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STRUCTURE OF SARGASSUMLACTAM, A NEW β,γ-UNSATURATED-γ-LACTAM, FROM THE MARINE ALGA *SARGASSUM KJELLMANIANUM*

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A new dehydro-γ-lactam, sargassumlactam, has been isolated from the brown alga *Sargassum kjellmanianum*, and its structure was determined to be 4,5-dehydro-3-methoxy-3,5-dimethoxycarbonyl-2-pyrrolidone by the spectroscopic and X-ray diffraction analysis.

In a previous paper, we reported the isolation and structure determination of kjellmanianone (1), a highly oxygenated cyclopentenone, from the brown alga *Sargassum kjellmanianum*.[1] Our continuous investigation on this seaweed resulted in the isolation of a new β,γ-unsaturated-γ-lactam, named sargassumlactam (2), which displayed a moderate antibacterial effect against *Staphylococcus aureus* FDA 209P and *Escherichia coli* K12. We described here the evidence for the proposed structure.

Sargassumlactam (2) was isolated as colorless plates, mp 140-141.5 °C, $[\alpha]_D \pm 0°$, from the methanol extract by repeated chromatography. The molecular formula of (2), $C_9H_{11}NO_6$, was established by high resolution mass spectrometry (M^+ 229.0565, calcd 229.0585) and elemental analysis (Found: C 47.38, H 4.89, N 6.23. Calcd: C 47.16, H 4.84, N 6.11). The IR ($CHCl_3$) and UV (EtOH) spectra showed absorption bands at 3430 (N-H), 1770 (C=O), 1740, 1150 (COO), and 1635 (C=C) cm^{-1} and at 208 (ε 6100) and 293 (ε 3400) nm, respectively. Its ^1H NMR spectrum ($CDCl_3$) exhibited signals due to three methoxyl groups [δ 3.43, 3.77 and 3.90 (each 3H, s)] and one olefinic proton [δ 6.22 (1H, d, J=2)] showing a long-range coupling with an amide proton [δ 7.72 (1H, broad; this signal disappeared when D_2O was added, and the olefinic proton signal was sharpened)]. Catalytic hydrogenation (Pd-C, EtOH) yielded a dihydro derivative, $C_9H_{13}NO_6$, whose spectrum indicated the disappearance of the olefinic function and the presence of γ-lactam [ν($CHCl_3$): 3430, 1725 cm^{-1}; δ6.90 (1H, brs)]. In addition to the above evidence, ^{13}C NMR spectrum suggested the gross structure (2) for this compound, that is, three methoxyl carbons [δ 53.00, 53.31 and 54.08 (each q)], three carbonyl carbons [δ 159.64, 166.27 and 172.74 (each s)], one fully substituted carbon [δ 85.90 (s)] bearing a methoxyl group, and two olefinic carbons [one at δ 138.53 (s), the other at δ 113.26 (d)].[2]

In order to confirm the molecular structure, a single crystal X-ray analysis was, furthermore, carried out. Sargassumlactam (2) crystallized in the triclinic

crystal class with a=6.503(1), b=8.230(1), c=10.229(1) Å, α=99.60(1), β=97.71(1), and γ=97.66(1)°. All unique diffraction intensities with 2θ<55.0° were collected in a variable speed ω-scan mode on a Syntex R3 four-circle diffractometer with graphite-monochromated MoKα radiation (0.7107 Å). Of the 2422 reflections surveyed in this manner, 1906 (78.7 %) were judged to be observed after correction for Lorentz, polarization, and background effects. The distribution of normalized structure factors for observed reflections indicated the centrosymmetric space group $P\bar{1}$, and the density (ρ_{obsd}: 1.46, ρ_{calcd}: 1.44 g cm^{-3}) showed the presence of one molecule of (2) per asymmetric unit. A phasing model which was obtained from the program MULTAN[3] was refined using Syntex XTL program system. Full-matrix least-squares refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the hydrogen atoms converged to a final R factor of 0.055 for 1906 reflections.

Figure 1 shows a perspective drawing of the molecular structure, and the structure of sargassumlactam is represented as 4,5-dehydro-3-methoxy-3,5-dimethoxycarbonyl-2-pyrrolidone (2).[4] Dehydro γ-lactam ring is almost coplanar, and all bond distances and angles agree well with generally accepted values within experimental error. The only short intermolecular contact is the hydrogen bond N-H···O(5)^{I} (2.079 Å).[5]

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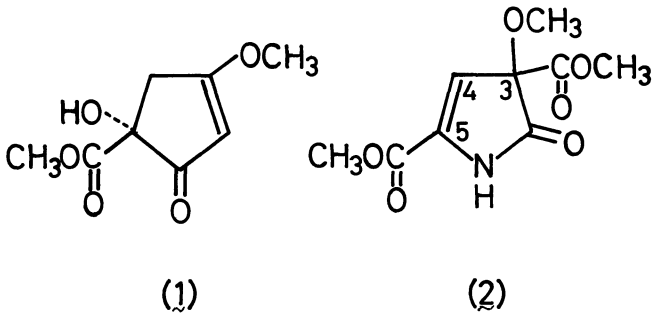

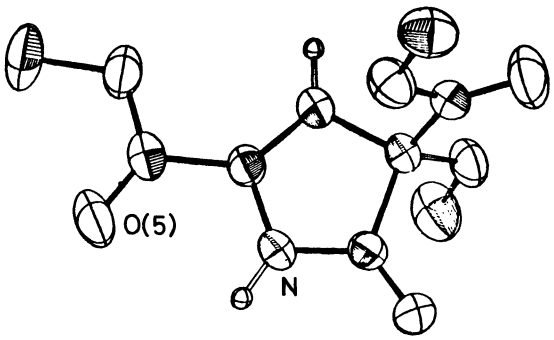

Fig. 1. A diagram of molecule (2)

References and Notes

1) M. Nakayama, Y. Fukuoka, H. Nozaki, A. Matsuo, and S. Hayashi, *Chem. Lett.*, in press.

2) The ^{13}C NMR spectrum was taken in $CDCl_3$ solution on a Hitachi R42-FT spectrometer (22.6 MHz).

3) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, Sect B, 24, 274(1970).

4) We also isolated this compound from *Sargassum thunbergii* (collected at Hiroshima bay and Oki island). The compound (2) was isolated as a racemate, and its details are now under investigation.

5) Roman numeral, I, as superscript refers to the equivalent position, 1-x, 1-y, 1-z, relative to the reference molecule at x, y, z. The atomic co-ordinates for this work are available on request from CSJ.

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