more, since every dialkylamine is expected to be an auxiliary of this class of reducing agents, this study should extend the scope of selective reduction in organic synthesis.

Experimental Section

All glassware used was dried in an oven, assembled hot, and cooled with a stream of nitrogen. All reaction were carried out under nitrogen atmosphere. Experimental techniques used in handing air-sensitive materials are described elsewhere.[4] Tetrahydrofuran was dried over a 4-Å molecular sieve and distilled from sodium benzophenone ketyl just prior to use. Lithium aluminum hydride (LAH) was from the Aldrich Company and was standardized by measurement of the H_2 produced by hydrolysis prior to use. All of the dialkylamines were high grade commercial reagent (Aldrich) and distilled after drying over KOH. ^{27}Al-NMR spectra were recorded on a Bruker WP 80 SY spectrometer and all ^{27}Al-NMR chemical shifts were reported in δ (ppm) relative to $[Al(H_2O)_6]^{3+}$. IR spectra were recored on a Perkin-Elmer 1330 spectrometer.

Reaction of Lithium Aluminum Hydrides with Excess Dialkylamines. The reaction of LAH with 4 equiv of Et_2NH is representative. An oven-dried, 100 m*l*, round-bottomed flask with a side arm, a condenser, and an adaptor was attached to a mercury bubbler. The flask flushed with N_2 and maintained under a static pressure of N_2. In the flask was placed 5.0 m*l* LAH-THF solution (2.0 M, 10.0 mmol) and the flask was brought to 0℃ by using an ice-bath. A total of 2.93 g (40.0 mmol) of Et_2NH was added dropwise with stirring. The evolution of 3.01 equiv of hydrogen was observed in 3 h at 0℃ and no further hydrogen evolution was apparent. An aliquot of the resulting solution was hydrolyzed to evolve 1.00 equiv of hydrogen.

Preparation of Lithium Dialkylaminoaluminum Hydrides. The preparation of lithium tris(diethylamino)aluminum hydride (LTDEA) is illustrative. In a 100 m*l*, round-bottomed flask was placed 50 m*l* of 2 M solution of LAH (100 mmol) in THF and the solution was kept at 25℃ by using a water bath. To this solution was added 23 g of Et_2NH (315 mmol, 5% excess) dropwise with vigorous stirring. The reaction mixture was stirred for 6 h at 0℃ until the evolution of hydrogen was complete. There resulting LTDEA solution in THF was diluted with THF to be 1.0 M, and the ^{27}Al-NMR spectrum of the solution showed a broad singlet at 120 ppm. The IR spectrum of the solution displayed a strong absorption at 1695 cm^{-1}, attributed to the Al-H stretching vibration.

In the case of morpholine, a white solid was precipitated from the reaction mixture after evolution of 3 equiv of hydrogen. The precipitate was filtered and washed with THF. The white solid, LTMPA, melted at 312℃. LTMPA, **11**, was also insoluble in CH_2Cl_2, Et_2O, or pentane.

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References

1. (a) H. C. Brown and P. M. Weissman, *Israel J. Chem.*, **1**, 430 (1963); (b) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958); (c) P. M. Weissman and H. C. Brown, *J. Org. Chem.*, **31**, 283 (1966); (d) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1085 (1964); (e) H. C. Brown and A. Tsukamoto, *ibid.*, **86**, 1089 (1964); (f) H. C. Brown and P. M. Weissman, *ibid.*, **87**, 5614 (1965); (g) H. C. Brown and H. R. Deck, *ibid.*, **87**, 5620 (1965).
2. (a) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958); (b) H. C. Brown and C. J. Shoaf, *ibid.*, **86**, 1079 (1964).
3. (a) J. S. Cha, J. C. Lee, S. E. Lee, J. M. Kim, O. S. Kwon, H. S. Lee, and S. J. Min, *Tetrahedron Lett.*, **32**, 6903 (1991); (b) J. S. Cha, S. E. Lee, and H. S. Lee, *Bull. Korean Chem. Soc.*, **12**, 644 (1991); (c) J. S. Cha, J. C. Lee, S. E. Lee, and H. S. Lee, *ibid.*, **12**, 598 (1991); (d) J. S. Cha, J. C. Lee, S. E. Lee, and H. S. Lee, *Org. Prep. Proced. Int.*, **24**, 327 (1992); (e) J. S. Cha, S. E. Lee, and H. S. Lee, *ibid.*, **24**, 331 (1992); (f) J. S. Cha, S. J. Min, J. C. Lee, H. S. Lee, and S. E. Lee, *ibid.*, **24**, 335 (1992).
4. H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses *via* Boranes", Wiley-Interscience, New York, 1975.

New Glyceroglycolipids from the Brown Alga *Sargassum thunbergii*

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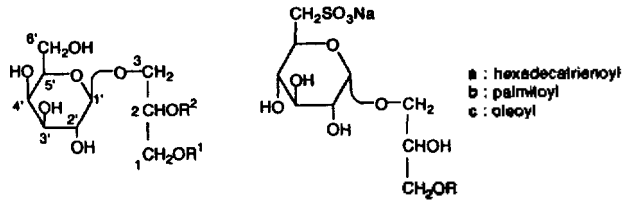
The brown alga *Sargassum thunbergii* is growing on rocks in the lower littoral and sublittoral belts, and this species is the most common *Sargassum* in our coast.[1] This alga metabolites antitumor polysaccharide,[2] iodoamino acid of depressing the blood cholesterol level,[3] and particular calcium-binding substances.[4] As a part of search for new biologically active substances from marine organisms, we have examined the metabolites of the brown alga *S. thunbergii*. Here we describe the isolation and characterization of two new glyceroglycolipids (**1**, **3**).

The methanol extract of *S. thunbergii* (1.5 kg, collected at Chungmu, Kyung-nam Prefacture in August 1990) was concentrated into an aqueous residue, which was successively extracted with ethyl acetate and *n*-butanol. The ethyl acetate soluble portion was concentrated to give a brown solid (10 g). Repeated column chromatography of this residue with silica gel (Merck, Kiesel gel 60) ($CHCl_3$-MeOH = 7 : 1 → 3 : 1), TSK gel (Toyo pearl HW-40F) (MeOH), octadecyl silica gel (Waters, μ-Bondapak C_{18}) (MeOH-H_2O = 5 : 1), and HPLC

Table 1. ^{13}C-NMR data for compounds **1**, **2**, **3**, and **4**

Carbon	1[a]	2[a]	3[a]	4[b]
1	66.4 t[c]	64.0 t	66.5 t	63.5 t
2	71.7 d	71.9 d	69.7 d	71.6 d
3	68.6 t	72.1 t	70.5 t	69.7 t
1′	105.0 d	105.1 d	100.1 d	99.1 d
2′	72.3 d	72.5 d	73.6 d	72.2 d
3′	74.6 d	74.7 d	75.0 d	73.8 d
4′	70.0 d	70.2 d	74.8 d	73.3 d
5′	76.4 d	76.6 d	69.7 d	68.9 d
6′	62.2 t	62.4 t	54.2 t	52.9 t

[a]Measured at 75 MHz in CD_3OD. [b]Measured at 75 MHz in D_2O : δc(TMS)=δc(tsp)−1.6 ppm. [c]Abbreviations denote the signal patterns observed in INEPT experiments.



1 : R^1, R^2 = (a : b : c = 8 : 5 : 87)
2 : R^1, R^2 = H
3 : R = (b : c = 96 : 4)
4 : R = H

(Cosmosil 5C_{18}) (MeOH-H_2O=5 : 1), finally led to the isolation of two new metabolites.

Compound (**1**), a white amorphous powder, showed a hydroxyl (3400 cm^{-1}) and ester functions (1720 cm^{-1}) in its IR spectrum. The ^{1}H-NMR (300 MHz, CD_3OD) spectrum of **1** indicated the presence of terminal methyls [δ 0.89(6H, t-like, J=6.0 Hz) and δ 0.97(3H, t, J=7.5 Hz)], a number of methylene groups (δ 1.30), anomeric proton (δ 4.24, d, J=7.0 Hz), and olefinic protons (δ 5.33-5.35). The ^{13}C-NMR (75 MHz, CD_3OD) data of **1** showed signals due to glycerol-glycoside moiety (Table 1) and fatty acid moiety.[5] The physicochemical features outlined above suggested that **1** was a galactolipid. Treatment of **1** with 10% NaOMe-MeOH gave monogalactosyl glycerol (**2**)[6] and a mixture of fatty acid methyl esters. Compairing the ^{13}C-NMR spectrum of **1** with that of **2** showed that in **1** the carbon signals due to the C-3 of **1** appeared in a higher field and that due to the C-1 of **1** appeared in a lower field, while that due to the C-2 of **1** showed similar chemical shift (Table 1). Thus, the fatty acid residues would attach to C-1 and C-2 in the glycerol moiety.

The monogalactosyl glycerol (**2**), $[\alpha]_D$-7.9°(H_2O), was identical in all respects with (2*R*)-1′-O-glyceryl β-D-galactopyranoside.[7]

The GC and GC-MS analyses of the above mentioned fatty acid methyl esters defined the composition as a mixture of hexadecatrienoate, palmitate and oleate in a ratio of 8 : 5 : 87.[8] Based on these findings, the structure of the galactolipid (**1**) was determined as (2*S*)-1,2-O-diacylglyceryl β-D-galactopyranoside (acyl; 8 : 5 : 87 mixture of hexadecatrienoate, palmitate and oleate).

The IR spectrum of compound (**3**) showed absorption bands at 3460 (hydroxyl), 1720 (ester), 1180 and 1060 (sulfonate) cm^{-1}. The ^{1}H-NMR and ^{13}C-NMR spectra of **3** showed signals characteristic of sulfonoglycolipid (Table 1).[9] On treatment with 10% NaOMe-MeOH, compound **3** furnished sulfonoquinovosyl glycerol (**4**) (Table 1)[10] and a mixture of fatty acid methyl esters. The composition of the fatty acid methyl esters was shown to be methyl palmitate and methyl oleate (96 : 4 mixture) by GC and GC-MS.[11] The anomeric carbon signal observed at δc 99.1 indicates the presence of an α-glycosidic linkage in **4**. Comparison of the ^{13}C-NMR data of the glycerol moiety in compound **3** and **4** suggests that the fatty acid moiety in compound **3** is attached at C-1 of the glycerol moiety rather than C-2 (Table 1). Consequently, the structure of **3** was found to be 96 : 4 mixture of the sodium salts of 1-O-palmitoyl-and 1-O-oleoyl-3-O-(6′-sulfo-α-D-quinovopyranosyl) glycerol.

Since glycolipids are shown to take part in several membrane functions in plants,[12] the unique functions and structural features of heterocyst cell walls may be related to a specific glycolipid and the biological significance of these metabolites is of interest.

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References and Notes

1. J. W. Kang, *Bull. Pusan Fish. Coll.*, **7**, 1 (1966).
2. H. Ito and M. Sugiura, *Chem. Pharm. Bull.*, **24**, 1114 (1976).
3. K. Ito, K. Ishikawa, and Y. Tsuchiya, *Tohoku J. Agric. Res.*, **27**, 53 (1976).
4. T. Misonou, M. Okazaki, K. Furuya, and K. Nishizawa, *Jpn. J. Phycol.*, **28**, 105 (1980).
5. The ^{13}C-NMR data for fatty acid moiety of **1** are as follows: δc 175.2(s), 175.1(s), 175.0(s), 132.6(d), 130.7(d), 130.6 (d), 130.5(d), 129.3(d), 129.1(d), 129.0(d), 128.0(d), 35.0(t), 34.8(t), 34.7(t), 32.9(t), 32.7(t), 32.4(t), 30.6(t), 30.4(t), 30.3 (t), 30.1(t), 30.0(t), 29.9(t), 28.0(t), 27.7(t), 26.4(t), 26.3(t), 25.8(t), 25.4(t), 23.5(t), 23.4(t), 21.3(t), 14.6(q), 14.4(q).
6. $[\alpha]_D$-7.9°(c 1.1, H_2O), FAB-MS (m/z): 277 $[M+Na]^+$, 255 $[M+H]^+$; ^{1}H-NMR (300 MHz, CD_3OD, δ): 3.46-3.64 (10H, m), 3.91(1H, ABq, J=5.0 Hz), 4.24(1H, d, J=7.0 Hz, anomeric-H); ^{13}C-NMR (75 MHz, CD_3OD, δc): see Table 1.
7. Lit. $[\alpha]_D$-7.4°(H_2O). B.-W. Son, *Bull. Korean Chem. Soc.*, **9**, 264 (1988).
8. A mixture of fatty acid methyl esters was identified by direct GC (3% SE-30, 3 mm×1 m, column temp. 195°, N_2 flow rate 30 ml/min.) with authentic samples [t_R(min.) = a 5′04″, b 5′52″, c 11′04″; a : b : c = 8 : 5 : 87] and GC-MS [Ultra-2 (5% diphenyl+95% dimethyl polysiloxane, 0.2 mm×25 m)] comparisons [MS (m/z): a 264 (M^+), 194, 135, 107, 67, 41; b 270(M^+), 227, 171, 143, 101, 74, 43; c 296(M^+), 264, 222, 220, 180, 110, 74, 41].
9. **3**; ^{1}H-NMR (300 MHz, CD_3OD, δ): 0.90(3H, dd, J=7.0, 6.0 Hz, terminal methyl), 1.29(24H, s, methylenes of fatty acid side chain), 1.61(2H, m), 2.37(2H, t, J=7.5 Hz), 2.92(1 H, m), 3.09(1H, t, J=6.5 Hz), 3.31-3.45(4H, m), 3.66(1H, t, J=6.5 Hz), 4.04-4.11(3H, m), 4.20(1H, t, J=6.5 Hz), 4.77

(1H, d, J=3.5 Hz, anomeric-H); ^{13}C-NMR (75 MHz, CD_3OD, δc) of fatty acid moiety: 175.6(s), 34.9(t), 33.0(t), 30.7 (t), 30.6(t), 30.4(t), 30.2(t), 25.9(t), 23.7(t), 14.4(q).

10. **4**; $[\alpha]_D$+51°(c 0.6, H_2O); SIMS (m/z): 363 $[M+Na]^+$, 703 $[2M+Na]^+$; ^{1}H-NMR(300 MHz, D_2O, δ): 3.08(1H, dd, J=14.5, 10.0 Hz), 3.27(1H, dd, J=9.5, 9.0 Hz), 3.36(1H, d, J=4.5 Hz), 3.42-3.49(1H, m), 3.57-3.63(2H, m), 3.68-3.78 (2H, m), 3.93-4.06(3H, m), 4.90(1H, d, J=3.5 Hz, anomeric-H); ^{13}C-NMR (75 MHz, D_2O, δc): see Table 1, and B.-W. Son, *Phytochemistry*, **29**, 307 (1990).
11. Analytical conditions for GC and GC-MS were the same as described in that of a mixture of fatty acid methyl esters of **1**,[8] [t_R(min.)=**b** 5'57", **c** 10'40"; **b** : **c**=96 : 4].
12. I. Ishizuka and T. Yamakawa, "New Comprehensive Biochemistry", Vol. 10, ed. by A. Neuberger, L. L. M. Van Deenen, and H. Wiegant, Elsevier, Amsterdam, 1985, pp. 101-198.

A Convenient Method for the Formation of *p*-Methoxylbenzyl Ethers and Esters over Perfluorinated Resinsulfonic Acid (Nafion-H)

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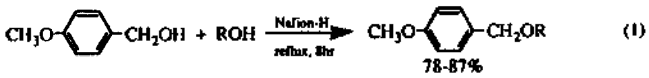
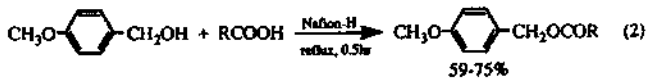
Nafion-H (a solid perfluorinated resinsulfonic acid having sulfonic acid group in the amount of 0.01 to 5 mequiv/gram resin)[1-3] has been used as an efficient catalyst in a number of acid catalyzed reactions.[4-7] Earlier we described convenient methods for esterification and benzylation over Nafion-H catalyst.[8,9] The esterification reactions between alkyl alcohols with carboxylicc acids proceeded cleanly to afford the desired products in nearly quantitative yields. Similarly, benzyl alcohol reacted readily with arenes to produce the benzylated products in excellent yields. However, benzyl alcohol did not react with alkyl alcohols and produced polymeric material when reacted with carboxylic acids. We now report that *p*-methoxybenzyl alcohol reacts readily with alcohols and carboxylic acids in the presence of catalytic amount of Nafion-H to afford *p*-methoxybenzyl ethers and esters, which have been prepared by different methods and used as protecting groups for alcohols and carboxylic acids.[10] (Eq 1 & 2)



(1)



(2)

The reaction was carried out by refluxing a mixture of *p*-methoxybenzyl alcohol (1.0 g), alkyl alcohol (5.0 m*l*), and Nafion-H (0.2 g) for 8 hours. Water was removed with small amount of silica gel in a soxhlet thimble suspended just below refluxing condenser. The product were simply isolated by filtering the hot reaction mixture and distilling off the excess alcohol. The results are summarized in Table 1. The reactions are very clean and produce the desired ethers in high yields. The esterification reactions of *p*-methoxybenzyl alcohol with carboxylic acids were conducted either by refluxing the reaction mixture for 30 min or by stirring the mixture for 8 hrs at room temperature to produce the *p*-methoxybenzyl esters in moderate to excellent yields (Table 2).

Table 1. Yield of Reaction between *p*-Methoxybenzy Alcohol and Alcohols (ROH) Catalyzed by Nafion-H

R	Yield (%)[a]	bp/mmHg	lit.[b] bp/mmHg
CH_3	86.5	66-8/1.5	102- 3/9
C_2H_5	78.4	90-4/2.3	109-10/9
C_3H_7	84.2	83-4/1.5	127- 8/11
C_4H_9	78.4	94-6/1.5	134- 5/10

[a]Isolated yield after reflux for 8 hrs, [b]Reference 11.

Table 2. Yield of Reactions Between *p*-Methoxybenzyl Alcohol and Carboxylic Acids (ROOH) Catalyzed by Nafion-H

R	Yield (%)[a]	bp/mmHg	lit.[b] bp/mmHg
CH_3	72.3(100)[b]	95-7/1.4	137-9/12[c]
C_2H_5	75.4(90.9)[b]	94-9/1.4	d
C_3H_7	58.7(74.6)[b]	102-7/1.4	158-68/11[c]
C_4H_9	60.0(52.9)[b]	99-103/1.5	d

[a]Isolated yield after reflux for 0.5 hour, [b]G.C. yield after 8 hrs at room temperature, [c]Reference 12, [d]Identified by NMR and IR.

The remarkable difference in reactivity between benzyl alcohol and its *p*-methoxy derivative can be attributed to the substituent effect. *p*-Methoxybenzyl cation should be more stable than benzyl cation and thus should exist in higher concentration than the latter. Although the former should be less reactive than the latter, the difference in reactivity between these two electrophiles is not expected to be as great as that of their concentration because the reactions between the benzylic cations and the oxygen nucleophiles must be highly exothermic. Therefore, it is reasonble to expect that the former should react faster than the latter with alcohols and carboxylic acids. The faster rate of ester formation may be attributed to the participation of the carboxylic acids as a catalyst in these reactions.

The present procedure provides an efficient method for the formation of *p*-methoxybenzyl ethers and esters. In this procedure, only a catalytic amount of the acidic resin is needed, and the heterogeneous catalyst provides for a very simple work-up. Application of Nafion-H on other acid catalyzed reactions are in progress in our laboratory.

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References

1. G. A. Olah and G. K. S. Prakash, and J. Sommer, "Supe-