STUDIES ON THE CONSTITUENTS OF THE VOLATILE OIL FROM THE LEAF OF *CHAMAECYPARIS OBTUSA*, SIEB. ET ZUCC., F. *FORMOSANA*, HAYATA, OR ARISAN-HINOKI. PART II.

By Kinzô KAFUKU and Tetsuo NOZOE.

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In the previous paper, the authors and C. Hata have reported on the terpenic as well as the terpenic alcoholic constituents of the essential oil from the leaf of "arisan-hinoki" or *chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata.(1) The present paper is its sequel and deals with the higher boiling ingredients of the same. As regards the high-boiling constituents of similar essential oils, R. Tsuchihashi and S. Tasaki(2) have reported that cadinene and a dicyclic sesquiterpene alcohol-chamaecypariol were present in the wood oil from the same plant as the authors', while S. Uchida,(3) who examined the leaf oil of "hinoki" or Japanese *chamaecyparis*, has proved, besides cadinene, a tricyclic sesquiterpene, a dicyclic sesquiterpene alcohol, and an inactive tetracyclic diterpene in it. The present authors' oil, however, showed a marked difference from the foregoing in various respects, a brief account of which will be described first.

The authors' sesquiterpene fraction, which occupied about 38% by weight of the whole oil, consisted for the most part of three sesquiterpenes, among which the most predominating was a new tricyclic sesquiterpene, the rest represent *d*-cadinene and another tricyclic sesquiterpene. The name "sesquichamene" is suggested by the authors to this predominant tricyclic sesquiterpene. From point of view of physical constants, sesquichamene is almost identical with many of the hitherto known sesquiterpenes of the tricyclic class, such as cedrene,(4) tricyclogurjunene,(5) or longifolene,(6) but it differs decidedly from the others in many chemical behaviours. The most characteristic of all is that it gives a crystalline nitrosochloride which melts with decomposition at 78°-79°C. It is rather unstable and cannot be kept for more than a few hours even in the purest state, but, unstable as it is, it should be remarked, that this is the only crystalline nitrosochloride ever prepared out of tricyclic sesquiterpenses. The nitrolbenzylamine can also be prepared from this nitrosochloride. It

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(1) This Bulletin, **6** (1931), 40.
(2) *Report of Govern. Research Inst. Formosa* (1920).
(3) *J. Soc. Chem. Ind. Japan*, **19** (1916), 611.
(4) Semmler, *Ber.*, **40** (1907), 3521; **45** (1912), 355.
5) Semmler, *Ber.*, **47** (1914), 1029, 1141.
6) Simonsen, *J. Chem. Soc*., **117** (1920), 570; **123** (1923), 2642.

melts at 158°-159°C. The nitrosochloride dissolves readily in chloroform and acetone forming blue solutions, from which the original nitrosochloride can be reprecipitated by the addition of ethyl or methyl alcohol, and thus it can be purified by repeating this treatment. It should be remembered, however, that the nitrosochloride is also very unstable in the dissolved state, and the blue colour of the solutions rapidly fades away into yellow minute by minute, and once it becomes yellow, then the reprecipitation impossible.

Sesquichamene slowly oxidizes in the air, and the yield of the characteristic nitrosochloride is maximal only directly after its distillation but declines steadily and ultimately into nil on standing. By oxidizing sesquichamene with potassium permanganate in acetone solution, a glycol melting at 89°-91°. a diketone whose disemicarbazone melting with decomposition at 233°, and a crystalline substance of an undefined nature, have been obtained. By the action of alcoholic sulphuric acid, sesquichamene undergoes isomerization and gives rise to an isomer which should be named "isosesquichamene." Isosesquichamene has a far lower rotatory power and a greater stability than the original sesquichamene. It should be noted that in our sesquiterpene fraction, a small quantity of isosesquichamene was found to be present. Whether this sesquiterpene had been present in the original oil, or had it arisen from sesquichamene during the processes of fractional distillations, remains to be discussed later. Uchida's tricyclic sesquiterpene also seems possibly to be the same, but in his case, it is to be anticipated that it resulted from sesquichamene by the action of heat, as his fractionations were carried out under the atmospheric pressure. Table 1 shows the physical constants and the melting points of characteristic derivatives of hitherto known tricyclic sesquiterpenes and those of sesquichamene and isosesquichamene:

Table 1.

	Cedrene	Tricyclogurjunene	Longifolene
	(Semmler)(4)	(Semmler)(5)	(Simonsen)(6)
B. p.	$121°-124°/_{12}$	$120°-123°/_{13}$	$150°-151°/_{35}$
d	$0.9354/_{15}$	$0.9348/_{15}$	$0.9284/_{30}$
n_D	1.5030	1.5028	$1.495/_{30}$
α_D	−56° (86°)	+74.5°	+42.7°
Hydrochloride	liq.	liq.	59°−60°
Ketone $C_{15}H_{24}O$	43°	43°	....
Semicarbazone	242°−243°	237°	....
Diketone	....	....	94°−95°
Disemicarbazone	234°	....	....
Glycol	168° (172°)	....	....
Nitrosochloride	....	....	....
Nitrolbenzylamine	....	....	....

Table 1.—(*Concluded*)

	Sesquichamene	Isosesquichamene	Isosesquichamene(3)
	(Authors')	(Authors')	(Uchida)
B. p.	122°—123°/$_{12}$	129°—131°/$_{12}$	265°—268°/$_{760}$
d	0.9277/$_{28}$	0.9320/$_{20}$	0.9367/$_{20}$
n_D	1.5012/$_{28}$	1.5109/$_{21}$	1.5009/$_{20}$
α_D	−89.4°/$_{28}$	−8.5°/$_{21}$	−15.7° (alcohol)
Hydrochloride	liq.	liq.	liq.
Ketone $C_{15}H_{24}O$	....	....	....
Semicarbazone	....	....	....
Diketone	....	....	....
Disemicarbazone	233° (dec.)	....	....
Glycol	89°—91° (dec.)	....	....
Nitrosochloride	78°—79° (dec.)	....	....
Nitrolbenzylamine	165°–166° (dec.)	....	....

The sesquiterpene alcohol fraction amounted to about 8% of the whole oil and contained a dextro-rotatory dicyclic sesquiterpene alcohol and cadinol. Besides, it contained also a very small quantity of tricyclic sesquiterpene alcohol which was not cedrol. The dicyclic sesquiterpene alcohol present was probably identical with that which had been found by Uchida in Japanese chamaecyparis oil. The only definitely identified compound among these was cadinol.

The diterpene fraction was very poor, amounting to only 1% of the original oil. Its physical properties showed that it consisted mainly of a laevo-rotatory tetracyclic diterpene. Its rotatory power, however, on treatment with acids, or by the action of heat, went diminutive and gave rise to an inactive diterpene which was most probably identical with Uchida's inactive diterpene in the above-mentioned oil. We wish to propose the name "chamaecyparene" to this active diterpene, and also the name "isochamaecyparene" to the racemized or isomerized inactive diterpene. The following table shows the physical properties of the dicyclic sesquiterpene alcohol and the diterpene obtained by Uchida and by us:

Table 2.

	Sesquiterpene Alcohol		Diterpene	
	(Uchida)	(Authors')	(Uchida)	(Authors')
B. p.	290°—295°/$_{760}$	146°—148°/$_{12}$	340°—343°/$_{760}$	185°—186°/$_{12}$
d	0.9599/$_{4}$	0.9492/$_{25}$	0.9624/$_{15}$	0.9648/$_{25}$
n_D	1.5020/$_{20}$	1.4995/$_{25}$	1.5190/$_{20}$	1.5158/$_{25}$
α_D	+18° (alcoh.)	+4.0°	±0°	−25.1°

Experimental.

The Sesquiterpene Fraction. After eight consecutive systematic fractional distillations under 12 mm. pressure (the last three times over metallic sodium) the following eleven fractions were obtained:—

	B. p. / $_{12}$ mm.	Distillate	n_D^{25}	d_4^{25}	α_D^{25}	M. R.
(1)	115°—120°	10	1.4940	0.9240	−37.0°	64.27
(2)	120°—122°	34	1.4990	0.9272	−51.8°	64.60
(3)	122°—124°	467	1.5031	0.9297	−85.8°	64.87
(4)	124°—126°	57	1.5035	0.9283	−70.6°	65.01
(5)	126°—128°	14	1.5048	0.9274	−52.8°	65.22
(6)	128°—130°	8	1.5049	0.9261	−31.5°	65.32
(7)	130°—132°	31	1.5062	0.9244	−13.7°	65.59
(8)	132°—134°	24	1.5075	0.9232	+18.0°	65.59
(9)	134°—136°	68	1.5073	0.9226	+43.1°	65.84
(10)	136°—140°	23	1.5056	0.9238	+44.2°	65.56
(11)	140°—142°	18	1.5024	....	+14.0°	....

A glance at these constants enables us to notice that the main constituent is represented by the fraction (3) where a preponderating maximum of the quantity of distillate as well as maxima of density and laevo-rotation are to be observed. From considerations of the molecular refraction it is evident that the predominant sesquiterpene belongs to the tricyclic class. The fraction (9) is also peculiar, corresponding to a small maximum of the quantity of distillate, a minimum of density, and a maximum of the dextro-rotation. This fraction should represent a dicyclic sesquiterpene as its molecular refraction is much greater than that of the fraction (3).

Sesquichamene. On rectification of the fraction (3), its physical constants exhibited the following values:

B. p. 122.5°—123.5° / $_{12}$ mm.; n_D^{28} 1.5021; d_4^{28} 0.9277; α_D^{28} −89.85°;

M. R. found 64.81, calculated as $C_{15}H_{24}\big|^{=}_{1}$ 64.45;

Anal. Subst. = 0.1627; CO_2 = 0.5254; H_2O = 0.1687 gr. Found: C = 88.01; H = 11.52%. Calc. for $C_{15}H_{24}$: C = 88.16; H = 11.84%.

Sesquichamene Nitrosochloride. A pure, freshly distilled sesquichamene was dissolved in twice its volume of absolute ether, and a current of dry nitrosyl chloride gas was passed through the cold solution contained in a vessel surrounded by freezing mixtures. After a while, the vessel became filled with crystals. The vessel was left in the cold for half an hour more, and then the crystals were filtered, washed with cold ether and alcohol, and dried in vacuo. The yield of this crystalline substance amounted to about 75-80%. It was then purified by reprecipitating its chloroformic solution with methyl alcohol, and was obtained as colourless needles melting with methyl alcohol, and was obtained as colourless needles melting with decomposition at 77.5°-78.5°. A very pure sample obtained by repeating this process several times, could be kept for three to five hours without any appreciable decomposition. It is very soluble in chloroform and benzol, pretty soluble in petroleum ether, ethyl acetate, aceton, and ether, but very slightly so in methyl alcohol, ethyl alcohol, and water.

Sesquichamene Nitrolbenzylamine. A weighed quantity of the nitrosochloride was suspended in a small volume of alcohol to which a slight excess of an alcoholic solution of benzylamine was slowly added in the cold. The crystals of the nitrosochloride was seen to disappear gradually as the temperature of the solution reached the room temperature, and then the product of reaction was precipitated by adding water thereto, filtered, washed with ether, and recrystallized from dilute alcohol. Sesquichamene nitrolbenzylamine thus prepared melted with decomposition at 165°-166°.

By the action of sodium nitrite and glacial acetic acid on sesquichamene, a semicrystalline deposit of sesquichamene nitrosite was obtained, but no further means of purification was possible as the crude nitrosite, on dissolving it in any of the ordinary solvents, was liable to pass into the oily state never to crystallize again. The preparation of the nitrosate was also tried but with negative results.

Oxidation of Sesquichamene. A mixture of 40 gr. of sesquichamene, 250 gr. acetone, and 80 c.c. of water was put into a vessel and kept agitated. To this mixture 80 gr. of finely powdered potassium permanganate was added in small portions, the temperature being kept under 40° the while. In half an hour the reaction was over, so the solution was filtered, the precipitate of manganese dioxide thoroughly extracted with hot acetone, the acetone solutions combined, evaporated, and then the whole mass was subjected to steam distillation. Nextly the products of reaction were divided into an acidic and a neutral portions in the usual manner.

The neutral products were collected and they were fractionated by three successive fractional distillations, when the fractions with following properties came over :—

	B. p.	Pressure	gr.	n_D^{28}	α_D^{28}
(1)	up to 140°	12 mm.	5	1.5140	− 80.0°
(2)	140°—155°	,,	2	1.5067	....
(3)	155°—160°	,,	7	1.5028	− 89.3°
(4)	160°—165°	,,	11	1.5040	−79.3°
(5)	165°−170°	,,	1	1.5044	....
(6)	170°−175°	,,	2	1.5059	....
(7)	175°—180°	,,	1	1.5068	....
(8)	161°—163°	4 mm.	26	1.5090	−21.3°

The residue from these distillations represented a solid mass, which when extracted with acetone while hot, left a white powder. This powder was soluble in chloroform and benzol, but insoluble in alcohol, acetone, or ethyl acetate. The chloroformic solution, on addition of methyl alcohol, deposited an oil which solidified in course of time but looked possibly amorphous. It sintered at 220° and melted with decomposition at 240°-245°.

The fraction (8) on standing gave a little crystalline deposit which could not be separated from its mother liquor by ordinary filtration on account of its excessive viscidness. Therefore, it was dissolved in 3-5 volumes of petroleum ether and kept still for a length of time in the ice box, until at last an aggregation of fine needle crystals separated out. It was filtered and washed with ice-cold petroleum ether, and then recrystallized from hot petroleum benzine. It melted at 89°-91°.

Anal. Subst. = 3.333 mg.; CO_2 = 9.20 mg.; H_2O = 3.311 mg. Found: C = 75.35; H = 11.12%. Calc. for $C_{15}H_{26}O_2$: C = 75.6; H = 10.9%.

The fractions (3) to (8) were treated with solutions of sodium acetate and semicarbazide hydrochloride and the crystalline deposit formed thereby filtered, washed with alcohol and ether, and dried. From each of the fractions the same semicarbazone resulted which melted with decomposition at 233°. It differed from hydrazodicarbonamide (m.p. 257°) in being insoluble in all ordinary organic solvents and also in its crystalline form and solubility in hot water. The result of analysis is as follows :—

1.89 mg. substance gave 0.414 c.c. nitrogen (23.5°C; 765.4 mm.).

	Found	$C_{17}H_{30}O_2N_6$	$C_{17}H_{28}O_2N_6$	$C_{16}H_{28}O_2N_6$	$C_{16}H_{26}O_2N_6$
N %:	24.9	24.0	24.1	25.0	25.2

It follows that the substance in question was either a semicarbazide-semicarbazone of an unsaturated monoketone $C_{14}H_{20}O$ or a disemicarbazone of a diketone $C_{14}H_{20}O_2$. But since this substance was not soluble in mineral acids, it is to be expected that this substance represents a disemicarbazone of a diketone or a keto-aldehyde.

Isosesquichamene. Shaking with aqueous sulphuric acid brought no action on sesquichamene, but when alcoholic sulphuric acid was used, its optical activity gradually demolished. Thus, 25 gr. sesquichamene was treated with 10 gr. of alcoholic sulphuric acid (1:1) at 40°-50°, when in course of 1.5 hours its activity depressed to the value -9.5°. It was then twice rectified over metallic sodium and a main fraction with the following properties was obtained :—

B. p. 129°—131° / 12 mm. ; $n_D^{21.5}$ 1.5109 ; $d_4^{21.5}$ 0.9320 ; $\alpha_D^{21.5}$ −8.52° ;

M. R. Found : 65.60. Calc. : 64.79 as $C_{15}H_{24}|^{=}_{1}$; 65.60 as $C_{15}H_{24}|^{=}_{2}$.

This sesquiterpene showed a fairly more stable quality against the action of the air but afforded no crystalline hydrochloride by treatment with hydrogen chloride gas.

d-Cadinene. The fractions (9) and (10) when dissolved in twice the volume of absolute ether, treated with a current of dry hydrogen chloride gas, and kept in cold for two days, deposited a quantity of needle crystals on evaporating off ether. After recrystallization from alcohol these crystals melted at 118°-119°, and were proved to be identical with cadinene dihydrochloride, as they showed no depression of the melting point on admixture with pure cadinene dihydrochloride from known source. From these fractions no nitrosite, nitrosate or nitrosochloride could be obtained in the crystalline state.

The fraction (7) gave neither hydrochloride nor nitrosochloride on usual treatment. Judging from its physical constants it seems most probable that it contained isosesquichamene.

The Sesquiterpene Alcohol and Diterpene Fractions. The portion containing sesquiterpene alcohols and diterpenes was fractionated six times under 12 mm. pressure and separated into the following eleven fractions, the physical constants of which are tabulated below :—

	B. p. / 12 mm.	Distillate	n_D^{25}	d_4^{25}	α_D^{25}
(1)	136°—140°	17 gr.	1.5018	0.9388	+14.8°
(2)	140°—145°	23	1.5006	....	+ 8.3°
(3)	145°—149°	55	1.5001	0.9482	+ 3.5°
(4)	149°—151°	15	1.5021	....	+ 5.6°
(5)	151°—154°	35	1.5033	0.9680	+ 7.8°
(6)	154°—157°	39	1.5062	0.9773	+ 8.8°
(7)	157°—159°	11	1.5113	0.9824	− 5.3°
(8)	159°—163°	23	1.5130	0.9860	−10.4°
(9)	163°—170°	5	1.5170	....	−20.0°
(10)	170°—180°	11	1.5184	....	−23.6°
(11)	180°—186°	22	1.5185	0.9650	−22.8°

d-Cadinol. On rectification the fractions (5) and (6) gave a main part having the following characteristics:

B. p. 146°—148°/$_{12\,\mathrm{mm.}}$; $n_D^{22.5}$ 1.5043; $d_4^{22.5}$ 0.9706; α_D^{22} +7.76°;
M. R. Found: 67.91. Calc. as $C_{15}H_{26}O$ 68.12.

By the action of hydrogen chloride, cadinene dihydrochloride melting at 118°-119° resulted, which showed no depression of melting point on mixing it with a pure specimen obtained from known sources. This fraction gave no other characteristic derivatives.

From considerations of physical properties, the fraction (3) and (8) seemed likely to consist of sesquiterpene alcohols of dicyclic and tricyclic structure respectively, but all attempts to get definite proofs failed.

The fraction (11) was further rectified in vacuo and a main fraction consisting chiefly of diterpenes was obtained. It showed the following constants:—

B. p. 185°—186°/$_{12\,\mathrm{mm.}}$; n_D^{25} 1.5185; d_4^{25} 0.9648; α_D^{25} −25.1°;
M. R. Found: 85.56. Calc. as $C_{20}H_{32}\,|^{\overline{=}}_{1}$ 85.21.

On treatment with alcoholic sulphuric acid (1:1), the optical activity of the diterpene enfeebled pretty rapidly. Also on heating it to 350° for several hours inactiviation ensued.

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Department of Industry,
Government Research Institute of Formosa,
Taihoku, Formosa.