

# STUDIES ON THE VOLATILE CONSTITUENTS OF THE LEAF OF CHAMAECYPARIS FORMOSENSIS, MATSUM.

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*Chamaecyparis formosensis*, Matsum. or "benihi" is a conifer indigenous to Formosa and one of the most important timber trees of the island. Its older growths are found along the central mountain range at an altitude of 7000 to 8500 ft. above sea level. Most of these trees are gigantic in size, the biggest tree on Mt. Ari is said to be more than two thousand years old and measures indeed 160 ft. in height and 25 ft. in diameter. The leaf of this conifer has a peculiarly pleasant odour of its own, but as to the nature of its volatile constituents, nothing has yet been reported. The authors, with a view to study such, distilled the live leaves of freshly felled trees on Mt. Ari with steam then and there, and could obtain a quantity of a reliable material for examination, in form of a faintly reddish coloured mobile oil with the characteristic odour, the yield of the oil amounting to 0.16% as referred to the whole weight of the leaf. This oil, on being stood in the air, was liable to oxidize and thicken into a viscid dark reddish-brown mass, however, without any appreciable change in odour. The properties of the oil, a week after its preparation, were as follows :

$d_4^{24}$	$n_D^{24}$	$\alpha_D^{24}$	Acid value	Ester value	Do. after acetylation
0.8645	1.4724	-24.67°	1.06	5.78	26.35

This oil consisted for the most part of terpenes, with smaller quantities of terpene alcohols, sesquiterpenes, and sesquiterpene alcohols. In addition

to these, the authors could detect the presence of minute quantities of a crystalline ketone, a liquid acid and a solid phenol. The ketone had a melting point  $139^{\circ}$ – $140^{\circ}$  and boiled between  $157^{\circ}$  and  $161^{\circ}$ . The authors propose to name this ketone "benihione." The liquid acid and the solid phenol showed a remarkable resemblance to citronellic acid and homopyrocatechin respectively but on account of the small quantity of the substance available, it was impossible to carry out any positive means of identification. Among the terpenes, there predominated a highly active *l*- $\alpha$ -pinene in quantity, while *l*-camphene, dipentene,  $\alpha$ - and  $\gamma$ -terpinene were also present with a little cineol. The terpene alcohol fraction represented chiefly borneol and its esters, while in the sesquiterpene fraction the authors detected cadinene and humulene. The highest boiling fraction as a whole seemed to consist of a dicyclic sesquiterpene alcohol of a tertiary nature perhaps identical with "cadinol" of Semmler and Jonas.<sup>(1)</sup>

### Experimental.

**Acids and Phenols.** 2800 gr. of the crude oil was shaken on the machine with a quantity of 3% caustic alkali solution and acids and phenols were regenerated from this aqueous layer in the usual manner. After due purifications 2.14 gr. of acidic and 1.2 gr. of phenolic portions were obtained. Both of these were reddish black in colour but smelled differently,—the former was of a strong fatty odour while the latter reminded of pyrocatechin and cresol at the same time.

**The Acid.** The acidic portion on fractionation in a small distilling apparatus came over chiefly between  $135^{\circ}$  and  $136^{\circ}$  under 6 mm. pressure, and the distillate was found to possess the following characteristics :—

$d_4^{24}$	$n_D^{24}$	Acid value	Bromine value	Ag % of Ag-salt
0.9507	1.4800	330.2	935	38.9

The molecular weight calculated as a monobasic acid from the above data is 169.6 corresponding to a formula  $C_{10}H_{18}O_2$  (M.W. = 170); the calculated value of Ag (%) from  $C_{10}H_{17}O_2Ag$  is 38.96% agreeing well with the experimental result. The bromine value points to the presence of one ethylene linkage, as such requires 940.2 for  $C_{10}H_{18}O_2$ . The odour of this acidic fraction reminded of citronellic acid, but attempts to prepare its acid amide and other derivatives turned out to be futile.

(1) *Ber.*, **47** (1914), 2063.

**The Phenol.** The phenolic portion showed a marked tendency to get darker in colour and to resinify on exposure to the air. On fractional distillation under 8 mm. pressure it furnished the following fractions :—

	B. p. / 8 mm.	$d_4^{24}$	$n_D^{23}$	Colour Reactions		
				aqueous $\text{FeCl}_3$	alcoholic $\text{FeCl}_3$	vanillin+HCl
(1)	123°—130°	0.974	1.5000	red	green	blue
(2)	130°—135°	0.973	1.4959	„	„	purple
(3)	135°—150°	0.976	1.5010	„	„	„
(4)	150°—156°	0.978	1.5013	„	„	„

(3) and (4), on cooling to  $-5^\circ\text{C}$ ., deposited a quantity of scaly crystals which, after purifications showed a melting point  $57^\circ\text{--}62^\circ$ , and seemed likely to be homopyrocatechin (m.p.  $=63^\circ$ ), but owing to the lack of material no further means of identification were possible.

**The Neutral Part.** The lye-washed neutral oil was almost devoid of the reddish tinge as seen in the crude state, and represented a golden yellow transparent oil of the following properties :—

$d_4^{24}$	$n_D^{24}$	$\alpha_D^{21}$	$\eta_{24}$	Ester value	Do. after acetylation
0.8654	1.4717	$-28^\circ$	1.00	5.75	26.44

This oil was four times fractionated under 3 mm. pressure using Wiedmer's fractionating column, when the fractions with the following characteristics came over :—

	B. p. / 3 mm.	$n_D^{28}$	$d_4^{29}$	$\alpha_D^{29}$	Yield %
(1)	31°—40°	1.4640	0.8505	$-39.40^\circ$	83.70
(2)	40°—50°	1.4725	0.8584	$-2.86^\circ$	0.57
(3)	50°—55°	1.4788	0.8621	$-1.23^\circ$	0.42
(4)	55°—60°	1.4839	0.8771	$-1.03^\circ$	0.25
(5)	60°—65°	1.4902	1.0049	$+0.85^\circ$	0.11
(6)	65°—70°	1.4870	1.0114	$+0.30^\circ$	0.07
(7)	70°—80°	1.4683	0.9263	$+7.20^\circ$	0.14
(8)	80°—85°	1.4706	0.9322	$-0.30^\circ$	0.88
(9)	85°—90°	1.4715	0.9319	$-0.45^\circ$	0.67
(10)	90°—95°	1.4740	0.9299	$-12.44^\circ$	0.28

	B. p. /3 mm.	$n_D^{25}$	$d_4^{25}$	$\alpha_D^{25}$	Yield %
(11)	95°—100°	1.4782	0.9281	—17.68°	0.11
(12)	100°—105°	1.4892	0.9152	—27.00°	0.78
(13)	105°—110°	1.4989	0.9053	—30.25°	2.87
(14)	110°—115°	1.5030	0.9054	—13.43°	3.97
(15)	115°—120°	1.5050	0.9141	+18.82°	2.51
(16)	120°—125°	1.5048	0.9331	+27.08°	0.32
(17)	125°—130°	1.5040	0.9478	+13.60°	0.32
(18)	130°—135°	1.5033	0.9583	— 7.00°	0.99
(19)	135°—140°	1.5052	0.9680	—19.59°	1.03

In the above, we notice that maxima of the amount of distillate per degree occur at (1), (8), (14), and (19), while maxima and minima of refractive indices and densities are observable at (1), (5), (7), (15), (19), and (1), (6), (13), (19) respectively. It is also of interest that while most of the fractions are laevo-rotatory, strongly dextro-rotatory fractions are met with at (7) and (16). These features are graphically shown in Fig. 1.

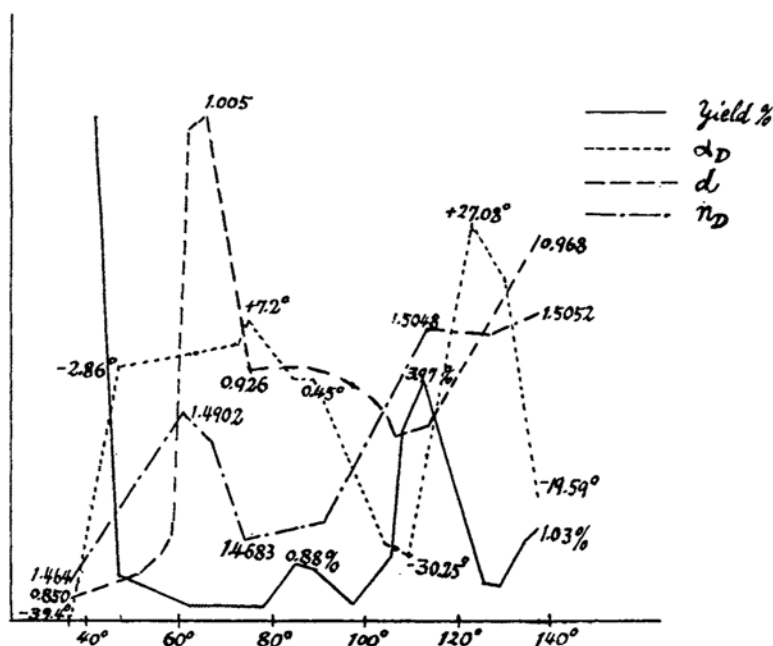


Fig. 1.

**The Terpenes.** Fractions (1) and (2), which represented the greater part of the terpenic constituents, were boiled over metallic sodium for 6 hours under 70 mm. pressure, and then fractionally distilled under the atmospheric pressure using Wiedmer's column for dephlegmation. After seven successive fractionations the greater part accumulated at the 156°–157° fraction and showed the following properties:—

$d_4^{21}$	$n_D^{21}$	$\alpha_D^{21}$	$[\alpha]_D$	M. R.	M. R. calc.
0.8483	1.4608	−40.78°	−48.07°	43.98	43.54 as $C_{10}H_{16}$ $\overline{1}$

That this fraction represented *l*- $\alpha$ -pinene is almost self-evident, but in order to prove its identity more rigorously, the following derivatives were prepared from it:

(a) *Pinene Hydrochloride.* On passing dry hydrogen chloride gas through well-cooled hydrocarbon, a quantity of the crystalline hydrochloride was obtained, which after recrystallizations from alcohol, melted at 128°C., and showed no depression of the melting temperature on admixture with a known sample of pinene hydrochloride. Its specific rotation in alcoholic solution amounted to −31.25°. (0.817 gr. of the crystal in 8.02 c.c. of alcohol.)

(b) *Pinonic Acid.* By oxidizing 25 gr. of the hydrocarbon with 83 gr. of potassium permanganate in 500 c.c. of water at 5°–10°C., and treating the product of oxidation in the usual manner, a syrupy acidic substance was obtained, which on rectification under 4 mm. pressure, distilled chiefly at 194°–199°. This distillate, on being kept for three weeks in an ice-cold chamber, deposited a mass of crystals with m.p. 67°–69°. The residual fluid part showed a specific rotation −25.0° and afforded a semicarbazone (m.p. = 203.5°) and an oxime (m.p. = 189°–190°). The oxime was insoluble in glacial acetic acid and its specific rotation amounted to +38.40° in alcoholic solution. All these data agree with the previous data about pinonic acid.

(c) *Pinene Nitrosochloride.* By passing a current of dry nitrosyl chloride into a well-cooled ethereal solution of the terpene (1:1), and subsequently adding an equal volume of cold absolute alcohol. The needle crystals thus precipitated were filtered, washed, redissolved in chloroform, and reprecipitated by methyl alcohol. The purified product showed a melting point 89°–90°, which even after several successive purifications remained unaltered. This is in accordance with the results of Tsuchihashi-

Tasaki<sup>(1)</sup> and of Lynn<sup>(2)</sup> who worked with highly active pinenes from *Chamaecyparis obtusa*, Sieb. et Zucc., and from *Chamaecyparis Lawsoniana*, (Murr.) Parl. respectively. It is worthy of note that in the present case up to 38% by weight of the nitrosochloride was obtainable, whereas it is generally stated that the preparation of nitrosochloride from highly active pinenes are accompanied by difficulties. Our nitrosochloride showed a specific rotation—292°. (2.00 gr. in 15.03 c.c. of chloroform.)

(d) *Nitrosopinene*. Two grams of the nitrosochloride was heated for five hours on the water bath with 2 gr. of metallic sodium and 5 c.c. of 85% alcohol, the whole mass was then thrown into 25 c.c. of water and kept for six days in the ice chamber, when a quantity of crystals separated out. These crystals after recrystallizations from acetic ester showed a melting point 129°–131°.

(e) *Pinene Nitrolbenzylamine*. On treating 1 gr. the nitrosochloride with 1 gr. of benzylamine and 5 c.c. of alcohol in the warm, crystals of the benzylamine were obtained, which after recrystallizations melted at 143°–145°. This melting point is somewhat too high for the ordinary pinene nitrolbenzylamine—122°–123°; but coincides with the data of Lynn who prepared it from pinene of *Chamaecyparis Lawsoniana*.

The next fraction b.p. 157°–161° seemed to consist of mixtures of pinene and camphene, and by carrying out the hydratation according to Bertram and Walbaum, isoborneol was duly identified, (phenylurethane m.p. 136°–137°), while by oxidizing it with concentrated aqueous permanganate pinonic acid could be obtained. Attempts to prove nopinene or sabinene proved to be fruitless.

The portion boiling between 173° and 175° gave dipentene tetrabromide (m.p. 124°) on treatment with bromine. The odour of this fraction reminded the presence of cineol in it, and analyses also revealed the presence of some oxygenated substances, thus:—

Sample	CO <sub>2</sub>	H <sub>2</sub> O	C %	H %	O %
0.2021	0.6241	0.2037	84.21	11.19	4.60
0.1673	0.5169	0.1689	84.26	11.21	4.53

So, the fraction was shaken with 50% resorcinol solution when a small quantity of cineol-like substance could be regenerated from this resorcinol

(1) Report of Dep't of Industry, Gov. Research Inst. of Formosa No. 1, p. 119.

(2) Ber. Schimmel & Co., 1919 S. 132.

solution. In order to identify cineol, it was treated with iodol and a iodol compound was obtained which melted at  $107^{\circ}$ – $110^{\circ}$ . On account of the small quantity no further purifications were possible, but it is most likely that this was cineol-iodol. (m.p. =  $112^{\circ}$ ).

The next two fractions b.p.  $175^{\circ}$ – $180^{\circ}$  and  $180^{\circ}$ – $187^{\circ}$  were twice rectified and a main fraction with the following properties was obtained :

B. p. / 757 mm.	$d_4^{23}$	$n_D^{13}$	$\alpha_D^{23}$
$179^{\circ}$ – $182^{\circ}$	0.8503	1.4766	$-3.65^{\circ}$

This gave two crystalline products on oxidation with dilute permanganate solution, the one melting at  $235^{\circ}$ – $236^{\circ}$  and the other at  $186^{\circ}$ – $188^{\circ}$ . The first of these corresponded to terpinene erythritol while the latter to  $\alpha$ - $\alpha'$ -dihydroxy- $\alpha$ -methyl- $\alpha'$ -isopropyl-adipic acid. These results show that the fraction consisted of  $\alpha$ - and  $\gamma$ -terpinenes.

**Benihione.** The fractions (2)–(5) contained a crystalline ketonic compound soluble in dilute  $\text{NaHSO}_3$ -solution, and on being regenerated from such solution a crystalline substance was obtained, which after recrystallization from 70% ethyl alcohol melted at  $139^{\circ}$ – $140^{\circ}\text{C}$ . This substance does not reduce Tollen's solution, but an attempt to prepare its semicarbazone resulted in a failure.

**The Terpene Alcohols and Esters.** The fractions (8), (9), and (10) represented terpene alcohols and esters as their saponification values before and after acetylation clearly showed :—

	Sap. V.	Sap. V. a. acet'n
(8)	88	132.4
(9)	99	129.8
(10)	86	146.3

These were separately fractionated under 15 mm. pressure, and rectified three times in the same manner, when the laevorotatory part accumulated at higher boiling fraction, thus,—

	B. p. / 15 mm.	Distillate gr.	$d_4^{23}$	$n_D^{23}$	$\alpha_D^{23}$
(a)	$97^{\circ}$ – $99^{\circ}$	16	0.9324	1.4705	+ $7.64^{\circ}$
(b)	$101^{\circ}$ – $102.5^{\circ}$	17	0.9354	1.4695	+ $3.16^{\circ}$
(c)	$106^{\circ}$ – $107^{\circ}$	9	0.9297	1.4712	$-11.40^{\circ}$

All of these fractions did not congeal even when they were cooled to  $-20^{\circ}$ . On treatment with phenyl isocyanate each gave the same phenyl urethane melting at  $137^{\circ}\text{C}$ , showing the presence of borneol or isoborneol in every one of them. Next, they are benzoylated after Schotten-Baumann, and after standing over night, the products were subjected to steam distillation. Then the residues from steam distillation were separately saponified with excess of alcoholic potash and steam distilled for the second time. The distillates were then ethered out, the ethereal solutions evaporated, when, from each of them crystals of borneol separated out. It was identified as such by testing the melting point and preparing the phenyl urethane. By directly saponifying the fractions and testing for the acids contained therein, the authors could detect formic and acetic acids. (Reducing action towards  $\text{HgCl}_2$ ; behaviour of the silver salt analyses of silver salts);

**The Sesquiterpenes.** The fractions (12), (13), and (14) consisted chiefly of sesquiterpenes but contained small quantities of alcoholic and ester constituents, so they were boiled for 6 hours under reduced pressures over metallic sodium at  $80^{\circ}$ – $90^{\circ}$  and then carefully fractionated seven times under reduced and atmospheric pressures. The resulting distillates showed the following properties:—

	B. p.	gr.	$d_4^{24}$	$n_D^{27}$	$\alpha_D^{26}$	M. R.
( i )	Up to $257^{\circ}$	3.5	—	—	—	—
( ii )	$257^{\circ}$ – $259^{\circ}$	4.8	0.9016	1.4970	$-24.36^{\circ}$	66.20
( iii )	$259^{\circ}$ – $260^{\circ}$	1.0	—	—	—	—
( iv )	$260^{\circ}$ – $263^{\circ}$	29.0	0.9046	1.5004	$-19.30^{\circ}$	66.38
( v )	$263^{\circ}$ – $264^{\circ}$	3.0	—	—	—	—
( vi )	$264^{\circ}$ – $267^{\circ}$	71.0	0.9065	1.5030	$+4.99^{\circ}$	66.52
( vii )	$267^{\circ}$ – $268^{\circ}$	8.0	—	—	—	—
( viii )	$268^{\circ}$ – $273^{\circ}$	10.0	0.9096	1.5050	$+21.04^{\circ}$	66.53

Fractions (ii) and (iv) gave liquid hydrochloride while (vi) and (viii) deposited cadinene dihydrochloride on treatment with dry hydrogen chloride. The cadinene dihydrochloride showed a specific rotation  $[\alpha]_D = -31.49^{\circ}$  (0.1023 gr. in 7.00 c.c. chloroform) and a melting point  $117^{\circ}\text{C}$ .

Fractions (ii) and (iv) gave a nitrosochloride which dissolved with difficulty in ether or alcohol but easily in chloroform, and melting at  $173^{\circ}$ – $175^{\circ}$ . It was optically inactive. Action of hydrogen chloride on these fractions produced no dihydrochloride. Also no isocaryophyllene alcohol could be obtained by applying Aschan's hydration method.



The nitrosite was obtained by adding 5 c.c. of glacial acetic acid into a well-cooled mixture of 3 c.c. of the substance in 3 c.c. of petroleum ether (b.p. 60°–70°) with some saturated solution of sodium nitrite in water, and stood over night at 5°C. A blue crystalline substance separated out, which was filtered, washed, and dried. It melted at 116°–118°C. When this was recrystallized from absolute alcohol, two kinds of crystals were obtained; viz.: a faintly blue-coloured crystal melting at 164°–166°, and a colourless needle crystal melting at 140°–141°C. These results agree with the description by A. Chapman<sup>(1)</sup> about the recrystallization of humulene nitrosite from ethyl alcohol.

Nextly, the nitrosate was prepared by the action of a mixture of nitric and acetic acids (1:1) on a solution of the hydrocarbon in amyl nitrite and glacial acetic acid (5:5:8). The white crystalline substance obtained, melted at 163°C. The nitrosate and the nitrosite were optically inactive.

**The Sesquiterpene Alcohol.** The fractions (18) and (19) were rectified twice under 12 mm. pressure and a main fraction with the following characteristics was obtained:

B. p. / 12 mm.	$d_4^{23}$	$n_D^{23}$	$\alpha_D^{23}$	M. R.	M. R. calc.
154°–156°	0.9695	1.5059	–14.00°	68.05	68.12 as $C_{15}H_{26}O$ $\bar{I}_1$

These data show that the fraction consists of a sesquiterpene alcohol of the bicyclic nature. On Liebermann's test it exhibited a beautiful green colour at first, which gradually changed into blue and then greyish violet. It did not react with phthalic anhydride neither in benzol solution nor without the solvent by heating to 130°, from which it seems probable that this alcohol represented a tertiary alcohol.

By the action of dry hydrochloric acid gas on this fraction an almost quantitative yield of cadinene dihydrochloride (m.p. 118°) resulted, while by dehydration with sulphur it afforded cadaline, its identity proved as its picrate. From these behaviours it is most probable that this alcohol is identical with cadinol of Semmler and Jonas.<sup>(2)</sup>

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1) *J. Chem. Soc.*, **67**, 60; *Ibid.*, **1928**, 133;

(2) *Loc. cit.*