Studies of Tritylated Pentoses and Methyl Pentoses. I. The *O*-Tritylation of Methyl α-D-Fucopyranoside

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Two trityl derivatives of fucose, methyl 2-*O*- (II) and 3-*O*-trityl α-D-fucopyranoside (III), were obtained in good yields by the reaction of methyl α-D-fucopyranoside (I) and trityl chloride in pyridine. The ratio of II and III in the reaction mixture was about 3 : 2. The structures were mainly established by NMR with appropriate derivatives. The gas chromatography-mass spectrometry of the partial methyl ethers of I was also discussed.

O-Tritylation[1] usually proceeds much more rapidly on primary hydroxyl groups. It has been used to determine quantitatively the number of primary hydroxyl groups in a molecule, or to protect the group for further synthetic procedures. However, in some cases, equatorial secondary hydroxyl groups are also tritylated rapidly. Hocket and Hudson[2] reported that methyl α-L-fucopyranoside, which contains only secondary hydroxyl groups, reacted readily with trityl chloride to form a mono-*O*-trityl ether. However, they did not describe its structure.

This paper will deal with the *O*-tritylation of I and with the etherified positions of the trityl derivatives. The *O*-tritylation of various pentoses and methyl pentoses can give information about the reactivity of secondary hydroxyl groups in different environments and can be used to protect a certain hydroxyl group for further synthetic procedures. This paper will also deal with the mass spectra of the partially methylated methyl fucosides prepared from the trityl derivatives.

Results and Discussion

The reaction of I with trityl chloride in a 1 : 2 mole ratio readily formed substituted derivatives under the conditions described by Helferich.[1] The tritylated product gave two adjacent spots on a thin-layer chromatogram and two peaks on a high-speed liquid chromatogram, as is shown in Fig. 1. The compound corresponding to the first peak(II) was isolated as a pyridine complex and was then recrystallized as monoethyl alcoholate. The second peak(III) was separated by liquid chromatography, and crystallized as monohydrate. The analyses and PMR spectra of the appropriate derivatives of II and III indicated that they both consisted of mono-*O*-trityl ether of I.

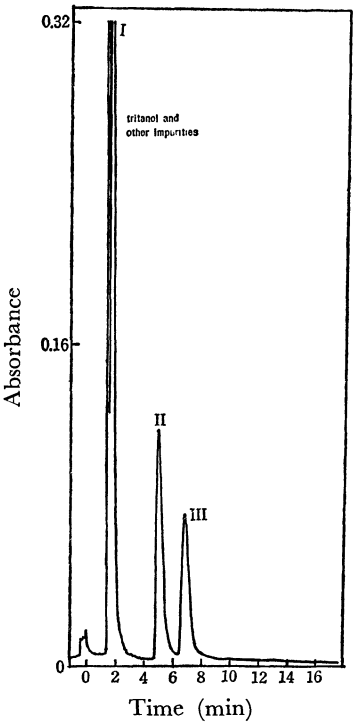
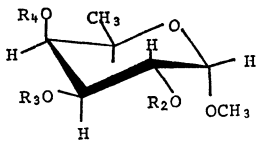


Fig. 1. Liquid chromatogram of the reaction mixture column: MicroPak si-10 2 mm×20 cm; solvent: 20% hexane/methylene chloride; flow rate: 50 ml/h; detector: UV (254 nm).



I	$R_2=R_3=R_4=H$	VIII	$R_3=Tr$, $R_2=Ac$, $R_4=H$
II	$R_2=Tr$, $R_3=R_4=H$	IX	$R_3=Tr$, $R_2=R_4=CH_3$
III	$R_3=Tr$, $R_2=R_4=H$	X	$R_3=H$, $R_2=R_4=CH_3$
IV	$R_2=Tr$, $R_3=R_4=Ac$	XI	$R_3=Ac$, $R_2=R_4=CH_3$
V	$R_2=Tr$, $R_3=R_4=CH_3$	XII	$R_4=H$, $R_2=R_3=CH_3$
VI	$R_2=H$, $R_3=R_4=CH_3$	XIII	$R_4=Ac$, $R_2=R_3=CH_3$
VII	$R_2=Ac$, $R_3=R_4=CH_3$		

All the methine-proton signals in a PMR spectrum of the peracetyl derivative of II (IV) were assigned with the aid of the decoupling technique shown in Fig. 2. The signals of H-3 and H-4 lay in the *O*-acetylmethine-proton area, while the H-2 resonated at a higher field than would be expected for an *O*-tritylmethine-proton. Most of the methine protons attached to alkoxylated or hydroxylated carbon resonate at δ4.0—2.5. However, trityl groups may sometimes cause anomalous chemical shifts of the adjacent protons by means of their strong anisotropic effect.[3,4] To confirm the structure, the PMR of a methyl di-*O*-methyl mono-*O*-acetylfucoside (VII) which had been derived from permethyl ether of II (V) was analyzed by the aid of the homodouble-resonance technique,[5]

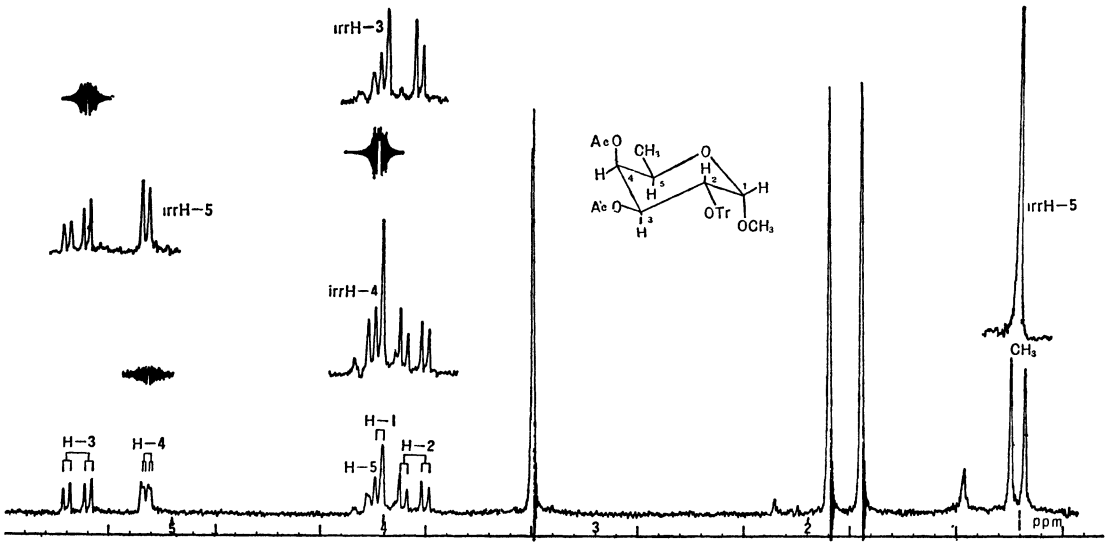


Fig. 2. Parts of the NMR spectrum at 100 MHz of IV.

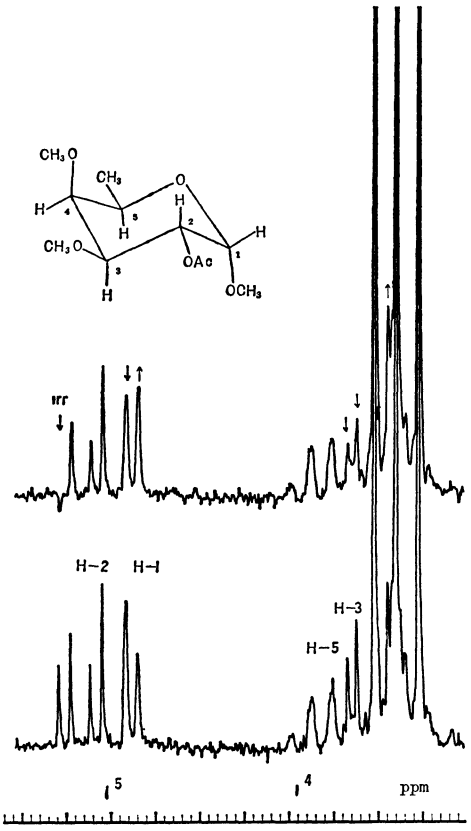


Fig. 3. A part of the NMR spectrum at 60 MHz (FT-mode) of VII. No. of scans: 10. Arrows show increasing or decreasing of signal intensities compared with those on the normal spectrum.

irradiating with a selective π-pulse at a resonance line of δ5.25, and observing the signal intensities using the Fourier transform mode, as is shown in Fig. 3. The spectrum showed that the H-2 was an *O*-acetylmethine proton, judging from the chemical shift. Accordingly, Compound II was confirmed to be 2-*O*-trityl α-D-fucopyranoside.

A PMR spectrum of the acetylation product of III (VIII) indicated that the hydroxyl group at C-2 alone was replaced by an acetyl group. Since protons of hydroxylmethine and alkoxylmethine resonate in a common area, however, the complete identification of VIII is difficult. In the PMR spectrum of di-*O*-methyl mono-*O*-acetylfucoside (XI) derived from the permethyl ether of III (IX) through its detritylation product (X), all the methine-proton signals were

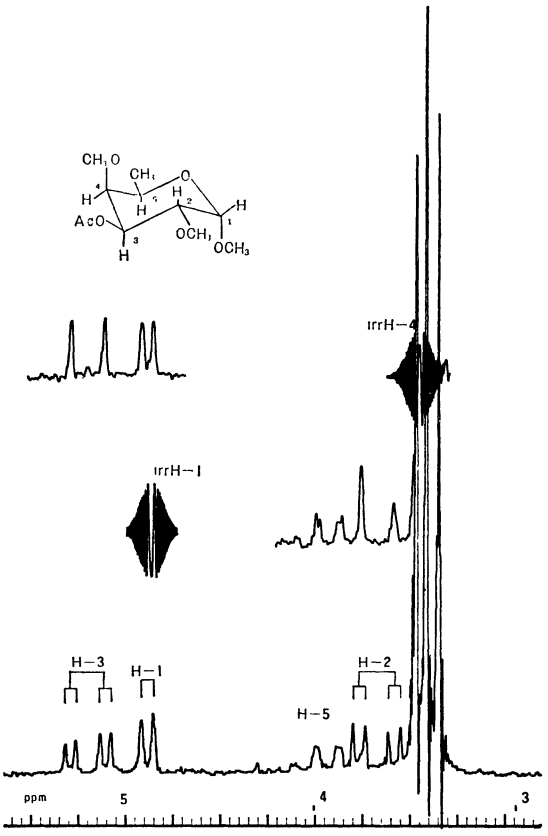
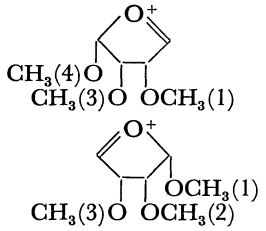


Fig. 4. A part of the NMR spectrum at 60 MHz of XI.

assigned with the aid of the decoupling technique, as is shown in Fig. 4. The H-3 was regarded as an acetylmethine proton from its chemical shift, and Compound III was identified as methyl 3-*O*-trityl α-D-fucopyranoside.

During these studies, the mass spectra of methyl di-*O*-methylfucoside (VI and X) were also analyzed. The mass spectra of methyl ethers of methyl glycosides have previously been studied in detail. For example, Kochetkov *et al.*[6-9] and Heyns *et al.*[10-11] have assigned the peaks on the mass spectra of permethylated methyl glycosides and calculated the contributions of isomeric ions to the total peak intensities. Later, Heyns *et al.*[12] analyzed the peaks of partially methylated methyl glucoside.

Some of the structures of ions and their contributions to the total peak intensities are presented below.

m/e	Structure[a]	Designation[9,12]	Contribution[b]
58 72	$[CH_3\text{-}CH{=}CH\text{-}OR(4)]^+$	K_1	100
74 88	$[R(2)O\text{-}CH{=}CH\text{-}OR(3)]^+$	H_1^2	78
75	$[CH_3(3)O{=}{=}CH{=}{=}OCH_3(1)]^+$	J_1^1	60
87 101	$R(4)O\text{-}CH{=}CH\text{-}CH{=}O^+R(2)$	F_1^2	62
87 101	R(2)-O-C(+CH(1,4))-C-OR(3)	G_1^4	15
119	$CH_3\text{-}CH{=}O^+\text{-}CH(OCH_3(1))(OCH_3(3))$	D_1	100
115 129	$CH_3\text{-}C^+H\text{-}CH(OR(4))\text{-}CH{=}CH\text{-}OR(2)$	C_2	48
161		J_4	
		J_3	

a) R's are CH_3 or OH, and the numbers in parentheses agree with the attached positions of the OR-groups in the original ethers.

b) The contributions were calculated with methyl 2,3,4-tri-*O*-methyl β-D-fucoside.

c) The peaks at *m/e* 119 and 75 are mainly formed by the migration of the methoxyl (3). Therefore, their hydroxyl analogues are scarcely afforded at all.

The relative intensities of the characteristic peaks of VI, X, and those of methyl 2,3-di-*O*-methyl α-D-fucopyranoside (XII) are presented in Table 1, while the mass spectra of these compounds are in Fig. 5.

The mass spectra of these ethers are well elucidated by the structures of ions and their contributions to the total peak intensities. For example, the comparatively low intensities of the peaks at *m/e* 75, 88, and 119 in the spectrum of X indicate the absence of methoxyl (3). The major ions which contribute to these peak intensities all include this methoxyl group.

TABLE 1. THE RELATIVE INTENSITIES ON MASS SPECTRA OF PARTIALLY METHYLATED METHYL α-D-FUCOPYRANOSIDES

m/e	VI	X	XII	Permethyl α-D-fucose[14]
72	50	42	2	20
74	91	100	15	1
75	54	18	30	38
85	14	8	42	2
87	19	8	10	2
88	100	43	100	100
101	6	23	18	20
102	2	15	3	1.5
115	6	5	2	1
119	5.2	0.4	2.2	1.7
129	1.5	3.9	0	1.6
130	4.5	0.6	6.5	0
143	1.8	2.4	2.4	0
157	0.2	0.6	0.1	0.4
161	2.0	0.2	1.3	0
175	0.5	1.9	0.7	0
176	0	0	0	1.0
189	0	0	0	1.4

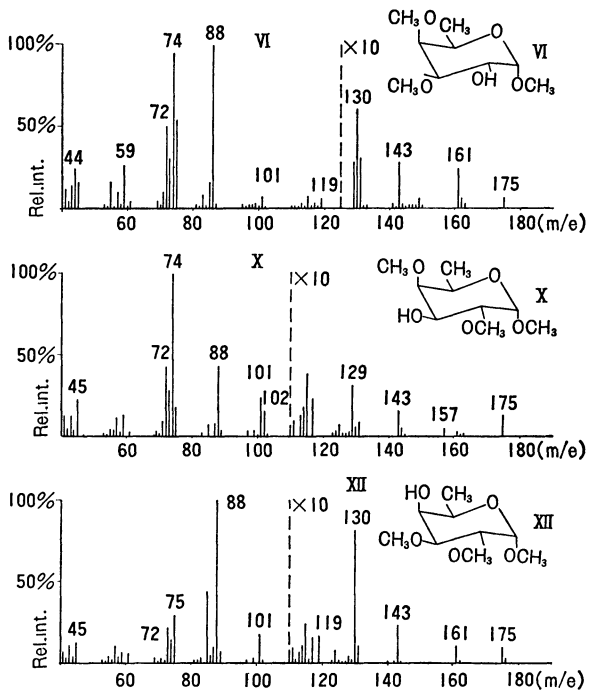


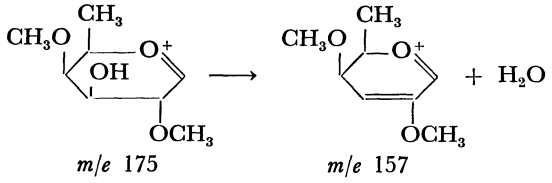
Fig. 5. Gas chromatography-mass spectra of VI, X and XII.

Similarly, the low intensity of the peak at *m/e* 101 in the spectrum of VI, and that of the peak at *m/e* 72 in the spectrum of XII, are elucidated by the absence of methoxyl (2) and methoxyl (4) respectively. The pathway of fragmentation should also be taken into consideration. The comparatively low intensity of the peak at *m/e* 101 in the spectrum of X may be explained by the lack of methoxyl (3). Because the F_1^2 ion is formed by the migration of methoxyl (3) from C-3 to C-1, in the case of permethylated methyl fucopyranoside, the absence of this group would reduce

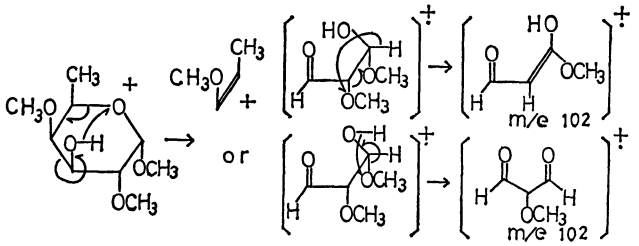
the contribution of F_1[2] to the peak intensity.

The formation of *m/e* 161 (J_3,J_4) accompanies proton-transfers from OH (2) or OH (4) to the ring oxygens of VI or XII, indicating the presence of hydroxyl gorups at C-2 or C-4 in molecular ions.

There were other peaks, like *m/e* 157, 130, and 102, which were characteristic of each isomeric ether. The peak at *m/e* 157 appeared only in the spectrum of X and was considered as a dehydrated fragment of an ion of *m/e* 175:



The peak at *m/e* 130 appeared in the spectra of VI and XII. The peak at *m/e* 102 appeared in the spectrum of X. The pathway of the fragmentation was assumed to be as follows:



Experimental

General Methods. For high-performance liquid chromatography, a Varian Model 8520 Liquid Chromatograph, equipped with a Micro Pak Si-10 column, was used. The solvent for elution was 20% hexane/methylene chloride. Thin-layer chromatography was effected using Merck silica gel G as an adsorbent in a thickness of 0.25 mm, with a solvent system of acetone-benzene. Preparative column chromatography was carried out using silica gel, 60—80 mesh (Kanto Chemical Co.). The PMR spectra were recorded on a Varian HA-100D (100 MHz) apparatus and an NV-14 (60 MHz) spectrometer equipped with Adapts, a computor system (Varian Data Machins), using chloroform-*d* with tetramethylsilane as the internal lock, the signal positions being expressed in δ values. Gas chromatography-mass spectrometry was carried out using a Varian MAT 111 GC/MS system.

Tritylation of I. A mixture of 0.593 g of I ($[\alpha]_D^{25}$+ 189°) and 1.853 g of recrystallized trityl chloride was dissolved in 20 ml of dry pyridine, and was then allowed to stand for 120 h at room temperature. At the end of the reaction period, 1 ml of water was added to the solution. The solution was then concentrated *in vacuo* at 40 °C until it became hard syrup. A thin-layer chromatogram with a solvent system of 20% acetone/benzene showed spots corresponding to II and III, with R_f values of 0.69 and 0.63 respectively. On a high-performance liquid chromatogram, two peaks corresponding to II and III had retention times of 5°00′ and 6°48′ respectively, with a flow rate of 50 ml/h. The reaction concentrate was chromatographed on 15 g of silica gel. After the column had been washed with benzene (300 ml), trityl ethers were eluted with 4% acetone/benzene (300 ml). The evaporation of the last solvent left 1061 mg of a glass which consisted of II and III. The combined yield of the ethers was about 71%.

Methyl 2-O-Trityl α-D-Fucopyranoside (II). The derivative, II, was crystallized as a pyridine complex from the pyridine solution of the glass. Then it was recrystallized several times from the ethanol solution as monoethyl alcoholate, which melted at 68—70 °C and which had an $[\alpha]_D^{20}$ of +55.5 °(*c* 1, chloroform).

Found: C, 72.07; H, 7.00%. Calcd for $C_{26}H_{28}O_5 \cdot C_2H_5OH$: C, 72.08; H, 7.35%.

The monoethyl alcoholate was dried over phosphorous pentoxide at 60 °C for 24 h.

PMR data for unhydrous II (100 MHz): δ 1.15 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3), δ 3.25 (s, 3H, OCH_3).

Found: C, 73.96; H, 6.74%. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71%.

Methyl 3-O-Trityl α-D-Fucopyranoside (III). The mother liquid of the recrystallization of II from the pyridine solution was dried *in vacuo* and chromatographed on 10 g of silica gel. The column was washed with 2% acetone/benzene (200 ml) and with 2.5% acetone/benzene (200 ml). The eluent was divided into eight 50-ml fractions. Each of them was dried *in vacuo*, and each residue was chromatographed on a thin-layer plate. The combined solid from the fractions which consisted of III weighed 417 mg. The crude III was recrystallized as monohydrate from a 60% methanol solution. The crystalline III had an $[\alpha]_D^{20}$ of +81.4° (*c* 1, chloroform) and melted at 71—74 °C.

PMR data for III (60 MHz): δ 0.98 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3), δ2.03 (dd, 1H, $J_{4,5}$ 1.5 Hz, $J_{3,4}$ 2.8 Hz, H-4), δ3.27 (s, 3H, OCH_3), δ3.41 (qd, 1H, H-5), δ 4.66 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1).

Found: C, 71.04; H, 6.62%. Calcd for $C_{26}H_{28}O_5 \cdot H_2O$: C, 71.23; H, 6.85%.

Acetylation of II and III. About 0.1 g of each sample was dissolved in 2 ml of dry pyridine and then acetylated with 0.2 ml of acetic anhydride and allowed to stand for 24 h. Each residue of the evaporation *in vacuo* was chromatographed on 10 g of silica gel. The peracetyl product of II (IV) was eluted with 1% acetone/benzene (200 ml) after the column had been washed with benzene (200 ml). The acetylation of III only gave a monoacetyl product (VIII). It was eluted with 2% acetone/benzene (200 ml) from the column. The yields were almost theoretical. The repeated crystallization of IV from 80% aqueous acetone gave needles; mp 172—174 °C, $[\alpha]_D^{20}$ +38.02° (*c* 1, chloroform).

Found: C, 71.00; H, 6.68%. Calcd for $C_{30}H_{32}O_7$: C, 71.41; H, 6.40%.

PMR data for IV (100 MHz): δ 1.01 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3), δ 1.75 (s, 3H, OAc), δ 1.90 (s, 3H, OAc), δ 3.30 (s, 3H, OCH_3), δ 3.80 (dd, 1H, $J_{1,2}$ 3.5 Hz, $J_{2,3}$ 10 Hz, H-2), δ 4.04 (qd, 1H, $J_{4,5}$ 1.5 Hz, H-5), δ 4.02 (d, 1H, H-1), δ 5.12 (dd, 1H, $J_{3,4}$ 3.5 Hz, H-4), δ 5.45 (dd, 1H, H-3).

PMR data for VIII (60 MHz): δ 1.00 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3), δ 2.02 (s, 3H, OAc), δ 2.25 (dd, 1H, $J_{4,5}$ 1.5 Hz, $J_{3,4}$ 3.5 Hz, H-4), δ 3.22 (s, 3H, OCH_3), δ 3.47 (qd, 1H, H-5), δ4.07 (dd, 1H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 3.5 Hz, H-3), δ4.75 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), δ 5.31 (dd, 1H, H-2).

Methylation of II and III. Each of the trityl ethers (0.1 g) was methylated in dry *N,N'*-dimethylformamide (5 ml) with methyl iodide (0.4 ml) and 0.8 g of a 1 : 1 mixture of silver oxide and barium oxide for 24 h. After filtration, each filtrate was concentrated *in vacuo*, and the residue was resolved in an admixture of methyl ethyl ketone and benzene (1 : 1 v/v) (20 ml), after which the solution was filtered to remove any insoluble matter. Each residue of the evaporation was chromatographed on 10 g of silica gel. The per-

methylated products, V and IX, were eluted with 1% acetone/benzene (200 ml). The yields were about 60% in both cases. The preparation of V and IX showed spots of R_f-values of 0.67 and 0.45 respectively on a thin-layer chromatogram with 6% acetone/benzene. Both derivatives were crystallized from 80% ethanol solutions as prisms; mp for V: 124 °C and mp for IX: 131—133 °C. The $[\alpha]_D^{20}$ of V was +24.5 ° (*c* 1.6, chloroform), and the $[\alpha]_D^{20}$ of IX was +131.1° (*c* 1.5, chloroform).

PMR data for V (60 MHz): δ 1.09 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3), δ 2.96 (s, 3H, OCH_3), δ 3.17 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1), δ 3.47 (s, 3H, OCH_3), δ 3.57 (s, 3H, OCH_3), δ 4.13 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2).

PMR data for IX (60 MHz-FT): δ 0.89 (d, 3H, $J_{5,6}$ 6.7 Hz, CH_3), δ 1.72 (s broad, 1H, H-4), δ 3.23 (s, 3H, OCH_3), δ 3.27 (s, 3H, OCH_3), δ^{ca} 3.33 (H-5), δ 3.63 (s, 3H, OCH_3), δ^{ca} 3.85 (dd, 1H, $J_{1,2}$ 3.3 Hz, $J_{2,3}$ 10.0 Hz, H-2), δ^{ca} 4.13 (dd, 1H, $J_{3,4}$ 2.2 Hz, H-3), δ 4.77 (d, 1H, H-1).

Found for V: C, 74.96; H, 7.25%. Calcd for $C_{28}H_{32}O_5$: C, 74.97; H, 7.19%.

Found for IX: C, 74.91; H, 7.20%. Calcd for $C_{28}H_{32}O_5$: C, 74.97; H, 7.19%.

Detritylation of V and IX. Each 50-mg portion of V and IX was dissolved with 80% acetic acid (0.5 ml) and heated at 90 °C in a sealed tube for 30 min. The solutions were then concentrated with toluene (3 ml) *in vacuo*. The residue of evaporation were chromatographed on 5 g of silica gel. The detritylation products, VI and X, were eluted with chloroform (100 ml). The subsequent evaporation of the eluting solvent left VI and X in almost theoretical yields. Retention index (I_R)[13] on GLC (He: 22 ml/min, column: 5′×1/8″, glass, column temperature: 140 °C) for VI: 2026 (5% NPGS/Chromosorb W) and 1526 (2% OV 17/Chromosorb W), for X: 2035 (5% NPGS) and 1584 (2% OV 17). Both ethers were crystallized from hexane solutions as needles; mp for VI: 82—85 °C, and mp for X: 74—78 °C, $[\alpha]_D^{20}$ for VI: +201.1 ° (*c* 0.9, chloroform) and $[\alpha]_D^{20}$ for X: +175.4° (*c* 1.2, chloroform).

Found for VI: C, 52.25; H, 8.57%. Calcd for $C_9H_{18}O_5$: C, 52.41; H, 8.80%.

Found for X: C, 52.23; H, 8.53%. Calcd for $C_9H_{18}O_5$: C, 52.41; H, 8.80%.

Methyl 2,3-Di-O-methyl α-D-Fucopyranoside (XII). Methyl 2-*O*-methyl α-D-fucopyranoside (0.5 g) was methylated in almost the same manner as is described above with methyl iodide (0.25 ml). After the removal of the catalyzer and the silver iodide, the residue of evaporation was chromatographed on 10 g of silica gel. The partially methylated products, X and XII, were eluted with 9% acetone/benzene (200 ml). The eluent was divided into five 40-ml fractions. Then it was re-chromatographed four times, while the fractions were gradually returned to the column with additional eluting solvent to get thirteen fractions. Each residue of evaporation was chromatographed on a thin-layer plate. The combined fractions, which contained only XII, were dried *in vacuo*. The residue weighed about 60 mg and had an $[\alpha]_D^{20}$ of +145.0 ° (*c* 1.0, chloroform). The structure of XII was confirmed by PMR as its acetylated derivative (XIII). I_R for XII: 2000 (5% NPGS) and 1584 (2% OV 17).

Found: C, 52.10; H, 8.60%. Calcd for $C_9H_{18}O_5$: C, 52.41; H, 8.80%.

Acetylation of VI, X and XII. The acetylation procedure used for these ethers was almost the same as that used for II and III. The acetylation products, VII, XI, and XIII, were purified by chromatography, after having been eluted with 1% acetone/benzene (200 ml) from silica gel column (10 g). The evaporation of the eluting solvent left the acetylation products in an almost theoretical yield as glass: $[\alpha]_D^{20}$ for VII; +156.4° (*c* 0.3, chloroform), for XI; +156.0° *c* 1.3, chloroform), and for XIII; +138.7° (*c* 0.6, chloroform). I_R for VII; 2095 (5% NPGS) and 1700 (2% OV 17), for XI; 2112 (5% NPGS) and 1770 (2% OV 17) and for XIII; 1981 (5% NPGS) and 1667 (2% OV 17).

PMR data for VII (60 MHz): δ 1.25 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3), δ 2.08 (s, 3H, OAc), δ 3.34 (s, 3H, OCH_3), δ 3.45 (s, 3H, OCH_3), δ 3.57 (s, 3H, OCH_3), δ 3.87 (qd, 1H, H-5), δ 4.85 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), δ 5.12 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2), for XI (60 MHz): δ 1.22 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3), δ 2.10 (s, 3H, OAc), δ 3.37 (s, 3H, OCH_3), δ 3.43 (s, 3H, OCH_3), δ 3.48 (s, 3H, OCH_3) δ^{ca} 3.48 (H-4), δ 3.70 (dd, 1H, $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 10.3 Hz, H-2), δ 3.93 (qd, 1H, H-5), δ4.82 (d, 1H, H-1), δ 5.10 (dd, 1H, $J_{3,4}$ 3.2 Hz, H-3), and for XIII (100 MHz): δ 1.17 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3), δ2.20 (s, 3H, OAc), δ 3.44 (s, 3H, OCH_3), δ 3.46 (s, 3H, OCH_3), δ 3.55 (s, 3H, OCH_3), δ 4.03 (qd, 1H, H-5), δ 4.89 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1), δ 5.36 (dd, 1H, $J_{4,5}$ 1.2 Hz, $J_{3,4}$ 3.0 Hz, H-4).

Relative peak intensities on MS for VII: *m/e* 72; 77, *m/e* 74; 82, *m/e* 75; 86, *m/e* 88; 100, *m/e* 97; 5.0, *m/e* 101; 18, *m/e* 116; 23, *m/e* 129; 14, *m/e* 157; 0.5, *m/e* 185; 4.0, *m/e* 204 ($M-CH_3$ CHO); 0.8, *m/e* 217 ($M-CH_3O$); 0.3, for XI; *m/e* 72; 51, *m/e* 74; 100, *m/e* 75; 38, *m/e* 88; 36, *m/e* 97; 20, *m/e* 101; 30, *m/e* 116; 40, *m/e* 129; 24, *m/e* 157; 6.0, *m/e* 185, 1.2, *m/e* 204 ($M-CH_3CHO$); 0, *m/e* 217 ($M-CH_3O$); 1.0, and for XIII: *m/e* 72; 2.0, *m/e* 73; 18, *m/e* 74; 10, *m/e* 75; 44, *m/e* 85; 24, *m/e* 88; 100, *m/e* 97; 4.5, *m/e* 101; 8.5, *m/e* 116; 3.0, *m/e* 125; 5.4, *m/e* 129; 5.5, *m/e* 157; 0.8, *m/e* 185; 1.2, *m/e* 204 ($M-CH_3CHO$); 1.0, *m/e* 217 ($M-CH_3O$); 1.4.

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