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Isopropylidenation of Raffinose[1)]

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A reaction of raffinose with an excess amount of 2,2-dimethoxypropane and *p*-toluenesulfonic acid as a catalyst in *N,N'*-dimethylformamide, followed by acetylation, gave seven kinds of mono-, di, or tri-*O*-isopropylideneraffinose peracetates with at least five kinds of minor products. A reaction of raffinose with a limited amount of 2,2-dimethoxypropane gave a new isopropylidene derivative with some of the derivatives described above. The isopropylidenation occurred at 1′,2-, 2,3-, 2″,3″-, 3,4-, 3″,4″-, and 4″,6″-positions. The structures of these compounds were established by ^{1}H and ^{13}C NMR analyses.

The importance of cyclic acetals for the selective blocking of hydroxyl groups in carbohydrate chemistry has long been recognized.[2)] However isopropylidenation of nonreducing sugars like sucrose and raffinose with acetone and an acidic catalyst had been unsuccessful. In 1975, Khan and Mufti[3–5)] investigated the reaction of sucrose with a combination of DMP,[*1] DMF,[*2] and TSA[*3] called reagent A. They obtained 4,6-*O*-isopropylidenesucrose and 1′,2:4,6-di-*O*-isopropylidenesucrose. The author[6)] has reported the isopropylidenation of 6,6′-di-*O*-palmitoylsucrose with reagent A. The main product was 1′,2-*O*-isopropylidene-6,6′-di-*O*-palmitoylsucrose.

Salam[7,8)] has reported that treatment of raffinose (**1**) with benzylidene bromide in pyridine followed by acetylation gave 3″,4″-*O*-benzylideneraffinose nonaacetate and 1′,2:4″,6″-di-*O*-benzylideneraffinose heptaacetate, and that treatment of **1** with reagent A yielded 4″,6″-*O*-isopropylideneraffinose in 21% yield. This paper will deal with mono-, di-, or tri-*O*-isopropylideneraffinose peracetates acetalated at 1′,2-, 2,3-, 2″,3″-, 3,4-, 3″,4″-, or 4″,6″-positions using reagent A.

Results and Discussion

Reaction of **1** with DMP in a molar ratio of 1:20 and TSA in DMF for 80 min, gave a mixture of isopropylidene(Ip) derivatives of **1**. By thin-layer chromatography(TLC), the complete consumption of **1** was confirmed. On a silica-gel TLC of the acetylation product of the above reaction mixture (developed four times with an admixture of diethyl ether and hexane (4:1 or 5:1)), at least seven spots were separately observed. They were designated in R_f's order (high to low) as **2** to **8**. After recycling column chromatography of the acetates about 35 times on an open column of silica gel eluted with a solvent system of diethyl ether and hexane or diisopropyl ether and hexane, the seven acetates were isolated as pure or almost pure forms on a TLC, and at least five minor components were also separated as almost pure forms. Yields of the seven acetates were 0.8 (**2**), 4.0 (**3**), 3.4 (**4**), 3.5 (**5**), 25.4 (**6**), 3.5 (**7**), and 5.5% (**8**), respectively. The major component was **6**. Compounds **3**, **6**, **7**, and **8** were crystallized as needles, respectively. From an elementary analysis, and ^{1}H and ^{13}C NMR analyses of acetyl methyl proton signals and methyl and quaternary carbon signals of the Ip-groups (Tables 1 and 2), the degree of isopropylidenation was estimated as shown in Table 3. Figure 1 shows schematic spectra of the acetates in the region of methyl and quaternary carbons of the Ip-group. By following common signals on the spectra of the eight compounds, at

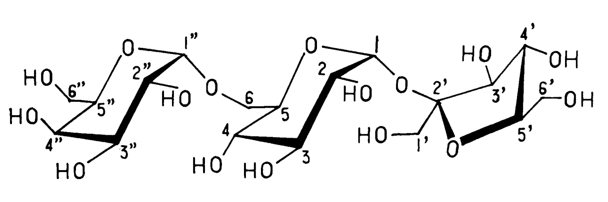


Table 1. ^{1}H Chemical Shifts(δ ppm) of the Ip- and Acetyl Groups of the *O*-Isopropylideneraffinose Peracetates

	Ip-methyl protons	Acetyl methyl protons
2	1.34, 1.40, 1.47(6H), 1.52, and 1.56.	2.08, 2.09, 2.12, 2.14, and 2.15.
3	1.27, 1.32, 1.48, and 1.50.	2.02, 2.05, 2.06, 2.10, 2.12, 2.14, and 2.24.
4	1.39, 1.42, 1.47(9H), and 1.54.	2.06, 2.07, 2.08, 2.10, and 2.14.
5	1.26, 1.47(9H), and 1.51.	2.01, 2.03, 2.08, 2.09, and 2.24.
6	1.27, 1.42, 1.46, and 1.49.	2.02, 2.05, 2.06, 2.07, 2.08, 2.12, and 2.24.
7	1.39, 1.42, 1.44 and 1.46.	2.08, 2.09(9H), and 2.12(9H)
8	1.38 and 1.43.	1.98, 2.00, 2.02, 2.05 2.06(6H), 2.07, 2.08, and 2.13.
9	1.31 and 1.49.	2.00, 2.04, 2.08, 2.09(6H), 2.10, 2.11, 2.13, and 2.15.

[*1] 2,2-Dimethoxypropane, [*2] *N,N'*-Dimethylfomamide, [*3] *p*-Tolueneesulfonic acid.

least, six sets of signals were distinguished. Compound **9** will be described later. Each set consists of signals of two methyl carbons and one quaternary carbon in the same Ip-group. The Ip-groups corresponding to each set were designated as Ip-1 to Ip-6. The mean δ-values of the carbons in each Ip-group are as follows: Ip-1, δ=26.26, 27.82, and 109.85; Ip-2, δ=26.62, 26.81, and 111.02; Ip-3, δ=26.57, 26.68, 110.23; Ip-4, δ=23.93, 25.43, and 101.51; Ip-5, δ=26.20, 26.91, and 111.57; Ip-6, δ=18.50, 29.38, and 98.79. Possible assignments of the Ip-groups to each compound are as follows: **2**, Ip-1, Ip-2, and Ip-4; **3**, Ip-1, and Ip-4; **4**, Ip-2, Ip-4, and Ip-6; **5**, Ip-3, Ip-4, and Ip-6; **6**, Ip-4 and Ip-6; **7**, Ip-5 and Ip-6; **8**, Ip-6; **9**, Ip-1.

Table 2. ^{13}C Chemical Shifts(δ ppm) of the Ip-Group and C-1, C-1″, and C-2′ of the *O*-Isopropylideneraffinose Peraceates

	Ip-methyl carbons
2	24.02, 25.46, 26.34, 26.58, 26.76, and 27.92.
3	23.86, 25.39, 26.30, and 27.88.
4	18.52, 24.06, 25.48, 26.65, 26.85, and 29.40.
5	18.47, 23.79, 25.45, 26.57, 26.68, and 29.28.
6	18.51, 23.93, 25.39, and 29.40.
7	18.50, 26.20, 26.91, and 29.40.
8	18.49 and 29.40
9	26.51 and 27.73

	C-1	C-1″	C-2′	Quaternary carbons of the Ip-group
2	91.42	96.52	104.26	101.62, 109.88, and and 111.02.
3	90.54	96.49	104.58	101.53 and 109.89.
4	91.11	97.24	104.03	98.78, 101.52, and 111.02.
5	90.57	96.47	104.55	98.74, 101.41, and 110.23.
6	90.34	93.33	104.44	98.78 and 101.47.
7	90.25	96.79	103.05	98.80 and 111.57
8	89.96	96.66	104.36	98.84.
9	90.08	96.00	104.40	109.77.

Table 3. Degree of Isopropylidenation of Each Compound Estimated by Elementary Analysis and Numbers of Signals of Under-Lined Atoms on NMR Spectra

	Ip-degree	Numbers of signals		
		$C\underline{H}_3CO$	$(\underline{C}H_3)_2CO_2$	$(CH_3)_2\underline{C}O_2$
2	Tri	5	6	3
3	Di	7	4	2
4	Tri	5	6	3
5	Tri	5	6	3
6	Di	7	4	2
7	Di	7	4	2
8	Mono	9	2	1
9	Mono	9	2	1

The structure of each compound was established by ^1H NMR with the aid of the 180° pulse-τ-90° pulse method[9,10] or others. The signal of the free induction decay of the 90° pulse was recorded and Fourier-transformed. At a τ-value of 0.15 s, the intensity of methylene-proton signal was almost zero, and methine protons showed negative signals. At a τ-value of 0.30—0.35 s, the intensities of methine-proton signals were low (positive or negative) and methylene protons showed positive signals.

First-order analyses of the eight compounds are summarized in Tables 4-1 and 4-2. Signals of the glycosylated methylene (H-6a and H-6b), Ip-*O*-methylene and methine protons are in a region between 3.3 and 4.3 ppm. Signals of acetoxy-substituted methylene and methine protons adjacent to the methylene group (H-5, H-5′, and H-5″) are in a region between 4.3 and 4.5 ppm, while signals of anomeric and other acetoxy-substituted methine protons fall in a region over 4.6 ppm.[11,12]

From the high-field shifts of H-4″ and H-6″ (2H), **8** was estimated to be 4″,6″-*O*-isopropylideneraffinose nonaacetate. Two symmetric proton signals, centered on 5.25 ppm, are regarded as signals of H-2″ and H-3″. This pattern is caused by a similar environment of the two protons:

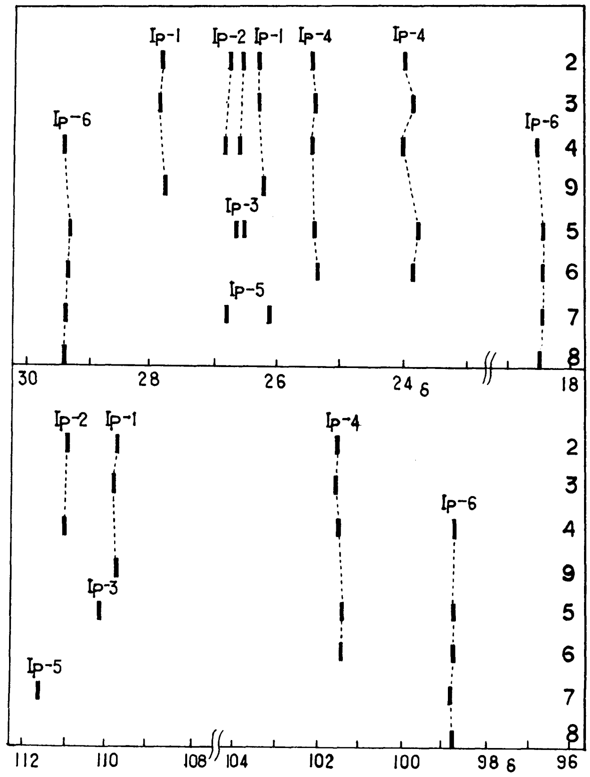
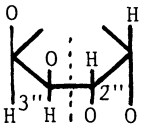


Fig. 1. Schematic ^{13}C NMR spectra of methyl (δ 18—30) and quaternary carbons (δ 96—112) of the Ip-group.



Other acetoxy-substituted methine signals (H-2, H-3, H-4, H-3′, and H-4′) were well analyzed, confirming the structure. Compounds having Ip-6 (**7**, **6**, **5**, and **4**) are also regarded as 4″,6″-*O*-isopropylidene derivatives. On a ^{1}H NMR spectrum of 6″-*O*-tritylraffinose decaacetate,[11] the coupling constants, $J_{5'',6''a}$ and $J_{5'',6''b}$ were 5 and 7 Hz, respectively. The small values of the corresponding coupling constants in the case of **8** may be caused by the rigid structure of the 4″,6″-*O*-Ip-ring.

In the case of **7**, the presence of a 4″,6″-*O*-isopropylidene group was confirmed by high-field shifts of the corresponding protons. A doublet and a triplet at 3.52 and 4.09 ppm were confirmed to be the signals of H-2 and H-3 by the decoupling method. Thus, **7** is expected to be 2,3:4″,6″-di-*O*-isopropylideneraffinose heptaacetate.

On a ^{1}H NMR spectrum of **6**, high-field shifts of H-1′ (2H) and H-2 were observed in addition to the high-field shifts of H-4″ and H-6″ (2H). Signals of acetoxy-substituted methine protons, H-3, H-4, H-3′, and H-4′ were wholly analyzed. A broad singlet of two protons centered on 5.25 ppm was assigned to the complex signals of H-2″ and H-3″. Thus, the main product **6** was confirmed to be 1′,2:4″,6″-di-*O*-isopropylideneraffinose heptaacetate. The Ip-4 type products, **2**, **3**, **4**, **5**, and **6** should be 1′,2-*O*-Ip-derivatives.

In the case of **5**, high-field shifts of H-1′ (2H), H-2, H-4″, and H-6″ (2H) were observed. All the signals involving acetoxy-substituted methine protons in a region over 4.6 ppm, H-3, H-4, H-3′, and H-4′ were wholly analyzed. At a τ of 0.15 s, in the 180° pulse-τ-90° pulse method, symmetric two-proton signals centered on 4.12 ppm were observed and assigned to the complex signals of H-2″ and H-3″. The assignments were supported by homonuclear correlated two-dimentional ^{1}H NMR.[13] A signal at 5.29 ppm (H-1″) correlated with a signal at 4.14 ppm

Table 4-1. Chemical Shifts (δ ppm) on ^{1}H NMR Spectra of the *O*-Isopropylideneraffinose Peracetates

	H-1 d	H-2 dd	H-3t(dd)		H-4t(dd)	H-6a dd	H-6b dd
2	6.20	3.96	3.80	or	3.35	3.85	3.72
3	6.12	3.84	5.31		5.11	3.74	3.52
4	6.17	3.96	3.79	or	3.30	3.76	3.69
5	6.16	3.85	5.30		5.16	3.81	3.67
6	6.16	3.78	5.33		5.04	3.79	3.53
7	5.71	3.52	4.09		5.21	3.77	3.63
8	5.67	4.82	5.46		5.06	3.78	3.54
9	5.63	4.78	5.43		5.09	3.69	3.49

	H-1′a d	H-1′b d	H-3′d	H-4′t(dd)	H-6′a dd	H-6′b dd
2	4.06	3.54	5.13	5.35	rd. 4.4	
3	4.04	3.53	5.16	5.37	rd. 4.4	
4	3.88	3.53	5.16	5.36	ca. 4.22	ca. 4.15
5	4.06	3.53	5.16	5.34	rd. 4.4	
6	3.86	3.53	5.19	5.38	4.53	4.27
7	4.27	4.07	rd. 5.46		rd. 4.4	
8	4.29	4.20	5.46	5.32	4.37	ca. 4.3
9	rd. 4.3		5.41	5.33	rd. 4.4	

	H-1″d	H-2″	H-3″	H-4″	H-5″	H-6″a dd	H-6″b dd
2	5.04	4.92 dd	rd. 4.3				
3	5.02	4.87 dd	4.38 dd	rd. 4.3			
4	5.19	ct. 5.30 m		3.79 bs	4.46 bs	4.09	3.89
5	5.29	ct. 4.12 m		3.46 bs	4.52 bs	4.17	3.90
6	5.19	ct. 5.27 m		3.72 bs	4.48 bs	4.08	4.01
7	rd. 5.2			3.71 bs	4.66 bs	4.07	3.84
8	5.17	ct. 5.25 m		3.72 bs	4.44 bs	4.10	3.85
9	4.97	4.85 dd	4.30 dd	rd. 4.2			

rd.: round, ct: centered on, bs: broad singlet, d: doublet, dd: doublet of doublets, t: triplet, m: multiplet.

Table 4-2. Coupling Constants(J Hz) on ^{1}H NMR Spectra of the *O*-Isopropylideneraffinose Peracetates

	1-2	2-3	3-4	4-5	5-6a	5-6b	6a-6b
2	3.8	10.4	10.0	10.0	5.0	ca. 2	10.4
3	3.4	9.6	10.0	10.0	4.0	ca. 2	12.0
4	3.5	9.8	9.8	9.8	5.6	ca. 2	9.0
5	3.8	9.5	9.5	9.5	4.0	ca. 2	10.6
6	3.5	9.8	9.8	9.8	5.0	ca. 3	ca.13
7	3.4	9.8	9.8	ca.10	3.8	2.3	8.8
8	4.0	10.4	10.4	10.4	5.2	2.5	11.0
9	3.8	10.0	10.0	10.0	3.8	ca. 2	12.0

	1′a-1′b	3′-4′	4′-5′	5′-6′a	5′-6′b	6′a-6′b
2	12.2	6.0	4.0	—	—	—
3	12.8	6.0	4.0	—	—	—
4	12.2	6.4	5.4	—	—	—
5	12.0	4.7	3.8	—	—	—
6	13.0	6.2	ca. 6	—	—	—
7	12.4	—	—	—	—	—
8	12.0	6.0	6.0	6.0	ca. 2	6.0
9	—	5.2	5.2	—	—	—

	1″-2″	2″-3″	3″-4″	4″-5″	5″-6″a	5″-6″b	6″a-6″b
2	3.4	8.4	—	—	—	—	—
3	3.6	7.8	—	—	—	—	—
4	4.0	—	ca. 1.5	ca. 1.5	ca. 1.5	ca. 1.5	13.5
5	2.8	—	ca. 1.5	ca. 1.5	ca. 1.5	ca. 1.5	13.6
6	3.5	—	ca. 1.5	ca. 1.5	ca. 1.5	0	12.8
7	—	—	ca. 1.5	ca. 1.5	ca. 1.5	ca. 1.5	12.6
8	2.5	—	ca. 1.5	ca. 1.5	ca. 1.5	ca. 1.5	12.4
9	3.3	8.0	—	—	—	—	—

to be assigned to H-2″, and a signal at 3.46 ppm (H-4″) correlated with a signal at 4.12 ppm to be assigned to H-3″. Thus, **5** was regarded as 1′,2:2″,3″:4″,6″-tri-*O*-isopropylideneraffinose pentaacetate, and Ip-3 is 2″,3″-*O*-Ip-group.

On a spectrum of **4**, high-field shifts of H-1′ (2H), H-2, H-3, H-4, H-4″, and H-6″ (2H) were recognized. In a region between 5.1 and 5.4 ppm, signals of acetoxy-substituted methine protons, H-1″, H-2″, H-3′, H-3″, and H-4′ were observed. The complex signals of H-2″ and H-3″ had almost the same symmetric pattern as that on the spectrum of **8**. Thus, **4** was recognized as 1′,2:3,4:4″,6″-tri-*O*-isopropylideneraffinose pentaacetate. Compound **2**, which also had an Ip-2 type Ip-group, was assumed to be a 3,4-*O*-isopropylidene derivative of **1**.

In the case of **3**, signals of five acetoxy-substituted methine protons, H-2″, H-3, H-3′, H-4, and H-4′ and an anomeric proton, H-1″ were observed in the region between 4.8 and 5.4 ppm. Signals of H-1′ (2H), H-2, and H-3″ were in a high field. Although the assignment of H-4″ could not be achieved due to the absence of an H-4″ signal in the region above 4.6 ppm, the high-field shift of H-4″ was clear. Thus, **3** is regarded to be 1′,2:3″,4″-di-*O*-isopropylideneraffinose heptaacetate, and Ip-1 is assumed to be a 3″,4″-*O*-isopropylidene group.

In the case of **2**, acetoxy-substituted methine protons were H-2″, H-3′ and H-4′. High-field shifts of H-1′ (2H), H-2, H-3, and H-4 were clearly recognized. Signals of H-3″ and H-4″ should be in the region between 4.3 and 4.5 ppm. Compound **2** was recognized as 1′,2:3,4:3″,4″-tri-*O*-isopropylideneraffinose pentaacetate.

In the above reaction, six types of isopropylidenation were observed. The main types were 4″,6″- and 1′,2-*O*-isopropylidenation. Isopropylidenations at 3′,4′-, and 4′,6′-positions were not found.

A reaction of **1** with DMP in a molar ratio of 1:6.5 in the presence of TSA in DMF for 80 min., also gave a mixture of Ip-derivatives without a free form of **1**. After recycling column chromatography of the corresponding acetates (about 30 times on a silica-gel column using the same method as for the former reaction), compounds, **3**, **6**, **8**, and **9** were isolated as pure or almost pure forms. A minor component and a mixture consisting of two components were also obtained. The yields of the four acetates were 1.7 (**3**), 11.3 (**6**), 10.6 (**8**), and 2.3% (**9**), respectively.

On ^{1}H and ^{13}C NMR spectra of **9**, 9 signals of acetyl methyl protons, 2 signals of Ip-methyl carbons and one signal of a quarternary carbon in an Ip-group were observed as shown in Table 1. Thus, **9** was estimated to be a mono-*O*-Ip-derivative, and the chemical shifts of the Ip-methyl carbons and the quaternary carbon in the Ip-group showed that **9** is 3″,4″-*O*-isopropylideneraffinose nonaacetate (Fig 1).

Table 5. Elementary Analysis, Optical Rotation ($[\alpha]_\mathrm{D}^{20}$) in Chloroform, Melting Point, and R_f and R_2 on TLC of the *O*-Isopropylideneraffinose Peracetates

	Found (%)		$[\alpha]_\mathrm{D}^{20}$	(c)	Mp(θ_m/°C)	R_f*	R_2*2
	C	H					
2	53.26	6.55	+ 59.50°	(1)	—	0.53	1.00
3	51.64	6.19	+ 78.16°	(1)	90—91	0.50	0.96
4	53.36	6.50	+ 82.67°	(1.5)	—	0.44	0.83
5	53.34	6.55	+ 75.33°	(1.5)	—	0.38	0.71
6	51.68	6.17	+104.00°	(1.5)	181—183	0.33	0.63
7	51.66	6.12	+113.58°	(1.5)	153—155	0.28	0.52
8	50.55	5.72	+115.46°	(1.5)	187—188	0.22	0.42
9	51.08	5.94	+122.27°	(1)	—	0.37	0.70

Calcd for $C_{39}H_{54}O_{21}$ (**8** and **9**): C, 50.76; H, 5.90%, for $C_{38}H_{54}O_{23}$ (**3**, **6**, and **7**): C, 51.94; H, 6.19%, for $C_{37}H_{54}O_{25}$ (**2**, **4**, and **5**): C, 53.23; H, 6.52%.

*1 TLC was performed with diethyl ether–hexane (4:1) in a quadruplicated development.

*2 R_2: migration length of **X**/ that of **2**.

In the acetoxy-substituted methine-proton region on a ^{1}H NMR spectrum of **9**, H-2, H-2″, H-3, H-3′, H-4, and H-4′ signals were observed. Due to an overlapping of the signals assignments of H-3″ and H-4″ could not be achieved; however **9** is difinitely regarded as a 3″,4″-*O*-Ip-derivative. Increases in mono-*O*-Ip-derivatives and decreases in tri-*O*-Ip-derivatives (compared to a high-DMP reaction) were reasonable.

Experimental

General Methods. Melting points were determined in capilary tubes and were uncorrected. Optical rotations were measured with a Japan Spectroscopic DIP-SL polarimeter. The ^{1}H and ^{13}C NMR spectra were recorded at 200 MHz (for ^{1}H) with a Varian XL-200 and at 300 MHz (for ^{1}H) with a Varian XL-300 spectrophotometer in deuteriochloroform with tetramethylsilane as an internal standard. With ^{1}H NMR, the spectral width was 2000 Hz (16000 data points) for the 200-MHz instrument and 4000 Hz (32000 data points) for the 300-MHz instrument. With ^{13}C NMR, the spectral width was 11574.1 Hz (16364 data points) and 16501.7 Hz (32000 data points). Acquisition times were 4.0 s for ^{1}H NMR and 0.7—0.97 s for ^{13}C NMR. Sixteen-times accumulation for ^{1}H NMR and 512-times accumulation for ^{13}C NMR were used. In the 180° pulse-τ-90° pulse method, the post delay (interval of the end of acquisition and 180° pulse) was 5 s, and the range of τ was 0.05—0.35 s TLC was performed on silica-gel plates (Art. 5554, DC-Alufolien Kieselgel 60 F_{254}, in a thickness of 0.2 mm, Merck) developed with a solvent system of 1-butanol–acetic acid–water (4:1:1.7) for the free Ip-derivatives and a solvent system of diethyl ether–hexane (4:1 or 5:1) in quadruplicated development for the *O*-isopropylideneraffinose peracetates. Open-column chromatography of the acetates was achieved on a silica-gel column (Wakogel C-200, Wako Pure Chemical Ind. Ltd.) eluted with diethyl ether–hexane (4:1 or 5:1). Recycling took place 30—35 times. Samples added to the column were dissolved in chloroform. The weight of the adsorbent that was used was about 20 times that of the submitted sample and the volume of eluting solvent was about 30 times that of the adsorbent (vol/wt). The eluent was divided into 50—60 fractions. Each fraction was inspected by TLC, and the fractions having the same R_f values were collected and dried for further inspection. An admixture of diisopropyl ether and hexane (3:1) was applied for the separation of **4** and **5**.

Isopropylidenation of 1 and Acetylation of the Reaction Products. To a solution of **1** (5.0 g, 0.01 mol as dehydrated material), 0.5 g of TSA and 25 ml (d=0.85, ca. 0.2 mol) of DMP in a "high-DMP reaction" and 8 ml (0.065 mol) of DMP in a "low-DMP reaction" in 250 ml of DMF were added and each mixture was settled for 80 min at room temperature. The solution was then neutralized with IR-410(OH) resin, filtered, and concentrated. The resultant syrupy residue was then acetylated with acetic anhydride (12 ml) in pyridine (20 ml). The reaction mixture was concentrated to give a syrupy product. The product was dissolved in chloroform and added to a silica-gel column. After recycling chromatography above-described, each reaction product of the high- and low-DMP reaction was divided into the isolates, **2** to **8** in the high-DMP reaction, and **3**, **6**, **8**, and **9** in the low-DMP reaction. The combined yields of the high- and low-DMP reaction were 4.03 g (46%), and 2.42 g (26%), respectively.

Elementary Analysis and Physical Data of the *O*-Isopropylideneraffinose Peracetates. The elementary analysis and physical data of 1′,2:3,4:3″,4″-tri-*O*-isopropylideneraffinose pentaacetate (**2**), 1′,2:3″,4″-di-*O*-isopropylideneraffinose heptaacetate (**3**), 1′,2:3,4:4″,6″-tri-*O*-isopropylideneraffinose pentaacetate (**4**), 1′,2:2″,3″:4″,6″-tri-*O*-isopropylideneraffinose pentaacetate (**5**), 1′,2:4″,6″-di-*O*-isopropylideneraffinose heptaacetate (**6**), 2,3:4″,6″-di-*O*-isopropylideneraffinose heptaacetate (**7**), 4″,6″-*O*-isopropylideneraffinose nonaacetate (**8**), and 3″,4″-*O*-isopropylideneraffinose nonaacetate (**9**) were summarized in Table 1, 2, 4, and 5. The weights obtained and yields were as follows; (i) high-DMP reaction: **2** 72.1 mg (0.8%), **3** 348 mg (4.0%), **4** 297 mg (3.4%), **5** 302 mg (3.5%), **6** 2227 mg (25.4%), **7** 309 mg (3.5%), and **8** 479 mg (5.5%); (ii) low-DMP reaction: **3** 159 mg (1.7%), **6** 1066 mg (11.3%), **8** 1000 mg (10.6%), and **9** 215 mg (2.3%).

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