Terpenoids. VIII. Sesquiterpenoids from the Wood Oil of "Sugi" (Cryptomeria japonica D. Don.)[*1,*2]

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The main components of the oil of Sugi wood have been shown to be sesquiterpenoids.[1-5] Among these, however, a cadinene has been the only component unsatisfactory characterized, except for the recent work by Sumimoto and his co-workers[6] on the isolation and characterization of cryptomeridiol (selinan-4α, 11-diol).

The results of experiments on two samples of Sugi-wood oil, kindly supplied by Professor Tamio Kondo, are described in this paper.

Oil I, obtained by steam-distillation, was analyzed by distillation, followed by chromatography; the complete results are given in Table I. Sesquiterpene alcohols are distributed over all fractions, and two alcohols are obtained

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[*2] Partly presented before the 6th Symposium on Perfumery, Terpene and Essential Oil Chemistry held at Shinshu University, Ina, August, 1962, and the 7th Symposium on the same subjects held at Kochi University, Kochi, October, 1963.

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1) C. Kimoto, *Tokyo Imp. Univ. Agr.*, **4**, 403 (1902); *Chem. Zent.*, **1902**, II, 382.

2) H. Kimura, a) *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), No. 284, 905 (1905); b) *Ber. Deutsch. Pharm. Ges.*, **19**, 369 (1909); *Chem. Zent.*, **1910**, I, 275.

3) K. Keimatsu, *J. Chem. Soc. Japan* (*Tokyo Kagaku Kaishi*), **26**, 315 (1905); *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), No. 277, 189 (1905).

4) M. Yano, *J. Soc. Chem. Ind. Japan* (*Kogyo Kagaku Zasshi*), **16**, 443 (1913).

5) K. Hoshino, ibid., **22**, 969 (1919).

6) M. Sumimoto, H. Ito, H. Hirai and K. Wada, *Chem. & Ind.*, **1963**, 780; M. Sumimoto, ibid., **1963**, 1356.

in the crystalline form. The one, $C_{15}H_{26}O$, (m. p. 140∼141°C), was identified as pilgerol (=δ-cadinol) by a direct comparison with the sample provided by Professor Erdtman.[*4] It seems quite probable that the "isocryptomeriol" (m. p. 135∼136°C) described by Kimura[2b] is identical with this alcohol. Another alcohol (m. p. 63∼74°C) was still impure, but its infrared spectrum was almost identical with that of β-eudesmol.[7],[*5] Furthermore, a new monocyclic ketone, named cryptomerion, $C_{15}H_{22}O$, was isolated from fraction 7.

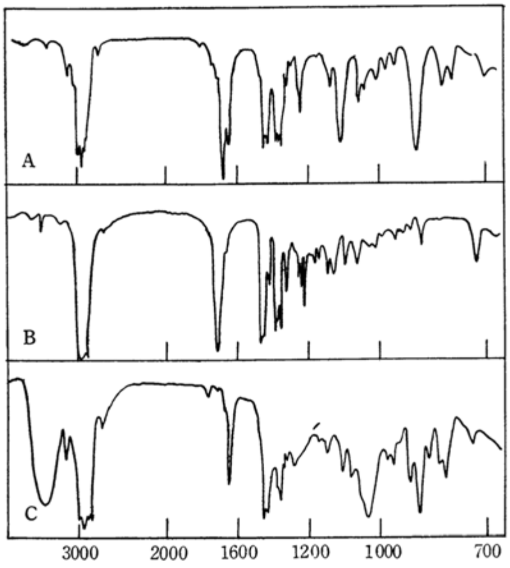


Fig. 1. Infrared spectra of cryptomerion (A); hexahydrocryptomerion (B); and unsaturated alcohol (C).

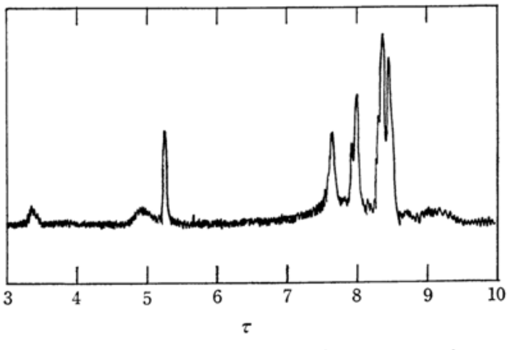
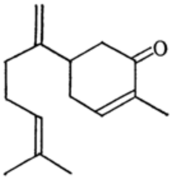
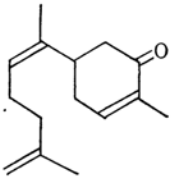


Fig. 2. NMR spectrum of cryptomerion (CCl_4 solution 10%).

Cryptomerion possesses an α,β-unsaturated ketone group (λ_{max} 236, 304 mμ and ν_{max} 1685 cm^{-1}; Fig. 1A). The infrared spectrum of the corresponding unsaturated alcohol (Fig. 1C) obtained by reduction of cryptomerion with lithium aluminum hydride clearly shows the presence of a terminal methylene group (ν_{max} 3130, 1650 and 888 cm^{-1}). The NMR spectrum[*6] of cryptomerion (Fig. 2) indicates the presence of the following groups; one hydrogen and one methyl group on the conjugated ketone system (τ value 3.38 and 8.00), one hydrogen on a trisubstituted double bond (4.98), one terminal methylene group (5.25), one methylene group adjacent to the carbonyl group (7.66), and two methyl groups on one (or two) double bond(s) (8.37 and 8.46). The catalytic reduction of cryptomerion gave a hexahydroderivative (Fig. 1B), which was reduced to the corresponding hydrocarbon by the Huang-Minlon method. The infrared spectrum of this hydrocarbon is identical with that of hexahydrobisabolene.[8],[*7] When the groups detected by the NMR spectrum are arranged on the bisabolane skeleton, the possible structures are limited to two, namely, I and II. Structure I is preferred for cryptomerion from the biogenetic point of view.[9]



(I)



(II)

Oil II, obtained by methanol extraction, was used for the analysis of sesquiterpene hydrocarbons. The fraction corresponding to fractions 1 to 4 of oil I was distilled by a spinning-band column (the results are shown in Table II) with each fraction subjected to the chromatographic separation. Fractions 10 to 13 show two main peaks in the gas chromatography. They were separated pure by chromatography and identified as δ-cadinene[10] and

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7) F. J. McQuillin and J. D. Parrack, *J. Chem. Soc.*, **1956**, 2973.

[*4] The author thanks Professor H. Erdtman for his kindness in providing him with the authentic sample.

[*5] The presence of eudesmol (=cryptomeradol) in the root oil of Sugi was reported by H. Wienhaus and H. Scholz, *Ber. Schimmel Jubiläum Ausgabe*, 267 (1929); *Chem. Zent.*, **1930**, I, 137. cf. L. Ruzicka, D. R. Koolhaas and A. H. Wind, *Helv. Chem. Acta*, **14**, 1178 (1931); Y. Sugii and T. Sengoku *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **51**, 196 (1931).

[*6] The NMR spectrum was measured with Varian A 60. The author is indebted to Dr. T. Matsuo and Mr. Y. Nakayama for the measurement and instructive discussions.

[*7] The author thanks Professor V. Herout for the donation of the reprints.

[*8] The author is indebted to Dr. Y. Hirose of the University of Tokyo for the identification of infrared spectrum of copaene.

8) J. Pliva, V. Herout and F. Šorm, *Chem. Listy*, **45**, 117 (1951).

9) J. B. Hendrickson, *Tetrahedron*, **7**, 82 (1959).

10) J. Pliva, V. Herout, B. Schneider and F. Šorm, *Coll. Czecko. Chem. Communs.*, **18**, 500 (1953).

TABLE I.

Fraction	B. p. °C/7 mmHg	n_D^{21}	Yield		Results of chromatography, %				
					Sesquiterpene				Diterpene
			g.	%	Hydrocarbon	Ether	Alcohol	Ketone	Hydrocarbon
1	105~110	1.5060	1.5	6.3	5.2	0.5	0.2		
2	110~115	1.5075	3.5	14.5	10.9	0.9	1.8		
3	115~120	1.5075	1.5	6.3	2.9		3.1		
4	120~125	1.5055	1.1	4.6	0.7		3.9		
5	125~130	1.5055	2.9	12.1	1.2		10.9		
6	130~140	1.5112	2.0	8.4			8.4		
7	140~155	1.5152	1.6	6.7			5.0	1.2	0.4
	Hold up		1.0	4.2			1.2	0.1	1.2
	Residue		7.5	31.1					4.1
	Total		22.6	94.2	20.9	1.4	34.5	1.3	5.7

calamenene.[10] From fraction 13 and from the pot residue a small amount of pure calacorene[10] was separated. Fractions 1 to 3 are complex mixtures of hydrocarbons; at least seven peaks were observed in gas chromatography, besides δ-cadiene and calamenene, and a small amount of copaene[*6] was separated from fractions 1 and 2.

Experimental

The Analysis of Oil I.—The oil obtained by steam distillation was brown and viscous n_D^{22} 1.5130, d_{22} 0.982. The neutral fraction (24 g.) was distilled with a concentric column 26 cm. high, and each fraction was chromatographed on an alumina or silica gel column. The results are tabulated in Table I.

Sesquiterpene Alcohols.—Fraction 6 (2.0 g.) was chromatographed on an alumina column (25 g.). A mixture of alcohols (oil) was eluted by a mixture of petroleum ether and ether. The next fraction was solidified (m. p. about 60°C) (300 mg.); the melting point was raised to 63~74°C after repeated crystallization from petroleum ether. 3, 5-Dinitrobenzoate, m. p. 125~136°C. This alcohol was considered to be impure β-eudesmol. The fractions eluted by ether gave another crystalline alcohol (257 mg.), which was recrystallized from petroleum ether and sublimed under reduced pressure. M. p. and mixed m. p. with authentic pilgerol, 140~141°C; $[\alpha]_D -100°$ (c 0.48, chloroform). The infrared spectra of the two alcohols are superimposable. Crued pilgerol was also obtained from fractions 4 (21 mg.), 5 (420 mg.) and 7 (42 mg.).

The Presence of Ethers.—Fraction 2 (3.33 g.) was chromatographed on a silica gel column (65 g.). After the elution of hydrocarbon (2.51 g.) with petroleum ether, a fraction (705 mg.) was eluted with ether. This fraction, on further chromatography on an alumina column (15 g.), afforded fractions of n_D^{24} 1.4745~1.4725 (total, 200 mg.). The infrared spectra of these fractions showed strong bands at 1135~1070 cm^{-1}.

Cryptomerion.—Fraction 7 (1.5 g.) was chromatographed on an alumina column (20 g.), Petroleum ether eluted an oily diterpene hydrocarbon (102 mg.) and a ketone (243 mg.) successively. The same ketone was obtained from a commercial (root ?) oil. The ketone (cryptomerion) showed n_D^{26} 1.5050, d_{26} 0.954, MR 68.19. Calcd. for $C_{15}H_{22}OF_3$, 67.90, $[\alpha]_D -38°$ (c 1.45, chloroform), λ_{max} 236 and 304 mμ (ε 9600 and 110, ethanol). Infrared spectrum, Fig. 1A. 2, 4-Dinitrophenylhydrazone m. p. 168~171°C.

Hexahydroketone. — n_D^{26} 1.4597, d_{26} 0.884, $[\alpha]_D$ +17° (c 0.92, chloroform) (infrared spectrum, Fig. 1B) was obtained by catalytic hydrogenation with Willstätter's platina black in ethanol. 2, 4-Dinitrophenylhydrazone, m. p. 74~77.5°C.

Found: C, 62.29; H, 8.08; N, 13.69. Calcd. for $C_{21}H_{32}O_4N_4$: C, 62.35; H, 7.97; N, 13.85%.

The Huang Minlon reduction of the hexahydroketone (208 mg.) gave a saturated hydrocarbon (123 mg., purified through an alumina column). Its infrared spectrum was identical with that of hexahydrobisabolene.[8] The lithium aluminum hydride reduction of cryptomerion gave an oily unsaturated alcohol (infrared spectrum, Fig. 1C). 3, 5-Dinitrobenzoate, m. p. 65.5~67°C (from petroleum ether).

Found: C, 63.33; H, 6.25; N, 6.68. Calcd. for $C_{22}H_{26}O_6N_2$: C, 63.75; H, 6.32; N, 6.76%.

The Separation of Sesquiterpene Hydrocarbons from Oil II.—The fractions (b. p. 105~115°C/10 mmHg (31.5 g.) and 115~140°C/10 mmHg (24 g.)) of oil II (which was obtained by methanol extraction) were distilled by a spinning-band column (Tokyo Kagaku Seiki Model SB 815); the fractions boiling below 131°C/11 mmHg were combined and distilled twice on sodium metal and finally by the same spinning-band column. The results of the final distillation is shown in Table II.

The Isolation and Identification of Individual Hydrocarbons.—The purity of the fractions was determined by gas chromatography.

Apparatus.—Shimadzu gas chromatograph, Type GC-2A. Column PEG 6000 on Shimalite; 2 m. Temp., 180°C. Carrier gas, H_2. The infrared spectra were compared with those published by F. Šorm,

TABLE II.

Fraction	B. p. °C/11 mmHg	cc.	n_D^{23}
1	108～114	1.20	1.4930
2	114～115.5	1.40	1.4945
3	115.5～117	1.18	1.4995
4	117～119	1.68	1.5040
5	119～120	1.20	1.5055
6	120～121	1.06	1.5056
7	121	2.30	1.5060
8	121	2.00	1.5069
9	121	1.64	1.5080
10	121	2.65	1.5080
11	121	1.65	1.5084
12	121	1.86	1.5097
13	121	1.30	1.5107

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Copaene.—Fraction 1 was chromatographed on an alumina column (100 g.), and the first fraction (412 mg.) was rechromatographed twice to yield copaene (70 mg. n_D^{26} 1.4813).

δ-Cadinene.—Fractions 8—13 were chromatographed on a hundred-fold of alumina. The first fraction yielded δ-cadinene, n_D^{28} 1.5072, d_4^{28} 0.9133, $[\alpha]_D$ +27.8° (*c* 4.1 1, chloroform). Dihydrochloride, m. p. 118°C, $[\alpha]_D$−36.1° (*c* 3.39, chloroform).

Calamenene.—The tail fractions of the chromatography of fractions 5—13 yielded calamenene, which was then purified by further chromatography. n_D^{28} 1.5155, d_4^{28} 0.9276, $[\alpha]_D$ −67.0° (*c* 2.40, chloroform).

Calacorene.—On chromatography the pot residue yielded a middle fraction calacorene of high purity (88 mg.) n_D^{23} 1.5405.

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