

ON THE ESSENTIAL OIL OF TAIWANIA CEDAR.

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The Taiwania cedar is one of the five big conifers indigenous to Formosa and is found along the central mountain range at an altitude of 6,000 to 7,000 ft. above sea level. It closely resembles Japanese Cryptomeria cedar (*Cryptomeria japonica*, D. Don.) in appearance, hence its Latin name,—*Taiwania Cryptomerioides*, Hayata. Its essential oil has hitherto never been studied but as it has a peculiar pleasant smell of its own, the authors undertook to investigate the nature of its volatile constituents, if any.

The material for examination forwarded by the Government Forestry Department at Taiheizan (Mt. Taihei) represented several root-stumps of a big, freshly hewn tree, of about 100 years of age, and they were chopped into small pieces of $1 \times 3 \times 8$ cm. in size, and put into a still. On prolonged steam distillation the authors obtained a very viscous oil of faintly yellow tinge with characteristic pleasant aroma, the yield amounting to 0.23% by weight of the material used. The oil, though very viscid, showed no tendency to deposit solid crystalline substance even on cooling with freezing mixtures. On fractional distillation it gave no terpene or terpene alcohol fractions, but seemed to consist practically of sesquiterpenes and sesquiterpene alcohols,—viz. about 34% cadinene, 2-3% humulene and caryophyllene, and 46% sesquiterpene alcohol. This last mentioned sesquiterpene alcohol closely resembled that isolated by L. Ruzicka⁽¹⁾ from West Indian sandalwood oil, in such respects as, the boiling point, the formation of hydrochloride, unaction towards phthallic anhydride, etc. etc. Thus, it is of interest whether this oil can be used or not as a substitute for the aforesaid oil for therapeutic purposes as a drug.

Experimental.

The oil directly after steam distillation, on being dried over anhydrous sodium sulphate, showed the following constants:—

d_4^{15}	0.9593
n_D^{15}	1.5104
α_D^{15}	-2.00°

(1) *Rec. trav. chim. Pay-Bas*, **47** (1928), 370, 381.

Acid value	0.38
Ester value	10.52
Do. after acetylation	83.00
Specific viscosity	137.1
Turbidity number (alcohol)	7.5 ⁽¹⁾

On shaking the oil with 40% sodium bisulphite solution, no formation of crystalline precipitate was observed, from this it follows likely that the oil contained neither aldehyde nor ketone. The result of five consecutive fractional distillations with Widmer's dephlegmator, is shown below. (Diagrammatically in Fig. 1.)

Fraction	Boiling point	Pressure	Distillate %
(1)	113°—115°	10 mm.	0.28
(2)	115°—120°	do.	0.16
(3)	120°—125°	do.	1.13
(4)	125°—130°	do.	2.06
(5)	130°—133°	do.	21.00
(6)	133°—135°	do.	13.70
(7)	135°—140°	do.	0.49
(8)	140°—145°	do.	1.23
(9)	145°—150°	6 mm.	46.20

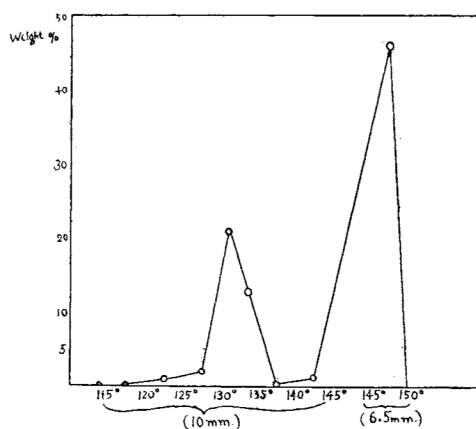


Fig. 1.

(1) Number of c.c. of water required to produce a permanent turbidity to 10 c.c. of an absolute alcohol solution of the oil in question (2 c.c. in 10 c.c. of alcohol).

The properties of these fractions are as follows :—

Fraction	d_4^{15}	n_D^{15}	α_D^{15}	M. R.
(1)	0.9104	1.4913	— 5.40°	—
(2)	0.9097	1.4979	— 1.40°	—
(3)	0.9089	1.5002	+ 1.08°	66.04 as $C_{15}H_{24}$
(4)	0.9134	1.5050	+ 7.20°	66.24
(5)	0.9189	1.5090	+ 35.20°	66.30
(6)	0.9215	1.5110	+ 54.60°	66.36
(7)	0.9641	1.5110	— 17.40°	—
(8)	0.9715	1.5104	— 33.40°	—
(9)	0.9742	1.5093	— 40.46°	68.01 as $C_{15}H_{26}O$

It is noteworthy that in the foregoing table, the first two fractions and the last three are laevo-rotatory, while the rest are all dextro-rotatory, and that the fraction (5) which forms the greater part of the sesquiterpene fraction still contains oxygen to an extent of 2.6%, while the next (6) is practically pure hydrocarbon. From these, it follows that there may be a certain oxygenous compound of laevo-rotatory nature in the lower boiling portions. Whether this oxygenous compound be of terpenic alcoholic nature or not, we leave it for the future to decide.

The Sesquiterpenes. From considerations on the boiling behaviour and other physical constants, it seemed most probable that the fractions (3), (4), (5), and (6) consisted for the most part of dicyclic sesquiterpenes, so that the authors tested for the presence of caryophyllene and humulene with the fractions (3) and (4), and of cadinene with (5) and (6).

Thus, 0.5 gr. each of (3) and (4), was dissolved in an equal volume of absolute ether, and a dry current of nitrosyl chloride was passed in the cold as suggested by Ehestädt, and stood overnight in the ice chamber, then ether expelled and treated with methyl alcohol, when, an amount of crystalline substance separated out. Then it was fractionally recrystallized from methyl alcoholic solution and the resulting nitrosochloride tested for the melting point.

It was found that the nitrosochloride from (3) melted at 165°–166°, while that from (4) at 105°–106°. That the former was identical with humulene nitrosochloride, could be proved by the unlowering of its melting point on admixture with humulene nitrosochloride from oil of *chamaecyparis Obtusa*, Sieb. et Zucc., but the latter, on examination, seemed likely to be a mixture of cadinene nitrosochloride with some other higher-melting nitrosochloride.

Thus, they were once more fractionated under 10 mm. pressure, and it was possible to separate them into a lower boiling inactive, and a higher boiling active fractions. These afforded on treatment with nitrosyl chloride following Ehestädt's method,⁽¹⁾ two nitrosochlorides, the one melting at 165°–166°, and the other at 175°. The former was of course identical with humulene nitrosochloride, and the latter proved to be that of caryophyllene, which identity was affirmed by observing the mixed melting point with a known sample of caryophyllene nitrosochloride from *Chamaecyparis* oil. This latter nitrosochloride with m.p. 175°, showed an optical activity of +3.82° (0.423 gr. in 10 c.c. of chloroform).

Nextly an attempt was made to prepare nitrosites but it was altogether fruitless, and no crystalline substance could be obtained. But the action of cold glacial acetic acid solution of nitric acid on a mixture of 2 c.c. each of the sesquiterpene, isoamyl nitrite, and glacial acetic acid, afforded crystalline nitrosates from both, which after recrystallization from methyl alcohol, melted both at 162° and was proved to be humulene nitrosate (*mischproben*).

The fraction (5) was boiled over metallic sodium for six hours to get rid of oxygenous substances, and then rectified in vacuo, and in this way, a rather pure product with the following constants was obtained.

B.p.	130°–131.5° / 10 mm.
d_4^{20}	0.9183
n_D^{20}	1.5093
α_D^{20}	+34.62°
M.R.	66.36; 66.15 calc. as $C_{15}H_{24} \frac{1}{2}$.

On Liebermann's colour test, the hydrocarbon produced indigo blue colour which gradually turned into blue and then pink. If dissolved in chloroform and a drop of concentrated sulphuric acid added, it imparted to the solution a deep red coloration. This agrees with the behaviours of cadinene, so that tests in this direction were carried out. One gram of the sample was dissolved in an equal amount of absolute ether, and a current of dry hydrogen chloride gas was passed into the ice-cold solution, after twenty minutes an amount of crystals separated out which was kept overnight, then ether and hydrogen chloride driven off in vacuo, and the resulting semisolid mass was thoroughly washed with cold glacial acetic acid and then recrystallized from acetic ether. The white needle crystal thus obtained showed a melting point 117°–118°, whose identity with cadinene dihydrochloride could be proved by "*mischproben*" method.

(1) *Schimmels Report*, April 1910, 164.

The nitrosate and the hydrobromide were prepared in the usual manner and after due purifications it was observed to melt at 110° – 111° and 124° – 125° respectively, which is in accordance with the data about the corresponding derivatives of cadinene. The fraction (6) had practically the same constants as this rectified product from (5) and on repeating the experiments as above, it gave precisely the same results. Only, it is worth mentioning, that in the second experiment, the hydrochloride (m. p. 117° – 118°) offered an optical activity of -39.64° (in chloroform solution), and that the cadinene regenerated from this hydrochloride rotated a laevorotation of -47.42° , whereas the original sesquiterpene gave a rotatory power $+56.60^{\circ}$. This is in accordance with the description by Semmler⁽¹⁾ that the hydrochloride obtained either from *d*- or *l*-cadinene, as well as the revived cadinene from the hydrochloride are all laevo-rotatory.

The oxidation of cadinene has been studied by L. Ruzicka and M. Stoll,⁽²⁾ and by D. T. Gibson, J. M. Robertson, and J. Sword,⁽³⁾ but no crystalline compound other than cadinene glycol has been obtained. The authors oxidized cadinene with acetone permanganate and obtained a substance melting at 142° – 143° with a composition corresponding to the formula $C_{12}H_{22}O_2$. It was carried out in the following manner. To a mixture of 20 gr. of the rectified hydrocarbon from (6), 150 gr. of acetone, and 40 gr. of water under stirring, 20 gr. of finely powdered potassium permanganate was added in small portions and the temperature maintained at 30° – 40° during the reaction. After the reaction was over, the mass was subjected to steam distillation to drive off acetone and unacted hydrocarbon, then the residue was extracted with ether. The ether extract was evaporated and distilled in vacuo, when, 12 gr. of unacted cadinene came over, and then about 4 gr. of higher-boiling oxidation product distilled at about 140° under 4 mm. pressure. This product was treated with petroleum ether when a crystalline substance deposited which melted at 142° – 143° after purification. The substance, on analysis, showed the composition $C_{12}H_{22}O_2$.

Anal. Subst.=0.1088, 0.1103; CO_2 =0.2895, 0.2930; H_2O =0.1070, 0.1100 gr. Found: C=72.56, 72.44; H=10.87, 11.08%. Calc. for $C_{12}H_{22}O_2$: C=72.70; H=11.10%.

As for the exact character of this substance the authors wish to communicate on the next available occasion, and retain it for the present.

The Sesquiterpene Alcohol. The fraction (9) practically consisted of sesquiterpene alcohol, as its physical properties as well as the analytical data show:—

(1) "Die ätherischen Oele," Bd. 2, S. 553.

(2) *Helv. Chim. Act.*, 7 (1924), 84.

(3) *J. Chem. Soc.*, 1926, 164.

B.p.	145°—150° / 6.5 mm.
d_4^{15}	0.9742
n_D^{15}	1.5093
α_D^{15}	-40.46°
M.R.	68.01; calculated as $C_{15}H_{26}O \frac{1}{1} = 68.12$.

Anal. Subst.=0.1267; $CO_2=0.3882$; $H_2O=0.1293$ gr. Found: C=81.42; H=11.34%.
Calc. for $C_{15}H_{26}O$: C=81.11; H=11.74%.

This fraction, on Liebermann's test, gave indigo blue colour at first which faded into pink, while the chloroformic solution, on addition of a few drops of concentrated sulphuric acid, turned into dark blue and changed into red in course of time.

Fifty grams of the fraction was boiled over a calculated amount of metallic sodium for 15 hours, the unacted oil was driven off in vacuo, the residual viscous mass of the alcoholate was decomposed by alcoholic sulphuric acid, then an excess of water was added and it was extracted with ether. The ethereal solution was washed out with water, dried, evaporated, and then distilled under a pressure of 6 mm. mercury. The distillate showed the following constants:—

B.p.	141°—143° / 6 mm.
d_4^{30}	0.9692
n_D^{30}	1.5045
α_D^{30}	-42.56°
M.R.	67.88; calculated as $C_{15}H_{26}O \frac{1}{1} = 68.01$.

Anal. Subst.=0.1355; $CO_2=0.4032$; $H_2O=0.1439$ gr. Found: C=81.15; H=11.79%
Calc.: C=81.11; H=11.70%.

Three grams of this substance, dissolved in dry ether was treated with a current of dry hydrogen chloride, when, a quantity of crystalline compound precipitated. Ether and excess of hydrogen chloride was then driven off at room temperatures, and the crystalline substance remaining behind was well washed with cold glacial acetic acid, drained until dry on the porous porcelain plate and then recrystallized from acetic ether. The pure hydrochloride showed a melting point 117°—118°, and proved to be identical with cadinene dihydrochloride as no lowering of melting point occurred on mixing it with cadinene dihydrochloride from other sources. Exactly the same thing had been experienced by Semmler and Jonas⁽¹⁾ in handling the sesquiterpene alcohol from galbanum oil, and they had given the name "cadinol" to it. They had stated that it represented a tertiary sesqui-

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

terpene alcohol, and that it was liable to break into cadinene and water, but failed to prepare any definite crystalline derivatives therefrom. For the sake of comparison, their data as regards this sesquiterpene alcohol, and the authors' data are given below:—

	Semmler and Jonas	Kafuku and Kato
B.p.	155°–165°/15 mm.	141°–143°/6 mm.
d_{20}^{20}	0.9720	0.9692 ($_{30}^{\circ}$)
n_D^{20}	1.50702	1.5045 ($_{30}^{\circ}$)
α_D^{20}	+22°	–42.56° ($_{30}^{\circ}$)
M.R.	67.97	67.88

With a view to obtain a crystalline phenyl urethane, the purified alcohol was let react with phenyl isocyanate. For this purpose, 2.2 gr. of the freshly distilled substance and 1.2 gr. of phenyl isocyanate was mixed in the warm and kept for 20 days in a desiccator, when the mixture congealed into a crystalline mass. Then, it was treated with petroleum ether and got rid of diphenyl urea in the usual manner, and at last, a crude phenyl urethane m.p.=128°–130° was obtained, which after recrystallizations from alcohol showed a melting point 134°–135°.

The attempt to prepare the benzoate, the acid phthalate, the paranitrobenzoate, the bromide, or the xanthogenate, turned out altogether to be futile, and no crystalline compound was obtained. Only, it is worthy of note that the petroleum ether solution of the sesquiterpene alcohol, on treatment with an aqueous chromic acid solution assumed a characteristic red colouration, which according to Wienhaus⁽¹⁾ showed the formation of chromic acid ester. Even though it was impossible to get any crystalline chromic ester, this colouration and its poor affinity towards phthalic anhydride suggests that the authors' sesquiterpene alcohol also to be of a tertiary nature.

Ten grams of the rectified product from (9) was oxidized in aqueous acetone solution with 25 gr. of potassium permanganate at 50°–60°, the resulting mass was steam distilled to expel the unoxidized oil, and then, the aqueous residue, as well as the manganic mud, were separately extracted with ether, the ethereal solutions united and evaporated, when a small quantity of a yellowish oil together with a little crystalline residue remained behind. On standing for a length of time, the whole coalesced into a gruel-like mass, which was dried on the clay plate and the crystalline body recrystallized from benzol. The resulting crystal melted at 170°, but, on account of the small quantity available, nothing has been done to determine the nature of the substance.

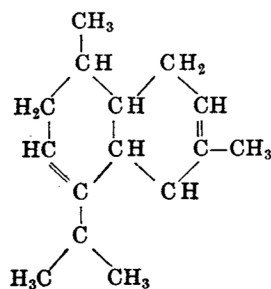
(1) *Ber.*, **47** (1914), 329.

Thirty grams of the substance was dissolved in an equal amount of pure formic acid, and warmed on the water bath for fifteen minutes, then the acid was neutralized with caustic soda, the hydrocarbon thus formed was extracted with ether, ether evaporated off, and the hydrocarbon boiled over metallic sodium at 165°–180° for 4 hours, and then rectified in vacuo. The distillate had the following properties:—

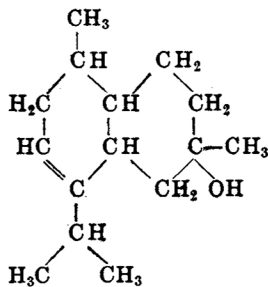
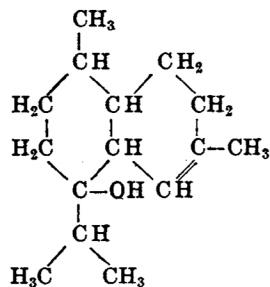
B.p.	134°–135°/10 mm.
d_4^{20}	0.9209
n_D^{20}	1.5100
α_D^{20}	–51.08°
M.R.	66.25 as $C_{15}H_{24} \overline{17} = 66.15$

This hydrocarbon gave a dihydrochloride m.p. 117°–118°, and a dihydrobromide m.p. 124°–125°, which turned out to be identical with those of cadinene, (mischproben). Also a nitrosate melting at 110°–111° was obtained in the usual manner. From these it is obvious that the product of dehydration is cadinene.

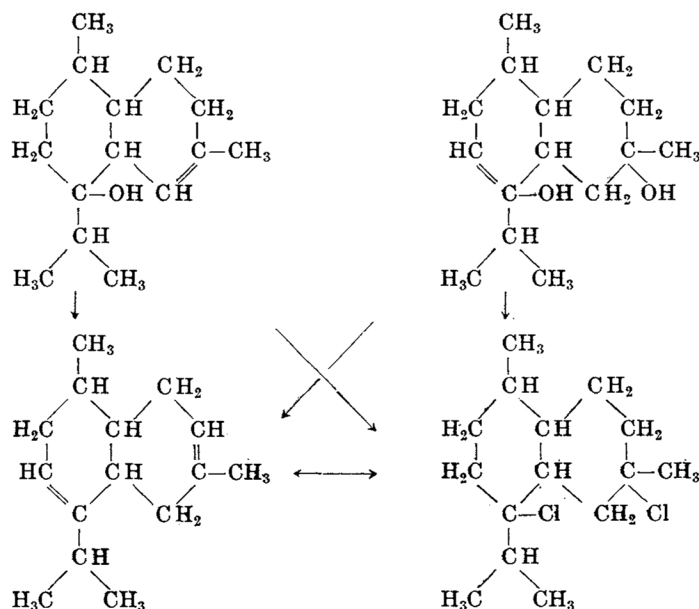
From the foregoing experiments it seems possible that the authors' sesquiterpene alcohol might be identical with Semmler's cadinol, but considering the assumed constitutional formula for cadinene, there still remains much to be determined before the identity is claimed. Supposing the constitutional formula for cadinene to be



the following two sesquiterpene alcohols of the formulae



may both be responsible for the formation of cadinene dihydrochloride by the action of hydrogen chloride, and at the same time the dehydration to cadinene by formic acid, thus:—



It therefore remains for the authors to determine which of these two formulae should more reasonably be adopted for the sesquiterpene alcohol in question. The authors hope to discuss the subject by studying the oxidative disintegration of the alcohol on the next available opportunity. For the present, the authors wish to name their sesquiterpene alcohol as "taiwanol," as it originates from *Taiwania Cryptomerioides*, Hayata.

Summary.

1. The wooden chips of *Taiwania Cryptomerioides*, Hayata, gives on steam distillation 0.23% of an oil, consisting chiefly of sesquiterpene and sesquiterpene alcohol.
2. The sesquiterpenes in the oil are chiefly cadinene, with a little humulene and caryophyllene.
3. From the cadinene, a new oxidation product C₁₂H₂₂O₂ (m.p.=142°-143°) was obtained.
4. The sesquiterpene alcohol in the oil, to which the authors suggest the name "taiwanol," closely resembles cadinol of Semmler and Jonas. From cadinol no crystalline phenyl urethane could be obtained, but in case

of taiwanol, it affords a crystalline phenyl urethane melting at 134° – 135° , and furthermore, it gives a neutral oxidation product (m.p. 170°) if oxidized with permanganate in acetone solution.

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