min exposure at 1 Torr, very small bands at 1576, 1475, 1438, and 1023 cm^{-1} appeared. However, those peaks disappeared completely after evacuation at room temperature. For the 22.3 wt% Mo/ γ-Al_2O_3 sample, any characteristic adsorption band was not observed even at higher pressure of benzenethiol.

Earlier studies of the reduction mechanism of Mo / γ-Al_2O_3 catalyst postulated that the Mo monolayer structure is not affected by reduction[17]. Later studies which viewed the calcined catalysts as formed by Mo clusters bonded to the Al_2O_3 surface suggest that, on reduction, the polymolybdate structure undergoes certain rearrangements to form MoO_2-like cluster of similar dimension[18]. Although the X-ray diffraction pattern does not provide the exclusive information on the surface layer, the X-ray analysis of the molybdenum containing sample in this work exhibited the co-existence of Mo, MoO, and MoO_2 clusters. Hence, we conclude tentatively that the benzenethiol molecule adsorbs hardly on these clusters.

For the bimetallic Ni-Mo/ γ-Al_2O_3 samples, the X-ray diffraction pattern evidenced that nickel is present as completely reduced state while molybdenum is composite of Mo, MoO, and MoO_2 clusters. The fact that, for the nickel-rich Ni-Mo/ γ-Al_2O_3 sample, the adsorbed benzenethiol peaks appeared at the same positions as observed on the Ni/ γ-Al_2O_3 surface suggests that the adsorption sites of benzenethiol to give the peaks in Figure 2 can be assigned to the nickel atoms. On the other hand, the relatively weak band intensities may indicate that, for the bimetallic Ni-Mo sample, the various Mo clusters are enriched at the surface layer inhibiting the exposure of bare nickel particles. The X-ray diffracted intensity of Ni(111) peak was observed to be substantially diminished by the incorporation of molybdenum to Ni/ γ-Al_2O_3. This would support the above argument.

In summary, it is concluded that benzenethiol is chemisorbed dissociatively on the nickel surface by rupture of its S-H bond and the benzenethiolate formed upon adsorption is bound to the surface via its sulfur atom as on the silver surface. Infrared desorption study suggests that sulfur atoms remain on the nickel surface even after the prolonged evacuation at 573 K. Benzenethiol appears hardly to adsorb on the molybdenum(Mo, MoO, and MoO_2) clusters. For the bimetallic Ni-Mo/ γ-Al_2O_3 sample, the molybdenum clusters seem to be enriched at the surface layer.

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Glycolipid from the Korean Marine Red Alga *Gracilaria verrucosa*

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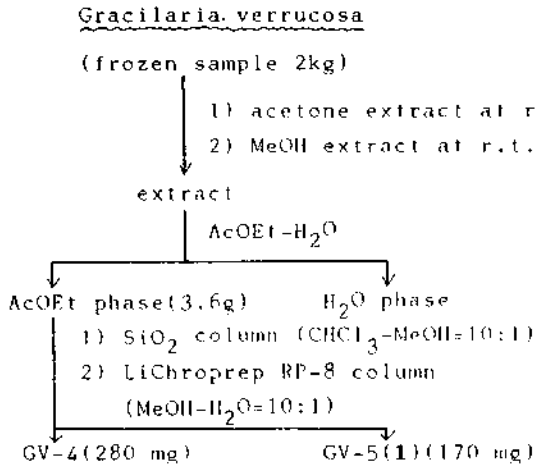
In 1969, Weinheimer and Spraggins reported the first high yield isolation of nonmammalian-type prostaglandins from the Caribbean gorgonean *Plexaura homomalla*.[1] This finding stimulated a world wide survey of prostaglandins in marine life. Especially, marine red alga *Gracilaria verrucosa* is one of the marine organism which metabolize the prostaglandins A_2 and E_2[2], and biological significance for the metabolites of this red alga is of interest.

From the red alga *G. verrucosa* collected at Chungmu, Kyung-Nam Prefecture in May 1987, I have isolated a mixture of fatty acids designated as GV-4 [palmitic acid, oleic acid and arachidonic acid (in a ratio of 2:1:6)] and a galac-



Scheme 1

tolipid designated as GV-5(**1**). This paper deals with the structure elucidation of these metabolites.

Acetone and methanol extracts of the frozen red alga was partitioned into an AcOEt-H_2O mixture and the AcOEt soluble portion was subjected to silica gel column chromatography($CHCl_3$-MeOH = 10:1). Each fractions containing GV-4 and GV-5 was further purified by LiChroprep RP-8 column chromatography(MeOH-H_2O = 10:1) to furnish GV-4 and GV-5(**1**) (8 and 5% yields respectively from the AcOEt soluble portion), as shown in Scheme 1.

GV-5(**1**) was shown by its infrared(IR) spectrum to have hydroxyl [3430(br) cm^{-1}] and ester(1725 cm^{-1}) groups. The ^1H NMR spectrum (90 MHz, $CDCl_3$) of **1** showed signals assignable to olefinic protons(δ 5.34, triplet like), sugar moiety(δ 4.27-3.56, a mass of signals), methylenes in fatty acids moiety(δ 1.24), and terminal methyl residue of fatty acids moiety(δ 0.87, a deformed triplet). The ^{13}C NMR data for **1** showed signals due to glycerol-glycoside moiety(Table 1) and fatty acids moiety.[3] Comparison of the above data for **1** with those reported for glyceroglycolipid[4] obtained from the alfalfa *Medicago sativa*, and for M-5[5] obtained from the marine sponge *Phyllospongia foliascens* have led us to assume a galactosyl diglyceride for GV-5.

Treatment of **1** with 10% sodium methoxide in dry-methanol provided a glycerol-galactoside(**2**), $[\alpha]_D$ 7.4° (H_2O), and a mixture of fatty acid methyl esters. The chemical-ionization(CI) mass spectrum of **2** showed an ion peak of m/z 255($M^+ + 1$). The anomeric proton and carbon signals of **2** observed at δ 4.27(1H, d, J = 7.6 Hz)(500 MHz, D_2O-CD_3OD = 2:1) and δ_c 105.2(Table 1) indicate the presence of a β-glycosidic linkage in **2**. Methanolysis of **2** with acetyl chloride in dry-methanol(9%) liberated methyl galactoside and glycerol which were identified by gas-liquid chromatography(GLC) of their trimethylsilyl(TMS) derivatives.[6] The ^{13}C NMR spectrum of **2**[7](Table 1) finally defined as the structure of glycerol β-D-galactopyranoside.[5]

In addition, C-2′ configuration in the glycerol moiety of **2** is presumed to be *R* on the basis of a comparison of the specific rotation with the reported value, $[\alpha]_D$(H_2O): -7° for C-2′ *R* and +2° for C-2′ *S*.[8]

The GLC and gas-liquid chromatography-mass spectrometry (GC-MS) analysis of the above-mentioned fatty acid methyl esters defined the composition as a mixture of methyl palmitate, methyl oleate, and methyl arachidonate in a ratio of 4:1:9.[9] Furthermore, the ^{13}C NMR analysis of glycerol galactoside moiety for **1** in comparison with that of **2** enabled us to identify the location of the fatty acid residues to be at C-1′ and C-2′ of the glycerol moiety(Table 1). Thus, the signal due to C-3′ of the glycerol moiety in **1** is observed at higher ppm(3.3 ppm)[10] as compared to that in **2**, while signals ascribable to C-1′ and C-2′ for **1** and **2** are observed in similar chemical shifts(Table 1).

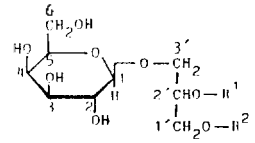
Table 1. ^{13}C NMR Data for Glycerol-glycoside Moiety of GV-5 (1), and for 2[a]

Carbon	GV-5(1)	2
1	105.4 (d)[b]	105.2 (d)
2	72.5 (d)	72.6 (d)
3	75.0 (d)	74.8 (d)
4	70.3 (d)	70.3 (d)
5	76.8 (d)	76.7 (d)
6	62.5 (t)	62.5 (t)
1′	64.2 (t)	64.1 (t)
2′	71.9 (d)	72.1 (d)
3′	68.9 (t)	72.2 (t)

[a] Measured at 22.5 MHz in CD_3OD. [b] Abbreviations given in parentheses denote the signal patterns observed in INEPT experiments: d = doublet, t = triplet.

Based on the above evidence, the chemical structure of GV-5 was determined as **1**, in which a mixture of fatty acid residues (**a**, **b**, and **c** in a ratio of 4:1:9) is attached to C-1′ and C-2′ of the glycerol moiety.

From the ^1H NMR and ^{13}C NMR analysis of GV-4[11], it was assumed to be a mixture of fatty acids. Esterification of GV-4 with CH_2N_2 in ether afforded a mixture of fatty acid methyl esters. The composition of the fatty acid methyl esters was shown to be methyl palmitate, methyl oleate, and methyl arachidonate(in a ratio of 2:1:6) by GLC.[12]



R^1, R^2:
a $-OC(CH_2)_{14}CH_3$
b $-OC(CH_2)_7CH=CH(CH_2)_7CH_3$ (*cis*)
c $-OC(CH_2)_2(CH_2CH=CH)_4(CH_2)_4CH_3$ (*cis*)

GV-5 (**1**): R^1, R^2 = (**a**:**b**:**c** = 4:1:9)
2: R^1, R^2 = H

A number of glycolipids have been isolated from the various organisms: *e.g.* cyanophyta[13], green alga[14], plants[10,15], sea urchin[16,17], and marine sponge[5], and exhibited diverse kinds of biological function. Since arachidonic acid which is a biosynthetic precursor of prostaglandins is abundantly contained in this red alga as free or binding types, the physiological functions of **1** is an interesting subject for investigation.

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6. TMS-glycerol and methyl TMS-galactoside were identified by direct GLC comparisons (2% SE-30 on Chromosorb WAW DMCS, 80-100 mesh, 3 mm × 2 m) with authentic samples: TMS-glycerol [column temp. 120°C, carrier gas N_2 at flow rate 25 ml/min., t_R(min.) = 5′18″] and methyl TMS-galactoside [column temp. 170°C, N_2 at flow rate 30 ml/min., t_R(min.) = 8′23″, 9′39″, 11′01″].
7. ^{13}C NMR data (22.5 MHz, D_2O-CD_3OD = 2:1, δ_c) of **2**: 104.4(C-1), 72.1(C-2), 74.0(C-3), 69.9(C-4), 76.4(C-5), 62.2(C-6), 63.6(C-1′), 71.7(C-2′), 71.9(C-3′).
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9. A mixture of fatty acid methyl esters was identified by direct GLC comparison (15% polyethylene glycol succinate on Chromosorb WAW DMCS, 80-100 mesh, 3 mm × 2 m, column temp. 210°C, carrier gas N_2 at flow rate 35 ml/min.) with authentic samples and its ratio was obtained by comparison of peak area for each of the fatty acid methyl esters: t_R(min.) = **a** 2′23″, **b** 4′14″, **c** 11′01″; **a**:**b**:**c** = 4:1:9.
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11. GV-4; ^1H NMR(90 MHz, $CDCl_3$, δ): 5.37(triplet like, olefinic protons) 1.26(methylene protons), 0.89(a deformed triplet, terminal methyl protons), ^{13}C NMR (22.5 MHz, $CDCl_3$, δ_c): 180.1(br.s), 130.5(d), 129.2(d), 128.8(d), 128.7(d), 128.3(d), 128.2(d), 127.9(d), 127.6(d), 34.1(t), 33.5(t), 32.0(t), 31.6(t), 29.8(t), 29.4(t), 29.2(t), 27.3(t), 26.6(t), 25.7(t), 24.8(t), 24.6(t), 22.6(t), 14.1(q), and methyl ester of GV-4; ^1H NMR(90 MHz, $CDCl_3$, δ): 5.35(triplet like, olefinic protons), 3.65(s), 1.25(methylene protons), 0.88 (a deformed triplet, terminal methyl protons).
12. Analytical conditions for GLC were the same as described in that of a mixture of fatty acid methyl esters of GV-5[9]: t_R(min.) = **a** 2′24″, **b** 4′19″, **c** 11′03″; **a**: **b**: **c** = 2:1:6.
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Theoretical Studies on [1,3] Sigmatropic Group Rearrangements†

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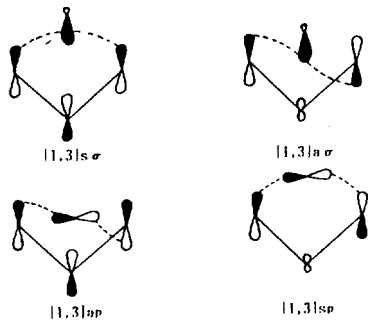
Sigmatropic rearrangements are not confined to hydrogen atoms.[1,2] Groups of nearly every type have been found to migrate. We report here semiempirical MO theoretical results on the course of such reactions involving migrating groups with lone pairs(F, OH, NH_2, SH, Cl) and those which can migrate by either σ- or p-type interactions (CH_3, NO) between 1,3-2p orbitals of propenyl system. Four types of orbital interactions can be envisaged, since both σ and p type can interact either suprafacially(s) or antarafacially(a) (Scheme 1).



Scheme 1

† Determination of Reactivity by MO Theory (part 53).