

# STUDIES ON THE CONSTITUENTS OF THE VOLATILE OIL FROM THE WOOD OF CHAMAECYPARIS FORMOSENSIS, MATSUM. .

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This paper is a sequel to a previous one—"Studies on the constituents of the volatile oil from the leaf of *Chamaecyparis formosensis*, Matsum..",<sup>(1)</sup> and deals with the chemistry of the volatile compounds contained in the wood of the same plant. The material for examination was prepared on Mt. Ari from a freshly felled tree about 250 years old. The tree was freed from its leaves, twigs, branches, and bark, and then chopped into small slices 3 × 10 × 15 cm. in size. These were put into an ordinary wooden still such as is employed in the manufacture of camphor, and were distilled with steam then and there. The yield of the volatile oil amounted to 1.10% on the average, the product representing a pale red viscous fluid of the characteristic odour, which darkened and thickened on standing. As a result of the authors' experiments, there were proved the presence of a strongly dextro-rotatory  $\alpha$ -pinene, *d*-camphene,  $\alpha$ -terpineol, *l*-cadinol, and allyl-protocatechin together with a number of newly discovered substances as listed below :—

(1) Benihiol  $C_{10}H_{18}O$ . A saturated primary alcohol of bicyclic nature, oxidizable into the corresponding aldehyde "benihial"  $C_{10}H_{16}O$  (Semicarbazone m.p. 169°C.), and further into a crystalline acid "benihic acid" melting at 110°C.

(2) Benihinol  $C_{10}H_{16}O$ . An unsaturated primary alcohol of monocyclic nature, giving the corresponding aldehyde "benihinal"  $C_{10}H_{14}O$  on oxidation.

(3) Benihinal  $C_{10}H_{14}O$ . The oxidation product of benihinol as stated above. Its oxime and semicarbazone are crystalline and melt at 65°C. and 216°C. respectively.

(4) *d*-Sesquibenihene  $C_{15}H_{24}$ . A bicyclic sesquiterpene closely akin to cadinene. It gives a crystalline dihydrochloride melting at 104°C. which is optically inactive, while the sesquiterpene regenerated from this dihydrochloride reverses the sign of its optical rotation and becomes laevo-rotatory. This regenerated hydrocarbon, on being acted on by hydrogen chloride,

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(1) K. Kafuku and N. Ichikawa, this Bulletin, **6** (1931), 1.

gives the inactive dihydrochloride perfectly identical with that from the dextro-rotatory sesquibeniene.

(5) A primary sesquiterpene alcohol. Not yet isolated in a state of sufficient purity, but probably of the composition  $C_{15}H_{24}O$ . No crystalline derivatives could be obtained from this substance.

(6) A crystalline phenolic body. Melting at  $127^{\circ}$ – $128^{\circ}C$ .

(7) A liquid acid. Composition corresponding to  $C_{10}H_{16}O_2$ .

### Experimental.

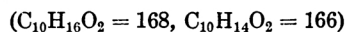
**The Crude Oil.** The crude oil used in the experiments showed the following properties :—

Colour	Dark red	—
Refractive Index	$n_D^{22}$	1.5020
Specific Gravity	$d_4^{22}$	0.9685
Rotation	$\alpha_D^{22}$	+4.76°
Acid Value	A.V.	6.13
Saponification Value	S.V.	24.0
Do. after Acetylation	S.V.a.A.	196.4
Specific Viscosity	$\eta_{22}$	67.7

**Acids and Phenols.** 1840 Gr. of the crude oil was shaken with an excess of 5% caustic soda solution on the machine for several hours, stood still, and then the aqueous layer separated. It was observed that the dark red colour of the oil passes over to the aqueous layer during this treatment. From this alkaline extract, acids and phenols were recovered in the usual manner and finally 12 gr. of acidic and 6 gr. of phenolic oils were obtained.

The acidic oil, after two consecutive fractionations in vacuo, exhibited the following properties :—

b.p.	146°–147°/7 mm.
	263°–265°/764 mm.
$n_D^{25}$	1.5010
$d_4^{19}$	1.0635
A.V.	335.8
Mol.W. from A.V.	167
Ag in Ag-salt	39.5%
Mol.W. from Ag%	165.8



That it does absorb but little bromine, and that it is not easily acted on by dilute permanganate in cold, show that it is a saturated compound. Its chloride, amide, and anilide are all fluid. The chloride was distillable in

vacuo, boiling approximately at about 100°C. under 10 mm. pressure. The ammonium salt showed a melting point at about 150°C. The insufficiency of the material made it impossible to carry on the experiments further.

The phenolic oil was distilled under the atmospheric pressure into two fractions, the one boiling within 235°C., whilst the other boiling between 270° and 274°C. These, on cooling, deposited crystals, those from the former melting at 47°–48°C., (after purification from petroleum ether), and those from the latter at 127°–128°C. (after recrystallization from 80% alcohol). The dilute alkaline solution of the former reddened rapidly on exposure to the air and gave on benzylation a crystalline ester melting at 71°C., which in every respect coincided with allyl-pyrocatechin dibenzoate. The other one did not give the characteristic colour reaction on addition of alcoholic ferric chloride alone, but on further addition of a drop or two of hydrochloric acid a faint colouration set in. The determination of methoxy-groups was made but to negative result, also the esterification after Schotten-Baumann by means of benzoyl chloride did not succeed.

**The Neutral Oil.** The crude oil after removal of acids and phenols, showed following constants :—

$d_4^{22}$	0.9689	S.V.	16.9
$n_D^{22}$	1.5020	S.V.a.A.	184.3
$\alpha_D^{22}$	+4.40°	$\gamma_{122}$	67.7

The oil was dried over anhydrous sodium sulphate and then it was fractionated five times consecutively under reduced pressures using Wiedemann's column of about 30 cm. length for dephlegmation. The fractions so divided exhibited the following characteristics :—

	b.p./5 mm.	$d_4^{21}$	$n_D^{16}$	$\alpha_D^{16}$	Yield (gr.)
1	Up to 30°C.	0.8603	1.4707	+40.58°	6
2	30°— 70°	0.9230	1.4886	+35.20°	2
3	70°— 75°	0.9761	1.4963	+ 5.75°	7
4	75°— 80°	0.9807	1.5000	+ 7.00°	21
5	80°— 85°	0.9786	1.4986	+14.55°	13
6	85°— 90°	0.9754	1.4988	+23.92°	106
7	90°— 95°	0.9700	1.4964	+30.94°	396
8	95°—100°	0.9658	1.4960	+23.75°	272
9	100°—105°	0.9512	1.5010	+21.75°	20
10	105°—110°	0.9325	1.5080	+21.50°	13

	b.p./5 mm.	$d_4^{21}$	$n_D^{16}$	$\alpha_D^{16}$	Yield (gr.)
11	110°—115°	0.9307	1.5100	+22.50°	124
12	115°—120°	0.9360	1.5106	+17.14°	62
13	120°—125°	0.9690	1.5108	-29.60°	5
14	125°—130°	0.9718	1.5112	-34.14°	9
15	130°—135°	0.9825	1.5120	-41.75°	250
16	135°—140°	0.9864	1.5136	-35.75°	153
17	140°—145°	0.9912	1.5179	-13.00°	5
18	145°—150°	0.9960	1.5216	-14.00°	85
19	150°—155°	1.0030	1.5238	- 2.50°	30
20	155°—159°	1.0087	1.5242	0°	20

**The Terpenes.** The fraction (1) consisted chiefly of terpenes as can be seen from the physical constants, so it was boiled over metallic sodium for some hours and then carefully distilled under atmospheric pressures into two portions, the one boiling between 156° and 157°C., and the other between 157.5° and 159.5°C., the properties of which were as follows :—

	b.p.	$d_4^{16}$	$\alpha_D^{16}$	Yield (gr.)
(a)	156°—157.3°	0.8430	+39.30°	3.1
(b)	157.5°—159.5°	0.8434	+29.30°	2.3

The former, on being treated with dry hydrogen chloride gas in cold, gave a crystalline hydrochloride melting at 127°—128°C., which, on further treatment with nitrosyl chloride was converted into an unstable nitrosochloride in form of white needles. This nitrosochloride readily decomposed on filtering. The higher boiling fraction, on hydration according to Bertram and Walbaum, gave isoborneol, which was identified as such by preparing the characteristic phenylurethane melting at 137°C.

**The Terpene Alcohols.** The fractions ranging from (2) to (8) consisted chiefly of terpene alcohols with a little ester, so they were separately saponified, and the liberated alcoholic portions were collected, and were fractionally distilled. After eight consecutive fractional distillations under 10 mm. using Wiedemann's column as dephlegmator, the following eleven fractions were obtained :—

	b.p./10 mm.	$d_4^{20}$	$n_D^{20}$	$\alpha_D^{20}$	Yield (gr.)
1'	86°—88°C.	0.9708	1.4982	— 4.0°	16
2'	88°—90°	0.9676	1.4982	— 1.6°	7
3'	90°—92°	0.9701	1.4974	+ 1.5°	9
4'	92°—94°	0.9662	1.4960	+12.0°	7
5'	94°—96°	0.9619	1.4946	+27.5°	13
6'	96°—98°	0.9644	1.4946	+44.0°	70
7'	98°—100°	0.9675	1.4944	+44.3°	40
8'	100°—102°	0.9688	1.4938	+38.4°	53
9'	102°—104°	0.9673	1.4934	+31.7°	41
10'	104°—106°	0.9766	1.4930	+28.0°	48
11'	106°—108°	0.9655	1.4938	+23.0°	276

**Benihinol and Benihinal.** The fraction (1') smelled like piperitone or some such aldehyde, so it was first shaken with 30% sodium bisulphite solution to get rid of the aldehydic component. The aqueous extract was then decomposed by means of alkali in the usual manner, and finally about 2 gr. of an oil (b.p. 86°—88°C./7.5 mm.;  $d_4^{17}$  0.9391;  $n_D^{17}$  1.4992) was obtained, exhibiting a remarkable reducing action on Tollen's solution and giving the characteristic colour reaction with Schiff's reagent. It gave a crystalline semicarbazone melting at 214°—215°C., and also a crystalline oxime melting at 64°—65°C. 0.3 Gr. of this aldehyde was digested with an excess of hydrogen peroxide and caustic potash solution at 60°—70°C., the turbidity ensuing at first gradually cleared up in course of time with formation of the corresponding potassium salt. This aldehyde was later proved to be identical with that which is obtained by oxidizing the fraction (6'). From the residual oil no crystalline derivatives could be obtained.

Nextly, the fractions (2') to (7') were separately boiled with phthalic anhydride in benzene solution, the resulting ester acids recrystallized from a mixture of ether and petroleum ether and finally saponified and distilled with steam. The main product amounted to 60 gr., and collected between 96° and 98°C. under 10 mm. pressure on fractionation. The properties of this main fraction as well as the results of analyses are shown below :—

Characteristic Constants.

b.p.	96.3°—97.7°C./10 mm. 216°C./766 mm.
$d_4^{19}$	0.9790
$n_D^{18.5}$	1.4960
$\alpha_D^{19}$	+46.80°

## Absorption of Bromine.

Substance 0.257 absorbed 0.529 bromine.

Calculated as  $C_{10}H_{16}O \text{ } \text{=}_2$  0.540.

## Elementary Analyses.

Substance	CO <sub>2</sub>	H <sub>2</sub> O	C%	H%
0.2298	0.6670	0.2142	79.15	10.35
0.2066	0.5975	0.1947	78.87	10.47
Calculated as $C_{10}H_{16}O$			79.0	10.4

## The Ester-Phthalic Acid and Its Silver Salt.

m.p.	107°—108°C.
Acid Value	190
Do. as $C_{18}H_{20}O_4$	187
m.p. of Ag Salt	88°—90°C.
Ag % in Ag Salt	25.92%
Do. as $C_{18}H_{19}O_4Ag$	25.86%

From the forgoing, the chief constituent of the fractions seems to consist of a primary alcohol  $C_{10}H_{16}O \text{ } \text{=}_2$ , so that, in order to ascertain this point, the substance was oxidized by means of chromic acid. Thus, 6 gr. of the substance was dissolved in 30 c.c. of glacial acetic acid, to which a calculated amount of chromic acid in the same solvent was slowly added, vigorously stirred keeping the reaction temperature within 15° and 20°C. Finally the whole mass was warmed to about 50°C. and then thrown into cold water. The oily substance separating out was caught by ether, the ethereal solution washed with 2% sodium bicarbonate solution and then treated with 30% sodium bisulphite solution. The bisulphite layer was then carefully separated, strong alkali added thereto, the regenerated aldehydic substance ethered out, washed, dried, evaporated, and then fractionated under reduced pressures. The main portion thus obtained exhibited the following characteristics:—

b.p.	87°C./8 mm.
$n_D^{15.5}$	1.5000
$d_4^{16}$	0.9893
Molecular Refraction	44.59
Do. as $C_{10}H_{14}O \text{ } \text{=}_2$	45.23

This aldehyde was proved to be perfectly identical with that isolated from fraction (1)—Cp. benihinal—the respective semi-carbazones melting at 216°C., and showing no depression of the melting temperature on 'mischproben.'

Analyses. Substance (mg)	Nitrogen (c.c.)	t°	p (mm)	N%
3.63	0.683	27	757	20.17
4.77	0.902	28	758	20.20
C <sub>10</sub> H <sub>14</sub> NNH—CO—NH <sub>2</sub> requires				20.3

To the alcohol the authors propose the name 'benihinol,' and to the aldehyde 'benihinal.'

**Benihiol and the Oxidation Products.** The fractions (8') to (11') when treated with phthalic anhydride in benzene solution, give esterphthalic acids, and if such be recrystallized from a mixture of ether and petroleum ether, from all of them, a crystalline esterphthalic acid melting at 123°–125°C. results, whose silver salt invariably decomposing at 165°C. Thus, from these fractions the alcohol was extracted as esterphthalic acid and such was ultimately saponified. The saponified mass was then distilled with steam, and the oily distillate finally fractionated in vacuo.

	b.p./10 mm.	b.p./atm.p.	$d_4^{21}$	$n_D^{21}$	$\alpha_D^{22}$	Yield (gr.)
(a)	106°–108°C.	234°–235°C.	0.9776	1.4903	+23.15°	135
(b)	108°–109°C.	234°–235°C.	0.9776	1.4910	+22.00°	85
(c)	109°–111.6°C.	235°–237°C.	0.9779	1.4910	+25.00°	45

Each one of these fractions gave the same esterphthalic acid on treatment with phthalic anhydride in benzene solution, which after purifications could be obtained in form of a compact crystalline mass. This esterphthalic acid was optically active and showed a specific rotation +4.55°(1.9 gr. in 8.6 c.c. of alcohol). Its silver salt represented a beautiful needle crystal which decomposed on heating at about 165°C. The titrimetric determination of its acid value agreed fairly well with the supposed composition C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>. Namely, for neutralizing 0.250 gr. of the acid with a decinormal caustic soda solution, 8.38 c.c. of the latter was consumed in place of 8.28 c.c., the amount theoretically required.

The absorption of bromine observed with these fractions varied considerably, but the amount was very small compared with the value as required for one double linking per molecule, so it might well be imputed to the presence of certain impurities.

	Substance	Br absorbed	Br Number
(a)	0.2230	0.0190	0.085
(b)	0.3136	0.0082	0.026
(c)	0.2024	0.0069	0.033
	Required for C <sub>10</sub> H <sub>18</sub> O   <sub>1</sub>		1.039

## Elementary analyses.

Substance	CO <sub>2</sub>	H <sub>2</sub> O	C%	H%
0.1272	0.3673	0.1302	78.75	11.37
0.1487	0.4283	0.1580	78.55	11.80
0.1542	0.4441	0.1616	78.54	11.64
0.1315	0.3749	0.1389	77.76	11.74
0.1542	0.4399	0.1636	77.81	11.79
0.1863	0.5317	0.1950	77.84	11.63
0.1444	0.4126	0.1528	77.92	11.76
C <sub>10</sub> H <sub>18</sub> O requires			77.9	11.7
C <sub>10</sub> H <sub>16</sub> O requires			79.0	10.4

**Oxidation by KMnO<sub>4</sub>.** These fractions are but slowly oxidized by potassium permanganate in cold but in the presence of KOH somewhat more rapidly. Thus, 10 gr. of the oil was shaken on the machine with 25 gr. KMnO<sub>4</sub>, 11 gr. KOH, 700 c.c. cold water, and 500 gr. shaved ice for four hours, then the unchanged oil and the neutral products of oxidation were driven off by steam, manganic slime was then filtered, and the filtrate was allowed to evaporate in an atmosphere of carbon dioxide. To the concentrated solution thus obtained an excess of dilute sulphuric acid was added, and the mass was ethered out, ethereal solution evaporated. The residue represented a sour-smelling viscid mass, boiling at 193°–195°C. under 7 mm. pressure. The distilled oil, on standing overnight in a cool place crystallized in needles. The crystals could be recrystallized from hot water and showed a melting point 175°–175.5°C.

**Oxidation by Chromic Acid.** A solution of 30 gr. of the forgoing alcohol in 100 c.c. of glacial acetic acid was prepared, into which a solution of 21 gr. of CrO<sub>3</sub> in the same solvent was allowed to drop down under stirring, keeping the reaction temperature below 15°C. for the whole while. After all the oxidizing agent had been added, the mass was warmed to about 50°C. and kept at that temperature for half an hour. It was then treated with sodium bicarbonate and then with sodium bisulphite in the usual manner, and thus acidic and aldehydic portions were separately obtained. The crude acid was crystalline, which after purifications—sublimation in a partial vacuum followed by recrystallization from 60% alcohol—melted at 110°C. This acid, on titration with alcoholic potash and on analyses of its silver salt as well as the elementary analyses, agreed fairly well with the composition C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>.

The acid value.

0.3000 gr. acid neutralized by	0.0986 gr. KOH
Calculated value for C <sub>10</sub> H <sub>16</sub> O <sub>2</sub> :	0.1000 gr. KOH



The silver salt.

Ag %	39.28	Calculated for $C_{10}H_{15}O_2Ag$	39.24
M.W. observed =	167.8	$C_{10}H_{16}O_2 =$	168.0

Elementary analyses.

Substance	CO <sub>2</sub>	H <sub>2</sub> O	C%	H%
0.1013	0.2660	0.0887	71.61	9.72
0.1118	0.2918	0.0970	71.81	9.64
	$C_{10}H_{16}O_2$ requires :		71.48	9.52

The aldehydic portion obtained as bisulphite compound was treated with dilute caustic soda, ethered out, ether evaporated, and distilled in vacuo. It distilled over at 83°–85°C. under 9.5 mm. pressure, and represented a colourless oil lighter than water. It was very unstable and was liable to oxidize into the forgoing acid on exposure to air. It was easily soluble in sodium bisulphite solution and was very sensitive to Schiff's reagent and Tollen's solution. The semicarbazone could easily be prepared and it melted after purification at 169°C.

The analyses.

Substance	N <sub>2</sub> (c.c.)	t°	p	N%
2.72 mg.	0.512	30	762.3	19.99
4.96 mg.	0.934	30	761.0	19.96
	$C_{10}H_{16} = N-NH-CO-NH_2$ requires			20.10

From the foregoing, it becomes clear that the chief constituent of the fractions (a), (b) and (c) is a primary terpene alcohol, dicyclic in structure, corresponding to a composition  $C_{10}H_{18}O$ . The terpene alcohol, as well as the corresponding aldehyde and acid have never been mentioned in the literature, so the authors proposed the names "benihiol," "benihial," and "benihic acid" for them.

**The Dehydration of Benihiol.** (i) *Dehydration by means of 50% Sulphuric Acid.* 30 Gr. benihiol was warmed with 100 gr. of 50% sulphuric acid on the water-bath to 80°–90°C. under vigorous stirring. After two hours' treatment, the whole was diluted with water and then distilled with steam. The pale yellow oil which distilled over was separated from water, dried, and then redistilled over metallic sodium. Thus, the following two fractions were obtained which showed the constants:—

	b.p./18 mm.	$n_D^{27}$	$d_4^{27}$	rotation
(i)	56°–58°C.	1.4693	0.8524	nil.
(ii)	58°–60°C.	1.4740	0.8524	nil.

Nextly, they were rectified under the atmospheric pressure and about 5 gr. of a colourless oil was obtained which smelled decidedly like terpenes.

b.p./757 mm.	162°–163°C.	$d_4^{27}$	0.8530
$n_D^{27}$	1.4693	M.R. obs.	44.43
Rotation	nil.	Do. as $C_{10}H_{16}$ $f=1$	43.53

This terpene, on oxidation, gave no defined products so as to identify itself with any known terpenes in the literature.

(ii) *Dehydration with Phosphoric Acid.* Benihiol, 30 gr. was warmed on the water-bath with syrupy phosphoric acid, 40 gr. The product in this case was similar to those in the foregoing experiment. The hydrocarbon boiled under 50 mm. pressure at 82°–84°C., the yield amounting to only 5 gr., and the remainder mostly passing into resinous mass. Nextly it was dehydrated in the following manner: viz., benihiol, 30 gr., was kept in a dropping funnel A, which was allowed to drip down into a double-necked flask B, containing 40 gr. of syrupy phosphoric acid at 150°C. and 15 mm.

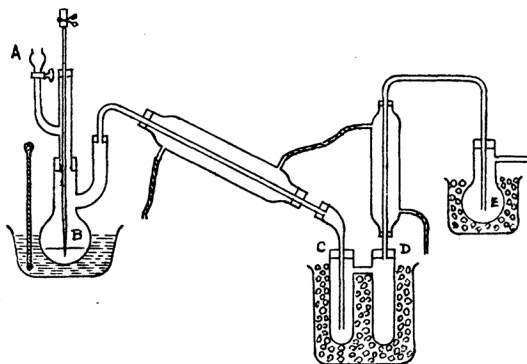


Fig. 1.

pressure. The rate of flow of benihiol was so adjusted that about 1 c.c. per minute dropped down into the acid. Thus, as soon as these drops of benihiol came in contact with the hot acid, they parted with their water to be distilled instantly over to the receivers C, D and E. After all benihiol reacted with the acid, the content of those receivers was collected, separated from water, dried over metallic sodium, and rectified in vacuo. In this way, about 20 gr. of a colourless mobile oil was obtained.

b.p./760.8 mm.	172.4–173°C.	Rotation	nil.
$d_4^{23}$	0.8537	Bromine value obs.	1.071
$n_D^{21.5}$	1.4730	Do. calc. as $C_{10}H_{16}$ $f=1$	1.176

This product was a little different from that obtained by dehydration with 50% sulphuric acid, however, all efforts to get crystalline derivatives therefrom were futile.

(iii) *Dehydration with Zinc Chloride.* Benihiol, 5 gr., was heated on the oil-bath to 160°–170°C. with an equal weight of anhydrous zinc chloride for an hour. After cooling, the whole mass was thrown into water, the separating oil recovered and rectified over metallic sodium. Thus, a hydrocarbon with the following characteristics was obtained:—

b.p./760 mm.	172°–173°C.
$d_4^{32}$	0.8493
$n_D^{32}$	1.4670

**Esters of Benihiol.** (i) *Benihyl Formate.* A mixture of an equal weight of benihiol and pure formic acid was treated with a current of dry hydrogen chloride, warmed on the water-bath for an hour, cooled, washed with water, shaken with a mixture of ether and very dilute alkali, dried over anhydrous sodium sulphate, ether evaporated, and then rectified in vacuo. Thus an ester with the following characteristics was obtained:—

b.p./10 mm.	101°–103°C.	M.R. observed	50.72
$n_D^{32}$	1.4720	Do. calc. as $C_{11}H_{18}O_2$	50.13
$d_4^{32}$	1.005	Sap. Value observed	311.3
$\alpha_D^{32}$	+20.50°	Do. calc. as $C_{11}H_{18}O_2$	308
Br-Value	nil.		

(ii) *Benihyl Acetate.* Benihiol was acetylated with an excess of acetic anhydride in presence of anhydrous sodium acetate at 140°–150°C., and the product was purified in the ordinary manner:—

b.p./10 mm.	107°–108°C.	M.R. observed	53.38
$n_D^{32}$	1.4680	Do. calc. as $C_{12}H_{20}O_2$	54.75
$d_4^{32}$	0.9888	Sap. Value observed	278.8
$\alpha_D^{32}$	+22.50°	Do. calc. as $C_{12}H_{20}O_2$	285
Br-Value	nil.		

(iii) *Benihyl Benzoate.* Benihiol, 10 gr., was dissolved in 80 c.c. of toluene, anhydrous potassium carbonate, 14 gr. and benzoyl chloride, 10 c.c. added, and warmed on the water-bath until evolution of  $CO_2$  ceased, then the whole was thrown into cold water, and the oily later was separated. The ester was then distilled under reduced pressure.

b.p./5 mm.	161°–162°C.	M.R. observed	76.8
$n_D^{30}$	1.5233	Do. calc. as $C_{17}H_{22}O_2$ $\frac{1}{3}$	74.24
$d_D^{30}$	1.0289	Sap. Value, observed	204.3
$\alpha_D^{30}$	+15.00°	Do. calc. as $C_{17}H_{22}O_3$	202.1

(iv) *Benihyl Propionate*. The propionic ester was prepared just as the formic ester. Its properties were as follows :—

b.p./10 mm.	117°–120°C.	$\alpha_D^{22}$	+14.24°
$n_D^{22}$	1.4685	Sap. Value, observed	249
$d_4^{22}$	0.9825	Do. calc. as C <sub>13</sub> H <sub>22</sub> O <sub>2</sub>	257

**Methyl-Benihyl Ether.** Benihiol 5 gr. was dissolved in 15 c.c. of toluene, and was boiled under reflux on an oil-bath with 0.7 gr. of metallic sodium. After all the sodium passed away into the alkoholate, the mass was cooled, and then 7 gr. of methyl iodide was added thereto, and was warmed under reflux for some hours. Then the mass was washed with water, ethered out, dried, ether and toluene expelled by distillation, and then the residual oil was fractionated in vacuo. The distillate, on rectification over metallic sodium, showed the following properties :

b.p./11 mm.	83°–84°C.	$d_D^{30}$	0.9096
$n_D^{30}$	1.4638	$\alpha_D^{30}$	+24.00°

**Halides of Benihiol.** (i) *Benihyl Chloride*. Benihiol, 10 gr., dissolved in petroleum ether, was allowed to drop slowly on phosphorus pentachloride, 13 gr., kept under a layer of the same solvent. After all had been added, the whole mass was heated to 50°–70°C. until all the solid matter disappeared. Then the solvent and phosphorus oxychloride thereby produced were distilled off, the residue rectified under a pressure of 10 mm., and thus 6 gr. of a colourless liquid was obtained :—

b.p./10 mm.	94°–97°C.	$\alpha_D^{21}$	+11.0°
$d_4^{21}$	1.007	M.R. observed	49.15
$n_D^{21}$	1.4860	Do. calc. as C <sub>10</sub> H <sub>17</sub> Cl	48.84

(ii) *Benihyl Iodide*. Benihiol, 20 gr., red phosphorus, 5.9 gr., and 30 gr. of 57% hydriodic acid were put into a sealed tube and was heated in a bomb furnace at 130°C. for the first two hours, and then at 150°C. for the next three hours. The product after cooling was freed from the admixing terpenes by distillation, and then was dissolved in ether, shaken with aqueous sulphurous acid in order to get rid of free iodine, washed with water, dried over anhydrous sodium sulphate, and ultimately the ether was carefully distilled off. The pale yellowish red liquid thus obtained was fairly difficultly soluble in 90% alcohol and in glacial acetic acid, also in pure methyl alcohol, but readily soluble in ether, absolute alcohol, carbon tetrachloride, benzene, etc., etc. It exhibited the following properties :—

$d_4^{28}$	1.2596	I-content	46.54
$n_D^{18}$	1.5215	Do. as $C_{10}H_{17}I$	48.11

It was likely that it contained some unchanged benihiol along with the iodide, and the authors tried to distil it in vacuo but with bad results.

**Reduction of Benihiol.** (i) *Catalytic Reduction of the Dehydrated Product.* The dehydrated product obtained by the action of phosphoric acid on benihiol was allowed to absorb hydrogen in presence of palladium chloride. The absorption proceeded smoothly until the absorption of hydrogen corresponded to one molecule of it against one of benihiol and the product obtained showed the following constants:—

b.p./760 mm.	162°	M.R. obs.	44.79
$n_D^{28}$	1.4608	Do. calc. as $C_{10}H_{18}$	43.98
$d_4^{22}$	0.8449		

(ii) *Catalytic Reduction of Benihyl Chloride.* Nextly benihyl chloride was catalytically reduced just as above, using about 1% its own weight of palladium chloride as catalyst. The product obtained was a little different from the hydrocarbon in the preceding experiment, and its properties after rectification were as follows:—

b.p./760 mm.	165°–167°C.	M.R. obs.	44.31
$n_D^{21}$	1.4648	Do. as $C_{10}H_{18}$	43.98
$d_4^{21}$	0.8603		

(iii) *Catalytic Reduction of Benihyl Iodide.* The iodide above described (40 gr.) was dissolved in 250 c.c. of 10% alcoholic potash, and was shaken in an atmosphere of hydrogen with 5 gr. of Pd-BaSO<sub>4</sub> at 30°C., 758 mm. Thus it absorbed 2830 c.c. of hydrogen instead of 3400 c.c. which is the theoretical amount. It was likely that part of the iodide had been converted into the corresponding alcohol so that the product was fractionated under reduced pressure and about 8 c.c. of a fraction 54°–56°/30 mm. and 6 c.c. of another 109°–130°/10 mm. were obtained. This latter fraction, on examination, was decidedly alcoholic and obviously represented an impure benihiol, so that the former fraction was carefully boiled over metallic sodium under reflux, and then it was rectified in vacuo. The hydrocarbon thus obtained, exhibited the following constants:—

b.p./753.4 mm.	165°C.	$\alpha_D^{28}$	+7.5°
Do./45 mm.	75°C.	Br. absorbed	nil.
$d_4^{28}$	0.846	M.R. obs.	44.25
$n_D^{28}$	1.4550	Do. calc. as $C_{10}H_{18}$	43.98

## Analyses :

Substance	CO <sub>2</sub>	H <sub>2</sub> O	C%	H%
0.1561	0.4966	0.1773	86.78	12.68
0.1209	0.3865	0.1398	86.47	12.69
	C <sub>10</sub> H <sub>18</sub> requires :		86.96	13.03

This hydrocarbon, as far as its boiling point and density are concerned, seems to be related to that which had formerly been obtained by Sabatier and Sendrens<sup>(2)</sup> by the reduction of camphene with hydrogen in presence of nickel catalyser.

**Oxidation of Benihiol.** (i) *Formation of Benihial.* Benihiol, as has been described, when oxidized with chromic acid, gives benihial and benihic acid but, in this case, the best part of the product is benihic acid. In order to obtain the aldehyde in a better yield, it is best to use Beckmann's solution. Thus, 20 gr. of benihiol was dissolved in 30 c.c. of glacial acetic acid, then, 100 gr. of ice-cold Beckmann's solution was added thereto, stood still for a while, then warmed at 40°-45°C. for twenty minutes, and finally the whole mass was thrown into cold water and extracted with ether. The ethereal solution was washed with water, then with dilute sodium bicarbonate solution, dried over anhydrous sodium sulphate, ether distilled away. The residual aldehydic substance amounted to about 12 gr. which could be distilled in vacuo. It represented a colourless oil after rectifications and showed the following characteristics :—

b.p./9.5 mm.	76°-77.8°
$d_4^{20}$	0.9698
$n_D^{20}$	1.4770
$\alpha_D^{20}$	+ 15.0°
Semicarbazone m.p.	169°C.
Do. (0.0457 gr. in 3.5 cc. CHCl <sub>3</sub> )	+151.6°
Phenylhydrazone m.p.	122°C.
Do. (0.0498 gr. in 2.5 cc. CHCl <sub>3</sub> )	+167.5°
Oxime	fluid

**$\alpha$ -Terpineol.** The alcoholic fractions (2) to (7), after repeated treatment with phthalic anhydride, became practically free from all primary alcohols, and such was then fractionated under 10 mm. pressure :—

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(2) *Compt. rend.* **132**, 1256; *Ann. chim. Phys.*, [8] **4**, 391.

	b.p./10 mm.	$d_4^{18}$	$n_D^{18}$	$\alpha_D^{18}$	Yield (gr.)
(i)	86°—88°C.	0.9836	1.4982	—	3
(ii)	88°—90°C.	0.9633	1.4866	—	2
(iii)	90°—94°C.	—	—	—	2
(iv)	94°—98°C.	0.9395	1.4831	+35.7°	8
(v)	98°—100°C.	0.9397	1.4836	+43.6°	12
(vi)	100°—118°C.	0.9680	1.4953	+23.0°	28

On examination of these fractions the first was proved to consist chiefly of benihinal (semicarbazone m.p. 214°–216°C.), and the last one to represent benihol (benihic acid m.p. 110°C.). The fourth and the fifth exhibited constants similar to  $\alpha$ -terpineol, so, they were oxidized with potassium permanganate to obtain 1-2-8-trioxy-menthane therefrom. The oxidation was carried out exactly as Wallach prescribed with 6 gr. of the substance, and a crystalline product with m.p. 121°C. was obtained. This substance, on mixing with 1-2-8-trioxy-menthane showed no depression of the melting point. Furthermore, on preparing the nitrosochloride directly from the fractions,  $\alpha$ -terpineol nitrosochloride m.p. 112°C. was obtained.

**The Sesquiterpenes.** The fractions (10) to (13) in the foregoing table (p. 373-374) namely, those fractions boiling between 105° and 125°C. under 5 mm. pressure seemed likely to represent sesquiterpenes as their saponification number as well as that after acetylation were very small, so they were boiled with metallic sodium for several days under reflux, and then they were rectified. The greater part of the distillate, on such treatment, collected between 127° and 131°C., and showed the following properties:—

b.p./10 mm.	127°—131°C.	$\alpha_D^{24}$	+35.7°
$d_4^{24}$	0.9162	M.R. obs.	66.45
$n_D^{24}$	1.5088	M.R. as $C_{15}H_{24}$   = <sub>2</sub>	66.15

This was then repeatedly fractionated with Widmer's dephlegmator on, under 10 mm. pressure, and thus it was divided into the following five fractions:—

	b.p./10 mm.	$d_4^{21}$	$n_D^{21}$	$\alpha_D^{21}$	M.R.	gr.
(l)	128.5°—130°C.	0.9176	1.5081	+22.0°	66.26	25
(m)	130°C.	0.9177	1.5088	+31.6°	66.23	30
(n)	130°C.	0.9182	1.5093	+37.0°	66.35	35
(o)	130°C.	0.9194	1.5095	+38.0°	66.30°	35
(p)	130°—131°C.	0.9232	1.5097	+40.2°	66.05	38

On testing Liebermann's reaction with each of these fractions, each showed yellowish green colour at first which passed gradually into purple-violet.

If acetic anhydride be used as solvent, the initial colouration was bright green and changed gradually into blue. With chloroform as solvent the colouration at first was yellow green which passed to orange yellow with lapse of time.

(i) *Action of Hydrogen Halides.* (a) *Action of Hydrogen Chloride.* These fractions, dissolved in absolute ether, were exposed to the action of dry hydrogen chloride in cold. From all of the fractions crystalline hydrochloride m.p.  $103^{\circ}$ – $104^{\circ}$ C. deposited which after purification if mixed half in half with cadinene hydrochloride, m.p.  $117^{\circ}$ C., showed a considerable depression of the melting point, viz. the mixture melting around  $110^{\circ}$ C.

(b) *Action of Hydrogen Bromide.* All fractions, if dissolved in glacial acetic acid, and a proper quantity of hydrogen bromide in form of 48% aqueous acid gradually added thereto, and shaken vigorously, solidified into a crystalline mass. The crystalline mass was stood still overnight in an ice chamber, filtered while cold, washed with cold alcohol, and was recrystallized from acetone. Alcohol and ethyl acetate were not suitable solvents for the recrystallization, as the crystals were liable to decompose on dissolution in these solvents. The melting point of the pure recrystallized product was  $112^{\circ}$ – $114^{\circ}$ C., which if mixed with pure cadinene dihydrobromide, m.p.  $125^{\circ}$ C., showed a remarkable depression of the melting point, viz., the mixture melting around  $98^{\circ}$ – $106^{\circ}$ C. It was optically inactive.

(c) *Action of Hydrogen Iodide.* Glacial acetic acid solutions of the fractions, on treatment with hydriodic acid s.g. 1.56 in cold, deposited a large amount of crystalline hydriodide,—a remarkable absorption of heat was experienced during the reaction. This hydriodide, after filtration, was washed with cold alcohol, dried, and then recrystallized from acetone. The pure product melted at  $117^{\circ}$ – $118^{\circ}$ C., but seemed likely to be rather unstable, and was apt to decompose, even if kept dry in vacuo. It was also optically inactive. The pure crystal mixed with pure cadinene dihydriodide, melted around  $96^{\circ}$ – $103^{\circ}$ C.

(ii) *The Nitrosite, the Nitrosate, and the Nitrosochloride.* Preparations of nitrosite, nitrosate, and nitrosochloride were tried with each of the fractions, but with no fruitful results.

(iii) *The Regeneration of the Sesquiterpene from the Hydrochloride.* The hydrochloride, m.p.  $103^{\circ}$ – $104^{\circ}$ C., 7 gr., was dissolved in 30 c.c. of glacial acetic acid, 7 gr. of anhydrous sodium acetate added, boiled under reflux for some hours and the regenerated hydrocarbon was rectified by distillation under reduced pressures. The sesquiterpene showed the following characteristics :—



b.p./10 mm.	129°–130°C.	$\alpha_D^{21}$	–10.32°
$d_4^{21}$	0.9191	M.R. obs.	66.10
$n_D^{21}$	1.5074	Do. as $C_{15}H_{24} =2$	66.15

On treating this sesquiterpene with hydrogen chloride, the selfsame hydrochloride melting at 103°–104°C. resulted, and on observing the mixed melting point with the original hydrochloride, no lowering of the melting point was to be found. It was optically inactive.

On experimenting with hydrogen bromide or hydrogen iodide, the identical hydrobromide or hydriodide resulted, and these also, on isolating the sesquiterpene as above, equally gave rise to laevo-rotatory sesquiterpene. The purest sample of the regenerated sesquiterpene obtained from the dihydrochloride from the fraction (p) exhibited the following constants:—

b.p./10 mm.	130°–131°C.	$\alpha_D^{21}$	–40.34°
$d_4^{21}$	0.9189	M.R. obs.	66.17
$n_D^{21}$	1.5080	Do. as $C_{15}H_{24} =2$	66.15

That this sesquiterpene reverses its sign of optical rotation through a transformation into an inactive hydrochloride, is most remarkable, and it reminds us of the behaviour of *d*-cadinene, which transforms into the *l*-modification through formation of laevo-rotatory hydrochloride.

(iv) *Catalytic Reduction.* The fraction (p), 2.707 gr., was dissolved in 50 c.c. of glacial acetic acid, 0.03 gr. of freshly prepared platinum black added thereto, was shaken in an atmosphere of pure hydrogen at 25°C., 762.3 mm. pressure. In about three hours it absorbed 679 c.c. of the gas, which amount is a little too high—by about 5%—but practically corresponds with the calculated quantity for saturating the two ethylene linkages. The reduced product, after rectifications, showed the following constants:—

b.p./10 mm.	123°–124.2°C.	$\alpha_D^{21}$	–9.52°
$n_D^{20.5}$	1.4820	M.R. obs.	66.92
$d_4^{21}$	0.8860	Do. as $C_{15}H_{28}$	67.07

(v) *Reduction by Sodium and Alcohol.* 4 Gr. of the fraction (p) was treated with 10 gr. of metallic sodium and hot amyl alcohol and heated under reflux for many hours, but no perceptible change took place. The substance recovered from the reaction mixture proved to be quite identical with the starting material.

(vi) *Bromine Number.* The fraction (p) 0.2207 gr. was treated with an excess of a standardized solution of bromine in carbon tetrachloride and then was titrated back with thiosulphate. The consumed bromine in this

case, amounted to 0.3459 gr., while that calculated for the same weight as  $C_{15}H_{24}|_2$  is 0.3458 gr.

(vii) *Racemization by Sulphuric Acid.* The fraction (p), on being shaken with 50% sulphuric acid, loses its optical activity with lapse of time. The features of such racemization with respect to time and temperature are as follows :—

Hours	0	2	4	6	8	10	12	14	28
Temp.	20°	20°	20°	80°	80°	80°	80°	80°	80°
$\alpha_D^{20}$	+40°	+36°	+30°	+25°	+18°	+14°	+7°	+1.4°	+0.35°

(viii) *Dehydrogenation.* The sesquiterpene was treated, exactly as Ruzicka had done in the case of dehydrogenating cadinene, with sulphur, and the product of reaction distilled. It came over at 287° to 291°C., with a refractive index  $n_D^{20}$  1.5820, the melting points of the picrate and styphnate being 115°C. and 138°–139°C. respectively. They did not show any depression of melting points if mixed with cadalin picrate or cadalin styphnate.

Thus, it becomes obvious, that the sesquiterpene is one which contains a cadalin nucleus and two double bonds that are not conjugated, but different from ordinary cadinene. To this sesquiterpene the authors propose the name “*sesquibenihene*,” whose chemical constitution will be discussed on another occasion.

**The Sesquiterpene Alcohols.** The fractions (15), (16), (17) and (18) look likely to consist of sesquiterpene alcohols from their constants. On observing their saponification numbers before and after acetylation, they gave the following values :—

	Sapo. V.	Sapo. V. after Acetylation
(15)	17.3	143.8
(16)	17.2	143.6
(17)	—	—
(18)	11.7	200.7

(i) *The Tertiary Alcohol.* The fractions (15) and (16) were separately saponified by means of alcoholic potash, the saponified product after due treatment was rectified in vacuo. Thus, from both of these, the same product resulted, the physical properties of which are given below :—

b.p./10 mm.	149°–152°C.	Br. Value obs.	0.737
$d_4^{18}$	0.9818	Do. calc. as $C_{15}H_{26}O _1$	0.720
$n_D^{16}$	1.5122	M.R. obs.	67.87
$\alpha_D^{18}$	–33.00°	Do. as $C_{15}H_{26}O _1$	68.03

The substance, on Liebermann's test, with chloroform, glacial acetic acid, and acetic anhydride as solvents, showed respectively bordeaux, violet, and blue colours.

(a) Action of Hydrogen Chloride. The substance was dissolved in ether (1/1) and exposed to the action of dry hydrogen chloride under cooling. Thus, after a while, beautiful needle crystals separated out in abundance, which after recrystallizations from alcohol showed a melting point  $117^{\circ}\text{C}$ . These crystals were proved to be identical with cadinene dihydrochloride, as they showed no depression of the melting temperature if mixed with a pure specimen of cadinene dihydrochloride.

(b) Dehydration by Formic Acid. The substance 8 gr. was boiled under reflux with 25 gr. of pure formic acid for two hours. Then the mass was thrown into cold water and the oil separating out was collected and rectified. The product represented a sesquiterpene with the following properties :

b.p./10 mm.	$126^{\circ}-127^{\circ}\text{C}$ .	m.p. of Dihydrochloride	$117^{\circ}\text{C}$ .
$d_4^{17}$	0.9181	M.R. obs.	66.48
$n_D^{17}$	1.5103	Do. as $\text{C}_{15}\text{H}_{24} =2$	66.15
$\alpha_D^{17}$	$+5.6^{\circ}$		

The dihydrochloride mentioned above also proved to be identical with cadinene dihydrochloride.

(c) Action of Phthalic Anhydride. The substance, on treatment with phthalic anhydride either in benzene solution or directly at  $120^{\circ}-130^{\circ}\text{C}$ ., no ester formation was observable. Thus, it seems likely that this alcohol is tertiary in structure, and closely related to cadinol of Semmler and Jonas<sup>(3)</sup> as well as to taiwanol which one of the present authors<sup>(4)</sup> (K) had isolated from the volatile principle of Formosa cedar or *Taiwania Cryptomerioides* Hay.

	The Substance in question	Cadinol (Semmler)	Taiwanol (Kafuku)
b.p.	$149^{\circ}-152^{\circ}/_{10}$	$155^{\circ}-165^{\circ}/_{15}$	$141^{\circ}-143^{\circ}/_{6}$
$d_4^{20}$	0.9802	0.9720	0.9772
$n_D$	1.5122 ( <sub>16</sub> )	1.50702 ( <sub>20</sub> )	1.5045 ( <sub>30</sub> )
$\alpha_D^{20}$	$-33.00^{\circ}$	$+22^{\circ}$	$-42.56^{\circ}$
M.R. obs.	67.87	67.97	67.88
m.p. of phenyl urethane	—	—	$134^{\circ}-135^{\circ}\text{C}$ .

(3) *Ber.*, **47** (1914), 2068.

(4) This Bulletin, **6** (1931), 7.

(ii) *The Primary Alcohol.* The fraction (18), after saponification by an excess of alcoholic potash, was rectified in vacuo. The main portion exhibited the following properties :—

b.p./10 mm.	162°—164°C.	Br. V.	1.19
b.p./758 mm.	294°—296°C.	Do. calc. as $C_{15}H_{26}O \mid_1$	0.721
$d_4^{15}$	0.9896	M.R. obs.	68.18
$n_D^{15}$	1.5200	M.R. calc. as above	68.13
$\alpha_D^{16}$	—13.00°		

On being acted on by hydrogen in presence of platinum black, 0.4720 gr. of the substance absorbed 537.6 c.c. of the gas under 758.3 mm. at 18°C. The calculated quantity for the above amount being about 4% lower than this value.

(a) *Colour Reaction.* The dilute chloroformic solution of the sesquiterpene, on addition of a drop of concentrated sulphuric acid, assumes beautiful crimson colour which passes with time to reddish brown. The glacial acetic acid solution under the same conditions is coloured purple red at first and passes into blue, while the solution in acetic anhydride takes the green colour which changes into blue.

(b) *Action of Hydrogen Chloride.* On passing dry hydrogen chloride gas into the ethereal solution (1/1), no dehydrating action is perceptible, and no separation of crystalline substance takes place.

(c) *Action of Formic Acid.* On boiling the sesquiterpene alcohol with pure formic acid under reflux, no dehydrating action took place, but formation of the formic ester was observed.

(d) *Action of 50% Sulphuric Acid.* On stirring the substance vigorously with 50% sulphuric acid, some sesquiterpene is formed but the yield is very poor, most part of the substance remaining unchanged. A small portion passes at the same time into a resinous mass.

(e) *Action of Phthalic Anhydride.* On boiling it with a calculated amount of phthalic anhydride in benzene solution on the water-bath for 2 hours, it is converted almost quantitatively into the acidic phthalate. Thus, after eliminating the unchanged portion by ethering out, the semi-ester was saponified with alcoholic potash, and about 86% of the pure sesquiterpene alcohol was obtained, which after rectifications exhibited the following constants :—

b.p./10 mm.	163°C.	$\alpha_4^{22}$	-12.00°
b.p./760 mm.	294°C.	M.R. obs.	68.16
$d_4^{22}$	0.9890	Do. calc. as $C_{15}H_{26}O$	68.13
$n_D^{22}$	1.5192		

## Analyses.

Substance	CO <sub>2</sub>	H <sub>2</sub> O	C%	H%
0.2154	0.6384	0.2059	80.83	10.58
0.2237	0.6737	0.2214	80.34	10.76
		C <sub>15</sub> H <sub>24</sub> O requires :	81.82	10.91
		C <sub>15</sub> H <sub>26</sub> O requires :	81.08	11.71

These data show that the substance under investigation may not be a simple alcohol but a mixture of alcohols, so various attempts were made in order to carry out their separation but without result.

## Summary.

(i) The volatile oil from the wood of *Chamaecyparis formosensis*, Matsum., or Formosa cypress (benihi), contains much less terpenes and much more terpene alcohols as compared with the volatile oil from the leaf of the same plant.

(ii) The predominant terpenes in the oil are *d*- $\alpha$ -pinene and *d*-camphene, and they are optically strongly active.

(iii) Among the terpenic alcoholic components there have been proved two new substances 'benihol' C<sub>10</sub>H<sub>18</sub>O, and 'benihinol' C<sub>10</sub>H<sub>16</sub>O.

(iv) In the sesquiterpene fraction, a new sesquiterpene whose hydrochloride has the melting point 103°-104°C. was isolated, and it was named sesquibenihene.

(v) Among the sesquiterpene alcohol fraction, there are, along with a tertiary alcohol of cadinol type, at least one more primary alcohol the exact nature of which is not yet definitely known.

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