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LAURENONES A AND B, NEW SESQUITERPENES, FROM THE RED ALGA *LAURENCIA NIPPONICA* YAMADA

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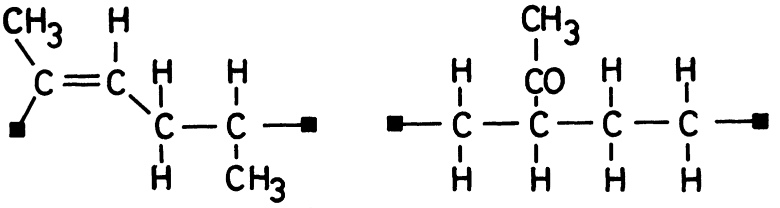
The structure of two new sesquiterpenes, isolated from the title alga and named laurenones A and B, was determined on the basis of the X-ray crystallography as well as the spectral data.

In a continuing study[1)] on components of the red alga *Laurencia nipponica* Yamada, we isolated new sesquiterpenes, designated as laurenones A and B, from the neutral oil of methanol extracts of the alga, collected at Oshoro Bay (*inside* Oshoro Bay) early in July (1981), in 0.0025 and 0.0017% yields (from the wet alga) along with laurallene[2)] (0.04%) and laureatin[3)] (0.007%).[4)] These sesquiterpenes possess a new skeleton, 2-ethyl-6,7,10-trimethylspiro[4.5]decane, and are regarded as biogenetic transformation products of spirolaurenone[5)] (**1**). We report herein the structure of these compounds.

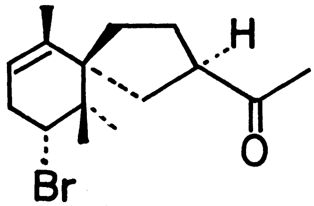
Laurenone A (**2**), colorless oil, $[\alpha]_D$ +152° ($CHCl_3$), had molecular formula $C_{15}H_{24}O_2$ [m/z 236.1764 (M^+)]. The IR, and the ^1H and ^{13}C NMR spectra of **2**,[6)] coupled with the decoupling experiments of the ^1H NMR spectra in the presence of the shift reagent $Eu(fod)_3$,[7)] revealed the partial structures described below. While a combination of these structural units, combined with close resemblance between the mass spectra of **2** and debromospirolaurenone,[5)] narrowed the probable structures for **2** into a few formulas, the complete structure (relative configuration) was reduced from the X-ray crystallography. Hydride reduction ($LiAlH_4$ in ether) of **2** afforded two glycols (**3**), mp 109.5-110.5 °C, $[\alpha]_D$ +72.0°, and (**4**), mp 106-107 °C, $[\alpha]_D$ +94.5°. The X-ray measurement of **3** was made at about -20 °C. The crystal data of **3** were as follows: $C_{15}H_{26}O_2$, monoclinic, space group $P2_1$, a = 10.918(3), b = 7.559(1), c = 8.707(2) Å, β = 91.03(4)°, Z = 2, D_c = 1.102 g cm^{-3}. The intensities of 1243 independent reflections (2Θ < 126°) were collected on a Rigaku four-circle diffractometer with graphite-monochromated Cu Kα radiation. The structure was solved by the Monte Carlo direct method,[8)] using the 15 strongest reflections as the starting set. The final R value was 0.041. The molecular framework thus obtained is illustrated in Fig. 1. It follows that laurenone A is represented by formula **2** or its enantiomer. The absolute configuration was determined as shown by formula **2** by transformation of **1** into **2** (21%) on acid treatment [1 M HCl and MeOH (1:1), 50 °C, 20 h].

Laurenone B (5), colorless oil, $[\alpha]_D$ +58.2° ($CHCl_3$), had the same molecular formula $C_{15}H_{24}O_2$ [m/z 236.1770 (M^+)] as 2. The IR, and the ^1H (in the absence and presence of the shift reagent)$^{7)}$ and ^{13}C NMR spectra$^{6)}$ indicated that 5 contained the same partial structures as 2, suggesting that 5 would be a C-2 epimer of 2. In fact, treatment of 5 with acid (p-TsOH in C_6H_6, room temperature, 0.5 h) gave 2 in moderate yield. The equlibrium ratio of 2 and 5 under the acidic conditions was 10:1.$^{9)}$ These facts indicate that laurenone B is represented by formula 5.



■— CH_3 ■— OH

Partial Structures



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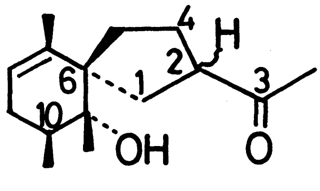

2 2β-H

5 2α-H

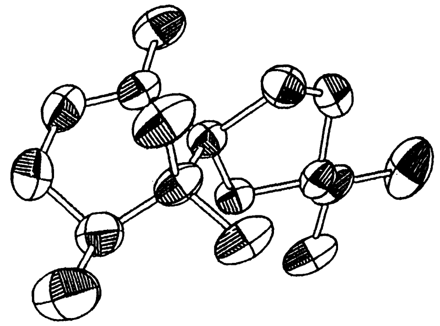

Fig. 1.

References

1) A. Fukuzawa, C. M. Shea, T. Masamune, A. Furusaki, C. Katayama, and T. Matsumoto, Tetrahedron Lett., 22, 4087 (1981).

2) A. Fukuzawa and E. Kurosawa, Tetrahedron Lett., 1979, 2797.

3) T. Irie, M. Izawa, and E. Kurosawa, Tetrahedron, 26, 851 (1970).

4) Spironippol was not isolated from this alga; *cf.*, Ref. 1.

5) M. Suzuki, N. Kowata, and E. Kurosawa, Tetrahedron, 36, 1551 (1980); A. Murai, K. Kato, and T. Masamune, Tetrahedron Lett., 23, 2887 (1982).

6) 2: MS, m/z 236, 218, 175, 164 (base), 149, and 121; IR ($CHCl_3$), 3500, 1710, 1175, 1095, and 990 cm^{-1}; ^1H NMR ($CDCl_3$), δ 0.96 (3H, d, J = 6.4 Hz), 0.98 (3H, s), 1.69 (3H, br s), 2.16 (3H, s), 2.21 (1H, dd, J = 14 and 8 Hz), 2.90 (1H, m), and 5.15 (1H, br s); ^{13}C NMR ($CDCl_3$), δ 14.7, 16.8, 19.6, and 29.2 (each q), 30.9, 31.6, and 33.5 (each t), 35.2 (d), 38.4 (t), 54.2 (d), 54.9 (s), 76.7 (s), 120.2 (d), 140.8 (s), and 210.8 (s). 5: MS, m/z 236, 218, 175, 164 (base), 149, and 121; IR ($CHCl_3$), 3500, 1705, 1170, 1125, and 990 cm^{-1}; ^1H NMR ($CDCl_3$), δ 0.95 (3H, s), 0.96 (3H, d, J = 6.8 Hz), 1.69 (3H, br s), 2.17 (3H, s), 2.40 (1H, dd, J = 14 and 4 Hz), 2.99 (1H, m), and 5.16 (1H, br s); ^{13}C NMR ($CDCl_3$), δ 14.9, 17.0, 20.5, and 28.3 (each q), 29.7, 30.0, and 35.5 (each t), 37.2 (t), 52.5 (d), 56.2 (s), 120.5 (d), 140.6 (s), and 211.8 (s).

7) The details will be described in a full paper.

8) A. Furusaki, Acta Crystallogr., Sect. A, 35, 220 (1979).

9) The possibility that 2 may be a product formed by epimerization of 5 during isolation process is not completely eliminated.

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