High-boiling Constituents of Swedish Sulphate Turpentine (*Pinus silvestris* L.)*, **

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Commercial high-boiling fractions of Swedish sulphate turpentine (mainly derived from *Pinus silvestris* L.) have been investigated. The following compounds were shown to be present (*cf*. Tables 2—4): α-longipinene, copaene, longicyclene, longifolene, β-ylangene, β-copaene, α-, γ-, and ε-muurolene, γ- and δ-cadinene, calamenene, α-calacorene, δ-cadinol, pimaradiene, isopimaradiene, pimarinol, pimarinal, isopimarinal, isoeugenol methyl ether, and a new sesquiterpene alcohol, m.p. 48°.

From the sulphate pulp industry turpentine and tall oil are obtained as by-products. The wood of Scots pine (*Pinus silvestris* L.) is a principal raw material for Swedish sulphate pulp. Varying amounts of spruce wood (*Picea exelsa*) and different hardwoods are pulped together with the pine wood. The main constituents of Swedish sulphate turpentine and tall oil, the monoterpenes and the resin acids, respectively, have been fairly well investigated,[1,2] but little is known about the minor constituents.

Investigations by Bergström [3] showed that Swedish sulphate turpentine and tall oil contained cadinenes and cadinols, as certain fractions on dehydrogenation gave cadalene. Recently, Pentegova and Lebedova [4] reported the isolation of ylangene (*24*), longifolene (*4*), "muurolene", γ-cadinene (*10*) and δ-cadinene (*11*) from Russian tall oil (*Pinus silvestris*).

The present paper describes an investigation of the high-boiling constituents of Swedish sulphate turpentine derived from pine wood (*ca*. 90 %), spruce wood (*ca*. 10 %) and hardwood (a few per cent). Some of the results reported in this paper have been published in three preliminary communications.[5-7]

The turpentine fractions investigated were obtained from the tall oil factory of Marma-Långrör. At this factory the crude turpentine was first distilled to separate monoterpenes from more high-boiling components. The

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latter were then distilled through a column under reduced pressure for the production of so-called "Pinol" mainly consisting of monoterpene alcohols. The highest boiling fractions contained sesquiterpene hydrocarbons. The pot residue consisted of sesquiterpene hydrocarbons and alcohols as well as di-terpenes.

The commercial sesqui- and diterpene fractions were distilled *in vacuo* through a packed column. A carbonyl fraction was obtained by treating the highest boiling fraction with Girard reagent.

The various fractions were analysed by gas-liquid chromatography (GLC) and argentative thin layer chromatography (Ag-TLC). Most of the components, which were detected by these methods, were isolated by further fractional distillation and by mainly alumina and argentative column chromatography.

Table 1. The occurrence of monoterpenes in Swedish sulphate turpentine and in the wood of *Pinus silvestris* (+ = isolated and characterized, × = presence indicated by GLC).

	Extract from wood [1]	Sulphate turpentine Ref. 1	this work *
α-Pinene	×	+	×
Camphene	×	+	×
β-Pinene	×	+	×
Δ^3-Carene	×	+	×
Limonene	×	+	×
p-Cymene	×	+	×
Terpinolene	×	+	×

* Column 1 % Reoplex,[8] temperature 50°.

Table 2. The occurrence of sesquiterpenes in Swedish sulphate turpentine and in the wood of *Pinus silvestris* (+ = isolated and characterized, × = presence indicated by GLC and/or Ag-TLC).

		Extract from wood [8] (*Peridermium* infested)	Sulphate turpentine
α-Longipinene	*(1)*	×	+
Copaene	*(2)*	+	+
Longicyclene	*(3)*	×	+
Longifolene	*(4)*	+	+
β-Ylangene	*(5)*	×	+
β-Copaene	*(6)*	+	+
ε-Muurolene	*(7)*	+	+
γ-Muurolene	*(8)*	+	+
α-Muurolene	*(9)*	+	+
γ-Cadinene	*(10)*	+	+
δ-Cadinene	*(11)*	+	+
Calamenene	*(12)*	×	+
α-Calacorene	*(13)*	×	+
δ-Cadinol	*(14)*	×	+
New sesquiterpene alcohol m.p. 48°		×	+

Table 3. The occurrence of diterpenes in Swedish sulphate turpentine and in the wood of *Pinus silvestris* (+ and × same significance as in Table 2).

		Extract from wood [8] (*Peridermium* infested)	Sulphate turpentine
Pimaradiene	*(15)*	+	+
Isopimaradiene	*(16)*	+	×
Pimarinol	*(17)*	+	×
Isopimarinol	*(18)*	+	
Abietinol	*(19)*	+	
Pimarinal	*(20)*	+	+
Isopimarinal	*(21)*	+	×
Dehydroabietinal	*(22)*	+	
Abietinal	*(23)*	+	

Table 4. Non-terpenoid high-boiling neutral compounds isolated from Swedish sulphate turpentine and from the wood of *Pinus silvestris*.

	Extract from wood [8] (*Peridermium* infested)	Sulphate turpentine
Eugenol methyl ether	+	
Isoeugenol methyl ether		+
Pinosylvin dimethyl ether	+	
β-Sitosterol	+	
Mixture of fatty alcohols	+	

The results are summarized in Tables 2—4. Table 1 shows the occurrence of monoterpenes in crude sulphate turpentine. For comparison the tables include the composition of the high-boiling neutral parts of extracts from Scots pine wood.[8]

As mentioned before, sulphate turpentine not only contains pine wood constituents but also compounds derived from other species. Moreover, the forced conditions of the sulphate cooking process may lead to the formation of artefacts. Hence, it was essential to subject the terpenes from Scots pine wood and from sulphate turpentine to parallel comparative investigations in order to ascertain if compounds isolated from the latter source were true pine wood constituents.

The commercial sulphate turpentine was found to contain many of the neutral pine constituents in an unchanged form (*cf.* Tables 1—4), thus constituting a convenient starting material for isolation of large amounts of the various terpenes when so required.

The terpenes isolated from the high-boiling sulphate turpentine fractions were identified with the pine wood terpenes by GLC and Ag-TLC comparisons. In most cases the compounds were isolated from both sources and the identity was confirmed by comparison of IR spectra and optical rotations.

α-Longipinene (*1*) [24] was isolated from the sulphate turpentine and was shown [8] to occur in the pine wood by GLC (*cf*. Table 2). **The IR and NMR** spectra of α-longipinene were found to be almost identical with those of a sesquiterpene recently isolated from the wood of *Pinus longifolia*.* The hydrocarbons gave the same crystalline ketoacid (*25*) on ozonolysis.

As already mentioned Russian tall oil from *Pinus silvestris* has been reported to contain ylangene (*24*). Copaene (*2*) was not detected. In the present study copaene has been proved to be a constituent of sulphate turpentine from the same species (*cf*. footnote of Table 7). The reason for this discrepancy may be the fact that ylangene has not been well characterized. Thus, it is possible that the hydrocarbon fraction isolated from the Russian tall oil and claimed to be ylangene in fact consisted mainly of copaene.

δ-Cadinene (*11*) is present in larger quantity in the sulphate turpentine than in the wood extracts as shown by GLC and Ag-TLC. Formation of δ-cadinene by isomerization of other cadinenes or of muurolenes is probably a thermodynamically favoured process, which may occur under the drastic conditions of the sulphate cook. The δ-isomer has one tri- and one tetrasubstituted double bond, and could thus be more stable than other cadinenes or than muurolenes having di- and/or trisubstituted double bonds. Thus, some of the δ-cadinene present in sulphate turpentine may probably have been formed from other cadinenes or from muurolenes. It is also possible that a portion of the δ-cadinene occurring in the sulphate turpentine is derived from, *e.g.*, spruce wood.
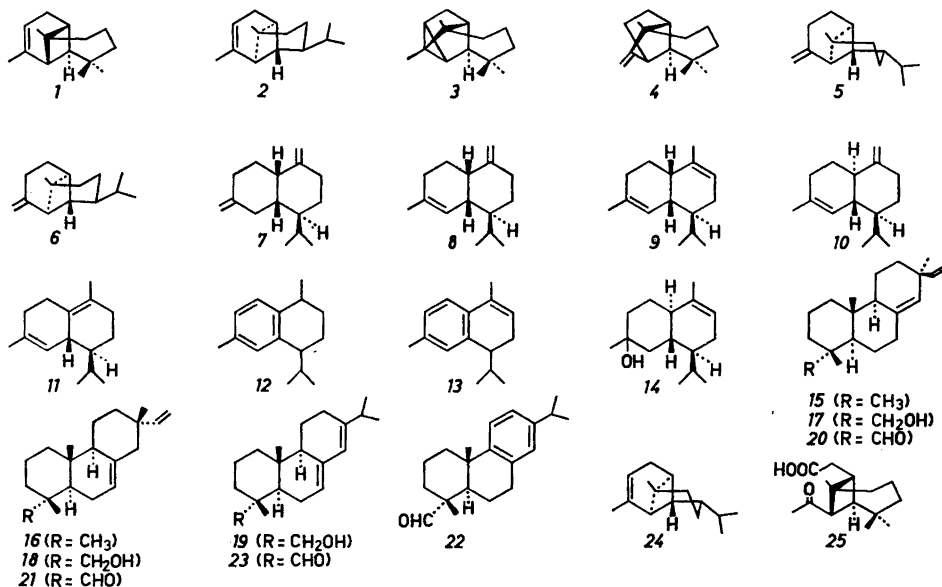
The diterpene hydrocarbon fraction of sulphate turpentine contained more components than the corresponding fractions of the wood extracts. The additional components of sulphate turpentine of course may be derived from spruce wood or some hardwood, but also might have been formed during the pulping process, *e.g.* by decarboxylation of resin acids. Remarkably, the diterpene aldehydes pimarinal and isopimarinal at least partly survived the drastic conditions during the sulphate cook.

Eugenol methyl ether was isolated from the pine wood extract,[8] while isoeugenol methyl ether was obtained from sulphate turpentine. As one could have expected, eugenol methyl ether had undergone isomerization under the alkaline conditions of the sulphate cooking process.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. IR spectra were recorded on a Perkin-Elmer No. 21 instrument (NaCl prism, sample as liquid film, or, for solids, in KBr), UV spectra on a Beckman DK 2 recording spectrophotometer (solvent ethanol) and NMR spectra on a Varian A 60 instrument operating at 60 Mc/s (solvent carbon tetrachloride, internal standard tetramethylsilane). For gas-liquid chromatography (GLC) a PYE argon chromatograph (column length 1.2 m, inner diameter 4 mm) was used.

Identifications of isolated compounds were made by comparison with authentic samples, when applicable, by mixed melting point determinations, by GLC and thin layer chromatography (TLC) and by comparison of IR spectra, UV spectra and optical rotations.

The procedures used to prepare columns for GLC, plates for argentative TLC (Ag-TLC) and adsorbent (Ag-silica) for argentative column chromatography have been described previously.[23]

Rotations were measured in chloroform. Light petroleum refers to the fraction b.p. 40—60°.

The monoterpenes. The composition of the monoterpenes of Swedish sulphate turpentine has been determined by Groth.[1] The present investigation includes a GLC analysis of crude sulphate turpentine, which confirms these results (see Table 1).

The sesqui- and diterpenes. Two high-boiling fractions of Swedish sulphate turpentine obtained from the "pinol-distillation" have been investigated, namely the highest boiling fraction (*A*, b.p. 115—130°/20 mm) and the pot residue (*B*, b.p. above 130°/20 mm).*

Fraction A. Fractional distillation of this fraction (302 g) through a vacuum jacketed packed column at 15 mm gave the following fractions (upper limit of boiling point range given): I, b.p. 107°, 148 g; II, b.p. 118°, 78 g; III, b.p. 125°, 41 g; IV, b.p. 130°, 22 g.

Table 5. Chromatography of fraction II *a* on Ag-silica. Longicyclene and α-longipinene.

Fraction	Volume ml	Weight g
1_5	250	0.05
2_5	170	1.12
3_5	250	0.05
4_5	500	1.74

Table 6. Chromatography of fraction II *c* on Ag-silica. Longicyclene and copaene.

Fraction	Volume ml	Weight g
1_6	300	0.01
2_6	200	0.82
3_6	600	0.24
4_6	1300	5.58

Fraction B. Similar distillation of fraction *B* (360 g) at 10 mm gave the following fractions: V, b.p. 114°, 7.0 g; VI, b.p. 126°, 22.0 g; VII, b.p. 128°, 10.4 g; VIII, b.p. 129°, 27.6 g; IX, b.p. 130°, 41.1 g; X, b.p. 133°, 15.7 g; XI, b.p. 140°, 3.3 g; XII, b.p. 151°, 16.0 g; XIII, b.p. 180°, 57.6 g; XIV, b.p. 190°, 62.0 g; XV, b.p. 200°, 21.5 g.

Investigation of the sesquiterpene hydrocarbon fractions II — XI. Isolation of longicyclene, α-longipinene, and copaene. According to GLC (conditions and retention data see Ref.8) fraction II consisted essentially of two components (ratio about 1:6) the predominating one having slightly larger retention time than the other. The fraction was chromatographed on alumina (basic, activity I, 2000 g) using light petroleum (4500 ml) as eluent to give a colourless oil (36 g).

Fractional distillation at 10 mm of this hydrocarbon fraction using a spinning band column resulted in partial separation of the components. The first fractions were combined to give a sample (fraction II *a*, 6.8 g) in which the ratio between the two components was about 4:3. The next fractions when combined (fraction II *b*, 12.2 g) showed approximately the same gas chromatogram as fraction II. As judged from GLC the last fractions contained the main component of fraction II in an almost pure state (combined to fraction II *c*, 8.0 g).

Table 7. Physical constants of longicyclene, α-longipinene and copaene.

Fraction	Compound	$[\alpha]_D°$	n_D^{22}	d_4^{22}	M_D*
2_5 (Table 5)	Longicyclene	+28.0 (*c* 2.2)	1.4880	0.9288	63.37
2_6 (Table 6)	»				
4_5 (Table 5)	α-Longipinene	+36.9 (*c* 2.2)	1.4924	0.9122	65.01
4_6 (Table 6)	Copaene **	+ 7.5 (*c* 2.8)	1.4897	0.9106	64.89

* Calculated values:

$C_{15}H_{24}$ + one cyclopropane ring 63.4

$C_{15}H_{24}$ + one double bond + one cyclobutane ring *ca.* 64.8

** Like copaene, $[\alpha]_D$ −6° [10,21] this sample gave [14] (−)-cadinene dihydrochloride. The positive rotation of fraction 4_6 (Table 6) could be accounted for by assuming that this sample was contaminated by (+)-ylangene, $[\alpha]_D$ +50.5°.[22] The value +7.5° corresponds to a *ca.* 1:3 mixture of (+)-ylangene and (−)-copaene. According to the results of Hunter and Brogden [13] such a high content of ylangene should be revealed by IR spectroscopy (copaene 780, ylangene 790 cm⁻¹) and by GLC.

The IR spectra of copaene (Büchi), ylangene (Motl) and a 1:1 mixture of these hydrocarbons were recorded. The absorption band due to the double bond of copaene appeared at a *higher* frequency (784 cm⁻¹) than the corresponding band of ylangene (779 cm⁻¹). GLC (conditions as in Ref. 13) did not resolve the 1:1 mixture.

The IR and GLC analysis performed does not exclude the possibility that fraction 4_6 (Table 6) contained *ca.* 25 % ylangene as indicated by the optical rotation.

Fractions II a and II c were chromatographed on Ag-silica (250 and 350 g, respectively; eluent light petroleum). The results are shown in Tables 5 and 6.

Longicyclene. Fractions 2_5 (Table 5) and 2_6 (Table 6) were identified as *longicyclene* [9] by their IR bands at 3060 and 840 cm^{-1}, physical constants (see Table 7) and by conversion [9] to longifolene.

α-Longipinene.[24] Fraction 4_5 (Table 5) was found to consist of *α-longipinene.* The physical constants are given in Table 7. (Found: C 88.0; H 11.6. $C_{15}H_{24}$ requires C 88.2; H 11.8). The IR spectrum showed bands characteristic of trisubstituted double bonds (3000, infl., 1656, 1570, overtone, and 787 cm^{-1}).

Ozonolysis of α-longipinene. The hydrocarbon (0.70 g) in ethyl acetate:methanol (6:1, 10 ml) was treated with ozone at $-80°$ until the solution turned blue. Excess ozone was removed with nitrogen and the solution was allowed to reach room temperature. The ozonide was decomposed by adding zinc dust, pre-activated with acetic acid, (2 g) and boiling under reflux for a few minutes. After cooling, ether (25 ml) and dilute sulphuric acid (1 %, 10 ml) were added, the mixture was filtered and the filtrate was extracted with aqueous sodium hydroxide (10 %, three portions, 10 ml each). Acidification of the combined aqueous phases followed by extraction with ether gave after drying (sodium sulphate) and evaporation the *ketoacid (25)* (0.44 g), which, after recrystallization from light petroleum, b.p. $60-70°$, and sublimation, had m.p. $92-92.5°$, $[\alpha]_D + 16.4°$ (c 0.9), strong IR absorption at 1690 and 1700 cm^{-1}. (Found: C 71.3; H 9.4. $C_{15}H_{24}O_3$ requires C 71.4; H 9.6). The *2,4-dinitrophenylhydrazone* melted at 138°.

Copaene. The IR spectrum of fraction 4_6 (Table 6) was found to be superimposable onto that of an authentic sample of *copaene* [10],* (for physical constants, see Table 7).

Dehydrogenation of copaene. Fraction 4_6 (Table 6) (0.250 g) was dehydrogenated with selenium (0.250 g) by heating the mixture at 280° for 28 h. *Cadalene* (0.115 g) was isolated from the products by extraction with light petroleum and filtration of the solution

Table 8. Chromatography of fraction VI (redistilled and passed through alumina) on Ag-silica. β-Ylangene, β-copaene, and ε-muurolene.

Fraction	Solvent *	Volume ml	Weight g
1_8	E. (1 %) in L.P.	800	0.36
2_8	»	200	0.15
3_8	»	400	0.83
4_8	»	400	0.95
5_8	E. (2 %) in L.P.	1000	0.65
6_8	E. (5 %) in L.P.	600	0.23
7_8	»	800	1.05

* Ether: E.; light petroleum: L. P.

Table 9. Physical constants of β-ylangene, β-copaene, α-, γ-, and ε-muurolene.

Fraction	Compound	$[\alpha]_D°$	$n_D{}^{22}$	$d_4{}^{22}$	M_D*
2_8 (Table 8)	β-ylangene	$+19.3$ (c 1.0)	1.5026	0.9256	65.4
4_8 (Table 8)	β-copaene	-7.6 (c 2.0)	1.4993	0.9138	65.12
2_{10} (Table 10)	α-muurolene	-85.3 (c 2.3)	1.5063		
4_{10} (Table 10)	γ-muurolene	-1.8 (c 2.5)	1.5059		
7_8 (Table 8)	ε-muurolene	$+50.7$ (c 2.3)	1.5049		

* Calculated values, see Table 7.

Table 10. Chromatography of fraction VIII (passed through alumina) on Ag-silica.
α- and γ-Muurolene.

Fraction	Solvent	Volume ml	Weight g
1_{10}	L.P.	3000	0.93
2_{10}	E. (1 %) in L.P.	2000	7.60
3_{10}	»	1000	2.34
4_{10}	E. (2 %) in L.P.	3000	6.82

through alumina. The picrate was recrystallized twice from methanol and was identified as *cadalene picrate*, m.p. 116—117°.

Osmium tetroxide oxidation of copaene. From fraction 4_6 (Table 6) as well as from copaene * the crystalline diol obtained from copaene by de Mayo, Büchi *et al.*[10] was prepared as follows. To the sesquiterpene (0.22 g, from fraction 4_6) in dry ether (25 ml) dry pyridine (0.39 ml) was added and, after cooling to 0°, an ice-cold solution of osmium tetroxide (0.46 g) in dry ether (15 ml). The mixture was left at room temperature for two days. The solution was concentrated at room temperature to a volume of about 15 ml by evaporation under reduced pressure. Crystallization commenced and was completed by cooling. The mother liquor was decanted from the crystals, which were then washed with a small portion of ice-cold, dry ether. Mannitol (2.0 g) and aqueous potassium hydroxide (1 M, 4 ml) were added to the crystals and the mixture was shaken for 4 h. The mixture was diluted with water and extracted with three portions of ether. The combined ether fractions were washed with water and dried over sodium sulphate. Evaporation of the solvent gave an oil (0.30 g), which was chromatographed on alumina (basic, activity III, 9 g). Elution with light petroleum:ether (1:1, 50 ml) furnished a crystalline product (0.09 g), which was recrystallized twice from light petroleum. It melted at 72—73° and had $[\alpha]_D$ + 3° (*c* 0.15).

Isolation of longifolene. Fraction IV (22 g) was chromatographed on alumina (500 g). The oil (19 g) eluted with light petroleum (1500 ml) was fractionally distilled twice through a spinning band column to give pure *longifolene* (3.3 g), $[\alpha]_D^{20}$ + 48.6° (*c* 2.3) as the main fraction. It was identical with longifolene from *Juniperus communis* wood. *Longibornyl chloride*, m.p. 60—61°, $[\alpha]_D^{20}$ + 12.9° (*c* 1.8) was prepared from the hydrocarbon in the usual manner.

Isolation of β-ylangene, β-copaene, and *ε-muurolene.* Fractional distillation of fraction VI through a spinning band column gave as the middle cut an oil (5.9 g), which was rapidly passed through an alumina column (basic, activity I, 100 g) using light petroleum (250 ml) as the eluent. Evaporation of the solvent gave a colourless oil (4.7 g), which showed three main peaks on GLC (conditions and retention data see Ref.8). The components were separated by chromatography on Ag-silica (200 g) as shown in Table 8.

β-Ylangene. A compound identical with β-ylangene [11] was obtained from fraction 2_8 (Table 8) and had the physical constants shown in Table 9. For comparison β-ylangene was prepared [14] from ylangene [12,13,**] by selenium dioxide oxidation followed by Wolff-Kishner reduction.

β-Copaene. Fraction 4_8 (Table 8) consisted of *β-copaene*,[14] physical constants, see Table 9. (Found: C 88.4; H 11.6. $C_{15}H_{24}$ requires C 88.2; H 11.8).

ε-Muurolene. Fraction 7_8 (Table 8, physical constants in Table 9) was found to consist of *ε-muurolene*.[15] The IR spectrum was identical with that of "ε-cadinene".[16a]

Isolation of α- and γ-muurolene. Fraction VIII (27 g) was passed through alumina and then chromatographed on Ag-silica (18 g oil on 500 g adsorbent) as described in Table 10.

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* I thank Professor G. Büchi for a generous gift of copaene.
** I thank Dr. O. Motl for a generous gift of ylangene.

α-*Muurolene.* Fraction 2_{10} (Table 10) consisted of α-*muurolene* [15] (physical constants in Table 9). (Found: C 88.2; H 11.6. $C_{15}H_{24}$ requires C 88.2; H 11.8). It had IR absorption bands at 1675, 844, 826, and 798 cm⁻¹. The UV spectrum indicated that the compound contained isolated double bonds.

γ-*Muurolene.* γ-*Muurolene* [15] was obtained from fraction 4_{10} (Table 10) by filtration through alumina. It had the physical constants given in Table 9. (Found: C 88.1; H 11.8. $C_{15}H_{24}$ requires C 88.2; H 11.8). The compound showed IR absorptions at 3080, 1780, 1670, 1649, 883, and 831 cm⁻¹. The UV spectrum indicated that the compound contained isolated double bonds.

Isolation of γ- *and* δ-*cadinene.* Fraction IX (41.1 g) was fractionally redistilled at 10 mm using a spinning band column. The first fraction (23.3 g) was a mixture of muurolenes and cadinenes. The next fraction (10.5 g), which was free from α-muurolene, was chromatographed on Ag-silica (Table 11).

δ-*Cadinene.* Fraction 2_{11} (Table 11) was found to consist of δ-cadinene, $[\alpha]_D$ + 80.3° (c 1.7). The IR spectrum was identical with that published by Plíva *et al.*[16b] The compound was characterized by conversion into the *diepoxide*, m.p. 82—84°,[17] and to (−)-*cadinene dihydrochloride,* m.p. 116—118°, $[\alpha]_D$ −35°.

Table 11. Chromatography of fraction IX (redistilled) on Ag-silica. δ- and γ-Cadinene

Fraction	Solvent	Volume ml	Weight g
1_{11}	L.P.	200	0.02
2_{11}	»	500	0.83
3_{11}	»	750	0.21
4_{11}	E. (4 %) in L.P.	1000	0.27
5_{11}	»	600	0.12
6_{11}	»	1500	0.06

γ-*Cadinene.* Fraction 5_{11} (Table 11), after filtration through alumina, had an IR spectrum identical with that of γ-cadinene,[16c] $[\alpha]_D^{24}$ + 117° (c 2.4). It gave *cadinene dihydrochloride,* m.p. 116—118°, with hydrogen chloride.

Isolation of calamenene. Fraction X (15.7 g) was ozonised and the product was worked up as described for the ozonolysis of α-longipinene. The neutral fraction (0.466 g) was chromatographed on alumina (basic, activity I, 125 g, eluent light petroleum) to give as the main fraction an oil (0.265 g), $[\alpha]_D$ −23° (c 0.8). The IR spectrum was almost identical with that of *calamenene;*[16d] UV extrema $\lambda_{infl.}$ 263 mμ (log ε 2.59); λ_{max} 269 (log ε 2.74); $\lambda_{infl.}$ 272 (log ε 2.68); λ_{max} 278 (log ε 2.76). (Found: C 88.7; H 11.5. $C_{15}H_{22}$ requires C 89.0; H 11.0).

Isolation of α-*calacorene.* Fraction XI (3.3 g) was chromatographed on alumina (basic, activity I, 600 g, eluent light petroleum). After 950 ml of eluate had been collected, an oil (0.50 g) was eluted by the following 750 ml portion. This oil had $[\alpha]_D$ + 56.1° (c 2.1). The IR spectrum was identical with that of α-*calacorene;*[16e] UV extrema λ_{max} 214 mμ (log ε 4.06); λ_{max} 220 (log ε 4.10); λ_{max} 227 (log ε 3.96); λ_{max} 265 (log ε 3.68); $\lambda_{infl.}$ 297 (log ε 2.74). (Found: C 89.6; H 10.1. $C_{15}H_{20}$ requires C 89.9; H 10.1).

Investigation of the sesquiterpene alcohol fraction XII. Isolation of δ-*cadinol.* Fraction XII (16 g) slowly deposited crystals on standing. They were collected by filtration and washed with a small amount of ice-cold light petroleum. The crude crystalline material (0.5 g) thus obtained was recrystallized from isopropyl ether and vacuum sublimed to give pure δ-*cadinol (pilgerol),* m.p. 138—139°, $[\alpha]_D^{21}$ −98.5°, identical with pilgerol isolated from *Pilgerodendron uviferum.*[18]

Isolation of isoeugenol methyl ether. The combined mother liquors (15.5 g) obtained after the isolation of δ-cadinol from fraction XII were chromatographed on alumina (basic, activity I, 500 g). Three fractions were collected, the first fraction, XII *a*, (1.48 g)

Table 12. Chromatography of fraction XII *c* on alumina. Sesquiterpene alcohols.

Fraction	Solvent	Volume ml	Weight g
1_{12}	E.	200	0.37
2_{12}	»	100	3.65
3_{12}	»	800	1.77
4_{12}	Methanol (1 %) in E.	300	1.18
5_{12}	»	200	0.62

by elution with light petroleum (1500 ml), the second, XII *b*, (3.90 g) with ether (3000 ml) and the third, XII *c*, (7.80 g) with ethanol (5 %) in ether (1000 ml).

Fraction XII *b* (1.25 g) was rechromatographed on alumina (basic, activity II, 50 g) using ether (10 %) in light petroleum as the eluent. The main fraction obtained (0.26 g) was found to consist of *isoeugenol methyl ether.*

Isolation of a new sesquiterpene alcohol, m.p. 48°. Rechromatography of fraction XII *c* on alumina (basic, activity I, 250 g) was carried out as described in Table 12.

Fraction 2_{12} (3.65 g) was chromatographed on Ag-silica (140 g) using ether (2 %) in light petroleum as the eluent. After 1100 ml had been collected, the next portion (3200 ml) eluted the main fraction (2.58 g, almost pure according to Ag-TLC). The product obtained crystallized on being kept in the refrigerator for a few days. Recrystallization from light petroleum followed by sublimation *in vacuo* afforded *an alcohol,* m.p. 47.5—48°, $[\alpha]_D^{22} + 27.4$ (*c* 1.0). (Found: C 81.1; H 11.7. $C_{15}H_{26}O$ requires C 81.2; H 11.8). It showed IR absorption at 3350 and 1037 cm^{-1} but no bands indicating the presence of double bonds.

The alcohol gave no colouration with a tetranitromethane solution (5 % in chloroform) and when dehydrogenated with selenium at 290° no cadalene or azulene was formed.

Investigation of the diterpene fractions XIV and XV. Isolation of pimaradiene. Fraction XIV (62.0 g) was distilled through a spinning band column. The main part (26.7 g) was followed by a fraction (6.9 g) containing pimaradiene and isopimaradiene as shown by GLC comparison with these compounds from Scots pine wood extract.[8] Chromatography of the latter fraction (6.9 g) on alumina (150 g, elution with light petroleum, 400 ml) gave a colourless oil (5.7 g). The oil was chromatographed on Ag-silica (160 g); 80 ml fractions were collected using ether (2 %) in light petroleum as the eluent. Fractions 14—20 consisted of almost pure *pimaradiene,*[19] which, after filtration through alumina and distillation, had m.p. 24—26°, $[\alpha]_D + 105°$ (*c* 2.7).

Isolation of pimarinal. According to GLC fraction XV contained pimarinol, pimarinal, and isopimarinal. This fraction (21.5 g) was treated with Girard reagent P (5.5 g) in absolute ethanol (50 ml) and glacial acetic acid (5 ml) at reflux for 2 h. The hot solution was poured into a stirred mixture of sodium hydroxide (2.7 g), water and ice (200 ml) and ether (150 ml). The aqueous phase was shaken with ether and then acidified with hydrochloric acid (conc., 8.5 ml). The mixture was left at room temperature overnight and then extracted with ether. The ether extract was washed once with aqueous sodium hydroxide (10 %), four times with water, dried (sodium sulphate) and taken to dryness. The residual brown oil (4.2 g) was chromatographed on alumina (neutral, activity I, 130 g) and the following fractions were collected. XV *a*, light petroleum (400 ml), 1.07 g; XV *b*, ether (2 %) in benzene (550 ml), 2.68 g; XV *c*, ether (400 ml), 0.41 g. Fraction XV *b* was chromatographed on Ag-silica (100 g) using ether (5 %) in light petroleum as the eluent to give as the main fraction *pimarinal*[20] (1.1 g), which, after recrystallization from acetone/water, had m.p. 52—54°, $[\alpha]_D + 98°$.

Added in proof. From Polish extraction turpentine (*Pinus silvestris* L.) Zabża *et al.* recently isolated longifolene, α- and γ-muurolene.[25]

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