

THE ESSENTIAL OIL OF *PHYLLOCLADUS TRICHOMANOIDES*

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Received May 6, 1941

The genus *Phyllocladus* is a small one of six species, three being endemic to New Zealand, one to Tasmania, another to Borneo, while the final species is distributed in New Guinea and the Philippine Islands. The Tasmanian species, *P. rhomboidalis*, contains an essential oil shown by Baker and Smith (1) to contain *l*- α -pinene, an unidentified sesquiterpene and the diterpene, phyllocladene. A small specimen of the winter oil of *P. alpinus* appeared to be mainly phyllocladene (Briggs, 2) but a larger sample examined by Brandt (3) contained unidentified terpene and sesquiterpene constituents in addition.

An examination of the winter and summer essential oils of *P. trichomanoides* has now been made, six constituents being isolated from the winter oil, while seven constituents have been identified from the summer oil, which contains other unidentified compounds in small amount. The work was commenced in 1937 but through various circumstances had to be discontinued for some years with consequent loss of material because fractions for later examination had to be repeatedly distilled to free them from oxidized or polymerized products.

Samples of oil collected at various times of the year showed some variation of the physical constants, a variation which was more marked in a detailed study of the constituents of the winter and summer oils.

The winter oil, obtained in 0.20% yield, had d_{16}^25 0.9031, n_D^{25} 1.4855, $[\alpha]_D^{25}$ +16.29°; the acid and saponification number and the saponification number after acetylation showed the presence of only traces of acids, esters or alcohols while aldehydes and phenols were absent. The oil was repeatedly fractionated with a Widmer column, the hydrocarbon fractions over sodium-potassium alloy, the terpene section at atmospheric pressure, and the higher fractions *in vacuo*. The results of the main fractionation are recorded in Table I.

α -Pinene and dipentene were identified through known derivatives while two sesquiterpene fractions were obtained neither of which was identified. One, b.p. 110–114°/10 mm., d_{25}^25 0.9189, n_D^{25} 1.4928, $[\alpha]_D^{25}$ +20.0°, $[R_L]_D^{25}$ 64.69, gave a crystalline nitrosite, m.p. 92.5–94°, not recorded from any other sesquiterpene, and cadalene on dehydrogenation. These facts, and its physical constants, suggest that it is a new tricyclic sesquiterpene, from which ozonization failed to yield any well characterized product. This constituent does not appear to be present in the summer oil; $[\alpha]_D^{25}$ +5.66°.

The second sesquiterpene, b.p. 122–127°/10 mm., d_{25}^25 0.9158, n_D^{25} 1.5038, $[R_L]_D^{25}$ 65.89, has physical constants of a dicyclic sesquiterpene, possibly identical with calamene for which the following constants are recorded: b.p. 123–126°/10.5 mm., d_{19}^{20} 0.9224, n_D^{20} 1.50572 (4). Like calamene it affords cadalene on dehydrogenation with palladized charcoal but, on the other hand, cadinene dihydrochloride by the action of hydrogen chloride, a derivative not obtained from

calamene. It may, however, be an impure cadinene which was definitely identified from the summer oil (*q. v.*). Ozonization failed to yield any well characterized product.

Crystals separated from the last high-boiling fractions on long standing, and were shown to be a mixture of the diterpenes, phyllocladene, and isophyllocladene, with a third unknown constituent.

The summer oil obtained in 0.13% yield had d_{25} 0.8876, n_D^{25} 1.4839, $[\alpha]_D^{20}$ +8.48°, acid number 1.1, saponification number 3.7, saponification number after acetylation 9.2. Distillation was carried out at 10 mm. using a Widmer column with a 10:1 reflux ratio for the earlier fractionations, and a Bower and Cooke type

TABLE I
DISTILLATION OF WINTER OIL

FRACTION	B. P., C°	PRESSURE, MM.	n_D^{15}	WEIGHT, G.	FRACTION %
1	154	752	1.4592	7.57	1.9
2	154	"	1.4550-1.4567	70.97	17.7
3	154-155	"	1.4567-1.4570	26.90	6.7
4	155-156	"	1.4570-1.4575	21.29	5.3
5	50	8	1.4625	12.93	3.2
6	50-80	"	1.4772	7.82	2.0
7	80-103	"	1.4870	8.82	2.2
8	103-110	"	1.4874	38.31	9.6
9	110-120	9	1.4913	79.19	19.8
10	120-130	"	1.4977	24.22	6.1
11	130-180	"	1.5054	21.34	5.3
12	180-185	"	1.5109	46.51	11.6
13	ca. 165	3	1.5148	5.73	1.4
14	Residue			14.22	3.6
	Loss			14.18	3.5
				400.00	

column (5) for the later sesquiterpene fractions; the results of the main fractionation are recorded in Table II. Only those fractions were examined whose physical constants indicated reasonable homogeneity.

The constants of fraction A1 corresponded to those of α -pinene the presence of which was confirmed by oxidation to pinonic acid according to Delépine (6). In agreement with the rotation +17.79°, both the active and *dl* forms were isolated.

Refractionation of A2 and A3 produced further quantities of α -pinene, together with a small fraction, with constants approximating those of myrcene. Treatment of this fraction with maleic anhydride furnished the adduct of myrcene, and the corresponding dicarboxylic acid after saponification, thus establishing its presence.

From the refractionation of A4 and the forerunnings from the redistillation of A5, small fractions of high-boiling terpenes were obtained. Addition of bromine

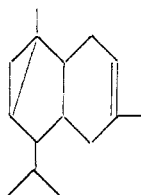
in amyl alcohol-ether to the first of these gave a tetrabromide, m.p. 125.5–126.5°, crystallizing from ethyl acetate in clusters of plates and thus agreeing with γ -terpinene tetrabromide, which has the melting point 128° (7) and crystallizes in the same manner. This was confirmed by the permanganate oxidation of the next fraction, which gave a product, m.p. 235°, which is the m.p. recorded for *p*-menthane-1,2,4,5-tetrol similarly obtained from γ -terpinene (8).

The physical constants of a sesquiterpene obtained by refractionation of A5 agree with those of copaene, whose identity is rigidly confirmed by the following reactions. The hydrogenation value corresponded to the presence of 87% of tricyclic sesquiterpene which gave cadinene dihydrochloride by the action of hydrogen chloride in ether, and cadalene, characterized through the picrate, on

TABLE II
DISTILLATION OF SUMMER OIL

FRACTION	B.P./10 MM., °C	n_D^{25}		d_{25}^4	$[\alpha]_D^{25}$	WEIGHT, G.
		1st Drop	Main Fraction			
A 1	37-39	1.4618	1.4618	0.8506	+17.79	22.9
A 2	39-44	1.4619	1.4629	.8447	+16.59	52.4
A 3	45-49	1.4640	1.4668	.8069	+11.99	10.4
A 4	50-100	1.4702	1.4773	.8875	+18.39	4.0
A 5	100-113	1.4800	1.4882	.9078	-0.99	22.8
A 6	112-120	1.4895	1.4939	.9069	-8.71	16.0
A 7	124-129	1.5008	1.5033	.9220	-2.34	19.0
A 8	131/5 mm.	1.5030	1.5065	very viscous—added to residue		27.0
A 9	Residue	Solidified on standing				27.0
	Loss					1.5
						176.0

dehydrogenation with palladium-charcoal. Oxidation with potassium permanganate afforded copaene ketonic acid, characterized as the semicarbazone, and as the semicarbazone of its methyl ester; the melting points agreed with those recorded by Semmler and Stenzel (9). The copaene from this oil has been used for degradative purposes, and the constitution has now been shown to be (10)



Copaene

The forepart of fraction A6 also consisted mainly of copaene.

From the refractionation of A7 two small dicyclic sesquiterpene fractions were obtained, both of which gave cadinene dihydrochloride by the action of hydrogen

chloride, while cadalene, as the picrate, could also be obtained from the second fraction by dehydrogenation with palladized charcoal. Since both fractions had constants agreeing with those of cadinene, the presence of this constituent is confirmed.

The residue in the main distillation partly solidified on standing. After separation of the solid, the residual oil was repeatedly distilled systematically, filtering off any solid separating on cooling. Finally a fraction was obtained, b.p. 134–137°/5 mm., n_D^{25} 1.5040, d_{25} 0.9674, $[\alpha]_D$ -9.5° in chloroform. The molecular refraction 67.92, agreed with that of a dicyclic sesquiterpene alcohol (calculated for $C_{15}H_{26}O$, $\sqrt{2}$ 68.07). It failed to give a crystalline acid phthalate or 3,5-dinitrobenzoate and is therefore probably tertiary. Hydrogen chloride in acetic acid, but not in dry ether, yielded *l*-cadinene dihydrochloride, undepressed by an authentic specimen, indicating its carbon framework. The constants do not agree well with any of the known cadinols.

The residual solid from the first distillation after repeated crystallization from alcohol and ethyl acetate melted at 94–95°, and its identity with phyllocladene was confirmed by mixed melting point, and isomerization with alcoholic sulfuric acid to isophyllocladene.

Further systematic crystallization of the mother liquors from which phyllocladene separated was carried out using ethyl acetate, and afforded isophyllocladene, m.p. 108–110°, identified by mixed melting point and conversion to α -dihydrophyllocladene. This is the first record of the occurrence of both phyllocladene and isophyllocladene in an essential oil, but this has since been observed also in the oil of *Araucaria excelsa* (11).

Still further investigation of the mother liquors gave 50 mg. of material, m.p. 68–83°, obviously still impure but with $[\alpha]_D$ $+41^\circ$, a higher rotation than either phyllocladene or isophyllocladene, indicating another compound of this range.

Finally, by distillation of the liquid diterpene residues, nearly 5 grams of an apparently homogeneous tetracyclic diterpene was obtained, which failed, however, to give crystalline products on attempted isomerization with alcoholic sulfuric acid, dehydrogenation with palladized charcoal, or oxidation with permanganate.

EXPERIMENTAL

A. The Winter Oil

The leaves and terminal branchlets of *Phyllocladus trichomanoides* growing near Auckland were collected in May and steam distilled the next day in two batches with an average yield of 0.20%.

The physical and chemical constants already enumerated were determined by standard methods. The oil was then systematically fractionated through jacketed Widmer columns with an electrically controlled manostat, the results of the first fractionation being recorded in Table I. The records of the various refractionations are omitted but the details of the relatively homogeneous fractions obtained are included in the following.

α -Pinene. Refractionation of fractions 1–4 failed to yield any component other than α -pinene, the main fraction having b.p. 154–154.5°/765 mm. (from sodium), n_D^{25} 1.4633,

d_{25}^{12} 0.8522, $[\alpha]_D^{12}$ +19.35°. Its identity with α -pinene was proved by preparation of the nitroschloride, m.p. 110–112°, undepressed by an authentic specimen (12), the nitrobenzylamine, m.p. 123–124° (lit. m.p. 122–123°) and the nitrolpiperide, m.p. 118–118.5° (lit. m.p. 118–119°).

Dipentene. Refractionation of fraction 5 gave a small fraction, b.p. 158–162°/766 mm., n_D^{12} 1.4727, which in the light of the results from the summer oil (*q. v.*) could well be myrcene, and a further fraction, b.p. 170–172°, n_D^{12} 1.4770, identified with dipentene by the preparation of the tetrabromide, m.p. 123–124° from ethyl acetate (lit. m.p. 125–126°). The small amount of dipentene probably arises in this case from the α -pinene by isomerization under the influence of heat during the protracted fractionation (13).

Sesquiterpenes. (a) In the subsequent series of fractionations under reduced pressure a sodium-potassium alloy was employed, leading to the almost complete removal of the small amounts of oxygenated constituents. Of the two sesquiterpenes isolated, the first had b.p. 111–112°/10 mm., d_{25} 0.9144, n_D^{25} 1.4912, $[\text{R}_L]_D$ 64.65. After standing for some years this fraction had oxidized considerably but after repeated distillation from sodium and refractionation it showed but slight change in its constants *viz.* b.p. 110–114°/10 mm., d_{25} 0.9189, n_D^{25} 1.4928, $[\alpha]_D$ +20.0°, $[\text{R}_L]_D$ 64.49, indicating a tricyclic sesquiterpene, (calculated for $\text{C}_{15}\text{H}_{24}$ $|\frac{-}{1}$ 64.40).

When bromine vapor was added to a solution of the original fraction in glacial acetic acid a bluish green color was produced passing to greenish blue on standing and disappearing on shaking; on heating it turned to indigo blue. Concentrated sulfuric acid gave a brownish lower layer with a pink-red coloration above.

A crystalline nitrosite could be prepared from the original fraction by passing nitrous fumes (prepared by the action of concentrated sulfuric acid on sodium nitrite) through an ethereal solution of the sesquiterpene cooled in a freezing mixture, the solution first turning blue-green, then dark green, and finally brown. The colorless crystals formed had m.p. 92.5–94°, unchanged by recrystallization from ether. Despite the fact that the same derivative was also prepared in alcohol-acetic acid solution (2:1) to which a little ether was also added to effect homogeneity, it could not be obtained from the later repurified material.

The sesquiterpene did not form a solid hydrochloride or nitroschloride.

A mixture of the sesquiterpene (750 mg.) and palladized charcoal (80 mg.) was boiled for 4 hours. The picrate from the product, after repeated crystallization from absolute alcohol formed orange-red needles, m.p. 114–115°, undepressed by an authentic specimen of cadalene picrate (14).

(b) The second sesquiterpene isolated had b.p. 124–127°/10 mm., d_{25} 0.9149, n_D^{25} 1.5053 $[\text{R}_L]_D$ 66.17. The same fraction purified some years later had b.p. 122–127°/10 mm., d_{25} 0.9158, n_D^{25} 1.5038, $[\alpha]_D^{25}$ +5.6°, $[\text{R}_L]_D$ 65.89, constants with little change and which indicated a bicyclic hydrocarbon (calculated for $\text{C}_{15}\text{H}_{24}$ $|\frac{-}{2}$ 66.14).

The following color reactions were produced in a solution of the oil in glacial acetic acid: concentrated sulfuric acid—crimson; concentrated hydrochloric acid—light crimson; phosphoric acid—madder-rose at the interface; bromine vapor—crimson changing to blue as it passed down the solution.

The sesquiterpene (1.22 g.) was dehydrogenated by heating with palladized charcoal (100 mg.) for 4 hours. Picric acid added to the blue oil on the water-bath formed brown needles, which after recrystallization from alcohol had m.p. 114–116°, undepressed by an authentic sample of cadalene picrate (yield 25%).

When dry hydrogen chloride was passed through an ethereal solution of the sesquiterpene in a freezing mixture, the solution remained colorless for about 10 minutes and then suddenly turned dark red with evolution of excess acid fumes shortly afterwards. After standing in the ice-chest overnight the ether was removed from the reddish-blue oil, which crystallized on addition of glacial acetic acid and cooling. The colorless needles, after recrystallization from alcohol, had m.p. 115–117°, undepressed by *l*-cadinene dihydrochloride (yield 3%) (15).

From the highest-boiling fractions crystals separated on long standing, m.p. 86.5–87.5° after recrystallization from alcohol. Repeated crystallization from alcohol and methyl alcohol raised the melting point to 92°, at which stage the melting point was raised to 93–95° by phyllocladene and to 94.5–104.5° by isophyllocladene. The material of m.p. 92° is thus a mixture of phyllocladene and isophyllocladene [compare the mixed melting point curve for these isomers (Briggs and Taylor, 11) and their isolation from the summer oil]. Since the eutectic of the phyllocladene-isophyllocladene mixture is 90°, the melting point of the original mixture, 86.5–87.5°, indicates admixture with a third unknown solid component. The total quantity, however, was too small for further investigation.

B. The Summer Oil

This was obtained in November from trees of the Waipoua Forest, supplied through courtesy of the State Forest Service to whom we express our sincere thanks. The leaves were steam distilled in the usual way and when the distillation was finished, steam was passed through the empty condenser to remove a small quantity of the diterpene phyllocladene which had crystallized out.

The results of the preliminary distillation carried out with a 50-cm. Widmer column and a 10:1 reflux ratio are recorded in Table II. Later distillations, particularly of the higher fractions, were effected through a three-foot Bower and Cooke type column (5). Only the constants of the relatively homogeneous fractions so obtained are recorded in the following text.

α -Pinene. By refractionation of fractions A1–A3 a main cut was obtained, b.p. 39–39.5°/10 mm., d_{25}^{20} 0.8512, n_D^{20} 1.4621, $[\alpha]_D^{20} + 21.03^\circ$ agreeing with the constants of specially purified α -pinene by Fugitt, Stalleup, and Hawkins (16). Oxidation according to Delépine (6) furnished pinonic acid, b.p. 159°/5 mm., from which the *cis-dl*-acid, m.p. 104–105°, could be obtained by repeated crystallization from benzene. The low-melting product from the mother liquors was converted to the oxime, and the optically active β -form of pinonic acid oxime crystallized from methyl alcohol in needles, m.p. 123–125° (lit. m.p. 128°).

Myrcene. Refractionation of A3 afforded 3.3 g. of an oil having b.p. 40–50°/10mm., d_{25}^{20} 0.8060, n_D^{20} 1.4660, $[\alpha]_D^{20} + 7.76^\circ$. An exothermic reaction occurred on warming a mixture of this fraction (1 g.) with maleic anhydride (1 g.). The distilled product, 0.85 g., b.p. 178°/5 mm., solidified on cooling. The crystals obtained on recrystallization from light petroleum had m.p. 34–35°, with zero rotation. The dicarboxylic acid obtained after saponification was recrystallized from aqueous alcohol and acetonitrile and then melted at 123–123.5°. Diels and Alder (17) record m.ps. of 34–35° and 122–123° for these respective compounds.

γ -Terpinene. This was identified from a fraction, b.p. 58–62.5°/10 mm., d_{25}^{20} 0.8361, n_D^{20} 1.4696, $[\alpha]_D^{20} + 36.0^\circ$, 0.6 g., obtained by refractionation of A4 and the forerunnings from the refractionation of A5. Bromine (1.25 g.) in ethereal solution was added to a solution of the fraction (0.53 g.) in amyl alcohol (0.6 cc.) and ether (1.2 cc.) in a freezing mixture. The crystalline precipitate which formed overnight, after repeated crystallization from ethyl acetate, produced clusters of plates, m.p. 125.5–125.6°. Richter and Wolf (7) record m.p. 128° for γ -terpinene tetrabromide. Dipentene tetrabromide of similar melting point crystallizes from ethyl acetate in needles and considerably depressed the melting point of the above product.

Further evidence for the presence of γ -terpinene was afforded by oxidation of the next fraction, similarly obtained, which had b.p. 63–80°/10 mm., d_{25}^{20} 0.8530, n_D^{20} 1.4796, $[\alpha]_D^{20} + 14.1^\circ$ (0.7 g.). A suspension of this fraction (440 mg.) in an aqueous solution of potassium hydroxide (100 mg. in 50 cc.) was mechanically shaken for three hours, potassium permanganate (680 mg.) being added in four equal portions at half-hourly intervals. The precipitated manganese dioxide was extracted three times with boiling water, the combined filtrates saturated with carbon dioxide and evaporated to dryness. The brown oil so obtained deposited 5 mg. of colorless crystals, m.p. ca. 235°, after standing in aqueous alcoholic solution. Wallach (8) obtained *p*-menthane-1,2,4,5-tetrol, m.p. 237°, from a similar oxidation of γ -terpinene.

Copaene. The main fraction (6.67 g.) obtained on redistillation of A5 had b.p. 112.5–114.5°/10 mm., $d_{25} 0.9061$, $n_D^{25} 1.4877$, $[\alpha]_D^{25} +0.19^\circ$, $[R_L]_D 64.84$. Catalytic hydrogenation on a semi-micro scale using Adams' catalyst and glacial acetic acid as solvent gave the double bond content as 1.13 ± 0.03 indicating a mixture of 87% tricyclic sesquiterpene and 13% dicyclic.

A mixture of this fraction (850 mg.) with palladized charcoal (100 mg.) was boiled under reflux for 9 hours. The crude picrate of the product, prepared in methyl alcohol, was filtered, the hydrocarbon regenerated and then treated with the calculated quantity of picric acid. The picrate, after crystallization from alcohol, had m.p. 114–115°, undepressed by an authentic specimen of cadalene picrate.

Dry hydrogen chloride was passed into an ethereal solution of the same fraction in a freezing mixture. After standing for some days in the refrigerator, two crops of crystals were obtained, (a) m.p. 110–115° (160 mg.), and (b) m.p. 70–75° (250 mg.). The first product, after repeated crystallization from alcohol had $[\alpha]_D -38^\circ \pm 2^\circ$ in chloroform and m.p. 117–117.5°, undepressed by *l*-cadinene dihydrochloride. The second crop after repeated crystallization from methyl alcohol formed plates m.p. 85–86°, but was unfortunately lost before analysis.

A suspension of this fraction (2.04 g.) in ice and water (40 g.) containing potassium permanganate (3.6 g.) and ammonium sulfate (1.55 g.) was shaken mechanically for 2 hours. The manganese dioxide was dissolved by passage of sulfur dioxide and the organic matter extracted with chloroform. Distillation afforded a main fraction, b.p. 155–175°/0.5 mm., 0.9 g., partly soluble in sodium hydroxide solution. Sodium carbonate solution added to its ethereal solution removed the acid (0.5 g.), recovered by acidification. The semicarbazone separated in warty masses on allowing the acid (250 mg.) to react with semicarbazide hydrochloride in dry pyridine overnight. After repeated crystallization from alcohol, clusters of colorless needles separated, m.p. 222°. Semmler and Stenzel (9) record m.p. 221° for the semicarbazone of copaene ketonic acid.

Anal. Calc'd for $C_{16}H_{27}N_3O_3$: C, 62.10; H, 8.80.

Found: C, 62.34; H, 8.70.

The methyl ester was prepared as a pale yellow oil by the interaction of excess diazomethane with the acid (250 mg., dried at 100° over P_2O_5 for 2 hours) in dry ethereal solution. The semicarbazone, as above, separated from aqueous methyl alcohol in needles, m.p. 194–196°, $[\alpha]_D +25^\circ \pm 3^\circ$ ($l = 1$, $c = 0.37$ in methyl alcohol). Semmler and Stenzel (9) found $[\alpha]_D +27^\circ$ for this ester and m.p. 193–194° for its semicarbazone.

Cadinene. Refractionation of the higher-boiling sesquiterpene portions gave two similar fractions, (a) b.p. 128–130°/10 mm., $d_{25} 0.9149$, $n_D^{25} 1.5041$, $[\alpha]_D -15.8^\circ$, 1.11 g., and (b) b.p. 130–131°/10 mm., $d_{25} 0.9170$, $n_D^{25} 1.5058$, $[\alpha]_D -9.4^\circ$, 1.09 g.

The first fraction (580 mg.) in dry ethereal solution was saturated with dry hydrogen chloride in a freezing mixture. The red solution deposited no crystalline material on standing, but the residue, after removal of the ether and acid, crystallized on standing in the refrigerator. Recrystallization from alcohol afforded colorless needles, m.p. 116.5–118°, undepressed by pure *l*-cadinene dihydrochloride. The second fraction yielded the same derivative.

Dehydrogenation of the second fraction (550 mg.) with palladized charcoal in a stream of carbon dioxide yielded cadalene, isolated as its picrate (40 mg.), m.p. 113–115° after crystallization from alcohol; undepressed by an authentic specimen.

Sesquiterpene alcohol. From the final liquid portions of the oil from which the solid diterpenes had separated, repeated fractionation yielded a fairly homogeneous sesquiterpene alcohol, 1.8 g., b.p. 134–137°/5 mm., $d_{25} 0.9674$, $n_D^{25} 1.5040$, $[\alpha]_D -9.5^\circ$ ($l = 1$, $c = 2.21$ in chloroform), $[R_L]_D 67.92$, (calculated for $C_{16}H_{26}O$ $\sqrt{2}$ 68.07).

Dry hydrogen chloride was passed through a solution of the alcohol (200 mg.) in glacial acetic acid kept in a freezing mixture. The crystals separating from the blue liquid, after recrystallization from alcohol, had m.p. 117–118°, undepressed by *l*-cadinene dihydrochloride.

Phyllocladene. The solid residues from fractions A8 and A9, after repeated crystallization from alcohol, had $[\alpha]_D +16.5^\circ$ ($l = 1$, $c = 13.15$ in chloroform) and m.p. 94–95°, undepressed by pure phyllocladene.

The product, after isomerization in alcoholic sulfuric acid, crystallized from ethyl acetate in needles, $[\alpha]_D +23.4^\circ$ ($l = 1$, $c = 2.06$ in chloroform), m.p. 109–111°. Briggs (18) records $[\alpha]_D^{25} +15.8^\circ$ for phyllocladene and $[\alpha]_D +23.4^\circ$ for isophyllocladene.

Isophyllocladene. The solid separating from the phyllocladene mother liquors was repeatedly crystallized from alcohol and ethyl acetate and finally formed needles, $[\alpha]_D +22.2^\circ$ ($l = 1$, $c = 4.06$ in chloroform), m.p. 108–110°, undepressed by pure isophyllocladene (yield ca. 1 g.).

The dihydro derivative, prepared in glacial acetic acid with Adams' catalyst, formed needles (not plates as recorded in the literature) from methyl alcohol, m.p. 72–72.5°, undepressed by pure α -dihydrophyllocladene (18).

Solid diterpene. Still further working up of the solid diterpene mixture afforded small quantities (ca. 50 mg.) of low-melting material, usually with m.p. ca. 70–80°, and with rotations higher than that of either phyllocladene or its isomeride, the highest rotation found being $[\alpha]_D +41^\circ$. Attempted purification by chromatographing on alumina effected only a partial separation. Isomerization of one such fraction with alcoholic sulfuric acid furnished a product, m.p. 108–110° from ethyl acetate, obviously isophyllocladene.

Since the eutectic of phyllocladene and isophyllocladene is 90° (11) the low-melting material must contain a third solid component but the amount available was too small for further investigation.

Liquid diterpene. Final distillation of the liquid diterpene residues yielded 4.96 grams of an apparently homogeneous colorless constituent, b.p. 156–157°/1 mm., d_{25} 0.9640, n_D^{25} 1.5168, $[\alpha]_D +22.6^\circ$, $[\text{R.L}]_D$ 85.36 (calculated for $\text{C}_{20}\text{H}_{32}$ $\left[\frac{1}{T} \right]$ 85.29), from which no solid derivatives could be obtained.

All melting points are uncorrected.

The analyses are by J. Mills, Adelaide University.

We are greatly indebted to W. Wright for assistance with the examination of the winter oil, to the Chemical Society and the Department of Scientific and Industrial Research Council for grants, to the Royal Society of New Zealand for the loan of apparatus and one of us (M.D.S.) for a National Research Scholarship.

SUMMARY

The essential oil from the leaves of *Phyllocladus trichomanoides* has been shown to contain the following constituents. The winter oil: α -pinene, dipentene, a possibly new tricyclic sesquiterpene, a second sesquiterpene (possibly calamene or cadinene), phyllocladene, and isophyllocladene.

The summer oil: α -pinene, myrcene, γ -terpinene, copaene, cadinene, a cadinol, phyllocladene, isophyllocladene, and an unidentified solid and liquid diterpene.

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