CHEMISTRY LETTERS, pp. 1633-1634, 1980. © The Chemical Society of Japan 1980

ISOLATION AND STRUCTURE OF NEODICTYOPROLENE, A NEW C_{11}-COMPOUND OF BIOGENETIC SIGNIFICANCE FROM A BROWN ALGA *DICTYOPTERIS PROLIFERA*

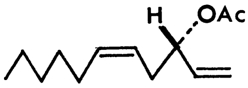
Kiyoyuki YAMADA,* Makoto OJIKA, and Hiroaki TAN
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

Neodictyoprolene isolated as a trace component of a brown alga *Dictyopteris prolifera* was shown to be the acetate of *cis*, *cis*-1,5,8-undecatrien-3-ol postulated to be a pivotal biosynthetic intermediate leading to biologically active C_{11}-substances such as sex attractants of brown algae (*e.g.*, ectocarpene).

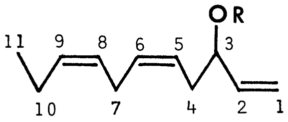
Some of the brown algae (*e.g.*, *Dictyopteris*, *Ectocarpus*, and *Cutleria*) have been known to contain various C_{11}-hydrocarbons[1] and related compounds.[2] Examination of the structures of these compounds led Moore to propose a hypothesis that three kinds of undec-1-en-3-ols derived from oleic, linoleic, and linolenic acid, respectively, were precursors in the biosynthesis of these C_{11}-compounds.[3,4] Recently we have reported the isolation of dictyoprolene (1)[5] from *Dictyopteris prolifera*, which was proved to be the acetate of one of the undec-1-en-3-ols postulated by Moore.

We describe herein the isolation and the structure of a trace component of *Dictyopteris prolifera*, neodictyoprolene (2) structurally related to dictyoprolene (1). Isolation of neodictyoprolene (2) is of particular significance from the biogenetic viewpoint, because some of the novel C_{11}-substances such as sex attractants of brown algae [ectocarpene (6) and multifidene] and an odoriferous compound dictyopterene B (5), which was also found in *Dictyopteris prolifera* (0.001% based on the weight of fresh wet alga) in the present study, have been postulated to be biosynthesized from the desacetyl compound (3) of neodictyoprolene (2) as depicted (3 → 5 and 3 → 6).[3,4]

The acetone extracts of the fresh alga were treated with hexane and the hexane-soluble portion was chromatographed on silica gel with chloroform. Early fractions (R_f values 0.7-0.9 on silica gel TLC (Merck, No. 5715) with $CHCl_3$) were further separated by repeating preparative TLC [(i) silica gel, $CHCl_3$-hexane (1:1), four times: (ii) silica gel impregnated with $AgNO_3$, EtOAc-hexane (1:6)] to give neodictyoprolene (2)[6,7] (0.000004% based on the weight of fresh wet alga), $C_{13}H_{20}O_2$, as colorless liquid: IR ($CHCl_3$) 3020 (olefinic ν_{C-H}), 1730 (acetate C=O), 1243 (acetate C-O) cm^{-1}; ^1H-NMR (90 MHz, $CDCl_3$) δ 0.96 (3H, t, J = 7.5 Hz, H-11), 2.05 (3H, s, OAc), 1.9-2.2 (2H, m, H-10), 2.42 (2H, dd, J = 6.5, 6.5 Hz, H-4), 2.79 (2H, dd, J = 5.5, 5.5 Hz, H-7), 5.1-5.6 (7H, complex pattern, H-1, H-3, H-5, H-6, H-8, H-9), 5.84 (1H, ddd, J = 17.0, 10.0, 5.5 Hz, H-2);

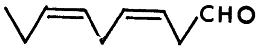


1

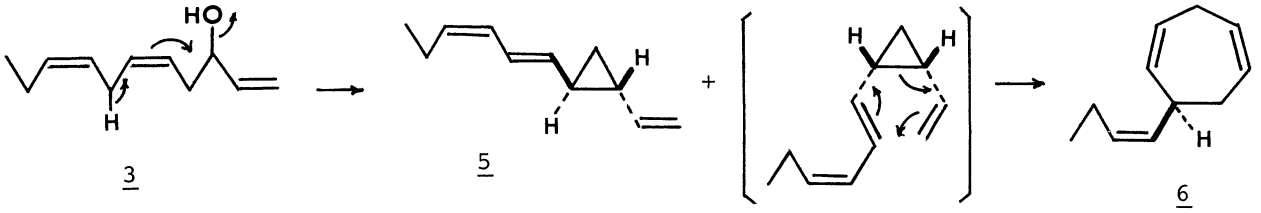


2, R = Ac

3, R = H



4



MS (70 eV), m/e (rel intensity) 208 (M$^+$, 5), 148 (M$^+$ - AcOH, 15), 99 (CH_2=CH-$\overset{+}{C}$H-OAc, 31), 43 (Ac, 100). Based on the comparison of the spectral data of neodictyoprolene (2) with those of dictyoprolene (1), the structure of the former was deduced to be (2), which was unambiguously confirmed by synthesis. The reaction of cis, cis-3,6-nonadienal (4)[8] with vinylmagnesium bromide (THF, 0°C, 25 min) afforded a hydroxy triene (3)[6,9] as a pale yellow oil [10%, after purification by preparative TLC (silica gel, $CHCl_3$-EtOAc (15:1)]. Acetylation of (3) with acetic anhydride and pyridine (room temp., 10 h) followed by purification by preparative TLC (silica gel, $CHCl_3$) gave an acetate[6] (98%), which was shown to be identical with natural neodictyoprolene (2) by spectral (IR, ^{1}H-NMR, and MS) and chromatographic comparison.[10]

REFERENCES AND NOTES

1. (a) R. E. Moore, J. A. Pettus, Jr., and M. S. Doty, Tetrahedron Lett., 1968, 4787; (b) J. A. Pettus, Jr. and R. E. Moore, Chem. Comm., 1970, 1093; (c) J. A. Pettus, Jr. and R. E. Moore, J. Am. Chem. Soc., 93, 3087 (1971); (d) D. G. Müller, L. Jaenicke, M. Donike, and T. Akintobi, Science, 171, 815 (1971); (e) L. Jaenicke, D. G. Müller, and R. E. Moore, J. Am. Chem. Soc., 96, 3324 (1974); (f) R. E. Moore, J. A. Pettus, Jr., and J. Mistysyn, J. Org. Chem., 39, 2201 (1974).
2. (a) P. Roller, K. Au, and R. E. Moore, Chem. Comm., 1971, 503; (b) R. E. Moore, ibid., 1971, 1168; (c) R. E. Moore, J. Mistysyn, and J. A. Pettus, Jr., J.C.S. Chem. Comm., 1972, 326; (d) R. E. Moore and G. Yost, ibid., 1973, 937.
3. R. E. Moore, Lloydia, 39, 181 (1976).
4. R. E. Moore, Acc. Chem. Res., 10, 40 (1977).
5. K. Yamada, H. Tan, and H. Tatematsu, J.C.S. Chem. Comm., 1979, 572.
6. Satisfactory exact mass spectral data were obtained.
7. Chiroptical data ($[\alpha]_D$ and CD) of neodictyoprolene (2) could not be obtained, because the isolated amount of 2 (0.8 mg from ca. 20 kg of fresh wet alga) was too minute to measure these properties.
8. T. Kajiwara, Y. Odake, and A. Hatanaka, Agr. Biol. Chem., 39, 1617 (1975).
9. This compound had IR, ^{1}H-NMR, and mass spectra in agreement with the structure assigned.
10. Financial support from the Ministry of Education, Science, and Culture (Grant-in-Aid for Scientific Research No. 447025) is gratefully acknowledged.

(Received September 25, 1980)