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BIOGENETIC-TYPE SYNTHESIS OF (±)-DICTYOPTERENE A, AN ODORIFEROUS SUBSTANCE OBTAINED FROM BROWN SEAWEEDS, *DICTYOPTERIS*

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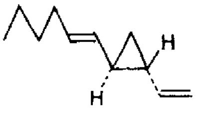
Abstract: Biogenetic-type synthesis of (±)-dictyopterene A (1) was achieved employing 1,*cis*-5-undecadien-3-ol (2) postulated to be a biosynthetic intermediate of 1: this synthesis means that transformation of dictyoprolene (4) into dictyopterene A (1) was formally made.

An odoriferous substance, dictyopterene A (1) belonging to a novel class of C_{11} hydrocarbons was isolated as one of the major constituents of the essential oils of the Hawaiian brown seaweeds (genus *Dictyopteris*).[1,2] Moore postulated that 1,*cis*-5-undecadien-3-ol (2) was a precursor for the biosynthesis of dictyopterene A (1), the former being converted to the latter as illustrated in 2A.[1,2] Moore's hypothesis was strongly supported by our recent isolation of (+)-dictyoprolene (4) from *Dictyopteris prolifera*, which was shown to be the (3*S*)-1,*cis*-5-undecadien-3-ol acetate (4).[3]

We herein report the biogenetic-type synthesis of (±)-dictyopterene A (1) employing 2 previously prepared in our laboratory during the synthesis of dictyoprolene (4).[3,4] The present synthesis means that transformation of dictyoprolene (4) into dictyopterene A (1) was formally accomplished, since 2 was obtained from 4 by methanolysis (NaOMe/MeOH). The crucial reaction in the present synthesis is the formation of a cyclopropane ring from 2 by biogenetically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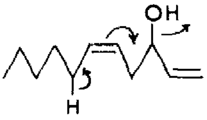
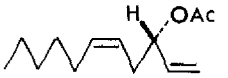
2, R = H
3, R = Ms


2A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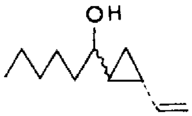
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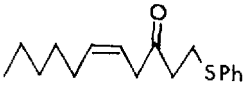
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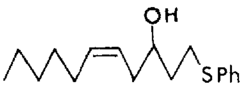
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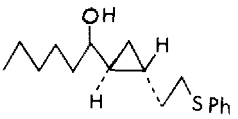
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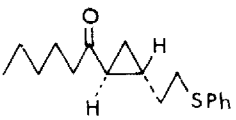
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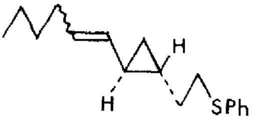
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patterned homoallyl - cyclopropylcarbinyl rearrangement, which was extensively examined under various conditions: the mesylate (**3**)[5] of **2** was solvolyzed (AcOK/acetone-H_2O (1:1), 80°C, 2.5 h), affording a cyclopropane compound (**5**)[5,6a,6b] only in 1.4% yield, other products being **2**[6a] (54%) and the rearranged alcohol (**6**)[5,6a,6b] (17%). It was therefore necessary to protect the terminal double bond in **2** prior to the cyclopropane-forming reaction.

Oxidation of **2** with pyridinium chlorochromate[7] (CH_2Cl_2, room temp., 1 h) gave a conjugated ketone (**7**)[5,6a] (41%). The Michael addition of thiophenol to **7** (toluene, 0°C, 15 min.) afforded a keto sulfide (**8**)[5,6a] (42%), which was reduced with $NaBH_4$ (MeOH, 0°C, 30 min.), producing a hydroxy sulfide (**9**)[5,6a,8] (92%). The terminal double bond of **2** was thus protected. The hydroxy sulfide (**9**) was mesylated (MsCl/Py, 0°C, 1 h) and the crude mesylate[5] was subjected to solvolysis under a variety of conditions: the mesylate was converted under the particular conditions (AcOK/acetone-H_2O (1:1), 80°C, 20 h) to a mixture of two stereoisomeric cyclopropylcarbinols, (**10a**)[5,6a,8] (64%) and (**10b**)[5,6a,8] (27%). Based on the fact that the mild oxidation of two stereoisomers (**10a** and **10b**) with MnO_2 (CH_2Cl_2, 50°C, 2 h) afforded a single ketone (**11**),[5,6a] the two compounds are shown to be diastereomeric at the carbon bearing the hydroxyl group. Since the cyclopropylcarbinols (**10**) are labile under acidic conditions, giving homoallylic derivatives, dehydration of **10** was examined under neutral or basic conditions. On treatment of **10** with (carboxysulfamoyl)triethylammonium hydroxide inner salt methyl ester ($\mathrm{MeOOC}\text{-}\bar{\mathrm{N}}\mathrm{SO_2}\overset{+}{\mathrm{N}}\mathrm{Et_3}$)[9] and NaH in DME (room temp., 5 h then 80°C, 12 h) dehydration of **10** occurred to give a *ca.* 1:1 mixture[10] of *trans*- and *cis*-olefins (**12a**[5,6c,8] and **12b**[5,6c,8]) (14%). Elimination of thiophenol from **12** was effected under conditions developed by Vedejs[11] ($CF_3SO_3CH_2COOEt$/MeCN, room temp., 20 h → DBU/DMF, 50°C, 3 h), affording a mixture of **1** and its geometrical isomer (86%). The mixture was separated by column chromatography on silica gel impregnated with $AgNO_3$ (9:1 pentane-ether), giving pure (±)-dictyopterene A (**1**),[8] identical with natural specimen by spectral and chromatographic comparison.

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REFERENCES AND NOTES

1. (a) R. E. Moore, *Lloydia*, **39**, 181 (1976). (b) R. E. Moore, *Acc. Chem. Res.*, **10**, 40 (1977).
2. R. E. Moore, J. A. Pettus, Jr., and J. Mistysyn, *J. Org. Chem.*, **39**, 2201 (1974).
3. K. Yamada, H. Tan, and H. Tatematsu, *J. C. S. Chem. Comm.*, 572 (1979).
4. Previous synthesis of dictyopterene A without biogentic consideration:
   (a) G. Ohloff and W. Pickenhagen, *Helv. Chim. Acta*, **52**, 880 (1969). (b) K. Das and B. Weinstein, *Tetrahedron Lett.*, 3459 (1969). (c) W. E. Billups, W. Y. Chow, and J. H. Cross, *J. C. S. Chem. Comm.*, 252 (1974).
5. This oily compound had IR, NMR, and mass spectra in agreement with the structure assigned.
6. Purified by plc on silica gel with (a) $CHCl_3$; (b) 1:1 hexane-ether; (c) hexane.
7. E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975).
8. Satisfactory exact mass spectral data were obtained.
9. E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *J. Org. Chem.*, **38**, 26 (1973).
10. Each isomer (**10a** and **10b**) was dehydrated to give a *ca.* 1:1 mixture of **12**, respectively, indicating that the stereochemistry of the hydroxyl group in **10** does not affect the ratio of isomers of **12**.
11. E. Vedejs and D. A. Engler, *Tetrahedron Lett.*, 3487 (1976).

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