Short Paper

Two new Methyl Sulfones from the Red Alga *Grateloupia fillicina* J. AgardhHiroshi Nozaki,*¹ Susumu Ohira,*¹ and Fukue Shirane*²^{*1}Department of Biological Chemistry, Faculty of Science, Okayama University of Science, Ridai-cho, Okayama 700 Japan^{*2}Faculty of School Education, Hiroshima University, Kagamiyama Higashihiroshima 739 Japan

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In the course of our investigation on constituents of algae from the inland Sea of Seto,¹⁾ we reported the isolation and structure determination of four new phenolic compounds, one of which was a unique sulfone derivative, from the red alga *Grateloupia fillicina* (Wulfen) J. Agardh in the previous papers.^{2,3)}

Our continuous investigation on this seaweed resulted in the isolation of two new aliphatic sulfone derivatives. Described here are the structural characterization of these sulfones.

The fresh alga (ca. 10.7 kg), collected in the Bay of Hiroshima in March 1994, was extracted with methanol, and the dried extract was extracted successively with n-hexane and ethyl acetate. The ethyl acetate soluble material was repeatedly chromatographed on silica gel with chloroform-benzene-methanol (9:1:0.5) and ethyl acetate-methanol (10:1) to furnish sulfone A (12.5 mg) and sulfone B (10.0 mg).

Sulfone A (**1**), colorless needles with mp 86.5–88.0°C, showed a (M+H)⁺ peak at *m/z* 151 along with a (M+NH₄)⁺ peak at *m/z* 168 in CI-MS (i-C₄H₁₀, NH₃). The characteristic IR bands indicated the presence of a carbonyl group (ν_{CHCl₃}, 1728 cm⁻¹) and a sulfonyl group (ν₁₃₁₆, 1130, and 1044 cm⁻¹), as evident from the diagnostic EI-MS fragment ions at *m/z* 107 (M-COCH₃)⁺, 71 [base peak, (M-SO₂CH₃)⁺], together with the positive hydroiodic acid test.⁴⁾ The ¹H- and ¹³C-NMR spectra of **1** exhibited signals assignable to an acetyl [δ_H (CDCl₃) 2.26 (3H, s); δ_C (CDCl₃) 29.8 q, 204.1 s], a methylsulfonyl [δ_H 2.95 (3H, s); δ_C 41.6 q], and two mutually coupled methylene [δ_H 3.03 and 3.33 (each 2H, t, *J*=6.6 Hz); δ_C 35.6 t and 48.9 t] groups. These spectral data suggested that the molecular formula of sulfone A (**1**) is C₅H₁₀O₃S. From the ¹H-¹H decoupling measurement in addition to the above data, the structure of A (**1**) was determined to be 4-methylsulfonylbutane-2-one.

Sulfone B (**2**), viscous oil, [α_D] -14.5° (c 1.1, CHCl₃), was also positive to hydroiodic acid test and showed typical IR bands (ν₁₃₅₀, 1120, and 1030 cm⁻¹) for sulfonyl group. The presence of a hydroxy and a conjugated diene groups was inferred by the IR (ν₃₄₀₀, 1680, and 980 cm⁻¹) and UV [λ_{EtOH} 243 nm (ε₆₁₀₀)] spectra. This was supported by signals assignable to an oxymethine [δ_H 4.08 (1H, q,

J=6.4 Hz); δ_C 73.8 d] and a conjugated double bond [δ_H 5.81 and 6.37 (each 2H, m); δ_C 119.3 d, 128.7 d, 138.0 d, and 138.3 d] in the ¹H- and ¹³C-NMR spectra of **2**, which were fully analyzed by the aid of ¹H-¹H and ¹H-¹³C COSY spectra. The presence of an ethyl [δ_H 0.92 (3H, t, *J*=7.3 Hz), 1.54 (2H, dq, *J*=7.3 and 6.6 Hz); δ_C 9.6 q and 30.1 t], an active methylene [δ_H 3.51 (2H, d, *J*=7.8 Hz); δ_C 57.2 t], and a methylsulfone [δ_H 2.55 (3H, s); δ_C 37.1 q] was also inferred from NMR data. The formula of C₉H₁₀O₃S was established by CI-MS (i-C₄H₁₀) [*m/z* 205 (M+H)⁺] and EI-MS [*m/z* 125 (base peak), (M-SO₂CH₃)⁺] as well as NMR data. The geometries of the conjugated diene were assigned as *E, E* by detailed analysis of 2D NMR J-spectroscopy (*J*_{4,5}=13.6 and *J*_{6,7}=14.6 Hz) of the acetate **3**: [α_D] 11.6° (c 1.4, CHCl₃); CI-MS (i-C₄H₁₀), *m/z* 247 (M+H)⁺ and 167 [base peak, (M-SO₂CH₃)⁺]. Therefore, these chemical and spectral properties indicated that sulfone B (**2**) is 8-methylsulfonylocta-4*E, 6E*-diene-3-ol. The absolute configuration of the secondary hydroxy group is now under investigation.

The isolation from marine algae of these sulfone derivatives, which are likely to be derived from methionine, seems to be a unique example,⁵⁾ and their physiological roles are an interesting subject.

1 **2** R=H**3** R=OAc

References

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