and 6), 1.42 (s, H-10), 0.96 and 0.98 (2 *d*, $J = 7$ Hz, H-8 and 9). ^{13}C NMR ($CDCl_3$): 94.5 and 88.0 (C-1 and 4), 77.2 (C-2), 45.6 (C-3), 32.6 (C-7), 16.2 and 18.0 (C-8 and 9), 30.0 (C-10), 32.6 and 33.1 C-5 and 6).

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REFERENCES

1. Anon. (1948). *The Wealth of India*, p. 23. CSIR, New Delhi.
2. Gulati, B. C., Shawl, A. S. and Channa, O. N. (1976). Perfumery and Flavour Association of India, IIIrd Seminar, Calcutta, p. 1.
3. Garg, S. N., Misra, L. N., Agarwal, S. K., Mahajan, V. P. and Rastogi, S. N. (1987) *Phytochemistry* **26**, 449.
4. Garg, S. N. and Agarwal, S. K. (1987) *Planta Med.* **53**, 311.
5. Garg, S. N., Agarwal, S. K., Mahajan, V. P. and Rastogi, S. N. (1987) *J. Nat. Prod.* **50**, 253.
6. Chaudhury, S. S. and Handa, K. L. (1959). *Indian J. Pharm.* **21**, 39.
7. Vashist, V. N., Nath, Y., Nazir, B. N. and Handa, K. L. (1962) *Indian Oil Soap J.* **27**, 229.
8. Kapahi, B. K., Thappa, R. K., Agarwal, S. G. and Sarin, Y. K. (1985) *Pafai.* **7**, 23.
9. Garg, S. N. and Agarwal, S. K. (1988) *Phytochemistry* **27**, 936.
10. Misra, L. N. (1986) *Phytochemistry* **25**, 2892.
11. Misra, L. N. and Singh, S. P. (1986) *J. Nat. Prod.* **49**, 941.
12. Misra, L. N. and Husain, A. (1987) *Planta Med.* **53**, 379.
13. Chandra, A., Misra, L. N. and Thakur, R. S. (1987) *Tetrahedron Letters* **28**, 6377.
14. Ahmad, A., Siddiqui, M. S. and Misra, L. N. (1988) *Phytochemistry* **27**, 1065.
15. Misra, L. N., Shawl, A. S. and Raina, V. K. (1988) *Planta Med.* **54**, 165.
16. Swigar, A. A. and Silverstein, R. M. (1981) *Monoterpenes*. Aldrich, Milwaukee, Wisconsin.

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VOLATILE CONSTITUENTS FROM MARINE BROWN ALGAE OF JAPANESE *DICTYOPTERIS*

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Key Word Index—*Dictyopteris*; brown algae; dictyopterenes; sesquiterpenes; chemotaxonomy

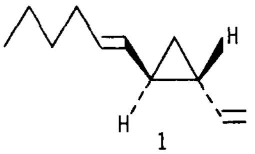
Abstract—*cis*-3-Butyl-4-vinylcyclopentene, *trans*-1-[(1*Z*)-hexenyl]-2-vinylcyclopropane, 4-[(1*E*)-hexenyl]-cyclopentene, and 6-[(1*E*)-butenyl]-cyclohepta-1,4-diene were newly identified in the essential oils from fresh *Dictyopteris prolifera* and *D. undulata*. On the other hand, the oil of *D. divaricata* was found to consist mostly of a single sesquiterpene, cubenol (over 95%) instead of the C_{11}-compounds. The growth-locality variation in the chemical compositions of the essential oils in the genus *Dictyopteris* was discussed.

INTRODUCTION

We have previously reported the occurrence of 'ocean smell' which consist of dictyopterene A (**1**), dictyopterene B (**2**), dictyopterene C′ (**3**), dictyopterene D′ (**4**), and dictyoprolene (**5**) including some unidentified compounds in Japanese *Dictyopteris* [1–3]. We here describe growth-locality variation of the volatile compounds in the essential oils from this genus, *D. prolifera*, and *D. divaricata* on the basis of GC and GC/MS analyses using a capillary column, and discuss taxonomic relationships within the genus of *Dictyopteris*.

RESULTS AND DISCUSSION

Essential oils obtained from the steam distillate of fresh fronds of *D. prolifera* (*ca* 0.09–0.1%), and *D. divaricata* (0.3–0.4%).The two oils displayed very different chromatographic profiles. In the essential oils of *D. prolifera*, *cis*-3-butyl-4-vinylcyclopentene (**6**), *trans*-1-[(1*Z*)-hexenyl]-2-vinylcyclopropane (**7**), 4-[(1*E*)-hexenyl]-cyclopentene (**8**) and 6-[(1*E*)-butenyl]-cyclohepta-1,4-diene (**9**) together with the known C_{11}-compounds (**1**–**5**), were newly identified by comparison of retention indices and GC/MS with those of authentic specimens syn-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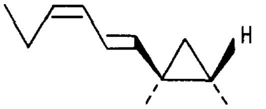
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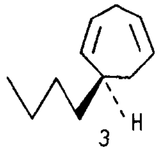
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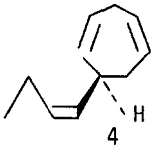
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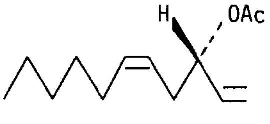
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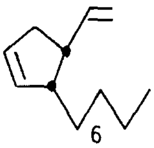
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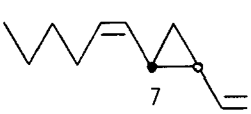
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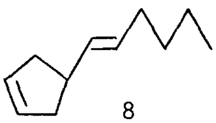
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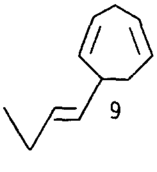
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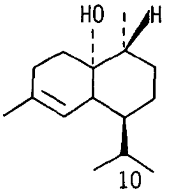
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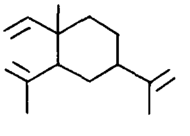
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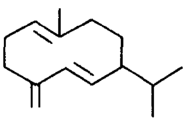
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thesized through unequivocal routes. Very recently the three C_{11}-hydrocarbons (**6**, **8**, **9**) have been identified from the European member of this genus, *D. membranacea* (Stock.) Batt [4]. However, *trans*-1-[(1*Z*)-hexenyl]-2-vinylcyclopropane (**7**) was identified for the first time as a natural product of *D. prolifera* collected at two different places. Particularly, the occurrence of the (*Z*)-isomer (**7**) of dictyopterene A (**1**) was also confirmed in the volatiles extracted by the closed-loop-stripping technique without heating. Dictyopterene B (**2**) and C′ (**3**) were not resolved well on DB-1 (0.25 mm x 50 m), whereas **2** (*ca* 80%), and **3** (*ca* 20%) was isolated by a silver nitrate-impregnated silica gel column chromatography of the steam-distillate from *D. prolifera*. Thus, the significant isomerization of dictyopterene B (**2**) to dictyopterene D′ (**4**) did not occur during the steam-distillation. However, silver nitrate and/or steam distillation could cause rearrangement and/or decomposition of some natural components.

Growth-locality variation in chemical compositions of the essential oil of *Dictyopteris*, which were collected from five locations in Japan (Muroran; the Pacific coast of Hokkaido, the northern Japan, Osaka; the Pacific coast of Mid-Japan, Susa; the Japan sea coast of the northern Yamaguchi, southern Japan, Yoshimo; the Japan sea coast of mid-Yamaguchi, Hikoshima; the Japan sea coast of the southern Yamaguchi) was explored (Table 1). With *D. prolifera*, the compositions of dictyopterene A (**1**) and dictyoprolene (**5**) were higher in the oils from the algae along the Japan sea coast, Susa and Yoshimo, than were in those from Osaka and Hikoshima, whereas the compositions of dictyopterene B, C′, and D′ (**2**$\sim$**4**) were greater in the latter than in the former. The difference in compositions of the C_{11}-compounds might be due to the algal growing conditions, e.g. nutrient, mineral compositions, and temperature of the sea waters in open-sea and inland-sea. The difference in compositions of **2**$\sim$**4** reflects particularly on the quality of 'ocean smell' of the essential oil, and the oil from the open-sea was found to possess an odour more reminiscent of ocean than that from inland-sea. On the other hand, a sesquiterpene alcohol, cubenol (**10**) was isolated from the steam distillate of fresh *D. divaricata* by a silica gel column chromatography. Instead of the C_{11}-compounds, over 95% was comprised of cubenol (**10**) in the oils from *D. divaricata* collected at two different places, northern Japan and southern Japan, along with a small amount of the structurally related sesquiterpenes, *β*-elemene and germacrene D. Although only a few species have been studied, it seems that *Dictyopteris* species might be divided into two groups on the basis of their major constituents: (i) C_{11}-compounds, (ii) sesquiterpenes. On the other hand, the oil of *D. undulata* was found to consist of the C_{11}-compounds (**1**$\sim$**9**) (20%) that were lacking in *D. divaricata*, cubenol ($\sim$10%) that was only in trace in *D. prolifera*, and a characteristic sesquiterpene (70%, unidentified) as major constituents of *D. undulata* oil. This suggests another group of the genus *Dictyopteris* in Japan. A survey of the literature showed that the essential oils of four species of *Dictyopteris* have been chemically investigated. *Dictyopteris zonarioides* (syn. *D. undulata*) collected from lower California was reported to contain sesquiterpenes, but the C_{11}-compounds was not explored [5]. With *D. membranacea*, *D. plagiogramma* and *D. australis*, the occurrence of the C_{11}-compounds was described, whereas sesquiterpenes in the oils have not been reported so far.

EXPERIMENTAL

The fresh algae of *Dictyopteris* were subjected to the analysis of volatile constituents immediately after collection at different growth-locality (see text).

Table 1. Compositions of C_{11}-compounds and sesquiterpenes in the essential oils from the *Dictyopteris* in different growth localities

		Composition (%)*					
		D. prolifera				*D. divaricata*†	
RI	Compounds	S	Y	H	O	M	H
1065	*cis*-3-Butyl-4-vinylcyclopentene	0.38	0.85	0.73	1.34	—	—
1090	*trans*-2-[(1*Z*)-Hexenyl]-2-vinylcyclopropane	—	tr.	0.07	0.16	—	—
1117	Dictyopterene A	32.9	23.7	0.24	4.90	—	—
1122	4-[(1*E*)-Hexenyl]-cyclopentene	2.89	3.63	2.66	5.14	—	—
1149	Dictyopterene D′	13.4	10.4	30.4	23.2	—	—
1157	6-[(1*E*)-Butenyl]-cyclohepta-1,4-diene	5.91	tr.	0.23	0.50	—	—
1169	Dictyopterene B + Dictyopterene C′	3.14	12.3	59.9	37.4	—	—
1171	(1, 3*E*, 5*Z*, 8*Z*)-Undecatetraene	0.31	tr.	0.11	0.51	—	—
1173	$C_{11}H_{16}$	tr.	tr.	tr.	0.14	—	—
1177	(1, 3*E*, 5*E*)-Undecatriene	0.40	tr.	0.07	0.23	—	—
1379	Dictyoprolene	39.2	47.7	5.22	25.4	—	—
1395	β-Elemene (**11**)	—	—	—	—	1.82	2.19
1485	Germacrene D (**12**)	—	—	—	—	0.09	0.73
1496	Sesquiterpene (161/204)	—	—	—	—	tr.	1.18
1519	Sesquiterpene (161/222)	—	—	—	—	1.05	1.10
1641	Cubenol	1.46	1.41	0.32	1.08	97.0	94.8

*% total of C_{11}-compounds and sesquiterpenes.

†Collected around June in 1986–1987

Ri: Kovats index. tr.: trace (~0.01%).

S: Susa, Y; Yoshimo, H; Hikoshima, O; Osaka, M; Muroran.

Sample preparation. The fresh marine algae fronds were homogenized in H_2O. The homogenate was steam-distilled. The distillate was satd with NaCl and extracted with pentane. The extract was dried over Na_2SO_4 and concd to give an essential oil *in vacuo*. The essential oil was analysed by GC and GC-MS. GC analysis was carried out on a Shimadzu 7A equipped with fused silica glass capillary column (50 m × 0.22 mm, SF-96). The column temp. was programmed from 70° (5 min hold) to 220° at 2°/min. GC/MS analysis was carried out on a Hitachi K-80A GC-MS equipped with fused silica glass capillary column (0.25 mm × 50 m, DB-1). The column temp. was programmed from 75° (10 min hold) to 240° at 3°/min. The ionization energy was 20 eV. Most peaks were identified by comparison of retention indices and their mass spectra with those of authentic compounds. *cis*-3-Butyl-4-vinylcyclopentene (**6**) was prepared according to ref. [6]. From 3-cyclopentene-1-carboxylic acid prepared by the method of ref. [7], 4-[(1*E*)-hexenyl]-cyclopentene (**8**) was obtained as reported in ref. [4]. The (*E*)-isomers of **1** and **4** (**7** and **9**) were separated by preparative GC (Varian Model 920 gas chromatograph: 5 mm × 1.5 m, polyethylene glycol 20 M 5% column, injection/detector temp. 250°, column temp. 160°) from the (*Z*), (*E*)-mixtures, which were synthesized as previously reported [1]. The retention indices and mass spectra of peaks (RI: 1065, 1090, 1122, and 1157) unidentified previously, were identical with those of synthetic specimens (**6**, **7**, **8**, **9**) [4], **6**: *m/z* (%) 41 (20), 55 (9.0), 66 (28), 67 (28), 76 (33), 77 (16), 79 (100), 91 (29), 93 (75), 107 (9), 121 (7), 150 (5, M^+); **7**: 29 (18), 39 (6.7), 41 (40), 55 (18), 66 (32), 67 (51), 77 (21), 78 (17), 79 (100), 80 (52), 91 (20), 93 (29), 94 (9.0), 107 (13), 109 (10), 121 (3), 150 (6, M^+); **8**: 29 (18), 41 (40), 54 (20), 67 (51), 79 (10), 93 (29), 107 (9), 150 (6, M^+); **9**: 39 (23), 41 (69), 55 (26), 66 (51), 79 (100), 91 (90), 105 (20), 119 (36), 133 (8), 148 (12, M^+). On the other hand, the essential oil obtained by steam distillation of *D. prolifera* was chromatographed (10% ether–hexane) on 17% $AgNO_3$–silica gel to afford dictyopterene B (**2**), and the structure was confirmed by comparison of ^1H and ^{13}C NMR data with those of authentic specimen [9].

Extraction of volatile compounds by CLHS. The volatile compounds emanated from *D. prolifera* (*ca* 2 g fresh weight) were adsorbed on charcoal (*ca* 100 mg, GC grade, 30–60 mesh, Wako Chem. Co., Japan) for 2 hr looping according to the CLHS procedure [8]. After that, the adsorbed compounds were desorbed from the charcoal with dichloromethane (3 ml). The extract was subjected to GC analysis.

Isolation of sesquiterpene alcohol (**10**). The sesquiterpene, which comprised *ca* over 95% of the volatiles, was isolated from the distillate of *D. divaricata* by column chromatography on silica gel and was identified as cubenol (**10**) by comparison of spectral data with those of authentic cubenol (**10**); IR 3500, 1660 cm^{-1}; and ^{13}C NMR (δ, $CHCl_3$), 135.1 (C), 119.6 (CH), 70.7 (CO), 46.1 (CH), 39.9 (2CH), 31.9 (CH_2), 30.0 (CH_2), 26.8 (CH_2), 25.9 (CH), 24.1 (CH_2), 23.6 (Me), 21.4 (Me), 15.0 (Me), 14.7 (Me); MS, *m/z* (%) 160 (100), 179 (56), 204 (44), 222 (4, M^+). IR: KBr disc. ^{13}C NMR spectra were measured with *d*-chloroform.

REFERENCES

1. Kajiwara, T., Kodama, K. and Hatanaka, A. (1980) *Bull. Jap. Soc. Sci. Fish.* **46**, 771.
2. Kajiwara, T., Kodama, K. and Hatanaka, A. (1982) *Bull. Jap. Soc. Sci. Fish.* **48**, 211.

3. Yamada, K., Tan, H., Tatematsu, H. and Ojika, M. (1986) *Tetrahedron* **42**, 3775.
4. Boland, W. and Müller, D. G. (1987) *Tetrahedron Letters* **28**, 307.
5. Fenical, W., James, J. S., Wing, R. M., and Radlick, P. C. (1972) *Phytochemistry* **11**, 1161.
6. Boland, W. and Mertes, K. (1984) *Helv. Chim. Acta.* **67**, 616.
7. Murdock, K. C. and Angier, R. B. (1962) *J. Org. Chem.* **27**, 2395.
8. Grob, K. and Zürcher, F. (1976) *J. Chromatogr.* **117**, 285.
9. Suzuki, M., Kowata, N., and Kurosawa, E. (1981) *Bull. Chem. Soc. Jpn* **54**, 2366.
10. Kajiwara, T., Nakatomi, T., Sasaki, Y. and Hatanaka, A. (1980) *Agric. Biol. Chem.* **44**, 2099.

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CAROTA-1,4-β-OXIDE, A SESQUITERPENE FROM *DAUCUS CAROTA*

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Key Word Index—*Daucus carota*; plant growth regulators; sesquiterpene; caryophylla-2,6-β-oxide; carota-1,4β-oxide

Abstract—A new sesquiterpene ether, carota-1,4-β-oxide, has been isolated from the essential oil of the seeds of carrot (*Daucus carota*). The structure and stereochemistry of this compound have been established by spectroscopic and chemical methods by its synthesis from carotol.

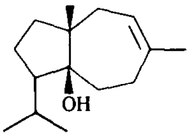
INTRODUCTION

A previous study of the essential oil from the carrot seeds, *Daucus carota* L. revealed the presence of several terpenoids like α-pinene, β-pinene, limonene, bergamotene, caryophyllene, γ-bisaboline, geranyl acetate, geraniol, carotol (**1**) and daucol (**2**) [1–8]. In our continued attempt to isolate the various terpenoids from different essential oils [4–8] and to test them as plant growth regulators we have isolated a new hitherto unknown sesquiterpene ether (**3**) from the hydrocarbon fraction of the essential oil of carrot seeds. The work was undertaken since the carrot plant is not attacked by the insects in the field [9] due to the presence of antifeedants. The present paper reports the isolation and identification of this new sesquiterpene carota-1, 4-β-oxide and its synthesis from carotol (**1**).

RESULTS AND DISCUSSION

The hexane fraction of the essential oil from carrot seeds of the northern part (Punjab State) of India afforded, after extensive column chromatography, a pure yellow liquid (**3**), $C_{15}H_{26}O$, which on mass spectral analysis at 70 eV showed *m/z* 222.3658 $[M]^+$(calculated for $C_{15}H_{26}O$; 222.3654). The IR bands at 1480, 1460, 1450, 1080 and 1090 cm^{-1} showed the absence of any other oxygenated functional group except an ether linkage. This finding was supported by NMR spectral signals at δ0.81 (3H, *d*, $J = 6.15$ Hz), 1.05 (3H, *d*, $J = 6.15$ Hz), 1.0 (3H, *s*) and 1.32 (3H, *s*). The comparison of this ^1H NMR spectrum with those of the major components of the oil, viz. carotol (**1**) and daucol (**2**), hints that this new compound might be related to them. Consequently, the C-skeleton of **3** was confirmed by its dehydrogenation studies over Pd/C, where it yielded mainly daucalene (**4**), a component also obtained from carotol and daucol under similar reaction conditions [**10**] and was identified as the TNB complex by comparison of IR, mp and mmp. This established the carbon skeleton of compound **3** as in carotol or daucol.

Biogenetically, it appears that either carotol or daucol is the immediate precursor of the new compound **3**. It looks probable that **3** is either produced by the removal of hydroxyl from daucol, or by electrophilic attack of an enzyme on the double bond with concomitant neutralization by the hydroxyl group, of the carbonium ion formed at C-3. A survey of the literature revealed that caryophylla-2,6-β-oxide, a natural product from *Lippia citriodora* [11] has been synthesized from 2-hydroxy-



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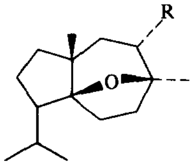

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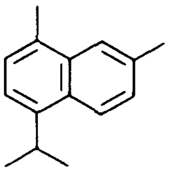

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