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The Absolute Stereochemistry of Okamurallene and Its Congeners, Halogenated C_{15} Nonterpenoids from the Red Alga *Laurencia intricata*[1]

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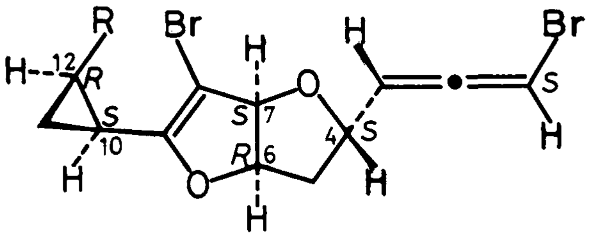
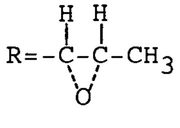
The absolute stereochemistry of okamurallene and the related metabolites, unusual C_{15} nonterpenoid bromoallenes from the red alga *Laurencia intricata* Lamouroux, were established by X-ray crystallographic analysis as well as chemical and spectral evidence.

During our continuing studies on halogenated metabolites from the red algae of the genus *Laurencia* (Rhodomelaceae; Rhodophyta), we reported in previous papers[2,3] structures of okamurallene (1), deoxyokamurallene (2), and isookamurallene (3) on the basis of spectroscopic evidence. However, further structure elucidation of those compounds by means of modern NMR technique (^1H-^1H, ^1H-^{13}C, and ^{13}C-^{13}C COSY and NOE spectra) indicated that the 2,7-dioxabicyclo[4.2.0]octene skeleton became questionable and should be revised to 2,6-dioxabicyclo[3.3.0]octene one.[4] In the revised structure of okamurallene (1), however, the relative configurations between C-3/C4, C-6/C-10, and C-12/C-13 remained to be resolved. Thus, in order to confirm the structure, including the absolute configuration, we carried out X-ray crystallographic analysis of the chlorohydrin 4.



1 :


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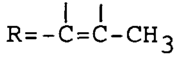
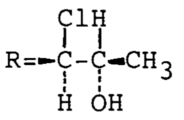

$R=-\overset{H}{C}=\overset{H}{C}-CH_3$

3 : $R=-CH_2-CO-CH_3$

4 :

$R=-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-CH_3$

The chlorohydrin 4, $C_{15}H_{17}O_3Br_2Cl$, mp 71-72 °C,[4)] crystallized from ether/hexane in the orthorhombic space group $P2_12_12_1$, a=22.48(3), b=5.715(5), c=13.24(2)Å, z=4, D_c=1.72 g/cm^3. The intensity of 1329 independent reflections with $2\theta < 45°$ were measured on a MAC Science imaging plate diffractometer DIP-100 with graphite-monochromated Mo Kα radiation. During the data collection, the crystal gradually turned brown, suggesting it suffered some deterioration. The structure was solved by the heavy atom method, and was refined by the block-diagonal least-squares method. The difference Fourier map revealed that two different conformers exist in the crystal by rotating around the C13-C14 single bond. Because of the difficulties mentioned above, the refinement terminated with R value being 0.125. The absolute configuration was, however, undoubtedly established by comparison of 24 Bijvoet pairs of reflections. The molecular skeleton of 4, including the absolute configuration, is illustrated in Fig. 1. As shown in Fig. 1, the chiral centers at C-4, C-6, C-7, C-10, C-12, C-13, and C-14 in 4 were *S*-, *R*-, *S*-, *S*-, *R*-, *R*- and *R*-configuration, respectively. Moreover, the absolute configuration of the bromoallene moiety in 4 was the same *S*-configuration as previously deduced from the Lowe's rule.[4)]

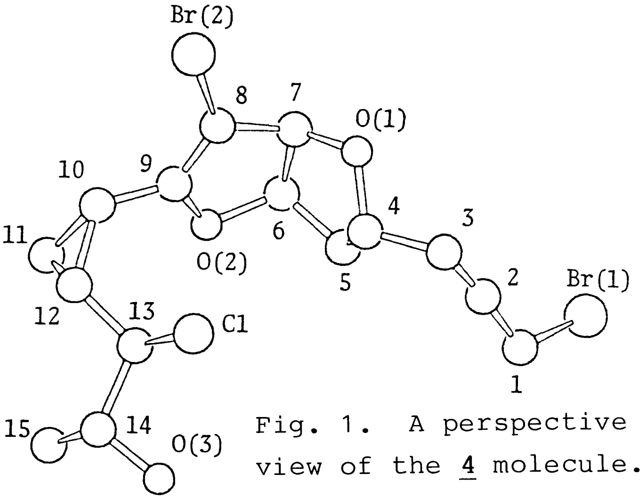


Fig. 1. A perspective view of the 4 molecule.

Treatment of the corresponding acetate of 4 with potassium carbonate in methanol gave okamurallene (1) in good yield.[4)] This internal S_N2 displacement reaction (epoxide formation) proceeds under *trans*-periplanar arrangement of the chlorine atom at C-13 and the hydroxyl group at C-14 in 4, giving only *cis* epoxide. Consequently, the absolute configurations at C-13 and C-14 in okamurallene (1) are *S* and *R*, respectively. In view of the close resemblance of the spectral data of deoxyokamurallene (2) and isookamurallene (3) to those of 1 and 4 along with the coexistence in the same alga, 2 and 3 must have the same configurations as those of 1 and 4.

References

1) Part 79 of "Constituents of Marine Plants." Part 78; H. Kikuchi, T. Suzuki, E. Kurosawa, and M. Suzuki, in preparation.
2) M. Suzuki and E. Kurosawa, *Tetrahedron Lett.*, 22, 3853 (1981).
3) M. Suzuki and E. Kurosawa, *Chem. Lett.*, 1982, 289.
4) M. Suzuki, Y. Sasage, M. Ikura, K. Hikichi, and E. Kurosawa, *Phytochemistry*, 28, 2145 (1989).

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