Chem. Pharm. Bull. 25(4) 624—631 (1977)

UDC 547.457.04.08 : 543.544.45.06

Chemical and Biochemical Studies on Carbohydrate Esters. IV.[1] Preparation and Analytical Properties of 1-O-Fattyacyl-α-D-glucopyranoses[2]

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(Received June 16, 1976)

A homologous series of 1-O-acyl-D-glucopyranoses (acyl=caproyl, lauroyl, myristoyl, palmitoyl, or stearoyl) were obtained as the anomeric mixtures by condensation of the appropriate fatty acid chlorides with 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose, followed by catalytic hydrogenation: the α anomers were predominant in all the products. Their gas–liquid chromatographic and thin–layer chromatographic behaviors were examined to establish the linear relations of log rt_R or *Rf* values to the acyl chain-lengths. From the anomeric mixtures, their α anomer components were isolated as crystallines by repeated recrystallization. Column chromatographic separation of the acetylated anomeric mixtures furnished the pure acetates of both anomers. The infrared nuclear magnetic resonance and mass spectral features were compared between the pairs of anomers.

Keywords——1-O-fattyacyl-α-D-glucopyranoses; 1-O-fattyacyl-α-D-glucopyranose tetraacetates; 1-O-fattyacyl-β-D-glucopyranose tetraacetates; NMR; IR; GLC; TLC

Recently natural occurrence of 1-O-fattyacyl-D-glucoses possessing various interesting biological activities has been reported by several groups of workers.[4–6] In order to provide analytical informations useful for the future systematic survey work on the distribution of this type of glycosyl ester constituents, we have previously prepared a homologous series of β anomers of 1-O-fattyacyl-D-glucopyranose as their tetra-O-acetyl derivatives and examined their infrared (IR), nuclear magnetic resonance (NMR), and mass spectral features, as well as their thin–layer and gas liquid chromatographic (TLC and GLC) behaviors.[7] To extend these studies, we now synthesized the corresponding α analogues in which all hydroxyl groups except hemiacetal hydroxyl group are either unprotected or masked as acetates.

The synthetic pathway employed is shown in Chart 1. According to the procedure described by Glaudemans and Fletcher, methyl α-D-glucopyranoside (I) was derived into methyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside (II), and then hydrolysed to give 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (III).[8] Treatment of the latter compound with appropriate fatty acid chlorides, such as caproyl, lauroyl myristoyl, palmitoyl, and stearoyl chlorides, in the

1) Part III: Y. Nishikawa, K. Yoshimoto, M. Okabe, and F. Fukuoka, *Chem. Pharm. Bull.* (Tokyo), **24**, 756 (1976).
2) This work was presented at the 96th Annual Meeting of the Pharmaceutical Society of Japan, Nagoya, April, 1976.
3) Location: *13–1 Takara-machi, Kanazawa, 920, Japan.*
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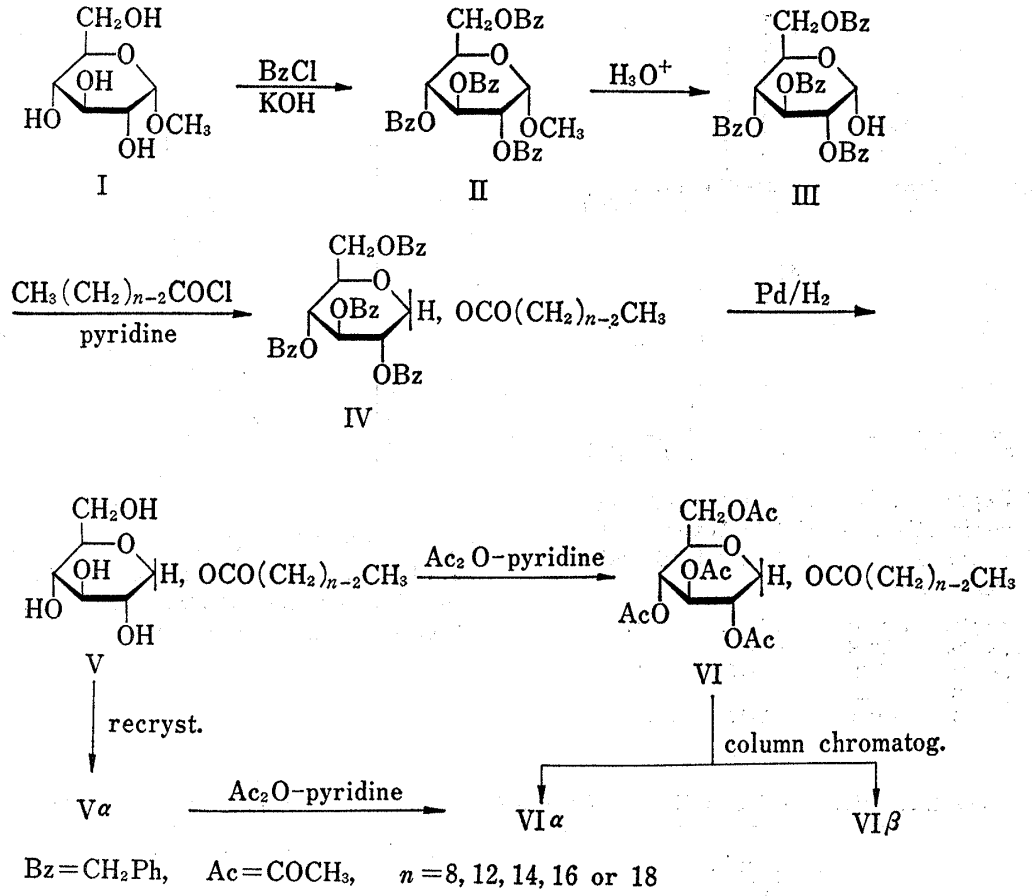

Chart 1

presence of pyridine yielded 1-O-acyl-2,3,4,6-tetra-O-benzyl-D-glucopyranoses (IV), which were subsequently de-benzylated by catalytic hydrogenation over palladium to afford the anomeric mixtures of 1-O-acyl-D-glucopyranoses (V). Proof for the presence of both anomers in these final products was provided by observing their NMR spectra (in pyridine-d_5 added with deuterium oxide). In all cases, two doublet signals ascribable to anomeric protons of α and β anomers were detected at δ 6.80 (J=3.8 Hz) and δ 6.30 (J=7.5 Hz), respectively: the intensity ratios between pairs of doublets were indicative of preponderant production of α anomers.

GLC analyses of the individual anomeric mixtures were performed as their acetyl and trimethylsilyl (TMS) derivatives, using OV-1 and OV-17 columns. Each chromatogram was found to consist of a major peak and a minor peak, together with some small peaks corresponding to the impurities derived from the contaminants originally present in the acid chloride specimens used as the starting materials. The representative chromatograms are illustrated in Fig. 1. TLC analyses of the anomeric mixtures and their acetyl derivatives were also carried out with chloroform–methanol (9:1) (solvent A) for the formers and *n*-hexane–ether (1:2) (solvent B) for the latters on silica gel layers. As depicted in Fig. 2, each sample showed a large spot and a small spot. The relative retention times (rt_R) of the minor peaks and the *Rf* values of the smaller spots given by the acetylated anomeric mixtures proved to be coincidental with those of the corresponding authentic specimens of β anomer acetates previously synthesized.[7] From these findings, it was considered that the minor peaks and the smaller spots detected by GLC and TLC would be all assignable to β anomers, and hence the major peaks and the larger spots to α counterparts: the conclusion agreed well with the NMR spectral observations mentioned above.

The exact proportion of both anomers in each anomeric mixture was determined by GLC, comparing the area ratio between a pair of anomer peaks. Thus it was found that the ratio of

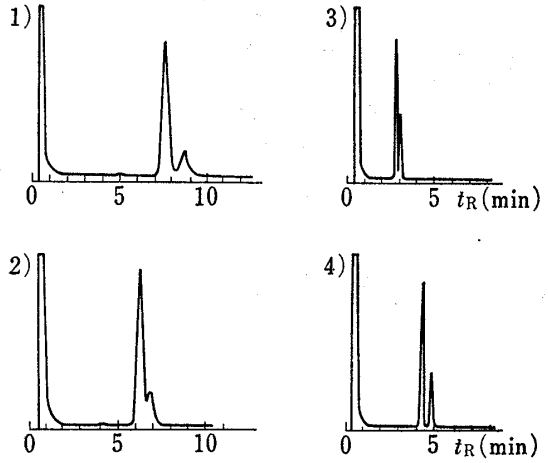

Fig. 1. Representative Gas Chromatograms of Anomeric Mixtures of 1-O-Acyl-α- and -β-D-glucopyranoses (V) as Their TMS and Acetyl Derivatives

Fig.	sample	derivative	column	Temp.
1)	V, n=14	TMS	OV-1	260°
2)	V, n=14	TMS	OV-17	260°
3)	V, n=12	acetate	OV-1	290°
4)	V, n=12	acetate	OV-17	290°

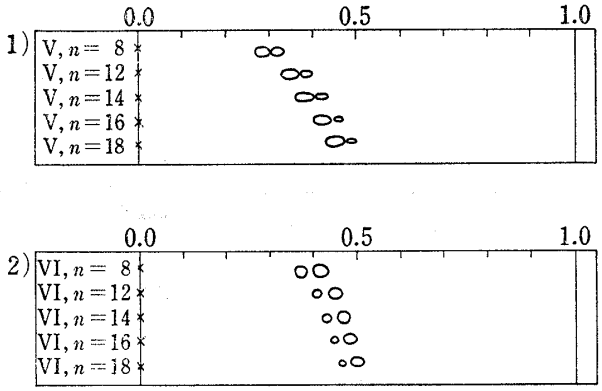

Fig. 2. Thin-Layer Chromatograms (Silica Gel G) of 1) Anomeric Mixtures of 1-O-Acyl-α- and -β-D-glucopyranoses (V) (Solvent A) and 2) Their Acetyl Derivatives (VI) (Solvent B)

TABLE I. Relative Molar Ratios of α and β Anomers in the Anomeric Mixtures (V)

Anomeric mixture (V)	Relative molar ratio (%)[a]	
	α Anomer	β Anomer
Caprylate (n= 8)	55	45
Laurate (n=12)	71	29
Myristate (n=14)	80	20
Palmitate (n=16)	83	17
Stearate (n=18)	85	15

a) determined by GLC (as TMS derivatives; column, OV-1), measuring the peak area ratios (see Fig. 1 and Table II)

TABLE II. Relative Retention Times of α and β Anomers of 1-O-Acyl-D-glucopyranoses (V) as TMS and Acetyl Derivatives[a]

Compd. (V)		rt$_R$ Values			
		TMS deriv.		Acetyl deriv.	
		OV-1 (260°)	OV-17 (260°)	OV-1 (280°)	OV-17 (290°)
Caprylate (n=8)	α	0.52	0.76	0.35	0.27
	β	0.57	0.81	0.36	0.30
Laurate (n=12)	α	1.16	1.71	0.75	0.53
	β	1.29	1.81	0.85	0.61
Myristate (n=14)	α	1.80	2.71	1.16	0.78
	β	2.00	2.95	1.30	0.91
Palmitate (n=16)	α	2.84	4.38	1.78	1.17
	β	3.13	5.03	1.98	1.39
Stearate (n=18)	α	4.50	7.10	2.65	1.89
	β	5.23	8.50	3.00	2.00
Sucrose[b]		1.00 (4.4 min)	1.00 (2.1 min)	1.00 (4.0 min)	1.00 (6.4 min)

a) See Fig. 1 and 3.
b) internal standard

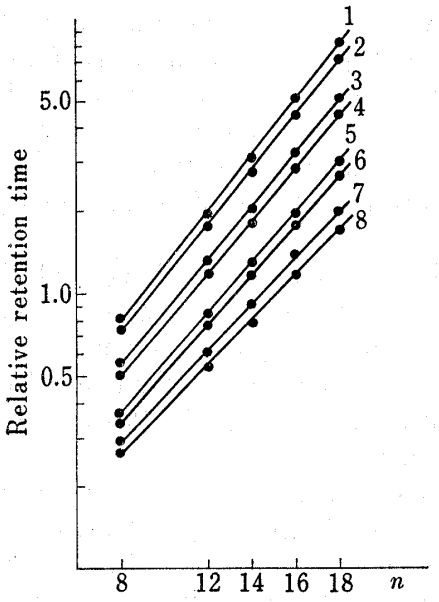

Fig. 3. Relationships between the Relative Retention Times (see Table II) and the Number (=n) of Carbon Atoms of Acyl Functions in GLC Analyses of 1-O-Acyl-α- and -β-D-glucopyranoses (V) as Their TMS and Acetyl Derivatives

1: β analogues as TMS, OV-17
2: α analogues as TMS, OV-17
3: β analogues as TMS, OV-1
4: α analogues as TMS, OV-1
5: β analogues as acetate, OV-1
6: α analogues as acetate, OV-1
8: β analogues as acetate, OV-17
8: α analogues as acetate, OV-17

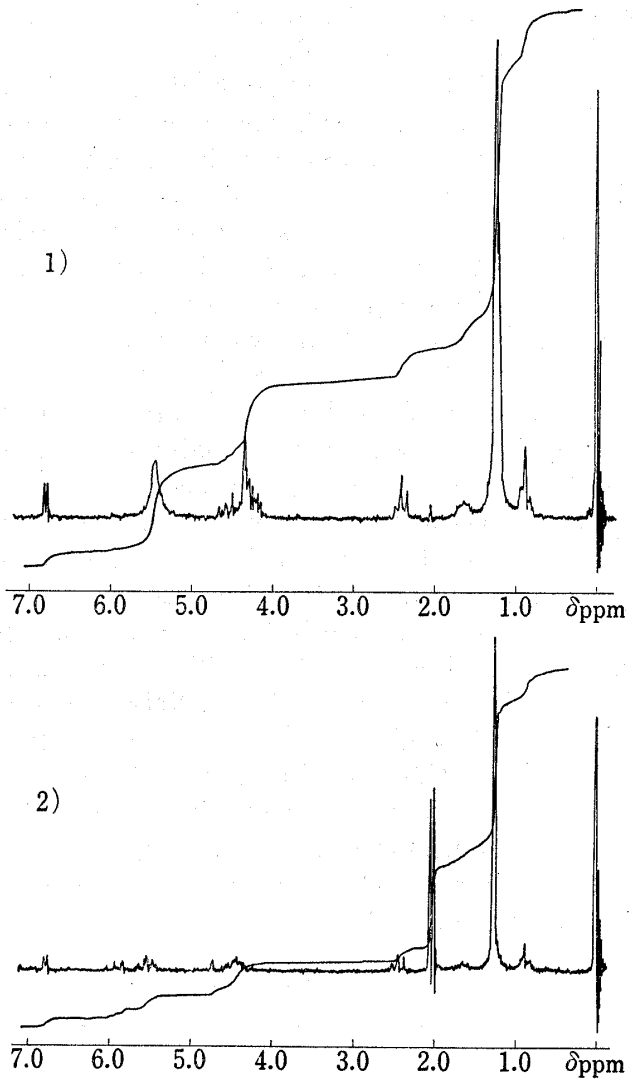

Fig. 4. NMR Spectra (100 MHz; Internal Standard, Tetramethylsilane)

1) 1-O-myristoyl-α-D-glucopyranose (V, n=14) (in pyridine-d_5 added with D_2O)
2) 1-O-myristoyl-α-D-glucopyranose tetraacetate (VI, n=14) (in $CDCl_3$)

TABLE III. TLC *Rf* Values of α and β Anomers of 1-O-Acyl-D-glucopyranoses (V) and Their Acetyl Derivatives (VI)[a]

Acyl	*Rf* Values			
	Unacetylated compd. (V)[b]		Acetyl deriv. (VI)[c]	
	α Anomer	β Anomer	α Anomer	β Anomer
Caproyl	0.28	0.32	0.41	0.38
Lauroyl	0.34	0.39	0.45	0.41
Myristoyl	0.38	0.43	0.47	0.43
Palmitoyl	0.41	0.46	0.48	0.44
Stearoyl	0.44	0.49	0.49	0.45

a) See Fig. 2.
b) Silica gel G, $CHCl_3$–MeOH (9:1) (selvent A)
c) Silica gel G, ether–n-hexane (2:1) (solvent B)

α anomer to β anomer tended to increase progressively with increasing chain-length of the acyl function introduced (Table I).

Table II lists the rt_R values obtained for the TMS and acetyl derivatives of both anomers. As can be seen in Fig. 1, it has been revealed that OV-1 column results in superior separation of anomeric mixture of TMS derivatives to OV-17 column, and that these two columns are both satisfactorily effective for resolution of pairs of anomer acetates. On GLC analysis of a series of 1-O-acyl-β-D-glucopyranose tetraacetates, strict linear relationships had been established previously between the log rt_R values and the number of carbon atoms of acyl functions.[7] Similar linearity has now been observed not only with the α analogous acetates but also with the α and β series of TMS derivatives: two straight lines given by a pair of anomer analogues run almost parallel to each other (Fig. 3).

The TLC *Rf* values obtained are presented in Table III. As shown in Table III and Fig. 2, the conditions chosen for TLC analyses in the present study failed to give good resolution between couples of anomers, and also between any two of the analogous compounds having adjacent carbon numbers. Some other conditions were also tested, but so far none of them gave the improved results. It is, however, of interest that the relations of the *Rf* values to the acyl chain-lengths appear to be linear in the present experiments.

By repeated recrystallization, the major components contained in the respective anomeric mixtures were isolated as crystalline compounds, which were chromatographically homogeneous and showed commonly the NMR spectral features (Fig. 4) consistent with α anomers. Their relatively higher optical rotations also provided the supporting evidence for the α-D-configuration. The analytical data of the resulting α anomers (Vα), which as far as we know, have never been reported in the literature, are presented in Table IV. Attempts to isolate the pure β anomers from the mother liquors were unsuccessful. Complete separation of each anomeric mixture into the corresponding both anomers was not accomplished by column chromatography, too.

Table IV. 1-O-Acyl-α-D-glucopyranoses (Vα)

Compd. (Vα)	Recrystallization		mp (°C)	$[\alpha]_D^{17a)}$ (c=1.0, pyridine)	Formula	Analysis (%)			
	Solvent	Appearance				Calcd.		Found	
						C	H	C	H
Caprylate (n=8)	petr. ether–ether	leaflets	96— 98	+68.3°	$C_{14}H_{26}O_7$	54.89	8.55	55.03	8.47
Laurate (n=12)	acetone	needles	74— 76	+66.4°	$C_{18}H_{34}O_7$	59.64	9.46	59.82	9.66
Myristate (n=14)	acetone	needles	113—115	+71.9°	$C_{20}H_{38}O_7$	61.51	9.81	61.29	10.05
Palmitate (n=16)	acetone	needles	108—110	+69.0°	$C_{22}H_{42}O_7$	63.13	10.11	63.13	10.28
Stearate (n=18)	acetone	needles	112—113	+67.6°	$C_{24}H_{46}O_7$	64.54	10.38	64.32	10.54

a) No alteration of the value was observed within 24 hr: this would be indicative of no occurrence of ready acyl migration.

On the other hand, the acetylated anomeric mixtures were satisfactorily fractionated on silica gel column with solvent B to furnish the pure acetates of α and β anomers (VIα and VIβ). These acetates were all crystallizable with one exception of α-capreyl ester acetate (VIα, n=8). The identity of the α anomer acetates thus obtained with the corresponding acetates derived directly from the purified α anomers has been confirmed. The resulting β anomer acetates were established to be indistinguishable from the authentic specimens of the corresponding 1-O-acyl-β-D-glucopyranose tetraacetates previously synthesized.[7] The analytical data of the α anomer acetates are summarized in Table V. In general, the α anomer acetates proved to

TABLE V. 1-O-Acyl-α-D-glucopyranose Tetraacetates (VIα)[a]

Compd. (VIα)	Recrystallization: Solvent	Recrystallization: Appearance	mp (°C)	$[\alpha]_D^{18}$ (c=1.0, $CHCl_3$)	Formula	Analysis (%): Calcd. C	Calcd. H	Found C	Found H
Caprylate (n=8)		semi-solid		+65.4°	$C_{22}H_{34}O_{11}$	55.69	7.22	55.41	7.32
Laurate (n=12)	aq. EtOH	needles	41	+67.6°	$C_{26}H_{42}O_{11}$	58.86	7.97	58.91	8.21
Myristate (n=14)	aq. EtOH	needles	36—37	+73.6°	$C_{28}H_{46}O_{11}$	60.20	8.30	60.02	8.51
Palmitate (n=16)	aq. EtOH	needles	41—42	+67.1°	$C_{30}H_{50}O_{11}$	61.41	8.59	61.79	8.76
Stearate (n=18)	aq. EtOH	needles	68—69	+71.2°	$C_{32}H_{54}O_{11}$	62.52	8.85	62.61	8.87

a) The data of the 1-O-acyl-β-D-glucopyranose tetraacetates (VIβ) obtained in the present study were identical with those of the corresponding authentic specimens prepared previously by the definitive method.[7]

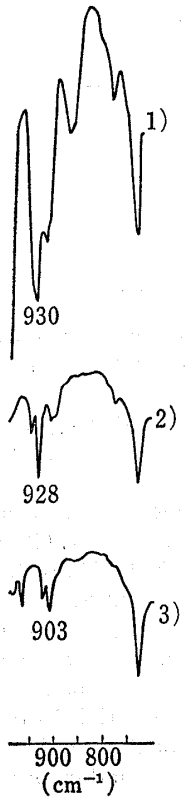

Fig. 5. IR Spectra

1) (KBr): 1-O-palmitoyl-α-D-glucopyranose (V, n=16)
2) (Nujol): 1-O-myristoyl-α-D-glucopyranose tetraacetate (VI, n=14)
3) (Nujol): 1-O-myristoyl-β-D-glucopyranose tetraacetate (VI, n=14)

have lower melting points and, as expected, considerably higher specific rotations than the corresponding β anomer acetates.

The NMR spectra of the α anomer acetates in pyridine-d_5 showed commonly the anomeric proton signals at δ 6.80 as doublets (J=3.5 Hz), indicating that the chemical shifts and the coupling constants of the unsubstituted parent esters were not altered significantly by acetylation (Fig. 4). As reported previously, the anomeric proton doublets of β anomer acetates appeared at δ 5.78 with coupling constant of 7.5 Hz, when chloroform-d was employed as a solvent. In contrast, the anomeric proton doublets of α anomer acetates were detected, in the same solvent, at δ 6.26 with the coupling constant of 4.0 Hz. The differences observed in the chemical shifts and the coupling constants are compatible with those found in the NMR spectra of penta-O-acetyl-β-D-glucopyranose (δ 5.72; doublet, J=7.5 Hz) and its α anomer (α 6.32; doublet, J=3.8 Hz).

The IR spectra of 1-O-acyl-α-D-glucopyranoses (Vα) generally exhibited the characteristic patterns in the region of 950—750 cm^{-1}, giving the absorption bands at 930 (strong), 910, 855, and 768 cm^{-1} (Fig. 5). Comparison of their IR spectral features with these of the corresponding β anomers could not be made, since the pure specimens of the latter compounds were unavailable in the present study. However, it has been revealed that the α anomer acetates show characteristic absorption patterns, in the region mentioned above, which differ significantly from those reported for the corresponding β anomer acetates: the formers gave the strongest absorption bands at 928±3 cm^{-1}, while the latters at 903±3 cm^{-1} (Fig. 5).

It is well known that the mass spectral method cannot at present claim any wide application to stereochemical studies in the field of carbohydrate derivatives. Thus it is not surprising that the mass spectral features, involving the relative intensities of the respective peaks,of the α anomer acetates were found to be identical with these of the corresponding β anomer acetates: the fragmentation patterns

of the latter compounds have already been fully interpreted in the preceding paper of this series.[7]

By Tschesche and co-workers, it has been reported that two antifungal principles, that is, 1-tuliposides A and B, both of which structurally belong to 1-O-acylglucose, occur in *Tulipa gesneriana* L., but, during the isolation procedures, they undergo the rapid conversion into inactive 6-tuliposides A and B, *via* 1→6 migration of their acyl residues.[4] Throughout the present experiments, we have, however, not encountered such a ready acyl migration. The discrepancy would be attributable to the different nature of the acyl functions attached. Detailed examination on this problem is now under progress.

Experimental[9]

Evaporations were performed in a rotary evaporator *in vacuo* at bath-temperature below 45°. The IR, NMR, and mass spectra were measured on a JASCO Model IR-G spectrophotometer, a JEOL JNM PS-100 spectrometer (100 MHz; internal standard, tetramethyl silane), and a JMS-01SG spectrometer, respectively.

Materials——Methyl α-D-glucoside (I) and fatty acid chlorides were purchased from commercial sources (Nakarai Chemicals, Ltd., and Wako Pure Chemical Ind. Ltd., respectively), and they were used without further purification: though the following contaminants were found to be present in the latter chemicals by GLC (These specimens were converted into the methyl esters of parent fatty acids by hydrolysis, followed by methylation, and then subjected to GLC analysis, using 5% DEGS on Shimalite W as a column packing). 1-O-Acyl-β-D-glucopyranose tetraacetates used as the authentic samples were the products previously synthesized in this laboratory by condensation of the silver salts of fatty acids with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide.[7]

Commercial specimens	Contaminants (% by weight)
Caproyl chloride	negligible
Lauroyl chloride	myristoyl chloride (trace)
Myristoyl chloride	lauroyl chloride (2%)
Palmitoyl chloride	myristoyl chloride (trace)
Steareyl chloride	palmitoyl chloride (27%) and myristoyl chloride (1%)

TLC Analyses——Throughout the present work, TLC was performed on Silica gel G (Merck), and detection was effected with 10% sulfuric acid and heating. The solvent systems used were: A, $CHCl_3$–MeOH (9: 1); B, ether–*n*-hexane (2: 1).

GLC Analyses——GLC was carried out with a Shimadzu Gas Chromatograph Model GC-4BPF attached with a hydrogen flame ionization detector, using glass column (2 m × 4 mm I.D.): carrier gas, N_2 (50 ml/min). The column packings employed were 1.5% OV-1 on Shimalite W (60—80 mesh) and 1.5% OV-17 on Shimalite W (60—80 mesh). Silylation was performed according to the Sweeley's procedure,[10] and acetylation was accomplished by treating a sample with a mixture of Ac_2O and pyridine at room temperature overnight.

Anomeric Mixture of 1-O-Acyl-α- and -β-D-glucopyranoses (V)——The synthetic pathway is shown in Chart 1. The benzyl ether (II) of methyl α-D-glucoside (I) was hydrolyzed to afford 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (III), colorless needles, mp 151—153° (lit.,[8] mp 151—152°), $[\alpha]_D^{18}$ +20.5° (c=2.0, $CHCl_3$) (lit.,[8] $[\alpha]_D^{20}$ +21.7° (c=2.19, $CHCl_3$)); yield, 67% from I. A stirred solution of III (10 mmoles) in dichloromethane (25 ml) was treated with a solution of an appropriate fatty acid chloride (13 mmoles) in a mixture of dichloromethane (25 ml) and dry pyridine (1 ml). The reaction mixture was stirred overnight at room temperature; it was then poured into ice-water, and extracted with $CHCl_3$. The extract was washed successively with water, cold 3 N sulfuric acid, and aqueous sodium bicarbonate solution. Moisture was removed with sodium sulfate, and the solution was concentrated under diminished pressure to a syrup which was purified by passing through the silica gel column (Wako gel 200) with a mixed solvent of ether and *n*-hexane (1: 1) to furnish the fraction consisting of an anomeric mixture of 1-O-acyl-2,3,4,6-tetra-O-benzyl-D-glucopyranose (IV). The solution of IV (9.8 mmoles) in a mixture of MeOH and dioxane (1: 1) (50 ml) was subjected to catalytic hydrogenation over Pd-black (300 mg) at room temperature under atmospheric pressure. At intervals, the reaction mixture was monitored by TLC (solvent A) and the reaction was continued until the spot (*Rf* 0.98) of IV became undetectable. After completion of the reaction (10—15 hr: prolongation of the reaction time tended to cause

9) Melting points are not corrected.

10) C.C. Sweeley, R. Bentley, M. Makita, and W.W. Wells, *J. Am. Chem. Soc.*, **85**, 2497 (1963).

slight scission of the C-1 ester bond, liberating a small amount of D-glucose.), the catalyst was removed by filtration, and the filtrate was evaporated *in vacuo* to a syrup, which was passed through the silica gel column with a mixed solvent of $CHCl_3$ and MeOH (15: 1) to afford an anomeric mixture of 1-O-acyl-α- and -β-D-glucopyranoses (V) as a colorless, amorphous powder; yields, 75—85% from III. The NMR spectra (in pyridine-d_5 added with D_2O) of the anomeric mixtures contained commonly two anomeric proton doublets at δ 6.80 (J=3.8 Hz) (α anomers) and δ 6.30 (J=7.5 Hz) (β anomers): the intensities of the former signals were always stronger than those of the corresponding latter signals. GLC analyses of the anomeric mixtures were carried out as their TMS and acetyl derivatives, using OV-1 and OV-17 columns. Each chromatogram showed a major peak (α anomer) and a minor peak (β anomer), accompanying occasionally with some small peaks attributable to the products derived from the contaminants which had been present in the acid chloride specimens used as the starting materials (Fig. 1). The relative proportions of α anomers to their β counterparts in these anomeric mixtures were determined by comparing the area ratios between pairs of the major and minor peaks. The results are presented in Table I. Table II lists the rt_R values obtained, and Fig. 3 indicates the linear relationships observed between the log rt_R values and the number (=n) of carbon atoms contained in the respective acyl functions. On TLC analysis (solvent A), each anomeric mixture gave a large spot (α anomer) and a small spot (β anomer) (Fig. 2). The *Rf* values are shown in Table III.

1-O-Acyl-α-D-glucopyranose (Vα)——The anomeric mixtures (V) obtained above were respectively subjected to the repeated recrystallization to yield their crystalline α anomer components whose analytical data, as well as the solvents employed, are presented in Table IV: attempts to isolate the corresponding β counterparts from the mother liquors were unsuccessful. On GLC (or TLC) examination, each α anomer thus isolated showed a single peak (or a single spot) whose t_R (or *Rf*) value was confirmed to be identical with that of the major peak (or the large spot) given by the corresponding parent anomeric mixture: the presence of impurities was almost undetectable. The NMR spectra (in pyridine-d_5 added with D_2O) of these α anomers each contained one anomeric proton doublet (δ 6.80, J=3.8 Hz) in addition to the following signals: *ca.* 0.88 (triplet, J=6.5 Hz; $-C\underline{H}_3$), 1.06—1.80 (multiplet; $-OCOCH_2(C\underline{H}_2)_{n-3}CH_3$), *ca.* 2.42 (triplet, J=7.0 Hz; $-OCOC\underline{H}_2-$), 4.10—4.80 (apparently as complex multiplet; C2–, C3–, C4–, C5–H, and C6–H_2 in the glucose residue) (Fig. 4). Their IR spectra (in KBr) were mutually similar, showing commonly the characteristic absorption bands at 1748, 930, 910, 855, and 768 cm^{-1} (Fig. 5).

1-O-Acyl-α- and -β-D-glucopyranose Tetraacetates (VIα and VIβ)——The anomeric mixtures (V) were respectively treated with Ac_2O–pyridine at room temperature overnight to afford the acetylated mixtures (VI) of both anomers. As mentioned above, the results of GLC analysis of these acetylated mixtures are presented in Fig. 1 and Table II. On TLC examination (solvent B), each acetylated mixture gave a large spot (α anomer) and a small spot (β anomer): the *Rf* values and the representative chromatograms are shown in Fig. 2 and Table III, respectively. The acetylated mixtures were fractionated, respectively, on silica gel (Wako gel 200) with the solvent of ether–*n*-hexane (2: 1) into the α anomer acetates (VIα) and the β anomer acetates (VIβ). These acetates were guaranteed to be homogeneous by TLC and GLC analyses, and all but one (VIα, n=8) were crystallizable from the solvents described in Table V. The α anomer acetates thus obtained were confirmed to be identical with the corresponding products derived from Vα by direct acetylation. The analytical data of VIα are summarized in Table V. The NMR spectral data of VIα were as follows: a) in pyridine-d_5; 0.86 (triplet, J=6.5 Hz; $-C\underline{H}_3$), 1.05—1.90 (multiplet; $-OCOCH_2(C\underline{H}_2)_{n-3}CH_3$), 1.92—2.22 (singlets; $-OCOC\underline{H}_3$), 2.22—2.56 (triplet, J=7.0 Hz; $-OCOC\underline{H}_2-$), 4.18—4.90 (multiplet; C_5–H and C_6–H_2), 5.40—6.10 (multiplet; C2–, C3–, C4–H), 6.80 (doublet, J=3.5 Hz; C1–H) (Fig. 4), and b) in $CDCl_3$; 0.86 (triplet, J=7.0 Hz; $-C\underline{H}_3$), 1.08—1.84 (multiplet; $-OCOCH_2(C\underline{H}_2)_{n-3}CH_3$), 1.90—2.20 (singlets; $-OCOC\underline{H}_3$), 2.22—2.50 (triplet, J=7.0 Hz; $-OCOC\underline{H}_2-$), 3.80—4.40 (multiplet; C_5–H and C_6–H_2), 4.80—5.40 (multiplet; C2–, C3–, C4–H), 6.26 (doublet, J=4.0 Hz; C_1–H) (*cf.* C1–H of glucose pentaacetate: α anomer, 6.32 (doublet, J=3.8 Hz); β anomer, 5.72 (doublet, J=7.5 Hz)). The IR spectral features of VIα were mutually similar: IR ν_{max}^{Nujol} cm^{-1}; 1742, 1755, 940, 928 (strong), 903 (Fig. 5). The mass spectra of VIα were indistinguishable from those of the corresponding VIβ (see ref. 7)). The identity of the present β anomer acetates with the corresponding authentic specimens of 1-O-acyl-β-D-glucopyranose tetraacetate was established (mixed melting points, TLC and GLC behaviors, and IR, NMR, and mass spectra).[7]

Acknowledgement The authors are grateful to Mr. Y. Itatani of this Faculty for elemental analyses, and NMR spectral measurement, and to Miss H. Hyuga of this Faculty for mass spectral measurement. Thanks are also due to Miss R. Murakami, and Mr. M. Nishijima for skillful technical assistance. This work was supported in part by a Grant-in-Aid from the Ministry of Health and Welfare.