[Contribution from Auckland University College]

THE ESSENTIAL OIL OF *CUPRESSUS MACROCARPA*

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Received May 23, 1942

A number of essential oils of the genus *Cupressus* have already been examined, including *C. sempervirens*, *C. sempervirens pyramidalis*, *C. aromatica*, *C. Goweniana*, *C. funebris* (1), *C. torulosa* (2), *C. lusitanica* (3). *Cupressus macrocarpa*, Hartweg (syn. *C. Lambertiana*, Carr.) or Monterey cypress has probably the most restricted range of any conifer, growing naturally only at Monterey and on the island of Guadaloupe, while at Monterey the main grove occupies an area only 2 miles long and 200 yards wide. It has been introduced into many parts of the world, including New Zealand, where it is grown extensively. The essential oil has not been previously examined in detail, Schimmel and Co. (4) reporting the physical constants, d_{15} 0.8656, $[\alpha]_D$ +31.35°, chemical constants, acid value 1.5, ester value 13.9, ester value after acetylation 50.82, and it was suggested without chemical confirmation that the oil contained citronellal and *p*-cymene.

A complete examination of the essential oil has now been made, ten different constituents being isolated with certainty, including two new compounds, a sesquiterpene alcohol and a diterpene, while at least five other unidentified constituents are also present. The winter oil, obtained in 0.20% yield from the leaves and terminal branchlets, is yellow in color and has the following constants: d_4^{25} 0.8607, n_D^{25} 1.4718, $[\alpha]_D^{25}$ +11.31°, acid number 1.0, saponification number 1.4, saponification number after acetylation 33.7. Phenols are absent, and the combined aldehyde and ketone content is less than 0.3%.

When an attempt was made to fractionate the oil at atmospheric pressure, decomposition occurred with apparent liberation of water, so that nearly all the fractionations were carried out at 10 mm. A typical preliminary distillation gave the fractions listed in Table I.

The fractions boiling below 65°/10 mm. were then systematically fractionated, twice at 10 mm. and finally at atmospheric pressure, the fractionation being controlled by the boiling point, as well as by the refractive index, density, and rotation, graphs being drawn of these four constants as the fractionation proceeded.

After the fourth fractionation it was apparent that some obvious mixtures were not being separated further, and separation and identification was then carried out by chemical means. The fractions boiling above 65°/10 mm. were also repeatedly fractionated at 10 mm., the solid separating in the higher-boiling fractions being filtered off before refractionation. In all cases where the molecular refraction indicated a hydrocarbon unmixed with any appreciable quantity of oxygenated compounds, the final distillations were carried out in the presence of sodium.

No attempt has been made to identify the constituents in each fraction but only those have been examined which a consideration of their physical properties showed to be reasonably homogeneous, or in some cases mixtures of constituents practically impossible to separate by fractionation. The numbers of the following fractions refer to those in Table II.

TABLE I
Fractionation of Cupressus Oil

FRACTION	B.P./10 MM., °C	n_D^{25}	d_4^{25}	$[\alpha]_D^{25}$	%
1	<45	1.4640	0.8473	+1.34	31.6
2	45–50	1.4672	.8431	+15.9	19.5
3	50–55	1.4712	.8373	+17.0	8.0
4	55–65	1.4757	.8459	+4.35	17.4
5	65–90	1.4770	.9228	+17.7	10.7
6	Residue	Solidified on cooling			9.1
	Loss				3.7
					100.0

TABLE II

FRACTION	B.P., °C	MM.	n_D^{25}	$[\alpha]_D^{25}$	d_4^{25}	WEIGHT, G.	FRACTION, %	CUMULATIVE, %
1	152–154	757	1.4612–1.4622	−19.64	0.8461	25.5	4.15	4.15
2	154–155.5	757	1.4622–1.4623	−14.57	0.8484	113	18.4	22.6
3	155.5	757	1.4623–1.4630	−7.29		49.1	7.9	30.5
4	155.5–156	743	1.4630–1.4639	−5.15		41.4	6.75	37.3
5	156–157	743	1.4639–1.4640	+4.54		45.2	7.36	44.7
6	157–157.5	743	1.4640–1.4651	+19.41	0.8457	24.4	3.98	48.6
7	157.5–163	743	1.4651–1.4675	+30.02	0.8420	29.7	4.85	53.5
8	163–164	743	1.4675–1.4680	+36.46	0.8366	37.4	6.10	59.4
9	164	743	1.4680–1.4688	+35.96	0.8373	13.3	2.16	61.8
10	164–167	749	1.4688–1.4720	+30.03	0.8360	35.9	5.85	67.5
11	167	749	1.4720–1.4722	+19.68	0.8332	11.3	1.84	69.4
12	167–170	749	1.4722–1.4735	+16.33	0.8352	22.2	3.54	73.0
13	170–174	754	1.4735–1.4748	+10.02	0.8381	29.9	4.87	77.9
14	174–176	754	1.4748–1.4755	+8.34		13.2	2.16	80.0
15	176–177	754	1.4755–1.4761	+4.68	0.8439	55.5	9.05	89.0
16	55–57	10	1.4761–1.4768	+1.41		37.6	6.10	95.1
17	58	10	1.4768–1.4778	+0.62		15.2	2.48	97.5
18	58	10	1.4778–1.4808	+0.26	0.8513	13.9	2.26	100
19	Residue		Red gummy mass					

The larger fraction 2 consisted mainly of a mixture of *dl*- and *l*-α-pinene, since it yielded the inactive nitrosochloride and *dl*-pinonic acid on oxidation with permanganate.

The constants of fraction 8 suggested the presence of sabinene, confirmed by oxidation with alkaline permanganate to the insoluble sodium sabinenate and hence to the free acid. Ozonization yielded sabina ketone, which was converted to an apparent mixture of isomeric dinitrophenylhydrazones, which could not, however, be conveniently separated into the pure optical isomerides. No trace of β-pinene could be detected in this or other fractions.

A minimum in the density curve indicated the presence of some acyclic terpene in fraction 10. Treatment with maleic anhydride furnished a mixture of adducts of myrcene and α-terpinene, separated by crystallization of their related potassium salts and the corresponding acids. The presence of α-terpinene in this case, is due probably to isomerization of sabinene under the conditions of the experiment, since there was no other evidence for its occurrence.

Treatment of fraction 15 with hydrogen chloride in glacial acetic acid furnished terpinene dihydrochloride, which might be derived from a number of terpenes, including the terpinenes, sabinene, thujene, and possibly the phellandrenes. The presence of α-phellandrene was confirmed by the preparation of the nitrosite (yield $< 1\%$) while the same fraction furnished the nitrosochloride (yield $< 5\%$) and the related nitrolpiperidide of γ-terpinene. *p*-Cymene was shown to be definitely absent, since the fraction was completely oxidized with very dilute permanganate. From the small yield of derivatives from this fraction it would appear that other terpenes besides α-phellandrene and γ-terpinene are also present, but neither a solid bromide nor a nitrosate could be isolated.

Oxidation of the highest-boiling terpene fraction 18 with dilute permanganate confirmed the presence of both γ-terpinene and terpinolene through the isolation of the corresponding erythritols, m.p. 236–237° and m.p. 149–150° respectively. Bromination with two moles of bromine yielded terpinolene tetrabromide, m.p. 117°, confirmed by mixed melting point with an authentic specimen, while with one mole, terpinolene dibromide, m.p. 69°, was formed. The presence of terpinolene is therefore definitely established and this is possibly the first authentic record of terpinolene existing in a naturally occurring oil. Clover (5) reported the presence of terpinolene in the oils distilled from two samples of resin from *Canarium luzonicum* but nineteen other samples of resin from different trees gave oils which contained no terpinolene. Bacon (6), however, examined over one hundred specimens but found no trace of terpinolene. The abstract of Clover's paper does not give the evidence for the identification of terpinolene. The occurrence of terpinolene in the oil of coriander (7) is listed in the abstract with a question mark. Escourrou (8) claimed to have proved as a result of experiments on the oxidation by ozone of limonene from oil of sweet oranges, that even the purest limonene is always a mixture of limonene, terpinolene, and α-terpinene. If Escourrou's claim is correct then the occurrence of terpinolene in essential oils would be as widespread as that of limonene (dipentene), which is second only to α-pinene in number of source species. The presence of terpinolene in Escourrou's limonene was not shown by the formation of derivatives, and the possibility of isomerization under the experimental conditions employed must be considered. However, in this oil terpinolene has been isolated and identified in the usual way and although attempts have been made to detect limonene, these have been fruitless.

The combined fractions, b.p. 65–90°/10 mm., after repeated fractionation gave a forerun of higher-boiling terpenes and a last fraction of sesquiterpenes but the bulk of the material passed over at 83–87°/10 mm. with practically no change of physical constants. The identity of this constituent was confirmed as *d*-terpinen-4-ol by oxidation with permanganate to the corresponding glycerol, hydration by means of dilute sulfuric acid to terpinene-terpin, and the formation of the corresponding naphthylurethan.

Since sabinene can be hydrated to terpinen-4-ol, this process also probably occurs in the plant, as sabinene is found in all the oils in which the alcohol occurs.[1] Simonsen (9) draws attention to the fact that 1,4-cineole also occurs where both sabinene and terpinen-4-ol are present in the same oil. 1,4-Cineole could not be detected, however, in this oil; if present, it would have revealed itself by its high density and low refractive index in the appropriate boiling fraction and by its characteristic odor.

The fractions boiling above 90°/10 mm., including all those from the refractionations, were united and separated into two main fractions, (a) b.p. $<$ 115°/5 mm. and (b) b.p. $>$ 115°/5 mm. The first fraction was refractionated at 10 mm. and from the curves derived from the physical constants the presence of at least five constituents was indicated but so far none of these have been identified.

The specific refraction, and the evolution of hydrogen with sodium, indicated the presence of an unsaturated monocyclic alcohol in the first fraction, b.p. *ca.* 100°/10 mm., which is apparently tertiary, since it does not form a naphthylurethan but is readily dehydrated. No solid phthalic ester could be formed, and the action of 5% sulfuric acid yielded no solid hydrated product.

The second fraction, b.p. *ca.* 110°/10 mm., had an ester value of 40.2, indicating the presence of about 15% of ester (as $C_{10}H_{15}OCOCH_3$). This corresponded to about one gram of ester in the fraction, and no attempt has been made to identify it.

The next three small fractions, b.p. 115–117°/10 mm., b.p. 120–121°/10 mm., b.p. 124–127°/10 mm., respectively, had physical constants agreeing with dicyclic sesquiterpenes and each gave a different color reaction with bromine in chloroform solution. Although dicyclic, however, the first and last fractions failed to yield a naphthalene or azulene hydrocarbon on treatment with palladized charcoal. The first fraction yielded no solid hydrochloride, and the third fraction also did not give a solid hydrochloride, nitrosochloride, nitrosite, or nitrosate. There was insufficient of the second fraction for examination. Although no solid derivatives have been obtained from these sesquiterpene fractions the physical constants approximate most closely those of the caryophyllenes.

A crystalline solid separated from the next higher-boiling fraction, b.p. 130–150°/5 mm., which when purified had the m.p. 108°, $[\alpha]_D^{25}$ +25.4°. This we believe to be a new saturated tricyclic sesquiterpene alcohol, $C_{15}H_{25}OH$, for

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[1] Sfiras (3), however, did not isolate salinen from the oil of *C. lusitanica* but reported the presence of terpinen-4-ol.

which we suggest the name macrocarpol. It was characterized as its naphthylurethan, m.p. 88–91°, purified with difficulty, and as a readily purified 3,5-dinitrobenzoyl ester, m.p. 157–158°. The alcohol did not react with chromic acid, nor did it form a chromate under conditions described by Wienhaus (10); it gave no coloration with tetranitromethane and was recovered unchanged after attempted hydrogenation with a platinum oxide catalyst. The melting point and rotation are both higher than those of the isomeric alcohols, ledol, m.p. 105°, $[\alpha]_D$ +7.98° (chromate, m.p. 92°) (11) and maalyl alcohol, m.p. 105°, $[\alpha]_D$ +18.33° (chromate, m.p. 111°) (12), and the crystalline form is also significantly different.

All the higher-boiling fractions from all the distillations deposited a crystalline solid on cooling, which proved to be almost entirely the diterpene, isophyllocladene, m.p. 112°, $[\alpha]_D^{25}$ +23.7° (in chloroform), identified by mixed melting point with an authentic specimen, and by the preparation of the hydrochloride, m.p. 106–107°, and dibromide, m.p. 133–133.5°. Isophyllocladene is not produced from phyllocladene in the course of distillation and isolation, since it could readily be isolated from the oil obtained in a pilot experiment after the more volatile constituents had been allowed to evaporate off, and it was also deposited in the condenser towards the end of the steam distillation. This is the first record of the occurrence of isophyllocladene in essential oils but the unidentified diterpene (13) from *Sciadopitys verticillata*, m.p. 111–112°, $[\alpha]_D$ −24.5°, (hydrochloride, m.p. 105–107°, dihydro derivative, m.p. 71–72°) is almost undoubtedly the levo form of isophyllocladene. It is possible too, that the diterpene, mirene, from *Podocarpus ferrugineus* (14), m.p. 105°, $[\alpha]_D$ −27.15° (hydrochloride, m.p. 97–98°, dihydro derivative, m.p. 73–74°) is also the levo modification of isophyllocladene. The *d* form also occurs with phyllocladene in the leaf-oil from *Phyllocladus trichomanoides* (unpublished results).

Systematic fractionation of the liquid diterpene fraction and crystallization of the solids separating furnished more isophyllocladene and a new diterpene, $C_{20}H_{32}$, m.p. 74–75°, $[\alpha]_D^{25}$ +59.2° (in chloroform), for which the name cupressene is suggested. Cupressene is more soluble in methyl and ethyl alcohol than isophyllocladene; it is tricyclic with two double bonds, forming a tetrahydro derivative, m.p. 56–57.5°, a hydrochloride, m.p. 80–85°, and is unchanged after boiling with either alcoholic sulfuric or alcoholic hydrochloric acid. The only product isolated from an attempted dehydrogenation with palladium charcoal was isophyllocladene in 30% yield. The isophyllocladene may have been formed by the action of the catalyst on cupressene but on the other hand it is quite conceivable that the isophyllocladene was present as an original impurity, for although the sample of cupressene used in this experiment had the m.p. 73–74°, the presence of isophyllocladene (or phyllocladene) causes practically no depression on the melting point of cupressene. There was insufficient material for the experiment to be repeated on an analytically pure specimen.

The small amount of liquid diterpene fraction remaining had $[\alpha]_D^{25}$ +25.7°. Experiments on the constitution of isophyllocladene are in active progress.

EXPERIMENTAL

The leaves and terminal branchlets of *Cupressus macrocarpa* growing in Auckland and collected during July were steam distilled in the usual way in three batches, the yield being 0.20% one day after cutting and 0.18% after two days.

The physical and chemical constants already recorded were determined by the standard methods. Four systematic refractionations were carried out, the fractionating column consisting of a 30-cm. jacketed Widmer column with a 10:1 reflux ratio, the pressure being maintained constant with an electrically controlled manostat. The results of the final fractionation of the constituents boiling below 65°/10 mm. are recorded in Table II.

α-Pinene. The nitrosochloride, m.p. 107°, was prepared from fraction 2 by Wallach's method (15) in 9% yield, undepressed by an authentic specimen, m.p. 110°. A liquid acid, b.p. 155–161°/5 mm., was obtained in 38% yield on oxidation with dilute permanganate according to Delépine (16), which deposited crystals of *dl*-pinonic acid on cooling, and after recrystallization from benzene had the m.p. 104–105° (*dl*-pinonic acid has the m.p. 103–104°). The low yields of these products and the low density of this fraction indicate the presence of another constituent.

Sabinene. The yield of sodium sabinenate (4.4 g. from 5 g. of sabinene) obtained by oxidation of fraction 8 with alkaline permanganate according to Short and Read (17) suggests a sabinene content in this fraction of 55%. Only the active acid, m.p. 56.5–57°, was isolated after acidification and crystallization from water, but none of the *dl*-acid, m.p. 84–85°. Wallach (18) records the m.p. 57° for the active acid. Ozonization of this fraction gave in 18% yield sabina ketone, b.p. 85–87°/10 mm., d_4^{25} 0.9472, n_D^{25} 1.4611, $[\alpha]_D^{23}$ −2.4°, which furnished a mixture of dinitrophenylhydrazones, separated from chloroform-methyl alcohol into two fractions, (a) m.p. 98–101°, and (b) m.p. 116–117°. Short and Read give 124.5° as the melting point of the pure derivative, but when the compound is derived from less pure ketone the melting point is markedly lower. The low rotation of the above ketone indicates that it is far from being optically pure.

Myrcene and α-terpinene. Ten grams of fraction 10 and freshly sublimed maleic anhydride (2 g.) were heated at 100° for 0.5 hour. Distillation at 10 mm. removed the terpenes and excess of maleic anhydride, followed by a mixture of adducts, b.p. 170–177°/5 mm., yield 4.24 g., forming a greasy solid on cooling, m.p. 25–28°. Saponification gave a mixture of potassium salts, one comparatively insoluble and the other freely soluble in water. The latter, after acidification followed by repeated crystallization from acetone-water and acetonitrile, furnished the pure acid, m.p. 123–124°, derived from the myrcene adduct, melting point undepressed by an authentic specimen. Diels and Alder (19) record the m.p. 122–123° for this acid.

The above insoluble potassium salt was twice recrystallized, and on acidification gave the free acid, m.p. 134.5–135°. Goodway and West (20) and Sfiras (21) record melting points of 134° and 131° respectively from the acid derived from the maleic anhydride adduct of α-terpinene, but Diels, Koch, and Frost (22) record the m.p. 158° for apparently the same compound. Repeated crystallization of the acid from acetonitrile raised the melting point to 141.5–143.5° but when heated at 130°/2 mm. for 1.5 hours it partly sublimed to a solid of m.p. *ca.* 60° and then had the m.p. 147–148°. Treatment of this product with acetyl chloride gave the anhydride, b.p. 155–165°/5 mm., which after repeated crystallization from light petroleum (b.p. 80–100°) had the m.p. 61–62°, unchanged by further recrystallization. Goodway and West (20), Sfiras (21), and Diels, Koch, and Frost (22) record melting points of 62°, 65–66°, and 66–67° respectively for this anhydride. Goodway and West were unable to raise the melting point of the anhydride above 62° and that of the acid above 134°. Although we cannot duplicate the high melting points of Diels, Koch, and Frost we have reconverted the above anhydride, m.p. 61–62°, into the acid of m.p. 135–140°, again raised after drying over phosphorus pentoxide at 100°/vac. to 147–148° with gas evolution.

α-Phellandrene and γ-terpinene. Fraction 15 (2 g.) when treated with dry hydrogen chloride in cooled glacial acetic acid gave a crystalline solid (yield 180 mg.) which after repeated crystallization from chloroform-methyl alcohol had the m.p. 51.5–52°. Wallach (23) records the m.p. 51–52° for terpinene dihydrochloride. The nitrosite prepared from this fraction (5 g.) in the usual way (yield 50 mg.) after repeated crystallization from chloroform-methyl alcohol and acetone had the m.p. 110–111°, undepressed by an authentic mixture of the α- and β-nitrosites of α-phelandrene, m.p. 110.5–111.5°. There was insufficient material to separate into the pure α- and β- forms, which exhibit marked mutarotation (24).

The same fraction gave a nitrosochloride in $<5\%$ yield, which after repeated crystallization from chloroform-methyl alcohol had the m.p. 108–109°, and the related nitrolpiperidide after crystallization from alcohol had the m.p. 148–149°. Richter and Wolff (25) record the m.p. 111° and m.p. 149° for these derivatives respectively for γ-terpinene.

γ-Terpinene and terpinolene. Fraction 18 (4.3 g.) was mixed with an ice-cold solution (400 cc.) of potassium permanganate (3.25 g.) and potassium hydroxide (1 g.) and shaken mechanically for one hour, and allowed to stand for two days. One and one-tenth grams of unchanged oil was separated and reoxidized separately as above. The combined filtrates were evaporated to dryness and extracted with alcohol. On concentration of this extract, γ-terpinene erythritol separated, which after repeated crystallization from aqueous alcohol melted at 236–237°. Wallach (23) records the m.p. 235–236° for this derivative.

The alcoholic mother liquors from the original extract were evaporated to dryness, the residue dissolved in water, and then repeatedly extracted with ethyl acetate. On concentration, terpinolene erythritol separated, and after repeated crystallization from ethyl acetate-ether had the m.p. 149–150°. Wallach (26) records 148–150° for this derivative.

Fraction 18 (0.85 g.) was dissolved in a mixture of amyl alcohol (1 cc.) and ether (2 cc.) and cooled in a freezing mixture. A cooled solution of bromine (2 g.) in ether (2 cc.) was slowly added. On removal of the ether a light yellow solid separated (0.95 g.), which after repeated crystallization from chloroform-methyl alcohol had the m.p. 116.5–117.5°, undepressed by an authentic specimen of terpinolene tetrabromide similarly prepared from terpinolene derived from terpineol by dehydration (27). Wallach (28) and Henry and Paget (29) record the m.p. 116° and m.p. 119° respectively for this derivative.

In a similar experiment using one gram of bromine, long needles of terpinolene dibromide separated (380 mg.), which after many crystallizations from chloroform-methyl alcohol and from acetone melted at 69°. Baeyer (27) records the m.p. 69–70° for the dibromide.

d-*Terpinen-4-ol.* By refractionation of the combined fractions, b.p. 65–90°/10 mm., an almost pure fraction was obtained, b.p. 86–87°/10 mm., d_4^{25} 0.9285, n_D^{25} 1.4765, $[\alpha]_D^{25}$ +21.36° corresponding to *d*-terpinen-4-ol which has the b.p. 92.5–94°/10 mm., d^{19} 0.9265, n_D^{19} 1.4785, $[\alpha]_D$ + 25.2° (30). Oxidation of this fraction with permanganate according to Wallach (30) gave *p*-menthane-1,2,4-triol hydrate, which after crystallization from ethyl acetate and then from chloroform melted at 112–113°. After heating at 100° for 24 hours the anhydrous compound was obtained of m.p. 128–129°. Wallach records 114–116° and 128–129° respectively for these derivatives. Hydration of this fraction with 5.5% sulfuric acid according to Wallach (31) gave terpinene-terpin, crystallizing from hot water in colorless crystals, m.p. 137.5–138.5° (lit. m.p. 137–138°).

The naphthylurethan prepared in the usual way was crystallized repeatedly from methyl alcohol and then had the m.p. 107–108°. Penfold (30) records m.p. 104–105° for this compound.

Terpene alcohol, terpene ester, and sesquiterpene fraction. The material boiling above 90°/10 mm. was separated into two major fractions, (a) b.p. below 115°/5 mm., and (b) b.p. above 115°/5 mm. The first portion was again fractionated, the physical constants indicating the presence of five constituents as in Table III.

Fraction A1 did not give a precipitate with Brady's reagent but liberated hydrogen on the addition of sodium, indicating the presence of an alcohol. When an attempt was made to prepare the naphthylurethan, dinaphthylurea was the only solid product which could be isolated. Similar attempts to form the phthalic ester and a hydrate with 5% sulfuric acid yielded no solid product. Calculation of the molecular refraction on a basis of formulas $C_{10}H_{16}O$ and $C_{10}H_{18}O$ indicated that it was a monocyclic alcohol with two or one double bonds respectively.

The second fraction A2 contained a small quantity of ester as already described.

The three sesquiterpene fractions gave pale green, reddish-brown, and deep blue colorations respectively with bromine in chloroform solution.

No aromatic nor azulene hydrocarbon could be obtained from the sesquiterpene fractions A3 or A5 using a palladized charcoal catalyst capable of yielding 520 mg. of cadalene from one gram of authentic cadinene (32).

In order to investigate the use of chloranil as a dehydrogenating agent in the sesquiterpene field, cadinene was treated as described by Arnold and Collins (33), but a yield of only 750 mg. of cadalene could be obtained from 2.7 g. of cadinene.

TABLE III

FRACTION	B.P./10 MM., °C	d_4^{25}	n_D^{25}	$[\alpha]_D^{25}$	$[R_L]_D$	YIELD, G.
A1	91–106	0.9149	1.4770	+6.62		10.6
A2	106–115	0.9028	1.4820	+4.86		7.0
A3	115–117	0.8965	1.4935	+7.34	66.4	6.9
A4	120–121		1.5020			1.7
A5	124–127	0.9031	1.5015	+16.83	66.6	2.4

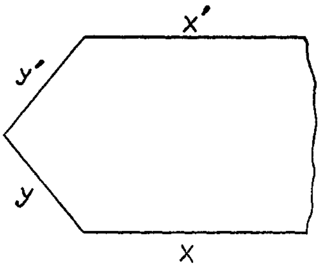
Macrocarpol. Refractionation of the second major fraction, b.p. above 115°/5 mm., gave a fraction of b.p. 130–150°/5 mm., which deposited a crystalline solid on cooling. Repeated crystallization from aqueous alcohol or light petroleum (b.p. 60–70°) furnished tabular crystals, m.p. 108°, $[\alpha]_D^{25}$ +25.4° ($l = 1, c = 5.24$ in alcohol). Yield *ca.* 0.5 gram.

Anal. Calc'd for $C_{15}H_{26}O$: C, 80.97; H, 11.79.

Found: C, 80.82, 80.95, 80.72; H, 11.55, 11.65, 11.49.

Molecular weight (Rast) 223, $C_{15}H_{26}O$ requires 222.

The optic axial angle of the crystals (2v) = 30° ± 1°, with the optic sign negative. The crystals are tabular in habit, bounded by edges having the following supplementary angles of intersection as seen under the microscope



x to y = x' to y' = 50.5° ± 1
y to y' = 79° ± 1

The compound is freely soluble in the common solvents with the exception of water and light petroleum.

The naphthylurethan prepared from 250 mg. separated as a gummy solid and could only be purified with difficulty from light petroleum as crystals of m.p. 88–91°.

The 3,5-dinitrobenzoyl ester prepared in the usual way from 140 mg. readily crystallized from alcohol and after repeated crystallization formed colorless needles, m.p. 157–158°.

Anal. Calc'd for $C_{22}H_{28}N_2O_6$: C, 63.42; H, 6.78.
Found: C, 63.60; H, 6.63.

Isophyllocladene. The fraction boiling above 150°/5 mm. deposited a considerable quantity of crystalline material, which after repeated crystallization from methyl and ethyl alcohol formed needles several centimeters long, m.p. 112°, $[\alpha]_D^{25}$ +23.7° (l = 1, c = 7.596 in chloroform). The melting point was not depressed by an authentic specimen formed by the isomerization of phyllocladene with alcoholic sulfuric acid (34).

The crystals are probably orthorhombic and prismatic or acicular in habit, elongated parallel to *c*. Interfacial angles, measured in the prism pinacoid cone only gave the following values (± 5′)

110 to 1 $\bar{1}$ 0 = 87° 42′
110 to 0 1 0 = 46° 9′

Optical properties: Optic axial angle (2v) = 18° ± 4°
Optic sign positive with β parallel to *c*.

The hydrochloride was prepared according to Uota (35), and after two crystallizations from ether-methyl alcohol had the m.p. 106–107°, undepressed by an authentic specimen.

The dibromide crystallized from alcohol in needles, m.p. 133–133.5°. Uota records 133–134°.

Cupressene. Systematic fractionation of the final diterpene liquid fractions, and crystallization of the solids separating on standing yielded more isophyllocladene and a further diterpene, m.p. 74–75°, separated from isophyllocladene by its greater solubility in methyl and ethyl alcohol (yield < 1 gram). $[\alpha]_D^{25}$ +59.2° (l = 1, c = 1.908 in chloroform).

Anal. Calc'd for $C_{20}H_{32}$: C, 88.24; H, 11.76.
Found: C, 88.14; H, 11.66.
Molecular weight (Rast) 309, $C_{20}H_{32}$ requires 272.

It gives a yellow coloration with tetranitromethane in chloroform solution.

Tetrahydrocupressene. Cupressene (180 mg.) was hydrogenated in glacial acetic acid at 45 lb. pressure for 20 hours in the presence of Adams' catalyst (30 mg.). Most of the acetic acid was removed by distillation *in vacuo*, the tetrahydro derivative being then precipitated by addition of water, crystallizing from alcohol in plates and needles. When crystallized from chloroform-methyl alcohol it formed plates, m.p. 56–57.5°, while from the mother liquors on standing, needles separated of approximately the same melting point; $[\alpha]_D^{17}$ (micro-tube) +62° (l = 1, c = 6.58 in chloroform).

Anal. Calc'd for $C_{20}H_{36}$: C, 86.96; H, 13.04.
Found: C, 86.93; H, 13.00.

The melting point was depressed on admixture with authentic β-dihydrophyllocladene (34) of m.p. 57–58°, $[\alpha]_D^{25}$ +12.5°.

Cupressene hydrochloride. Dry hydrogen chloride was passed through a solution of cupressene in ether in a freezing mixture. The solid product formed after the removal of ether was repeatedly crystallized from alcohol-ether and then had the m.p. 80–82°. The only analytical sample was unfortunately lost in the censoring of the mail.

A mixture of cupressene, m.p. 73–74°, (500 mg.) and active palladized charcoal (50 mg.) was heated in a stream of nitrogen at 270–280° for 3.5 hours. The catalyst was filtered off after dilution with ether, and the product after removal of the ether crystallized from ethyl acetate in needles, m.p. 98–100° (yield 150 mg.). Repeated crystallization from ethyl acetate raised the melting point to 107–108°, undepressed by an authentic specimen of isophyllocladene; $[\alpha]_D^{25}$ +25° (l = 1, c = 0.781 in chloroform).

Anal. Calc'd for $C_{20}H_{32}$: C, 88.24; H, 11.76.
Found: C, 88.10; H, 11.82.

The isophyllocladene was also confirmed by the preparation of α-dihydrophyllocladene (34), m.p. 73°, undepressed by an authentic specimen.

All melting points are uncorrected. The analyses are by Dr. Burger.

We are greatly indebted to Dr. F. J. Turner, Otago University, for the crystal measurements, to the Chemical Society and the Australian and New Zealand Association for the Advancement of Science for grants, and one of us (M. D. S.) for a National Research Scholarship.

SUMMARY

The essential oil from the leaves of *Cupressus macrocarpa* has been shown to consist of the following constituents expressed in approximate percentages:

1. Terpenes: α-pinene, 40%; sabinene, 15%; myrcene, 3%; α-phellandrene, 4%; α-terpinene (?)—; γ-terpinene and terpinolene, 6%; unidentified terpenes, 12%.
2. Sesquiterpenes: (a) unidentified sesquiterpene, b.p. 115–117°/10 mm., (b) b.p. 120–121°/10 mm., (c) 124–127°/10 mm., 0.7%.
3. Diterpenes: isophyllocladene, 3.5%; cupressene, 0.1%.
4. Alcohols: *d*-terpinen-4-ol, 8.8%; unidentified alcohol, b.p. *ca.* 100°/10 mm., 0.8%, macrocarpol, 0.1%.
5. Ester: unidentified ester, b.p. *ca.* 110°/10 mm., 0.5%.
6. Acids, aldehydes, ketones: traces.
7. Other compounds, including residue: 5.5%. Total, 100%.

Macrocarpol is probably a new sesquiterpene alcohol, $C_{15}H_{26}O$, m.p. 108°, while cupressene is a new diterpene, m.p. 74–75°. This is the first record of isophyllocladene and possibly terpinolene in essential oils.

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