water. The diastereomer **6** was obtained in an analogous manner from the glycal **4**.[1]

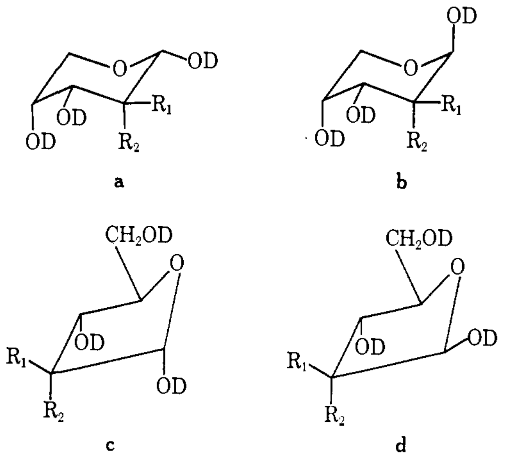
The pure sugars **5** and **6** could be obtained either from preparative paper chromatograms,[5] or alternatively by conversion to, and regeneration from their *N*-phenylglycosylamines ("anilides"),[6] although the latter route gave a somewhat lower overall yield (52 *vs.* 65%). However, since the favored derivative of 2-deoxyribose (**7**) is the *N*-phenylglycosylamine, it is advantageous to note that the corresponding derivatives of **5** and **6**[7] may be (i) mutarotated to equilibrium in pyridine, and/or (ii) hydrolyzed, then reconverted to the "anilide," without any change in the ratio of the M, M − 1, and M + 1 ion peaks in the mass spectra. Furthermore, there was absolutely no change in the nmr pattern (*vide infra*) for H-1 of **5** and **6** before conversion to, and after regeneration from, the *N*-phenylglycosylamines. Hence isolation, purification, and characterization of **5** and **6** as these derivatives and subsequent acid-catalyzed regeneration of the free sugars may be undertaken in confidence that no scrambling of the label will occur.

For the *N*-phenylglycosylamines of **5**, **6**, and **7** the melting points are 179.0–179.5, 178.0–178.5, and 173–174°.[8] The optical rotations, $[\alpha]^{23}\text{D}$, at equilibrium (*c* 0.85, pyridine) are +61.5 (120 hr), +133.8 (24 hr), and 41.7 (72 hr).[8]

Detailed analysis of the nuclear magnetic resonance spectra of **5** and **6** is underway, but some useful information available directly from the 220-MHz spectra of their equilibrated solutions in deuterium oxide is shown in Table I along with data for 2-deoxyribose (**7**). The values for H-1 are compatible with those determined earlier for **7** by Lemieux and Stevens.[9] The chemical shifts reported for H-2 of the pyranose contributors are in excellent agreement with the calculated values using Hall's data,[10] and the spacings J_{12} affirm the disposition of the deuterium in **5** and **6**. The latter affirmation and cognizance of the parameters for the methylene protons in some β-nucleosides[11] permit the assignments for the furanose systems c and d shown in Table I.[12]

Acknowledgment. Financial assistance from the National Research Council of Canada and from Bristol Laboratories is gratefully acknowledged.

Table I. Some 220-MHz Nuclear Magnetic Resonance Parameters for Equilibrated Solutions of **5**, **6**, and **7** in D_2O[a]



5, $R_1 = D$; $R_2 = H$
6, $R_1 = H$; $R_2 = D$
7, $R_1 = R_2 = H$

	H-1	H-2	J_{12}, Hz
5a	5.19	8.22	8.5
5b	4.97	8.00	3.3
5c	4.38	8.10	5.7
5d	4.44	7.83	∼1.5
6a	5.17	8.00[b]	5.0
6b	4.97	8.20[b]	4.5
6c	4.37	7.59	3.2
6d	4.43	7.85	5.4
7a	5.19		2.5, 8.4
7b	4.97		3.5, 3.5
7c	4.38	7.56	
7d	4.44	7.82, 7.82	

[a] Spectra were recorded at 60° with internal TSP as standard. Chemical shifts are in τ values and the *J* values shown were read directly from the spectra. [b] These signals were broad due, undoubtedly, to large geminal H–D coupling estimated to be ∼2.5 Hz.

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[5] P. A. J. Gorin and J. K. N. Jones, *Nature* (*London*), **172**, 1051 (1953).

[6] G. N. Richards, *Methods Carbohyd. Chem.*, **1**, 180 (1962).

[7] Per cent deuteration for both derivatives by mass spectrometry was 98.5. *Anal.* Calcd for $C_{11}H_{14}DO_3N$: C, 62.85; H, 7.67; N, 6.66. Found for the *N*-phenylglycosylamine of **5**: C, 63.29; H, 7.40; N, 6.61. Of **6**: C, 63.21; H, 7.28; N, 6.84.

[8] In agreement with literature values.[5]

[9] R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, **44**, 249 (1966).

[10] L. D. Hall and J. F. Manville, *Advan. Chem. Ser.*, **No. 74**, 228 (1968). Using the values for 2-deoxy-D-arabinohexopyranose as a guide, the expected difference in chemical shift for the pertinent protons in **6a** and **6b** should be 0.13 ppm. This is in good agreement with the observed value of 0.20 ppm.

[11] (a) M. P. Schweizer, S. I. Chan, and P. O. P. Ts'O, *J. Amer. Chem. Soc.*, **87**, 5241 (1965); (b) R. U. Lemieux, *Can. J. Chem.*, **39**, 116 (1961); (c) "High Resolution NMR Spectra," Vol. II, Varian Associates, Palo Alto, Calif., 1960, no. 566.

[12] In thymidine, for example, the methylene protons appear as a poorly resolved quartet.[11c] Against this precedent, the triplet at τ 7.82 in the spectrum of 2-deoxy-D-ribose 7 is assigned to the carbon-2 protons of the β-D-furanose form, **7d**. In accordance with this, both **5d** and **6d** show a signal at the same frequency (τ 7.83 and 7.85). There remains unassigned only the methylene protons for the α-D-furanose forms. The signal present in **9c** (τ 7.56) and in **6c** (τ 7.59) obviously arises when $R_1 = H$, since it is absent in **5c** (where $R_1 = D$). Accordingly, in the latter the proton ($R_2 = H$) has been assigned at τ 8.10.

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The Isolation and Structure Determination of Dictyopterenes C′ and D′ from *Dictyopteris*. Stereospecificity in the Cope Rearrangement of Dictyopterenes A and B

Sir:

The essential oil of *Dictyopteris*, one of the few genera of seaweed to possess odor, is composed of C_{11} hydrocarbons. Dictyopterene A [(+)-(*R*,*R*)-*trans*-1-(*trans*-hex-1′-enyl)-2-vinylcyclopropane (**1**)][1] and dictyopterene B [(−)-(*R*,*R*)-*trans*-1-(*trans*,*cis*-hexa-1′,3′-dienyl)-2-vinylcyclopropane (**2**)][2] are the major constituents and *trans*,*cis*,*cis*-undeca-1,3,5,8-tetraene (**3**),[2] *trans*,*trans*,*cis*-undeca-1,3,5,8-tetraene (**4**),[3] *trans*,*cis*-undeca-1,3,5-triene (**5**),[3] and *trans*-*trans*-undeca-1,3,5-triene (**6**)[3] are

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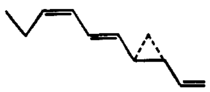
[1] R. E. Moore, J. A. Pettus, Jr., and M. S. Doty, *Tetrahedron Lett.*, 4787 (1968).

[2] J. A. Pettus, Jr., and R. E. Moore, *Chem. Commun.*, 1093 (1970).

found in smaller amounts. It has been suggested[2] that the biogenesis of the cyclopropane ring of the dictyopterenes involves a di-π-methane rearrangement.[4] Recently several compounds with sulfur attached to a linear C_{11} chain have been found in the nonvolatile extract of *Dictyopteris* and may be precursors of these hydrocarbons.[5]


1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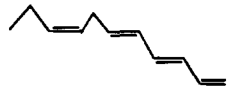
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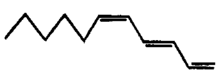
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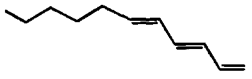
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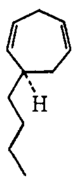
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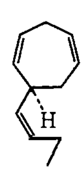
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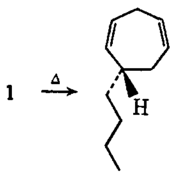
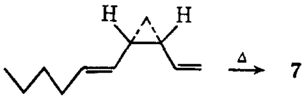
Fraction 2 from chromatography of the essential oil on 25% silver nitrate–silica gel[2] is a mixture of dictyopterene A (**1**) and still another C_{11} hydrocarbon, dictyopterene C′ [(−)-(*R*)-6-butylcyclohepta-1,4-diene (**7**)], separable by preparative gas chromatography. Natural **7**, $[\alpha]^{25}D$ −13° in $CHCl_3$, is identical in all respects, except optical properties, with the Cope rearrangement product **9** obtained by heating dictyopterene A at 170° for several hours.[6,7] Ozonolysis of **7** to (+)-(*R*)-butylsuccinic acid[8] establishes the configuration at C-6 in **7** as *R*.

It is highly improbable that **7** arises from Cope rearrangement of **1** *in vivo*. The Cope rearrangement of **1**, $[\alpha]^{25}D$ +72° in $CHCl_3$, occurs at a rather high temperature[9] and the product **9** differs from **7** not only in optical purity (*ca.* 16%)[10] but also in sign of optical rotation, $[\alpha]^{25}D$ +2.0° in $CHCl_3$. The configuration of C-6 in **9** is therefore predominately *S*.


9

Compound **7** is most likely the result of a concerted Cope rearrangement of dictyopterene C (**10**) in the plant, an isomerization reported to proceed at 15°.[6] Dictyopterene C itself has not been found in the essential oil.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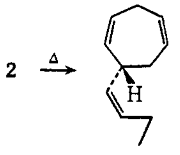
Fraction 6 (silver nitrate–silica gel chromatography) is a complex mixture from which a small amount of dictyopterene D′ [(+)-6-(*cis*-but-1′-enyl)cyclohepta-1,4-diene (**8**)] is obtained by gas chromatography. Compound **8**, which should have the *S* configuration at C-6 by analogy with **7**, is identical, except for optical properties, with the Cope rearrangement product **11** obtained by heating dictyopterene B at 90° for several hours.[11] Owing to the limited amount of material $[\alpha]D$ for **8** could not be measured precisely.[12]

The Cope rearrangement of **2**,[9] $[\alpha]^{25}D$ −43° in EtOH, also proceeds with stereospecificity as the product **11** has $[\alpha]^{25}D$ −24° in EtOH and should have predominately the *R* configuration at C-6 by analogy with **9**. The optical purity of **11**, however, remains to be determined, but preliminary results indicate that the optical purity of **11** is higher than **9** and hence **2** → **11** is a more stereospecific reaction than **1** → **9**.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(3) J. A. Pettus, Jr., and R. E. Moore, unpublished work. Reported at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstract No. ORGN 113.

(4) There is evidence [R. S. H. Liu and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 4936 (1967)] that the di-π-methane rearrangement of *cis,trans*-1,4,6-undecatriene to dictyopterene A *via* an excited singlet [H. E Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969); H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 1409 (1970)] or triplet may not proceed. *trans*-2,5,5-Trimethyl-1,3,6-heptatriene (artemisia triene) undergoes a facile di-π-methane rearrangement to *trans*-1-isopropenyl-2-vinyl-3,3-dimethylcyclopropane [T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Lett.*, 3895 (1970)] and it is proposed that the rearrangement proceeds *via* a triplet excitation and that the C_5-*gem*-dimethyl group provides the intermediate diradical with the proper stabilization.

(5) The isolation of undecan-3-onyl thiolacetate, diundecan-3-onyl disulfide, (−)-3-hexyl-4,5-dithiacycloheptanone, and *trans*-undec-4-en-3-onyl thiolacetate from *Dictyopteris* is described in P. Roller, K. Au, and R. E. Moore, *Chem. Commun.*, in press.

(6) G. Ohloff and W. Pickenhagen, *Helv. Chim. Acta*, **52**, 880 (1969).

(7) K. C. Das and B. Weinstein, *Tetrahedron Lett.*, 3459 (1969).

(8) M. Matel, *Ark. Kemi*, **5**, 17 (1953), and references therein.

(9) Preliminary data show that the Cope rearrangement of **1** → **9** proceeds at 140° ($t_{1/2}$ = 14 hr) and 173° ($t_{1/2}$ = 0.48 hr) with E_a = 37.4 kcal/mol whereas the Cope rearrangement of **2** → **11** proceeds at 70° ($t_{1/2}$ = 39 hr) and 92°($t_{1/2}$ = 2.9 hr) with E_a = 28.5 kcal/mol. Assuming that the intermediate is a diradical resulting from fission of the cyclopropane ring, the difference in activation energy for **1** → **9** and **2** → **11** (*ca.* 9 kcal) should reflect the difference in stabilization energy for the pentadienyl radical and allyl radical. Hitherto no data were available on the mechanism of the Cope rearrangement of *trans*-1,2-dialkenylcyclopropanes.

(10) Assuming the optical purity of **1** and **7** to be 100%.

(11) It has recently been reported [D. G. Müller, L. Jaenicke, M. Donike, and T. Akintori, *Science*, **171**, 815 (1971)] that 6-(*cis*-but-1′-enyl)cyclohepta-1,4-diene is the male-attracting substance produced by the female gametes of the brown alga *Ectocarpus siliculosus*. The optical properties of the sex attractant have not been reported.

(12) A specific rotation of +75° was obtained with a 1.6-mg sample of dictyopterene D′ contaminated with **11**. Nmr analysis of fraction 6 showed the presence of 5–10% dictyopterene B (relative to **8**) which presumably rearranges to **11** during the gas chromatography.

(13) NASA Predoctoral Fellow, 1970–1971.

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