

Studies on Sesquiterpenes, II Sesquiterpene and Sesquiterpene Alcohol from Japanese Cedar Oil (*Cryptomeria Japonica* or Sugi Oil)

By

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It is said in Japan that *sake* is usually preserved in a Japanese cedar wood tank in order to flavour the liquor with an essential oil that occurs naturally in the wood. Chemical studies of the essential oil have been made by many investigators; sesquiterpenes and sesquiterpene alcohols from the root and the trunk have been studied by T. Kimoto¹, S. Keimatsu² and H. Kimura³, and S. Uchida⁴ has reported on some sesquiterpene and alcohol isolated from leaves. The results of these researches are shown in the following table.

Researcher			B. p.	d	n _D	[α] _D
T. Kimoto	Sugiol	C ₃₀ H ₄₄ O	264	0.935	—	—
S. Keimatsu	Cryptene	C ₁₅ H ₂₄	267	0.925	—	+18.6
H. Kimura	{ Cryptomeriol	C ₁₅ H ₂₄	(150—160) ₁₇	—	—	—
		C ₁₅ H ₂₄	(150—160) ₁₇	0.918	—	-10.3
		C ₁₅ H ₂₅ OH	(162—163) ₁₀	0.964	—	-37.5
S. Uchida	{	C ₁₅ H ₂₄	266—268	0.934	1.5041	+15.2
		C ₁₅ H ₂₄	262—275	—	—	—
		C ₁₅ H ₂₆ O	284—286	0.962	1.5048	+16.8

Although many investigations of the chemistry of the sesquiterpene and sesquiterpene alcohol obtained from Japanese cedar oil have been

1. Complete Abstracts of Japanese Chemical Literatures, Series I, Vol. II, 62 (Japanese)
2. *Ibid.*, 226.
3. *Ber. Deutsch. Pharm. Ges.*, **19**, 369 (1909).
4. *J. A. C. S.*, **38**, 687 (1916).

carried out from different points of view, little definite information has been given about them beyond their chemical formula. The writers have therefore undertaken the present investigation of Japanese cedar oil which came to their hands through the courtesy of Dr. T. Kainosho, Director of the Takasago Perfumery Company near Tokyo, and which was prepared by steam distillation from cedar roots grown at Tosa.

The essential oil used in this research was a bluish green viscous liquid and showed the following physical constants: B. p. = (255–285)_{754mm}; $d_4^{25} = 0.936$; $n_D^{25} = 1.508$; $[\alpha]_D = -16.7$; acid val. = 0.9; ester val. = 8.9.

The separation of hydrocarbon and alcohol from the oil was performed by means of sodamide and the yield was 54 % hydrocarbon and 38 % alcohol. The crude sesquiterpene, thus obtained, was a pale yellow liquid, boiling at (140–155)_{17mm}, $d_4^{25} = 0.922$; $n_D^{25} = 1.515$; $[\alpha]_D = -20^\circ$. It was distilled in vacuo to isolate a hydrocarbon of definite composition, and a colourless liquid of the composition $C_{15}H_{24}$ was obtained, which, showing the physical constants; B. p. = (108–114)_{4.5mm}; $d_4^{25} = 0.9150$; $n_D^{25} = 1.5085$; $[\alpha]_D = -22.4$; M. R. = 66.4 (theory $C_{15}H_{24}F_2 = 66.1$), was assumed from its physical properties to contain two double bonds in the molecule.

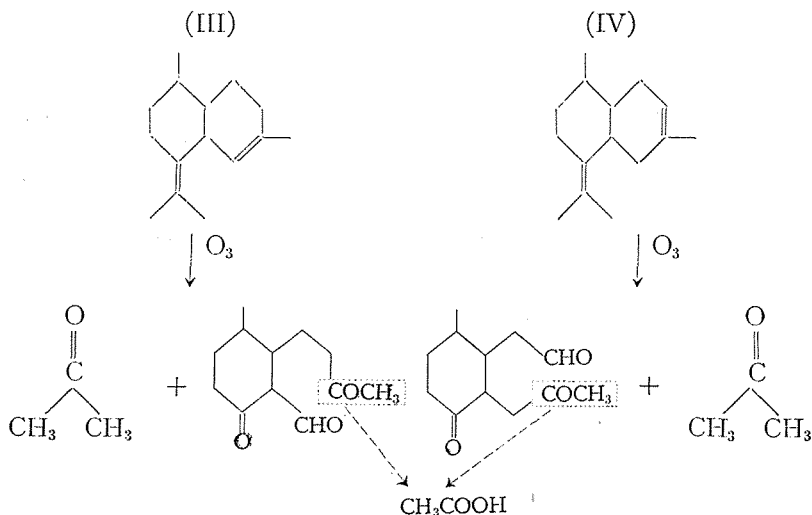
This hydrocarbon named *kiganene* by the writers resembles in its properties that of the sesquiterpene $C_{15}H_{24}$ B. p. = (150–160)_{17mm} obtained previously by H. Kimura but differs from that studied by other investigators.

It forms with hydrogen chloride cadinene dihydrochloride¹ and cadalene by catalytic oxidation at high temperature in the presence of palladium asbestos². These facts indicate that the kiganene is a bicyclic compound having the same carbon skeleton as the cadinene molecule and can be represented by one of the two formulae



1. F. W. Semmler: Die Aetherischen Oele, II, 561.
2. S. Kimura: These memoirs, A, 14, 186 (1931).

When, however, kiganene was oxidized with ozone, acetone and acetic acid were formed, and the reaction for their formation can be explained in the following manner by taking formula (III) or (IV) as its structure.



The structural formula for kiganene and the position of the double bonds in the molecule will be discussed later when the structure of the sesquiterpene alcohol occurring in the essential oil with the hydrocarbon has been decided, the two compounds being assumed to be intimately connected biochemically.

A crude sesquiterpene alcohol was separated from the hydrocarbon as a sodium compound by treating the oil with sodamide, showing the constants, $d_4^{25} = 0.953$; $n_D^{25} = 1.503$; $[\alpha]_D = -19^\circ$. It was purified by repeated vacuum distillation, and a very viscous yellowish liquid of the constants B. p. = (145–150)_{mm}; $d_4^{25} = 0.9657$; $n_D^{25} = 1.5055$; $[\alpha]_D = -6.34$; M. R. = 68.2 was isolated. From these properties and the analytical figures (C=80.8; H=11.4; O=7.8) we learned that the fraction consisted of alcohol $C_{15}H_{26}O$ with one double bond in the molecule ($C_{15}H_{26}OF_1 = 68.1$). It changes in colour, on being kept in a bottle, to bluish green.

These properties of the alcohol so far studied, resemble those of the cryptomerol isolated from the cedar root and studied by H. Kimura and also of the sesquiterpene alcohol obtained from cedar leaves by S. Uchida, and therefore the alcohol was called *kiganole*.

When kiganole was subjected to oxidation by the Vesterberg method¹, cadalene was formed, and a hydrocarbon $C_{15}H_{24}$, B. p. = $(115-146)_{6mm}$; $d_4^{25} = 0.928$; $n_D^{25} = 1.508$; $[\alpha]_D = -15^\circ$, resulted on heating with phthalic anhydride; it probably has two double bonds in its molecule.

On reduction, kiganole gave a saturated alcohol (dihydrokiganole) $C_{15}H_{26}O$, B. p. = $(124-128)_{1.5mm}$; $d_4^{25} = 0.9547$; $n_D^{25} = 1.4964$; $[\alpha]_D = -3^\circ$, which on being treated with acetic anhydride without formation of any ester, yielded an unsaturated hydrocarbon $C_{15}H_{26}$, B. p. = $(102-108)_{1.5mm}$; $d_4^{25} = 0.8999$; $n_D^{25} = 1.4932$; $[\alpha]_D = +2^\circ$, this hydrocarbon gives rise to acetone on oxidation with ozone.

These facts favour the view that the dihydrosesquiterpene alcohol is a tertiary alcohol represented by either formula V or VI, and the unsaturated hydrocarbon formed by dehydration has the double bond between 4 and 8 carbon atoms. The saturated sesquiterpene alcohol formed by reduction of kiganole is, therefore, isomeric with the alcohol prepared by the hydrogenation of the sesquiterpene alcohol from camphor blue oil.

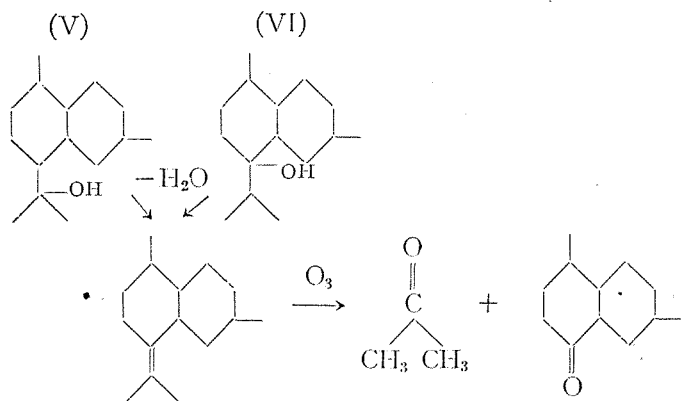
Dihydrosesquiterpene alcohol derived from kiganole of the Japanese cedar oil.

B. p. $(124-128)_{1.5mm}$,
 d_4^{25} 0.9547
 n_D^{25} 1.4964

Dihydrosesquiterpene alcohol derived from the sesquiterpene alcohol of camphor blue oil.

$(145-150)_{12mm}$,
 0.9388
 1.4901

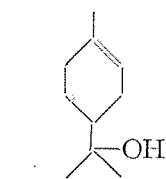
The properties of these compounds, as will be seen in the table,



1. Ber., **36**, 4260 (1903); L. Ruzicka und J. Meyer: Helv., **4**, 505 (1921).

will be different from each other, and are in agreement with structure V for our compound and VI for the isomer¹.

This opinion as to the structure of the sesquiterpene alcohols is based on the fact that the physical constants of monoterpene alcohols have a close connection with the position of the hydroxyl group in their molecule; i. e. α -terpineol² in which hydroxyl group is joined to carbon 8 shows higher values in its physical constants than terpinenol-4².

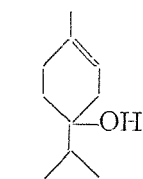


α -Terpineol

B. p. 217—218

d 0.940¹⁵

n_D 1.4808²⁰



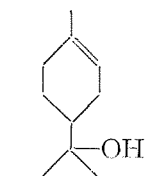
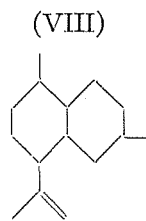
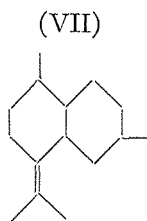
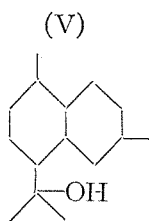
Terpinenol-4

209—212

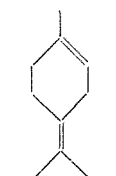
0.9265¹⁹

1.4785¹⁹

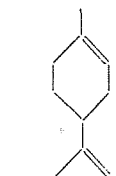
If such a relation between the physical constants and the position of the OH group of monoterpene alcohols holds in the case of sesquiterpene alcohols, dihydrokiganole which shows higher physical constants than the isomer obtained from camphor oil, should have formula V for its structure. If we accept the structural formula V for



α -Terpineol



Terpinolene



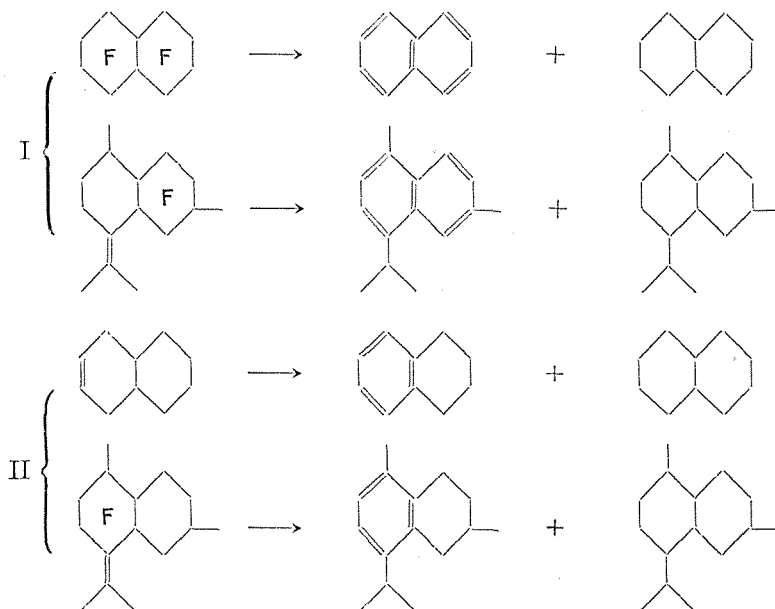
Limonene

1. S. Komatsu, H. Fujimoto and S. Tanaka: These Memoirs, A, 14, 149 (1931).
2. E. Gildemeister: Die Aetherischen Oele, Band I, 394, 400.

dihydrokiganole, the structure for the hydrocarbon $C_{15}H_{26}$ formed by dehydration of the alcohol should be represented by either formula VII or VIII, and the chemical relation between these two compounds is obviously alike to that in the formation of limonene and terpinolene from α -terpineol by dehydration as shown by Wallach¹.

The fact that the unsaturated hydrocarbon derived from dihydrokiganole yields acetone on oxidation with ozone disposes of the formula VII for this compound.

In order to determine the position of the hydroxyl group and the double bond in the molecule of kiganole the writers have applied the method of catalytic oxidation-reduction in the presence of palladium to the unsaturated hydrocarbon $C_{15}H_{24}$ generated from kiganole by dehydration, the process which has already been used by one of the writers (S. Kimura) in the investigation of hydronaphthalenes² for the determination of their chemical structure. It has been confirmed that a hydronaphthalene having the double bond in each hexamethylene ring yields naphthalene and decahydronaphthalene on oxidation-reduction, while from hydrocarbons, in which two double bonds occur in the



1. Ann., **275**, 103 (1893); **291**, 361 (1896).

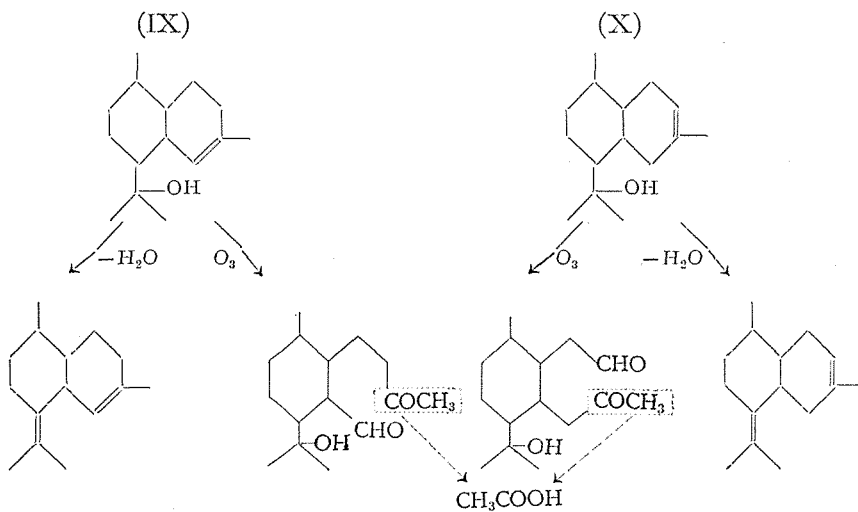
2. Loc. cit.

same ring, tetrahydro- and decahydronaphthalenes have actually been produced.

As a matter of fact, the hydrocarbon $C_{15}H_{24}$ obtained from kiganole $C_{15}H_{20}O$ catalytic oxidation-reduction at 320° in the presence of palladium asbestos, yielded cadalene and decahydrocadalene, and the reaction should be represented by scheme I but not by II; consequently, the two double bonds of the hydrocarbon occur in different rings.

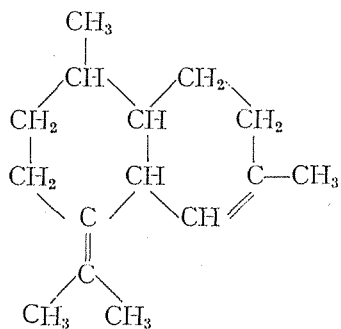
	$C_{15}H_{24}$	\rightarrow	$C_{15}H_{18}$	+	$C_{15}H_{28}$
B. p.	(108-114) _{4.5mm}		(118-125) _{4.5mm}		(96-99) _{4.5mm}
d_4^{25}	0.9138		0.921		0.8840
n_D^{25}	1.5058		1.523		1.4800

Furthermore, the fact that oxidation of the sesquiterpene alcohol with ozone gives acetic acid as one of the reaction products is explained by applying as its structure formula IX or X.



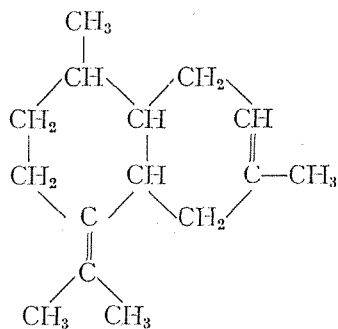
Accordingly, for the sesquiterpene kiganene occurring with the sesquiterpene alcohol kiganole of formula IX or X in cedar oil, either structure III or IV should be proposed and this proposition for the

structure is clearly endorsed by the hypothesis put forward by Prof. S. Komatsu and his collaborateurs¹ in their study of the sesquiterpene and alcohol obtained from camphor oil, 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.



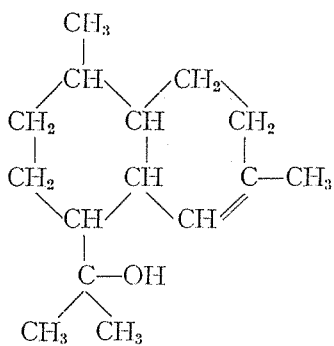
(III)

or



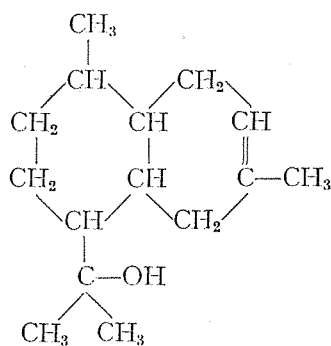
(IV)

Kiganene



(IX)

or



(X)

Kiganole

Experimental

The essential oil used in this experiment was prepared by steam distillation from the roots of Japanese cedars grown at Tosa. It is a

1. Loc. cit.

viscous yellowish green liquid, B. p. = (255–285)_{760mm}; $d_4^{25} = 0.936$; $n_D^{25} = 1.508$; $[\alpha]_D = -16.7$; acid val. = 0.9; ester val. = 8.9.

For the separation of hydrocarbon from alcohol, 2810 gms. of the oil were heated with sodamide on a water bath under reduced pressure until no more ammonia gas was evolved. After the hydrocarbon had been distilled under diminished pressure, the free alcohol was isolated from alcoholate by decomposition with water. The yield of crude sesquiterpene and crude sesquiterpene alcohol was 1528 gms. (54 %) and 1060 gms. (38 %) respectively with 172 gms. (6 %) of tarry matter, and the physical constants were ($d_4^{25} = 0.922$; $n_D^{25} = 1.515$; $[\alpha]_D = -20.1$) for the hydrocarbon and ($d_4^{25} = 0.953$; $n_D^{25} = 1.503$; $[\alpha]_D = -19.5$) for the alcohol.

I. Kiganene $C_{15}H_{21}$

(A) Cadinene dihydrochloride

When dry hydrogen chloride gas was passed into the crude sesquiterpene, cadinene dihydrochloride M. p. = 117–118°¹ was formed with a yield of about 60 %.

(B) Purification of Sesquiterpene

80 gms. of crude sesquiterpene containing 60 % cadinene hydrochloride yielding compound were purified by distillation with metallic sodium under 4.5 mm. pressures.

	Fraction	Yield (gms.)	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.
(1)	108–114°	47	0.9150	1.5085	-22.4	66.4
(2)	114–118°	17	0.9315	1.5119	—	—

Fraction (1) which formed the main portion of the essential oil was a colourless liquid turning to a yellowish brown colour gradually on standing in the air, and was assumed to be composed of a bicyclic sesquiterpene by reference to its physical constants (M. R. calculated for $C_{15}H_{21}F_2$ is 66.1), and named *kiganene*.

1. F. W. Semmler: Die Aetherischen Oele, II, 561.

(C) Oxidation of Kiganene with Ozone

Ozonized oxygen was passed into a solution of 4 gms. of kiganene in 40 c.c. of carbon tetrachloride, and some iodoform was found in a potassium iodide solution placed after the reaction tube.

The ozonide, separated from carbon tetrachloride solution, was decomposed with water, and the aqueous solution separated from oily matter gave a blood-red colour with ferric chloride and sodium carbonate and also mercurous acetate with mercurous nitrate¹, due to the presence of acetic acid in the solution, but no reaction for formaldehyde and formic acid was noticed with the aqueous solution.

II. Kiganole $C_{15}H_{25}O$

(A) Purification of Sesquiterpene Alcohol

587 gms. of crude sesquiterpene alcohol separated from sesquiterpene by means of sodamide were fractionated under 9 mm. pressure into the following fractions:—

	Fraction	Yield gms.	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.
(1)	122—132	61	0.9399	1.5074	—14.04	—
(2)	132—142	24	0.9462	1.5061	—21.56	—
(3)	142—145	120	0.9523	1.5050	—11.0	—
(4)	145—150	212	0.9657	1.5055	—6.34	68.2
(5)	150—167	21	0.9750	1.5132	—	—

Fractions (1), (2) and (3) were assumed from their physical constants to be composed mostly of hydrocarbon. Fraction (4) which was a viscous, yellowish green liquid changed its colour to bluish green gradually on standing in air. The physical constants and the analytical results indicate that this fraction consists of a bicyclic sesquiterpene alcohol of M. R. $C_{15}H_{25}OF_1=68.1$ and named *kiganole*. The analytical results are as follows: 0.1490 gm. subst., gave 0.4415 gm. CO_2 and 0.1534 gm. H_2O . Found: C=80.8; H=11.4; requires C=81.1; H=11.7 for $C_{15}H_{25}O$.

1. L. Rosenthaler: Der Nachweis Organischer Verbindungen, 284, 285.

(B) Dehydrogenation of Kiganole with Sulphur

10 gms. of kiganole were heated with 5 gms. of sulphur at 150–180°C for about 10 hours and the reaction product was distilled under reduced pressure, and then on metallic sodium, and 1.7 gms. of hydrocarbon of the following physical constants were obtained: B.p.= (172–175)_{21mm}; $d_4^{25}=0.9667$; $n_D^{25}=1.5785$. It yielded cadalene picrate¹ melting at 114–115°.

(C) Reaction of Kiganole with Phthalic Anhydride

10 gms. of kiganole were heated with an equal weight of phthalic anhydride at 120° for about 8 hours and the hydrocarbon formed by the reaction gave the following constants: B.p.= (115–146)_{6mm}; $d_4^{25}=0.928$; $n_D^{25}=1.508$; $[\alpha]_D=-15.1$.

(D) Catalytic Reduction of Kiganole

(a) The Reduction of Kiganole by colloidal Palladium and Hydrogen²

5 gms. of the alcohol were dissolved in 25 gms. of glacial acetic acid and reduced with hydrogen of 1.6 atmospheric pressures in the presence of colloidal palladium. The absorption of hydrogen gas was about 85 % of the theoretical value to saturate one double bond in the molecule. Thus, 54 gms. of kiganole yielded 46.1 gms. of the hydrogenated compound, B.p.= (115–130)_{4.5mm}; $d_4^{25}=0.945$; $n_D^{25}=1.495$; $[\alpha]_D=-5.4$, which were fractionated under 4.5mm. pressures into the following 3 portions.

	Fraction	Yield gms.	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.
(1)	107–124	16.6	0.9316	1.4928	–13.0	–
(2)	124–128	16.4	0.9547	1.4964	– 3.2	68.7
(3)	128–134	5.4	–	–	–	–

Fraction (1) was assumed from its physical constants to be composed of hydrocarbon formed by dehydration of the alcohol, and fraction

1. L. Ruzicka u. J. Meyer: *Helv.*, **4**, 508 (1921).

2. Skita: *Ber.*, **45**, 3589 (1912).

(3) was the unchanged kiganole. Fraction (2) was a colourless viscous liquid and was supposed from the physical constants and analytical results to consist of dihydrokiganole $C_{15}H_{23}O$ (theory for M.R.=68.6).

On analysis 0.1618 gm. of subst., gave 0.4769 gm. CO_2 and 0.1760 gm. H_2O . Found: C=80.4; H=12.1; requires C=80.4; H=12.5 for $C_{15}H_{23}O$.

(b) *Catalytic Reduction under High Pressure and Temperature*

46 gms. of kiganole were reduced in the presence of reduced nickel at 140° under 70 atmospheric pressures of hydrogen, and the absorption of hydrogen was 25.9 atmospheric pressures, whereas the theoretical value of hydrogen for the saturation of one double bond corresponds to 23.2 atmospheric pressures. The reaction product ($d_4^{25}=0.941$; $n_D^{25}=1.493$) was fractionated under 4.5 mm. pressures into the following 3 portions.

	Fraction	Yield gms.	d_4^{25}	n_D^{25}	$[\alpha]_D$
(1)	112-125	13	0.9209	1.4922	+2.04
(2)	125-129	25	0.9492	1.4940	+7.07
(3)	129-135	3	—	1.4982	—

The physical constants indicate that fraction (3) consists of dihydrokiganole $C_{15}H_{23}O$.

(E) *Dehydration of the Dihydrokiganole $C_{15}H_{23}O$*

12 gms. of the dihydrokiganole obtained by reduction in the presence of colloidal palladium were heated in a sealed tube with an equal weight of acetic anhydride at 150° for about 5 hours, the reaction product being distilled under diminished pressure with metallic sodium after being separated from the acid, and 8.6 gms. of hydrocarbon were obtained. It showed the constants: B.p.=(102-108)_{imm}; $d_4^{25}=0.8999$; $n_D^{25}=1.4932$; $[\alpha]_D=+2.1$; M.R.=66.7 (theor. val. for $C_{15}H_{26}F_1=66.6$).

In the second experiment, 15 gms. of the dihydrokiganole prepared by catalytic reduction under high temperature and pressure were dehydrated in the same manner as in the former case, and 9.8 gms. of the hydrocarbon, B.p.=(102-106)_{imm}, $d_4^{25}=0.8944$; $n_D^{25}=1.4915$; $[\alpha]_D=+8.27$; M.R.=66.4) were obtained.

The hydrocarbon $C_{15}H_{26}$, thus formed by dehydration of the dihydrokiganole, was oxidized with ozone in the usual way and the formation of acetone was recognised in the reaction product.

(F) Dehydration of Kiganole $C_{15}H_{26}O$

30 gms. of kiganole were heated in a sealed tube, with an equal weight of acetic anhydride at 150° for about 6 hours, and 18.4 gms. of hydrocarbon $C_{15}H_{24}$ of the following physical constants resulted: B.p. = $(108-114)_{4.5\text{mm}}$; $d_4^{25} = 0.9138$; $n_D^{25} = 1.5058$; $[\alpha]_D = +21.23$; M.R. = 66.2 (theor. val. for $C_{15}H_{24}F_2 = 66.1$).

(G) Catalytic Oxidation-Reduction of Hydrocarbon $C_{15}H_{24}$

11 gms. of the hydrocarbon prepared by dehydration of kiganole mentioned in F were passed with dry carbon dioxide gas over palladium asbestos heated at 320° for about 2 hours, and 10.4 gms. of the reaction product ($d_4^{25} = 0.908$; $n_D^{25} = 1.511$) were fractionated under 5 mm. pressures into the following 3 portions.

	Fraction	Yield gms.	d_4^{25}	n_D^{25}
(1)	99-106	2.3	0.9002	1.5050
(2)	106-118	6.4	—	1.5110
(3)	118-125	1.2	0.9210	1.5225

Fraction (1) after being treated with conc. sulphuric acid to remove any unsaturated hydrocarbon was distilled under diminished pressure, and decahydrocadalene¹ was isolated, which was confirmed to be so by the constants: B.p. = $(96-99)_{4.5\text{mm}}$; $d_4^{25} = 0.8840$; $n_D^{25} = 1.4800$.

Fraction (3) should consist of cadalene which yields a picrate of M.p. = 112° , the melting point not showing any depression when it was mixed with pure cadalene picrate.

(H) Oxidation of Kiganole $C_{15}H_{26}O$ with Ozone

4 gms. of the sesquiterpene alcohol were oxidized with ozone in the usual way, and acetic acid was noticed to occur in the reaction product but no trace of formaldehyde and formic acid.

1. S. Kimura, Loc. cit.

In conclusion, the writers wish to express their hearty thanks to Prof. S. Komatsu for his kind guidance and valuable suggestions throughout this work and also to Dr. T. Kainosho, the Director of the Takasago Perfumery Co. for his generous gift of the valuable material, which has made this investigation possible.

May 1930.

Laboratory of Organic- & Bio-Chemistry.
