

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

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It was S. Uchida<sup>(1)</sup> who first studied the oil of *Chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata, or Arisan-Hinoki. His oil, however, consisted of the product of dry distillation of the wood, and he reported to have found *d*- $\alpha$ -pinene and *l*-cadinene in the oil. Nextly, R. Tsuchihashi and S. Tasaki<sup>(2)</sup> studied the oil obtained by steam distillation of old root-stumps of the same plant, and proved the presence of *d*- $\alpha$ -pinene, *d*- $\alpha$ -terpineol, isoborneol, *d*-cadinene, a dicyclic sesquiterpene alcohol, an acid of the formula  $C_9H_{16}O_2$  or  $C_9H_{14}O_2$ , and a phenolic substance of the formula  $C_{10}H_{12}O_2$ . Later, N. Hirao<sup>(3)</sup> examined a similar oil and found camphene, borneol, camphor, and an acid of the formula  $C_{10}H_{16}O_2$  aside from those previously mentioned. To this acid Hirao gave the name "chamaenic acid," he also suggested that terpinolene and  $\beta$ -terpineol might probably be present. In all of these cases, the main component of the oil were *d*- $\alpha$ -pinene, *d*- $\alpha$ -terpineol, and cadinene. More recently, S. Uchida<sup>(4)</sup> published the result of his studies of the oil from the leaves of Japanese Hinoki (*Chamaecyparis obtusa*, Sieb. et Zucc.) and the following constituents are stated to have been found:—*d*- $\alpha$ -pinene; *d*-limonene; borneol, bornyl acetate; bornyl nonylate; a tricyclic sesquiterpene with a little cadinene; a dicyclic sesquiterpene alcohol; a tetracyclic diterpene; a new acid  $C_{16}H_{24}O_2$ . The last substance was named "hinokic acid" by the author. In quantity, *d*- $\alpha$ -pinene, *l*-limonene, and bornyl acetate predominated.

So far as the present authors are aware, however, there has been no report concerning the constituents of Formosa Hinoki leaf oil, and the authors took to the study of this oil which turned out to be quite different in composition from those cited above.

The main constituents of the acidic part was an unsaturated fatty acid possessing the physical properties resembling those of the acid described by Tsuchihashi and Tasaki (loc. cit.), but the results of analyses, molecular

(1) *J. Soc. Chem. Ind. Japan*, **19** (1916), 611.

(2) *Report of Gov. Research Inst. Formosa*, **1** (1920).

(3) *J. Chem. Soc. Japan*, **47** (1926), 666, 743.

(4) *J. Soc. Chem. Ind. Japan*, **31** (1928), 650.

weight determinations, and the molecular refraction corresponded to  $C_{10}H_{16}O_2$  instead of  $C_9H_{16}O_2$  or  $C_9H_{14}O_2$ . Chamaenic acid described by Hirao (loc. cit.) could not be found in our oil. The following table shows the data as regards these acids.

Table 1.

	Tsuchihashi-Tasaki	Hirao	Kafuku-Nozoe-Hata
Origin	wood	wood	leaf
B. p.	134°–140°/5mm.	130°–134°/6mm.	133°–135°/6mm.
Density	0.9507 (24/4)	1.0092 (20/4)	0.9544 (20/4)
$n_D$	1.4784 (24)	1.5271 (20)	1.4732 (20)
Formula	$C_9H_{16}O_2$	$C_{10}H_{16}O_2$	$C_{10}H_{16}O_2$
Mol. refr.	—	51.10	49.40
Br-absorption	—	2 Br.	2 Br.
Coloration with $FeCl_3$	—	deep red	deep red

Our acid, which perhaps is an aliphatic acid of the terpene series, gave a deep red coloration with a drop of dilute alcoholic solution of ferric chloride, precisely as is stated by Hirao in case of chamaenic acid (loc. cit.)—and moreover, it deposited a minute quantity of dark red crystals; but, as regards the exact nature of this acid, we must leave it for the future study.

On fractionation of the acid-free oil, the fraction boiling between 165° and 175° showed a density too low for an ordinary terpene and moreover it was very unstable and liable to oxidize on exposure to the air and ready to undergo polymerization. With a view that it might contain some new terpenes possessing definite properties, we carefully fractionated it repeatedly over metallic sodium under partial vacua and obtained at last a hydrocarbon of a characteristic odor with following constants: Boiling point=86°–88° under 50 mm.;  $d_4^{25}=0.8228$ ;  $n_D^{25}=1.4686$ ; rotatory power $^{25}_D$ =about+35°.

From considerations of its molecular refraction, its bromine number, and its non-reducibility by sodium and alcohol, it becomes evident that the hydrocarbon is neither a menthene nor a mixture of cyclic and chain terpenes, but a hitherto unknown new terpene of monocyclic nature. The authors wish to propose the name "*chamene*" to this new terpene, which, so far as the authors are aware, has the lowest density among all naturally occurring monocyclic terpenes, as shown in Table 2.

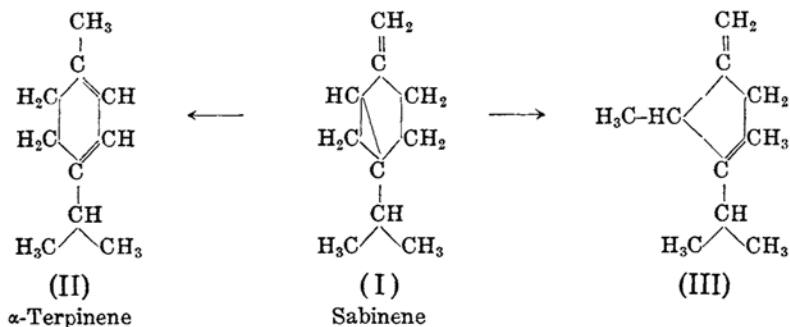
Table 2.

	B. p.	$d_{20}$	$n_D^{20}$	M.R.	M.R. as $C_{10}H_{16} \left  \frac{\infty}{2} \right $
Limonene	175°-176°	0.845	1.4746	45.24	45.24
Terpinolene	184°-188°	0.857	—	—	—
Terpinene	179°-181°	0.846	1.480	45.65	—
Phellandrene	170°-176°	0.845	1.4788	45.63	—
Sylvestrene	175°-176°	0.848	1.4753	45.23	—
Chamene	168°-170°	0.827	1.472	46.0	—

Chamene is easily oxidized on being kept in the air, thereby changing into a viscous oxygenous compound of higher density, and if shaken with an amount of dilute sulphuric acid it loses its optical activity and changes into another new terpene, to which we propose the name "*isochamene*." Isochamene is fairly more stable than chamene but the physical properties remain almost unchanged, and it is not yet fully explained whether this change is due to isomerization or racemization. If alcoholic potash is used instead of dilute sulphuric acid, then an inactive diterpene "*diisochamene*" results.

Semmler,<sup>(1)</sup> on treating sabinene with concentrated formic acid at -20°C., obtained besides  $\alpha$ -terpinene and formic ester of origanol (terpinenol-4), a hydrocarbon  $C_{10}H_{16}$  with the following properties: Boiling point=50°-54° under 10mm., 169°-173° under 760mm.;  $d_{20}^0=0.829-0.831$ ;  $n_D^{20}=1.470$ ;  $\alpha_D=+13^\circ-+24^\circ$ .

From the fact that this hydrocarbon showed a very low density and that its optical activity did not enfeeble even when it was boiled with an acid, and from the supposition that a semicyclic double linking is less influenced by acids than the cyclopropane ring, he assumed this hydrocarbon to be a derivative of cyclopentadiene of the formula (3) given below, but as to its chemical behaviors nothing is described in his paper:



(1) Ber., **39** (1906) 4414.

It is not difficult to consider that this hydrocarbon and chamene or isochamene to be in close connection,—although may or may not be the same substance,—as Semmler's formula is in accordance with such properties of chamene as the tendency to polymerize, isomerize or oxidize by itself. But it is absolutely necessary to determine at first whether this hydrocarbon does actually possess a pentamethylene ring, or not; and experiments are being carried out in this direction.

Fractions distilling below  $158^{\circ}$  had a fairly low specific gravity and were still unstable even though sabinene and chamene had been removed by repeated fractionations, which fact led us to test for the presence of  $\alpha$ -thujene and  $\alpha$ -pinene. For this purpose we oxidized this fraction with dilute potassium permanganate and ketonic acids formed thereby were isolated as their semicarbazones. After repeated fractional crystallizations from dilute alcohol we succeeded in separating them into two parts, the one of which represented the semicarbazone of pinonic acid melting at  $206^{\circ}$ — $207^{\circ}$  while the other that of thujaketonic acid,<sup>(1)</sup> melting with decomposition at  $180.5^{\circ}$ — $181.5^{\circ}$ . Thus, it is most probable that  $\alpha$ -thujene is contained in the oil, although any further identification could not be made.

An intermediate portion distilling between the terpene and terpene alcohol fractions possessed a characteristic pleasant odour reminding esters, so that it was saponified and a free alcohol of the formula  $C_8H_{16}O$  was obtained. This alcohol represented an octenol, secondary in nature, but quite different from ordinary methyl heptenol. It had a peculiar musty odour and on oxidation with Beckmann's mixtures, it gave a product other than the ordinary methyl heptenone. The exact nature of this alcohol, however, could not be determined because of the small quantity available.

To summarize our results briefly :

1. The acidic portion which amounted to about 0.85% of the whole oil, consisted mainly of an unsaturated fatty acid of the formula  $C_{10}H_{16}O_2$ , and hinokic acid,  $C_{16}H_{24}O_2$ , melting at  $165^{\circ}$ — $166^{\circ}$ , together with a small quantity of an acid, probably caproic acid, and a trace of phenolic substances.

2. The terpene part occupied about 34% of the oil, of which about 50% consisted of *d*-sabinene, and 20—30% of a new terpene "*chamene*," the remainder represented *d*- $\alpha$ -pinene, *p*-cymene,  $\alpha$ -terpinene,  $\gamma$ -terpinene,  $\alpha$ -thujene, and a trace of dipentene.

3. The constitutional formula for chamene was partly deduced, but not yet fully established.

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(1) Wallach (*Ber.*, **30**, 426), Thuja-ketonic Acid m.p.= $182^{\circ}$ — $183^{\circ}$ .  
Semmler (*Ber.*, **35**, 552), Thuja-ketonic Acid m.p.= $198.5^{\circ}$ .



4. The terpene alcohol fraction occupied about 11.6% of the original oil, which consisted mainly of *d*-terpinenol-4. Besides, there were found a small amount of a laevo-rotatory alcohol of the formula  $C_8H_{16}O$  and *l*-linalool, both for the most part in form of esters, and in addition to these a trace of borneol was found to present.

N.B. It is of interest that the chief constituents of the leaf oil, *d*-sabinene, *d*-chamene, and *d*-terpinenol-4, have never been found in the oils from root or wood, while *d*- $\alpha$ -pinene, dipentene, and  $\alpha$ -terpineol which form the main part of the latter oils are to be found in the former oil either in very small quantities or not at all. Moreover, it seems peculiar, that almost all the constituents found in this oil are to some extent related to sabinene as may be seen from the scheme in the foregoing page.

### Experimental.

The oil used for these experiments was obtained at Arisan (Mt. Ari) by steam distillation of the fresh leaves of "benihi"-cypress or *Chamaecyparis Obtusa*, Sieb. et Zucc. f. *formosana*, Hay.; the yield amounting to 0.3% of the weight of live leaves. The oil had a characteristic pleasant odour and was of slightly yellow colour which gradually changed into deep red on standing. The properties of the oil were as follows:  $d_{25}^{25}=0.8988$ ;  $n_D^{25}=1.4878$ ;  $\alpha_D^{25}=-5.83^\circ$ ; Acid value=0.96; Ester value=12.63; Do. after acetylation=54.81.

**The Acidic Part.** The acid part was extracted from the oil by shaking with 5% caustic potash, and it was then regenerated from the aqueous solution in the usual way by means of carbon dioxide and dilute sulphuric acid. From 5 kg. of oil 12 gr. of the acidic part and 1.5 gr. of phenolic part were obtained.

This acidic mixture was fractionally distilled in vacuo three times successively, and from the fractions we could identify the following constituents:

i) *An Unsaturated Fatty Acid*,  $C_{10}H_{16}O_2$ . This formed the main fraction which had the following constants: B.p.= $133^\circ-135^\circ$ ;  $d_4^{20}=0.9544$ ;  $n_D^{20}=1.4732$ ;  $\alpha_D=0^\circ$ ; M.R.=49.40 as  $C_{10}H_{16}O_2$ , calculated value 48.99.

Anal. Subst.=0.1365;  $CO_2=0.3558$ ;  $H_2O=0.1233$  gr. Found: C=71.08; H=10.03%. Calc. for  $C_{10}H_{16}O_2$ : C=70.58; H=10.58%. Calc. for  $C_{10}H_{18}O_2$ : C=71.42; H=9.50%.

0.0999 gr. substance in carbon tetrachloride at  $0^\circ C$ . absorbed 0.0948 gr. bromine. Calculated for  $C_{10}H_{16}O_2Br_2$ : Br=0.0950 gr.

Molecular weight. 0.2067 gr. acid required 12.65 c.c. of normal caustic soda ( $N=0.969$ ) for neutralization, corresponding to a molecular weight of 168.6.  $C_{10}H_{16}O_2=168.2$ . 2.80 mg. of the silver salt gave 1.07 mg. silver, corresponding to a molecular weight of 168.4.

Neither an acid amide nor an anilide could be obtained in the crystalline form.

The solution of this acid gave an intense red coloration on shaking with a few drops of ferric chloride solution and deposited a small amount of dark red crystalline precipitate on standing, but the nature of this precipitate, however, has not been studied further.

ii) *Hinokic Acid*. The fraction boiling above 150° under 2 mm. pressure, solidified on standing and after recrystallization from dilute alcohol melted at 165°–166°. This acid is in all probability identical with Uchida's hinokic acid.

iii) Besides, there was a trace of lower fatty acid, which judging from the results of analyses of its silver salt, seemed likely to be caproic acid.

iv) Phenols, with lower boiling point, gave reddish violet coloration to alcoholic ferric chloride, while the higher ones, a deep bluish green on the same treatment, but on account of the small quantity we could not identify any of the individual phenols.

**The Neutral Part.** A preliminary examination has shown that the oil did not contain any noticeable quantity of aldehydes or ketones (shaking with concentrated sodium bisulphite solution), and moreover, that it was rather unstable to the action of the acid, so we fractionated the oil directly without any treatment beforehand.

2500 c.c. of the oil was fractionated carefully under reduced pressures, and after four consecutive fractionations the whole was divided into the following six sections :

Table 3.

(A)	40°–80°/50 mm.	1362 gr.	34.1% (Terpenes)
(B)	80°–120°/50 mm.	456 gr.	11.4% (Terpene alcohols)
(C)	120°–140°/50 mm.	1607 gr.	40.2% (Sesquiterpenes)
(D)	140°–160°/50 mm.	394 gr.	9.6% (Sesquiterpene alcohols)
(E)	160°–180°/50 mm.	52 gr.	1.8% (Diterpenes)
(F)	The residue	16 gr.	0.4%

In all of the fractional distillations the authors used Widmer's fractionating column.

**The Terpenes.** The fraction (A) in the foregoing table was further fractionated over metallic sodium under 50 mm. pressure and separated into the following eleven fractions as shown below :

Table 4.

No.	B.p./50 mm.	Yield	$d_4^{22}$	$n_D^{22}$	$\alpha_D^{22}$
1	76°—78°	53 gr.	0.842	1.4651	+30.4°
2	78°—80°	131	0.839	1.4662	+40.9°
3	80°—82°	171	0.835	1.4673	+48.3°
4	82°—84°	128	0.830	1.4685	+48.7°
5	84°—86°	76	0.830	1.4698	+42.3°
6	86°—88°	44	0.829	1.4705	+35.2°
7	88°—90°	12	0.831	1.4712	+27.5°
8	90°—92°	40	0.833	1.4726	+20.4°
9	92°—94°	50	0.837	1.4746	+13.1°
10	94°—98°	67	0.847	1.4773	+ 5.5°
11	98°—106°	5	0.870	1.4740	+ 3.0°

*The New Terpene "Chamene."* As the fractions (3) to (7) had a very low specific gravity, and were liable to deposit a viscous liquid (not water) on exposure to the air, we studied these fractions first of all. These were once again repeatedly and systematically fractionated over metallic sodium and at last we could obtain a rather pure sample with the following constants: B.p. = 86°—88° under 50 mm., 168°—170° under 760 mm.;  $d_4^{25} = 0.8228$ ;  $n_D^{25} = 1.4686$ ;  $\alpha_D = +35.0^\circ$ ; M.R. = 46.00, calculated as  $C_{10}H_{16}\overline{f}_2 = 45.2$ .

As chamene was ready to oxidize in the air, the authors experienced difficulty in getting good results in analyses.

0.2745 gr. substance absorbed 0.7033 gr. bromine, the amount calculated for  $C_{10}H_{16}Br_2$  being 0.6443 gr.

The hydrochloride was obtained by saturating the ethereal solution of the hydrocarbon with dry hydrogen chloride for two days in the cold. The product was a liquid which boiled at 80°—90° under 11 mm. pressure with a density 1.0196 at 25°C., and a refractive index 1.4783 at the same temperature. The molecular refraction found was 58.09 as  $C_{10}H_{18}Cl_2$  or 50.58 as  $C_{10}H_{17}Cl$ , while those calculated were 55.91 as  $C_{10}H_{18}Cl_2$  ( $\overline{f} = 0$ ) and 50.58 as  $C_{10}H_{17}Cl$  ( $\overline{f} = 1$ ).

Attempts to reduce the hydrocarbon itself or this hydrochloride with sodium and alcohol were not effective; also all efforts to get characteristic crystalline substance proved unsuccessful.

Chamene, especially in the pure state, was very unstable and liable to change into a viscous liquid insoluble in the original terpene which seemed



likely to be a peroxide. As for the exact nature of the products of oxidation it should remain to be reported until the next opportunity.

Isomerisation of chamene was carried out by shaking 20 gr. of chamene with 20 c.c. of dilute sulphuric acid (1:3) for two hours at room temperatures, when its optical activity all but disappeared and a new isomeric terpene was obtained, which was thoroughly washed with water, dried over anhydrous sodium sulphate, and then rectified in vacuo. This terpene, to which we suggest the name "*isochamene*," was found to possess the following constants: B.p.=88°–90° under 50 mm.;  $d_4^{25}=0.8222$ ;  $n_D^{25}=1.4726$ ;  $\alpha_D^{25}=-0.27^\circ$ ; M.R.=46.42, calculated as  $C_{10}H_{16}$   $\frac{1}{2}=45.2$ .

Anal. Subst.=0.1088;  $CO_2=0.3475$ ;  $H_2O=0.1123$  gr. Found: C=87.11; H=11.46%.  
Calc. for  $C_{10}H_{16}$ : C=88.23; H=11.77%.

Contrary to chamene, isochamene was found to be fairly more stable than chamene against the action of the air.

Polymerization of isochamene to its dimeride ensued when alcoholic sulphuric acid (1:1) was used instead of the aqueous in the experiment described above; the rotatory power being destroyed almost to nothing in half an hour with appreciable evolution of heat. The product represented a mixture of a diterpene with a little isochamene, which was rectified in the usual manner and the diterpene with the following properties was obtained: B.p. = 155°–156° under 4 mm.;  $d_4^{20}=0.9150$ ;  $n_D^{20}=1.5134$ ;  $\alpha_D^{20}=-0.7^\circ$ ; M.R.=89.40, calculated as  $C_{20}H_{32}$   $\frac{1}{3}=88.76$ .

The name "*diisochamene*" is given by the authors to this new diterpene as it was obtained by the condensation of two molecules of isochamene.

To a well-cooled mixture of a benzol solution of isochamene and a calculated amount of sodium nitrite solution under stirring, glacial acetic acid was added drop by drop, when the solution assumed a blue colour at first which gradually turned into yellow. No crystal formation set in before the solution was warmed once again to about 50° when it suddenly deposited a quantity of colourless needles which after recrystallization from dilute alcohol, melted at 154°–155°. Strangely enough, this crystal was proved to be identical with  $\alpha$ -terpinene nitrosite by observing the mixed melting point with an authentic specimen of the same. Whether this nitrosite resulted from by-mixed terpinene really existent in the isochamene fraction or from an intramolecular rearrangement of isochamene nitrosite, is not clear, but from consideration of the feature and quantity of crystal formation, the latter course seems the more probable.

Chamene dissolved in acetic anhydride, if treated with a drop of concentrated sulphuric acid, a deep red coloration is produced.

The total amount of chamene in the oil perhaps amounted to 20–30% although the final product in the pure condition was rather small in quantity.

**The Terpenes boiling lower than Chamene.** The fractions of lower boiling terpenes—No. 1 to No. 6 were further fractionated under ordinary pressures over metallic sodium and they were divided into the following eleven fractions taking into consideration their optical activities:—

Table 5.

No.	$\alpha_D^{18}$	B.p./760 mm.	$n_D^{18}$	$d_4^{19}$	Yield	M.R.
1	– 4° – + 0°	153.0° – 155.0°	1.4628	0.8463	14 gr.	44.6
2	+ 0° – + 5°	155.0° – 155.5°	1.4642	0.8475	20	44.3
3	+ 5° – + 10°	155.5° – 156.0°	1.4647	0.8477	13	44.3
4	+ 10° – + 15°	156.0° – 156.5°	1.4651	0.8477	21	44.4
5	+ 15° – + 20°	156.5° – 157.0°	1.4655	0.8474	29	44.4
6	+ 20° – + 32°	157.0° – 157.5°	1.4661	0.8469	24	44.5
7	+ 32° – + 40°	157.5° – 158.0°	1.4665	0.8462	18	44.6
8	+ 40° – + 50°	158.0° – 159.0°	1.4669	0.8453	35	44.6
9	+ 50° – + 60°	159.0° – 160.0°	1.4677	0.8435	30	44.8
10	+ 60° – + 62°	160.0° – 161.0°	1.4680	0.8425	15	44.9
11	+ 62° – + 66°	161.0° – 162.0°	1.4690	0.8420	150	45.0

From these fractions we could identify  $\alpha$ -pinene,  $\alpha$ -thujene, and *d*-sabinene.

**$\alpha$ -Pinene.** The presence of  $\alpha$ -pinene was proved by preparing nitroso-chloride, nitrolbenzylamine, nitrolpiperidine, and pinonic acid melting at 106°–107°, 121°–122.5°, 118°–119°, and 206.5°–207° respectively.

***d*-Sabinene.** Fraction (11) represented nearly pure sabinene, whose presence being confirmed by preparing the sparingly soluble sodium salt of sabinic acid, and the free acid melting at 58°–58.5° from the products of oxidation of the fraction with alkaline permanganate. Besides, we obtained sabina ketone and its semicarbazone (m.p. 141°–142°). It should be mentioned that our sabinene was found to possess the highest optical activity. The hitherto observed highest data being + 68.54°<sup>(1)</sup> while the authors' sabinene after careful rectifications showed the following constants: B.p.=161°–163°;  $d_4^{17.5}$ =0.8442;  $n_D^{17.5}$ =1.4695;  $\alpha_D^{17.5}$ =+72.94°;  $[\alpha]_D^{17.5}$ =+86.4°; M.R.=44.90, calc. as  $C_{10}H_{16}$   $\bar{M}_1$ =43.51.

(1) Ber. von Schimmel & Co. – Gildemeister u. Hoffmann, "Die Ätherischen Öle," Vol. 1, p. 356.

*$\alpha$ -Thujene.* A well-cooled mixture of the fractions No. 3 to No. 6 (45 gr.) was oxidized by means of alkaline permanganate solution, and the resulting oxidized products were treated in the usual manner and obtained 30 gr. of acid. This was extracted with ether and the extract was neutralized with sodium hydroxide. On evaporation 3.5 gr. of sodium sabinat separated out as crystals while from the filtrate 22 gr. of other acids were recovered. These gave on treatment with semicarbazide hydrochloride, about 12 gr. of a crystalline body melting at  $190^{\circ}$ – $198^{\circ}$ , seemingly a mixture of more than two semicarbazones. Thus, it was fractionally recrystallized from dilute alcohol and at last we obtained two different products, the one melting at  $201^{\circ}$ – $203^{\circ}$  and the other at  $184^{\circ}$ – $186^{\circ}$ . These were further fractionated in the same medium eight consecutive times and were differentiated into (a) the more difficultly soluble prismatic crystals—pinonic acid semicarbazone m.p.  $206^{\circ}$ – $207^{\circ}$ , and (b) the more easily soluble thin needle crystals melting with decomposition at  $181^{\circ}$ – $181.5^{\circ}$ . This latter melting point coincides with that of  $\alpha$ -tanaceto-keto-carboxylic acid semicarbazone,<sup>(1)</sup> but whether it be such or not is not clear.

Anal. Subst. = 3.61 mg.;  $N_2$  = 0.579 c.c. ( $30^{\circ}$ , 759 mm.) Found: N = 16.95%. Calc. for  $C_{11}H_{19}O_3N_3$ : N = 17.4%.

**The Higher Boiling Terpenes.** The fractions (8), (9), (10), and (11), were further fractionated over metallic sodium into the following five fractions:

Table 6.

	B.p./760 mm.	Yield	$n_D^{22}$	$d_4^{22}$	$\alpha_D^{22}$
1)	$168^{\circ}$ – $172^{\circ}$	84 gr.	1.4710	0.8300	+ $30.0^{\circ}$
2)	$172^{\circ}$ – $175^{\circ}$	16	1.4735	0.8354	+ $16.6^{\circ}$
3)	$175^{\circ}$ – $178^{\circ}$	44	1.4759	0.8418	+ $8.5^{\circ}$
4)	$178^{\circ}$ – $181^{\circ}$	45	1.4782	0.8471	+ $3.5^{\circ}$
5)	$181^{\circ}$ —	8	1.4832	0.8545	+ $1.1^{\circ}$

In the above, 1) consisted mainly of chamene, while 3) and 4) contained *p*-cymene,  $\alpha$ -terpinene,  $\gamma$ -terpinene and dipentene. The first of these, *p*-cymene, was isolated after repeated treatments with dilute permanganate solution as a mobile, highly refracting liquid of the characteristic smell, from which on oxidation with a more concentrated solution of potassium

(1) Wallach, *Ber.*, **30**, 426.

permanganate, crystals of *p*-oxy-isopropyl-benzoic acid<sup>(1)</sup> (m.p. 115°—Mischproben) was obtained. The presence of  $\alpha$ -, and  $\gamma$ -terpinenes was proved by preparing *aa'*-dioxy- $\alpha$ -methyl- $\alpha'$ -isopropyl adipic acid<sup>(2)</sup> (m.p. 188°—189°—Mischproben) and  $\gamma$ -terpinene erythrite (m.p. 236°—238°—Mischproben) respectively. Dipentene was found in small quantity in 4) from which the tetrabromide could be prepared in the ordinary way.

The presence of  $\Delta_3$ -, and  $\Delta_4$ -carenes,  $\alpha$ -, and  $\beta$ -phellandrenes was suspected and tests in these directions were made but without success.

**The Terpene Alcohols.** The fraction (B), which consisted mainly of terpene alcohols, was submitted to a careful and systematic fractionation under reduced pressures (at first under 12 mm., and finally under 50 mm. pressure), and ultimately it was divided into the following twelve fractions:

Table 7.

	B.p./50 mm.	Yield	$d_4^{20}$	$n_D^{20}$	$\alpha_D^{20}$	Ester value
(1)	up to 105°	11 gr.	0.853	1.476	+ 2.5°	—
(2)	105°—112°	3	—	1.465	+ 3.8°	—
(3)	112°—115°	2	0.884	1.458	+ 4.9°	78.5
(4)	115°—118°	7	0.899	1.464	+ 9.5°	44.2
(5)	118°—121°	17	0.907	1.468	+13.5°	—
(6)	121°—124°	78	0.931	1.475	+20.1°	29.1
(7)	124°—127°	22	0.930	1.472	+19.2°	51.8
(8)	127°—130°	12	0.928	1.468	+14.5°	—
(9)	130°—133°	13	0.926	1.466	+ 4.3°	157.2°
(10)	133°—136°	5	—	1.467	+ 0.5°	157.8
(11)	136°—140°	6	0.932	1.477	— 12.5°	109.0
(12)	140°—145°	7	0.934	1.481	—25.6°	80.5

With these fractions the following identifications were made:

i) *An Octenol C<sub>8</sub>H<sub>16</sub>O and its Ester.* The fractions (2) and (3) had a characteristic pleasant odour reminding the presence of an ester, therefore we mixed the fractions (1) to (4) and saponified the mixture by heating with alcoholic potash for two hours. The free alcohol thus obtained was purified by distillation in vacuo, the constants of which are:  $d_4^{20}$ =0.8454;  $n_D^{20}$ =1.4441;  $\alpha_D^{20}$ =—10.62.

Anal. Subst.=0.1189; CO<sub>2</sub>=0.3290; H<sub>2</sub>O=0.1298 gr. Found: C=75.8; H=12.12%.  
Calc. for C<sub>8</sub>H<sub>16</sub>O: C=75.00; H=12.50%.

(1) Wallach, *Ann.*, **264** (1891), 10.

(2) Wallach, *Ann.*, **362** (1908), 297.

The purified alcohol had a peculiar not-unpleasant odour but reminding of mouldy cellar, did react with phthalic anhydride not at 100°C., but at 130° with formation of an ester-acid. The physical constants of this alcohol almost coincided with those of methyl heptenol, but these two differed distinctly in their odour as well as their behaviour towards Beckmann's chromic acid mixture,—the former in not giving the ordinary methyl heptenone while the latter did. The attempt to prepare crystalline derivatives from the alcohol were altogether futile.

ii) *d*- $\Delta_1$ -Terpinenol-4. The fractions (5) to (7) represented a free terpene alcohol with a little ester, so they were saponified to get rid of the latter, and then distilled, when, it was found that the main fraction boiled very constantly at 122°–123° under 50 mm. pressure. The properties of the main distillate are as follows:  $d_4^{14}=0.9410$ ;  $n_D^{14}=1.4806$ ;  $\alpha_D^{14}=+23.58^\circ$ ; M.R.=45.9°, calc. as  $C_{10}H_{16}OH$   $\bar{M}_r=45.04$ .

These constants agree fairly well with those of *d*- $\Delta_1$ -terpinenol-4 so the following derivatives were prepared for the identification. *Nitrosochloride*. The nitrosochloride was prepared just in the same way as in the case of pinene, and was found to melt at 109°–110°. The nitrolpiperidin derived from this melted after purifications at 178°–179°, and showed no depression of the melting point on admixture with pure  $\beta$ -nitrolpiperidin of *i*- $\Delta_1$ -terpinenol-4 (m.p. 181°). *1, 2, 4-Trioxysterpane*. The alcohol, on treatment with an ice-cold, dilute, alkaline permanganate solution, gave 1, 2, 4-trioxysterpane<sup>(1)</sup> which melted after recrystallization from water at 115°–116° (with a molecule of water of crystallization) and after being dried at 80° in vacuo at 124°–125°.

iii) *Borneol*. In course of the above described experiment, during the steam distillation of the oxidized products, a small quantity of needle-like crystal was observed to separate out in the colder part of the receiver which on examination was found to possess an unmistakable odour of borneol.

iv) *l*-Linalool and its Ester. The fractions (9) and (10) consisted of esters of very pleasant smell which after saponification and subsequent extraction and distillation gave an alcohol having the characteristic odour of linalool with the following constants: B.p.=116°–118° under 50 mm.;  $d_4^{20}=0.8695$ ;  $n_D^{20}=1.4648$ ;  $\alpha_D=-14.28^\circ$ .

The alcohol was identified as linalool by obtaining the phenyl urethane melting at 60°–63° whose melting point did not lower on admixture with a known sample of linalool phenyl urethane from 'Ho'-oil. Besides, it gave

(1) Wallach, *Ann.*, **356** (1907), 215; also K. Nagai, Investigation of Shogyu- and Yuju-oils (Monopoly Bureau, Government of Formosa, 1914).

rise to an unmistakable odour of citral on treatment with Beckmann's chromic mixture.

From the caustic residue of the saponification, the acidic constituents were recovered in the usual manner. The recovered acid possessed a smell more like caproic acid, but the analysis of the silver salt, however, showed that the greater part was acetic acid, viz. :—

4.82 mg. substance gave 3.04 mg. silver. Found: Ag=63.1%. Calc. for  $\text{CH}_3\text{CO}_2\text{Ag}$ : Ag=64.7%.

It follows that linalool existed in the oil chiefly as acetate and a fraction as an ester of higher fatty acid.

Attempts to prove the presence of  $\alpha$ -terpineol as its phenyl urethane or its nitrosochloride did not succeed.

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