STRUCTURE OF (+)-KJELLMANIANONE, A HIGHLY OXYGENATED CYCLOPENTENONE FROM THE MARIN ALGA, SARGASSUM KJELLMANIANUM

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The structure and absolute configuration of a new cyclopentenone derivative, (+)-kjellmanianone, isolated from the brown alga Sargassum kjellmanianum has been determined as 5-carbomethoxy-5hydroxy-3-methoxy-2-cyclopenten-1-one on the basis of the chemical and spectroscopic evidence and the X-ray analysis.

In our search for the components of the *Sarugassum* (brown algae),¹⁾ we have isolated a highly oxygenated cyclopentenone (1), named (+)-kjellmanianone, from *Sargassum kjellmanianum* Yendo. This compound possessed a moderate antibacterial activity against *Escherichia coli* K12 and *Bacillus subtilis* var. *niger*, grampositive microorganisms. The present paper deals with the chemical and spectral evidence and the result of X-ray diffraction analysis for the proposed structure (1).

(+)-Kjellmanianone (1), $[\alpha]_{D}$ +1.6° (c 1.80, CHCl₃), was isolated as colorless crystals melting at 139-139.5°C by repeated chromatography of the methanol extract of the seaweeds which were collected at the Bay of Hiroshima early in March, 1978. The composition of $C_8H_{10}O_5$ was determined by high resolution mass spectrometer (M^{+} 186.0530) and confirmed by elemental analysis. The presence of a β -substituted- α,β -unsaturated five-membered ketone was exhibited by the IR band at 1705 cm⁻¹, the UV absorption maximum at 242 nm (ϵ 14300), and the ¹H NMR signal at δ 5.32 (1H, t, J=1.0 Hz) showing a long-range coupling with a methylene proton [δ 2.72 and 3.17 (each 1H, dd, J=18.0, 1.0 Hz)]. A sharp band at 3350 cm⁻¹ and no signal due to carbinyl proton suggested it contained a tertiary hydroxyl group. The ¹H NMR spectrum,

furthermore, had the two signals assigned to methoxyl groups [δ 3.78 and 3.92 (each 3H, s)], one of which was classified into that of a carbomethoxyl group(ν 1740 and 1270 cm⁻¹).

The hydroxyl group of kjellmanianone (1), despite of a tertiary one, was acetylated by using normal conditions(Ac_2O -pyridine, 25°C) to afford a monoacetate (2), $C_{10}H_{12}O_6$, mp 119-121°C. Catalytic hydrogenation (PtO₂-EtOAc) of (1) yielded a saturated secondary alcohol (3), $C_8H_{14}O_5$, acetylation of which gave a diacetate (4), $C_{12}H_{18}O_7$, containing an acetoxyl proton [δ 5.23 (1H, t, J=6.0 Hz)] and a methoxyl proton [δ 3.98 (1H, ddd, J=14.0, 7.0; 1.5 Hz)].²⁾ The above chemical and spectral properties indicated that kjellmanianone (1) was a β -substituted- α , β -unsaturated five-membered ketone with a tertiary hydroxyl group, a carbomethoxyl group, and a methoxyl group attached to the double bond. This gross structure was also supported by the off-resonance ¹³C NMR spectrum which contained four singlets [one carbonyl carbon (C-1): δ 199.6, one carbomethoxyl carbonyl carbon (C-6): δ 171.6, one olefinic carbon (C-3) bearing a methoxyl group: δ 190.1, and one fully substituted carbon (C-5): δ 79.2], one doublet [one olefinic carbon (C-2): δ 101.1], one triplet [one methylene carbon (C-4): δ 40.7], and two quartets [two methoxyl carbons (C-7 and C-8): δ 59.2 and/or 53.4].³



For the further confirmation of the structure and the elucidation of the absolute configuration, the single-crystal X-ray analysis was undertaken. Crystals of (1) belonged to the space group $P2_12_12_1$, with a=7.880(2), b=8.813(2), c=12.317(5) Å. The density ($P_{calcd.}=1.45$ g cm⁻³) indicated one molecule of $C_8H_{10}O_5$ per asymmetric unit. All intensity data in a 20 sphere of 55.0° were collected on a Syntex R3 diffractometer using graphite monochromated Mo-K α radiation (0.7107 Å). A total of 1157 reflections was measured and 936 (80.9 %) were judged to be observed after correction for Lorentz, polarization, and background effect. The structure was solved by direct methods using MULTAN in a Syntex XTL program system.⁴) The largest 140 normalized structure factors were phased and a three-dimensional E-synthesis of the

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best set revealed completely the non-hydrogen atom skeleton. Ten hydrogens were also located in the difference electron density synthesis. The full matrix least-squares refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the hydrogen atoms converged for a final residual of 0.049 for the observed reflections. The absolute configuration was determined by the Bijvoet method using Cu-Ka radiation (1.5418 Å) with Rigaku AFC-5 diffractometer.⁵⁾ The Bijvoet differences were calculated with the anomalous scattering of oxygen atoms. Figure 1 shows a perspective drawing of the X-ray model including the absolute configuration. Therefore, the structure and absolute configuration of (+)-kjellmanianone should be represented by 5-carbomethoxy-5-hydroxy-3-methoxy-2-cyclopenten-1-one (1).



Fig. 1. A diagram of the molecule (1) showing atom numbering

Fig. 2. Arrangement of the molecules in the unit cell projecting down the *a*-axis

The cyclopentene ring approximated to a half-chair form with C(4) and C(5) displaced to opposite sides of the plane through atoms C(1)—C(3). The presence of intramolecular hydrogen bond between O(3)-H and O(4) (2.212 Å) is of interest in respect to the molecule. All bond lengths and angles agree well with the accepted values within experimental error. The crystal packing was shown in Figure 2, and the molecules in crystal were linked by intermolecular hydrogen bond, O(3)-H···O(1)^I (H···O, 2.145 Å).⁶

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References and Notes

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- 2) The spectral data of (2), (3), and (4) were as follows; (2): $C_{10}H_{12}O_6$ (M⁺ 228); $[\alpha]_D \pm 0^\circ$; mp 119-121°C; v_{CHCl_3} 1750, 1715, 1600, 1245 cm⁻¹; δ_{CDCl_3} 2.17, 3.75, 3.93, (each 3H, s), 2.68, 3.63 (each 1H, dd, J=18.0, 1.0), 5.30 (1H, t, J=1.0). (3): $C_8H_{14}O_5$ (M⁺ 190); $[\alpha]_D \pm 6.45^\circ$ (c 0.62, CHCl_3); v_{CHCl_3} 3615, 3580-3200, 1740 cm⁻¹; δ_{CDCl_3} 1.84-2.85 (4H, complex), 2.92-3.50 (1H, m), 3.60-4.26 (1H, m), 3.25, 3.70 (each 3H, s). (4): $C_{12}H_{18}O_7$ (M⁺ 274); $[\alpha]_D \pm 4.0^\circ$ (c 1.0, CHCl_3); v_{CHCl_3} 1745, 1265 cm⁻¹; δ_{CDCl_3} 1.63-2.87 (4H, complex), 2.03, 2.10, 3.20, 3.70 (each 3H, s), 3.98 (1H, ddd, J=14.0, 7.0, 1.5), 5.23 (1H, t, J=6.0).
- 3) The ¹³C NMR spectrum was taken in CDCl₃ solution on Hitachi R42-FT spectrometer (22.6 MHz).
- 4) G. Germain, P. Main, and M. M. Woolfson, Acta Crystallogr., Sect. B, 24, 274 (1970).
- 5) J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, <u>168</u>, 271 (1951); D. W. Engel, *Acta Crystallogr.*, Sect. B, <u>28</u>, 1496 (1972); K. Fukuyama, K. Hamada, T. Tsukihara, and Y. Katsube, *Bull. Chem. Soc. Jpn.*, <u>51</u>, 37 (1978). Bijvoet differences were calculated with Δf "=0.020. All of 15 reflections indicated that the correct absolute configuration was equal to that of the trial structure. All calculation related to the determination of absolute configuration was carried out by the computer program of Prof. Y. Katsube. (The CD spectral datum of (1) is $[\theta]_{240}$ -5995.)
- 6) Roman numeral, I, as superscript refers to the equivalent position, -x, $\frac{1}{2} + y$, $\frac{1}{2} z$, relative to the reference molecule at x, y, z.

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