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CEMBRENENE AND MAYOL, TWO NEW CEMBRANOID DITERPENES FROM THE SOFT CORAL *SINULARIA MAYI*

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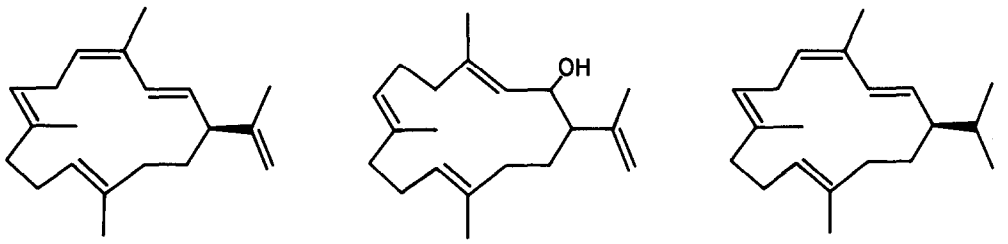
Summary: Two new cembranoid diterpenes, cembrenene (1) and mayol (2), have been isolated from *Sinularia mayi* Lütschw, along with the first reported cembrene (3) from marine organism. The structures were determined from spectral data and chemical transformations.

Among numerous cembranoid diterpenes isolated from marine organisms,[1a~c] the parent hydrocarbon cembrene itself has not been reported to date from marine sources. In this communication, we report the occurrence of cembrene, and isolation of a new simple cembrene derivative (1) and an oxygenated cembranoid (2), named cembrenene and mayol, respectively, from a soft coral, *Sinularia mayi*, collected around the Yayeyama islands, Japan. Silica gel chromatography of the dichloromethane-soluble material from the methanol extracts of the soft coral, followed by preparative TLC, gave two new cembranoid diterpenes (1) and (2), along with (-)-cembrene (3).

Cembrenene (1) is an oil, $C_{20}H_{30}$ ($M^{+\cdot}$ 270.2384, calc. 270.2346), $\{\alpha\}_D$ +78.1°($CHCl_3$). Since the ^{13}C NMR ($CDCl_3$) spectrum exhibited the presence of five double bonds (ten sp^2 carbons: δ 149.7s, 135.1s, 132.3s, 131.4s, 130.5d, 130.5d, 126.7d, 126.3d, 126.3d, 108.8t) and ten saturated carbons (δ 49.0d, 38.9t, 36.4t, 29.1t, 26.3t, 23.5t, 21.5q, 19.8q, 14.4q, 14.4q), and (1) has six degrees of unsaturation, it was assigned a monocyclic 14-membered ring of the cembrane skeleton. The IR (CCl_4) and ^1H NMR ($CDCl_3$) spectra of (1) indicated the presence of an isopropenyl group (ν 3090, 1645, 899 cm^{-1}; δ 1.71, 3H, t, J=1.5Hz, 4.69, 2H, octet, J=1.5), which was confirmed by NMDR experiment, three methyl groups attached to trisubstituted double bonds (3H: δ 1.52, br s, 1.60, t, J=1.0, 1.79, t, J=1.0. 1H: δ 4.92, br d, J=6.0, 5.11, br d, J=10.0, 5.56, br t, J=7.0), and a *trans*-disubstituted double bond (ν 1670, 975 cm^{-1}; δ 5.24, dd, J=16.0 and 9.0, 6.18, d, J=16.0) whose low field shifts indicated that it was a part of a conjugated diene system. Comparison of the ^1H and ^{13}C NMR spectra of (1) with those of cembrene (3)[2] showed a close similarity and indicated that (1) contained an isopropenyl group instead of the isopropyl group of cembrene (3). Thus, formula (1) was proposed for cembrenene whose four double bonds of 14-membered ring had the same geometry as cembrene double bonds (3). Hydrogenation of (1) over 5% Pd-C in AcOEt afforded a dihydro-derivative, $C_{20}H_{32}$ ($M^{+\cdot}$ 272), resulting from 1,4-addition of hydrogen to the conjugated double bond, and a slight amount of tetrahydro-derivative, $C_{20}H_{34}$ ($M^{+\cdot}$ 274). The former dihydro compound was identical with cembrene-A by comparison of the IR and



(1) (2) (3)

^{1}H NMR spectra, and also shown to have structure antipodal to that from terrestrial source[1c] because of its positive rotation, $\{\alpha\}_D$ +15.3°($CHCl_3$). Hence, the structure and absolute configuration of cembrenene should be represented by formula (1).

The second oily compound mayol (2), $C_{20}H_{32}O$ ($M^{+\cdot}$ 288.2488, calc. 288.2451), $\{\alpha\}_D$ +138.5°($CHCl_3$), on acetylation (Ac_2O/Py), gave a monoacetate (4), $C_{22}H_{34}O_2$ ($M^{+\cdot}$ 330), $\{\alpha\}_D$ +76.3°($CHCl_3$). Like cembrenene (1), the ^{1}H and ^{13}C NMR spectra suggested that mayol (2) was a monocyclic 14-membered ring of cembrane skeleton. Fortunately, the IR and ^{1}H NMR spectra of (2) and (4) showed a good correspondence to those of reported data of synthetic intermediates[3] for a termite trail pheromone, neocembrene (cembrene-A), and the structure (2), which had a *cis*-relationship between the hydroxyl and vicinal isopropenyl groups, was determined for mayol by spectral coincidence with the synthetic compound, although the absolute configuration of mayol (2) have not been established because of limited amount material available.

It is noteworthy that cembrenene (1) and cembrene (3) isolated in this work are shown to be the antipodal memberes of cembranoids to those of terrestrial source,[1c] as well as the sesquiterpenes[4] from the soft coral *Sinularia mayi* from Indonesia.

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2. (3): mp 59.0-60.0°; $\{\alpha\}_D$ -136.6°($CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.83 and 0.87 (each 3H, d, J=7.0), 1.50 (3H, br s), 1.59 (3H, t, J=1.0), 1.79 (3H, t, J=1.5), 4.89 (1H, br d, J=6.0), 5.11 (1H, br d, J=10.0), 5.17 (1H, dd, J=15.5 and 9.0), 5.53 (1H, br t, J=7.0), 6.09 (1H, d, J=15.5); ^{13}C NMR ($CDCl_3$): δ 135.3s, 132.6s, 131.2s, 131.1d, 130.5d, 126.6d, 125.9d, 125.5d, 48.3d, 38.9t, 36.6t, 32.9d, 27.9t, 26.3t, 23.6t, 20.9q, 19.9q, 19.9q, 14.4q, 14.4q.
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