*Sesquiterpenes from Dictyopteris divaricata. I**

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In 1951, Takaoka and Ando[1] isolated a sesquiterpene alcohol from *Dictyopteris divaricata*, Okamura, and they suggested that it was a new type of cadinol. Recently acquired knowledge about the constitution and stereochemistry of sesquiterpenes[2] has prompted us to re-examine the sesquiterpenes of the brown alga.

The methanol extracts of the air-dried seaweed, *Dictyopteris divaricata*[3] (92 kg.), were concentrated to a small volume in vacuo, and the residual light brown oil was then distilled with steam. The ether extracts of the distillate were washed with 5% aqueous potassium hydroxide and then by 1 N hydrochloric acid. The neutral essential oil (790 g.)[4] thus obtained was subjected to fractional distillation in vacuo; each fraction was chromatographed on alumina or silica gel, the homogeneity was tested by gas chromatography and thin-layer chromatography, and six components were isolated in a pure state.

Four sesquiterpenes among them were identified as (−)-copaene,[5] (−)-γ_1-cadinene,[6] cadalene and (−)-δ-cadinol[7] by a comparison of their infrared absorption spectra and other physical constants with those the corresponding sesquiterpenes given by Šorm.[8] The alcohol was also shown to be identical with that isolated by Takaoka and Ando.[1]

A new hydrocarbon (b. p. 97°C/5 mmHg, $[\alpha]_D^{23}$ +12.8°) showed an infrared spectrum which was superimposable on that of (−)-β-elemene.[8] The NMR spectrum showed the presence of one quaternary methyl ($\tau=9.07$, s), two methyls attached to the double bond ($\tau=8.38$, ss), one vinyl group ($\tau=4.45$, q; 5.35, d; 5.43, d) and four olefinic protons ($\tau=5.45\sim5.65$). These data have shown that the hydrocarbon is the optical antipode of (−)-β-elemene. This was further confirmed by a comparison of the retention time on gas chromatography with that of authentic (−)-β-elemene.[9]

The further investigation of another sesquiterpene, a newly isolated secondary alcohol, $C_{15}H_{24}O$, $[\alpha]_D^{23.5}$ −13.6°, is now in progress; details will be presented elsewhere.

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* "Terpenoids from Marine Plants," Part I.

[1] M. Takaoka and Y. Ando *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon kagaku Zassi*), **72**, 999 (1951).

[2] Cf. P. de Mayo, "Mono- and Sesquiterpenoids", Interscience Publ., New York (1959); F. Šorm, "Fortschritte der Chemie Organischer Naturstoffe," XIX, Wien-Springer-Verlag (1961) p. 1; T. G. Halsall and D. W. Theobald, *Quart. Rev.*, **16**, 101 (1962).

[3] Collected at Oshoro Bay, Hokkaido.

[4] The gas chromatogaphic analysis showed that it consisted of at least thirteen components.

[5] G. Büchi and S. H. Feairheller, *Proc. Chem. Soc.*, **1963**, 214; V. K. Kapadia, B. A. Nagasampagi, V. G. Naik and S. Dev, *Tetrahedron Letters*, **1963**, 1933.

[6] V. Herout and V. Sykora, *Tetrahedron*, **4**, 246 (1958).

[7] W. G. Dauben, B. Weinstein, P. Lim and A. B. Anderson, ibid., **15**, 217 (1961).

[8] J. Pliva, M. Herac, V. Herout and F. Šorm, "Die Terpene. Sammlung der Spektren und physikalischen Konstanten," Teil I, Akademie-Verlag, Berlin (1960).

TABLE I. THE FRACTIONAL DISTILLATION OF THE NEUTRAL ESSENTIAL OIL (774 g.)

Fraction	B. p., °C/mmHg	Yield, g.	Principal component*
D-1	65~85/9	0.15	
2	100~105/9	1.47	
3	109~129/9	21.00	crude (−)-copaene
4	89.5~91/5	18.51	two components
5	96~98/5	75.90	crude (+)-β-elemene
6	102~104/5	12.86	two or three components
7	104.5~108/5	26.53	three components
8	108.5~110/5	73.45	two or three components
9	105~109/4.5	42.86	two or three components containing γ_1-cadinene
10	109~110/4.5	33.55	
11	110.5~114/4.5	13.53	
12	114.5/4.5	90.05	two components
13	101~104/4	80.00	five or six components
14	105~106.5/4	27.53	five or six components
15	106.5/4	4.93	
16	residue	ca. 80	

* Checked by gas chromatography on PEG-4000

Experimental

The melting points are uncorrected. Fractional distillation was carried out with a high-efficiency concentric-tube Kyowa fractionator. The gas chromatographic analyses were carried out with a Hitachi gas chromatograph KGL-2 at 200°C, using PEG-4000 and helium gas. The ultraviolet and infrared spectra were measured using a Hitachi ESP-2 spectrophotometer and a Nippon Bunko 401-G spectrophotometer respectively. The NMR measurements were performed with a Nippon Denshi 60 Mc. spectrophotometer, and carbon tetrachloride and tetramethylsilane were used as the solvent and the internal standard respectively.

The Extraction and Fractionation of the Essential Oil.—The air-dried seaweed, *Dictyopteris divaricata*, Okamura (92 kg.), was extracted with methanol at room temperature for two weeks, after which the methanol extracts were concentrated in vacuo. The light brown residual oil then distilled with steam, and the distillate was extracted with ether. After the solvent had been removed from the ethereal extracts, 890 g. of a light yellow essential oil was obtained (yield, 0.97%).

The crude essential oil was dissolved in ether, and the ethereal solution was washed with 5% aqueous potassium hydroxide and then by 1 N hydrochloric acid. The neutral fraction thus obtained amounted to 790 g. (0.86%). Gas chromatography showed that this fraction consisted of at least thirteen components. The neutral fraction was then fractionated in a nitrogen stream under diminished pressure using a high-efficiency (theoretical plates about 80) fractional column. The results are shown in Table I.

(−)-Copaene. — Fraction D-3 was subjected to redistillation in vacuo, and a fraction boiling at 87 ~87.5°C/3 mmHg was then chromatographed on silica gel. (−)-Copaene, $C_{15}H_{24}$ ($n_D^{21.5}$ 1.4922, $[\alpha]_D^{23}$ −26.1°, IR (liquid film): 3040, 1642, 1320, 1177, 1166, 1156, 1045, 1032, 1010, 930, 879, 824, 777, 740 cm^{-1}) was obtained from the fraction eluted with petroleum ether.

The NMR spectrum showed peaks at 5.20 (1H, singlet), 8.28 (3H, doublet, J=2.4 c.p.s.), 9.02 (3H, singlet), and 9.08 τ (6H, doublet, J=6.6 c.p.s.).

(+)-β-Elemene.—Fraction D-5 was redistilled in vacuo, and a fraction boiling at 97°C/5 mmHg (yield 66.2%) was collected. This was chromatographed on silica gel. A pure hydrocarbon n_D^{22} 1.4920, $[\alpha]_D^{23}$ +12.8°, was obtained.

Found: C, 87.87; H, 11.69. Calcd. for $C_{15}H_{24}$: C, 88.16; H, 11.84%.

The infrared spectrum (liquid film) (3080, 1640, 1003, 907, 885 cm^{-1}) was superimposable on that of (−)-β-elemene.[8] The NMR spectrum showed peaks at 4.45 (1H, quartet, J=9.5, 17.5 c.p.s.), 5.35 (1H, doublet, J=9.5 c.p.s.), 5.43 (1H, doublet, J=17.5 c.p.s.), 5.45~5.65 (4H), 8.38 (6H, singlet), and 9.07 τ (3H, singlet). When the comparison of this hydrocarbon and authentic (−)-β-elemene was carried out by Šorm[9] using gas chromatography, the same retention time was observed.

(−)-γ_1-Cadinene.—Fractions D-9, 10, and 11 were combined and redistilled in vacuo, and a fraction boiling at 108.5~109°C/5 mmHg was identified as (−)-γ_1-cadinene ($[\alpha]_D^{25}$ −19.6°, IR (liquid film): 3070, 1642, 886, 833, 812 cm^{-1}).

Cadalene.—Fraction D-15 was chromatographed on neutral alumina, and the first petroleum ether eluate yielded cadalene, $C_{15}H_{18}$, (picrate, m. p. 111 ~113°C. UV: λ_{max}^{EtOH} 231 (4.67), 290 (3.72), 325 mμ (log ε 2.75); IR (liquid film): 3070, 1625, 1603, 1517, 828, 806, 777 cm^{-1}; NMR: 2.23 (2H, multiplet), 2.75 (1H, doublet, J=2 c.p.s.), 2.92 (2H, singlet), 6.38 (1H, multiplet), 7.42 (3H, singlet), 7.50 (3H, singlet), 8.64 (3H, doublet, J=5.7 c.p.s.) and 8.66 τ (3H, doublet, J=5.7 c.p.s.).

(−)-δ-Cadinol.—The D-16 residue was distilled in vacuo; the results are shown in Table II.

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[9] F. Šorm, private communication.

TABLE II. VACUUM DISTILLATION OF THE RESIDUE D-16 (10 ml.)

Fraction	B. p., °C/mmHg	Yield, ml.
D-16-1	123.5~128/3	1.60
2	128~131/3	1.00
3	131.5~132.5/3	0.54
4	130.5/2.5	0.51
5	130.5~133/2.5	0.53
6	139~146.5/1.5	0.52
7	149.5~170/1.5	0.58

Fraction D-16-3, boiling at 131.5~132.5°C/3 mmHg, (417 mg.) was chromatographed on neutral alumina, and from the benzene-ether (3 : 2) eluate, colorless crystals (m. p. 110~130°C) were isolated (71 mg.); these were repeatedly recrystallized from methanol to have an m. p. of 137.5~138.5°C and $[\alpha]_D^{27}$ −108°.

Found: C, 81.22; H, 11.75. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79%.

The infrared spectra in chloroform, 3590, 1133, 1117, 1101, 947, 873 cm^{-1}, and in Nujol, 3305, 1108, 871 cm^{-1}, were identical with those of (−)-δ-cadinol. NMR: 4.64 (1H, doublet), 8.37 (3H, singlet), 8.77 (3H, singlet), 9.11 (3H, doublet, J=5.5 c.p.s.) and 9.21 τ (3H, doublet, J=5.5 c.p.s.). The cadinol isolated by Takaoka and Ando[1] was found to be identical with this (−)-δ-cadinol on the basis of a mixed melting point determination and the infrared spectra.[10]

A Sesquiterpene Alcohol.—The D-16 residue (25 g.) was chromatographed on neutral alumina, and from the benzene-ether (4 : 1) eluate, a sesquiterpene alcohol (1.73 g.) was obtained, $[\alpha]_D^{23.5}$ −13.6°C.

Found: C, 81.87; H, 10.91. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98%.

IR (liquid film): 3360, 1033, 1015 (OH), 3080, 1643 885 cm^{-1} ($>C=CH_2$); NMR: 4.77 (1H, multiplet), 5.36 (2H, broad singlet), 6.65 (1H, multiplet), 8.27 (3H, singlet), 8.42 (3H, singlet) and 9.29 τ (3H, doublet). The structure elucidation of this alcohol is in progress.

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[10] Cf. Footnote 6 and B. Weinstein, *Experientia*, in press.