Pyranose Benzoates. An Additivity Relation in the Amplitudes of Exciton-Split CD Curves[1]

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Abstract: The circular dichroism (CD) curves of over 40 bis-, tris-, and tetrakis(*p*-bromobenzoates) of various methyl pyranosides have been measured. This has led to the finding that an additivity relation exists in the amplitudes of the sigmoid-shaped CD curves characteristic of coupled oscillators. Namely, the CD amplitudes of the various classes of bis(benzoate) units shown in Tables I and II only reflect the spatial disposition of the interacting chromophores and are independent of the nonchromophoric substituents; they can thus be regarded as constants representative of the interacting bis(benzoate) moieties. The CD amplitude of a tris(benzoate) can then be approximated by the sum of three component bis(benzoate) amplitudes; similarly, the amplitude of a tetrakis(benzoate) can be approximated by adding the amplitudes of the six component bis(benzoate) units (Table III, Figure 4). This additivity relation, in addition to the large amplitudes of the coupled CD, forms the basis of a micromethod for determining the oligosaccharide structures; it should also greatly simplify the CD analysis of natural products containing multiple chromophores.

When two or more chromophores which absorb strongly around the same wavelength are located nearby in space, the system will exhibit a Davydov-split[2] circular dichroism (CD) curve with extrema of opposite signs centered around its absorption maximum; if the chirality of the spatially interacting electric transition moments is positive, the signs of the longer (first) and shorter (second) Cotton effects will be positive and negative, respectively (and vice versa). In the hypothetical cyclohexylbis(*p*-bromobenzoates) shown in Figure 1, the electric transition moments of the ^1L_a bands (244 nm, ϵ ca. 19 500) are always approximately parallel to the C_{aliph}–O bond despite the rotational mobility of the ester bond, and hence, the transition moments of the two benzoate groups as well as the C(1)–O/C(2)–O bonds constitute a counterclockwise or negative chirality. The dibenzoate shown in Figure 1 will thus exhibit a split CD curve centered at 244 nm with negative first and positive second Cotton effects (Figure 2b), the sign of the first Cotton effect reflecting the twist of the transition moments or the two C–O linkages. This splitting is accounted for by the so-called coupled oscillator theory,[3,4] which provides the basis for the only general method other than the X-ray Bijvoet method for determination of the absolute configuration or conformation of molecules in a nonempirical manner. It was first applied to the natural products calycanthine[4a] and argemonine[4b] by Mason and co-workers.

The exciton chirality method,[5] which is based on the coupled oscillator theory,[6] and which is an extension of the dibenzoate chirality method[7] (Figure 1), was developed as a practical tool for determination of the absolute configurations of complex natural products.[8] It has been applied to many types of compounds[5a,d] including terpenoids,[9a] alkaloids,[9b] antibiotics,[9c] sugars,[9d] and arene oxide adducts with nucleic acids.[9e,f,10] We had noted earlier that in molecules containing three interacting chromophores,[11] the amplitudes ("*A* values") of split CD curves, i.e., the difference in $\Delta\epsilon$ of split extrema (Figure 2), are greatly augmented if the chiralities between the chromophores are all of identical signs;[9d,12] in contrast, when opposing chiralities are present, the coupled interactions cancel out and give rise to a noncharacteristic unsplit CD curve.[9d]

Frequently, the $\Delta\epsilon$ intensities of the two split Cotton effects are uneven, the second Cotton effect band having a broader half-bandwidth.[5b,d] A more accurate representation of the "amplitudes" of split CD curves would have been to measure the areas of positive and negative Cotton effects. However, the following discussions are based on *A* values, because they are readily measurable from CD charts plotted against $\Delta\epsilon$ values, whereas this is not the case for the integrated areas. Several aspects of practical significance have been deduced from our past studies on dibenzoates: (i) a linear relation exists between the *A* values of para-substituted benzoates and the UV ϵ values;[13] (ii) the *A* value is inversely proportional to the square of the interchromophoric distance, provided other factors remain the same;[5b] and (iii) in vicinal dibenzoates, the sign of split CD curves is unchanged from 0° to 180°, the largest *A* value being encountered around a dihedral angle of. ca. 70°.[5b]

During the course of a systematic re-investigation of over 40 pyranose benzoates, a study which was initiated to develop a micromethod for determining the glycosidic linkages of oligosaccharides without reference to authentic methylated methyl glycosides,[14] we have found the existence of an interesting ad-

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(13) Reference 11, Figure 2.

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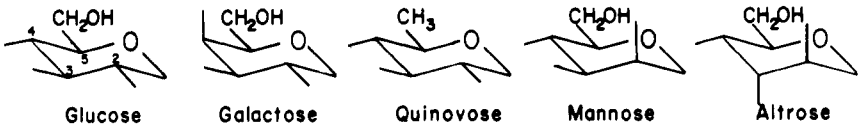
Table I. CD Data of Methyl D-Pyranoside *p*-Bromobenzoates, in MeOH



class	entry	compound	236 nm/ 253 nm[b]	A- (obsd)[c]	class	entry	compound	236 nm/ 253 nm[b]	A- (obsd)[c]
I	1	α-Glu-2(e),3(e)-[a]	−19/+41	+60	III	16	α-Glu-3,6-di-OAc-2(e),4(e)-	+2/−4	−6
	2	α-Glu-4,6-*O*-Bnzd-2(e),3(e)-[d]	−26/+42	+68		17	α-Glu-3-OMe-2(e),4(e)-	0/−1	−1
	3	α-Gal-2(e),3(e)-	−17/+49	+66	IV	18	α-Man-3,6-di-OAc-2(a),4(e)-	+1/−13	−14
	4	α-Gal-4,6-*O*-Bnzd-2(e),3(e)-	−14/+50	+64		19	β-Gal-3,6-di-OAc-2(e),4(a)-	0/+18	+18
	5	α-Gal-6-*O*-TBDMS-2(e),3(e)-[e]	−19/+41	+60	V	20	α-Glu-2,3-di-OMe-4(e),6-	−4/+11	+15
	6	α-Gal-4-OAc-6-*O*-TBDMS-2(e),3(e)-	−20/+46	+66		21	α-Man-3(e),6-	−4/+7	+11
	7	α-Gal-6-OAc-2(e),3(e)-	−19/+44	+63		22	α-Glu-2(e),6-	+1/−6	−7
	8	α-Qui-2(e),3(e)-	−16/+40	+56		23	α-Man-2(a),6-	−2/+8	+10
	9	β-Qui-2(e),3(e)-	−16/+40	+56	VI	24	α-Gal-2,3-di-OMe-4(a),6-	+4/−11	−15
	10	α-Glu-2,6-di-OAc-3(e),4(e)-	+17/−42	−59		25	β-Gal-3(e),6-	+2/−7	−9
	11	α-Man-2,6-di-OAc-3(e),4(e)-	+17/−40	−57		26	β-Gal-2(e),6-	+2/−2	−4
	12	α-Gal-2,6-di-OMe-3(e),4(a)-	−16/+48	+64					
	13	α-Gal-3(e),4(a)-	−14/+50	+64					
II	14	α-Alt-2(a),3(a)-	0/−6	−6					
	15	α-Alt-4,6-*O*-Bnzd-2(a),3(a)-	+1/−4	−5					

[a] Substitution and configuration of *p*-bromobenzoate groups. [b] The $\Delta\epsilon$ values of split Cotton effect extrema at 236 ± 1 nm/253 ± 1 nm. Sample concentrations were estimated from the following standard UV ϵ values: 38 200, 57 200, and 76 400 for bis-, tris-, and tetrakis(*p*-bromobenzoates), respectively. [c] Amplitudes of split CD curves; the sign is that of the first (or longer) Cotton effect (Figure 2). [d] Bnzd = benzylidene. [e] TBDMS = *tert*-butyldimethylsilyl.

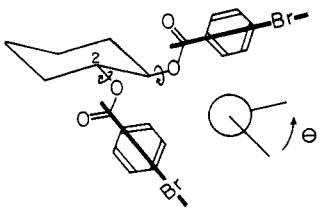


Figure 1. A hypothetical 1(e),2(e)-bis(*p*-bromobenzoate). The bold lines indicate direction of electric transition moments, which give rise to the UV maximum around 244 nm (^1L_a band). The chirality of the depicted dibenzoate system is counterclockwise or negative. Curved arrows denote rotational mobility.

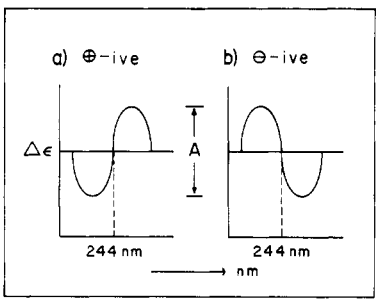


Figure 2. Split Cotton effects centered at 244 nm due to two or more chirally interacting *p*-bromobenzoates. (a) A positively split CD. (b) A negatively split CD.

ditivity relation in the *A* values of split CD curves of compounds containing three or more interacting chromophores. Thus, *in the case of a molecule with three interacting chromophores A, B, and C, the amplitude of the split CD can be approximated by the summation of component amplitudes A/B, B/C, and C/A.* We have found that this relationship holds also for hexopyranose tetrakis(benzoates) which now have six component interactions. The data leading to this conclusion are presented in the following.

The *p*-bromobenzoates were used for the present studies because of the relatively facile preparation and strong UV absorptions (and hence large *A* values). The specific benzoylations were carried out on the methyl glycosides (mostly α), the hydroxyl groups of which had been appropriately blocked or derivatized as acetonides, benzylidenes, acetates, methyl ethers, *tert*-butyldimethylsilyl ethers, etc. However, since the selectivity among the sugar hydroxyl groups is not high, the preparation of specific benzoates frequently

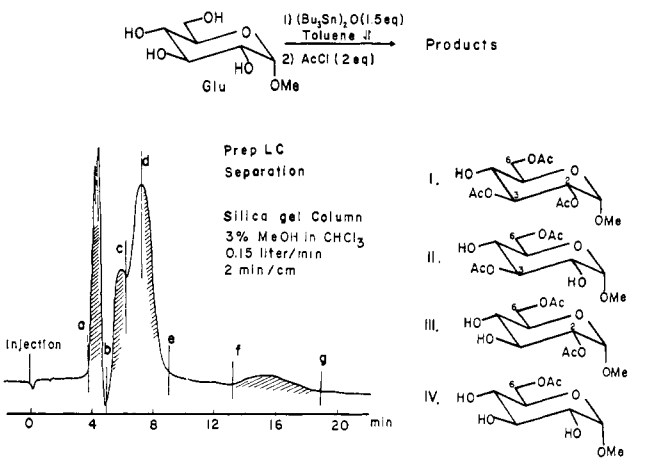


Figure 3. Preparation and prep LC separation of methyl glucoside partial acetates. Shaded fractions a–b, b–c, d–e, and f–g yielded acetates I, II, III, and IV, respectively.

required repeated protection–deprotection steps[15] as well as tedious separations. For example, the conversion of galactose into methyl 3,4-bis(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (**13**) (Table I) required the multistep procedure shown in Scheme I (see Experimental Section); perbenzoylation and debenzylation of intermediate **c** yielded the 2,3,4-tris(benzoate) (**29**) (Table III) in addition. Benzoylations were carried out by reacting with *p*-bromobenzoyl chloride and pyridine at 60 °C overnight. The *p*-bromobenzoate chromophore was occasionally found to be labile to normal catalytic hydrogenolysis conditions employed for removal of *O*-benzyl groups (H_2, 10% Pd–C) as was the case shown for **g** (Scheme I). Under such circumstances debenzylation was carried out by catalytic transfer hydrogenation[16,17] with palladium as catalyst and cyclohexadiene[18] as hydrogen donor.

An alternative method for preparing various benzoates was to obtain a mixture of various derivatized glycosides in one reaction

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(17) Rao, V. S.; Perlin, A. S. *Carbohydr. Res.* **1980**, *83*, 175.
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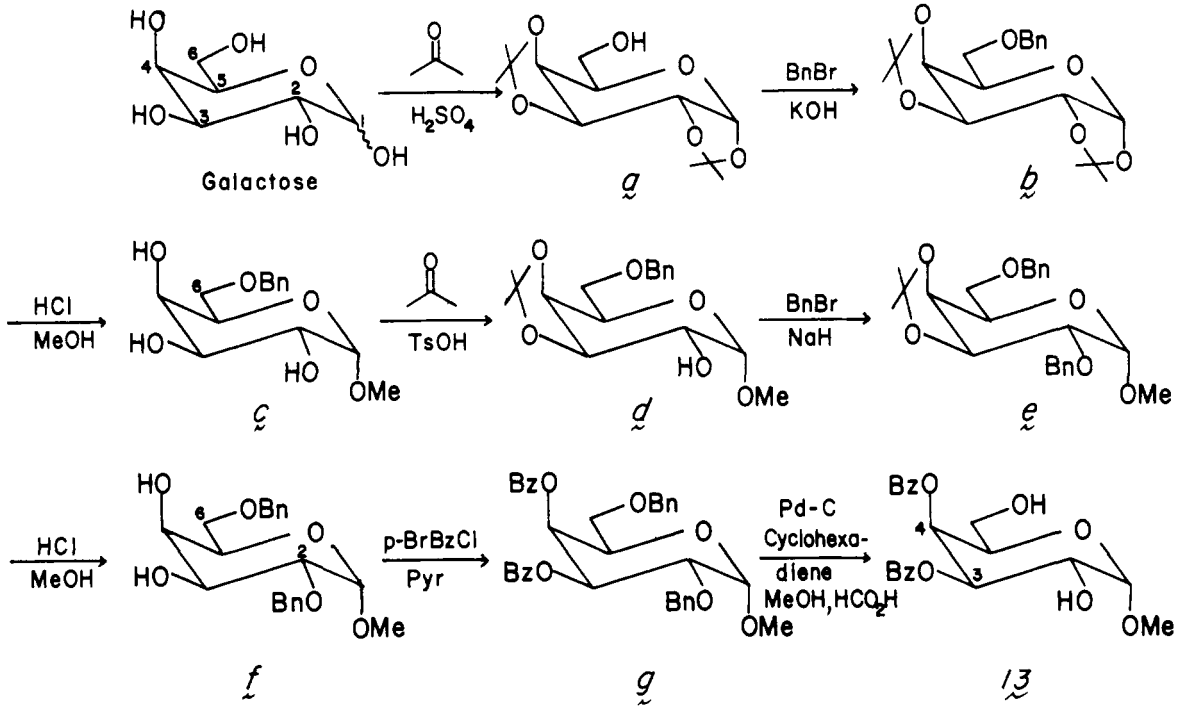
Scheme I. Preparation of Methyl 3,4-Bis(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (**13**) (and Methyl 2,3,4-Tris(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (**29**) from Intermediate C)



(Figure 3). This was performed by enhancing the nucleophilicity of specific oxygen atoms by treating the glycosides with bis(tributylstannyl) oxide with continuous removal of water;[19,20] evaporation of the solvent gave partially stannylated products which were then acetylated[19] or alkylated.[20] This usually gave one major acetate accompanied by several other minor acetates. For example, methyl α-D-glucopyranoside (Figure 3) gave methyl 2,3,6-tri-O-acetyl-α-D-glucopyranoside, methyl 3,6-di-*O*-acetyl-α-D-glucopyranoside, methyl 2,6-di-*O*-acetyl-α-D-glucopyranoside, and methyl 6-*O*-acetyl-α-D-glucopyranoside in 15%, 10%, 70%, and 5% yield, respectively. These partially acetylated compounds were separated by high-performance liquid chromatography (HPLC) or preparative LC, normal phase silica gel column, 3% MeOH in $CHCl_3$, and then benzoylated by treating them with *p*-bromobenzoyl chloride in pyridine at 60 °C overnight. The partial acetates in Figure 3 yielded methyl 3,6-di-*O*-acetyl-2,4-bis(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (**16**) and methyl 2,6-di-*O*-acetyl-3,4-bis(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (**10**) upon benzoylation.

All benzoates were fully characterized by CI-MS (CH_4 carrier gas) and ^1H NMR. Several milligrams of benzoates were made in all cases except for entries 7, 8, 9, 14, and 35 (Tables I and III), where the quantities were less than 1 mg. Measurements of 3-4 samples of respective benzoates led to the following standard UV ε values: mono(*p*-bromobenzoate) ε 19 500; bis(*p*-bromobenzoate) ε 38 200; tris(*p*-bromobenzoate) ε 57 200; and tetrakis(*p*-bromobenzoate) ε 76 400. These standard ε values were then used for deriving the concentrations of the solutions submitted to UV and CD measurements. Moreover, the large amplitudes of the CD curves enable one to deal with only microgram quantities of the sample.

The data for six classes of bis(*p*-bromobenzoates) are listed in Table I and summarized in Table II.

Class I: 1,2 ee and 1,2 ea, *A* = 62. The *A* values for 1,2-ee (Table I, entries 1–11; Table II, units **1**, **2**) and 1,2-ea (Table I, entries 12, 13; Table II, unit **3**) dibenzoates are ca. 62, or from 56 to 68. This spread could be due to any one of the following subtle factors: (i) the pyranose ring is distorted from an idealized chair geometry; (ii) the ^1L_a transition is not precisely polarized along the C_2 rotation axis of the benzoate group; and (iii) the overall direction of the ^1L_a transition is not exactly parallel to the C_{aliph}–O bond due to the existence of preferred conformers around this bond. However, from a practical viewpoint, we may regard the *A* value of 62 as a constant representing the 1,2-ee and 1,2-ea class of vicinal bis(*p*-bromobenzoates).

Class II: 1,2 aa, *A* = 5. If the two C_{aliph}–O bonds had a dihedral angle of 180°, no split CD would have been observed. However, the fact that split CD curves with small amplitudes are observed is not surprising because 1,3-diaxial interactions between the benzoate groups and 1α-OMe, 4β-H, 4β-benzylidene, and 5α-H would tend to bend the two C–O bonds outwards (hence negative chirality between the benzoates in entries 14, 15).

Class III: 1,3 ee, *A* = 0. Theoretically no split CD should result since the two C–O bonds are coplanar. That the experimental values are not zero is attributable to the factors mentioned above. A similar weakly split CD was encountered in 5α-cholestane-3β,7β-bis(*p*-dimethylaminobenzoate).[21]

Class IV: 1,3 ea, *A* = 16. The fact that the *A* value is smaller than that of *vic*-ea bis(benzoates) (*A* = 62) is due to the larger interchromophoric distance in the 1,3-bis(benzoates).

Class V: Bis(benzoates) Involving 6-OBz with 4(e) Substituents. Entries 20, 21, and 23 (or units **8**, **9**, **11**) all have positively split CD curves whereas entry 22 (unit **10**) has a negatively split CD. In all four cases, the C-4 substituent is equatorial, i.e., entry 20 has a 4(e)-benzoate and entries 21–23 have 4(e)-hydroxyl groups. It is thus clear that despite the possibility of rotational freedom of the 6-OBz group, its conformation can be depicted as pointing toward the "right".

Class VI: Bis(benzoates) Involving 6-OBz with 4(a) Substituents. Entry 24 (unit **12**) has a 4(a)-benzoate group and entries 25 and 26 (units **13**, **14**) have 4(a)-hydroxyl groups. The negative *A* values in all three cases indicate that in 4(a)-substituted hexopyranose benzoates, the 6-OBz group has a conformation pointing toward the left. These specific conformations of the 6-benzoates in classes V and VI are corroborated by the additivity relations discussed below. Although it would have been difficult to predict these conformations beforehand, the results can be rationalized by inspections of space-filling models.[22] The fact that the 6-

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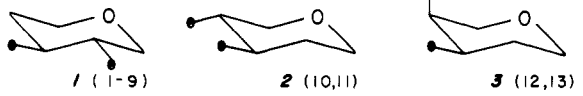
(20) Ogawa, T.; Matsui, M. *Carbohydr. Res.* **1977**, *56*, C1.
(21) Reference 5b, Table II, entry 7 and Figure 10.

Table II. Approximate A Values (in MeOH) of Various Pyranose p-Bromobenzoates, Classes I-VI, Units **1-26**[a]

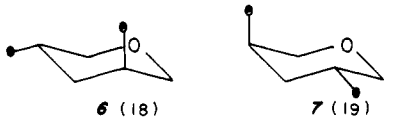
I) 1,2 ee and 1,2 ea : 62



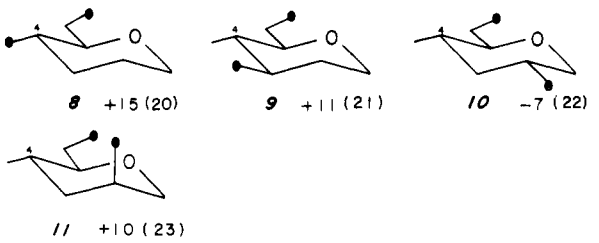
II) 1,2 aa : 5

III) 1,3 ee : 0

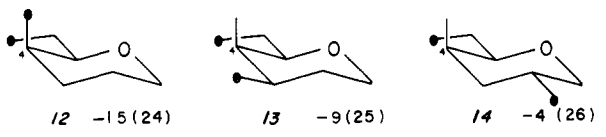
IV) 1,3 ea : 16



V) *Dibenzoates involving 6-OBz, 4e-Substituted*



VI) *Dibenzoates involving 6-OBz, 4a-Substituted*



[a] The signs of A values are dependent on chiralities of benzoate groups. The numbers in the parentheses correspond to the entries in Table I. Benzoate groups are indicated by hatched circles. The anomeric carbon is normally α-OMe but occasionally β-OMe; the "unsubstituted" carbons at other locations are either methylenes or substituted with "nonchromophoric" groups, e.g., OAc, OMe, CH_2OH, Me, etc. However, in the 6-benzoates (units **9**, **10**, **11**, **13**, **14**), the nonbenzoate substituents at C-4 are also depicted because the 6-benzoate conformation is affected by the C-4 substituent (see text).

benzoates can be represented by specific preferred conformations in solutions, however, was extremely fortunate because if this were not the case, they would have had to be excluded from the additivity treatment, which, in turn, would have greatly restricted the applicability of current investigation in oligosaccharide structure determination.[14]

The A values summarized in Table II reflect only the spatial arrangement of the benzoate group, are independent of other nonchromophoric substituents on the pyranose ring, and are equally applicable to $^4C_1$ and $_1C^4$ conformers of the pyranoses.[23]

The data for tris- and tetrakis(benzoates) are summarized in Table III.

i. Entry 27. This 1,2,3-eee tris(benzoate) shows only a weakly split CD because the opposing 1,2- and 2,3-chiralities (class I, +62 and −62) cancel out while the 1,3-chirality (class III) is nil.

ii. Entries 28–30. In 1,2,3-eea (or aee) tris(benzoates), the A values are large (±140) because the 1,2-, 2,3- and 1,3-chiralities all have identical signs. Moreover, it was found that the overall CD amplitude of these trichromophoric systems could be approximated by the sum of the three component dichromophoric systems as exemplified for entry 28 in Figure 4 (and Table III).

iii. Entries 31–37. These are tris(benzoates) involving the 6-benzoate groups. As shown in Figure 4 (and in Table III) for entries 32 and 37, there is again good agreement between the overall A value and the sum of component A values. This agreement also supports the above-mentioned preferred conformation of the 6-benzoyloxy group which is governed by the presence or absence of a 4-axial substituent.

iv. Entries 38–42. The additivity relation still holds to a remarkable extent even in these tetrakis(benzoates) which now consist of six component bis(benzoate) moieties (Figure 4). It should be noted that the A values for a pair of anomeric methyl glycosides are identical or very similar, i.e., entries 8(+56)/9(+56),

(22) It would be interesting to check the conformations of the 4(e)- and 4(a)-substituted 6-benzoates in the solid state.

Table III. Observed and Calculated A Values of Tris- and Tetrakis(p-bromobenzoates)

entry	compound	236 nm/ 253 nm	A- (obsd)	A- (calcd)[a]
27	β-Xyl-2(e),3(e),4(e)-	−1/+1	+2	0
28	β-Ara-2(e),3(e),4(a)-	−32/+101	+133	+140
29	α-Gal-2(e),3(e),4(a)-	−42/+95	+137	+140
30	α-Man-6-*O*-TBDMS-2(a),3(e),4(e)-[b]	+29/−91	−120	−140
31	α-Glu-3-OMe-2(e),4(e),6-	−1/+8	+9	+8
32	α-Glu-2(e),3(e),6-	−22/+47	+69	+66
33	α-Glu-2-OMe-3(e),4(e),6-	+11/−22	−33	−36
34	α-Glu-2-OAc-3(e),4(e),6-	+10/−22	−32	−36
35	α-Gal-3-OAc-2(e),4(a),6-	0/+6	+6	−3
36	α-Gal-2(e),3(e),6-	−14/+31	+45	+49
37	β-Gal-2(e),3(e),6-	−16/+30	+46	+49
38	β-Glu-2(e),3(e),4(e),6-	−7/+25	+32	+19
39	α-Glu-2(e),3(e),4(e),6-	−4/+20	+24	+19
40	β-Gal-2(e),3(e),4(a),6-	−26/+74	+100	+112
41	α-Gal-2(e),3(e),4(a),6-	−29/+70	+99	+112
42	α-Man-2(a),3(e),4(e),6-	+23/−66	−89	−104

[a] Estimated A value from sum of component dibenzoate units **1-26** (Table II). [b] TBDMS = *tert*-butyldimethylsilyl.

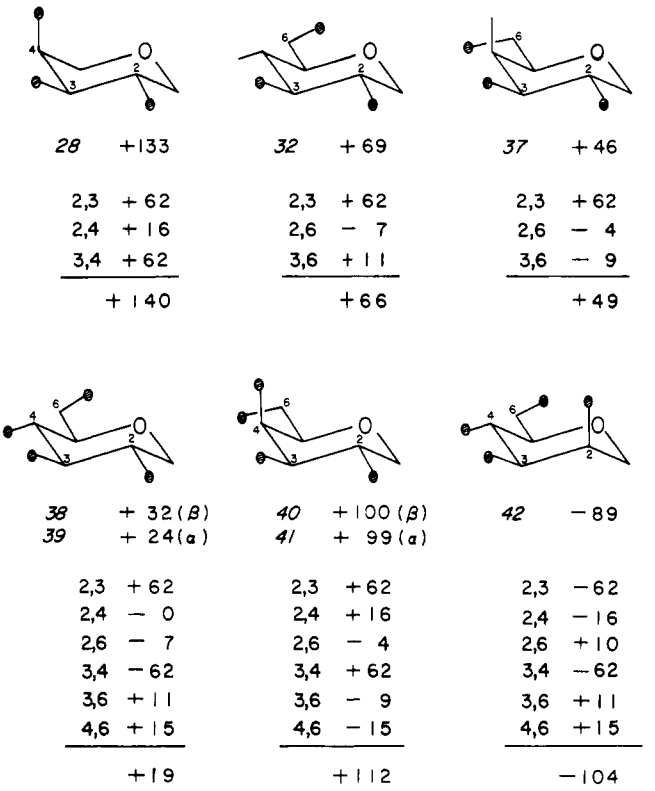


Figure 4. Observed and calculated A values of some tris- and tetrakis-(p-bromobenzoates). Italicized numbers correspond to entry numbers in Table III.

entries 36(+45)/37(+46), entries 40(+100)/41(+99). This was not the case for glucose, entry 38(+32)/39(+24), which has an A value ratio of 1.33; however, the integrated areas of the split CD curves of the two anomers were comparable (the ratio being 1.1).

In summary, the amplitudes given in Table II can be handled as constants reflecting only the spatial disposition of the two benzoate groups and are independent of other nonchromophoric substituents; furthermore, the A values of these bis(benzoate) units can be used in estimating the overall amplitudes of tris- and tetrakis(benzoate) systems consisting of four and six component bis(benzoate) units, respectively. In addition, the intensities of exciton-split CD curves are greatly enhanced. These attributes form the basis of the micromethod for determining oligosaccharide structures without reference to standard samples.[14] The additivity relations found in the amplitudes of split CD curves, which should not be restricted to benzoate interactions, simplify the CD analysis of multichromophoric systems and should have general applicability in configurational studies of complex natural products.[24]

Experimental Section

The spectroscopic measurements were carried out with the following instruments: MS (CI and EI), Finnigan 3300, methane as carrier gas in CI-MS; UV, JASCO UVIDEC-505; CD, JASCO J-40; NMR (^{1}H and ^{13}C), Bruker WM-250 or Bruker WP-80, chemical shifts were reported in ppm on the δ scale relative to a Me_4Si internal standard or appropriate solvent peaks. The preparative LC was performed on a Waters Prep LC/system 500 instrument. The analytical HPLC was performed with a Waters Model 6000A pump equipped with a U6K injector and a Schoeffel Model SF770 variable wavelength detector. Open column chromatography was performed utilizing J.T. Baker 60–200 mesh silica gel, eluted with the solvents mentioned. Flash column chromatography was performed according to the procedures of Still et al.,[25] using Merck silica gel 60 (230–400 mesh) eluted with the solvents mentioned. Solvents were reagent grade and purified by standard methods.

General Procedures. 1. Alkylation with Methylsulfinyl Anion and Alkyl Halide in Dimethyl Sulfoxide (Hakomori Method). a. Preparation of Methylsulfinyl Anion. Into a dry three-necked round-bottomed flask fitted at one neck with a rubber serum cap and containing a magnetic stirring bar is weighed 0.5 g of NaH (55%, coated with mineral oil). The sodium hydride is washed three times by stirring with anhydrous ether and decanting the wash. After the third wash, the flask is fitted with a condensor, and residual ether is removed by successive evacuations with a water aspirator through a needle inserted into the serum cap. After each evacuation, the flask is regassed with nitrogen. Dimethyl sulfoxide, 5 mL, is then transferred into the flask. This heterogeneous mixture is placed in an oil bath and stirred at 50–60 °C until the solution becomes green and evolution of hydrogen gas ceased (about 1 h). The concentration of anion in this Me_2SO solution is ca. 2.3 mequiv per mL.

b. Alkylation with Alkyl Halide. To a solution of the starting material (underivatized or partially derivatized sugars) in Me_2SO, cooled to ca. 20 °C with an ice-water bath, is added the methylsulfinyl anion solution obtained from preparation a. The amount of base is three times excess (3×) over the number of equivalents of hydroxyl present. A gel forms immediately upon addition of anion but gradually liquifies to a homogeneous, viscous solution after being stirred for a few hours (alkoxide formation is usually complete in a few hours; however, for polyhydroxyl compounds, stirring is continued overnight). The solution of sugar alkoxide is cooled in an ice-water bath, and 5 equiv of alkyl halide is added dropwise. A clear solution with markedly reduced viscosity is formed immediately and this solution is usually kept stirring at room temperature for a few hours. The reaction mixture is then quenched with water and extracted with chloroform. The purification process includes flash column chromatography, prepTLC and sometimes recrystallization.

2. Benzoylation. The solution of the starting material in dry pyridine is treated with 1.5 times excess of p-bromobenzoyl chloride. The resulting pale yellow solution is heated at 60 °C and stirred overnight (12 h). The reaction is quenched with a few drops of methanol and the excess solvent is removed under reduced pressure in the presence of benzene or toluene. The residue is then spotted on prepTLC or fractionated on flash column chromatography to give the benzoate. The samples submitted to CD measurement are further purified by recrystallization or HPLC.

1,2:3,4-Diisopropylidene-D-galactopyranose (a). D-Galactose (2 g) was stirred for 18 h with 1.6 L of acetone containing 1.6 mL of concentrated sulfuric acid, during which time most of the sugar dissolved. The reaction mixture was then cooled in an ice-water bath, and the acid was neutralized by passing ammonia gas through the solution. The precipitated salt was removed by filtration, and the filtrate was concentrated to a syrup which was dissolved in 20 mL of $CHCl_3$ and washed with 2 mL of H_2O. The organic fraction was purified by flash column chromatography (3% MeOH/$CHCl_3$). The yield was 75%; ^{1}H NMR ($CDCl_3$, 250 MHz) 5.377 (d, 1, J = 4.78, 1-H), 4.352 (dd, 1, J = 8.09, and 2.21, 3-H), 4.159 (dd, 1, J = 4.78, and 2.21, 2-H), 4.111 (d, 1, J = 8.09, 4-H),, 3.692–3.511 (m, 3, 5-H, 6-H's), 1.359 (s, 3, Me), 1.265 (s, 3, Me), 1.161 (s, 6, Me's); ^{13}C NMR ($CDCl_3$) 108.9 and 108.2 (ketalic-C's), 95.9 (C-1), 70.9 (C-2), 70.3 and 70.2 (C-4/C-3), 68.1 (C-5), 61.3 (C-6), 25.6, 24.5, and 24.0 (Me's).

1,2:3,4-Diisopropylidene-6-O-benzyl-D-galactopyranose (b). Compound **a** (2.2 g) was stirred with 10 mL of toluene, 10 mL of benzyl bromide, and 7 g of powdered KOH at 100 °C for 5 h. After the mixture had cooled to room temperature, 20 mL of ice water was added, and the stirring was continued until the salts dissolved. The organic layer was separated and washed with water. It was finally concentrated to a syrup and purified by flash column chromatography (5% EtOAc/benzene). The yield was quantitative. ^{1}H NMR ($CDCl_3$, 250 MHz) 7.389–7.280 (m, 5, aromatic-H's), 5.567 (d, 1, J = 4.78, 1-H), benzylic AB at 4.647 (d, 1, J = 12.13) and 4.566 (d, 1, J = 12.13), 4.614 (dd, 1, J = 8.09, and 2.58, 3-H), 4.328 (dd, 1, J = 4.78, and 2.58, 2-H), 4.293 (dd, 1, J = 8.09, and 1.84, 4-H), 4.028 (ddd, 1, J = 6.62, 5.88, and 1.84, 5-H), 3.721 (dd, 1, J = 9.93, and 5.88, 6-H), 3.649 (dd, 1, J = 9.93, and 6.62, 6′-H), 1.556 (s, 3, Me), 1.461 (s, 3, Me), 1.353 (s, 3, Me), 1.349 (s, 3, Me); ^{13}C NMR ($CDCl_3$) 138–127 (aromatic-C's), 108.9 and 108.1 (ketalic-C's), 96.2 (C-1), 73.1 (benzylic-C), 71.0 (C-2), 70.5 (C-3,4), 68.8 (C-6), 66.8 (C-5), 25.8, 24.7, and 24.3 (Me's).

Methyl 6-O-Benzyl-α-D-galactopyranoside (c). Compound **b** (2.2 g) was dissolved in 15 mL of dry methanol containing 4% hydrogen chloride gas, and the solution was refluxed for 3 h. The cooled solution was stirred with Ag_2O (1 g) until neutral, and the AgCl formed was removed by filtration through Celite. The filtrate was then concentrated in vacuo, during which the product crystallized spontaneously. It was recrystallized from absolute ethanol to give the desired product in 75% yield. ^{1}H NMR ($CDCl_3$, 250 MHz) 7.358–7.292 (m, 5, aromatic-H's), 4.842 (d, 1, J = 3.68, 1-H), 4.602 (br s, 2, benzylic-H's), 4.055–3.487 (m, 6, 2-H, 3-H, 4-H, 5-H, 6-H's), 3.427 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 135–128 (aromatic-C's), 99.6 (C-1), 73.8 (benzylic-C), 71.4 (C-2), 70.1 and 70.0 (C-4/C-3), 69.8 (C-6), 68.8 (C-5), 55.5 (1-OMe).

Methyl 6-O-Benzyl-3,4-O-isopropylidene-α-D-galactopyranoside (d). Compound **c** (568 mg) was dissolved in dry acetone (35 mL) containing a catalytic amount of p-toluenesulfonic acid. The reaction mixture was stirred at room temperature for 24 h and neutralized with $NaHCO_3$. The excess salt was filtered through Celite, and the filtrate was evaporated in vacuo. The resulting residue was dissolved in water followed by $CHCl_3$ extraction. Compound **d** was isolated from the organic fraction by flash column chromatography (3% MeOH/$CHCl_3$) in 97% yield. ^{1}H NMR ($CDCl_3$, 250 MHz) 7.352–7.276 (m, 5, aromatic-H's), 4.761 (d, 1, J = 3.68, 1-H), benzylic AB at 4.695 (d, 1, J = 12.13) and 4.547 (d, 1, J = 12.13), 4.215 (br s, 1, 4-H), 4.195–3.545 (m, 5, 2-H, 3-H, 5-H, 6-H's), 3.446 (s, 3, OMe), 1.492 (s, 3, Me), 1.330 (s, 3, Me); ^{13}C NMR ($CDCl_3$) 138.2 (subst-C), 128.1 (p-C), 127.4 (o-, m-C's), 109.3 (ketalic-C), 98.4 (C-1), 76.0 (C-4), 73.2 (C-3, benzylic-C), 69.4 (C-2,6), 67.2 (C-5), 55.2 (OMe), 27.6 and 25.7 (Me's).

Methyl 2,6-Di-O-benzyl-3,4-isopropylidene-α-D-galactopyranoside (e). Compound **d** (630 mg) was stirred with 15 mL of dry benzene, 93 mg of NaH, and 0.46 mL of BnBr at room temperature for 1 h and then refluxed for another 4 h. After being cooled to room temperature, the excess solvent was evaporated in vacuo and the product was extracted into the $CHCl_3$ solution which, after purification on flash column chromatography (5% EtOAc/benzene), afforded 75% of the pure product. ^{1}H NMR ($CDCl_3$, 250 MHz) 7.439–7.280 (m, 10, aromatic-H's), two benzylic AB's at 4.851 (d, 1, J = 12.24), 4.735 (d, 1, J = 12.24), and 4.678 (d, 1, J = 12.13), 4.558 (d, 1, J = 12.13), 4.701 (d, 1, J = 3.68, 1-H), 4.368 (dd, 1, J = 7.72, 5.52, 3-H), 4.227–4.164 (m, 2, 4-H, 6-H), 3.805–3.687 (m, 2, 5-H, 6′-H), 3.538 (dd, 1, J = 7.72, and 3.68, 2-H), 3.423 (s, 3, OMe), 1.405 (s, 3, Me), 1.355 (s, 3, Me); ^{13}C NMR ($CDCl_3$) 138.0 (subs-C), 128.0 (p-C), 127.6 (o-C), 127.1 (m-C), 108.7 (ketalic-C), 97.9 (C-1), 76.2 (C-4), 75.7 (C-2), 73.4 and 73.0 (benzylic-C's), 72.0 (C-3), 69.2 (C-6), 66.3 (C-5), 55.0 (OMe), 27.7 and 26.0 (Me's).

Methyl 2,6-Di-O-benzyl-α-D-galactopyranoside (f). A solution of compound **e** (350 mg) in MeOH (15 mL) containing 2 N HCl (5 mL) was refluxed for 30 min and cooled to room temperature. The reaction

(23) The benzoates of sugars which are in conformation equilibrium between the $^4C_1$ and $_1C^4$ conformers are under investigation.

(24) The additivity relation has been applied to trichilin, a complex limonoid insect antifeedant (Dr. M. Nakatani) and an insect molting hormone related to ecdysteroids (Dr. A. Trainor): manuscript in preparation.

(25) Still, W. C.; Mitra, A.; Khan, M. *J. Org. Chem.* **1978**, *41*, 2923.

solution was neutralized with diluted $NaHCO_3$ solution and excess solvent was evaporated in vacuo. The reaction product was extracted into $CHCl_3$ solution which, after concentration, was purified by flash column chromatography (3% MeOH/$CHCl_3$) to give the desired product **f** in quantitative yield. ^1H NMR ($CDCl_3$, 250 MHz) 7.397–7.276 (m, 10, aromatic-H's), 4.702 (d, 1, J = 3.68, 1-H), two benzylic AB's at 4.716 (d, 1, J = 12.14), 4.631 (d, 1, J = 12.14), 4.603 (d, 1, J = 12.13), 4.547 (d, 1, J = 12.13), 3.995–3.374 (m, 6, 2-H, 3-H, 4-H, 5-H, 6-H's), 3.354 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 138–127 (aromatic-C's), 97.9 (C-1), 76.6 (C-2), 73.4 and 72.7 (benzylic-C's), 69.7 (C-4,6), 69.2 (C-3), 68.4 (C-5), 55.1 (OMe).

Methyl 2,6-Di-*O*-benzyl-3,4-bis(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (g). Compound **g** was prepared from compound **f** (160 mg) and *p*-bromobenzoyl chloride (282 mg) in dry pyridine (3 mL) according to the standard procedure for benzoylation. The reaction mixture was purified by flash column chromatography (5% EtOAc/benzene) to afford the pure product in 91% yield. ^1H NMR ($CDCl_3$, 250 MHz) 7.876–7.307 (m, 18, aromatic-H's), 5.959 (br d, 1, J = 2.94, 4-H), 5.834 (dd, 1, J = 10.30 and 2.94, 3-H), 5.040 (d, 1, J = 2.94, 1-H), 4.761 (s, 2, benzylic-H's), benzylic AB at 4.614 (d, 1, J = 12.13), 4.481 (d, 1, J = 12.13), 4.439–4.415 (m, 1, 6-H), 4.188 (dd, 1, J = 10.30 and 2.94, 2-H), 3.679–3.640 (m, 2, 5-H, 6′-H), 3.583 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 164.6 and 164.4 (2 C=O's), 138–127 (aromatic-C's), 98.2 (C-1), 73.4 and 73.2 (benzylic-C's), 72.7 (C-2), 70.4 and 70.0 (C-4/C-3), 68.0 (C-6), 67.4 (C-5), 55.4 (OMe).

Methyl 3,4-Bis(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (13). Compound **g** (25 mg) was dissolved in methanol (3 mL) containing cyclohexadiene (2 mL) and 5% of formic acid. This solution was added to a stirred suspension of 10% Pd/C (5 mg) in the same solvent mixture (5 mL), maintained under a nitrogen atmosphere. Reaction was over in 3 h. The catalyst was filtered off and washed with methanol and water; the filtrates were combined and evaporated. Compound 13 was the only product. CI-MS 561 $(M + 1)^+$, 529 $(M - OMe)^+$; ^1H NMR ($CDCl_3$, 250 MHz) 7.956–7.356 (m, 8, aromatic-H's), 5.725 (br d, 1, J = 3.31, 4-H), 5.582 (dd, 1, J = 10.30 and 3.31, 3-H), 5.006 (d, 1, J = 4.05, 1-H), 4.329–3.590 (m, 4, 2-H, 5-H, 6-H's), 3.541 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 164.8 and 164.2 (2 C=O's), 138–127 (aromatic-C's), 99.9 (C-1), 71.5 and 71.2 (C-4/C-3), 69.7 (C-5), 68.3 (C-2), 60.9 (C-6), 55.8 (OMe).

Partial Acetates of Methyl α-D-Glucopyranoside (Acetates I-IV, Figure 3). Methyl α-D-glucopyranoside (970 mg) was treated with 1.5 M proportions (3 equiv) of bis(tributylstannyl) oxide in boiling toluene for 4 h with continuous removal of water to give a clear solution. After the solution was cooled to room temperature, the excess solvent was evaporated to give the partially stannylated products as an oil. Addition of 3.0 M proportions (0.71 mL) of acetyl chloride to this ice-cooled reaction mixture initiated a mildly exothermic reaction, to afford, after standing for 12 h at room temperature, compound II (10%), compound III (70%), and two other partially acetylated products, I (15%) and IV (5%). Reaction was quenched with water and extracted with $CHCl_3$. The crude mixture was separated by prep LC (3% MeOH/$CHCl_3$) with silica gel column (prep LC trace is shown in Figure 3).

Methyl 2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (acetate I, Figure 3): CI-MS 321 $(M + 1)^+$, 289 $(M - OMe)^+$, 229 $(M - OMe - HOAc)^+$; ^{13}C NMR ($CDCl_3$) 170.5, 170.2, and 169.7 (3 C=O's), 96.3 (C-1), 72.2 (C-3), 70.5 (C-2), 69.0 (C-4), 68.5 (C-5), 62.6 (C-6), 54.4 (OMe), 19.9 (OAc's).

Methyl 3,6-di-*O*-acetyl-α-D-glucopyranoside (acetate II, Figure 3): CI-MS 279 $(M + 1)^+$, 247 $(M - OMe)^+$, 187 $(M - OMe - HOAc)^+$; ^{13}C NMR ($CDCl_3$) 172.1 and 171.0 (2 C=O's), 99.2 (C-1), 75.9 (C-3), 70.4 (C-2), 69.4 (C-4), 68.3 (C-5), 63.0 (C-6), 54.9 (OMe), 20.6 and 20.3 (OAc's).

Methyl 2,6-Di-*O*-acetyl-α-D-glucopyranoside (acetate III, Figure 3): CI-MS 279 $(M + 1)^+$, 247 $(M - OMe)^+$, 187 $(M - OMe - HOAc)^+$; ^{13}C NMR ($CDCl_3$) 171.1 and 170.6 (2 C=O's), 96.6 (C-1), 72.8 (C-2), 70.9 (C-3), 70.2 (C-4), 68.9 (C-5), 63.0 (C-6), 54.6 (OMe), 20.3 (OAc's).

Methyl 6-*O*-acetyl-α-D-glucopyranoside (acetate IV, Figure 3): CI-MS 237 $(M + 1)^+$, 205 $(M - OMe)^+$, 187 $(M - OMe - H_2O)^+$; ^{13}C NMR ($CDCl_3$) 171.2 (C=O), 99.3 (C-1), 73.8 (C-3), 71.7 (C-2), 70.1 (C-4), 69.4 (C-5), 63.5 (C-6), 54.9 (OMe), 20.5 (OAc).

A trace of methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside was also isolated from the prep LC fraction eluting at 2–3 min and gave the following physical data: ^{13}C NMR ($CDCl_3$) 169.9, 169.5, and 169.0 (4 C=O's), 96.5 (C-1), 70.4 (C-2), 69.8 (C-3), 68.3 (C-4), 66.9 (C-5), 61.7 (C-6), 54.9 (OMe), 20.5 (OAc's).

Methyl 2,6-Di-*O*-acetyl-3,4-bis(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (10). Acetate III (Figure 3) (285 mg) was reacted with *p*-bromobenzoyl chloride (678 mg) in dry pyridine (3 mL) and the reaction mixture was purified by flash column chromatography (5% EtOAc/benzene) to afford the pure product in 84% yield. CI-MS 644 $(M)^+$, 613 $(M - OMe)^+$, 585 $(M - OAc)^+$, 553 $(M - OMe - HOAc)^+$; ^1H NMR ($CDCl_3$, 250 MHz) 7.741–7.396 (m, 8, aromatic-H's), 5.886 (dd, 1, J = 9.93 and 9.93, 3-H), 5.454 (dd, 1, J = 9.93 and 9.93; 4-H), 5.153 (dd, 1, J = 9.93 and 3.68, 2-H), 5.028 (d, 1, J = 3.68, 1-H), 4.260 (dd, 1, J = 8.09 and 1.10, 6-H), 4.200 (dd, 1, J = 8.09 and 2.57, 6′-H), 4.160 (m, 1, 5-H), 3.475 (s, 3, OMe), 2.054 (s, 3, OAc), 1.977 (s, 3, OAc); ^{13}C NMR ($CDCl_3$) 170.1 and 169.7 (OAc, C=O's), 164.6 and 164.2 (OBz, C=O's), 132–127 (aromatic-C's), 96.8 (C-1), 70.6 and 70.5 (C-3/C-2), 69.5 (C-4), 67.2 (C-5), 62.0 (C-6), 55.3 (OMe), 20.3 (OAc's).

Methyl 3,6-Di-*O*-acetyl-2,4-bis(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (16). Compound **16** was prepared from acetate II (Figure 3) (246 mg) with *p*-bromobenzoyl chloride (583 mg) in dry pyridine (3 mL) according to the standard procedure for benzoylation. The reaction mixture was purified by open column chromatography (4% EtOAc/benzene) to afford the pure product in 86% yield. CI-MS 644 $(M)^+$, 613 $(M - OMe)^+$, 585 $(M - OAc)^+$, 553 $(M - OMe - OAc)^+$; ^1H NMR ($CDCl_3$, 250 MHz) 7.892–7.545 (m, 8, aromatic-H's), 5.852 (dd, 1, J = 9.93 and 9.93, 3-H), 5.372 (dd, 1, J = 9.93 and 9.93, 4-H), 5.139 (dd, 1, J = 9.93 and 3.68, 2-H), 5.084 (d, 1, J = 3.68, 1-H), 4.281 (dd, 1, J = 12.87 and 5.52, 6-H), 4.206–4.130 (m, 2, 5-H, 6′-H), 3.425 (s, 3, OMe), 2.052 (s, 3, OAc), 1.836 (s, 3, OAc); ^{13}C NMR ($CDCl_3$) 170.1 and 169.7 (OAc, C=O's), 164.7 and 164.4 (OBz, C=O's), 132–127 (aromatic-C's), 96.7 (C-1), 71.7 (C-3), 69.6 (C-2), 69.5 (C-4), 67.2 (C-5), 62.2 (C-6), 55.3 (OMe), 20.4 and 20.3 (OAc's).

Methyl 2,3-bis(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (1): CI-MS 558 $([M - OMe] + 29)^+$, 529 $(M - OMe)^+$; ^1H NMR ($CDCl_3$, 250 MHz) 7.952–7.523 (m, 8, aromatic-H's), 5.717 (dd, 1, J = 9.56 and 9.56, 3-H), 5.176 (dd, 1, J = 9.56 and 3.68, 2-H), 5.100 (d, 1, J = 3.68, 1-H), 3.975–3.649 (m, 4, 4-H, 5-H, 6-H's), 3.447 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 167.3 and 166.0 (2 C=O's), 133–128 (aromatic-C's), 97.1 (C-1), 74.2 (C-3), 71.6 and 71.4 (C-2/C-5), 69.8 (C-4), 62.0 (C-6), 55.3 (OMe).

Methyl 2,3-bis(*O*-(*p*-bromobenzoyl))-4,6-*O*-benzylidene-α-D-glucopyranoside (2): CI-MS 649 $(M + 1)^+$, 617 $(M - OMe)^+$; ^1H NMR ($CDCl_3$, 250 MHz) 7.895–7.325 (m, 13, aromatic-H's), 6.051 (dd, 1, J = 9.93 and 9.93; 3-H), 5.594 (s, 1, ketalic-H), 5.262 (dd, 1, J = 9.93 and 3.68, 2-H), 5.185 (d, 1, J = 3.68, 1-H), 4.407 (dd, 1, J = 9.93 and 4.78, 6R-H), 4.086 (m, 1, 5-H), 3.927 (dd, 1, J = 9.93 and 9.93, 4-H), 3.887 (dd, 1, J = 10.30 and 9.93, 6S-H), 3.464 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 102.3 (ketalic-C), 98.1, (C-1), 79.6 (C-4), 74.6 (C-2), 73.0 (C-3), 68.9 (C-6), 62.5 (C-5), 55.5 (OMe).

Methyl 2,3-bis(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (3): CI-MS 529 $(M - OMe)^+$; ^{13}C NMR ($CDCl_3$) 165.3 and 165.0 (2 C=O's), 138–125 (aromatic-C's), 97.9 (C-1), 71.5 (C-3), 70.4 (C-5), 69.6 (C-4), 69.0 (C-2), 61.2 (C-6), 55.3 (OMe).

Methyl 2,3-bis(*O*-(*p*-bromobenzoyl))-4,6-*O*-benzylidene-α-D-galactopyranoside (4): ^1H NMR ($CDCl_3$, 250 MHz) 7.875–7.278 (m, 13, aromatic-H's), 5.765–5.755 (m, 2, 2-H, 3-H), 5.577 (s, 1, ketalic-H), 5.260 (d, 1, J = 2.21, 1-H), 4.631 (br s, 1, 4-H), 4.371 (dd, 1, J = 12.50 and 1.84, 6S-H), 4.152 (dd, 1, J = 12.50 and 1.47, 6R-H), 3.907 (br, s, 1, 5-H), 3.474 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.2 and 165.0 (2 C=O's), 138–126 (aromatic-C's), 100.6 (ketalic-C), 97.9 (C-1), 74.1 (C-4), 69.4 (C-3), 69.0 (C-2,6), 62.1 (C-5), 55.6 (OMe).

Methyl 2,3-bis(*O*-(*p*-bromobenzoyl))-6-*O*-(*tert*-butyldimethylsilyl)-α-D-galactopyranoside (5): ^1H NMR ($CDCl_3$, 250 MHz) 7.884–7.501 (m, 8, aromatic-H's), 5.666 (br d, 1, J = 2.57, 2-H), 5.657 (br d, 1, J = 1.84, 3-H), 5.179 (d, 1, J = 2.57, 1-H), 4.491 (br s, 1, 4-H), 4.052–3.951 (m, 3, 5-H, 6-H's), 3.425 (s, 3, OMe), 0.931 (s, 9, $(CH_3)_3C$–), 0.137 (s, 3, CH_3Si), 0.130 (s, 3, CH_3Si); ^{13}C NMR ($CDCl_3$) 165.2 and 165.0 (2 C=O's), 135–128 (aromatic-C's), 97.5 (C-1), 71.5 (C-3), 69.4, 69.2, and 69.0 (C-5/C-4/C-2), 63.6 (C-6), 55.3 (OMe), 25.8 ($(CH_3)_3C$–), 18.2 ($(CH_3)_2Si$), −5.6 (>CSi).

Methyl 4-*O*-acetyl-2,3-bis(*O*-(*p*-bromobenzoyl))-6-*O*-(*tert*-butyldimethylsilyl)-α-D-galactopyranoside (6): ^1H NMR ($CDCl_3$, 80 MHz) 7.88–7.42 (m, 8, aromatic-H's), 5.69 (m, 1, 3-H), 5.57 (m, 1, 2-H), 5.13 (d, 1, J = 2.69, 1-H), 3.42 (s, 3, OMe), 2.11 (s, 3, OAc), 0.87 (s, 9, $(CH_3)_3C$–), 0.03 (s, 6, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$) 169.7 (OAc, C=O), 165.3 and 164.8 (OBz, C=O's), 135–128 (aromatic-C's), 97.4 (C-1), 69.5 (C-3), 69.2, 69.0, and 68.4 (C-2/C-4/C-5), 61.2 (C-6), 55.5 (OMe), 25.7 ($(CH_3)_3C$–), 18.2 ($(CH_3)_2Si$), 16.4 (CH_3CO), −5.6 (>CSi).

Methyl 6-*O*-acetyl-2,3-bis(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (7): CI-MS 571 $(M - OMe)^+$, 512 $([M - OMe - HOAc] + 1)^+$.

Methyl 2,3-bis(*O*-(*p*-bromobenzoyl))-α-D-quinovopyranoside (8): CI-MS 553 $([M - HOMe] + 41)^+$, 541 $([M - HOMe] + 29)^+$, 513 $([M - HOMe] + 1)^+$; ^1H NMR ($CDCl_3$, 250 MHz) 7.850–7.510 (m, 8, aromatic-H's), 5.638 (dd, 1, J = 9.19 and 9.19, 3-H), 5.236 (dd, 1, J = 9.19 and 3.68, 2-H), 5.023 (d, 1, J = 3.68, 1-H), 3.918–3.450 (m, 2, 4-H,

5-H), 3.434 (s, 3, OMe), 1.405 (d, 3, J = 6.25, 5-Me).

Methyl 2,3-bis(*O*-(*p*-bromobenzoyl))-β-D-quinovopyranoside (9): CI-MS 553 ([M − HOMe] + 41)$^+$, 541 ([M − HOMe] + 29)$^+$, 513 ([M − HOMe] + 1)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.837–7.518 (m, 8, aromatic-H's), 5.374 (dd, 1, J = 9.10 and 9.10, 3-H), 5.333 (dd, 1, J = 9.10 and 7.72, 2-H), 4.588 (d, 1, J = 7.72, 1-H), 3.605–3.505 (m, 2, 4-H, 5-H), 3.527 (s, 3, OMe), 1.460 (d, 3, J = 5.88, 5-Me).

Methyl 2,6-di-*O*-acetyl-3,4-bis(*O*-(*p*-bromobenzoyl))-α-D-mannopyranoside (11): CI-MS 645 (M + 1)$^+$, 613 (M − OMe)$^+$, 585 (M − OAc)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.888–7.443 (m, 8, aromatic-H's), 5.682 (m, 2, 3-H, 4-H), 5.417 (dd, 1, J = 1.84 and 1.47, 2-H), 4.819 (d, 1, J = 1.47, 1-H), 4.332 (dd, 1, J = 12.50 and 5.88, 6-H), 4.215 (br, d, 1, J = 12.50, 6′-H), 3.887 (m, 1, 5-H), 3.465 (s, 3, OMe), 2.145 (s, 3, OAc), 2.053 (s, 3, OAc); ^{13}C NMR ($CDCl_3$) 170.1 and 169.4 (OAc, C=O's), 164.3 (OBz, C=O's), 135–125 (aromatic-C's), 98.3 (C-1), 69.7 (C-3), 69.4 (C-2), 68.1 (C-5), 67.0 (C-4), 62.4 (C-6), 55.0 (OMe), 20.3 (OAc's).

Methyl 3,4-bis(*O*-(*p*-bromobenzoyl))-2,6-di-*O*-methyl-α-D-galactopyranoside (12): CI-MS 589 (M + 1)$^+$, 557 (M − OMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.954–7.356 (m, 8, aromatic-H's), 5.880 (br s, 1, 4-H), 5.668 (dd, 1, J = 10.30 and 3.31, 3-H), 5.262 (d, 1, J = 3.31, 1-H), 4.352 (m, 1, 6-H), 3.669–3.521 (m, 3, 2-H, 5-H, 6′-H), 3.500 (s, 3, OMe), 3.340 (s, 3, OMe), 3.315 (s, 3, OMe).

Methyl 2,3-bis(*O*-(*p*-bromobenzoyl))-α-D-altropyranoside (14): CI-MS 561 (M + 1)$^+$, 529 (M − OMe)$^+$.

Methyl 4,6-*O*-benzylidene-2,3-bis(*O*-(*p*-bromobenzoyl))-α-D-altropyranoside (15): ^{1}H NMR ($CDCl_3$, 250 MHz) 8.022–7.317 (m, 13, aromatic-H's), 5.726 (s, 1, ketalic-H), 5.677 (dd, 1, J = 2.94 and 2.57, 3-H), 5.407 (d, 1, J = 2.94, 2-H), 4.845 (br s, 1, 1-H), 4.586–4.418 (m, 2, 4-H, 5-H), 4.237 (dd, 1, J = 9.93 and 2.94, 6R-H), 3.930 (dd, 1, J = 9.93 and 9.93, 6S-H), 3.496 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 164.6 and 164.0 (2 C=O's), 137–126 (aromatic-C's), 102.1 (ketalic-C), 98.8 (C-1), 74.8 (C-4), 70.1 (C-2), 69.2 and 67.4 (C-6/C-3), 58.9 (C-5), 55.7 (OMe).

Methyl 2,4-bis(*O*-(*p*-bromobenzoyl))-3-*O*-methyl-α-D-glucopyranoside (17): ^{13}C NMR ($CDCl_3$) 164.5, 164.0 (2 C=O's), 133–128 (aromatic-C's), 97.3 (C-1), 73.7 (C-3), 71.2 (C-2), 70.1 and 69.9 (C-4/C-5), 61.8 (C-6), 55.5 (OMe).

Methyl 3,6-di-*O*-acetyl-2,4-bis(*O*-(*p*-bromobenzoyl))-α-D-mannopyranoside (18): CI-MS 645 (M + 1)$^+$, 613 (M − OMe)$^+$, 585 (M − OAc)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.979–7.531 (m, 8, aromatic-H's), 5.508 (m, 2, 3-H, 4-H), 5.417 (dd, 1, J = 1.84 and 1.47, 2-H), 4.897 (d, 1, J = 1.47, 1-H), 4.332 (dd, 1, J = 12.50 and 5.88, 6-H), 4.215 (br d, 1, J = 12.50, 6′-H), 3.887 (m, 1, 5-H), 3.465 (s, 3, OMe), 2.145 (s, 3, OAc), 2.053 (s, 3, OAc); ^{13}C NMR ($CDCl_3$) 170.2 and 169.6 (OAc, C=O's), 164.5 (OBz, C=O's), 135–125 (aromatic-C's), 98.3 (C-1), 70.2 (C-3), 68.8 and 68.3 (C-2/C-5), 67.2 (C-4), 62.6 (C-6), 55.2 (OMe), 20.3 (OAc's).

Methyl 3,6-di-*O*-acetyl-2,4-bis(*O*-(*p*-bromobenzoyl))-β-D-galactopyranoside (19): CI-MS 645 (M + 1)$^+$, 613 (M − OMe)$^+$, 585 (M − OAc)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.985–7.532 (m, 8, aromatic-H's), 5.694 (br d, 1, J = 3.31, 4-H), 5.503 (dd, 1, J = 10.20 and 8.09, 2-H), 5.327 (dd, 1, J = 10.20 and 3.31, 3-H), 4.619 (d, 1, J = 8.09, 1-H), 4.334–4.087 (m, 3, 5-H, 6-H's), 3.533 (s, 3, OMe), 2.020 (s, 3, OAc), 1.850 (s, 3, OAc).

Methyl 4,6-bis(*O*-(*p*-bromobenzoyl))-2,3-di-*O*-methyl-α-D-glucopyranoside (20): CI-MS 629 (M + 41)$^+$, 617 (M + 29)$^+$, 589 (M + 1)$^+$, 557 (M − OMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.931–7.507 (m, 8, aromatic-H's), 5.283 (dd, 1, J = 9.56 and 9.56; 4-H), 4.910 (d, 1, J = 3.68, 1-H), 4.517 (dd, 1, J = 12.13 and 2.94, 6-H), 4.328 (dd, 1, J = 12.13 and 5.15; 6′-H), 4.172–4.099 (m, 1, 5-H), 3.759 (dd, 1, J = 9.56 and 9.56, 3-H), 3.565 (s, 3, OMe), 3.491 (s, 3, OMe), 3.486 (s, 3, OMe), 3.402 (dd, 1, J = 9.56 and 3.68, 2-H); ^{13}C NMR ($CDCl_3$) 165.3 and 164.6 (2 C=O's), 132–128 (aromatic-C's), 97.7 (C-1), 81.4 (C-3), 80.9 (C-2), 71.5 (C-4), 67.4 (C-5), 63.5 (C-6), 60.9 (3-OMe), 59.2 (2-OMe), 55.4 (1-OMe).

Methyl 3,6-bis(*O*-(*p*-bromobenzyl))-α-D-mannopyranoside (21): CI-MS 560 (M)$^+$, 529 (M − OMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.965–7.553 (m, 8, aromatic-H's), 5.358 (dd, 1, J = 9.96 and 3.31, 3-H), 4.800 (d, 1, J = 1.84, 1-H), 4.769 (dd, 1, J = 12.13 and 4.78, 6-H), 4.608 (dd, 1, J = 12.13 and 2.20, 6′-H), 4.182 (dd, 1, J = 3.31 and 1.84, 2-H), 4.134–3.999 (m, 2, 4-H, 5-H), 3.312 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.9 and 165.6 (2 C=O's), 132–128 (aromatic-C's), 100.7 (C-1), 75.2 (C-3), 70.6 and 68.9 (C-5/C-2), 65.7 (C-4), 64.3 (C-6), 54.8 (OMe).

Methyl 2,6-bis(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (22): CI-MS 529 (M − OMe)$^+$, 345 (M − OMe − [*p*-BrBz])$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.981–7.584 (m, 8, aromatic-H's), 5.047 (d, 1, J = 3.68 1-H), 4.940 (dd, 1, J = 9.93 and 3.68, 2-H), 4.832 (dd, 1, J = 12.13 and 4.15, 6-H), 4.523 (dd, 1, J = 12.13 and 2.21, 6′-H), 4.176 (dd, 1, J = 9.93 and 9.93, 3-H), 3.938 (ddd, 1, J = 12.13, 4.15, and 2.21, 5-H), 3.561 (dd, 1, J = 9.93 and 9.93, 4-H), 3.415 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 166.6 and 165.7 (2 C=O's), 132–128 (aromatic-C's), 97.3 (C-1), 73.9 (C-2), 71.6 (C-3), 70.8 (C-4), 69.5 (C-5), 63.8 (C-6), 55.4 (OMe).

Methyl 2,6-bis(*O*-(*p*-bromobenzoyl))-α-D-mannopyranoside (23): CI-MS 561 (M + 1)$^+$, 529 (M − OMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.916–7.342 (m, 8, aromatic-H's), 5.292 (dd, 1, J = 3.31 and 1.84, 2-H), 4.800 (d, 1, J = 1.84, 1-H), 4.738 (dd, 1, J = 12.14 and 3.68, 6-H), 4.559 (dd, 1, J = 12.14 and 1.84, 6′-H), 4.170 (dd, 1, J = 8.83 and 3.31, 3-H), 3.893–3.478 (m, 2, 4-H, 5-H), 3.440 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.6 and 165.0 (2 C=O's), 132–128 (aromatic-C's), 98.2 (C-1), 72.4 (C-2), 70.3 (C-5), 69.6 (C-3), 67.5 (C-4), 63.5 (C-6), 54.8 (OMe).

Methyl 4,6-bis(*O*-(*p*-bromobenzoyl))-2,3-di-*O*-methyl-α-D-galactopyranoside (24): CI-MS 589 (M + 1)$^+$, 558 ([M − OMe] + 1)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.952–7.536 (m, 8, aromatic-H's), 5.807 (br d, 1, J = 3.31, 4-H), 5.014 (d, 1, J = 3.68, 1-H), 4.493 (dd, 1, J = 12.87 and 9.19, 6-H), 4.449–4.209 (m, 2, 5-H, 6′-H), 3.766 (dd, 1, J = 9.93 and 3.31, 3-H), 3.644 (dd, 1, J = 9.93 and 3.68, 2-H), 3.550 (s, 3, OMe), 3.466 (s, 3, OMe), 3.452 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.3 and 165.0 (2 C=O's), 132–128 (aromatic-C's), 98.2 (C-1), 78.0 (C-3), 77.6 (C-2), 68.1 (C-4), 66.8 (C-5), 63.2 (C-6), 59.3, 57.9, and 55.5 (OMe's).

Methyl 3,6-bis(*O*-(*p*-bromobenzoyl))-β-D-galactopyranoside (25): CI-MS 529 (M − OMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.975–7.526 (m, 8, aromatic-H's), 5.121 (dd, 1, J = 9.93 and 3.31, 3-H), 4.689–4.523 (m, 2, 6-H's), 4.358 (d, 1, J = 7.72, 1-H), 4.219 (br s, 1, 4-H), 4.066–3.947 (m, 2, 2-H, 5-H), 3.608 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 166.2 and 165.9 (2 C=O's), 132–128 (aromatic-C's), 104.5 (C-1), 75.6 (C-3), 72.4 (C-5), 69.5 (C-2), 67.4 (C-4), 64.9 (C-6), 57.3 (OMe).

Methyl 2,6-bis(*O*-(*p*-bromobenzoyl))-β-D-galactopyranoside (26): CI-MS 529 (M − OMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.923–7.522 (m, 8, aromatic-H's), 5.242–5.163 (m, 2, 2-H, 3-H), 4.691 (d, 1, J = 1.47, 1-H), 4.518 (dd, 1, J = 12.13 and 4.41, 6-H), 4.329 (br d, 1, J = 12.13, 6′-H), 3.840–3.816 (m, 2, 4-H, 5-H), 3.396 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.3 and 165.1 (2 C=O's), 131–127 (aromatic-C's), 101.5 (C-1), 72.5 and 72.2 (C-2/C-5), 71.1 (C-3), 68.5 (C-4), 63.2 (C-6), 55.2 (OMe).

Methyl 2,3,4-Tris(*O*-(*p*-bromobenzoyl))-β-D-xylopyranoside (27): CI-MS 713 (M)$^+$, 681 ([M − OMe] − 1)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 8.019–7.500 (m, 12, aromatic-H's), 5.739 (dd, 1, J = 8.09 and 8.09, 3-H), 5.358 (dd, 1, J = 8.09 and 5.88, 2-H), 5.333 (ddd, 1, J = 8.09, 8.09, and 4.41, 4-H), 4.706 (d, 1, J = 5.88, 1-H), 4.415 (dd, 1, J = 12.13 and 4.41, 5R-H), 3.677 (dd, 1, J = 12.13 and 8.09, 5S-H), 3.540 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 164.7 and 164.4 (3 C=O's), 132–128 (aromatic-C's), 101.3 (C-1), 71.2 (C-3), 70.8 (C-2), 69.6 (C-4), 61.6 (C-5), 56.5 (OMe).

Methyl 2,3,4-tris(*O*-(*p*-bromobenzoyl))-β-L-arabinopyranoside (28): CI-MS 714 (M + 1)$^+$, 682 (M − OMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 8.034–7.190 (m, 12, aromatic-H's), 5.933 (dd, 1, J = 10.66 and 3.31, 3-H), 5.766 (br d, 1, J = 3.31, 4-H), 5.696 (dd, 1, J = 10.66 and 3.31, 2-H), 5.242 (d, 1, J = 3.31, 1-H), 4.181 (br d, 1, J = 12.50, 5R-H), 3.968 (br d, 1, J = 12.50, 5S-H), 3.465 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.0, 164.8 and 164.6 (3 C=O's), 132–128 (aromatic-C's), 97.7 (C-1), 70.3 (C-3), 69.4 (C-2), 68.1 (C-4), 61.5 (C-5), 55.5 (OMe).

Methyl 2,3,4-tris(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (29): CI-MS 712 (M − OMe)$^+$; ^{13}C NMR ($CDCl_3$) 165.5, 164.7, and 164.3 (3 C=O's), 132–128 (aromatic-C's), 71.0 (C-4), 69.7 (C-3,5), 69.0 (C-2), 63.1 (C-6), 55.6 (OMe).

Methyl 2,3,4-tris(O-(*p*-bromobenzoyl))-6-(*O*-*tert*-butyldimethylsilyl)-α-D-mannopyranoside (30): CI-MS 857 (M)$^+$, 826 (M − OMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.969–7.402 (m, 12, aromatic-H's), 5.915 (dd, 1, J = 9.93 and 9.93, 4-H), 5.790 (dd, 1, J = 9.93 and 2.94, 3-H), 5.650 (dd, 1, J = 2.94 and 1.84, 2-H), 4.953 (d, 1, J = 1.84, 1-H), 4.108 (m, 1, 5-H), 3.855 (m, 2, 6-H's), 3.519 (s, 3, OMe), 0.918 (s, 9, $(CH_3)_3C$), 0.044 (s, 3, CH_3Si), 0.018 (s, 3, CH_3Si); ^{13}C NMR ($CDCl_3$) 165.2, 164.3, and 164.2 (3 C=O's), 132–128 (aromatic-C's), 98.3 (C-1), 70.9, 70.4 (C-2/C-3/C-5), 66.7 (C-4), 61.8 (C-6), 54.9 (OMe), 25.6 ($(CH_3)_3C$), 17.9 ($(CH_3)_2Si$), −5.7 (>CSi).

Methyl 3-*O*-methyl-2,4,6-tris(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (31): CI-MS 757 (M)$^+$, 725 (M − HOMe)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.972–7.528 (m, 12, aromatic-H's), 5.424 (dd, 1, J = 9.56 and 9.56, 4-H), 5.145–5.103 (m, 2, 1-H, 2-H), 4.555 (dd, 1, J = 12.13 and 2.94, 6-H), 4.389 (dd, 1, J = 12.13 and 5.15, 6′-H), 4.269–4.216 (m, 1, 5-H), 4.074 (dd, 1, J = 9.56 and 9.56, 3-H), 3.458 (s, 3, OMe), 3.434 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.3, 165.0, and 164.4 (3 C=O's), 132–128 (aromatic-C's), 97.1 (C-1), 78.8 (C-3), 73.6 (C-2), 71.4 (C-4), 67.4 (C-5), 63.4 (C-6), 60.6 (3-OMe), 55.5 (1-OMe).

Methyl 2,3,6-tris(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (32): CI-MS 743 (M)$^+$, 711 (M − HOMe)$^+$, 528 (M − OMe − *p*-Br-Bz)$^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.954–7.478 (m, 12, aromatic-H's), 5.764 (dd, 1, J = 9.93 and 9.93, 3-H), 5.227 (dd, 1, J = 9.93 and 3.68, 2-H), 5.116 (d, 1, J = 3.68, 1-H), 4.783 (dd, 1, J = 12.13 and 4.41, 6-H), 4.620 (br

d, 1, J = 12.13, 6′-H), 4.128–4.082 (m, 1, 5-H), 3.847 (dd, 1, J = 9.93 and 9.93, 4-H), 3.456 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 166.1 and 165.2 (3 C=O's), 132–128 (aromatic-C's), 97.0 (C-1), 73.9 (C-3), 71.6 (C-2), 69.8 and 69.5 (C-4/C-5), 63.7 (C-6), 55.3 (OMe).

Methyl 2-*O*-methyl-3,4,6-tris(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (33): CI-MS 757 $(M)^+$, 725 $(M - HOMe)^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.891–7.465 (m, 12, aromatic-H's), 5.867 (dd, 1, J = 9.93 and 9.93, 3-H), 5.464 (dd, 1, J = 9.93 and 9.93, 4-H), 5.039 (d, 1, J = 3.68, 1-H), 4.553 (dd, 1, J = 12.14 and 2.94, 6-H), 4.427 (dd, 1, J = 12.14 and 5.15, 6′-H), 4.343–4.269 (m, 1, 5-H), 3.635 (dd, 1, J = 9.93 and 3.68, 2-H), 3.540 (s, 3, OMe), 3.453 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.4, 165.0, and 164.3 (3 C=O's), 132–128 (aromatic-C's), 97.2 (C-1), 79.5 (C-2), 72.5 (C-3), 70.2 (C-4), 67.4 (C-5), 63.3 (C-6), 59.2 (2-OMe), 55.6 (1-OMe).

Methyl 2-*O*-acetyl-3,4,6-tris(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (34): CI-MS 754 $(M - OMe)^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.954–7.455 (m, 12, aromatic-H's), 5.933 (dd, 1, J = 9.93 and 9.93, 3-H), 5.535 (dd, 1, J = 9.93 and 9.93, 4-H), 5.178 (dd, 1, J = 9.93 and 3.68, 2-H), 5.051 (d, 1, J = 3.68, 1-H), 4.565 (dd, 1, J = 12.13 and 3.31, 6-H), 4.435 (dd, 1, J = 12.13 and 4.78, 6′-H), 3.335 (m, 1, 5-H), 3.505 (s, 3, OMe), 2.010 (s, 3, OAc); ^{13}C NMR ($CDCl_3$), 170.1 (OAc, C=O), 165.3, 164.9, and 164.6 (OBz, C=O's), 132–128 (aromatic-C's), 97.1 (C-1), 70.8 (C-2,3), 70.0 (C-4), 67.4 (C-5), 63.1 (C-6), 55.6 (OMe), 20.5 (OAc).

Methyl 3-*O*-acetyl-2,4,6-tris(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (35): CI-MS 786 $(M + 1)^+$, 755 $([M - OMe] + 1)^+$.

Methyl 2,3,6-tris(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (36): CI-MS 712 $(M - OMe)^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.922–7.522 (m, 12, aromatic-H's), 5.230–5.179 (m, 2, 2-H, 3-H), 4.691 (d, 1, J = 1.47, 1-H), 4.516 (br d, 1, J = 12.13, 6-H), 4.327 (br d, 1, J = 12.13, 6′-H), 3.838–3.815 (m, 2, 4-H, 5-H), 3.396 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.8, 165.3, and 165.1 (3 C=O's), 132–128 (aromatic-C's), 97.4 (C-1), 71.1 (C-3), 69.0 (C-2), 68.1 (C-4), 67.8 (C-5), 63.7 (C-6), 55.5 (OMe).

Methyl 2,3,6-tris(*O*-(*p*-bromobenzoyl))-β-D-galactopyranoside (37): CI-MS 712 $(M - OMe)^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.967–7.372 (m, 12, aromatic-H's), 5.716 (dd, 1, J = 10.30 and 7.72, 2-H), 5.320 (dd, 1, J = 10.30 and 2.94, 3-H), 4.676 (d, 1, J = 7.72, 1-H), 4.736–4.575 (m, 2, 6-H's), 4.323 (br d, 1, J = 2.94, 4-H), 4.063 (m, 1, 5-H), 3.544 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.8, 165.1, and 164.7 (3 C=O's), 132–128 (aromatic-C's), 102.1 (C-1), 74.3 (C-3), 72.3 (C-5), 69.8 (C-2), 67.4 (C-4), 62.9 (C-6), 56.9 (OMe).

Methyl 2,3,4,6-tetrakis(*O*-(*p*-bromobenzoyl))-β-D-glucopyranoside (38): CI-MS 955 $(M + 29)^+$, 927 $(M + 1)^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 8.002–7.432 (m, 16, aromatic-H's), 5.827 (dd, 1, J = 9.56 and 9.56, 3-H), 5.629 (dd, 1, J = 9.56 and 9.56, 4-H), 5.471 (dd, 1, J = 9.56 and 7.72, 2-H), 4.748 (d, 1, J = 7.72, 1-H), 4.643 (dd, 1, J = 12.13 and 2.94, 6-H), 4.427 (dd, 1, J = 12.13 and 4.47, 6′-H), 4.285–4.198 (m, 1, 5-H), 3.526 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.4 and 164.3 (4 C=O's), 132–128 (aromatic-C's), 101.9 (C-1), 73.2 (C-3), 71.9 (C-2,5), 70.0 (C-4), 63.2 (C-6), 57.0 (OMe).

Methyl 2,3,4,6-tetrakis(*O*-(*p*-bromobenzoyl))-α-D-glucopyranoside (39): CI-MS 927 $(M + 1)^+$, 895 $(M - OMe)^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 8.002–7.438 (m, 16, aromatic-H's), 6.105 (dd, 1, J = 9.93 and 9.93, 3-H), 5.621 (dd, 1, J = 9.93 and 9.93, 4-H), 5.280 (dd, 1, J = 9.93 and 3.68, 2-H), 5.215 (d, 1, J = 3.68, 1-H), 4.606 (dd, 1, J = 11.77 and 2.57, 6-H), 4.382 (dd, 1, J = 11.77 and 4.36, 6′-H), 4.340 (m, 1, 5-H), 3.498 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.2, 164.9, and 164.4 (4 C=O's), 132–127 (aromatic-C's), 96.9 (C-1), 71.8 (C-3), 70.6 (C-2), 69.7 (C-4), 67.3 (C-5), 63.0 (C-6), 55.6 (OMe).

Methyl 2,3,4,6-tetrakis(*O*-(*p*-bromobenzoyl))-β-D-galactopyranoside (40): CI-MS 895 $(M - OMe)^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.960–7.368 (m, 16, aromatic-H's), 5.942 (br d, 1, J = 3.31, 4-H), 5.716 (dd, 1, J = 10.30 and 7.72, 2-H), 5.563 (dd, 1, J = 10.30 and 3.31, 3-H), 4.746 (d, 1, J = 7.72, 1-H), 4.691 (dd, 1, J = 10.30 and 6.25, 6-H), 4.445–4.293 (m, 2, 5-H, 6′-H), 3.603 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.6, 165.3, and 165.0 (4 C=O's), 132–128 (aromatic-C's), 102.4 (C-1), 72.0 (C-3), 71.2 (C-5), 70.0 (C-2), 68.4 (C-4), 62.1 (C-6), 57.2 (OMe).

Methyl 2,3,4,6-tetrakis(*O*-(*p*-bromobenzoyl))-α-D-galactopyranoside (41): CI-MS 927 $(M + 1)^+$, 895 $(M - OMe)^+$; ^{1}H NMR ($CDCl_3$, 250 MHz) 7.957–7.363 (m, 16, aromatic-H's), 6.015 (br s, 1, 4-H), 5.989 (dd, 1, J = 10.29 and 3.31, 3-H), 5.667 (dd, 1, J = 10.29 and 3.31, 2-H), 5.325 (d, 1, J = 3.31, 1-H), 4.642–4.228 (m, 3, 5-H, 6-H's), 3.502 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.1, 164.8 and 164.6 (4 C=O's), 132–128 (aromatic-C's), 97.5 (C-1), 69.4 and 69.2 (C-3/C-2), 68.5 (C-4), 66.6 (C-5), 62.4 (C-6), 55.6 (OMe).

Methyl 2,3,4,6-tetrakis(*O*-(*p*-bromobenzoyl))-α-D-mannopyranoside (42): CI-MS 927 $(M + 1)^+$, 895 $(M - OMe)^+$; ^{1}H NNR ($CDCl_3$, 250 MHz) 7.950–7.407 (m, 16, aromatic-H's), 5.993 (dd, 1, J = 9.93 and 9.93, 4-H); 5.865 (dd, 1, J = 9.93 and 2.94, 3-H), 5.671 (dd, 1, J = 2.94 and 1.84, 2-H), 4.983 (d, 1, J = 1.84, 1-H), 4.762 (dd, 1, J = 12.14 and 2.57, 6-H), 4.512–4.219 (m, 2, 5-H, 6′-H), 3.546 (s, 3, OMe); ^{13}C NMR ($CDCl_3$) 165.2, 164.7, and 164.5 (4 C=O's), 132–127 (aromatic-C's), 98.5 (C-1), 70.4 and 70.1 (C-3/C-2), 68.5 (C-5), 67.2 (C-4), 62.9 (C-6), 55.6 (OMe).

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Registry No. 1, 80326-06-3; **2**, 80326-07-4; **3**, 80326-08-5; **4**, 80326-09-6; **5**, 80326-10-9; **6**, 80326-11-0; **7**, 80326-12-1; **8**, 80326-13-2; **9**, 80326-14-3; **10**, 80326-15-4; **11**, 80326-16-5; **12**, 80339-88-4; **13**, 80326-17-6; **14**, 80326-18-7; **15**, 80326-19-8; **16**, 80326-20-1; **17**, 80326-21-2; **18**, 80326-22-3; **19**, 80326-23-4; **20**, 80326-24-5; **21**, 80326-25-6; **22**, 80326-26-7; **23**, 80326-27-8; **24**, 80339-89-5; **25**, 80326-28-9; **26**, 80326-29-0; **27**, 80326-30-3; **28**, 78950-12-6; **29**, 78950-13-7; **30**, 78966-81-1; **31**, 78950-14-8; **32**, 78950-15-9; **33**, 78966-82-2; **34**, 78950-16-0; **35**, 78950-17-1; **36**, 78950-18-2; **37**, 78950-19-3; **38**, 78950-20-6; **39**, 78950-21-7; **40**, 78950-22-8; **41**, 78950-23-9; **42**, 78950-24-0; I, 18031-51-1; II, 50694-98-9; III, 50694-97-8; IV, 4201-66-5; **a**, 4064-06-6; **b**, 35526-05-7; **c**, 23392-30-5; **d**, 28542-03-2; **e**, 80326-31-4; **f**, 53685-11-3; **g**, 53008-63-2; methyl α-D-glucopyranoside, 97-30-3; methylsulfinyl anion, 80326-32-5; *p*-bromobenzoyl chloride, 586-75-4; D-galactose, 59-23-4; methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside, 604-70-6.

Oxidation of Mandelic Acid by Fenton's Reagent[1]

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Abstract: Mandelic acid forms a stable 1:1 complex with Fe^{2+} at pH 1–3. Its oxidation by H_2O_2 and $S_2O_8^{2-}$ has been investigated in the hope of detecting intramolecular oxidation–reduction of any intermediate Fe^{IV} species, rather than the usual hydroxyl radical process. Products are benzaldehyde and hydroxymandelic acids, consistent with either, but added hydroxyl radical traps—acetone or crotonic acid—are able to intercept only about half of the reaction. However, they reduce yields of benzaldehyde but not hydroxymandelic acids, and it is concluded that the balance of the reaction involves cage reactions of newly formed hydroxyl radicals rather than a high-valence iron species.

Reactions between oxygen or peroxides and organic substrates catalyzed by transition-metal ions are of great importance in both technology and biochemistry. A critical question in understanding their mechanisms is the nature of the "primary oxidant" which

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