Tetrahedron Letters, Vol.22, No.41, pp 4087 - 4088, 1981
Printed in Great Britain

0040-4039/81/414087-02$02.00/0

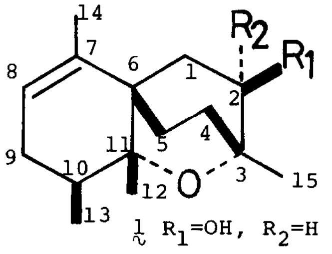
STRUCTURE OF SPIRONIPPOL, A NEW SESQUITERPENE, FROM THE RED ALGA LAURENCIA NIPPONICA YAMADA

Akio Fukuzawa, Chie Ming Shea, Tadashi Masamune,* Akio Furusaki,
Chuji Katayama,† and Takeshi Matsumoto
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060, Japan
†Department of Chemistry, Faculty of Science, Nagoya University,
Chikusa-ku, Nagoya 464, Japan

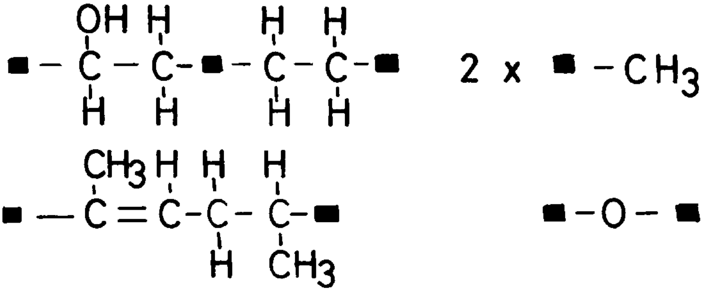
Abstract   A new sesquiterpene, designated as spironippol, was isolated from the title alga. The structure, which was determined on the basis of the spectral data and X-ray crystallography, represents the biogenetic transition between chamigrane and perforane sesquiterpenes.

In a continuing study[1] on components of the red alga Laurencia nipponica Yamada, we isolated a new sesquiterpene, designated as spironippol, from the neutral oil of methanol extracts of the alga, collected at Pon-Oshoro Bay (outside Oshoro Bay) in late June, in 0.11% yield along with laurallene.[2] The sesquiterpene consists of a 3,7,10,11-tetramethylspiro[5,5]dodecane skeleton and is regarded as a biogenetic intermediate in the transition from chamigrane into perforane sesquiterpenes.

Spironippol (1), mp 135-136 °C, $[\alpha]_D$ +59.1, had molecular formula $C_{15}H_{24}O_2$ [m/e 236.178 (M^+)] and gave the corresponding monoacetate (2) and ketone (3) on acetylation and oxidation, respectively. The IR, and the ^1H and ^{13}C NMR spectra of 1 ∿ 3,[3] coupled with decoupling experiments of the ^1H NMR spectra of 1 in the presence of the shift reagent Eu(fod)$_3$,[4] revealed the following partial structures. While a combination of these structural units had narrowed the probable structure for 1 into a few formulas, the complete structure (relative configuration) was elucidated by the X-ray crystallography.



1 R_1=OH, R_2=H
2 R_1=OAc, R_2=H
3 R_1,R_2=O



The X-ray measurement was made at about -20 °C. The crystal data of **1** were as follows: $C_{15}H_{24}O_2$, orthorhombic, space group $P2_12_12_1$, a = 10.384(1), b = 18.645(2), c = 6.879(5) Å, Z = 4, D_c = 1.179 g cm^{-3}. 1302 unique intensity data for $2\theta < 130°$ were collected on a Rigaku four-circle diffractometer with graphite-monochromated CuKα radiation. The structure was elucidated by the Monte Carlo direct method,[5] using the 15 strongest reflections as the starting set. The final R value was 0.040. The molecular skeleton of **1** thus obtained is shown in Fig. 1.[6]

In view of the co-ocurrence of 10-bromo-α-chamigrene[7] and its 2,3-epoxide[8] (**4**) in the same alga <u>L</u>. <u>nipponica</u> (collected at Oshoro Bay) as well as the proposed biogenesis of perforane sesquiterpenes,[9] spironippol would be formed biogenetically by migration of one of geminal methyl groups of a hypothetical glycol (**5**) as shown in Scheme 1, implying that the absolute configuration would be represented by formula **1**.

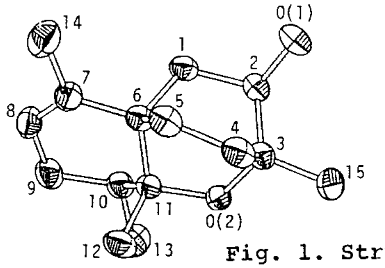
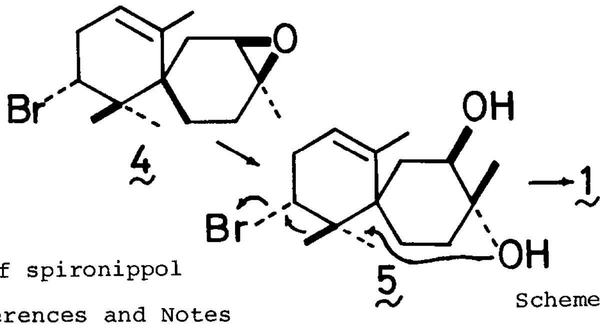


Fig. 1. Structure of spironippol



Scheme 1

References and Notes

1. A. Fukuzawa and E. Kurosawa, Tetrahedron Lett., <u>1980</u>, 1471.
2. A. Fukuzawa and E. Kurosawa, Tetrahedron Lett., <u>1979</u>, 2797.
3. **1**: IR ($CHCl_3$), 3425 and 1062 cm^{-1}; ^1H NMR ($CDCl_3$), δ 0.92 (3H, d, J = 6 Hz), 1.09, 1.12, and 1.58 (each 3H, s), 1.64 (1H, s, OH), 2.27 (1H, ddd, J = 14, 10, and 3 Hz, 1-H), 3.67 (1H, br d, J = 10 Hz, -C<u>H</u>OH), and 5.18 (1H, br d, J = 4 Hz); ^{13}C NMR ($CDCl_3$), δ 14.3, 17.1, 18.5, 24.0 (each q), 24.8, 26.1, 33.4 (each t), 33.8 (d), 39.9 (s), 41.5 (t), 71.5 (s), 71.8 (d), 76.5 (s), 121.3 (d), and 138.1 (s). **2**: IR ($CHCl_3$) 1722 and 1280 cm^{-1}; ^1H NMR, δ 2.04 (3H, s) and 4.62 (1H, br dd, J = 10 and 3 Hz); MS, m/e 278 (M^+). **3**: IR ($CHCl_3$), 1736 cm^{-1}; ^1H NMR, δ 2.37 (1H, d, J = 18 Hz, 1-H) and 2.56 (1H, dd, J = 18 and 4 Hz); MS, m/e 234.162 (M^+).
4. The details will be described in a full paper.
5. A. Furusaki, Acta Crystallogr., Sect. A, <u>35</u>, 220 (1979).
6. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center.
7. B. M. Howard and W. Fenical, Tetrahedron Lett., <u>1976</u>, 2519.
8. M. Suzuki, A. Furusaki, and E. Kurosawa, Tetrahedron, <u>35</u>, 823 (1979).
9. A. G. González, J. M. Aguir, J. D. Martin, and M. Norte, Tetrahedron Lett., <u>1975</u>, 2499; A. G. González, J. Darias, and J. D. Martin, ibid., <u>1977</u>, 3375.

(Received in Japan 15 June 1981)