; $d_4^{25}=0.9162$; $n_D^{25}=1.5066$; $(\alpha)_D=-23.7°$;
M. R.=66.29 (M. R. for $C_{15}H_{24}F_2=66.14$)

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	87.9
Hydrogen	11.85	11.5

Neither fraction gave solid hydrochloride with hydrochloric acid nor a mercury derivative with mercury acetate. On oxidation with

ozone, fraction (1) yielded a large quantity of acetone and a carbonyl-compound, and the latter, which gave a semicarbazone with M. p. 55°-57°, was analysed.

	Calc. for $C_{12}H_{18}O_4$	Found	
		I	II
Carbon	63.70	62.2	62.1
Hydrogen	7.90	8.2	8.5

On oxidation with ozone fraction (2) gave acetone and a carbonyl compound $C_{11}H_{18}O_3$, which showed the following analytical results :—

	Calc. for $C_{11}H_{18}O_3$	Found	
		I	II
Carbon	66.70	65.6	66.2
Hydrogen	9.10	8.9	9.0

B. Sesquiterpene

I. Isolation of sesquiterpene

3 kgms. of the camphor blue oil were treated with 30 gms. of sodamide at 50° under diminished pressure for 60 hours, and after the evolution of ammonia had ceased, the reaction product was distilled under reduced pressure, 1.1 kgms. of distillate being obtained.

It was fractionated several times on metallic sodium and the following 5 portions were obtained.

Fraction	B. p.	Yield	
		gms.	%
1	(50°—87°)$_3$	150	5.0
2	(87°—98°)„	165	5.5
3	(98°—112°)„	360	12.0
4	(112°—125°)„	135	4.5
5	(125°—)„	275	9.1

Fraction (3) was divided into the following 3 fractions and the physical constants of each were determined. The analytical results agree with those for sesquiterpene, $C_{15}H_{24}$ (C=88.15 ; H=11.85).

Fraction	B. p.	Yield	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.	C	H
1	(119°—121°)$_8$	92 gms.	0.9128	1.5046	+16.2°	66.25	87.7	11.8
2	(121°—124°)„	134	0.9100	1.5046	+17.7	66.45	87.9	11.8
3	(124°—127°)„	83	0.9162	1.5055	+17.3	66.72	87.8	11.9
				M. R. for $C_{15}H_{24}F_2$		66.14		

Preparation of Hydrochloride

In an etherial solution of the three fractions, hydrochloric gas was passed until the solution was saturated with the gas. It was then left to stand for a long time in an ice box, but no solid hydrochloride was noticed to form in the solution.

Preparation of Nitrosate

A mixture of 5 gms. of each fraction, 15 gms. of glacial acetic acid and 5 gms. of amyl nitrite, was cooled with a cooling mixture of ice and salt, and 5 gms. of conc. nitric acid were added slowly to the solution and the mixture was kept in a refrigerator for a few days but no crystalline substance appeared from the solution.

Preparation of Nitrosochloride

5 gms. of each hydrocarbon dissolved in 15 gms. of glacial acetic acid, and 5 gms. of amyl nitrite were mixed under cooling, and absolute alcohol saturated with hydrochloric gas was added slowly. No solid substance separated out from the solution when it was kept in a cold place for a long time.

II. Addition of bromine to the sesquiterpene

In accordance with Allen's method, a carbon tetrachloride solution of the sesquiterpene was mixed with a known quantity of 1/3 N carbon tetrachloride solution of bromine, and the mixture was left to stand for 18 hours, and free and combined bromines were determined as usual. The bromine required for the double bonds in the compound was calculated, with the following results :—

Fraction	Substance	Br_2 absorbed	Br_2 substituted	Br_2 added	% of Br_2 (add. product)
1	0.4242 gm.	0.8646 gm.	0.2964 gm.	0.5682 gm.	57.25
2	0.4292	0.8919	0.3019	0.5900	57.89
3	0.6566	1.2367	0.3193	0.9174	58.29
			Br_2 Calc. for $C_{15}H_{24}Br_4$		61.05

These results show that these three fractions consist of the same sesquiterpene, of a bicyclic nature, having two double bonds in the molecule.

III. Oxidation of sesquiterpene with sulphur

30 gms. of the sesquiterpene were heated with 15 gms. of sulphur at 180°-200° for 10 hours, and the reaction product, purified by distillation on metallic sodium, showed the following constants :—

B. p. $(120°\text{-}135°)_9$; $d_4^{25}=0.9573$; $n_D^{25}=1.5419$; M. R.$=65.08$;

(M. R. for $C_{15}H_{18}F_5=64.72$)

This substance gave a picrate of orange coloured needles which were identical in M. p. (114°) with cadaline picrate.

IV. Reduction of the sesquiterpene with metallic sodium and amyl alcohol

An amyl alcohol solution of 20 gms. of the sesquiterpene was heated to boiling and 15 gms. of sodium were added to the solution. The reduced sesquiterpene was purified on metallic sodium and showed the following constants :—

B. p. $(100°\text{-}110°)_4$; $d_4^{25}=0.9189$; $n_D^{25}=1.4981$; $(\alpha)_D=+12.7°$;

M. R.$=65.73$ (M. R. for $C_{15}H_{24}F_2=66.14$)

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	87.9
Hydrogen	11.85	11.6

These results show that two double bonds in the sesquiterpene remained without entering into any reaction with amyl alcohol and metallic sodium.

V. Oxidation of the sesquiterpene with potassium permanganate

20 gms. of the sesquiterpene were dissolved in a mixture of 200 gms. of acetone and 50 gms. of water, and 22 gms. of powdered potassium permanganate were added gradually under vigorous agitation at the room temperature. This was filtered from manganese dioxide, and acetone was distilled off under reduced pressure, and an oily neutral substance which separated out on the surface of the solution

was extracted with ether. The aqueous solution separated from the oily matter, gave 1.3 gms. of a white crystalline acidic substance together with oxalic acid on acidifing with hydrochloric acid. This acidic substance was easily separated from the oxalic acid by transforming into their calcium salts. The free acid, purified by sublimation, melted at 228° with decomposition and gave on micro-analysis the following results:—

	Calc. for $C_8H_6O_4$	Found	
		I	II
Carbon	57.80	57.3	57.3
Hydrogen	3.60	3.3	3.7

The physical and chemical properties of this substance were identical with those of isophthalic acid.

VI. Oxidation of the sesquiterpene with manganese dioxide and sulphuric acid

30 gms. of the sesquiterpene were oxidized in a boiling state with 500 gms. of conc. sulphuric acid, 600 c. c. of water and 37 gms. of manganese dioxide.

An aqueous solution separated from unchanged manganese dioxide was treated with ether to extract an acidic substance which was formed from the hydrocarbon by the oxidation; this was isolated in a syrupy form. It was converted into a silver salt by means of alcoholic silver nitrate solution, and by being transformed into the methyl ester was identified as prehnitic acid. The dimethyl ester purified from its alcohol solution melted at 172° and gave the following analytical results:

	Calc. for $C_{12}H_{10}O_8$	Found
Carbon	51.10	52.2
Hydrogen	3.50	3.6

VII. Oxidation of the sesquiterpene with ozone

The sesquiterpene dissolved in chloroform was oxidized with ozone by the usual method, and after the completion of the reaction the solvent was distilled off under reduced pressure and a white syrupy ozonide, thus obtained, was decomposed with boiling water.

An aqueous solution separated from an oily substance formed from the ozonide was proved to contain formaldehyde by;

(1) the reduction of an ammoniacal silver oxide,

(2) reduction of Fehling's solution,

(3) the colour reaction to a sodium nitroprusside solution and phenylhydrazine hydrochloride solution,

(4) the formation of the phenylhydrazone, M. p. 168°.

The occurrence of formic acid and acetic acid in the solution was confirmed by the fact that it formed white silver salts with silver nitrate solution and also by;

(1) the colour reaction to ferric chloride solution,

(2) formation of a white precipitate with mercurous acetate,

(3) formation of the ethyl ester with ethyl alcohol and conc. sulphuric acid.

The presence of acetone in the solution was also confirmed by;

(1) a purple-red colouration with sodium nitroprusside and ammonium sulphate,

(2) a red colouration with sodium nitroprusside and caustic soda solution,

(3) Lieben's iodoform reaction,

(4) a dark red colouration with salicylaldehyde and caustic soda,

(5) Dibenzalacetone, M. p. 110° obtained by treating it with benzaldehyde and a large amount of alcoholic potash.

The oily reaction product separated from the acidic solution was subjected to steam distillation and the volatile substance thus obtained was fractionated under reduced pressure. The main fraction boiling at $(100°\text{-}110°)_4$, consisted of a ketone with the formula $C_{11}H_{22}O_2$, which gave a semicarbazone with M. p. 219° and the analytical results.

N = 29.1; theory requires N = 31.2 for $C_{11}H_{22}O_2N_6$.

A resinous substance formed from the oily reaction substance by steam distillation showed an intense reducing action and on oxidation with ammoniacal silver oxide gave a carboxylic acid, the structure of which could not be decided owing to the small amount of the substance.

In conclusion, the writers wish to express their hearty thanks to the Government Monopoly Bureau, Camphor Department, Taiwan for a research grant.

April, 1930.

Laboratory of Organic- & Bio-Chemistry.