# Preparations and Reactions of Alkyl Ethers of Some Aldohexoses

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**ABSTRACT:** Aldohexose, such as D-glucose, D-galactose or D-mannose, reacted with acetone to give the following O-isopropylidene derivatives: 1,2;5,6-di-O-isopropylidene-D-glucofuranose (IA), 1,2;3,4-di-O-isopropylidene-D-galactopyranose (IB) or 2,3;5,6-di-O-isopropylidene-D-mannofuranose (IC). The O-isopropylidene derivative (IA~IC) reacted with alkyl/alkenyl halogenide to yield aldohexose ether compounds containing di-O-isopropylidene group, 3-O-alkyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose (II), 6-O-alkyl-1,2;3,4-di-O-isopropylidene-D-galactopyranose (III) or 1-O-alkyl-2,3;5,6-di-O-isopropylidene-D-mannofuranoside (IV), in good yields. The Williamson ether synthesis was carried out using phase-transfer catalysis (PTC). The derived aldohexose alkyl ether containing di-O-isopropylidene group was hydrolyzed to give 3-O-alkyl-1,2-O-isopropylidene-D-glucofuranose (V) as a partial hydrolysis product; the complete hydrolysis of I~IV gave, as expected, 3-O-alkyl-glucopyranose (VI), 6-O-alkyl-galactopyranose (VII) or 1-O-alkyl-mannofuranoside (VIII). Further alkylation of (V) with MeI under PTC and subsequent acid hydrolysis gave 3-O-alkyl-5,6-di-O-methyl-D-glucofuranose (X). Methanolysis of III with catalytic amounts of $H_2SO_4$ gave 1-O-methyl-6-O-alkyl-D-galactofuranoside (XI). The elucidation of the galactofuranoside skeleton of (XI) was determined by means of its $^{13}C$ nuclear magnetic resonance spectra. The O-alkyl aldohexoses, e.g., X and XI, were evaluated and found to be emulsifiers.
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**KEY WORDS:** Aldohexose, alkylation, D-galactofuranoside, D-galactopyranose, D-galactose, D-glucofuranose, D-glucose, D-mannofuranoside, D-mannose, emulsification, hydrolysis, isopropylidene group, methanolysis, PTC, Williamson ether synthesis.

Surfactants based on carbohydrates have long been known and are widely used as emulsifiers, solubilizers, surfactants, etc. In recent years, alkyl polyglycoside surfactants, derived by the reaction of glucose with a fatty alcohol, have been used as nonionic surfactants with good detergency and a very high degree of biodegradability (1–4). However, alkyl polyglycoside surfactants are polymerization products of glucose in which the average number of glucose units per unit of alcohol is 1–5.0. Thus, on account of their polymeric structures, the relationship between the chemical structures and the properties of this class of substances has not been fully understood. In contrast, studies on the synthesis and properties of alkyl aldohexoses bearing the lipophilic chain at various positions through different types of linkages, such as an ester bond, an ether bond and so on, have been reported in detail (5,6).

We report here on the preparation and reactions of nonionic surfactants with defined structures derived from the reactions of some aldohexoses, such as D-glucose, D-galactose and D-mannose, bearing di-O-isopropylidene groups with alkyl halides in Williamson ether synthesis. Isopropylidene compounds can be formed into cyclic sugars by the reaction of acetone with *cis* vicinal hydroxyl groups on furanose or pyranose rings. Isopropylidene compounds are easily crystallizable and distillable in a vacuum without decomposition. They are usually stable with respect to alkali, but are hydrolyzed by aqueous acids. Sometimes two isopropylidene groups on the same molecule differ in their rates of hydrolysis; in these cases it is possible to selectively remove only one isopropylidene group. We have also investigated the chemical transformations of these isopropylidene compounds of some aldohexoses, and found that the Williamson ether synthesis can be easily carried out under phase-transfer catalysis (PTC) under conditions that are mild compared to the conventional methods, which use alkali metal, alkali metal hydrides or large amounts of alkali metal hydroxides and polar solvents with high dielectric constant such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), dioxane, and so on (7,8). The great stability of isopropylidene groups to alkali allowed us to use the Williamson ether synthesis under the PTC reaction conditions to form alkyl ether derivatives of these aldohexose isopropylidene compounds.

## EXPERIMENTAL PROCEDURES

All melting points are uncorrected. Infrared (IR) spectra were obtained with a Hitachi (Tokyo, Japan) 260-50 IR spectrometer. Both $^1H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ using a Varian (Palo Alto, CA) EM 360L NMR spectrometer. Chemical shifts were measured in ppm downfield from internal tetramethylsilane

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($\delta = 0$). The abbreviations *s, d, t* and *m* denote singlet, doublet, triplet and multiplet resonances, respectively.

*Preparation of di-O-isopropylidene aldohexoses (IA–IC) (Fig. 1).* Three types of di-O-isopropylidene aldohexoses (D-glucose, D-galactose and D-mannose) were prepared following previously published procedures. 1,2;5,6-Di-O-isopropylidene-D-glucofuranose (IA) (9), 1,2;3,4-di-O-isopropylidene-D-galactopyranose (IB) (10) and 2,3;5,6-di-O-isopropylidene-D-mannofuranose (IC) (11) were prepared from D-glucose, D-galactose and D-mannose, respectively.

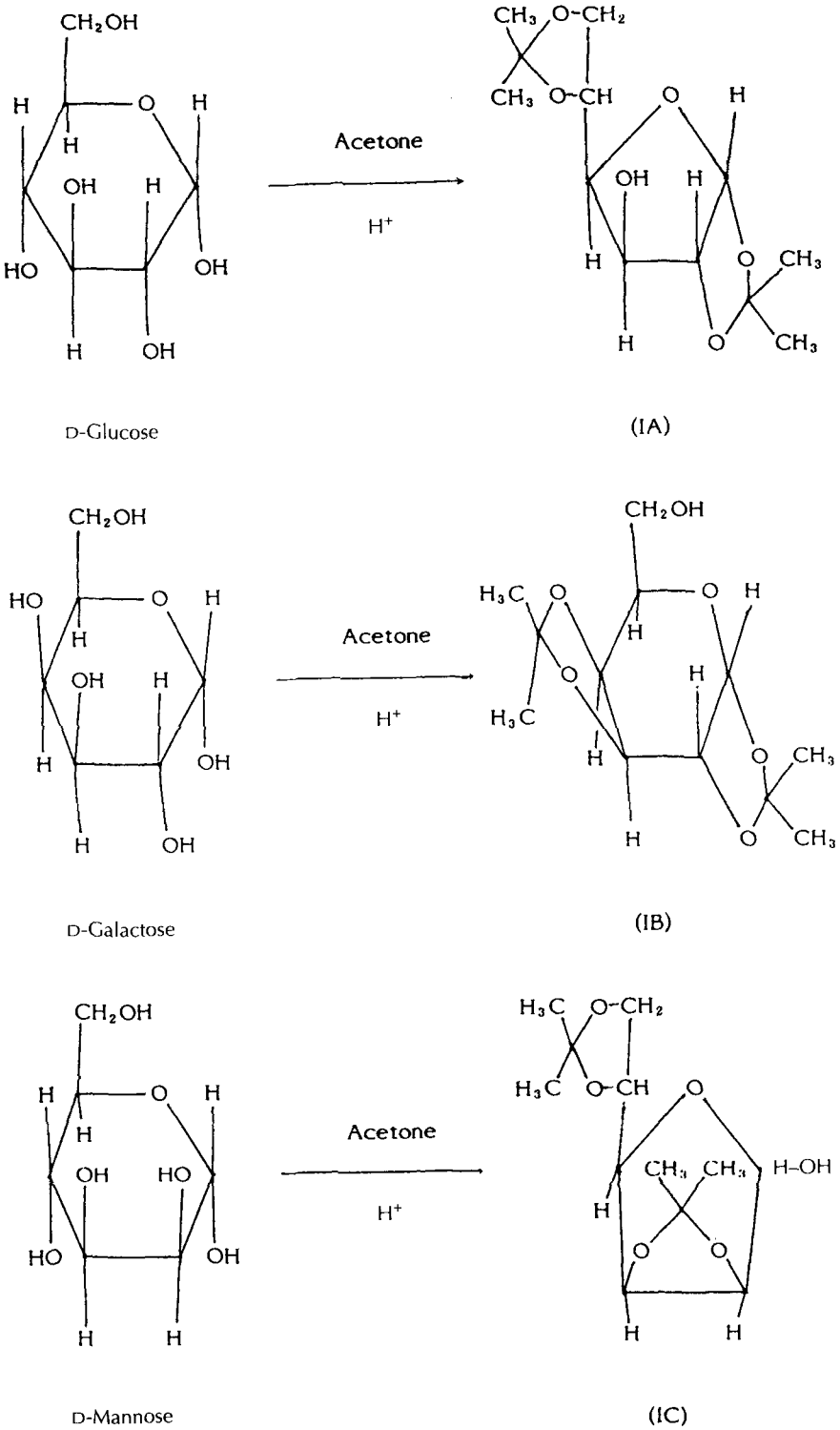



**FIG. 1.** Di-O-isopropylidene aldohexoses (IA–IC).

*Preparation of O-alkyl-di-O-isopropylidene aldohexoses (II–IV): general procedure.* Aqueous sodium hydroxide solution (48%; 3.0 mols as sodium hydroxide), quaternary ammonium salt, such as tetrabutyl ammonium bromide (0.05 mols) and hexane (500 mL) was added dropwise alkyl bromide (1.0 mols) over a period of 30 min at room temperature to a vigorously stirred mixture of di-O-isopropylidene aldohexose (IA–IC) (1.1 mols). After addition of alkyl bromide, the mixture was stirred vigorously at 30–50°C for 2–5 h. The mixture was then cooled, the organic layer separated and the solvent evaporated under reduced pressure. The residue was distilled *in vacuo* to give O-alkyl-di-O-isopropylidene aldohexoses (II–IV) (see Table 1 and Fig. 2).

*Hydrolysis of O-alkyl-di-O-isopropylidene aldohexose (II) [1].* A mixture consisting of 3-O-alkyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose (II; 1.0 mols), $H_2SO_4$ (0.02 mols), methanol (200 mL) and water (200 mL) was heated to 40–50°C for 1–2 h. The resulting mixture was cooled to room temperature, neutralized with a diluted aqueous $NaHCO_3$ solution, and the oily organic phase separated and dried. The solvent was distilled *in vacuo* to give 3-O-alkyl-1,2-O-isopropylidene-D-glucofuranose (V) (Fig. 3). The analytical and spectral data are summarized in Table 2.

*Hydrolysis of 3-O-alkyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose (II) [2].* A mixture of 3-O-alkyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose (II; 1.0 mols), $H_2SO_4$ (0.03 mols) and water (500 mL) was heated under reflux (90–100°C) during stirring for 5–6 h. The resulting mixture was cooled (50°C) and neutralized with a diluted aqueous sodium hydroxide solution. The organic phase was separated and dried under reduced pressure at 80–90°C for a few hours. Recrystallization of the oily mass from ethanol (300 mL) gave 3-O-alkyl-D-glucopyranose (IV) as white crystals (Fig. 4). The analytical and spectral data are summarized in Table 3.

*Hydrolysis of 6-O-alkyl-1,2;3,4-di-O-isopropylidene-D-galactopyranose (III) and 1-O-alkyl-2,3;5,6-di-O-isopropylidene-D-mannofuranoside (IV).* In the analogous method described above, hydrolysis of 3-O-alkyl-1,2;5,6-O-isopropylidene-D-glucofuranose (II) (2), the hydrolysis of 6-O-alkyl-1,2;3,4-di-O-isopropylidene-D-galactopyranose (III) and 1-O-alkyl-2,3;5,6-di-O-isopropylidene-D-mannofuranoside (IV) was carried out at a temperature of 90–100°C to give the 6-O-alkyl-D-galactopyranose (VII) and 1-O-alkyl-D-mannofuranoside (VIII), respectively (Fig. 5). The analytical and spectral data are summarized in Table 4.

*3-O-alkyl-5,6-di-O-methyl-1,2-O-isopropylidene-D-glucofuranose (IX).* Aqueous sodium hydroxide solution (48%; 3.0 mols as NaOH), tetrabutyl ammonium bromide (0.05 mols) and *n*-hexane (500 mL) was added dropwise, 2.1 mols of methyl iodide over a period of 30 min at room temperature to a vigorously stirred mixture of 3-O-alkyl-1,2-O-isopropylidene-D-glucofuranose (V) (1.0 mols). The reaction mixture was stirred vigorously at 30–50°C for 2–5 h, then cooled to room temperature, and the organic layer was separated and the solvent was evaporated under reduced pressure. The residue was distilled *in vacuo* to give 3-O-alkyl-5,6-di-O-methyl-1,2-O-isopropylidene-D-glucofuranose (IX) (Fig. 6). The analytical and spectral data are summarized in Table 5.

*3-O-alkyl-5,6-di-O-methyl-D-glucofuranose (X).* A mixture of 3-O-alkyl-5,6-di-O-methyl-1,2-O-isopropylidene-D-glucofuranose (0.5 mols) prepared as mentioned previously and acetic acid (200 mL) was heated to 80–90°C. Then, to the reaction mixture, 200 mL of water were added dropwise while vigorously stirring for 3 h under the same reaction temperature.

**TABLE 1**
**Preparation of O-Alkyl-Di-O-Isopropylidene Aldohexoses (II–IV)**

| Product | Yield (%)[a] | b.p./mm Hg | Literature[b] b.p./(mm Hg) | $^1$H NMR[c] ($CDCl_3$) δ (ppm) $C_1$-H | $C_3$-$OCH_2$ |
|---|---|---|---|---|---|
| IIA | 95 | 154/0.3 | | 5.77(*d*,1H), | 3.48(*t*,2H) |
| IIB | 93 | 176–180/0.3 | 130/0.005 (5) | 5.84(*d*,1H), | 3.53(*t*,2H) |
| IIC | 88 | 206–220/0.3 | 180–182/0.25 (7) | 5.83(*d*,1H), | 3.54(*t*,2H) |
| IID | 88 | 221–230/0.4 | | 5.84(*d*,1H), | 3.58(*t*,2H) |
| IIE | 88 | 220–230/0.4 | | 5.82(*d*,1H), | 3.55(*t*,2H) |
| IIIA | 83 | 155–165/0.4 | | 5.50(*d*,1H), | $C_2$–$C_6$-H, $C_6OCH_2$ |
| IIIB | 76 | 185–192/1.0 | Oil (5) | 5.50(*d*,1H), | 3.40–4.70 (*m*, 8H) |
| IIID | 75 | 220–225/0.4 | | 5.50(*d*,1H), | |
| IIIE | 79 | 205–230/0.3 | | 5.50(*d*,1H), | |
| IVA | 70 | 150–160/0.55 | | $C_1$–$C_6$-H, $C_1$-$OCH_2$ 3.2–5.0 (*m*,9H) | |
| IVD | 72 | 210–222/0.35 | | | |
| IVE | 77 | 220–228/0.4 | | | |

[a]Yields are based on di-O-isopropylidene aldoxexoses, and the microanalyses were in satisfactory agreement with the calculated values: C, ±0.21; H, ±0.31.
[b]Number in parentheses is the reference number.
[c]NMR, nuclear magnetic resonance.

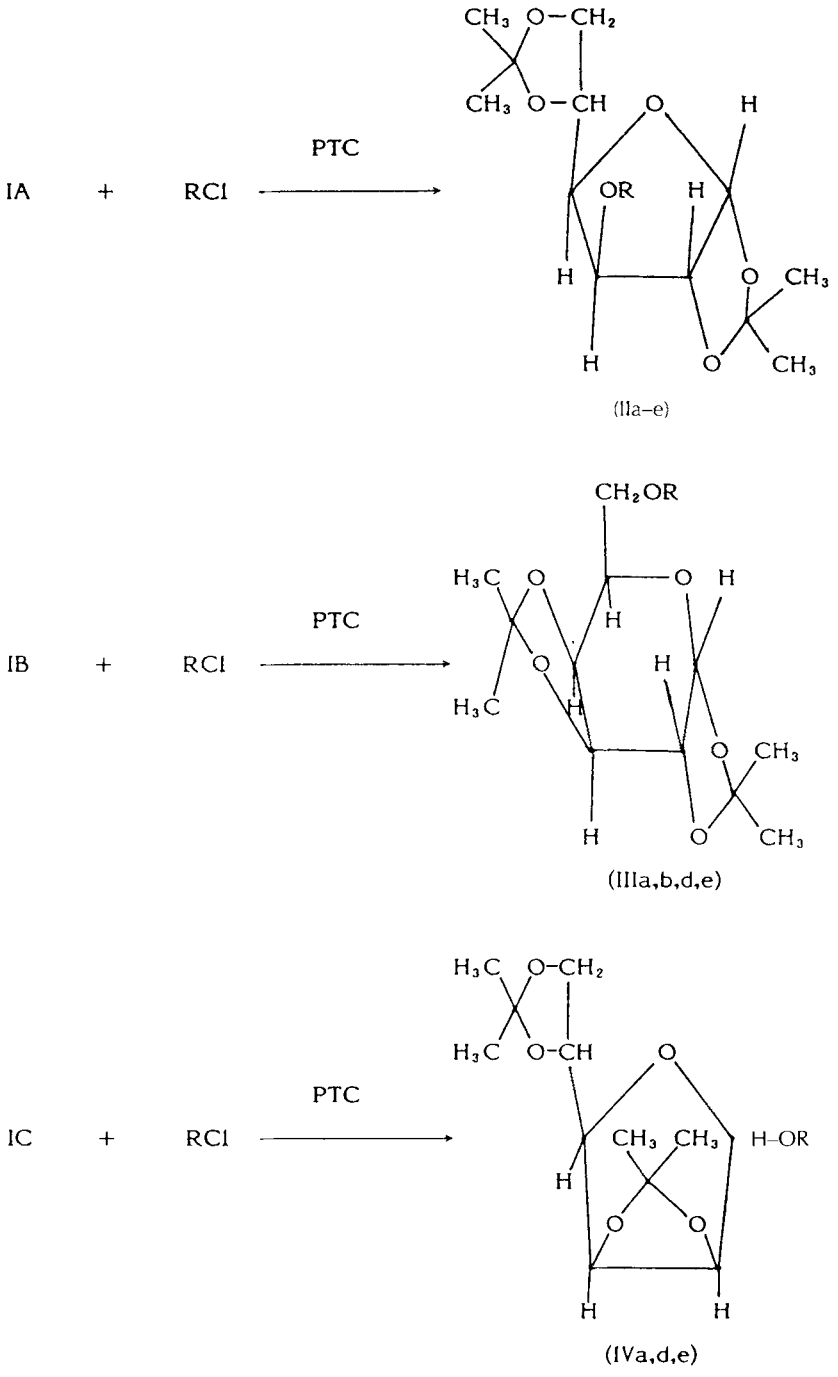



**FIG. 2.** O-Alkyl-di-O-isopropylidene aldohexoses (II–IV). a: R=$C_{18}H_{17}$; b: R=$C_{12}H_{25}$; c: R=$C_{16}H_{33}$; d: R=$C_{18}H_{37}$; e: R=$C_{18}H_{35}$ (oleyl).

After cooling the reaction mixture to room temperature, excess acetic acid was evaporated under reduced pressure. The residue thus obtained was purified by silica gel column chromatography using chloroform at first and then chloroform/methanol (9:1) as the eluant. Thus, the expected 3-O-alkyl-5,6-di-O-methyl-D-glucofuranose (X) was obtained (Fig. 7). The analytical and spectral data are summarized in Table 6.

*1-O-methyl-6-O-alkyl-D-galactofuranoside (XI).* A mixture of 6-O-alkyl-1,2;3,4-di-O-isopropylidene-D-galactopyranose (III; 0.5 mols), methanol (500 mL) and conc. sulfuric acid (10 g) was heated to 40°C for 7–10 h. The resultant mixture was cooled to room temperature and neutralized with an aqueous diluted $NaHCO_3$ solution. The oily organic mass was separated and dried under reduced pressure at 50–60°C for

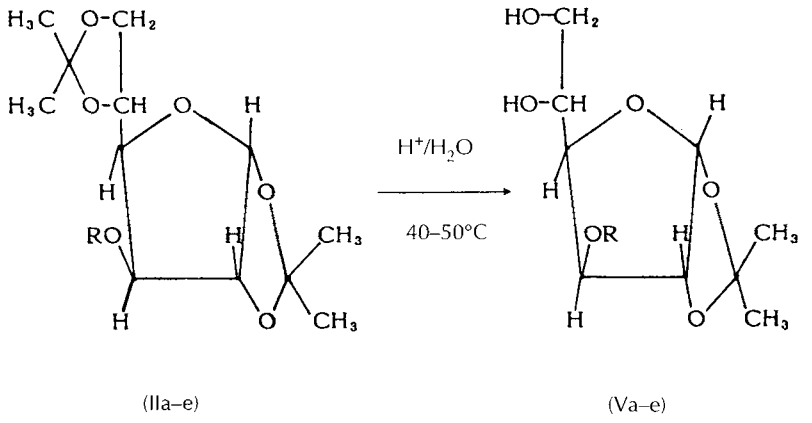



**FIG. 3.** 3-O-Alkyl-1,2-O-isopropylidene-D-glucofuranose (V). a–e are the same as in Figure 2.

**TABLE 2**
**Preparation of 3-O-Alkyl-1,2-O-Isopropylidene-D-Glucofuranose (V)**

| Product | Yield (%)[a,b] | $^1$H NMR ($CDCl_3$) δ (ppm)[c] $C_1$-H | $C_2$-H | $C_3$–$C_6$-H + $C_3$-$OCH_2$ | $C(CH_3)_2$ |
|---|---|---|---|---|---|
| VA | 94 | 5.83*d* | 4.50*d* | 3.3–4.3*m* | 1.47*s* |
| VB | 93 | 5.90 | 4.53 | 3.1–4.3*m* | 1.47 |
| VC | 87 | 5.89 | 4.54 | 3.4–4.3*m* | 1.47 |
| VD | 87 | 5.87 | 4.52 | 2.9–4.4*m* | 1.47 |
| VE | 88 | 5.86 | 4.53 | 3.0–4.4*m* | 1.47 |

[a]Yields are based on 3-O-alkyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose (II).
[b]The microanalyses were in satisfactory agreement with the calculated values: C, ±0.32; H, ±0.10.
[c]Infrared spectra also showed OH (3440 $cm^{-1}$) and C-O-C (1080 $cm^{-1}$) absorption. Abbreviations as in Table 1.

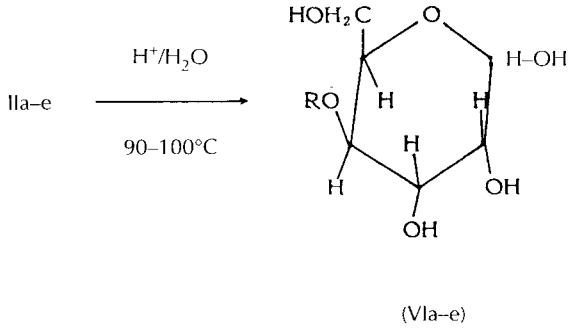



**FIG. 4.** 3-O-Alkyl-D-glucopyranose (VI). a–e are the same as in Figure 2.

1–2 h. The crude product was purified by silica gel column chromatography using chloroform/methanol (15:1) at first and then chloroform/methanol (5:1) as an eluent. The purified product, 1-O-methyl-6-O-alkyl-D-galactofuranoside (XI), was recrystallized by column chromatography from ethanol as a white solid (Fig. 8). The analytical and spectral data are also summarized in Table 7.

## RESULTS AND DISCUSSION

The alkylation of isopropylidene aldohexoses (IA–IC) such as D-glucose, D-galactose and D-mannose, with $C_8$, $C_{12}$, $C_{16}$

**TABLE 3**
**Preparation of 3-O-Alkyl-D-Glucopyranose (VI)**

| Product | Yield (%)[a] | m.p. | $^1$H NMR[b] ($CDCl_3$) δ (ppm) $C_1$-H | $C_2$–$C_6$-H + $C_3$-$OCH_2$ | IR[b] ($cm^{-1}$) -OH | C-O-C |
|---|---|---|---|---|---|---|
| VIA | 40 | 133–137 | 6.55*d* | 2.9–4.9*m* | 3450 | 1000–1200 |
| VIIB | 60 | 140–142 (138–141)[c] | 6.60*d* | 2.8–4.9m | 3450 | 1010–1190 |
| VIC | 55 | 133–136 (134–135)[c] | 6.60*d* | 2.8–5.0*m* | 3450 | 1050–1200 |
| VID | 50 | 124–126 (125–127)[c] | 6.60 | 2.8–5.0*m* | 3450 | 1000–1150 |
| VIE | 40 | 120–122 | 6.60 | 2.8–4.9*m* | 3450 | 1050–1190 |

[a]Yields are based on 3-O-alkyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose (II).
[b]NMR, nuclear magnetic resonance; IR, infrared.
[c]Reference 6.

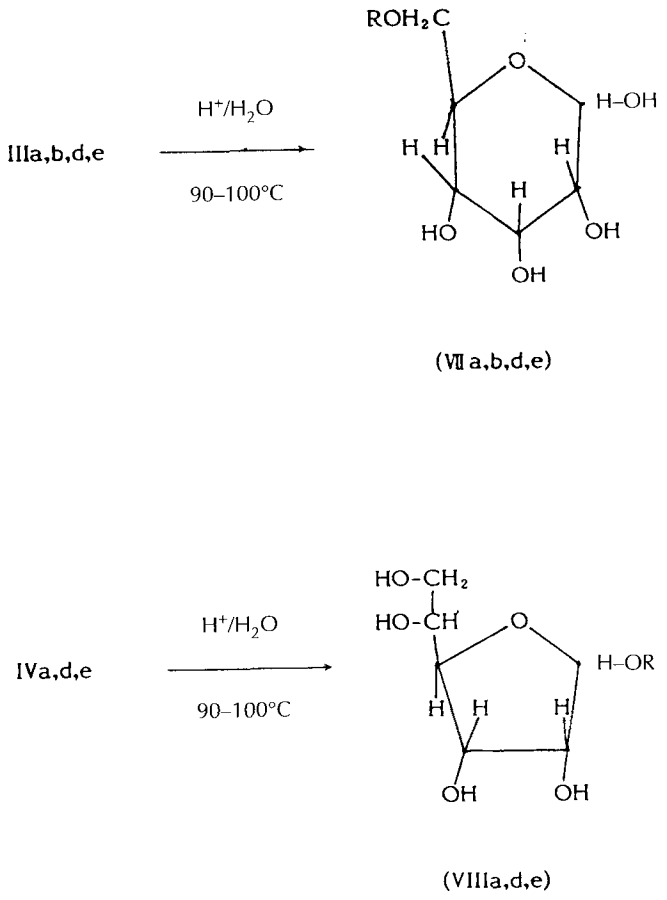



**FIG. 5.** 6-O-Alkyl-D-galactopyranose (VII) and 1-O-alkyl-D-mannofuranoside (VIII). a–e are the same as in Figure 2.

and $C_{18}$ halides under PTC was described. PTC offers distinct advantages over the classical alkyl halide/caustic route. It avoids the use of anhydrous or expensive aprotic solvents, and allows the reactions to be carried out at lower temperatures, e.g., below 50°C (12,13). Even the sterically hindered OH group, especially 3-hydroxyl group in the 1,2:5,6-di-O-isopropylidene-D-glucofuranose (II) compound, could be alkylated in high yields using this procedure (Table 1). This demonstrated that PTC offers an effective general tool for the alkylation of OH-containing compounds. Additionally, the milder reaction conditions prevent the occurrence of unfavorable side reactions, such as the formation of olefinic compounds by dehydrohalogenation of the alkyl halide, which are typically observed under strong alkaline conditions.

The solvolysis reaction of the alkylated isopropylidene aldohexoses at 50–100°C using aqueous acids gave the corresponding O-alkyl aldohexoses. However, in the case of 3-O-alkyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose (II), the careful control of the reaction conditions (40–50°C) yields the selectively deprotected 3-O-alkyl-1,2-O-isopropylidene-D-glucofuranose (V), partial solvolysis reaction product, in good yields. According to the appearance of the two free OH groups in the 5,6-position of the abovementioned partial solvolysis reaction product (V), further methylation at the same OH groups with MeI gave 3-O-long alkyl ($C_8$–$C_{18}$)-5,6-di-O-methyl-D-glucofuranose (IX). In further methylation, the PTC Williamson ether synthesis also could be used effectively. The ability to selectively alkylate at the 3-, 5-, or 6-position of the glucofuranose skeleton adds further versatility to this procedure.

The solvolysis reaction of 6-O-alkyl-1,2;3,4-di-O-isopropylidene-D-galactopyranose (III) using methanol in the presence of catalytic amounts of protonic acid gave 1-O-methyl-6-O-alkyl-D-galactofuranoside compound (XI). A similar alcoholysis reaction using *n*-butanol has been reported to give the kinetically favored 1-O-butyl-D-glucofuranoside, which isomerized to the more thermodynamically stable 1-O-butyl-D-glucopyranoside (14). The same reaction was observed in our studies. That is, the kinetically controlled 1-O-methyl-6-O-alkyl-D-galactofuranoside (XI) was able to be

**TABLE 4**
**Preparation of 6-O-Alkyl-D-Galactopyranose (VII) and 1-O-Alkyl-D-Mannofuranoside (VIII)**

| | | | $^1$H NMR[b] ($CDCl_3$) δ (ppm) | | IR[b] ($cm^{-1}$) | |
|---|---|---|---|---|---|---|
| Product | Yield (%)[a] | m.p. | $C_1$-H | $C_2$–$C_6$-H + $C_6$-$OCH_2$ | -OH | C-O-C |
| VIIA | 60 | 127–130 | 6.05*d* | 3.2–4.3*m* | 3440 | 1050–1200 |
| VIIB | 65 | 118–120 (120–122)[c] | 6.09*d* | 3.3–4.4*m* | 3400 | 1000–1200 |
| VIID | 45 | 106–108 | 6.10*d* | 3.3–4.6*m* | 3450 | 1000–1150 |
| VIIE | 40 | 95–98 | 6.10*d* | 3.3–4.6*m* | 3450 | 1050–1190 |
| VIIIA | 50 | 86–88 | $C_1$–$C_6$-H,$C_1$–$OCH_2$ | | 3500 | 1080–1200 |
| VIIID | 50 | 106–108 | 2.8–5.0 | | 3450 | 1050–1200 |
| VIIIe | 45 | Oil | | | 3450 | 1000–1200 |

[a]Yields are based on 6-O-1,2;3,4-di-O-isopropylidene-D-galactopyranose (III) and 1-O-alkyl-2,3;5,6-di-O-isopropylidene-D-mannofuranoside (IV), respectively. The microanalyses were in satisfactory agreement with the calculated values: C, ±0.34; H, ±0.22.
[b]Abbreviations as in Table 3.
[c]Reference 5.

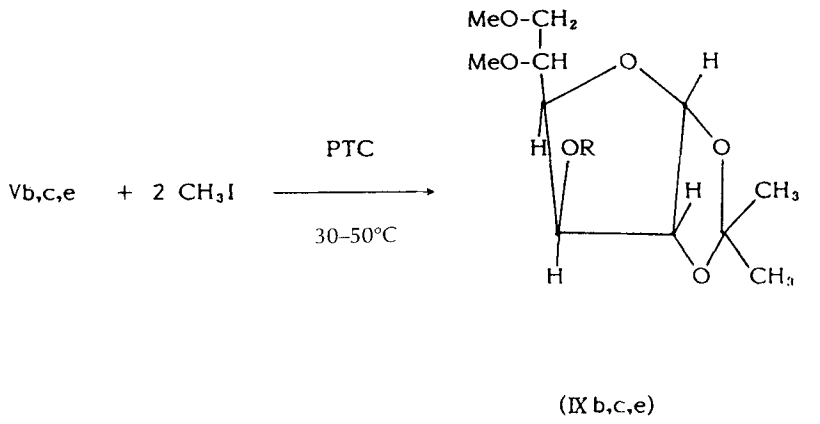


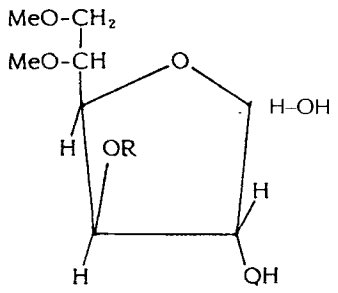

**FIG. 6.** 3-O-Alkyl-5,6-di-O-methyl-1,2-O-isopropylidene-D-glucofuranose (IX). b–e are the same as in Figure 2.

**TABLE 5**
**Preparation of 3-O-Alkyl-5,6-Di-O-Methyl-1,2-Di-O-Isopropylidene-D-Glucofuranose (IX)**

| | | | $^1$H NMR[b] ($CDCl_3$) δ (ppm) | | | | |
|---|---|---|---|---|---|---|---|
| Product | Yield (%)[a] | b.p./mm Hg | $C_1$-H | $C_2$-H | $C_3$–$C_6$-H + $C_6$-$OCH_2$ | -$OCH_3$ | $C(CH_3)_2$ |
| IXB | 90 | 175–179/0.2 | 5.87*d* | 4.53*d* | 3.3–4.3*m* | 3.40*s*<br>3.45*s* | 1.47*s* |
| IXC | 83 | 190–200/0.5 | 5.87*d* | 4.53*d* | 3.3–4.3*m* | 3.40*s*<br>3.45*s* | 1.47*s* |
| IXE | 80 | 220–230/0.8 | 5.87*d* | 4.53*d* | 3.3–4.3*m* | 3.40*s*<br>3.45*s* | 1.46*s* |

[a]Yields are based on 3-O-alkyl-1,2-O-isopropylidene-D-glucofuranose (V) and the microanalyses were in satisfactory agreement with the calculated values: C, ±0.25; H, ±0.30.
[b]Abbreviations as in Table 3.

isolated as a pure solid by column chromatography. The structural elucidation of the compound (XI) was determined by comparing its $^{13}$C NMR spectra with that reported by George *et al.* (15) (see Table 8).




(X b,c,e)

**FIG. 7.** 3-O-Alkyl-5,6-di-O-methyl-D-glucofuranose (X). b–e are the same as in Figure 2.

Further solvolysis reaction of the compound XI gave 1-O-methyl-6-O-alkyl-D-galactopyranoside as thermodynamically stable compounds. The alkyl derivatives of aldohexoses, particularly the di- and tri-O-alkylated aldohexose derivatives, such as 3-O-long chain alkyl-5,6-di-O-methyl-D-glucofuranose (X) or 1-O-methyl-6-O-long chain alkyl-D-galactofuranoside (XI), would be of potential interest as surfactants in cosmetics (16).

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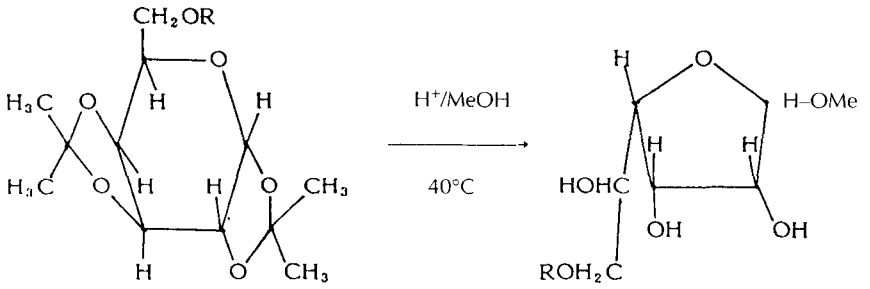
**TABLE 6**
**Preparation of 3-O-Alkyl-5,6-Di-O-Methyl-D-Glucofuranose (X)**

| Product | Yield (%)[a] | m.p. | $^1$H NMR[b] ($CDCl_3$) δ (ppm) | | IR[b] ($cm^{-1}$) | |
|---|---|---|---|---|---|---|
| | | | $C_1$-H–$C_6$-H | -$OCH_3$ | -OH | C-O-C |
| XB | 54 | Oil | 3.2–4.5*m* | 5.14*s*,5.45*s* | 3650–3050 | 1160–970 |
| XC | 35 | Oil | 3.2–4.5*m* | 5.14*s*,5.45*s* | 3650–3050 | 1160–970 |
| XE | 45 | Oil | 3.2–4.4*m* | 5.13*s*,5.45*s* | 3650–3050 | 1160–970 |

[a]Yields are based on 3-O-alkyl-5,6-di-O-methyl-1,2-O-isopropylidene-D-glucofuranose (IX) and the microanalyses were in satisfactory agreement with the calculated values: C, ±0.31; H, ±0.35.
[b]Abbreviations as in Table 3.




(IIIa,b,d,e) (XI a,b,d,e)

**FIG. 8.** 1-O-Methyl-6-O-alkyl-D-galactofuranoside (XI); a–e are the same as in Figure 2.

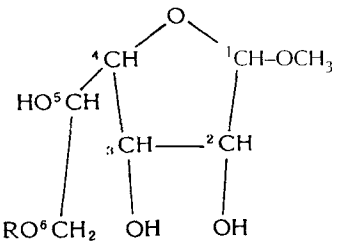
**TABLE 7**
**Preparation of 1-O-Methyl-6-Alkyl-D-Galactofuranoside (XI)**

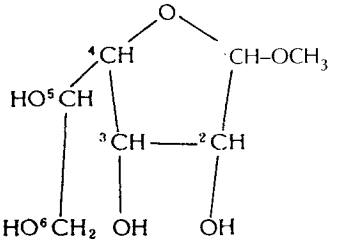
| Product | Yield (%)[a] | m.p. | $^1$H NMR[b] ($CDCl_3$) δ (ppm) | | | IR[b] ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|
| | | | $C_1$-H | $C_1$-$OCH_3$ | $C_2$–$C_6$-H | -OH | C-O-C |
| XIA | 55 | Oil | 4.90*d* | 3.39*s* | 3.4–4.4*m* | 3700–3050 | 1170–970 |
| XIB | 60 | Oil | 4.85*d* | 3.39*s* | 3.3–4.3*m* | 3700–3050 | 1170–970 |
| XID | 60 | 67–71 | 4.87*d* | 3.38*s* | 3.3–4.3*m* | 3700–3050 | 1170–970 |
| XIE | 75 | Oil | 4.86*d* | 3.36*s* | 3.3–4.3*m* | 3700–3050 | 1160–970 |

[a]Yields are based on 6-O-alkyl-1,2;3,4-di-O-isopropylidene-D-galactopyranose (III) and the microanalyses were in satisfactory agreement with the calculated values: C, ±0.44; H, ±0.38.
[b]Abbreviations as in Table 3.

**TABLE 8**
**$^{13}C$ NMR Spectra of 1-O-Methyl-6-O-Alkyl-D-Galactofuranoside (XI)[a]**

(XI)




| R / $C_n$ | $C_8H_{17}$(XIA) | $C_{12}H_{25}$(XIB) | $C_{18}H_{37}$(XIC) | $C_{18}H_{35}$(XIE) | Literature values[b] |
|---|---|---|---|---|---|
| $C_1$ | 109.1 | 109.1 | 109.2 | 109.1 | 109.9 |
| $C_4$ | 84.7 | 84.4 | 85.1 | 83.9 | 84.7 |
| $C_2$ | 80.4 | 80.7 | 80.2 | 81.0 | 81.3 |
| $C_3$ | 80.0 | 77.9 | 78.1 | 77.6 | 78.4 |
| $C_5$ | 69.2 | 69.3 | 69.4 | 69.0 | 71.7 |
| $C_6$ | 71.7 | 71.8 | 71.8 | 71.8 | 63.6 |
| $OCH_3$ | 54.8 | 54.8 | 54.9 | 54.8 | 55.6 |

[a]$^{13}C$ NMR ($CDCl_3$, δ in ppm). Abbreviations as in Table 3.
[b]Reference 15.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