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ISOLATION AND STRUCTURES OF TRANS-LAURENCENYNE, A POSSIBLE PRECURSOR OF THE C_{15} HALOGENATED CYCLIC ETHERS, AND TRANS-NEOLAURENCENYNE FROM LAURENCIA OKAMURAI

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Abstract: Isolation and structural elucidation of two new acetylenic polyenes, trans-laurencenyne 1 and trans-neolaurencenyne 2 from the marine red alga Laurencia okamurai were carried out, the former compound 1 very recently being proposed to be a biosynthetic precursor of the C_{15} halogenated cyclic ethers, 7 and 8.

The marine red algae of the genus Laurencia have been known as rich sources of a variety of acetylenic halogenated cyclic ethers, the carbon skeleton of which consisted of pentadec-3-en-1-yne. Previously, trans- and cis-laurediols, 5 and 6 from Laurencia nipponica were reported as possible biosynthetic precursors of these halogenated cyclic ethers.[1] Very recently we have isolated laurencenyne 3[2] from Laurencia okamurai, which may be regarded as an intermediate in the earlier stage of the biosynthetic pathway for various cyclic ethers than laurediols, 5 and 6.

In this paper we describe the isolation and structures of two new acetylenic polyenes, trans-laurencenyne 1 and trans-neolaurencenyne 2 from L. okamurai collected off the coast of Goza, Mie Prefecture, Japan in July. Isolation of trans-laurencenyne 1 is particularly significant, because Fukuzawa and Masamume quite recently described concerning the biogenesis of laurepinnacin 7 and isolaurepinnacin 8 that these two cyclic ethers, 7 and 8 could not be formed from laurediol 5 but must be derived from a new, hypothetical precursor 1 from the viewpoint of the stereostructures of 7 and 8.[3] Thus the isolation of 1 from L. okamurai strongly supports the validity of the biogenesis of the C_{15} cyclic ethers, 7 and 8, proposed by Masamume.[3]

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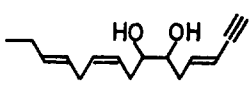

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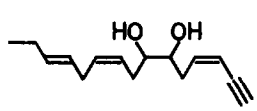

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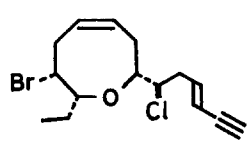

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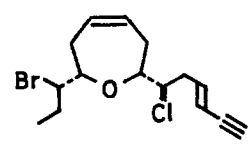

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The EtOAc-soluble fraction of the acetone extract of fresh L. okamurai was chromatographed on silica gel. The eluate from hexane was separated repeatedly by preparative TLC (silica gel, hexane) to give trans-laurencenyne 1 (0.0005%) and trans-neolaurencenyne 2 (0.0004%), which were further purified by preparative GLC[4], affording pure 1[5] and 2[6].

trans-Laurencenyne 1:[7] colorless liquid, $C_{15}H_{20}$; UV (MeOH) nm (ε) 223 (13,400); IR (film) cm^{-1} 3300 (acetylenic ν_{C-H}), 3010 (olefinic ν_{C-H}), 2170 ($\nu_{C\equiv C}$), 1650 and 1630 ($\nu_{C=C}$), 960 (δ_{C-H}, trans -CH=CH-); ^{1}H-NMR (90 MHz, $CDCl_3$) δ 0.98 (3H, t, J=7.5 Hz, H-15), 2.07 (2H, m, H-14), 2.6 - 3.0 (7H, m, H-1, H-5, H-8, H-11), 5.1 - 5.7 (7H, m, H-3, H-6, H-7, H-9, H-10, H-12, H-13), 6.25 (1H, dt, J=16.0, 6.5 Hz, H-4); ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ 14.3 (q), 20.6 (t), 25.6 (t), 25.6 (t), 30.6 (t), 76.2 (d), 82.4 (s), 109.1 (d), 125.4 (d), 127.0 (d), 127.5 (d), 128.8 (d), 130.2 (d), 132.1 (d), 144.2 (d); MS (m/e) 200 (M^+).

trans-Neolaurencenyne 2:[7] colorless liquid, $C_{15}H_{22}$; UV (MeOH) nm (ε) 223 (15,100); IR (film) cm^{-1} 3300 (acetylenic ν_{C-H}), 3010 (olefinic ν_{C-H}), 2150 ($\nu_{C\equiv C}$), 1650 and 1625 ($\nu_{C=C}$), 960 (δ_{C-H}, trans -CH=CH-); ^{1}H-NMR (90 MHz, $CDCl_3$) δ 0.89 (3H, br.t, J=6.0 Hz, H-15), 1.1 - 1.6 (6H, m, H-12, H-13, H-14), 2.03 (2H, m, H-11), 2.6 - 3.0 (5H, m, H-1, H-5, H-8), 5.1 - 5.7 (5H, m, H-3, H-6, H-7, H-9, H-10), 6.25 (1H, dt, J=16.0, 6.5 Hz, H-4); ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ 14.0(q), 22.6 (t), 25.6 (t), 27.2 (t), 29.3 (t), 30.6 (t), 31.5 (t), 76.2 (d), 82.4 (s), 108.9 (d), 125.0 (d), 127.1 (d), 130.6 (d), 130.7 (d), 144.3 (d); MS (m/e) 202 (M^+).

Similarity of the spectral properties of the compound 1 and laurencenyne 3[2] together with the fact that both compounds possessed the identical molecular formula indicated that 1 was a geometrical isomer of 3. The compound 1 showed a very strong band at 960 cm^{-1} in the IR spectrum and a characteristic signal at δ 6.25 (1H, dt, J=16.0, 6.5 Hz) in the ^{1}H-NMR spectrum, suggesting that 1 was a trans isomer at C-3 of 3. The structure of the compound 1 was unambiguously established as the C-3 trans isomer of laurencenyne by comparison of the spectral properties of natural 1 with those of authentic 1, the latter being synthesized[2] in our laboratory in connection with the structural study of laurencenyne 3. Based on the comparison of the spectral behaviors of the compound 2 and neolaurencenyne 4[2], 2 was deduced to be the trans isomer at C-3 of 4. This inference was confirmed by the finding that the spectral data of 2 were identical with those of the synthetic C-3 trans isomer of neolaurencenyne, which was obtained as a minor product in the synthesis of neolaurencenyne 4.

It is noteworthy that trans-laurencenyne 1 and trans-neolaurencenyne 2 occur together with laurencenyne 3 and neolaurencenyne 4 in L. okamurai in view of the biogenesis of the C_{15} halogenated cyclic ethers.

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REFERENCES AND NOTES

1. E. Kurosawa, A. Fukuzawa, and T. Irie, Tetrahedron Lett., 2121 (1972).
2. H. Kigoshi, Y. Shizuri, H. Niwa, and K. Yamada, Tetrahedron Lett., 22, 4729 (1981).
3. A. Fukuzawa and T. Masamune, Tetrahedron Lett., 22, 4081 (1981).
4. Conditions: a column of 6 mm x 1.5 m of 10% SILAR 10C, 135 °C, He flow rate 65.5 ml/min.
5. The retention time was 9.2 min. under the conditions employed.[4]
6. The retention time was 6.4 min. under the conditions employed.[4]
7. Satisfactory exact mass spectral data were obtained.

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