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# REGIOSELECTIVE *O*-DEACYLATION OF FULLY ACYLATED GLYCOSIDES AND 1,2-*O*-ISOPROPYLIDENEALDOFURANOSE DERIVATIVES WITH HYDRAZINE HYDRATE*

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ABSTRACT

On hydrazinolysis in 1:4 acetic acid–pyridine, and in pyridine, partial *O*-deacylation of fully acylated methyl glycosides and some other glycosyl compounds (23 compounds) was found to be induced, to give, in good yields, products bearing one free hydroxyl group; the results obtained indicated that, among the primary and secondary *O*-acyl groups, the 2-*O*-acyl groups were, in general, the most labile toward the nucleophile (hydrazine). Hydrazinolysis of 1,2-*O*-isopropylidenealdofuranose acylates (3 compounds), on the other hand, gave, in high yield, the corresponding monoacyl derivatives having the protecting group on their primary hydroxyl group. The factors possibly involved in the regioselectivity of the hydrazinolysis were discussed.

## INTRODUCTION

Investigation of the relative reactivity of the various hydroxyl groups in carbohydrates and their derivatives[2] is not only of theoretical interest, but also of practical importance for their partial protection and chemical derivatization, and a number of protecting groups for hydroxyl groups, or procedures for their introduction, have been reported. As regards partially acylated carbohydrate derivatives, they have usually been prepared through regioselective esterification of nonmasked compounds[2].

Alternatively, partial *O*-deacylation of fully acylated carbohydrates has also been found to be regioselective and effective for that purpose, *e.g.*, through treatment of (*a*) 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose with aqueous sodium hydroxide solution, giving 6-*O*-acetyl-D-glucopyranose[3]; (*b*) fully acylated monosaccharides with hydrazine acetate in *N*,*N*-dimethylformamide, giving the corresponding 1-hydroxy derivatives[4]; and (*c*) fully acylated purine and pyrimidine ribonucleosides with hydrazine hydrate in 1:4 acetic acid–pyridine[5], and with hydroxylaminium acetate in pyridine[6], giving the corresponding 2′-hydroxy derivatives in good yields.

*Partial Protection of Carbohydrate Derivatives, Part 6. For Part 5, see ref. 1.

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TABLE I

COMPARISON OF HYDROXYLAMINIUM ACETATE AND HYDRAZINE HYDRATE IN PARTIAL *O*-DEBENZOYLATION OF METHYL 2,3-DI-*O*-BENZOYL-4,6-*O*-BENZYLIDENE-α-D-GLUCOPYRANOSIDE (**1**)[a]

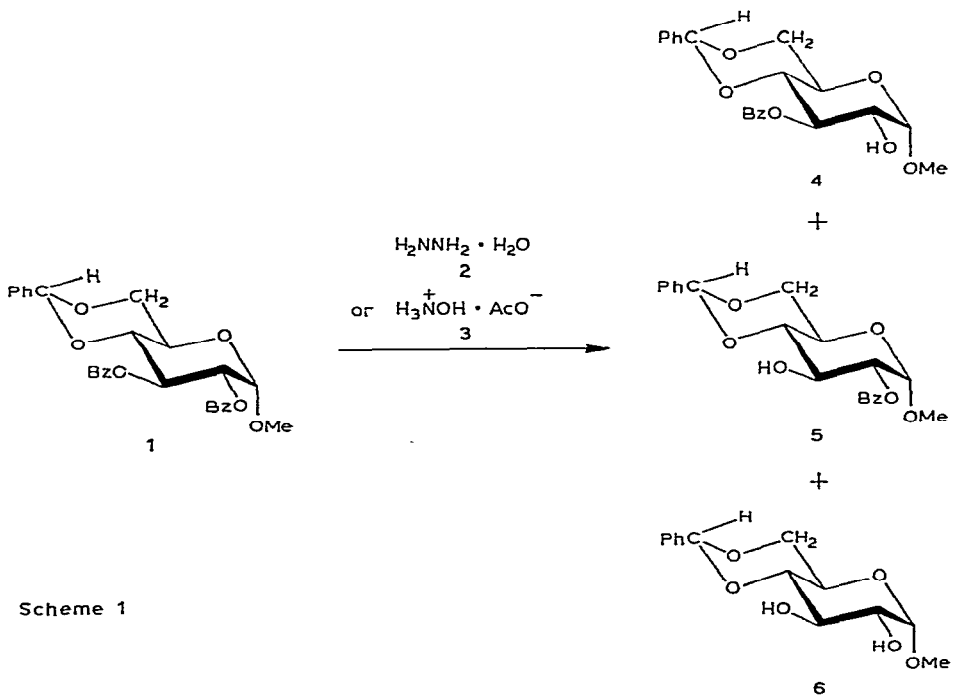
| *Entry* | *Reagent* | *Reaction conditions* | | | | *Yield (%) of* | | | *Recovery of* **1** *(%)* |
|---|---|---|---|---|---|---|---|---|---|
| | | *Mol. equiv. ratio* | *Solvent* | *Temp.* | *Time* | **4** | **5** | **6** | |
| 1 | $HON^+H_3 \cdot AcO^-$ | 4 | pyridine | room temp. | 7 days | — | — | — | quant. |
| 2 | $HON^+H_3 \cdot AcO^-$ | 4 | pyridine | 70–75° | 2 days | 39 | 6 | 20 | 18 |
| 3 | $NH_2NH_2 \cdot H_2O$ | 4 | pyridine–acetic acid[b] | room temp. | 7 days | — | — | — | quant. |
| 4 | $NH_2NH_2 \cdot H_2O$ | 4 | pyridine–acetic acid[b] | 70–75° | 6 h | 48 | 8 | 13 | 22 |
| 5 | $NH_2NH_2 \cdot H_2O$ | 2 | pyridine | room temp. | 20 h | 65 | 18 | — | 5 |

[a]All reactions were performed by use of **1** (5 mmol) in the solvent (25 mL). [b]The solvent was 4:1 (v/v).

The results[5,6], and the suggestion that the 2-hydroxyl groups of methyl aldosides are the most active among their hydroxyl groups, due to the electron-withdrawing effect of their methoxyl groups at the anomeric center[2], prompted us to extend the procedure to fully acylated sugar derivatives. We now describe the results of regioselective *O*-deacylation of fully acylated methyl glycosides, some other glycosyl compounds, and 1,2-*O*-isopropylidenealdofuranoses by means of hydrazinolysis.

## RESULTS AND DISCUSSION

An examination of the conditions for regioselective *O*-debenzoylation was started by use of methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**1**) as a model substrate, and hydrazine (**2**), or hydroxylaminium acetate (**3**), as the potential nucleophile for the partial *O*-deacylation reaction. Treatment of **1** with either **2** or **3** resulted in the favored formation of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**4**) over that of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**5**) or methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**6**), or both; the results thus obtained, and the conditions used, are summarized in Table I.




Scheme 1

As may be seen from Table I, the conditions used in Entry 5 (*i.e.*, **2** in pyridine at room temperature) were found to give the best result, affording **4** in 65% yield, whereas those in Entries 2 and 4 were inferior to that in Entry 5 as regards the yield of **4**, and gave **6** in addition to **5**. Those in Entries 1 and 3, on the other hand, were

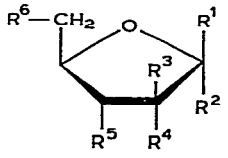
TABLE II

PARTIAL *O*-DEACYLATION OF FULLY ACYLATED METHYL D-PENTOFURANOSIDES AND 1,2-*O*-ISOPROPYLIDENEALDOFURANOSES WITH HYDRAZINE HYDRATE (2)

| *Entry* | *Sugar acylate* | *Reaction conditions* | | | *Yield (%) of O-acyl derivatives* | *Recovery (%) of starting material* |
|---|---|---|---|---|---|---|
| | | *2/the acylate* | *Procedure*[a] | *Time (h)* | | |
| 1 | **7** | 4 | A | 7 | 2,5-di- (**9**) (Mixture of 3,5-di- (**8**) & (**9**)) 23 44 (2:5) | 21 |
| 2 | **7** | 1.1 | B | 15 | **8** 25 **9** 32 | 22 |
| 3 | **12** | 2 | C | 72 | 3,5-di- (**13**) 2,5-di- (**14**) 23 44 | 2 |
| 4 | **15** | 1.1 | B | 20 | Mixture of 3,5- (**16**) and 2,5-di- (**17**) 51 (7:1) | 22 |
| 5 | **18** | 2 | B | 20 | 3,5-di- (**19**) 68 | 21 |
| 6 | **20** | 2 | B | 72 | 5- (**21**) 72 | — |
| 7 | **22** | 1.1 | B | 16 | 5- (**23**) 72 | — |
| 8 | **24** | 2 | B | 48 | 6- (**25**) 80 | — |

[a]Procedure A was performed in 1:4 (v/v) acetic acid–pyridine at 70–75°; B, in pyridine at room temperature; and C, in 1:4 (v/v) acetic acid–pyridine at room temperature.

inappropriate for the purpose of obtaining good regioselectivity, due to such an extremely slow reaction that **1** was recovered quantitatively; these conditions, however, proved fruitful in the regioselective, partial *O*-deacylation of fully acylated purine and pyrimidine ribonucleosides[5,6]. The conditions used in Entries 4, 5, and 3 are respectively termed Condition A, B, and C.




| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ |
|---|---|---|---|---|---|---|
| 7 | OMe | H | H | OBz | OBz | OBz |
| 8 | OMe | H | H | OH | OBz | OBz |
| 9 | OMe | H | H | OBz | OH | OBz |
| 10 | OMe | H | H | OBz | *m*-$MeC_6H_4CO_2$ | OBz |
| 11 | OMe | H | H | *m*-$MeC_6H_4CO_2$ | OBz | OBz |
| 12 | OMe | H | H | *p*-$O_2NC_6H_4CO_2$ | *p*-$O_2NC_6H_4CO_2$ | *p*-$O_2NC_6H_4CO_2$ |
| 13 | OMe | H | H | OH | *p*-$O_2NC_6H_4CO_2$ | *p*-$O_2NC_6H_4CO_2$ |
| 14 | OMe | H | H | *p*-$O_2NC_6H_4CO_2$ | OH | *p*-$O_2NC_6H_4CO_2$ |
| 15 | H | OMe | H | OBz | OBz | OBz |
| 16 | H | OMe | H | OH | OBz | OBz |
| 17 | H | OMe | H | OBz | OH | OBz |
| 18 | H | OMe | OBz | H | OBz | OBz |
| 19 | H | OMe | OH | H | OBz | OBz |

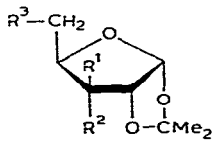
Based on the foregoing results, we next examined the conditions with respect to a series of methyl pentofuranosides and other furanoid derivatives; the conditions used, and the results thus obtained, are summarized in Table II. The behavior of methyl 2,3,5-tri-*O*-benzoyl-β-D-ribofuranoside (**7**) was of particular interest in comparison with that of fully acylated ribonucleosides, which gave the corresponding 2′-hydroxy 3′,5′-diacylates regioselectively[5,6]. Upon hydrazinolysis under Condition A (Entry 1), **7** gave a 2:5 mixture of methyl 3,5- (**8**) and 2,5-di-*O*-benzoyl-β-D-ribofuranoside (**9**) (44% yield), whose crystallization from ethanol gave **9** (23% yield). Decrease in the ratio of **2**:**7** from 4:1 to 1:1 and use of Condition B (Entry 2) gave **8** (25% yield) and **9** (32% yield). Incidentally, **9** (82% yield) was obtained by storing the ethanolic solution of **8** in a refrigerator for a week; this indicates that the benzoyl group involved in its 2,3-*cis*-diol system readily migrates under those conditions.

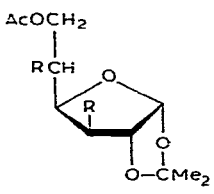
To make sure of the mutual lability of acyl groups in the *cis*-diol system, the behavior of the 2,5-di-*O*-benzoyl-3-*O*-*m*-toluoyl- (**10**) and 3,5-di-*O*-benzoyl-2-*O*-*m*-toluoyl derivative (**11**) of methyl β-D-ribofuranoside towards the nucleophile was scrutinized. [Compounds **10** and **11** were respectively derived from **9** and **8** by *m*-toluoylation in the usual way (85 and 83% yield, respectively).] Hydrazinolysis of **10** and **11** under Condition B gave the corresponding mixture of diacylates (55 and 51% yield, respectively); $^1$H-n.m.r.-spectroscopic analysis of each resulting mixture in terms of the area-ratios of the methyl-proton signals, *i.e.*, that of the *m*-toluoyl group at δ 2.30, and of the methoxyl group on C-1 at δ 3.43, respectively proved 70

and 25% survival of the *m*-tolyoyl group. The 2-*O*-acyl groups in fully acylated methyl β-D-ribofuranosides were thus confirmed as being the most labile towards **2**, a trend similar to that observed in the hydrazinolysis of fully acylated ribonucleosides[5,6]. Therefore, it was concluded that the favored formation of **9** over **8** must be due to acyl migration after removal of the benzoyl group on O-2 during the reaction, although it is at present difficult to discuss potential factors involved in the equilibration between **8** and **9**.

The lower reactivity of **7** than that of fully acylated ribonucleosides towards **2** caused us to examine the *p*-nitrobenzoyl group as the protecting group (instead of the benzoyl group); the conditions used here had been sufficiently fruitful to induce the highly regioselective 2′-*O*-deacylation of fully acylated ribonucleosides[5]. On hydrazinolysis under Condition C, methyl 2,3,5-tri-*O*-(*p*-nitrobenzoyl)-β-D-ribofuranoside, (**12**) gave the 3,5-bis(*p*-nitrobenzoate) (**14**) in 44% yield (Entry 3). On the other hand, the reactions of methyl 2,3,5-tri-*O*-benzoyl-α-D-ribofuranoside (**15**) and -D-arabinofuranoside (**18**) under Condition B (Entries 4 and 5) gave a 7:1 mixture of methyl 3,5- (**16**) and 2,5-di-*O*-benzoyl-α-D-ribofuranoside (**17**) (51% yield), and methyl 3,5-di-*O*-benzoyl-α-D-arabinofuranoside (**19**) (68% yield), respectively; the 2-*O*-benzoyl group was thus found to be the most labile toward **2** among the three *O*-benzoyl groups in these cases, as with fully benzoylated ribonucleosides.

We next examined the behavior of 3,5-di-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-ribofuranose (**20**), 3,5-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**22**), and 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**24**) (Entries 6, 7, and 8; under Condition B, respectively, in Table II). It was found that these reactions result in the formation of the corresponding derivatives bearing one acyl group on their primary alcoholic groups, giving 5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-ribofuranose (**21**) (72% yield), 5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**23**) (72% yield), and 6-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**25**) (80% yield), respectively. Such a remarkable difference in lability as between the primary and secondary esters in these sugar derivatives may be explained through a concept proposed by Zachau and Karau[7] and Bruice and Fife[8], namely, the electron-withdrawing effect of the

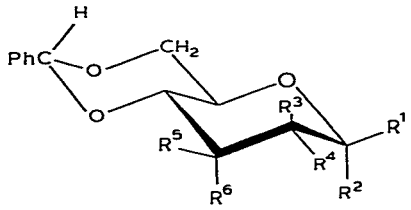



| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| 20 | H | OBz | OBz |
| 21 | H | OH | OBz |
| 22 | OAc | H | OAc |
| 23 | OH | H | OAc |

24 R = OAc

25 R = OH



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ |
|---|---|---|---|---|---|---|
| 26 | H | OMe | H | OBz | H | OBz |
| 27 | H | OMe | H | OH | H | OBz |
| 28 | H | OMe | H | OBz | H | OH |
| 29 | H | OMe | OBz | H | H | OBz |
| 30 | H | OMe | OH | H | H | OBz |
| 31 | H | OMe | OBz | H | H | OH |
| 32 | H | OMe | OBz | H | OBz | H |
| 33 | H | OMe | OH | H | OBz | H |
| 34 | H | OMe | OBz | H | OH | H |
| 35 | OMe | H | H | OBz | OBz | H |
| 36 | OMe | H | H | OH | OBz | H |
| 37 | OMe | H | H | OBz | OH | H |
| 38 | OMe | H | OBz | H | OBz | H |
| 39 | OMe | H | OH | H | OBz | H |
| 40 | OMe | H | OBz | H | OH | H |
| 41 | H | OMe | H | OAc | OAc | H |
| 42 | H | OMe | H | OH | OAc | H |
| 43 | H | OMe | H | OAc | OH | H |
| 44 | H | OMe | H | *p*-$O_2NC_6H_4CO_2$ | *p*-$O_2NC_6H_4CO_2$ | H |
| 45 | H | OMe | H | OH | *p*-$O_2NC_6H_4CO_2$ | H |
| 46 | H | OMe | H | *p*-$O_2NC_6H_4CO_2$ | OH | H |

alkoxy-oxygen atom in sugar backbones functionalized as ethers (or ring-oxygen) and esters, and the number of carbon atoms bearing such an oxygen atom vicinal to the carbon atom bearing an acyloxy group might bring about such a delicate difference in the lability towards **2** that is observed among the derivatives **20**, **22**, and **24**.

We then performed a series of reactions on methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-allo- (**26**), -altro- (**29**), -manno- (**32**), and -galactopyranoside (**47**), methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-gluco- (**35**) and -mannopyranoside (**38**), methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**41**), and methyl 4,6-*O*-benzylidene-2,3-di-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranoside (**44**), in addition to **1**, all of which had been found, by $^1$H-n.m.r. spectroscopy[9], to assume the $^4C_1$(D) conformation; it seemed probable that study of the reaction of these compounds would make possible a correlation of the configurational differences of their hydroxyl groups with their regioselectivity in hydrazinolysis. The conditions used, and the results thus obtained, are summarized in Table III. Among the reactions under Condition B, compounds **1** (Entry 2), **26** (Entry 3), **29** (Entry 4), and **47** (Entry 7) afforded the corresponding 3-benzoates (**4**, **27**, **30**, and **48**) in preference to the corresponding 2-benzoates (**5**, **28**, **31**, and **49**, respectively). However, compound **35** (Entry 9) gave the corresponding 3- (**36**) (8% yield) and 2-benzoate (**37**) (10% yield), and compound **38** (Entry 10) gave a 1:4 mixture of the 3- (**39**) and 2-benzoate (**40**) (27% total yield), respectively. The reactions under Condition A showed, by and large, the same trend as observed for those under Condition B (comparing the results

TABLE III

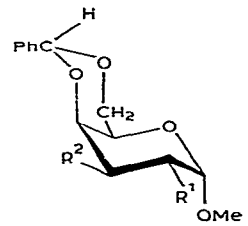
PARTIAL *O*-DEACYLATION OF METHYL 4,6-*O*-BENZYLIDENE-D-HEXOPYRANOSIDE ACYLATES WITH 2

| *Entry* | *Hexopyranoside acylate* | *Reaction conditions* | | | *Yield (%) of* | | | *Recovery (%) of hexopyranoside acylate* |
|---|---|---|---|---|---|---|---|---|
| | | *2/hexopyranoside* | *Time (h)* | *Temp. and solvent*[a] | *2-OH derivatives* | *3-OH* | *2,3-di-OH* | |
| 1 | **1** | 4 | 6 | A | 48 | 8 | 13 | 22 |
| 2 | **1** | 2 | 20 | B | 65 | 18 | — | 5 |
| 3 | **26** | 2 | 16 | B | 77 | 5 | — | 16 |
| 4 | **29** | 2 | 24 | B | 87 | 3 | — | 5 |
| 5 | **32** | 6 | 30 | A | 21 | 16 | 26 | 22 |
| 6 | **32** | 4 | 48 | B | 32 | 25 | — | 41 |
| 7 | **47** | 2 | 18 | B | 51 | 22 | — | 10 |
| 8 | **35** | 8 | 14 | A | 10 | 20 | 27 | 27 |
| 9 | **35** | 4 | 120 | B | 8 | 10 | —[b] | 29 |
| 10 | **38** | 4 | 120 | B | 27[c] | | 40 | 9 |
| 11 | **41** | 1.6 | 120 | C | 22 | 0 | 42 | 8 |
| 12 | **44** | 4 | 5 | C | 63 | 12 | — | 10 |

[a]Reaction A was performed in 1:4 (v/v) acetic acid–pyridine at 70–75°; B, in pyridine at room temperature; C, in 1:4 (v/v) acetic acid–pyridine at room temperature. [b]This product was obtained as a mixture with 1-benzoyl-2,2-isopropylidenehydrazine. [c]In this case, the 2-OH and 3-OH derivatives were obtained as a 1:4 mixture.

in Entries 1 and 2, and in Entries 5 and 6, with each other, except for that in Entries 8 and 9). Moreover, the reactions of compounds **41** (Entry 11) and of **44** (Entry 12) under Condition C gave the corresponding 3-acylates, **42** and **45**, in preference to the 2-acylates, **43** and **46**, respectively.

In order to make less ambiguous a discussion of the factors potentially in-




47 $R^1$ = OBz, $R^2$ = OBz
48 $R^1$ = OH, $R^2$ = OBz
49 $R^1$ = OBz, $R^2$ = OH

volved in the regioselectivity, the possibility of acyl migration between each pair of 3- and 2-hydroxyl groups was examined by treating each pure sample with **2** (1 mol. equiv.) in pyridine; the conditions used, and the results obtained, are summarized in Table IV.

Except for those of **32**, **36**, and **37**, the hydrazinolysis could be assumed to involve no substantial, acyl migration, provided that the reaction time was not much prolonged over 14 h, and it should, therefore, be possible to discuss the factors (in

TABLE IV

EXAMINATION OF ACYL MIGRATION BETWEEN METHYL 2-*O*- AND 3-*O*-BENZOYL-4,6-*O*-BENZYLIDENE-D-HEXOPYRANOSIDES[a]

| *Monobenzoate* | | *Yield (%) of* | |
|---|---|---|---|
| | | *2-Benzoate* | *3-Benzoate* |
| 2-Benzoate of | | | |
| α-D-allo- | (28) | 97 | — |
| α-D-altro- | (31) | 94 | — |
| α-D-gluco- | (5) | 86 | — |
| α-D-manno- | (34) | 85 | — |
| β-D-gluco- | (37) | 90 | 4 |
| 3-Benzoate of | | | |
| α-D-allo- | (27) | — | 94 |
| α-D-altro- | (30) | — | 90 |
| α-D-gluco- | (4) | — | 89 |
| α-D-manno- | (33) | 10 | 82 |
| β-D-gluco- | (36) | 6 | 86 |

[a]All reactions were performed by use of **2** (1 equiv.) in pyridine (B) for 14 h at room temperature, and the resulting mixtures were respectively separated by chromatography on a column of silica gel.

terms of the yields shown in Entries 1, 2, 3, 4, and 7) as a reflection of the electron-withdrawing effect of the anomeric methoxyl group, in addition to that of the ring-oxygen atom, which should make the 2-*O*-acyl groups more active than the 3-*O*-acyl groups, just as the heterocyclic moieties of fully acylated D-ribonucleosides affect their D-ribofuranosyl moiety[5,6]. Reaction of **1** (Entries 1 and 2) and of **35** (Entries 8 and 9) brought to notice the importance of a difference in the anomeric configuration of the aglycon, which may affect the regioselectivity, or the correlative activity, or both, of the *O*-benzoyl groups on O-2 and O-3, towards **2**.

The striking difference in the reaction time, as well as in the regioselectivity, may be attributed to the difference in anomeric configuration of the carbon atom bearing the methoxyl group, although it is at present impossible to discuss, without ambiguity, whether the electron-withdrawing effect of the methoxyl group varies with that configuration on account of the dipole–dipole interaction between the ring-oxygen atom and the methoxyl group (which should be in parallel in **35**, but not in **1***), or whether the steric effect of the aglycon on the 2-*O*-benzoyl group is enhanced on its occupying the equatorial orientation ($\beta$ configuration) in the $^4C_1$(D) conformation. Comparison of Entries 2 and 7 led us to conclude that the configurational difference at C-4, as between **1** and **47**, did not make so much difference in the regioselectivity as that observed between **1** and **35**. The excellent regioselectivity observed in the reaction of **26** (Entry 3) and **29** (Entry 4) might be due to the 1,3-diaxial interaction between the 1-methoxyl and the 3-benzoyloxy group; the reactivity of the 3-benzoyloxy group towards **2** might be considerably lessened, so that the reactivity of the 2-benzoyloxy group might apparently be enhanced, to give regioselectivity, even in the case of **29** (bearing an axial, 2-benzoyloxy group, which has been accepted as being less reactive than an equatorial group towards a nucleophile[12]).

On the other hand, the reaction of **32** (Entry 6) resulted in its 41% recovery, despite the longer reaction time (48 h), and the regioselectivity was strikingly lowered; this may be attributed to its equatorial 3-benzoyloxy group (free from the 1,3-diaxial interaction with the 1-methoxyl group that was involved in **26** and **29**), and to its 2-benzoyloxy group, sterically hindered because of its axial orientation. As with the relationship observed between **1** and **35**, the difference in the anomeric configuration brought about an extreme decrease in the reactivity of **38**, as compared with that of **32**; the 1-methoxyl group in the equatorial orientation might decrease the reactivity

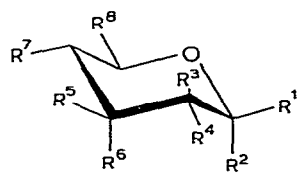
*In connection with the anomeric effect[10], it has generally been accepted that the O-5–C-1 bond assumes a double-bond character, and the C-1–$OCH_3$ bond has less bond character than the usual C–O single bond in a methyl $\alpha$-D-aldopyranoside, but not in the corresponding $\beta$ anomer. The difference found here could be a matter of controversy, based on such reliable evidence as that derived from X-ray crystal-structure analysis, which had mainly suggested our developing the novel procedure for regioselective 2′-*O*-deacylation of fully acylated purine and pyrimidine ribonucleosides (see refs. 5 and 6). The intramolecular hydrogen-bonding of the 2-hydroxyl group with the 1-methoxyl group involved in methyl $\alpha$-D-glucopyranoside has, incidentally, been used in an explanation of its higher reactivity towards an electrophile than of that in the corresponding $\beta$ anomer[11]; the fact revealed here seems to be in conflict with that, as in the previous discussion on the unusual acidity of the 2′-hydroxyl groups of purine and pyrimidine D-ribonucleosides[6].

TABLE V

PARTIAL *O*-DEBENZOYLATION OF METHYL 2,3,4,6-TETRA-*O*-BENZOYL-D-HEXO- AND -PENTO-PYRANOSIDES WITH **2**[a]

| *Entry* | *Hexo-pyranoside benzoate* | *Reaction conditions* | | *Yield (%) of* | | *Recovery (%) of starting material* |
|---|---|---|---|---|---|---|
| | | *2/the benzoate* | *Time (h)* | *2-OH* | *di-OH* | |
| 1 | **50** | 1.1 | 12 | 77 | — | — |
| 2 | **52** | 1.1 | 14 | 78 | — | — |
| 3 | **54** | 2.0 | 16 | 52[b] | 12 (2,3-) | 14 |
| 4 | **54** | 4.0 | 9 | 41[b] | 17 (2,3-) | 15 |
| 5 | **59** | 4.0 | 22 | 20 | 13 (2,4-) | 8 |
| 6 | **62** | 4.0 | 48 | — | 30 (2,3-) | 52 |
| 7 | **64** | 2.0 | 24 | 41 (29%[c]) | — | 14 |
| 8 | **64** | 4.0 | 6 | 36 (24%[c]) | — | 24 |

[a]All reactions were performed by Procedure B, except for Entries 4 and 8, which were performed by Procedure A. [b]This product was isolated as the corresponding tosyl derivative. [c]The yield of methyl 2,3-di-*O*-benzoyl-α-D-xylopyranoside (**66**).




| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | $R^7$ | $R^8$ |
|---|---|---|---|---|---|---|---|---|
| **50** | H | OMe | H | OBz | H | OBz | OBz | $CH_2OBz$ |
| **51** | H | OMe | H | OH | H | OBz | OBz | $CH_2OBz$ |
| **52** | H | OMe | OBz | H | H | OBz | OBz | $CH_2OBz$ |
| **53** | H | OMe | OH | H | H | OBz | OBz | $CH_2OBz$ |
| **54** | H | OMe | H | OBz | OBz | H | OBz | $CH_2OBz$ |
| **55** | H | OMe | H | OH | OBz | H | OBz | $CH_2OBz$ |
| **56** | H | OMe | H | OH | OBz | H | OH | $CH_2OBz$ |
| **57** | H | OMe | H | OH | OH | H | OBz | $CH_2OBz$ |
| **58** | H | OMe | H | OTs | OBz | H | OBz | $CH_2OBz$ |
| **59** | H | OMe | OBz | H | OBz | H | OBz | $CH_2OBz$ |
| **60** | H | OMe | OH | H | OBz | H | OBz | $CH_2OBz$ |
| **61** | H | OMe | OH | H | OBz | H | OH | $CH_2OBz$ |
| **62** | OMe | H | H | OBz | OBz | H | OBz | $CH_2OBz$ |
| **63** | OMe | H | H | OH | OH | H | OBz | $CH_2OBz$ |
| **64** | H | OMe | H | OBz | OBz | H | OBz | H |
| **65** | H | OMe | H | OH | OBz | H | OBz | H |
| **66** | H | OMe | H | OBz | OBz | H | OH | H |
| **67** | H | OMe | H | $OCOC_6H_4NO_2$-*p* | $OCOC_6H_4NO_2$-*p* | H | $OCOC_6H_4NO_2$-*p* | $CH_2OCOC_6H_4NO_2$-*p* |
| **68** | H | OMe | H | OH | $OCOC_6H_4NO_2$-*p* | H | $OCOC_6H_4NO_2$-*p* | $CH_2OCOC_6H_4NO_2$-*p* |
| **69** | H | OMe | $OCOC_6H_4NO_2$-*p* | H | $OCOC_6H_4NO_2$-*p* | H | $OCOC_6H_4NO_2$-*p* | $CH_2OCOC_6H_4NO_2$-*p* |
| **70** | H | OMe | OH | H | $OCOC_6H_4NO_2$-*p* | H | $OCOC_6H_4NO_2$-*p* | $CH_2OCOC_6H_4NO_2$-*p* |
| **71** | H | OMe | $OCOC_6H_4NO_2$-*p* | H | OH | H | $OCOC_6H_4NO_2$-*p* | $CH_2OCOC_6H_4NO_2$-*p* |
| **72** | OMe | H | H | $OCOC_6H_4NO_2$-*p* | $OCOC_6H_4NO_2$-*p* | H | $OCOC_6H_4NO_2$-*p* | $CH_2OCOC_6H_4NO_2$-*p* |
| **73** | OMe | H | H | OH | $OCOC_6H_4NO_2$-*p* | H | $OCOC_6H_4NO_2$-*p* | $CH_2OCOC_6H_4NO_2$-*p* |

of the 2-benzoyloxy group in the axial orientation, giving 2-hydroxy, 3-hydroxy, and 2,3-dihydroxy derivatives in 5, 22, and 44% yield, respectively. The reactions of **41** and **44**, respectively, with **2** were performed in 1 : 4 acetic acid–pyridine, in anticipation of their enhanced reactivity; however, excellent regioselectivity was obtained only in the reaction of the latter, which was complete within 5 h, in contrast to that of **41**.

Extension of the foregoing procedure to fully acylated methyl aldo-hexo- and -pento-furanosides was next attempted; the conditions used, and the results obtained, are summarized in Table V. Among the derivatives used, methyl 2,3,4,6-tetra-*O*-benzoyl-α-D-allo- (**50**) and -altro-pyranoside (**52**) were found to give the highest regioselectivity, as shown in Entries 1 and 2, and a little less regioselectivity was obtained in the reaction of methyl 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranoside (**54**). The regioselectivity was further lowered in the reactions of methyl 2,3,4,6-tetra-*O*-benzoyl-α-D-manno- (**59**) and -β-D-gluco-pyranoside (**62**); both of the resulting mixtures were complex (according to t.l.c.). The 2,4- and 2,3-dihydroxy derivatives were respectively isolated, and the former reaction produced, as an inseparable mixture, a considerable proportion of further debenzoylated derivatives (Entries 5 and 6). On the other hand, the reaction of methyl 2,3,4-tri-*O*-benzoyl-α-D-xylopyranoside (**64**) gave comparable amounts of the 2- and 4-hydroxy derivatives (Entries 7 and 8); this may be attributed to the absence of a 5-(benzoyloxymethyl) group (thus differing from the hexopyranosides used), and the favored formation of the 2-hydroxy derivative may be ascribed to the extra electron-withdrawing effect of the 1-methoxyl group.

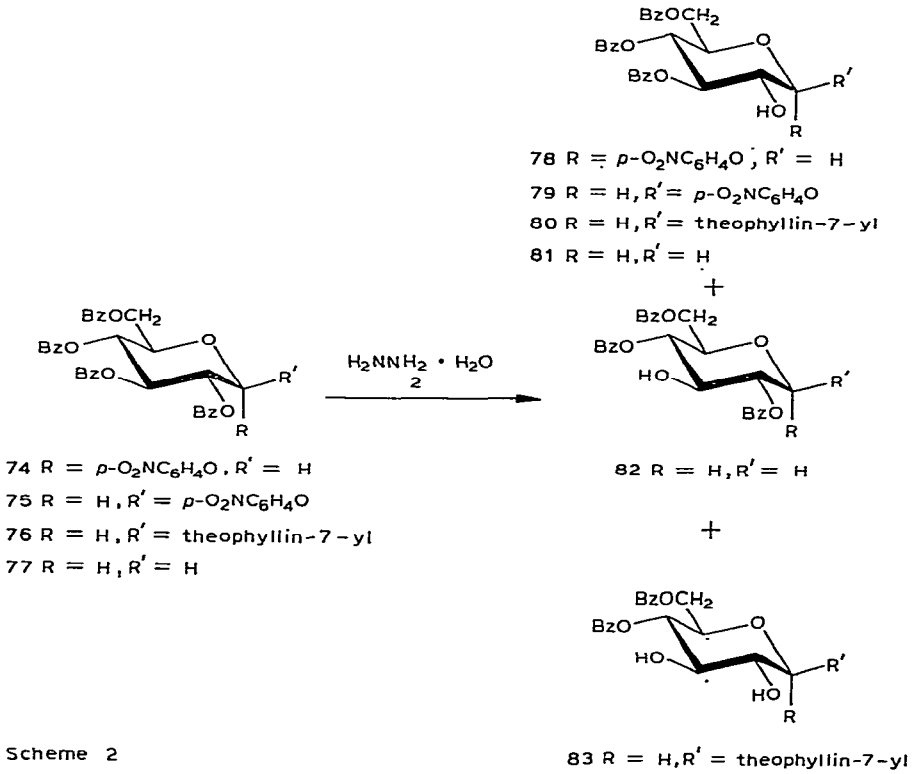
Confronted with the results shown in Entries 3, 5, and 6 in Table V, the corresponding tetrakis(*p*-nitrobenzoates) (**67**, **69**, and **72**, respectively) of methyl α-D-gluco-, α-D-manno-, and β-D-gluco-pyranoside were examined under Condition C, and the results thus obtained are summarized in Table VI. The utility of the *p*-nitrobenzoates was proved by these results, although **69** afforded the corresponding 3,4,6- (**70**) and 2,4,6-tris(*p*-nitrobenzoate) (**71**), judging from the improved results (compared with those shown in Entries 3, 5, and 6 in Table V). The favored formation of the 2,4,6-

TABLE VI

PARTIAL *O*-DE-(*p*-NITROBENZOYL)ATION OF METHYL 2,3,4,6-TETRA-*O*-(*p*-NITROBENZOYL)-D-HEXOPYRANOSIDES WITH **2**[a]

| *Hexopyranoside* p-*nitrobenzoate* | *Reaction conditions* | | *Yield (%) of tris*(p-*nitrobenzoate*) | | *Recovery (%) of starting material* |
|---|---|---|---|---|---|
| | **2**/*the* p-*nitrobenzoate* | *Time (h)* | *3,4,6-* | *2,4,6-* | |
| **67** | 4 | 8 | 77 | — | 9 |
| **69** | 4 | 24 | 28 | 42 | 18 |
| **72** | 4 | 16 | 51 | — | 5 |

[a]All reactions were performed under Condition C.




Scheme 2

over the 3,4,6-tris(*p*-nitrobenzoate) in the reaction of **69** might be ascribed to the difference in the steric effect of an equatorial benzoyloxy group at C-3 and an axial one at C-2, on interacting with **2**.

Lastly, we examined the behavior of *p*-nitrophenyl 2,3,4,6-tetra-*O*-benzoyl-α-(**74**) and -β-D-glucopyranoside (**75**), 7-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-theophylline (**76**), and 1,5-anhydro-2,3,4,6-tetra-*O*-benzoyl-D-glucitol (**77**) under Condition B and C, respectively; the conditions used, and the results obtained, are summarized in Table VII. The trend observed, as between the reactions of **74** (Entries 1 and 2) and of **75** (Entries 3 and 4), was similar to that found between those of **54** and of **62** (Entries 4 and 6 in Table V, respectively), although the difference is not so striking as that between **54** and **62**; the stronger electron-withdrawing effect of the *p*-nitrophenoxyl than of the methoxyl group presumably decreases the difference observed between **1** and **35** (bearing the latter group at the anomeric center).

Comparable reactivity towards **2** was observed in the reaction of **76** and of **75**. Comparison of the reactivity of **77** (Entries 7 and 8) with that of **54** and **62** (Entries 4 and 6, respectively, in Table V) is of interest, as it showed that **77** is superior in reactivity, to **62**, but inferior to **54**, giving the 2-hydroxy preferentially over the 3-hydroxy derivative. That the reactivity of **62** is lower than that of **77** strongly supports the contention that assumption of the equatorial orientation (β configuration) by

TABLE VII

PARTIAL *O*-DEACYLATION OF 2,3,4,6-TETRA-*O*-BENZOYL-D-GLUCOPYRANOSYL DERIVATIVES WITH **2**

| *Entry* | D-*Glucopyranosyl derivatives* | | *Reaction conditions* | | | | *Yield (%) of* | | *Recovery (%) of starting material* |
|---|---|---|---|---|---|---|---|---|---|
| | *R* | *R'* | *2/Glc-Bz*$_4$ | | *Time (h)* | *Solvent and temp.*[a] | *3,4,6-Tri-O-Bz* | *Other product*[b] | |
| 1 | *p*-$O_2NC_6H_4O$- | H | **74** | 1.1 | 8 | B | 79 | — | 14 |
| 2 | *p*-$O_2NC_6H_4O$- | H | **74** | 2 | 48 | C | 82 | — | 9 |
| 3 | H | *p*-$O_2NC_6H_4O$- | **75** | 1.1 | 16 | B | 37 | *P-a*, 22 | 32 |
| 4 | H | *p*-$O_2NC_6H_4O$- | **75** | 4 | 96 | C | 66 | — | 29 |
| 5 | H | theophyllin-7-yl | **76** | 2 | 12 | B | 49 | *P-b*, 29 | 17 |
| 6 | H | theophyllin-7-yl | **76** | 4 | 96 | C | 29 | — | 49 |
| 7 | H | H | **77** | 4 | 96 | B | 41 | *P-c*, 18 | 36 |
| 8 | H | H | **77** | 4 | 48 | B | 16 | *P-c*, 9 | 62 |

[a]Reactions indicated with B in column 6 were performed in pyridine at room temperature, and those with C, in 1:19 (v/v) acetic acid–pyridine at room temperature. [b]*P-a*, obtained as a mixture of dibenzoates; *P-b*, 4,6-dibenzoate; *P-c*, 2,4,6-tribenzoate.

the 1-methoxyl group makes it difficult to obtain excellent regioselectivity. That the regioselectivity in the reaction of **77** is superior to that of **62** is, presumably, brought about by the electron-withdrawing effect of the ring-oxygen atom, in addition to the steric effect of the 5-(benzoyloxymethyl) group.

It may be noted that, on the whole, acyl migration was not observed at all during separation of the products on a column of silica gel, in contrast to ribonucleoside diacylates[5,6], for which the migration was remarkably induced in the separation process.

Partial *O*-deacylation by **2** was thus proved to be achieved regioselectively for fully acylated glycosyl compounds also, parallel to that of fully acylated ribonucleosides, giving products having the 2-hydroxyl group free; this hydroxyl group has been chemically characterized by its greater susceptibility to esterification on treating nonacylated glycosyl compounds with acylating agents in the usual way.

## EXPERIMENTAL

*General methods.* — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Specific rotations were determined with a Nippon Bunko JASCO-DIP-4 apparatus. $^1$H-N.m.r. spectra were recorded with a Varian T-60 instrument, unless noted that a Varian EM-390 instrument was used. T.l.c. was performed on plates precoated with Merck silica gel 60 $F_{254}$ (thickness 0.25 mm), employing 4:1 benzene–ethyl acetates or 9:1 chloroform–methanol as the eluant, and detection of spots with a u.v. lamp (253.7 nm) or by heating the plate after spraying with 5% aqueous sulfuric acid solution. Elementary analysis was performed with a Perkin–Elmer 240-002 instrument. The pyridine used was preheated with 5% aqueous potassium permanganate solution at 50–60° before distillation, and then redistilled from calcium hydride.

*General procedures for partial O-deacylation.* — *Condition A.* A solution of a fully acylated carbohydrate derivative (1 mmol) in 1:4 acetic acid–pyridine (2 mL) was treated with **2** (the amount used being given in each case) for a chosen time at 70–75°, after which, the reaction was terminated by quenching with an excess of acetone, followed by evaporation below 40°. The resulting syrup was dissolved in chloroform, and chromatographed on a column of silica gel (Wakogel C-300). Elution with 7:3 and 1:1 cyclohexane–chloroform and then 50:1 chloroform–methanol, respectively gave unchanged starting-material, a product having a free hydroxyl group, and one with two free hydroxyl groups, in admixture with 1-acyl-2,2-isopropylidenehydrazine.

*Condition B.* A solution of a fully acylated carbohydrate derivative ( 1 mmol) in pyridine (5 mL) was treated with **2** for a chosen time at room temperature, after which, the reaction was quenched with an excess of acetone by stirring for 1–2 h at room temperature. The mixture was then evaporated below 40° to a syrup, which was chromatographed on a column of silica gel (Wakogel B-0). Elution with 19:19:2, 9:9:2, and then 2:2:1 benzene–cyclohexane–ethyl acetate gave, respectively, un-

changed starting-material, a product having a free hydroxyl group, and one with two free hydroxyl groups, in admixture with the hydrazine derivative.

*Condition C.* This procedure was as described under Condition B, but using 1:4 acetic acid–pyridine as the solvent instead of pyridine.

*Regioselective hydrazinolysis of methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-glucopyranoside* (**1**). — Using Condition A, **1** (2.45 g, 5 mmol) was treated with **2** (0.98 mL, 20 mmol) for 5 h, and the usual processing gave **1** (0.54 g, 22% recovery) as the first fraction, methyl 2-*O*-benzoyl- (**5**) (0.14 g, 7% yield) as the second fraction, and methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**4**) (0.91 g, 47% yield) as the third fraction, in addition to a fourth fraction consisting of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**6**) (0.18 g, 13% yield).

Compound **4** had m.p. 217–218° (from ethanol), $[\alpha]_D^{23}$ +32° (*c* 1.0, chloroform) {lit.[14] m.p. 217–218°, $[\alpha]_D^{21}$ +33.5° (*c* 2.55, chloroform)}.

Compound **5** had m.p. 171–172° (from diethyl ether–cyclohexane), $[\alpha]_D^{23}$ +113.3° (*c* 1.0, chloroform) {lit.[14] m.p. 171–172°, $[\alpha]_D^{21}$ +109.5° (*c* 2.09, chloroform)}.

Compound **6** had m.p. 163–164° (from chloroform–diethyl ether) {lit.[15] m.p. 163–164°}.

Treatment of **1** (2.45 g, 5 mmol) with **2** (0.49 mL, 10 mmol) under Condition B for 20 h, followed by the same processing, gave **1** (0.12 g, 5% recovery), **5** (0.35 g, 18% yield), and **4** (1.25 g, 65% yield); that of **1** (2.45 g, 5 mmol) with **2** (0.98 mL, 20 mmol) under Condition C for 7 days, followed by the same processing, gave **1** (2.40 g, 98% recovery); that of **1** (2.45 g, 5 mmol) with **3** (1.83 g, 20 mmol) in pyridine (30 mL) for 7 days at room temperature gave **1** (2.38 g, 97% recovery); and that of **1** (2.45 g, 5 mmol) with **3** (1.86 g, 20 mmol) in pyridine (30 mL) for 2 days at 70–75°, followed by the same processing, gave **1** (0.44 g, 18% recovery), **5** (0.12 g, 6% yield), **4** (0.75 g, 39% yield), and **6** (0.28 g, 20% yield).

*Methyl 2,3,5-tri-*O*-benzoyl-β-*D*-ribofuranoside* (**7**). — To a solution of methyl β-D-ribofuranoside[16] (2.5 g, 15 mmol) in 1:2 anhydrous pyridine–chloroform (30 mL), was added benzoyl chloride (10 mL) dropwise, with ice-cooling, and the mixture was stirred for 45 min at 0°, and kept overnight at room temperature. The mixture was poured into ice–water, and the aqueous layer was extracted with chloroform (100 mL × 3). The organic layer and extracts were combined, successively washed with M hydrochloric acid, aqueous sodium hydrogencarbonate solution (saturated), and aqueous sodium chloride solution (saturated), dried (anhydrous magnesium sulfate), and evaporated to a syrup which was chromatographed with 1:1 benzene–chloroform containing acetone (0 → 1%) as the eluant, to give colorless, syrupy **7** (6.3 g, 95% yield); $[\alpha]_D^{23}$ +64.1° (*c* 1.26, chloroform); $^1$H-n.m.r. (chloroform-*d*): δ 3.42 (s, 3 H, OC$H_3$), 5.88 (s, 1 H, *H*-1), and 7.2–7.6 and 7.8–8.2 (m, 15 H, 3 OCOC$_6H_5$).

*Anal.* Calc. for $C_{22}H_{24}O_8$: C, 68.05; H, 5.10. Found: C, 68.25; H, 5.10.

*Partial hydrazinolysis of* **7**. — Using Condition A, **7** (2.20 g, 4.65 mmol) was treated with **2** (0.91 mL, 18.6 mmol) for 7 h, and the same processing as before

gave **7** (0.47 g, 21% recovery), methyl 3,5-di-*O*-benzoyl-β-D-ribofuranoside (**8**) as a mixture with the corresponding 2,5-dibenzoate (**9**) (0.77 g, 44% yield; **8**:**9** = 2:5), and methyl 5-*O*-benzoyl-β-D-ribofuranoside (0.35 g, 28% yield). Crystallization of the mixture of **8** and **9** gave pure **9** (0.40 g, 23% yield).

Performance of the reaction under Condition B by use of **7** (1.83 g, 3.8 mmol) and **2** (0.19 mL, 4 mmol) for 15 h, followed by chromatographic separation of the resulting mixture, and rechromatography of the mixture of **8** and **9** gave **7** (0.38 g, 22% recovery), **8** (0.35 g, 25% yield), and **9** (0.45 g, 32% yield).

Compound **8** was a syrup, $[\alpha]_D^{23}$ +9.2° (*c* 1.7, chloroform); $^1$H-n.m.r. (chloroform-*d*): δ 3.37 (s, 3 H, OC$H_3$), 4.40–4.84 (m, 4 H, *H*-2,4,5,5'), 5.50 (t, 1 H, $J_{2,3}$ 5.0, $J_{3,4}$ 5.0 Hz, *H*-3), 4.96 (s, 1 H, *H*-1), and 7.16–7.60 and 7.85–8.20 (m, 10 H, 2 OCOC$_6H_5$).

*Anal.* Calc. for $C_{20}H_{20}O_7$: C, 64.50; H, 5.40. Found: C, 64.35; H, 5.45.

Compound **9** had m.p. 131–132° (from ethanol), $[\alpha]_D^{23}$ −9.7° (*c* 1, chloroform) {lit.[17] m.p. 131–132°, $[\alpha]_D^{25}$ −8.7° (*c* 0.49, chloroform)}: $^1$H-n.m.r. (chloroform-*d*): δ 3.38 (s, 3 H, OC$H_3$), 4.35–4.90 (m, 4 H, *H*-3,4,5,5'), 5.40 (d, 1 H, $J_{2,3}$ 4.5 Hz, *H*-2), 5.03 (s, 1 H, *H*-1), and 7.10–7.65 and 7.90–8.25 (m, 10 H, 2 OCOC$_6H_5$).

Compound **7** had m.p. 101–102° (from methanol), (lit.[17] m.p. 103–105°), $[\alpha]_D^{23}$ −38.7° (*c* 1, chloroform).

*Methyl 2,5-di-*O*-benzoyl-3-*O*-*m*-tolyoyl-β-D-ribofuranoside* (**10**). — To a solution of **9** (0.74 g, 2 mmol) in anhydrous pyridine (20 mL) was added *m*-toluoyl chloride (1.1 mL, 8 mmol), dropwise, with ice-cooling, and the mixture was stirred overnight, poured into ice–water, and extracted with chloroform (30 mL × 3). The extracts were combined, washed successively with M hydrochloric acid, aqueous sodium hydrogencarbonate solution (saturated), and water, dried (anhydrous sodium sulfate), and evaporated to a syrup; chromatography gave syrupy **10** (0.85 g, 86% yield); $^1$H-n.m.r. (chloroform-*d*): δ 2.30 (s, 3 H, Ph-C$H_3$), 3.41 (s, 3 H, OC$H_3$), 5.15 (s, 1 H, *H*-1), 5.65 (d, 1 H, $J_{2,3}$ 5.1 Hz, *H*-2), and 5.88 (t, 1 H, $J_{3,4}$ 5.0 Hz, *H*-3).

*Anal.* Calc. for $C_{28}H_{26}O_8$: C, 68.55; H, 5.35. Found: C, 68.50; H, 5.35.

*Methyl 3,5-di-*O*-benzoyl-2-*O*-m-toluoyl-β-D-ribofuranoside* (**11**). — The same treatment of **8** (0.74 g, 2 mmol) gave syrupy **11** (0.81 g, 83% yield); $^1$H-n.m.r. (chloroform-*d*): δ 2.25 (s, 3 H, Ph-C$H_3$), 3.40 (s, 3 H, OC$H_3$), 5.15 (s, 1 H, *H*-1), 5.65 (d, 1 H, $J_{2,3}$ 5.0 Hz, *H*-2), and 5.68 (t, 1 H, $J_{3,4}$ 5.0 Hz, *H*-3).

*Anal.* Calc. for $C_{28}H_{26}O_8$: C, 68.55; H, 5.35. Found: C, 68.25; H, 5.30.

*Partial hydrazinolysis of* **10**. — Treatment of **10** (0.49 g, 1 mmol) with **2** (0.05 mL, 1 mmol) under Condition B for 15 h, and the same processing as already described, gave a mixture of the corresponding diacylates (0.21 g, 55% yield); $^1$H-n.m.r. integration of area-ratio with respect to Ph-C$H_3$ and O-C$H_3$ in the spectrum of the mixture was ~7:10.

*Partial hydrazinolysis of* **11**. — The same treatment of **11** (0.49 g, 1 mmol) with **2** (0.05 mL, 1 mmol) for 15 h gave a mixture of diacylates (0.19 g, 51% yield); $^1$H-n.m.r. integration of area-ratio of Ph-C$H_3$ and O-C$H_3$ in the spectrum was ~1:4.

*Partial hydrazinolysis of methyl 2,3,5-tri-*O*-(p-nitrobenzoyl)-β-D-ribofuranoside*

(**12**). — Treatment of **12**[18] (0.61 g, 1 mmol) with **2** (0.1 mL, 2 mmol) under Condition C for 3 days, followed by similar processing, gave **12** (0.03 g, 2% recovery) and a semi-crystalline, syrupy mixture of bis(*p*-nitrobenzoate) (0.34 g, 74% yield); fractional recrystallization from ethanol gave methyl 2,5-di-*O*-(*p*-nitrobenzoyl)-β-D-ribofuranoside (**14**) (0.21 g, 44% yield). The mother liquor was evaporated to a syrup, and its crystallization, and recrystallization of the solid, from diethyl ether gave methyl 3,5-di-*O*-(*p*-nitrobenzoyl)-β-D-ribofuranoside (**13**) (0.12 g, 23% yield).

Compound **13** had m.p. 63–64°, $[\alpha]_D^{23}$ +27° (*c* 1, chloroform) {lit.[19] m.p. 62–63°, $[\alpha]_D^{23}$ +31° (*c* 1.42, chloroform)}.

Compound **14** had m.p. 150–151°, $[\alpha]_D^{23}$ −6.5° (*c* 1, chloroform) {lit.[19] m.p. 149–150°, $[\alpha]_D^{23}$ +1.4° (*c* 0.19, chloroform)}.

*Methyl 2,3,5-tri-*O*-benzoyl-α-*D*-ribofuranoside* (**15**). — Hydrogenolysis of methyl 2,3,5-tri-*O*-benzyl-α-D-ribofuranoside[20] (2.5 g, 5.75 mmol) under hydrogen in the presence of 10% palladized charcoal in 2:1 1,4-dioxane–ethanol (150 mL) for 3 days at room temperature, with stirring, followed by filtration, evaporation of the filtrate, and chromatography of the residue on a column of silica gel (Wakogel C-300) by use of 9:1 chloroform–methanol as the eluant, gave syrupy methyl α-D-ribofuranoside (0.82 g, 87% yield). This product (0.57 g, 3.4 mmol) was dissolved in 1:2 pyridine–chloroform (30 mL), benzoyl chloride (5 mL) was added dropwise, under ice-cooling, and the mixture was stirred for 5 h, poured into ice–water, stirred for 3 h, and extracted with chloroform (50 mL × 3). The extracts were combined, successively washed with M hydrochloric acid, aqueous sodium hydrogencarbonate solution (saturated), and water, dried (anhydrous magnesium sulfate), and evaporated to a syrup which was chromatographed on a column of silica gel by use of 1:1 benzene–cyclohexane containing 0 → 1% of acetone, to give syrupy **15** (1.60 g, 98% yield); $[\alpha]_D^{23}$ −64.4° (*c* 0.81, chloroform); $^1$H-n.m.r. (chloroform-*d*): δ 3.48 (s, 3 H, $OCH_3$), 4.50–4.80 (m, 3 H, *H*-4,5,5′), 5.20–5.45 (m, 2 H, *H*-1,2), 5.78 (m, 1 H, *H*-3), and 7.10–8.15 (m, 15 H, 3 $OCOC_6H_5$).

*Anal.* Calc. for $C_{27}H_{24}O_8$: C, 68.05; H, 5.10. Found: C, 68.00; H, 5.50.

*Partial hydrazinolysis of* **15**. — Treatment of **15** (0.48 g, 1 mmol) with **2** (0.05 mL, 1 mmol) by Condition B for 20 h, and processing as usual, gave **15** (0.10 g, 22% recovery) and a mixture of methyl 3,5- (**16**) and 2,5-di-*O*-benzoyl-α-D-ribofuranoside (**17**) (0.19 g, 51% yield) (**16**:**17** = 17:3, based on the $^1$H-n.m.r. integration area-ratio of methoxyl signals).

Compound **16** was a syrup; $^1$H-n.m.r. (chloroform-*d*; $D_2O$ added): δ 3.50 (s, 3 H, $OCH_3$), 4.30 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 7.0 Hz, *H*-2), 4.40–4.73 (m, 3 H, *H*-4,5,5′), 5.00 (d, 1 H, *H*-1), 5.38 (dd, 1 H, $J_{3,4}$ 2.5 Hz, *H*-3), and 7.1–8.2 (m, 10 H, 2 $OCOC_6H_5$).

Compound **17** had $^1$H-n.m.r. (chloroform-*d*; $D_2O$ added): δ 3.45 (s, 3 H, $OCH_3$).

*Anal.* Calc. for $C_{20}H_{20}O_7$ (mixture of **16** and **17**): C, 64.60; H, 5.20. Found: C, 64.50; H, 5.40.

*Partial hydrazinolysis of methyl 2,3,5-tri-*O*-benzoyl-α-*D*-arabinofuranoside* (**18**). — Treatment of **18**[21] (0.96 g, 2 mmol) with **2** (0.2 mL, 4 mmol) under Condition B

for 20 h, followed by the usual processing, gave **18** (0.07 g, 7% recovery) and syrupy methyl 3,5-di-*O*-benzoyl-α-D-arabinofuranoside (**19**) (0.50 g, 68% yield); $[\alpha]_D^{23}$ +59.2° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*; $D_2O$ added): δ 3.47 (s, 3 H, *H*-4,5,5'), 4.65 (s, 1 H, *H*-2), 5.16 (s, 1 H, *H*-1), 5.28 (d, 1 H, $J_{3,4}$ 7.0 Hz, *H*-3), and 7.10–7.60 and 7.90–8.15 (m, 10 H, 2 $OCOC_6H_5$).

*Anal.* Calc. for $C_{20}H_{20}O_7$: C, 64.50; H, 5.40. Found: C, 64.40; H, 5.35.

*Partial hydrazinolysis of 3,5-di-*O*-benzoyl-1,2-*O*-isopropylidene-α-*D*-ribofuranose* (**20**). — Treatment of **20**[22] (3.97 g, 10 mmol) with **2** (1 mL, 20 mmol) under Condition B for 3 days, followed by processing as usual, gave 5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-ribofuranose (**21**) (2.11 g, 72% yield); m.p. 76.5–77.5° (from acetone–cyclohexane), $[\alpha]_D^{23}$ +25.5° (*c* 1, chloroform) {lit[23] m.p. 78–79°, $[\alpha]_D^{23}$ +20.05° (*c* 1, chloroform)}.

*Partial hydrazinolysis of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-*D*-xylofuranose* (**22**). — Treatment of **22**[24] (2.05 g, 7.48 mmol) with **2** (0.41 g, 8.2 mmol) under Condition B for 16 h, followed by the usual processing, gave 5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**23**) (1.25 g, 72% yield); m.p. 101° (from diethyl ether), $[\alpha]_D^{23}$ +20.0° (*c* 1, chloroform) {lit.[24] m.p. 100–100.5°, $[\alpha]_D^{23}$ +23°}.

*Partial hydrazinolysis of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-*D*-glucofuranose* (**24**). — Treatment of **24**[25] (1.04 g, 2 mmol) with **2** (0.11 mL, 2.2 mmol) under Condition B for 2 days, followed by the usual processing, gave 6-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**25**) (0.63 g, 80% yield); m.p. 142–143° (from ethanol) (lit.[26] m.p. 142–143°).

*Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-allopyranoside* (**26**). — To a solution of methyl 4,6-*O*-benzylidene-α-D-allopyranoside[27] (3.3 g, 10 mmol) in anhydrous pyridine (20 mL) was added benzoyl chloride (10 mL) under ice-cooling. After being stirred overnight at room temperature, the mixture was treated as usual, and the product was purified by chromatography on a column of silica gel, to give **26** (5.2 g, 94% yield); colorless syrup, $[\alpha]_D^{23}$ +70° (*c* 1.4, chloroform).

*Anal.* Calc. for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.67; H, 5.41.

*Partial hydrazinolysis of* **26**. — Treatment of **26** (1.02 g, 2.07 mmol) with **2** (0.21 mL, 4.1 mmol) under Condition B for 16 h, followed by the usual processing, gave, in succession, **26** (0.16 g, 16% recovery), methyl 2-*O*- (**28**) (0.04 g, 5% yield), and methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-allopyranoside (**27**) (0.62 g, 77% yield) on chromatographing.

Compound **27** was a syrup, $[\alpha]_D^{23}$ +86.7° (*c* 1.4, chloroform); $^1$H-n.m.r. (chloroform-*d*; $D_2O$ added): δ 3.48 (s, 3 H, $OCH_3$), 3.65–4.57 (m, 4 H, *H*-4,5,6,6'), 3.90 (dd, 1 H, $J_{1,2}$ 4.5, $J_{2,3}$ ~2 Hz, *H*-2), 4.78 (d, 1 H, *H*-1), 5.55 (s, 1 H, C*H*-Ph), 5.93 (t, 1 H, $J_{3,4}$ 2.0 Hz, *H*-3), and 7.05–7.65 and 7.90–8.24 (m, 10 H, 2 $C_6H_5$).

*Anal.* Calc. for $C_{21}H_{22}O_7$: C, 65.27; H, 5.74. Found: C, 65.15; H, 5.71.

Compound **28** had m.p. 114–116° (from ethanol), $[\alpha]_D^{23}$ +71° (*c* 1, chloroform) {lit.[27] 110–115°, $[\alpha]_D^{23}$ +74° (*c* 1.5, chloroform)}, $^1$H-n.m.r. (chloroform-*d*; $D_2O$ added): δ 3.50 (s, 3 H, $OCH_3$), 3.70–4.65 (m, 5 H, *H*-3,4,5,6,6'), 5.00–5.20 (m, 2 H, *H*-1,2), 5.63 (s, 1 H, C*H*-Ph), and 7.25–8.28 (m, 10 H, 2 $C_6H_5$).

*Partial hydrazinolysis of methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-altropyranoside* (**29**). — Treatment of[28] **29** (2.45 g, 5.04 mmol) with **2** (0.5 mL, 10 mmol) under Condition B for 24 h, followed by processing as usual, gave, in succession, **29** (0.12 g, 5% recovery), methyl 2-*O*- (**31**) (0.06 g, 3% yield), and methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-altropyranoside (**30**) (1.7 g, 89% yield).

Compound **30** was a syrup, $[\alpha]_D^{23}$ +133° (*c* 1, chloroform) {lit.[28] $[\alpha]_D^{20}$ +131.0 ±2° (chloroform)}; $^1$H-n.m.r. (chloroform-*d*; $D_2O$ added): δ 3.40 (s, 3 H, $OCH_3$), 3.80–4.54 (m, 4 H, *H*-4,5,6,6'), 4.17 (d, 1 H, $J_{2,3}$ 3.0 Hz, *H*-2), 4.70 (s, 1 H, *H*-1), 5.50 (m, 1 H, *H*-3), 5.62 (s, 1 H, C*H*-Ph), and 7.15–7.62 and 7.75–8.20 (m, 10 H, 2 $C_6H_5$).

Compound **31** had m.p. 139° (from diethyl ether–hexane), $[\alpha]_D^{23}$ −3.0° (*c* 1, chloroform) {lit.[29] m.p. 137–138.5°, $[\alpha]_D^{24}$ −5.2° (*c* 2, chloroform)}.

*Partial hydrazinolysis of methyl 2,3-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-mannopyranoside* (**32**). — Treatment of[29] **32** (2.88 g, 5.7 mmol) with **2** (1.1 mL, 2.2 mmol) under Condition A for 17 h, and further, with **2** (0.5 mL, 10 mmol) for 14 h, followed by the usual processing, gave, in succession, **32** (0.65 g, 22% recovery), methyl 2-*O*- (**34**) (0.36 g, 16% yield), methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-mannopyranoside (**33**) (0.46 g, 21% yield), and methyl 4,6-*O*-benzylidene-α-*D*-mannopyranoside (0.44 g, 22% yield).

Another experiment, with **32** (0.98 g, 2 mmol) and **2** (0.4 mL, 8 mmol) under Condition B for 48 h, gave **32** (0.41 g, 41% recovery), **34** (0.2 g, 25% yield), and **33** (0.24 g, 32% yield).

Compound **34** was identified as its 3-*p*-toluenesulfonate, which had m.p. 188–189° (from ethyl acetate–hexane), $[\alpha]_D^{23}$ −31° (*c* 1, chloroform) {lit.[29] m.p. 187–188°, $[\alpha]_D^{25}$ −34° (*c* 0.5, chloroform)}.

Compound **33** had m.p. 131–132° (from hexanol), $[\alpha]_D^{23}$ −26° (*c* 1, chloroform) {lit.[29] m.p. 131–132°, $[\alpha]_D^{25}$ −24° (*c* 1.3, chloroform)}.

*Partial hydrazinolysis of 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-galactopyranoside* (**47**). — Treatment of **47**[30] (0.98 g, 2 mmol) with **2** (0.4 mL, 8 mmol) under Condition B for 18 h, followed by the usual processing, gave, in succession, **47** (0.10 g, 10% recovery), methyl 2-*O*- (**49**) (0.17 g, 22% yield), and methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-galactopyranoside (**48**) (0.39 g, 51% yield).

Compound **48** had m.p. 138–139° (from diethyl ether–hexane), $[\alpha]_D^{23}$ +230° (*c* 1, chloroform) {lit.[30] m.p. 137–138°, $[\alpha]_D^{19}$ +235.7 ±2°}.

Compound **49** had m.p. 200–201° (from chloroform–diethyl ether), $[\alpha]_D^{23}$ +143° (*c* 1, chloroform) {lit.[30] m.p. 202–204°, $[\alpha]_D^{19}$ +145.8 ±1.7°}.

*Partial hydrazinolysis of methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**35**). — Treatment of **35**[13] (2.45 g, 5 mmol) with **2** (1 mL, 20 mmol) under Condition A for 7 h, followed by the usual processing, gave, in succession, **35** (0.7 g, 27% recovery), methyl 2-*O*- (**37**) (0.38 g, 20% yield), methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside (**36**) (0.18 g, 10% yield), and methyl 4,6-*O*-benzylidene-β-*D*-glucopyranoside (0.38 g, 27% yield).

Repetition of the reaction, with **35** (0.98 g, 2 mmol) and **2** (0.4 mL, 8 mmol)

for 120 h, afforded, in succession, **35** (0.29 g, 29% yield), **37** (0.08 g, 10% yield), **36** (0.06 g, 8% yield), and methyl 4,6-*O*-benzylidene-β-D-glucopyranoside as a mixture (0.41 g) with the hydrazine derivative.

Compound **36** had m.p. 177–178° (from diethyl ether–cyclohexane), $[\alpha]_D^{23}$ −102.3° (*c* 1, chloroform) {lit.[31] m.p. 177–178°, $[\alpha]_D^{20}$ −107° (*c* 1, chloroform)}.

Compound **37** had m.p. 196–197° (from diethyl ether), $[\alpha]_D^{23}$ −37.7° (*c* 1, chloroform) {lit.[31] m.p. 195–196°, $[\alpha]_D^{20}$ −34° (*c* 0.5, chloroform)}.

Compound **37** had m.p. 207°, and showed no depression in m.p. on admixture with an authentic sample[15].

*Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-*D*-mannopyranoside* (**38**). — Methyl 4,6-*O*-benzylidene-β-D-mannopyranoside[32] (1.65 g, 5 mmol) was dissolved in anhydrous pyridine (20 mL), and benzoyl chloride (5 mL) was added, dropwise, with stirring and ice-cooling; stirring was continued overnight at room temperature, the mixture was treated as usual, and chromatographic purification of the product on a column of silica gel gave **38** (2.5 g, 90% yield) as a colorless syrup, $[\alpha]_D^{23}$ −57.9° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*): δ 3.53 (s, 3 H, OC$H_3$), 3.70–4.60 (m, 4 H, *H*-4,5,6,6'), 4.73 (d, 1 H, $J_{1,2}$ ~1 Hz, *H*-1), 5.52 (dd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 8.5 Hz, *H*-3), 5.60 (s, 1 H, C*H*-Ph), 5.93 (dd, 1 H, *H*-2), and 7.20–7.60 and 7.60–8.10 (m, 15 H, 3 $C_6H_5$).

*Anal.* Calc. for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.57; H, 5.36.

*Partial hydrazinolysis of* **38**. — Treatment of **38** (0.49 g, 1 mmol) with **2** (0.2 mL, 4 mmol) under Condition B for 120 h, followed by the usual processing, gave **38** (0.05 g, 10% recovery), methyl 3-*O*- (**39**) and methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranoside (**40**) as a mixture (0.1 g, 27% yield; **39**:**40** = 21:4, calculated through the $^1$H-n.m.r. area-ratio of their 1-*O*-$CH_3$ signals). The mixture of **39** and **40** had $^1$H-n.m.r. (acetone-$d_6$–$Me_4Si$): δ 3.43 (s, 3 H, OC$H_3$ of **40**), 3.50 (s, 3 H, OC$H_3$ of **39**), 4.71 (d, 1 H, $J_{1,2}$ 0.5 Hz, *H*-1 of **39**), 4.78 (d, 1 H, $J_{1,2}$ 0.5 Hz, *H*-1 of **40**), and 5.23 (dd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 10.0 Hz, *H*-3 of **39**).

*Anal.* Calc. for $C_{21}H_{22}O_7$: C, 65.27; H, 5.74. Found: C, 65.48; H, 5.74.

*Partial hydrazinolysis of methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-*D*-glucopyranoside* (**41**). — Treatment of **41**[33] (1.83 g, 5 mmol) with **2** (0.4 mL, 8.2 mmol) under Condition C, followed by the usual processing, gave, in succession, **41** (0.15 g, 8% recovery), methyl 3-*O*- (**42**) (0.36 g, 22% yield), methyl 2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**43**) (0.33 g, 20% yield), and **6** (0.60 g, 42% yield).

Compound **42** had m.p. 178–179° (from diethyl ether), $[\alpha]_D^{23}$ +113.7° (*c* 1, chloroform) {lit.[34] m.p. 174°, $[\alpha]_D^{14}$ +110° (chloroform)}.

Compound **43** had m.p. 135–136° (from diethyl ether–cyclohexane), $[\alpha]_D^{23}$ +100.2° (*c* 1, chloroform) {lit.[34] m.p. 133–134°, $[\alpha]_D^{19}$ +112° (*c* 0.86, chloroform)}.

*Partial hydrazinolysis of methyl 4,6-*O*-benzylidene-2,3-di-*O*-(p-nitrobenzoyl)-α-*D*-glucopyranoside* (**44**). — Treatment of **44**[35] (1.45 g, 2.5 mmol) with **2** (0.5 mL, 10 mmol) under Condition C for 5 h, followed by processing as usual, gave, in succession, **44** (0.15 g, 10% recovery), methyl 4,6-*O*-benzylidene-3-*O*- (**45**) (0.67 g, 63% yield), and -2-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranoside (**46**) (0.12 g, 12% yield).

Compound **45** had m.p. 233–235° (from ethanol), $[\alpha]_D^{23}$ +16.7° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*): $\delta$ 2.39 (d, 1 H, $J_{2,2\text{-OH}}$ 11.5 Hz, *H*O-2), 3.52 (s, 3 H, O-C$H_3$), 4.88 (d, 1 H, $J_{1,2}$ 3.5 Hz, *H*-1), 5.51 (s, 1 H, C*H*-Ph), 5.62 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, *H*-3), 7.3 (m, 5 H, $C_6H_5$), and 8.22 (s, 4 H, $C_6H_4$-$NO_2$-*p*).

*Anal.* Calc. for $C_{21}H_{21}NO_9$: C, 58.46; H, 4.91; N, 3.25. Found: C, 58.70; H, 4.99; N, 3.34.

Compound **46** had m.p. 195–197° (from chloroform–cyclohexane), $[\alpha]_D^{23}$ +104.6° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*): $\delta$ 2.78 (br s, 1 H, *H*O-3), 3.41 (s, 3 H, OC$H_3$), 5.07 (m, 2 H, *H*-1,2), 5.57 (s, 1 H, C*H*-Ph), 7.4 (m, 5 H, $C_6H_5$), and 8.22 (s, 4 H, $C_6H_4NO_2$-*p*).

*Anal.* Calc. for $C_{21}H_{21}NO_9$: C, 58.46; H, 4.91; N, 3.25. Found: C, 58.70; H, 4.94; N, 3.34.

*Methyl 2,3,4,6-tetra*-O-*benzoyl*-α-D-*allopyranoside* (**50**). — A solution of methyl α-D-allopyranoside[36] (0.98 g, 5 mmol) in 1:2 pyridine–chloroform (30 mL) was treated with benzoyl chloride (5 mL), added dropwise under ice-cooling, with stirring, and the mixture was stirred overnight at room temperature, poured into ice–water, and stirred for 3 h. The mixture was extracted with chloroform (30 mL × 3), and the extracts were combined, washed successively with M hydrochloric acid, aqueous sodium hydrogencarbonate (saturated), and water, dried (anhydrous magnesium sulfate), and evaporated to a syrup which was then chromatographed on a column of silica gel by use of 1:1 benzene–cyclohexane to which acetone was gradually added, 0 → 2% (v/v), to give syrupy **50** (2.84 g, 93% yield); $[\alpha]_D^{23}$ +34.3 (*c* 1, chloroform).

*Anal.* Calc. for $C_{35}H_{30}O_{10}$: C, 70.34; H, 4.86. Found: C, 70.64; H, 4.83.

*Partial hydrazinolysis of* **50**. — After reaction under Condition B, **50** (0.61 g, 1 mmol) was treated with **2** (0.05 mL, 1.1 mmol) for 12 h, and processed as usual, to give **50** (0.05 g, 8% recovery) and methyl 3,4,6-tri-*O*-benzoyl-α-D-allopyranoside (**51**) (0.39 g, 77% yield); syrup, $[\alpha]_D^{23}$ +117° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*; with the EM-390 apparatus): $\delta$ 3.35 (s, 3 H, OC$H_3$), 4.07 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 6.0 Hz, *H*-2), 4.2–4.9 (m, 3 H, *H*-5,6,6′), 4.93 (d, 1 H, *H*-1), 4.42 (dd, 1 H, $J_{3,4}$ 2.5, $J_{4,5}$ 9.0 Hz, *H*-4), 5.9–6.1 (m, 1 H, *H*-3), and 7.15–7.65 and 7.75–8.20 (m, 15 H, 3 OCO$C_6H_5$).

*Anal.* Calc. for $C_{28}H_{26}O_9$: C, 66.39; H, 5.17. Found: C, 66.17; H, 5.11.

*Partial hydrazinolysis of methyl 2,3,4,6-tetra*-O-*benzoyl*-α-D-*altropyranoside* (**52**). — Treatment of[37] **52** (1.22 g, 2 mmol) with **2** (0.1 mL, 2.2 mmol) under Condition B, followed by the usual processing, gave methyl 3,4,6-tri-*O*-benzoyl-α-D-altropyranoside (**53**) (0.77 g, 78% yield) and a mixture of diacylates (0.18 g, 18% yield).

Compound **53** was a syrup, $[\alpha]_D^{23}$ +75° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*; with the EM-390 apparatus): $\delta$ 3.56 (s, 3 H, OC$H_3$), 4.28 (dd, 1 H, $J_{1,2}$ ~1.5, $J_{2,3}$ 3.0 Hz, *H*-2), 4.5–5.0 (m, 3 H, *H*-5,6,6′), 4.93 (br s, 1 H, *H*-1), 5.70–5.95 (m, 2 H, *H*-3,4), and 7.20–7.70 and 7.85–8.20 (m, 15 H, 3 OCO$C_6H_5$).

*Anal.* Calc. for $C_{28}H_{26}O_9$: C, 66.39; H, 5.17. Found: C, 66.17; H, 5.11.

*Partial hydrazinolysis of methyl 2,3,4,6-tetra*-O-*benzoyl*-α-D-*glucopyranoside*

(**54**). — Treatment of **54**[38] (6.10 g, 10 mmol) with **2** (2 mL, 40 mmol) for 9 h, followed by the usual processing, gave, in succession, **54** (0.93 g, 15% recovery), methyl 3,4,6-tri-*O*-benzoyl-α-D-glucopyranoside (**55**) containing a small amount of its 2,4,6-isomer (based on $^{13}$C-n.m.r. spectroscopy) (3.25 g, 65% yield), methyl 3,6-di-*O*- (**56**) (0.15 g, 4% yield), and methyl 4,6-di-*O*-benzoyl-α-D-glucopyranoside (**57**) (0.55 g, 13% yield). The mixture of the tribenzoates was dissolved in pyridine (20 mL), and treated with *p*-toluenesulfonyl chloride (4 g), under stirring, overnight at room temperature. The usual processing, followed by crystallization from methanol, gave methyl 3,4,6-tri-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**58**) (2.72 g, 41% yield).

In another experiment, **54** (2.44 g, 4 mmol) was treated with **2** (0.4 mL, 8 mmol) under Condition B for 16 h, followed by the usual processing, to afford, in succession, **54** (0.35 g, 14% recovery), a mixture of tribenzoates containing **55** (1.44 g, 71% yield), and **57** (0.19 g, 12% yield). The same treatment of the tribenzoate mixture with *p*-toluenesulfonyl chloride (0.5 g) in pyridine (5 mL) gave **58** (0.24 g, 73% yield).

Compound **55** was a syrup; $^1$H-n.m.r. (chloroform-*d*, $D_2O$ added): δ 3.95 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 9.5 Hz, *H*-2), 4.2–4.7 (m, 3 H, *H*-5,6,6′), 4.92 (d, 1 H, *H*-1) 5.56 (t, 1 H, $J_{3,4}$ 9.5 Hz, *H*-4), 5.78 (t, 1 H, *H*-3), and 7.1–7.6 and 7.8–8.2 (m, 15 H, 3 $OCOC_6H_5$).

Compound **56** had m.p. 136–137° (from ethyl acetate), $[\alpha]_D^{23}$ +136.4° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*; $D_2O$ added): δ 4.83 (d, 1 H, $J_{1,2}$ 4.0 Hz, *H*-1), 5.32 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.0 Hz, *H*-3), and 7.2–8.1 (m, 10 H, 2 $OCOC_6H_5$).

*Anal.* Calc. for $C_{21}H_{22}O_8$: C, 62.68; H, 5.51. Found: C, 62.79; H, 5.50.

Compound **57** had m.p. 131–133° (from diethyl ether), $[\alpha]_D^{23}$ +143.4° (*c* 1, chloroform) {lit.[39] m.p. 133–133.5°, $[\alpha]_D^{22}$ +145.7° (*c* 2, chloroform)}.

Compound **58** had m.p. 158–159° (from ethanol), $[\alpha]_D^{23}$ +62° (*c* 1, chloroform) {lit.[40] m.p. 158–159°, $[\alpha]_D^{25}$ +67.2° (*c* 2, chloroform)}; $^1$H-n.m.r. (chloroform-*d*): δ 2.21 (s, 3 H, Ph-C$H_3$), 3.25 (s, 3 H, OC$H_3$), 4.72 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.0 Hz, *H*-2), 5.13 (d, 1 H, *H*-1), 5.52 (t, 1 H, $J_{4,5}$ 9.0 Hz, *H*-4), 6.01 (t, 1 H, $J_{3,4}$ 9.0 Hz, *H*-3), and 6.8–8.1 (m, 19 H, aromatic protons).

*Partial hydrazinolysis of methyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside* (**59**). — Treatment of **59**[41] (1.22 g, 2 mmol) with **2** (0.4 mL, 8 mmol) under Condition B, followed by the usual processing, gave, in succession, **59** (0.10 g, 8% recovery), methyl 3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside (**60**) (0.20 g, 20% yield), a mixture of tribenzoates (0.06 g, 6% yield), and methyl 3,6-di-*O*-benzoyl-α-D-mannopyranoside (**61**) (0.10 g, 13% yield).

Compound **60** was a syrup, $[\alpha]_D^{23}$ +32° (*c* 0.5, chloroform); $^1$H-n.m.r. (chloroform-*d*; $D_2O$ added): δ 3.44 (s, 3 H, OC$H_3$), 4.20–4.73 (m, 4 H, *H*-2,5,6,6′), 4.90 (d, 1 H, $J_{1,2}$ 1.5 Hz, *H*-1), 5.69 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 9.5 Hz, *H*-3), 6.02 (t, 1 H, $J_{4,5}$ 9.5 Hz, *H*-4), and 7.10–7.63 and 7.84–8.30 (m, 15 H, 3 $OCOC_6H_5$).

*Anal.* Calc. for $C_{28}H_{26}O_9$: C, 66.39; H, 5.17. Found: C, 66.26; H, 5.10.

The tribenzoate mixture was composed mainly of the 2,3,6-tribenzoate; $^1$H-n.m.r. (chloroform-*d*): δ 4.48 (s, 3 H, OC$H_3$), 4.05–4.90 (m, 4 H, *H*-4,5,6,6′),

4.92 (d, 1 H, $J_{1,2}$ 1.5 Hz, *H*-1), 5.46 (dd, 1 H, $J_{2,3}$ 3.5 Hz, *H*-2), 5.64 (d, 1 H, $J_{3,4}$ 8.5 Hz, *H*-3), and 7.13–7.63 and 7.80–8.14 (m, 15 H, 3 $OCOC_6H_5$).

Compound **61** had m.p. 134–135° (from diethyl ether–cyclohexane) {lit.[42] m.p. 134–135°}; $^1$H-n.m.r. (chloroform-*d*): $\delta$ 3.49 (s, 3 H, $OCH_3$), 5.34 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8.5 Hz, *H*-3).

*Anal.* Calc. for $C_{21}H_{22}O_8$: C, 62.68; H, 5.51. Found: C, 62.63; H, 5.46.

*Partial hydrazinolysis of methyl 2,3,4,6-tetra-*O*-benzoyl-β-*D*-glucopyranoside* (**62**). — Application of Condition B to the reaction of **62**[41] (0.61 g, 1 mmol) with **2** (0.2 mL, 2 mmol) afforded **62** (0.32 g, 52% recovery) and methyl 4,6-di-*O*-benzoyl-β-D-glucopyranoside (**63**) (0.12 g, 30% yield); m.p. 135–136° (from ethanol), $[\alpha]_D^{23}$ +22° (*c* 1, chloroform) {lit.[42] m.p. 137–138°, $[\alpha]_D^{22}$ +20.7° (*c* 2, chloroform)}.

*Partial hydrazinolysis of methyl 2,3,4-tri-*O*-benzoyl-α-*D*-xylopyranoside* (**64**). — Treatment of **64**[44] (2.38 g, 5 mmol) with **2** (1 mL, 20 mmol) under Condition A for 6 h, followed by the usual processing, afforded, in succession, **64** (0.57 g, 24% recovery), methyl 3,4-di-*O*-benzoyl- (**65**) (0.67 g, 36% yield), and methyl 2,3-di-*O*-benzoyl-α-D-xylopyranoside (**66**) (0.45 g, 24% yield).

Another experiment, under Condition B, with **64** (0.95 g, 2 mmol) and **2** (0.4 mL, 8 mmol) for 24 h, gave, in succession, **64** (0.13 g, 14% recovery), **65** (0.31 g, 41% yield), and **66** (0.22 g, 29% yield).

Compound **65** had m.p. 106–107° (from cyclohexane), $[\alpha]_D^{23}$ +21.7° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*): $\delta$ 2.49 (d, 1 H, $J_{2,2\text{-OH}}$ 11 Hz, *H*O-2), 3.53 (s, 3 H, $OCH_3$), 4.88 (d, 1 H, $J_{1,2}$ 3.5 Hz, *H*-1), 5.32 (dt, 1 H, $J_{3,4} = J_{4,5a} = 9.0$ Hz, $J_{4,5e}$ 4.5 Hz, *H*-4), and 7.2–8.2 (m, 10 H, 2 $OCOC_6H_5$).

*Anal.* Calc. for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.71; H, 5.39.

*Partial hydrazinolysis of methyl 2,3,4,6-tetra-*O*-(p-*nitrobenzoyl*)-α-*D*-glucopyranoside* (**67**). — Treatment of **67**[45] (0.79 g, 1 mmol with **2** (0.2 mL, 4 mmol) for 8 h, followed by the usual processing, afforded **67** (0.07 g, 9% recovery), and methyl 3,4,6-tri-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranoside (**68**) (0.49 g, 77% yield); m.p. 185–187° (from ethanol), $[\alpha]_D^{23}$ +68° (*c* 0.5, chloroform); $^1$H-n.m.r. (chloroform-*d*–methanol-$d_4$): $\delta$ 3.42 (s, 3 H, $OCH_3$), 4.07 (dd, 1 H, $J_{1,2}$ 3.5 Hz, *H*-2), 4.30–4.90 (m, 3 H, *H*-5,6,6'), 5.55 (t, 1 H, $J_{4,5}$ 8.0 Hz, *H*-4), 5.85 (t, 1 H, $J_{3,4}$ 8.0 Hz, *H*-3), 8.05 (s, 4 H, $OCOC_6H_4NO_2$-*p*), 8.09 (s, 4 H, $OCOC_6H_4NO_2$-*p*), and 8.15 (s, 4 H, $OCOC_6H_4NO_2$-*p*).

*Anal.* Calc. for $C_{28}H_{23}N_3O_{15}$: C, 52.42; H, 3.61; N, 6.55. Found: C, 52.34; H, 3.55; N, 6.65.

*Methyl 2,3,4,6-tetra-*O*-(p-*nitrobenzoyl*)-α-*D*-mannopyranoside* (**69**). — A solution of methyl α-D-mannopyranoside[46] (0.97 g, 5 mmol) in pyridine (30 mL) was treated with *p*-nitrobenzoyl chloride (1.11 g, 6 mmol) overnight at 0°, with stirring. The mixture was poured into saturated, aqueous sodium hydrogencarbonate solution (100 mL), and the suspension of the crystalline precipitate was stirred for 3 h, and filtered. The material was recrystallized, to give **69** (3.59 g, 91% yield); m.p. 177.5–179° (from ethanol), $[\alpha]_D^{23}$ −118° (*c* 1.1, chloroform).

*Anal.* Calc. for $C_{35}H_{26}N_4O_{18}$: C, 53.17; H, 3.32; N, 7.09. Found: C, 53.52; H, 3.45; N, 6.91.

*Partial hydrazinolysis of* **69**. — Treatment of **69** (0.79 g, 1 mmol) with **2** (0.2 mL, 4 mmol) under Condition C for 24 h, followed by the usual processing, gave, in succession, **69** (0.15 g, 18% recovery), methyl 3,4,6- (**70**) (0.18 g, 28% yield), and methyl 2,4,6-tri-*O*-(*p*-nitrobenzoyl)-α-D-mannopyranoside (**71**) (0.27 g, 42% yield).

Compound **70** had m.p. 172–174° (from acetone), $[\alpha]_D^{23}$ +38.5° (*c* 1.3, chloroform); $^1$H-n.m.r. (acetone-$d_6$): δ 3.54 (s, 3 H, OC$H_3$), 4.43 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.0 Hz, *H*-2), 4.55–4.75 (m, 3 H, *H*-5,6,6′), 4.93 (d, 1 H, *H*-1), 5.65 (dd, 1 H, $J_{3,4}$ 10.0 Hz, *H*-3), 6.08 (t, 1 H, $J_{4,5}$ 10.0 Hz, *H*-4), 8.16 (s, 8 H, 2 OCOC$_6H_4$NO$_2$-*p*), and 8.26 (s, 4 H, OCOC$_6H_4$NO$_2$-*p*).

*Anal.* Calc. for $C_{28}H_{23}N_3O_{15}$: C, 52.42; H, 3.61; N, 6.55. Found: C, 52.39; H, 3.55; N, 6.46.

Compound **71** had m.p. 189–191° (from ethyl acetate), $[\alpha]_D^{23}$ −8.6° (*c* 1.03, chloroform); $^1$H-n.m.r. (acetone-$d_6$): δ 3.58 (s, 3 H, OC$H_3$), 4.3–4.9 (m, 3 H, *H*-5,6,6′), 4.40 (dd, 1 H, $J_{2,3}$ 4.0, $J_{3,4}$ 10.0 Hz, *H*-3), 5.03 (d, 1 H, $J_{1,2}$ 1.5 Hz, *H*-1), 5.48 (dd, 1 H, *H*-2), 5.81 (t, 1 H, $J_{4,5}$ 10.0 Hz, *H*-4), 8.22 (s, 4 H, OCOC$_6H_4$NO$_2$-*p*), 8.26 (s, 4 H, OCOC$_6H_4$NO$_2$-*p*), and 8.28 (s, 4 H, OCOC$_6H_4$NO$_2$-*p*).

*Anal.* Calc. for $C_{28}H_{23}N_3O_{15}$: C, 52.42; H, 3.61; N, 6.55. Found: C, 52.44; H, 3.52; N, 6.82.

*Methyl 2,3,4,6-tetra*-O-(p-*nitrobenzoyl*)-β-D-*glucopyranoside* (**72**). — The same treatment of methyl β-D-glucopyranoside[47] (0.97 g, 5 mmol) as described for the preparation of **69** afforded **72** (3.82 g, 97% yield); m.p. 226–228° (from ethanol), $[\alpha]_D^{23}$ −101° (*c* 1.48, chloroform).

*Anal.* Calc. for $C_{35}H_{26}N_4O_{18}$: C, 53.17; H, 3.32; N, 7.09. Found: C, 53.44; H, 3.26; N, 7.17.

*Partial hydrazinolysis of* **72**. — Treatment of **72** (1.58 g, 2 mmol) with **2** (0.4 mL, 8 mmol) under Condition C for 16 h, followed by the usual processing, gave **72** (0.08 g, 5% recovery) and methyl 3,4,6-tri-*O*-(*p*-nitrobenzoyl)-β-D-glucopyranoside (**73**) (0.66 g, 51% yield); m.p. 201–204° (from acetone–isopropyl ether), $[\alpha]_D^{23}$ −35° (*c* 1.07, chloroform); $^1$H-n.m.r. (acetone-$d_6$): δ 3.55 (s, 3 H, OC$H_3$), 3.84 (t, 1 H, $J_{1,2} = J_{2,3}$ = 8.0 Hz, *H*-2), 4.25–4.77 (m, 3 H, *H*-5,6,6′), 4.70 (d, 1 H, *H*-1), 5.54 (t, 1 H, $J_{4,5}$ 8.0 Hz, *H*-4), 6.73 (t, 1 H, *H*-3), 8.10 (s, 4 H, OCOC$_6H_4$NO$_2$-*p*), 8.14 (s, 4 H, OCOC$_6H_4$NO$_2$-*p*), and 8.17 (s, 4 H, OCOC$_6H_4$NO$_2$-*p*).

*Anal.* Calc. for $C_{28}H_{23}N_3O_{15}$: C, 52.42; H, 3.61; N, 6.55. Found: C, 52.77; H, 3.57; N, 6.32.

p-*Nitrophenyl 2,3,4,6-tetra*-O-*benzoyl*-α-D-*glucopyranoside* (**74**). — A solution of *p*-nitrophenyl α-D-glucopyranoside[48] (1.51 g, 5 mmol) in pyridine (20 mmol) was treated with benzoyl chloride (5 mL) in the usual way, and the resulting, crystalline mass was recrystallized, to give **74** (3.02 g, 84% yield); m.p. 142–143.5° (from ethanol), $[\alpha]_D^{23}$ +57.6° (*c* 1.65, chloroform).

*Anal.* Calc. for $C_{40}H_{31}NO_{12}$: C, 66.94; H, 4.35; N, 1.95. Found: C, 67.21; H, 4.40; N, 1.99.

*Partial hydrazinolysis of* **74**. — Treatment of **74** (0.72 g, 1 mmol) with **2** (0.05 mL, 1.1 mmol) under Condition B for 8 h, followed by the usual processing, gave **74** (0.10 g, 14% recovery) and *p*-nitrophenyl 3,4,6-tri-*O*-benzoyl-α-D-glucopyranoside (**78**) (0.49 g, 79% yield).

Repetition of the reaction under Condition C, using 1:19 acetic acid–pyridine as the solvent system, for 48 h, followed by the usual processing, gave **74** (0.06 g, 9% recovery) and **78** (0.51 g, 82% yield); m.p. 202–205° (from ethanol), $[\alpha]_D^{23}$ +90.1° (*c* 0.75, chloroform); $^1$H-n.m.r. (acetone-$d_6$): δ 4.35–5.00 (m, 4 H, *H*-2,5,6,6′), 5.72 (d, 1 H, $J_{1,2}$ 1.0 Hz, *H*-1), 5.95 (dd, 1 H, $J_{3,4}$ 9.5, $J_{4,5}$ 7.0 Hz, *H*-4), 6.13 (t, 1 H, $J_{2,3}$ 9.5 Hz, *H*-3), and 7.0–8.3 (m, 19 H, aromatic protons).

*Anal.* Calc. for $C_{33}H_{27}NO_{11}$: C, 64.60; H, 4.44; N, 2.28. Found: C, 64.61; H, 4.44; N, 2.12.

p-*Nitrophenyl 2,3,4,6-tetra*-O-*benzoyl-β-*D-*glucopyranoside* (**75**). — A solution of *p*-nitrophenyl β-D-glucopyranoside[48] (1.51 g, 5 mmol) in pyridine (20 mL) was treated with benzoyl chloride (5 mL) at 0°, and processed as usual; the product crystallized, to give **75** (3.0 g, 83% yield); m.p. 153.5–154.5° (from ethanol), $[\alpha]_D^{23}$ +18.7° (*c* 1.2, chloroform).

*Anal.* Calc. for $C_{40}H_{31}NO_{12}$: C, 66.94; H, 4.34; N, 1.95. Found: C, 67.21; H, 4.40; N, 1.99.

*Partial hydrazinolysis of* **75**. — Treatment of **75** (1.44 g, 2 mmol) with **2** (0.1 mL, 1.1 mmol) under Condition B, followed by the usual processing, gave **75** (0.46 g, 32% recovery) and *p*-nitrophenyl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside (**79**) (0.45 g, 37% yield), in addition to a third fraction composed of a mixture of unidentified dibenzoates (0.22 g, 22% yield).

Repetition under Condition C, with **75** (0.72 g, 1 mmol) and **2** (0.2 mL, 4 mmol) for 4 days, followed by the usual processing, gave **75** (0.2 g, 29% recovery) and **79** (0.40 g, 66% yield); m.p. 159–161° (from ethanol), $[\alpha]_D^{23}$ −25.8° (*c* 1.32, chloroform); $^1$H-n.m.r. (chloroform-*d*): δ 4.33 (t, 1 H, $J_{1,2} = J_{2,3} = 8.0$ Hz, *H*-2), 4.55–4.95 (m, 3 H, *H*-5,6,6′), 5.73 (d, 1 H, *H*-1), 5.82 (t, 1 H, $J_{3,4} = J_{4,5} = 8.0$ Hz, *H*-4), 6.00 (t, 1 H, *H*-3), and 7.20–7.75 and 7.80–8.30 (m, 19 H, aromatic protons).

*Anal.* Calc. for $C_{33}H_{27}NO_{11}$: C, 64.60; H, 4.44; N, 2.28. Found: C, 64.64; H, 4.50; N, 2.09.

*Partial hydrazinolysis of 7-(2,3,4,6-tetra*-O-*benzoyl-β-*D-*glucopyranosyl)theophylline* (**76**). — Treatment of **76**[49] (1.52 g, 2 mmol) with **2** (0.2 mL, 4 mmol) under Condition B for 12 h, followed by the usual processing, afforded, in succession, **76** (0.26 g, 17% recovery), 7-(3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl)theophylline (**80**) (0.65 g, 49% yield), and 7-(4,6-di-*O*-benzoyl-β-D-glucopyranosyl)theophylline (**83**) (0.32 g, 29% yield).

Repetition under Condition C, with **76** (1.52 g, 2 mmol) and **2** (0.4 mL, 8 mmol) in 1:19 acetic acid–pyridine for 4 days, followed by the usual processing, gave, in succession, **76** (0.75 g, 49% recovery) and **80** (0.39 g, 29% yield).

Compound **80** was an amorphous powder, $[\alpha]_D^{23}$ +22° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*): δ 3.24 (s, 3 H, N-C$H_3$), 3.44 (s, 3 H, N-C$H_3$), 4.2–4.8

(m, 4 H, *H*-2',5',6',6''), 5.70–6.00 (m, 2 H, *H*-3',4'), 6.22 (d, 1 H, $J_{1',2'}$ 9.0 Hz, *H*-1'), and 7.10–7.55 and 7.60–8.13 (m, 16 H, 3 $OCOC_6H_5$ and *H*-8); on irradiation at $\delta$ 4.67, the doublet at $\delta$ 6.22 changed to a singlet.

*Anal.* Calc. for $C_{34}H_{30}N_4O_{10}$: C, 62.38; H, 4.62; N, 8.55. Found: C, 62.07; H, 4.86; N, 8.48.

Compound **83** had m.p. 152–153° (from ethanol), $[\alpha]_D^{23}$ +12° (*c* 0.5, chloroform); $^1$H-n.m.r. (chloroform-*d*): $\delta$ 3.34 (s, 3 H, N-C$H_3$), 3.60 (s, 3 H, N-C$H_3$), 4.15–4.60 (m, 5 H, *H*-2',3',5',6',6''), 5.46 (t, 1 H, $J_{3',4'} = J_{4',5'} = 8.5$ Hz, *H*-4'), 5.92 (d, 1 H, $J_{1',2'}$ 9.0 Hz, *H*-1'), and 7.35–7.70 and 7.90–8.35 (m, 11 H, 2 $OCOC_6H_5$ and *H*-8); on irradiation at $\delta$ 4.53, the doublet at $\delta$ 5.92 and the triplet at $\delta$ 5.46 changed to a singlet and a doublet, respectively.

*Anal.* Calc. for $C_{27}H_{26}N_4O_9$: C, 58.91; H, 4.76; N, 10.18. Found: C, 58.65; H, 4.90; N, 10.33.

*1,5-Anhydro-2,3,4,6-tetra*-O-*benzoyl*-D-*glucitol* (**77**). — A solution of 1,5-anhydro-D-glucitol[50] (0.82 g, 5 mmol) in pyridine (20 mL) was treated with benzoyl chloride (5 mL), and processed as usual, and the resulting syrup was chromatographed on a column of silica gel by use of 1 : 1 benzene–cyclohexane with a gradient increase of the content of acetone from 0 to 2%, to give syrupy **77** (2.64 g, 91% yield); $[\alpha]_D^{23}$ +30.1° (*c* 1.05, chloroform); $^1$H-n.m.r. (chloroform-*d*): $\delta$ 3.65 (t, 1 H, $J_{1a,1e} = J_{1a,2} = 10.0$ Hz, *H*-1*a*), 4.10 (dd, 1 H, $J_{1e,2}$ 7.5 Hz, *H*-1*e*), 4.30–4.70 (m, 3 H, *H*-5,6,6'), 5.48 (t, 1 H, $J_{2,3}$ 10.0 Hz, *H*-2), 5.69 (t, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, *H*-4), 6.00 (t, 1 H, *H*-3), and 7.20–7.65 and 7.80–8.30 (m, 20 H, 4 $OCOC_6H_5$).

*Anal.* Calc. for $C_{34}H_{28}O_9$: C, 68.84; H, 4.95. Found: C, 68.72; H, 5.03.

*Partial hydrazinolysis of* **77**. — Treatment of **77** (0.90 g, 1.5 mmol) with **2** (0.3 mL, 6 mmol) under Condition B for 4 days, followed by the usual processing, gave, in succession, **77** (0.32 g, 36% recovery), 1,5-anhydro-3,4,6-tri-*O*-benzoyl-D-glucitol (**81**) (0.30 g, 41% yield), and 1,5-anhydro-2,4,6-tri-*O*-benzoyl-D-glucitol (**82**) (0.13 g, 18% yield).

Repetition under Condition B, with **77** (2.0 g, 3.3 mmol) and **2** (0.66 mL, 1.32 mmol) for 2 days, followed by the usual processing, gave, in succession, **77** (1.24 g, 62% recovery), **81** (0.27 g, 16% yield), and **82** (0.15 g, 9% yield).

Compound **81** had m.p. 145–146° (from chloroform–methanol), $[\alpha]_D^{23}$ −7.0° (*c* 1, chloroform); $^1$H-n.m.r. (chloroform-*d*): $\delta$ 3.50 (t, 1 H, $J_{1a,1e} = J_{1a,2} = 10.5$ Hz, *H*-1*a*), 3.60–4.80 (m, 5 H, *H*-1*e*,2,5,6,6'), 5.30–5.65 (m, 2 H, *H*-3,4), and 7.10–8.20 (m, 15 H, 3 $OCOC_6H_5$).

*Anal.* Calc. for $C_{27}H_{24}O_8$: C, 68.06; H, 5.08. Found: C, 67.82; H, 5.00.

Compound **82** was a syrup, $[\alpha]_D^{23}$ +9.2° (*c* 0.5, chloroform); $^1$H-n.m.r. (chloroform-*d*): $\delta$ 3.30–5.00 (m, 6 H, *H*-1*a*,1*e*,3,5,6,6'), 5.42 (dt, 1 H, $J_{1a,2} = J_{2,3} = 9.0$ Hz, $J_{1e,2}$ 5.0 Hz, *H*-2), 5.64 (t, 1 H, $J_{3,4} = J_{4,5} = 8.5$ Hz, *H*-4), and 7.10–8.25 (m, 15 H, 3 $OCOC_6H_5$).

*Anal.* Calc. for $C_{27}H_{24}O_8$: C, 68.06; H, 5.08. Found: C, 68.29; H, 5.25.

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