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Oligosaccharide microscale analysis by circular dichroic spectroscopy: Reference spectra for chromophoric D-fructofuranoside derivatives

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ABSTRACT

The microscale analytical method that is being developed in this group for the structure determination of oligosaccharides yields monosaccharide derivatives bearing two types of chromophores suitable for exciton-coupling, namely, 4-bromobenzoate (λ_{max} 245 nm) and 4-methoxycinnamate (λ_{max} 311 nm). Comparison of the circular dichroic (CD) curves of these subunits to those in the reference library allows for the determination of the sugar identities, linkage positions, and the absolute configurations. The 32 possible derivatives of methyl α- and β-D-fructofuranosides bearing four chromophores were prepared and their CD spectra recorded. These data serve to extend the CD library, which already encompasses pyranoside derivatives with the *gluco-*, *galacto-*, and *manno*-configurations, and extend the utility of this methodology to the analysis of fructose-containing oligosaccharides.

INTRODUCTION

Methylation analysis has been the standard method for obtaining the linkage information in oligosaccharides and involves GLC–MS measurement of partially methylated alditol acetates[1]. This linkage analysis generally follows a sugar component analysis, and additional analysis is necessary to determine the absolute configuration of the monosaccharides. The methylation analysis involves comparison of retention times of the unknown derivatives to those of a large number of authentic samples, which must be prepared synthetically.

An alternative strategy for sugar component and linkage analysis is based upon circular dichroic spectroscopy (CD) of monosaccharide fragments derivatized with exciton-coupling chromophores, a method currently under development in our laboratory[2]. This method employs the strongly absorbing chromophores 4-bromo-

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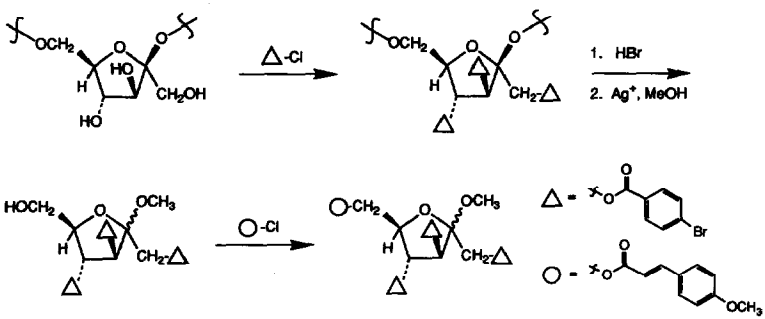
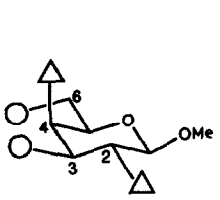
benzoate (λ_{max} 245 nm, ε 19 500) and 4-methoxycinnamate (λ_{max} 311 nm, ε 24 000) to differentially tag the hydroxyl groups that are free and those involved in glycosidic linkages. The HPLC purification of the monosaccharide components followed by UV (which gives the ratio of the two chromophores) and CD analysis allow for the identification of the sugar and its linkage pattern.

Previous work on this method focussed on the pyranoside derivatives of sugars (with the *gluco-*, *galacto-*, and *manno*-configurations)[3], and successful, although preliminary, applications to oligosaccharide analysis have been reported[2,4]. We here extend this methodology to the analysis of oligosaccharides containing fructofuranose units. Fructose is commonly found in many oligosaccharides in plants, which biosynthesize them by linking monosaccharide units to sucrose [α-D-Glc$p$-(1 ↔ 2)-β-D-Fru$f$]. Next to sucrose, α-D-galactosides of sucrose such as raffinose, lychnose, and stachyose are the most commonly found oligosaccharides in plants. Another class of oligosaccharides are the fructans[5], which incorporate multiple fructose units and are classified based on their various linkage patterns. They are isolated not only from plants but also from algae[6] and bacterial media[7]. These oligosaccharides have diverse functions in these organisms ranging from energy storage and structural support to recognition elements. In addition, many fructose-containing oligosaccharides are important commercially as dietary products and are produced industrially[8]. Methods for structural analysis are, therefore, important for the study and characterization of these oligosaccharides. Methylation analysis has been used for such studies; however, a chiroptical alternative of this methodology was believed to be a valuable tool for the analysis of fructose-containing oligosaccharides, since determination of glycosidic linkages and sugar identity involves only the comparison with CD spectra, and requires no authentic samples.

One of the possible schemes for the analysis of such oligosaccharides involves derivatization of the initially free hydroxyl groups with the 4-bromobenzoate chromophore, cleavage of the glycosidic bonds and derivatization of the liberated hydroxyl groups with the 4-methoxycinnamate chromophore (Scheme 1). The



Scheme 1. A possible cleavage–derivatization scheme.



2,3/ △ ○
2,4/ △ △
2,6/ △ ○
3,4/ ○ △
3,6/ ○ ○
4,6/ △ ○

calcd CD ≈ obsd CD

Fig. 1. Additivity principle: The summation of the six pairwise interactions of the basis set CD spectra yields a calculated CD spectrum that agrees well with the experimentally observed CD spectrum.

resulting fragments are separated by HPLC, and their CD curves are compared with those in the CD library. Their structures are unambiguously assigned by these comparisons in conjunction with their UV data and, if needed, their MS and chromatographic data.

In the pyranoside sugars (including deoxy, aminodeoxy, and *N*-acetylaminodeoxy sugars), the CD spectra covering the range of 220–360 nm are predicted with good accuracy by the summation of the six constituent pairwise interactions. For example, the CD spectrum of methyl β-D-galactopyranoside 2,4-bis(*p*-bromobenzoate)-3,6-bis(*p*-methoxycinnamate) (GalBCBC) can be represented[9] by the summation of the six interacting pairs of chromophores as shown in Fig. 1. These interacting pairs are taken from a CD library (called basis sets)[3a] containing the spectra of all 72 dichromophoric derivatives of methyl α-D-gluco-, galacto-, and manno-pyranosides.

The fact that the pairwise additivity principle holds for the pyranoside series is attributable to the conformational rigidity of the pyranose rings that do not vary greatly with the substitution pattern. However, because of the greater conformational flexibility exhibited by furanose ring systems[10,12], we questioned the applicability of this principle to the fructofuranoside systems. We therefore prepared all 32 fructofuranoside derivatives and recorded their CD spectra, as described next.

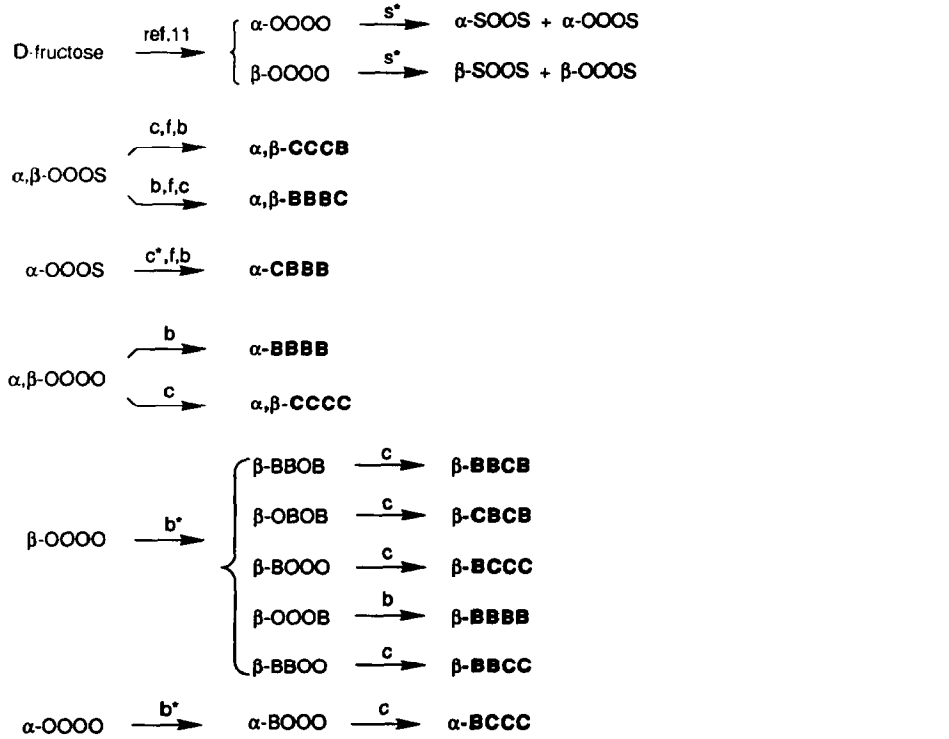
RESULTS AND DISCUSSION

Compounds and terminology.—The tetrachromophoric derivatives of methyl fructofuranoside (2 B_4, 2 C_4, 8 B_3C, 8 C_3B, and 12 B_2C_2) were prepared as summarized in Scheme 2. The 4-bromobenzoate chromophore is symbolized by (B), the 4-methoxycinnamate chromophore by (C), the underivatized hydroxyl group by (O) and the *tert*-butyldimethylsilyloxy group by (S). The fructofuranoside derivatives are abbreviated by the anomeric configuration followed by the chromophores at positions C-1, C-3, C-4, and C-6. The methyl α- and β-D-fructofuranosides were prepared from D-fructose by a literature procedure[11]. Selective *O*-silylation afforded the 1,6-bis-TBDMS and 6-mono-TBDMS intermediates, which were transformed to the tetrachromophoric derivatives by a combination of

full and partial acylation steps, and desilylation reactions. These compounds were purified by HPLC and characterized by ^{1}H NMR, UV, and MS.

Circular dichroic spectra.—The CD spectra of these compounds were measured and then found to be highly characteristic for each substitution pattern (Fig. 2). The wavelengths and $\Delta\varepsilon$ values of the extrema are given in Table I.

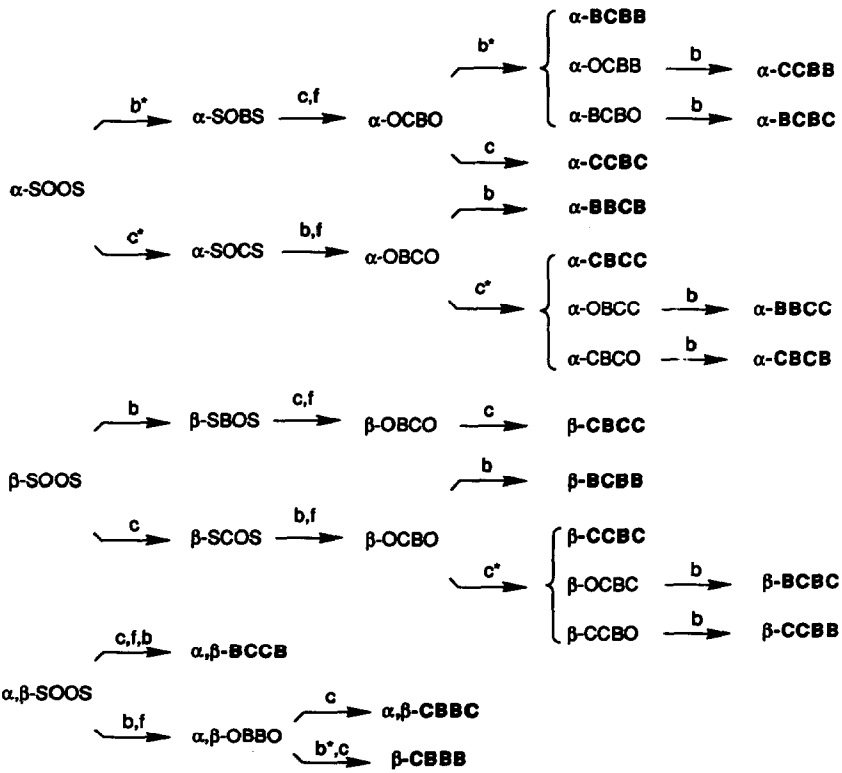
For the interpretation of the observed CD spectra, additional information about the solution conformations of these fructofuranoside derivatives is helpful. The conformational interconversions of furanose ring-containing systems have been described to occur on a circle of 10 envelope (E) and 10 twist (T) conformers, named the pseudorotational itinerary[12]. The envelope conformation disposes four ring atoms on a plate with the fifth atom displaced out of the plane. In the twist conformation, the three contiguous atoms lie on a plane with the remaining two disposed above and below the plane. The superscripted and subscripted indicators denote the atoms that lie above and below the plane of the ring, respectively. The β-D-fructofuranose unit of sucrose and methyl β-D-fructofuranoside has been recently reported to exist in the $^4T_5$–E_5 conformations[13]. Furthermore, the tetraacetate derivatives of methyl α-D-fructofuranoside and methyl β-D-fructofuranoside



Scheme 2. Preparation of the 32 fructofuranoside tetrachromophoric derivatives: s*, TBDMSCl, imidazole, DMF; b, 4-BrBzCl, AgOTf, DMAP, CH_2Cl_2-py (5:1); b*, 4-BrBzCl, py; c, 4-MeOCinnCl, AgOTf, DMAP, CH_2Cl_2-py (5:1); c*, 4-MeOCinnCl, py; f, py-HF·py$_x$ (5:1).

have been reported to exist roughly in the ${}^{0}E$–${}^{0}T_{2}$ and ${}^{4}T_{3}$–${}^{4}E$ conformations, respectively[14]. Because conformational changes are likely to be introduced in the ring with derivatization, the latter conformations may be more probable for the methyl fructofuranoside derivatives.

NMR spectra and conformations.—The ^{1}H NMR data, recorded in chloroform-*d*, (see Experimental) show that all 16 α-fructofuranoside derivatives display consistently small $J_{3,4}$ values, whereas the 16 β-fructofuranoside derivatives show large values (Table II; see also Fig. 4 later). These coupling constants were comparable to values obtained from measurements in acetonitrile-d_3. The $J_{4,5}$ and $J_{5,6}$ values for the two anomers also lie within a narrow range for each anomeric series. These values, which depend on the dihedral angles of the respective vicinal ring protons, and thus the conformation of the furanose ring, suggest that the α anomers all possess similar conformations or conformational distributions while the β anomers all possess a conformation different from that of α. The small $J_{3,4}$ values for the α anomers are consistent with a quasiaxial to eclipsed disposition of the C-3 and C-4 acyloxy groups, while the large $J_{3,4}$ values for β anomers suggest a quasiequatorial arrangement of these groups.



Scheme 2 (continued).

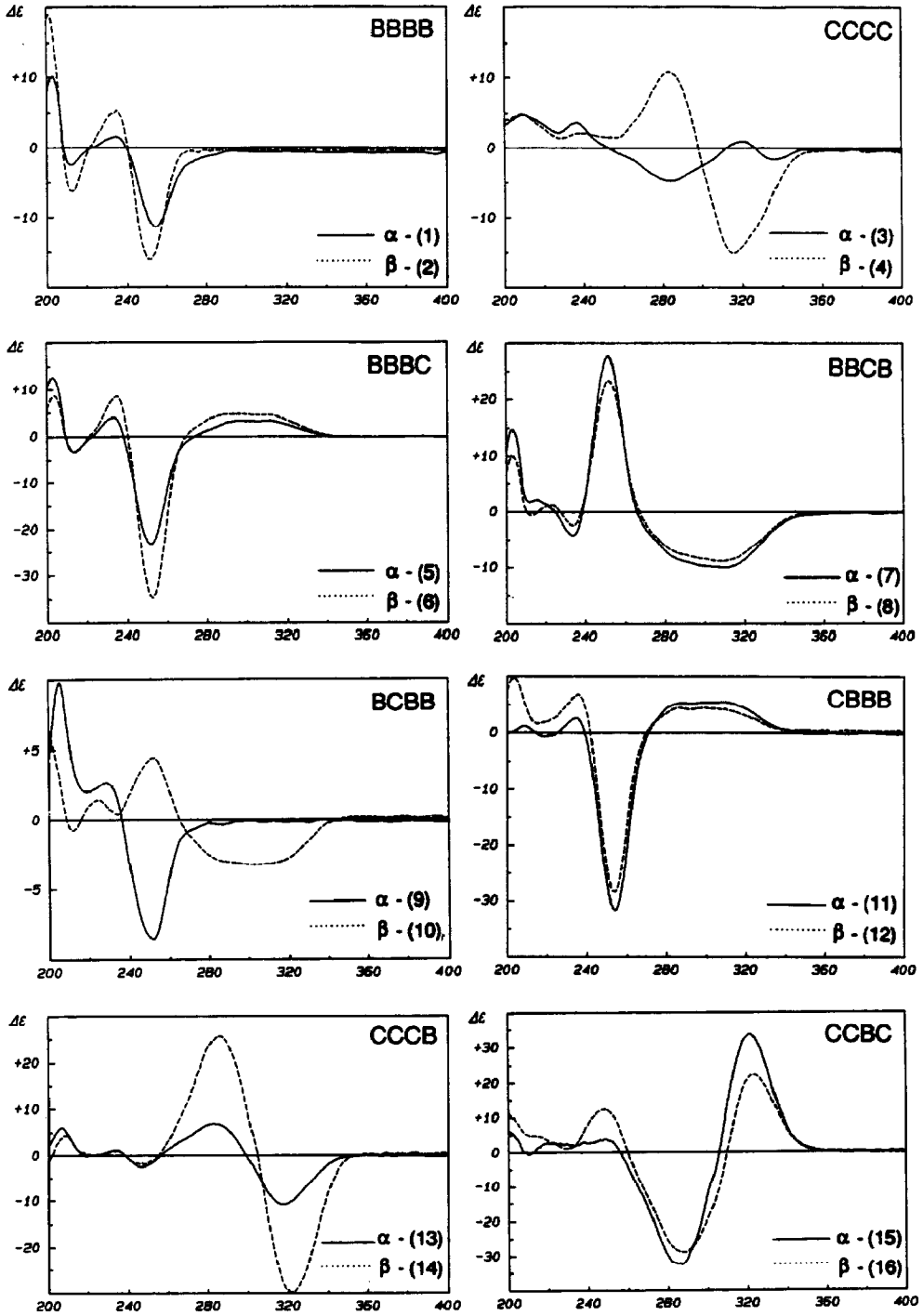


Fig. 2. The CD spectra of the 32 fructofuranoside tetrachromophoric derivatives in acetonitrile.

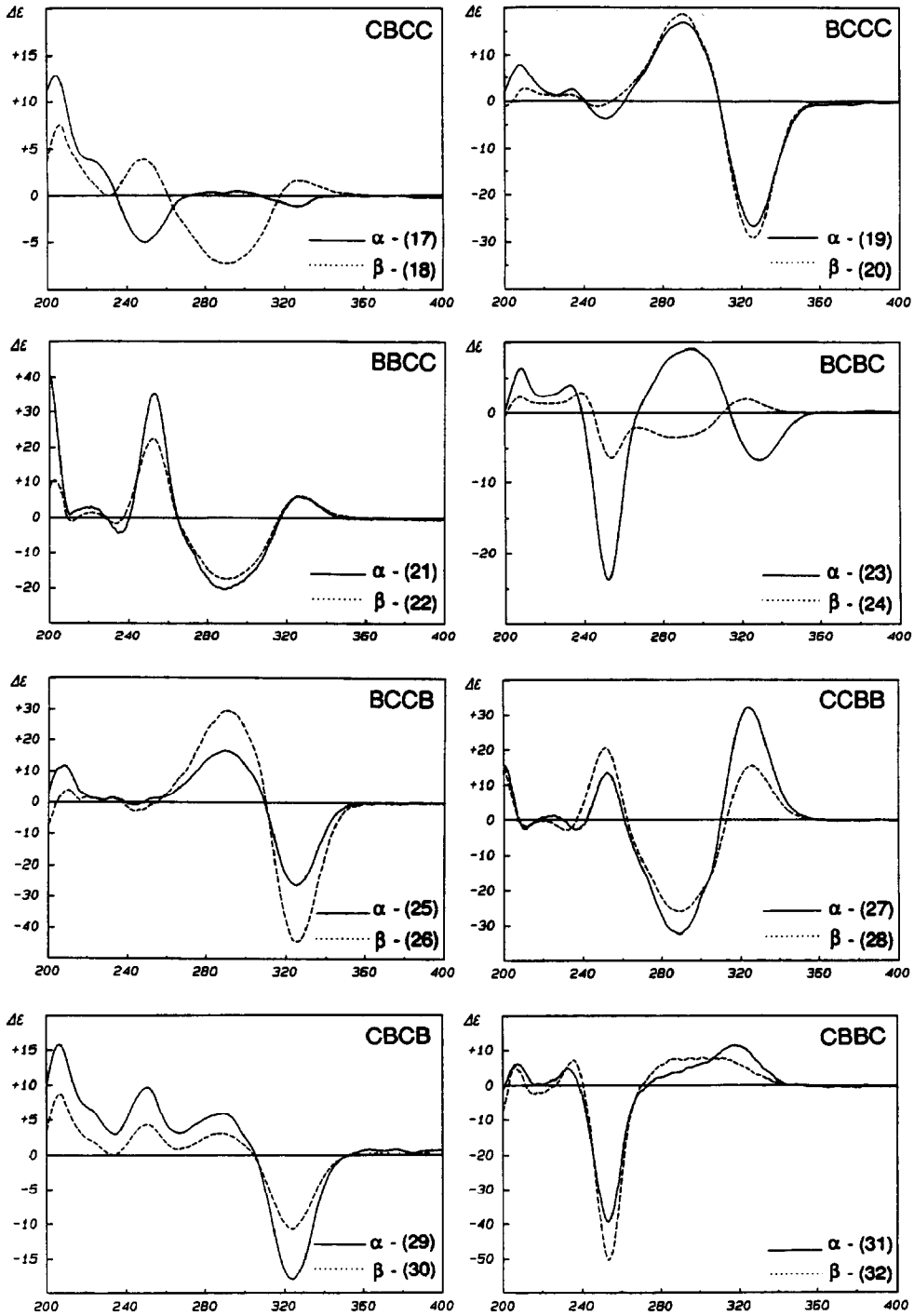


Fig. 2 (continued).

TABLE I

The observed CD data for the fructofuranoside derivatives in acetonitrile

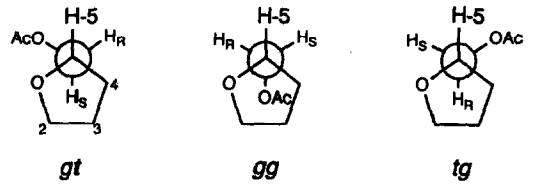
Compound	$[\lambda_{extr}(nm)/\Delta\varepsilon]$
1	203(+10.1), 212(−2.5), 234(+1.6), 254(−11.3)
2	202(+18.9), 212(−6.4), 234(+5.6), 252(−16.8)
3	209(+4.8), 236(+3.7), 284(−4.7), 320(+1), 336(−1.6)
4	209(+4.9), 239(+2.2), 283(+10.9), 316(−15)
5	203(+12.6), 213(−3.8), 234(+3.9), 252(−23), 296(+3.3), 312sh(+3.2)
6	204(+8), 213(−3.3), 235(+8.5), 253(−34.5), 296(+4.8), 309sh(+4.6)
7	203(+14.7), 215sh(+1.9), 234(−4.1), 252(+27.7), 309(−10)
8	203(+9.9), 223(+1.2), 234(−2.3), 252(+23.4), 308(−8.9)
9	229(+2.7), 252(−8.5)
10	225(+1.4), 252(+4.5), 311(−3.3)
11	209(+1.2), 218(−0.7), 235(+2.6), 254(−31.6), 288sh(+5.4), 309(+5.6)
12	236(+6.9), 254(−28.4), 285(+4.5), 308sh(+4.1)
13	233(+1.2), 247(−2.4), 283(+6.9), 317(−10.8)
14	234(+0.9), 246(−1.8), 286(+25.5), 322(−29.6)
15	223(+2.9), 249(+3.9), 287(−32.4), 322(+33.8)
16	214sh(+4.7), 249(+12.3), 287(−28.8), 324(+22.3)
17	222sh(+3.7), 249(−5), 296(+0.5), 326(−1.1)
18	249(+3.8), 290(−7.2), 328(+1.6)
19	236(+2.8), 249(−4), 291(+16.9), 328(−26.4)
20	233sh(+1.3), 247(−1.2), 290(+18.6), 326(−29)
21	221(+3.1), 235(−4.3), 253(+35.5), 289(−20.3), 326(+6.3)
22	222(+1.4), 233(−1.6), 253(+22.6), 290(−17.2), 327(+6.2)
23	233(+4), 252(−23.6), 295(+9.2), 329(−6.6)
24	239(+2.9), 254(−6.3), 285(−3.5), 323(+2)
25	208(+11.8), 233(+1.8), 244(−0.8), 290(+16.7), 326(−26.2)
26	211(+4), 232(+1.4), 243(−2.8), 289(+29.6), 326(−44.2)
27	210(−2.5), 225(+1.4), 236(−2.8), 252(+13.5), 289(−32.2), 325(+32.2)
28	232(−2.8), 252(+20.6), 289(−25.8), 326(+15.5)
29	207(+15.8), 221sh(+6.8), 251(+9.7), 289(+5.9), 324(−18)
30	207(+8.8), 221sh(+2.3), 251(+4.3), 288(+3.1), 324(−10.6)
31	234(+4.5), 253(−38.3), 302sh(+6), 318(+11.4)
32	218(−2.4), 236(+6.8), 254(−48.8), 291sh(+7.5), 311(+7.6)

The orientations of the acyloxymethyl groups about the furanose ring can also be inferred from the ^{1}H NMR data. The large difference in chemical shifts of the two H-1 signals for the α anomer ($\Delta\delta_{ave} = 0.50$ ppm) suggests a conformation in which one proton (possibly *pro-R*) lies closer to and is deshielded by the C-3 acyloxy group. The β anomers show every small chemical-shift differences for the two H-1 signals ($\Delta\delta_{ave} = 0.09$ ppm) since the C-3 acyloxy group lies on the opposite

TABLE II

^{1}H NMR coupling constants (Hz)

	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
α Derivatives	1.3–1.5	4.8–5.0	3.0–3.6/4.1–4.7
β Derivatives	6.9–7.2	5.4–6.1	3.6–4.3/6.4–6.7



Expected values:

gt	gg	tg
$J_{H\text{-}5,HR}$ ~3.3 Hz	$J_{H\text{-}5,HR}$ ~2.6 Hz	$J_{H\text{-}5,HR}$ ~10.7 Hz
$J_{H\text{-}5,HS}$ ~10.8 Hz	$J_{H\text{-}5,HS}$ ~1.0 Hz	$J_{H\text{-}5,HS}$ ~4.8 Hz

α anomer:

$J_{H\text{-}5,HR}$ ~3.3 Hz (obsd values)→ 0.31 (*gt*)/0.63 (*gg*)/0.06 (*tg*)
$J_{H\text{-}5,HS}$ ~4.4 Hz

β anomer:

$J_{H\text{-}5,HR}$ ~3.9 Hz (obsd values)→ 0.53 (*gt*)/0.36 (*gg*)/0.11 (*tg*)
$J_{H\text{-}5,HS}$ ~6.6 Hz

Fig. 3. The three staggered conformations of the C-6 acyloxymethyl group are shown with their coupling constants for the *pro-R* and *pro-S* H-6 atoms. Gauche (*g*)/trans (*t*) designations (the acyloxy group disposed gauche to ring oxygen/anti to C-4) are used. The conformational distributions are calculated based on averaged vicinal coupling constants.

side of the ring. The two diastereotopic H-6 atoms show small chemical-shift differences ($\Delta\delta_{ave} = 0.20$ ppm for α, $\Delta\delta_{ave} = 0.15$ ppm for β). As shown in Fig. 3, the calculations[15] using the averaged $J_{5,6}$ values for the two H-6 atoms lead to the populational distribution of the three fully staggered rotamers (with the expected coupling constants[16] shown) about C-5 and C-6. These fructofuranoside derivatives exhibit coupling constants for the ring protons that are similar to those reported for methyl fructofuranoside tetraacetate and, therefore, probably share the same ring conformations. In Fig. 4 are shown the ${}^0E$ and the ${}^4E$ ring conformations for the α and β anomers, respectively, representing the probable averaged conformations of these derivatives.

Chromophore interactions.—Most of the α and β anomers shown in Fig. 2 exhibit strong Cotton effects ($|\Delta\varepsilon| > \sim 20$) and show CD spectra with similar shapes but with different intensities. The similarity in shape apparently arises from the contributions of the same individual pairwise interactions possessing the same signs but different magnitudes that arise from differences in conformations between the two anomers. For those derivatives with weak $\Delta\varepsilon$ values ($< \sim 10$), the CD spectra for the two anomers are very different, i.e., CCCC (**3**, **4**), BCBB (**9**, **10**), CBCC (**17**, **18**), and BCBC (**23**, **24**). In the absence of strong Cotton effects (possibly due to the cancellation of some of the individual pairwise interactions) the conformational differences between the anomers have a greater influence on the shapes of the CD spectra.

The relative orientations of the chromophores can be determined from the signs and magnitudes of the individual CD pairwise interactions. The pairwise interactions of the 4-methoxycinnamate chromophores observable in the ~270–350 nm

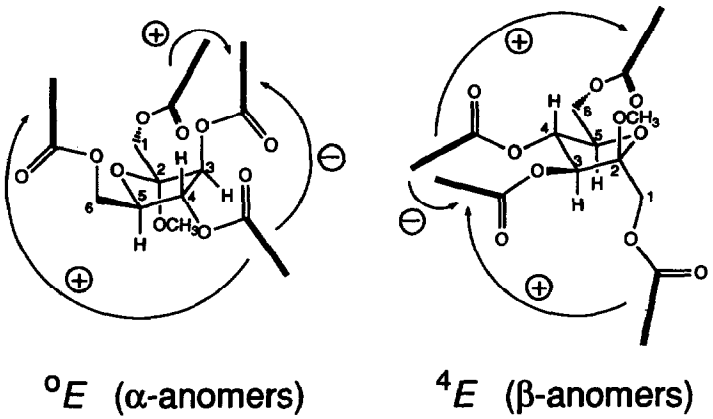


Fig. 4. The possible averaged conformations for the α- and β-fructofuranoside derivatives. The long-axis electric transition moments (^1L_a) are represented by bold lines, and the chirality of the interacting pairs of chromophores is designated as positive (+) or negative (−).

region of the CD spectra is useful for analysis because it is free from overlapping signals from the 4-bromobenzoate chromophore (centered at λ 245 nm). For example, the strong and negative interaction between chromophores attached to C-3 and C-4 (3,4-dichromophoric interaction) is evident in α- and β-BCCB (**25**, **26**). The 1,3-interaction yields a strong but positive CD that is observable for α- and β-CCBB (**27**, **28**). The 4,6-interaction is also positive but is weaker as seen with α- and β-BBCC (**21**, **22**). These data are consistent with the conformations shown in Fig. 4. The remaining interactions are weaker and less diagnostic: the 1,4-interactions appear to be negative as seen with α- and β-CBCB (**29**, **30**), while α-BCBC (**23**) and β-BCBC (**24**) show opposite CDs. The 1,6-interactions are very weak and not detectable, for example, in α- and β-CBBC (**31**, **32**).

The structural determination of the monosaccharide derivatives obtained by HPLC after the cleavage–derivatization sequence (Scheme 1) involves, initially, UV measurements to determine the derivative class (B_4, B_3C, B_2C_2, BC_3, or C_4) to which the compound belongs. The 4-bromobenzoate and 4-methoxycinnamate chromophores possess different λ_{max} values (245 and 311 nm, respectively), and thus the different ratio of these chromophores give different $Abs_{(245)}/Abs_{(311)}$ values. These values were determined for each derivative and are summarized in Table III.

The CD spectrum of the unknown derivative is measured and is compared with the reference CD spectra in the library for the pyranose and furanose sugars within the same class. The best match is used to assign the structure[2]. To allow for an unambiguous assignment, it is important that these CD reference spectra be unique. The CD spectra of the fructofuranoside derivatives were compared in detail with those of gluco-, galacto-, and manno-pyranoside derivatives within the same chromophoric class. The majority of them were very different and easily

TABLE III

Absorption ratios for each derivative type

Class	$Abs_{(245)}/Abs_{(311)}$
B_4	∞
B_3C	2.20–2.60
B_2C_2	0.71–0.88
BC_3	0.31–0.34
C_4	0.09

distinguishable. However, some of them showed similarities, and these are displayed in Fig. 5.

A few comments on these figures are given next (see also Fig. 2). Numbers in parentheses denote the total number of hexopyranoses[2] and fructofuranoses belonging to the specific class. The most-intense peaks occur in the 220–380 nm region of the CD spectra, and this region is used for comparative studies; the 200–220 nm region is less diagnostic because the weaker signal (resulting from the overlap of other transitions of opposite sign) and the lower S/N ratio that make the accurate estimation of $\Delta\varepsilon$ values difficult. In comparing similar spectra, the ratio of the extrema as well as their wavelengths and intensities should be taken into account. The CD spectra of α- and β-glycopyranoside derivatives are very similar and are thus represented by one spectrum.

B_3C (20). Fig. 5. (a) The intensities of the 250 nm Cotton effects (CEs) allow for the differentiation of the derivatives except for **5** and GlcCBBB; however, these two differ in the shapes of the spectra at 220–240 nm.

(b) The spectra for **7** and **8** cannot be differentiated. Of the 20 cases belonging to this group, only GlcBBCB has a CD of similar shape, but differentiation is facile because of the strong 250 nm CE.

(c) Except for small differences in the 220–240 nm region, all three spectra are similar.

BC_3 (20). Fig. 5. (d and e) The spectra of the six compounds possessing similar shapes are compared. Compound **14** is readily distinguishable. The other three spectra in (d) that have less distinctive CD couplets require careful comparisons of both intensity and location of the extrema. Discrimination between **19**/**20** is not possible; however, the two are quite different from GlcBCCC and GlcCCCB.

(f) GalCCBC can be readily distinguished. Compounds **15** and **16** are distinguishable comparing the ratios of the positive CEs at 320/250 nm. However, **15** and GlcCCBC are difficult to differentiate.

B_2C_2 (30). Fig. 5. (g) The negative couplets of **25**/**26** show significant differences. The discrimination of **26** from ManBCCB is practically not possible; however, **26** and GlcBCCB are distinguishable from comparing the ratios of CEs at 320/290 nm.

(h) These four can be distinguished by precise measurements in the > 270 nm region.

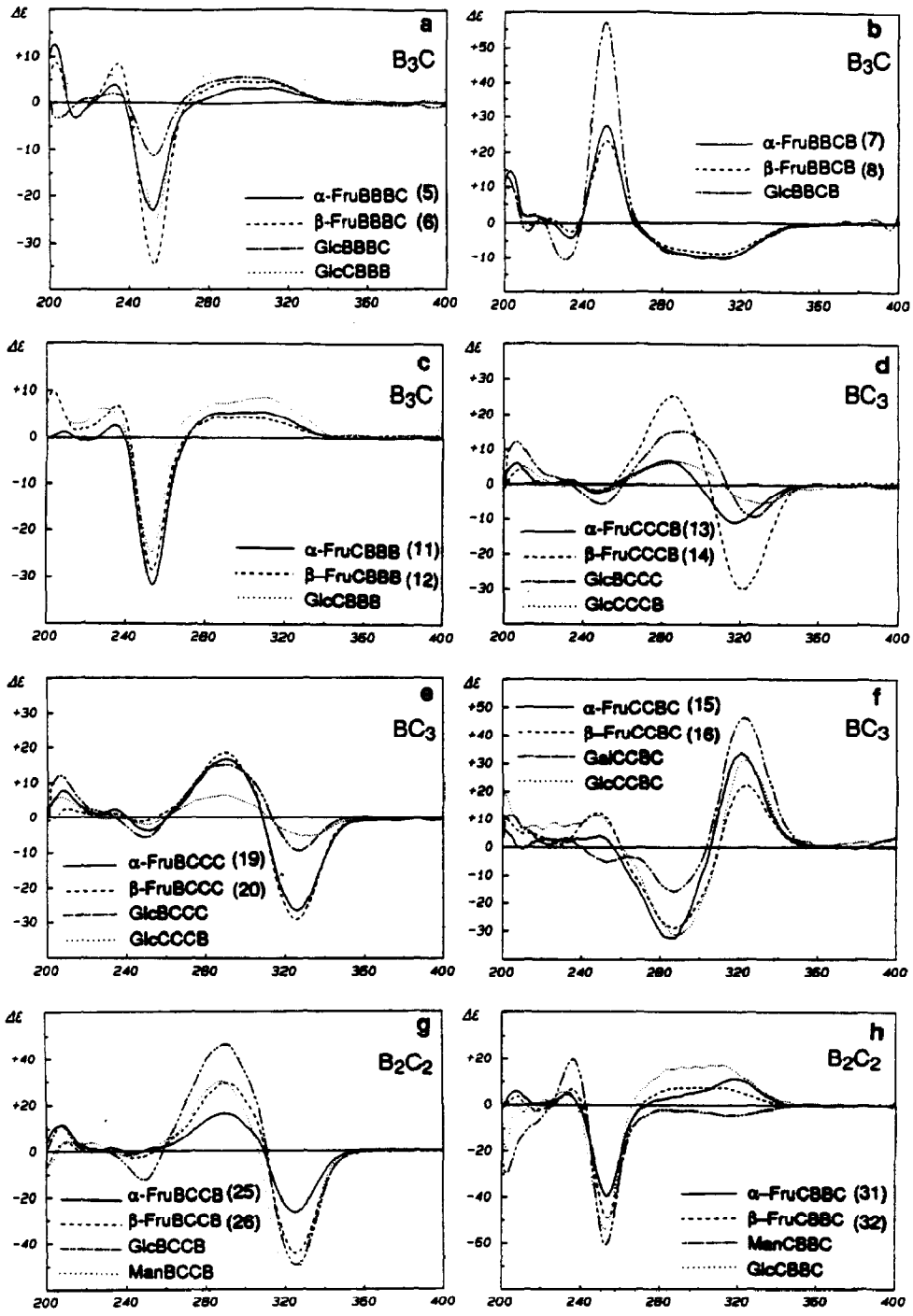


Fig. 5. Comparisons of the CD spectra (in acetonitrile) of the fructofuranoside and pyranoside derivatives in a given class that show similar spectral shape.

B_4 (5) and C_4 (5). The fructofuranoside derivatives **1/2** and **3/4** (see Fig. 2) can all be readily distinguished from each other as well as from the corresponding derivatives of the glucose, galactose, and mannose series[2].

Importantly, within a given class, all of the fructofuranoside derivatives, except for **6** and **11/12**, with different chromophore patterns can be readily differentiated. The linkage information for a given isolated fructofuranoside derivative can, therefore, be determined. As is evident from this analysis, few of the anomers with a given chromophoric arrangement possess very similar CD spectra; despite the ambiguity in assigning the anomeric configurations in these pairs, the desired information concerning the sugar identity, linkage positions, and absolute configuration can be obtained from the CD spectra. Most of spectra in Fig. 5 are distinguishable based on differences in shapes and intensities of the individual Cotton effects in the 245 and 311-nm region. Several of the fructofuranoside CD spectra are, however, very similar to those of pyranose sugars. For these cases, additional information such as HPLC retention times and MS fragmentation patterns is needed to make an unambiguous assignment.

Summary.—The 32 CD spectra of the tetrachromophoric fructose derivatives show highly characteristic CD spectra and, except for a few cases, are distinguishable from the spectra of the pyranoside derivatives. Together with the UV $Abs_{(245)}/Abs_{(311)}$ values, which indicates the ratio of the two different chromophores, these spectra are useful for assigning the identity and the linkage pattern of the fructose residue obtained after cleavage and derivatization. Some insight into the conformation of the derivatives was possible based on the analysis of the CD spectra and the ^1H NMR data. The tetrachromophoric derivatives can be detected at the nanomole level by CD spectroscopy and, in combination with an efficient derivatization–cleavage scheme, should provide a very effective methodology for the microscale analysis of oligosaccharides. Studies on the analysis of various fructose-containing sugars, such as fructans, are underway and will be reported in due course.

EXPERIMENTAL

General methods.—All intermediates and final products were characterized by ^1H NMR spectroscopy (Varian 200, 300, or 400 MHz) in $CDCl_3$ (referenced to 7.24 ppm). The final products were also characterized by low resolution (MS) and high resolution (HRMS) mass spectroscopies, measured on a Jeol JMS-DX303HF mass spectrometer. Significant fragments for MS are reported as follows: m/z and relative intensity. Purification was achieved by preparative TLC, run on E. Merck Silica Gel 60F glass plates (1.0-mm thick), or flash chromatography, using E. Merck Silica Gel 60 (230–400 mesh). High-performance liquid chromatography (HPLC) was used to purify the final products prior to UV and CD measurements. A Rainin HPLC system, equipped with a UV-vis spectrophotometer and controlled by a dynamax DA HPLC controller and data acquisition program, was

used. A normal-phase analytical silica column with a hexane–EtOAc elution system was used. The UV absorbance measurements were performed with a Perkin–Elmer Lambda 4B spectrophotometer to calculate the sample concentration and to obtain the A_{245}/A_{311} values. Acetonitrile solutions were prepared at concentrations of 5–15 μM, which were determined on the basis of the average 4-methoxycinnamate UV ε values, experimentally determined at 311 nm: mono, ε 24000; di, 45000; tri, 68000; tetra, 90000. For the tetra-4-bromobenzoate derivatives, an average value of ε 76400 at 245 nm was used. The CD measurements were made on the acetonitrile solutions in a 1 cm quartz cell, recorded in a Jasco J-720 spectropolarimeter utilizing four scans between 200 and 400 nm. An IBM-PC computer operated with the Jasco software was used to normalize all CD spectra to a concentration of 10 μM. Curve smoothing (DFT, discrete Fourier transform) and further CD data manipulations were carried out using a software developed in-house.

Dichloromethane and pyridine were distilled from CaH_2, and 4-dimethylaminopyridine was recrystallized from hexane–benzene. 4-Bromobenzoyl chloride was purified by dissolving in hexane–CH_2Cl_2 and evaporation. 4-Methoxycinnamoyl chloride was prepared from the acid and thionyl chloride (1.2 equiv) in refluxing benzene (2 h). Benzene and excess reagent were remove in vacuo, and distillation in a sublimation apparatus (140°C/13 Pa) afforded the pure acid chloride. Silver triflate was dried by several evaporations on a rotary evaporator with benzene in the dark followed by pumping under high vacuum.

The chromophoric derivatives were prepared directly from methyl α- and β-D-fructofuranosides or by way of the silylated intermediates. The primary hydroxyl groups (at C-1 and C-6) were selectively silylated over the secondary groups (at C-3 and C-4) with *tert*-butyldimethylsilyl chloride (TBDSMCl) to afford the bis-silyl intermediates. The C-6 position is less sterically hindered than the C-1 position and was selectively silylated to afford the mono-silyl intermediates. Full acylation was achieved via a silver-catalyzed acylation reaction with an excess of 4-bromobenzoyl chloride or 4-methoxycinnamoyl chloride in the presence of 4-dimethylaminopyridine (DMAP) as an acylation catalyst at room temperature or with slight heating. Desilylation was achieved by subjecting the silyl ether to dilute HF in pyridine at room temperature. Partial acylation was conducted without silver triflate at room temperature with stoichiometric amounts of the acyl chloride. Mono-acylation of the α-1,6-di-TBDMS intermediate occurred selectively at the C-4 position (presumably because of steric hindrance at the C-3 position located adjacent to the bulky C-1 silyloxy group) and occurred at the C-3 position for the β anomer. The representative reaction conditions are given for a few derivatives next.

Partial 4-bromobenzoylation of methyl β-D-fructofuranoside.—4-Bromobenzoyl chloride (20.0 mg) was added to a solution of methyl β-D-fructofuranoside (16.0 mg) in pyridine (1 mL) at 0°C. After 2 h of stirring at 0°C, the ice bath was removed, and the mixture was stirred at room temperature for 4 h. The reaction

was quenched with water, diluted with satd $NaHCO_3$ and extracted 4 times with EtOAc. The extracts were concentrated to dryness and purified by PTLC. The following compounds were isolated: β-BBOB (4.3 mg), β-OBOB (0.9 mg), β-BBOO (5.2 mg), β-OOOB (2.4 mg), and a mixture of β-OBOO and β-BOOO (8.1 mg). These partially acylated products were subsequently 4-methoxycinnamoylated to yield β-BBBB, β-BBCB, β-CBCB, and β-BBCC.

*Methyl 1,6-di-O-(*tert*-butyldimethylsilyl)-α- and β-D-fructofuranoside (α,β-SOOS) and methyl 6-O-(*tert*-butyldimethylsilyl)-α- and β-D-fructofuranoside (α,β-OOOS).* —To a solution of methyl β-D-fructofuranoside (130 mg, 0.67 mmol) and imidazole (136 mg, 2.0 mmol) in *N,N'*-dimethylformamide (DMF) (2 mL) at 0°C was added a solution of *tert*-butylchlorodimethylsilane (190 mg, 1.2 mmol) in DMF (1 mL) over 15 min. After 1.5 h of stirring at 0°C, the ice bath was removed and water was added. After 30 min, the mixture was diluted with more water extracted 4 times with EtOAc. The combined organic layers were dried ($MgSO_4$) and concentrated to give a crude oil, which was purified by silica gel column chromatography eluting with 5:1 hexane–EtOAc to EtOAc to afford the bis-silyl ether (0.19 g, 67%) and the mono-silyl ether (0.06 g, 30%). The α-derivatives were prepared similarly. ^{1}H NMR (200 MHz): (β-SOOS): δ 0.04, 0.05 (s, 6 H, $SiCH_3$), 0.86 (s, 18 H, Si^{t}Bu), 3.30 (s, 3 H, OCH_3), 3.8 (m, 4 H), 3.83–4.04 (m, 3 H). (β-OOOS): δ 0.06 (s, 6 H, $SiCH_3$), 0.86 (s, 9 H, Si^{t}Bu), 2.7 (br, 3 H, OH), 3.31 (s, 3 H, OCH_3), 3.76 (m, 4 H), 3.97 (m, 1 H), 4.06 (m, 1 H), 4.29 (m, 1 H). (α-SOOS): δ 0.04, 0.05 (s, 6 H, $SiCH_3$), 0.84 (s, 18 H, Si^{t}Bu), 3.30 (s, 3 H, OCH_3), 3.30 (m, 4 H), 3.77 (m, 1 H), 3.91 (br, 1 H), 4.02 (q, 1 H). (α-OOOS): δ 0.06 (s, 6 H, $SiCH_3$), 0.86 (s, 9 H, Si^{t}Bu), 3.0 (br, 3 H, OH), 3.31 (s, 3 H, OCH_3), 3.76 (m, 4 H), 3.95 (s, 1 H), 3.99 (m, 1 H), 4.06 (q, 1 H).

*Partial 4-bromobenzolation of methyl 1,6-di-O-(*tert*-butyldimethylsilyl)-α-D-fructofuranoside.* —4-Bromobenzoyl chloride (43.0 mg) was added to a solution of α-SOOS (82.8 mg) in pyridine (1 mL). The mixture was stirred at room temperature for 2 h and then quenched with water. The workup procedure is the same as that for partial bromobenzoylation of methyl β-D-fructofuranoside. The major product, α-SOBS (64.8 mg), along with two minor products, α-SBBS and α-SBOS, were isolated.

*Partial 4-bromobenzolation of methyl 1,6-di-O-(*tert*-butyldimethylsilyl)-β-D-fructofuranoside.* —4-Bromobenzoyl chloride (8.0 mg) was added to a solution of β-SOOS (15.0 mg) in pyridine (1 mL). The mixture was stirred at room temperature for 2 h and then quenched with water. The workup procedure is as above. The major product, β-SBOS (15.0 mg), and the minor product, β-SOBS (1.3 mg), were isolated.

Methyl 4-O-(4-bromobenzoyl)-3-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-OCBO). —4-Methoxycinnamoyl chloride (55.0 mg) was added to a mixture of α-SOBS (64.8 mg), silver triflate (55.0 mg), and DMAP (catalytic amount) in pyridine (1 mL). The mixture was stirred overnight at room temperature and then quenched with water. The workup procedure was the same as before. The product,

α-SCBS (53.2 mg), was purified by flash column chromatography and was desilylated as follows: The silyl ether was dissolved in HF–pyridine (0.1 ml) and pyridine (0.5 mL) and was stirred for 5 h at room temperature. The reaction was quenched with satd $NaHCO_3$ and extracted 3 times with EtOAc. The extracts were concentrated to dryness and purified by flash chromatography to afford the desired product (32.6 mg). This product was used to prepare α-BCBB, α-BCBC, α-CCBB, and α-CCBC.

*Methyl 3,4-di-*O*-(4-bromobenzoyl)-1,6-di-*O*-(4-methoxycinnamoyl)-α-*D*-fructofuranoside (α-CBBC).*—^{1}H NMR (400 MHz): δ 3.41 (s, 3 H, OCH_3), 3.81, 3.83 (s, 3 H, CinnOCH_3), 4.28 (d, 1 H, *J* 12.3 Hz, H-1), 4.40 (q, 1 H, H-5), 4.52 (dd, 1 H, H-6), 4.71 (dd, 1 H, *J* 12.0, 3.3 Hz, H-6), 4.73 (d, 1 H, *J* 12.3 Hz, H-1), 5.44 (dd, 1 H, *J* 4.8, 1.5 Hz, H-4), 5.71 (d, 1 H, *J* 1.5 Hz, H-3), 6.14, 6.15 (d, 1 H, *J* 16.0 Hz, alkenic), 6.85 (d, 4 H), 7.24, 7.38, 7.42, 7.57, 7.85, 7.92 (d, 2 H, aromatic), 7.55, 7.59 (d, 1 H, *J* 16 Hz, alkenic). FABMS: 878 (M^+, 1%), 847 ($M - OCH_3$, 28%). FABHRMS: 878.0585 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

*Methyl 3,4-di-*O*-(4-bromobenzoyl)-1,6-di-*O*-(4-methoxycinnamoyl)-β-*D*-fructofuranoside (β-CBBC).*—^{1}H NMR (400 MHz): δ 3.45 (s, 3 H, OCH_3), 3.82, 3.82 (s, 3 H, CinnOCH_3), 4.5 (m, 4 H), 4.59 (q, 1 H, H-5), 5.84 (dd, 1 H, *J* 6.8, 5.5 Hz, H-4), 5.93 (d, 1 H, *J* 6.9 Hz, H-3), 6.06, 6.28 (d, 1 H, *J* 16 Hz, alkenic), 6.84, 6.87, 7.18, 7.38, 7.50, 7.51, 7.86, 7.90 (d, 2 H, aromatic), 7.51, 7.63 (d, 1 H, *J* 16 Hz, alkenic). FABMS: 878 (M^+, 3%), 847 ($M - OCH_3$, 38%). HRFABMS: 847.0344 (calcd 847.0390 for $C_{40}H_{33}Br_2O_{12}$, $M - OCH_3$).

*Methyl 3,4,6-tri-*O*-(4-bromobenzoyl)-1-*O*-(4-methoxycinnamoyl)-α-*D*-fructofuranoside (α-CBBB).*—^{1}H NMR (400 MHz): δ 3.41 (s, 3 H, OCH_3), 3.81 (s, 3 H, CinnOCH_3), 4.26 (d, 1 H, *J* 12.3 Hz, H-1), 4.44 (q, 1 H, H-5), 4.64 (dd, 1 H, *J* 12.0, 4.7 Hz, H-6), 4.71 (d, 1 H, *J* 12.3 Hz, H-1), 4.82 (dd, 1 H, *J* 12.1, 3.4 Hz, H-6), 5.45 (dd, 1 H, *J* 5.0, 1.5 Hz, H-4), 5.71 (d, 1 H, *J* 1.5 Hz, H-3), 6.12 (d, 1 H, *J* 17.0 Hz, alkenic), 6.86, 7.35, 7.37, 7.47, 7.58, 7.73, 7.80, 7.90 (d, 2 H, aromatic), 7.53 (d, 1 H, alkenic). FABMS: 900 (M^+, 9%), 869 ($M - OCH_3$, 28%). FABHRMS: 899.9420 (calcd 899.9417 for $C_{38}H_{31}Br_3O_{11}$).

*Methyl 3,4,6-tri-*O*-(4-bromobenzoyl)-1-*O*-(4-methoxycinnamoyl)-β-*D*-fructofuranoside (β-CBBB).*—^{1}H NMR (300 MHz): δ 3.40 (s, 3 H, OCH_3), 3.82 (s, 3 H, CinnOCH_3), 4.48 (m, 4 H), 4.71 (dd, 1 H, *J* 11.3, 3.6 Hz, H-6), 5.85 (t, 1 H, *J* 6 Hz, H-4), 5.95 (d, 1 H, *J* 7.0 Hz, H-3), 6.05 (d, 1 H, *J* 16.0 Hz, alkenic), 6.83, 7.17, 7.84 (d, 2 H, aromatic), 7.52 (m, 7 H, aromatic + alkenic), 7.89 (d, 4 H, aromatic). FABMS: 900 (M^+, 3%), 869 ($M - OCH_3$, 25%). FABHRMS: 901.9383 (calcd 901.9396 for $C_{38}H_{31}Br^{79}{}_2Br^{81}O_{11}$).

*Methyl 1,3,4-tri-*O*-(4-bromobenzoyl)-6-*O*-(4-methoxycinnamoyl)-α-*D*-fructofuranoside (α-BBBC).*—^{1}H NMR (400 MHz): δ 3.41 (s, 3 H, OCH_3), 3.83 (s, 3 H, CinnOCH_3), 4.34 (d, 1 H, *J* 12.3 Hz, H-1), 4.42 (q, 1 H, H-5), 4.53 (dd, 1 H, *J* 12.2, 4.5 Hz, H-6), 4.72 (dd, 1 H, *J* 12.0, 3.3 Hz, H-6), 4.86 (d, 1 H, *J* 12.3 Hz, H-1), 5.44 (dd, 1 H, *J* 4.8, 1.4 Hz, H-4), 5.75 (d, 1 H, *J* 1.5 Hz, H-3), 6.16 (d, 1 H, *J* 15.9 Hz, alkenic), 6.86, 7.25, 7.40, 7.49, 7.57, 7.75, 7.80, 7.91 (d, 2 H, aromatic), 7.60 (d, 1 H,

J 15.9 Hz, alkenic). FABMS: 900 (M^+, 5%), 869 ($M - OCH_3$, 15%). FABHRMS: 899.9432 (calcd 899.9417 for $C_{38}H_{31}Br_3O_{11}$).

Methyl 1,3,4-tri-O-(4-bromobenzoyl)-6-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-BBBC).—^{1}H NMR (400 MHz): δ 3.46 (s, 3 H, OCH_3), 3.82 (s, 3 H, $CinnOCH_3$), 4.48 (m, 2 H), 4.58 (m, 3 H), 5.85 (dd, 1 H, *J* 6.9, 5.4 Hz, H-4). 5.93 (d, 1 H, 6.9 Hz, H-3), 6.28 (d, 1 H, *J* 15.9 Hz, alkenic), 6.87, 7.36, 7.38, 7.53, 7.72, 7.80, 7.83 (d, 2 H, aromatic), 7.63 (d, 1 H, *J* 15.9 Hz, alkenic). FABMS: 900 (M^+, 8%), 869 ($M - OCH_3$, 31%). FABHRMS: 901.9383 (calcd 901.9396 for $C_{38}H_{31}Br^{79}{}_2Br^{81}O_{11}$).

Methyl 1,6-di-O-(4-bromobenzoyl)-3,4-di-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-BCCB).—^{1}H NMR (400 MHz): δ 3.39 (s, 3 H, OCH_3), 3.82 (s, 6 H, $CinnOCH_3$), 4.28 (d, 1 H, *J* 12.2 Hz, H-1), 4.37 (q, 1 H, H-5), 4.63 (dd, 1 H, *J* 12.0, 4.3 Hz, H-6), 4.81 (d, 1 H, *J* 12.3 Hz, H-1), 4.82 (dd, 1 H, *J* 12.0, 3.1 Hz, H-6), 5.31 (dd, 1 H, *J* 4.8, 1.4 Hz, H-4), 5.66 (d, 1 H, *J* 1.2 Hz, H-3), 6.07, 6.34 (d, 1 H, *J* 16 Hz, alkenic), 6.88, 6.89, 7.29, 7.46, 7.48, 7.81, 7.92 (d, 2 H, aromatic), 7.53, 7.67 (d, 1 H, *J* 16 Hz, alkenic). FABMS: 878 (M^+, 9%), 847 ($M - OCH_3$, 28%). FABHRMS: 878.0583 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

Methyl 1,6-di-O-(4-bromobenzoyl)-3,4-di-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-BCCB).—^{1}H NMR (400 MHz): δ 3.41 (s, 3 H, OCH_3), 3.82, 3.83 (s, 3 H, $CinnOCH_3$), 4.41 (m, 1 H, H-5), 4.57 (m, 3 H), 4.69 (dd, 1 H, *J* 11.9, 4.1 Hz, H-6), 5.73 (dd, 1 H, *J* 7.0, 5.8 Hz, H-4), 5.83 (d, 1 H, *J* 7.0 Hz, H-3), 6.25, 6.30 (d, 1 H, *J* 16.0 Hz, alkenic), 6.88 (d, 4 H, aromatic), 7.40, 7.43, 7.45, 7.55, 7.88, 7.94 (d, 2 H, aromatic), 7.55, 7.62 (d, 1 H, alkenic). FABMS: 878 (M^+, 1%), 847 ($M - OCH_3$, 8%). FABHRMS: 878.0551 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

Methyl 1-O-(4-bromobenzoyl)-3,4,6-tri-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-BCCC).—^{1}H NMR (300 MHz): δ 3.39 (s, 3 H, OCH_3), 3.76, 3.79, 3.82 (s, 3 H, $CinnOCH_3$), 4.30 (m, 2 H, H-5 + H-1), 4.47, 4.71 (dd, 1 H, H-6), 4.82 (d, 1 H, *J* 12.4 Hz, H-1), 5.28 (dd, 1 H, *J* 5.0, 1.4 Hz, H-4), 5.62 (d, 1 H, *J* 1.4 Hz, H-3), 6.16, 6.29, 6.35 (d, 1 H, alkenic), 6.73, 6.75, 6.86, 7.23, 7.35, 7.47, 7.51, 7.80 (d, 2 H, aromatic), 7.54, 7.65, 7.67 (d, 1 H, alkenic). FABMS: 856 (M^+, 22%), 825 ($M - OCH_3$, 82%). FABHRMS: 825.1586 (calcd 825.1547 for $C_{43}H_{38}BrO_{12}$, $M - OCH_3$).

Methyl 1-O-(4-bromobenzoyl)-3,4,6-tri-O-(4-methoxycinnamoyl)β-D-fructofuranoside (β-BCCC).—^{1}H NMR (400 MHz): δ 3.46 (s, 3 H, OCH_3), 3.81, 3.82, 3.82 (s, 3 H, $CinnOCH_3$), 4.44 (m, 2 H), 4.57 (m, 3 H), 5.71 (t, 1 H, H-4), 5.79 (d, 1 H, *J* 7.1 Hz, H-3), 6.27, 6.31, 6.33 (d, 1 H, *J* 16 Hz, alkenic), 6.84, 7.89 (d, 2 H, aromatic), 6.87 (d, 4 H, aromatic), 7.64 (m, 6 H, aromatic), 7.55, 7.64, 7.67 (d, 1 H, *J* 16 Hz, alkenic). FABMS: 856 (M^+, 10%), 825 ($M - OCH_3$, 58%). FABHRMS: 856.1688 (calcd 856.1730 for $C_{44}H_{41}BrO_{13}$).

Methyl 6-O-(4-bromobenzoyl)-1,3,4-tri-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-CCCB).—^{1}H NMR (400 MHz): δ 3.39 (s, 3 H, OCH_3), 3.81, 3.82, 3.82 (s, 2 H, $CinnOCH_3$), 4.21 (d, 1 H, *J* 12.3 Hz, H-1), 4.36 (q, 1 H, H-5), 4.64 (dd, 1 H, *J* 12.0, 4.1 Hz, H-6), 4.69 (d, 1 H, *J* 12.4 Hz, H-1), 4.82 (dd, 1 H, *J* 12.0, 3.0

Hz, H-6), 5.31 (dd, 1 H, *J* 4.9, 1.4 Hz, H-4), 5.62 (d, 1 H, H-3), 6.14, 6.21, 6.35 (d, 1 H, *J* 16 Hz, alkenic), 6.85, 6.87, 6.89, 7.33, 7.39, 7.93 (d, 2 H, aromatic), 7.46 (d, 4 H, aromatic), 7.57, 7.59, 7.67 (d, 1 H, *J* 16 Hz, alkenic). FABMS: 856 (M^+, 22%), 825 ($M - OCH_3$, 82%). FABHRMS: 856.1705 (calcd 856.1730 for $C_{44}H_{41}BrO_{13}$).

Methyl 6-O-(4-bromobenzoyl)-1,3,4-tri-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-CCCB).—^{1}H NMR (400 MHz): δ 3.40 (s, 3 H, OCH_3), 3.76 (s, 3 H, CinnOCH_3), 3.81 (s, 6 H, CinnOCH_3), 4.39 (d, 1 H, *J* 12 Hz, H-1), 4.42 (q, 1 H, H-5), 4.48 (d, 1 H, *J* 12 Hz, H-1), 4.54 (dd, 1 H, *J* 11.8, 6.6 Hz, H-6), 4.69 (dd, 1 H, *J* 11.9, 4.0 Hz, H-6), 5.72 (dd, 1 H, *J* 7.2, 6.0 Hz, H-4), 5.85 (d, 1 H, *J* 7.2 Hz, H-3), 6.27, 6.27, 6.38 (d, 1 H, *J* 16 Hz, alkenic), 6.69, 6.84, 6.86, 7.31, 7.39, 7.41, 7.56, 7.93 (d, 2 H, aromatic), 7.61, 7.62, 7.66 (d, 1 H, alkenic). FABMS: 856 (M^+, 4%), 825 ($M - OCH_3$, 89%). FABHRMS: 825.1538 (calcd 825.1547 for $C_{43}H_{38}BrO_{12}$, $M - OCH_3$).

Methyl 1,3,4,6-tetra-O-(4-bromobenzoyl)-α-D-fructofuranoside (α-BBBB).—^{1}H NMR (400 MHz): δ 3.41 (s, 3 H, OCH_3), 4.33 (d, 1 H, *J* 12.4 Hz, H-1), 4.47 (q, 1 H, H-5), 4.63 (dd, 1 H, *J* 12.1, 4.7 Hz, H-6), 4.83 (dd, 1 H, *J* 12.1, 3.6 Hz, H-6), 4.85 (d, 1 H, *J* 12.4 Hz, H-1), 5.46 (dd, 1 H, *J* 5.0, 1.5 Hz, H-4), 5.76 (d, 1 H, *J* 1.5 Hz, H-3), 7.39, 7.46, 7.49, 7.58, 7.70, 7.74, 7.81, 7.90 (d, 2 H, aromatic). FABMS: 922 (M^+, 1%), 891 ($M - OCH_3$, 16%). FABHRMS: 890.8061 (calcd 890.8076 for $C_{34}H_{23}Br_4O_9$, $M - OCH_3$).

Methyl 1,3,4,6-tetra-O-(4-bromobenzoyl)-β-D-fructofuranoside (β-BBBB).—^{1}H NMR (400 MHz): δ 3.43 (s, 3 H, OCH_3), 4.52 (q, 1 H, H-5), 4.55–4.63 (m, 3 H, 2 H-1 + H-6), 4.72 (dd, 1 H, *J* 11.7, 4.3 Hz, H-6), 5.87 (dd, 1 H, *J* 6.8, 5.8 Hz, H-4), 5.96 (d, 1 H, *J* 6.8 Hz, H-3), 7.36 (d, 2 H, aromatic), 7.50–7.56 (m, 6 H, aromatic), 7.72 (d, 2 H, aromatic), 7.78–7.83 (m, 4 H, aromatic), 7.90 (d, 2 H, aromatic). FABMS: 922 (M^+, 1%), 891 ($M - OCH_3$, 15%). FABHRMS: 890.8040 (calcd 890.8076 for $C_{34}H_{23}Br_4O_9$, $M - OCH_3$).

Methyl 1,4,6-tri-O-(4-bromobenzoyl)-3-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-BCBB).—^{1}H NMR (400 MHz): δ 3.39 (s, 3 H, OCH_3), 3.83 (s, 3 H, CinnOCH_3), 4.29 (d, 1 H, *J* 12.2 Hz, H-1), 4.42 (q, 1 H, H-5), 4.67 (dd, 1 H, *J* 12.0, 4.2 Hz, H-6), 4.82–4.86 (m, 2 H, H-1 + H-6), 5.40 (dd, 1 H, *J* 4.5, 1.2 Hz, H-4), 5.70 (d, 1 H, *J* 1.2 Hz, H-3), 6.07 (d, 1 H, *J* 15.9 Hz, alkenic), 6.89 (d, 2 H), 7.30 (d, 2 H), 7.47–7.52 (m, 3 H), 7.56–7.59 (m, 4 H), 7.82 (d, 2 H), 7.90–7.93 (m, 4H). FABMS: 900 (M^+, 11%), 889 ($M - OCH_3$, 31%). FABHRMS: 899.9437 (calcd 899.9417 for $C_{38}H_{31}Br_3O_{11}$).

Methyl 1,4,6-tri-O-(4-bromobenzoyl)-3-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-BCBB).—^{1}H NMR (400 MHz): δ 3.43 (s, 3 H, OCH_3), 3.83 (s, 3 H, CinnOCH_3), 4.54 (q, 1 H, H-5), 4.57–4.65 (m, 3 H, 2 H-1 + H-6), 4.72 (dd, 1 H, *J* 11.9, 4.0 Hz, H-6), 5.81 (dd, 1 H, *J* 7.1, 5.8 Hz, H-4), 5.91 (d, 1 H, *J* 7.1 Hz, H-3), 6.27 (d, 1 H, *J* 15.9 Hz, alkenic), 6.88 (d, 2 H, *J* 8.8 Hz, aromatic), 7.38 (d, 2 H, *J* 8.9 Hz, aromatic), 7.42 (d, 2 H, *J* 8.6 Hz, aromatic), 7.51–7.57 (m, 5 H, 1 alkenic + 4 aromatic), 7.83–7.92 (m, 6 H, aromatic). FABMS: 900 (M^+, 2%), 869 ($M - OCH_3$, 12%). FABHRMS: 899.9435 (calcd 899.9417 for $C_{38}H_{31}Br_3O_{11}$).

Methyl 1,3,6-tri-O-(4-bromobenzoyl)-4-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-BBCB).—^{1}H NMR (400 MHz): δ 3.41 (s, 3 H, OCH_3), 3.83 (s, 3 H, $CinnOCH_3$), 4.30 (d, 1 H, *J* 12.3 Hz, H-1), 4.41 (q, 1 H, H-5), 4.62 (dd, 1 H, *J* 12.0, 4.8 Hz, H-6), 4.83 (d, 1 H, *J* 12.3 Hz, H-1), 4.84 (dd, 1 H, *J* 11.9, 3.6 Hz, H-6), 5.37 (dd, 1 H, *J* 5.3, 1.5 Hz, H-4), 5.73 (d, 1 H, *J* 1.6 Hz, H-3), 6.34 (d, 1 H, *J* 15.9 Hz, alkenic), 6.90 (d, 2 H, *J* 8.8 Hz, aromatic), 7.40 (d, 2 H, *J* 8.5 Hz, aromatic), 7.45 (d, 2 H, *J* 8.5 Hz, aromatic), 7.46 (d, 2 H, *J* 8.7 Hz, aromatic), 7.49 (d, 2 H, *J* 8.6 Hz, aromatic), 7.68 (d, 1 H, *J* 16.3 Hz, alkenic), 7.69 (d, 2 H, *J* 8.6 Hz, aromatic), 7.74 (d, 2 H, *J* 8.5 Hz, aromatic), 7.83 (d, 2 H, *J* 8.5 Hz, aromatic). FABMS: 900 (M^+, 4%), 869 ($M - OCH_3$, 14%). FABHRMS: 899.9455 (calcd 899.9417 for $C_{38}H_{31}Br_3O_{11}$).

Methyl 1,3,6-tri-O-(4-bromobenzoyl)-4-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-BBCB).—^{1}H NMR (400 MHz): δ 3.40 (s, 3 H, OCH_3), 3.82 (s, 3 H, $CinnOCH_3$), 4.45 (q, 1 H, H-5), 4.3–4.62 (m, 3 H, 2 H-1 + H-6), 4.67 (dd, 1 H, *J* 11.8, 4.3 Hz, H-6), 5.80 (dd, 1 H, *J* 6.7, 5.4 Hz, H-4), 5.88 (d, 1 H, *J* 6.7 Hz, H-3), 6.23 (d, 1 H), 6.89 (d, 2 H), 7.39–7.43 (m, 4 H), 7.53–7.56 (m, 4 H), 7.61 (d, 1 H), 7.77 (d, 2 H), 7.82 (d, 2 H), 7.93 (d, 2 H). FABMS: 900 (M^+, 6%), 869 ($M - OCH_3$, 29%). FABHRMS: 899.9411 (calcd 899.9417 for $C_{38}H_{31}Br_3O_{11}$).

Methyl 1,4-di-O-(4-bromobenzoyl)-3,6-di-O-(4-methoxycinnamoyl)-*α*-D-*fructofuranoside (α-BCBC).*—^{1}H NMR (400 MHz): δ 3.40 (s, 3 H, OCH_3), 3.78, 3.80 (s, 3 H, $CinnOCH_3$), 4.34 (d, 1 H, *J* 12.2 Hz, H-1), 4.40 (q, 1 H, H-5), 4.52 (dd, 1 H, *J* 12.1, 4.7 Hz, H-6), 4.71 (dd, 1 H, *J* 12.1, 3.3 Hz, H-6), 4.85 (d, 1 H, *J* 12.2 Hz, H-1), 5.38 (dd, 1 H, *J* 4.6, 1.3 Hz, H-4), 5.67 (d, 1 H, *J* 1.3 Hz, H-3), 6.17 (d, 1 H), 6.28 (d, 1 H), 6.75 (d, 2 H), 6.76 (d, 2 H), 7.24 (d, 2 H), 7.34 (d, 2 H), 7.50–7.58 (m, 5 H), 7.65 (d, 1 H), 7.83 (d, 2 H), 7.92 (d, 2 H). FABMS: 878 (M^+, 3%), 847 ($M - OCH_3$, 48%). FABHRMS: 878.0597 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

Methyl 1,4-di-O-(4-bromobenzoyl)-3,6-di-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-BCBC).—^{1}H NMR (400 MHz): δ 3.48 (s, 3 H, OCH_3), 3.818 (s, 3 H, $CinnOCH_3$), 3.823 (s, 3 H, $CinnOCH_3$), 4.43–4.46 (m, 2 H), 4.57–4.61 (m, 3 H), 5.79 (dd, 1 H, *J* 7.1, 5.6 Hz, H-4), 5.89 (d, 1 H, *J* 7.2 Hz, H-3), 6.27 (d, 1 H, *J* 15.9 Hz, alkenic), 6.30 (d, 1 H, *J* 16.0 Hz, alkenic), 6.868 (d, 2 H, *J* 8.9 Hz, aromatic), 6.873 (d, 2 H, *J* 8.9 Hz, aromatic), 7.36–7.43 (m, 6 H, aromatic), 7.53 (d, 1 H, *J* 15.9 Hz, alkenic), 7.55 (d, 2 H, *J* 8.6 Hz, aromatic), 7.64 (d, 1 H, *J* 16.0 Hz, aromatic), 7.86 (d, 4 H, *J* 8.5 Hz, alkenic). FABMS: 878 (M^+, 5%), 847 ($M - OCH_3$, 21%). FABHRMS: 878.0585 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

Methyl 1,3-di-O-(4-bromobenzoyl)-4,6-di-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-BBCC).—^{1}H NMR (400 MHz): δ 3.41 (s, 3 H, OCH_3), 3.827 (s, 3 H, $CinnOCH_3$), 3.833 (s, 3 H, $CinnOCH_3$), 4.32 (d, 1 H, *J* 12.3 Hz, H-1), 4.37 (q, 1 H, H-5), 4.49 (dd, 1 H, *J* 12.3, 4.5 Hz, H-6), 4.74 (dd, 1 H, *J* 12.3, 3.0 Hz, H-6), 4.85 (d, 1 H, *J* 12.3 Hz, H-1), 5.35 (dd, 1 H, *J* 5.1, 1.5 Hz, H-4), 5.71 (d, 1 H, *J* 1.4 Hz, H-3), 6.20 (d, 1 H, *J* 15.9 Hz, alkenic), 6.35 (d, 1 H, *J* 15.9 Hz, alkenic), 6.86 (d, 2 H, *J* 8.9 Hz, aromatic), 6.89 (d, 2 H, *J* 8.9 Hz, aromatic), 7.29 (d, 2 H, *J* 8.8 Hz, aromatic), 7.38 (d, 2 H, *J* 8.6 Hz, aromatic), 7.46 (d, 2 H, *J* 8.8 Hz, aromatic), 7.50

(d, 2 H, *J* 8.6 Hz, aromatic), 7.63 (d, 1 H, *J* 16.0 Hz, alkenic), 7.68 (d, 1 H, *J* 16.0 Hz, alkenic), 7.76 (d, 2 H, *J* 8.6 Hz, aromatic), 7.80 (d, 2 H, *J* 8.6 Hz, aromatic). FABMS: 878 (M^+, 3%), 847 ($M - OCH_3$, 15%), FABHRMS: 878.0585 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

Methyl 1,3-di-O-(4-bromobenzoyl)-4,6-di-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-BBCC).—^{1}H NMR (400 MHz): δ 3.44 (s, 3 H, OCH_3), 3.81, 3.82 (s, 3 H, CinnOCH_3), 4.41–4.47 (m, 2 H), 4.53–4.61 (m, 3 H), 5.78 (dd, 1 H, *J* 6.7, 5.6 Hz, H-4), 5.88 (d, 1 H, *J* 6.7 Hz, H-3), 6.25 (d, 1 H), 6.33 (d, 1 H), 6.84–6.88 (m, 4 H), 7.40–7.44 (m, 6 H), 7.53 (d, 2 H), 7.62 (d, 1 H), 7.67 (d, 1 H), 7.78 (d, 2 H), 7.84 (d, 2 H). FABMS: 878 (M^+, 3%), 847 ($M - OCH_3$, 22%). FABHRMS: 878.0593 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

Methyl 4,6-di-O-(4-bromobenzoyl)-1,3-di-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-CCBB).—^{1}H NMR (400 MHz): δ 3.40 (s, 3 H, OCH_3), 3.81, 3.82 (s, 3 H, CinnOCH_3), 4.23 (d, 1 H, *J* 12.2 Hz, H-1), 4.41 (q, 1 H, H-5), 4.66 (dd, 1 H, *J* 12.0, 4.2 Hz, H-6), 4.71 (d, 1 H, *J* 12.2 Hz, H-1), 4.82 (dd, 1 H, *J* 12.0, 3.2 Hz, H-6), 5.40 (dd, 1 H, *J* 4.6, 1.2 Hz, H-4), 5.66 (d, 1 H, *J* 1.2 Hz, H-3), 6.13 (d, 1 H), 6.22 (d, 1 H), 6.85 (d, 2 H), 6.87 (d, 2 H), 7.33 (d, 2 H), 7.40 (d, 2 H), 7.46 (d, 2 H), 7.56–7.61 (m, 4 H), 7.90–7.93 (m, 4 H). FABMS: 878 (M^+, 4%), 847 ($M - OCH_3$, 48%). FABHRMS: 847.0397 (calcd 847.0390 for $C_{40}H_{33}Br_2O_{12}$, $M - OCH_3$).

Methyl 4,6-di-O-(4-bromobenzoyl)-1,3-di-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-CCBB).—^{1}H NMR (400 MHz): δ 3.42 (s, 3 H, OCH_3), 3.78 (s, 3 H, CinnOCH_3), 3.82 (s, 3 H, CinnOCH_3), 4.43 (d, 1 H, *J* 12.0 Hz, H-1), 4.49–4.51 (m, 2 H, H-1 + H-5), 4.57 (dd, 1 H, *J* 11.5, 6.4 Hz, H-6), 4.75 (dd, 1 H, *J* 11.7, 3.8 Hz, H-6), 5.80 (dd, 1 H, *J* 7.1, 5.9 Hz, H-4), 5.93 (d, 1 H, *J* 7.1 Hz, H-3), 6.26 (d, 1 H, *J* 16.0 Hz, alkenic), 6.37 (d, 1 H, *J* 16.0 Hz, alkenic), 6.72 (d, 2 H, *J* 8.8 Hz, aromatic), 6.84 (d, 2 H, *J* 8.8 Hz, aromatic), 7.30 (d, 2 H, *J* 8.7 Hz, aromatic), 7.39 (d, 2 H, *J* 8.8 Hz, aromatic), 7.54 (d, 2 H, *J* 8.5 Hz, aromatic), 7.55 (d, 2 H, *J* 8.6 Hz, aromatic), 7.61 (d, 1 H, *J* 16.0 Hz, alkenic), 7.66 (d, 1 H, *J* 15.9 Hz, alkenic), 7.87 (d, 2 H, *J* 8.6 Hz, aromatic), 7.92 (d, 2 H, *J* 8.6 Hz, aromatic). FABMS: 878 (M^+, 1%), 847 ($M - OCH_3$, 22%). FABHRMS: 878.0540 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

Methyl 3,6-di-O-(4-bromobenzoyl)-1,4-di-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-CBCB).—^{1}H NMR (400 MHz): δ 3.40 (s, 3 H, OCH_3), 3.79 (s, 3 H, CinnOCH_3), 3.81 (s, 3 H, CinnOCH_3), 4.35 (d, 1 H, *J* 12.2 Hz, H-1), 4.40 (q, 1 H, H-5), 4.50 (dd, 1 H, *J* 12.0, 4.6 Hz, H-6), 4.73 (dd, 1 H, *J* 12.0, 3.4 Hz, H-6), 4.87 (d, 1 H, *J* 12.2 Hz, H-1), 5.40 (dd, 1 H, *J* 4.5, 1.3 Hz, H-4), 5.68 (d, 1 H, *J* 1.4 Hz, H-3), 6.19 (d, 1 H, *J* 15.9 Hz, alkenic), 6.29 (d, 1 H, *J* 16.0 Hz, alkenic), 6.76 (d, 2 H, *J* 8.8 Hz, aromatic), 6.77 (d, 2 H, *J* 8.8 Hz, aromatic), 7.25 (d, 2 H, *J* 8.8 Hz, aromatic), 7.36 (d, 2 H, *J* 8.9 Hz, aromatic), 7.52 (d, 2 H, *J* 8.7 Hz, aromatic), 7.57 (d, 1 H, *J* 15.3 Hz, alkenic), 7.59 (d, 2 H, *J* 8.7 Hz, aromatic), 7.67 (d, 1 H, *J* 16.0 Hz, alkenic), 7.85 (d, 2 H, *J* 8.6 Hz, aromatic), 7.93 (d, 2 H, *J* 8.6 Hz, aromatic). FABMS: 878 (M^+, 2%), 847 ($M - OCH_3$, 18%). FABHRMS: 878.0590 (calcd 878.0573 for $C_{41}H_{36}Br_2O_{12}$).

Methyl 3,6-di-O-(4-bromobenzoyl)-1,4-di-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-CBCB).—^{1}H NMR (400 MHz): δ 3.39 (s, 3 H, OCH_3), 3.82 (s, 6 H, CinnOCH_3), 4.40 (d, 1 H, *J* 11.9 Hz, H-1), 4.43–4.50 (m, 2 H, H-1 + H-5), 4.56 (dd, 1 H, *J* 11.8, 6.7 Hz, H-6), 4.69 (dd, 1 H, *J* 11.8, 4.3 Hz, H-6), 5.79 (dd, 1 H, *J* 7.0, 6.1 Hz, H-4), 5.99 (d, 1 H, *J* 7.0 Hz, H-3), 6.09 (d, 1 H), 6.26 (d, 1 H), 6.83 (d, 2 H), 6.86 (d, 2 H), 7.21 (d, 2 H), 7.41 (d, 2 H), 7.48–7.55 (m, 5 H), 7.61 (d, 1 H), 7.91–7.94 (m, 4 H). FABMS: 878 (M^+, 1%), 847 (M − OCH_3, 44%). FABHRMS: 847.0344 (calcd 847.0406 for $C_{40}H_{33}Br_2O_{12}$, M − OCH_3).

Methyl 4-O-(4-bromobenzoyl)-1,3,6-tri-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-CCBC).—^{1}H NMR (400 MHz): δ 3.40 (s, 3 H, OCH_3), 3.77, 3.79, 381 (s, 3 H, CinnOCH_3), 4.27 (d, 1 H, *J* 12.1 Hz, H-1), 4.38 (q, 1 H, H-5), 4.51 (dd, 1 H, *J* 12.0, 4.7 Hz, H-6), 4.70 (dd, 1 H, *J* 12.0, 3.2 Hz, H-6), 4.73 (d, 1 H, *J* 12.1 Hz, H-1), 5.38 (dd, 1 H, *J* 4.6, 1.5 Hz, H-4), 5.63 (d, 1 H, *J* 1.5 Hz, H-3), 6.24 (d, 1 H), 6.25 (d, 1 H), 6.28 (d, 1 H), 6.72 (d, 2 H), 6.74 (d, 2 H), 6.84 (d, 2 H), 7.28 (d, 2 H), 7.32 (d, 2 H), 7.41 (d, 2 H), 7.56–7.66 (m, 5 H), 7.92 (d, 2 H), FABMS: 856 (M^+, 2%), 825 (M − OCH_3, 89%). FABHRMS: 825.1549 (calcd 825.1547 for $C_{43}H_{38}BrO_{12}$, M − OCH_3).

Methyl 4-O-(4-bromobenzoyl)-1,3,6-tri-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-CCBC).—^{1}H NMR (400 MHz): δ 3.46 (s, 3 H, OCH_3), 3.78 (s, 3 H, CinnOCH_3), 3.81 (s, 3 H, CinnOCH_3), 3.82 (s, 3 H, CinnOCH_3), 4.41–4.51 (m, 4 H), 4.60 (q, 1 H, H-5), 5.78 (dd, 1 H, *J* 7.1, 5.4 Hz, H-4), 5.91 (d, 1 H, *J* 7.2 Hz, H-3), 6.26 (d, 1 H, *J* 16.0 Hz, alkenic), 6.30 (d, 1 H, *J* 16.0 Hz, alkenic), 6.37 (d, 1 H, *J* 15.9 Hz, alkenic), 6.71 (d, 2 H, *J* 8.8 Hz, aromatic), 6.83 (d, 2 H, *J* 8.7 Hz, aromatic), 6.87 (d, 2 H, *J* 8.8 Hz, aromatic), 7.30 (d, 2 H, *J* 8.8 Hz, aromatic), 7.38 (d, 2 H, *J* 8.8 Hz, aromatic), 7.40 (d, 2 H, *J* 8.9 Hz, aromatic), 7.53 (d, 2 H, *J* 8.6 Hz, aromatic), 7.61 (d, 1 H, *J* 16.0 Hz, alkenic), 7.64 (d, 1 H, *J* 16.0 Hz, alkenic), 7.65 (d, 1 H, *J* 16.0 Hz, alkenic), 7.89 (d, 2 H, *J* 8.6 Hz, aromatic). FABMS: 856 (M^+, 11%), 825 (M − OCH_3, 78%). FABHRMS: 825.1558 (calcd 825.1547 for $C_{43}H_{38}BrO_{12}$, M − OCH_3).

Methyl 3-O-(4-bromobenzoyl)-1,4,6-tri-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-CBCC).—^{1}H NMR (400 MHz): δ 3.41 (s, 3 H, OCH_3), 3.81 (s, 3 H, CinnOCH_3), 3.83 (s, 6 H, CinnOCH_3), 4.26 (d, 1 H, *J* 12.3 Hz, H-1), 4.35 (q, 1 H, H-5), 4.48 (dd, 1 H, *J* 12.0, 4.5 Hz, H-6), 4.73 (d, 1 H, *J* 12.3 Hz, H-1), 4.74 (dd, 1 H, *J* 12.3, 4.5 Hz, H-6), 5.35 (dd, 1 H, *J* 5.1, 1.6 Hz, H-4), 5.68 (d, 1 H, *J* 1.5 Hz, H-3), 6.14 (d, 1 H, *J* 15.9 Hz, alkenic), 6.19 (d, 1 H, *J* 15.9 Hz, alkenic), 6.36 (d, 1 H, *J* 15.9 Hz, alkenic), 6.85 (d, 2 H, *J* 8.8 Hz, aromatic), 6.86 (d, 2 H, *J* 8.8 Hz, aromatic), 6.89 (d, 2 H, *J* 8.8 Hz, aromatic), 7.27 (d, 2 H, *J* 8.9 Hz, aromatic), 7.39 (d, 2 H, *J* 8.7 Hz, aromatic), 7.41 (d, 2 H, *J* 8.6 Hz, aromatic), 7.46 (d, 2 H, *J* 8.8 Hz, aromatic), 7.51 (d, 1 H, *J* 15.9 Hz, alkenic), 7.62 (d, 1 H, *J* 16.0 Hz, alkenic), 7.69 (d, 1 H, *J* 16.0 Hz, alkenic), 7.85 (d, 2 H, *J* 8.6 Hz, aromatic), FABMS: 856 (M^+, 4%), 825 (M − OCH_3, 31%). FABHRMS: 825.1546 (calcd 825.1547 for $C_{43}H_{38}BrO_{12}$, M − OCH_3).

Methyl 3-O-(4-bromobenzoyl)-1,4,6-tri-O-(4-methoxycinnamoyl)-β-D-fructo-

furanoside (β-CBCC).—^{1}H NMR (400 MHz): δ 3.43 (s, 3 H, OCH_3), 3.81 (s, 9 H, $CinnOCH_3$), 4.39–4.50 (m, 4 H), 4.57 (m, 1 H), 5.78 (dd, 1 H, *J* 7.0, 5.8 Hz, H-4), 5.88 (d, 1 H, *J* 7.0 Hz, H-3), 6.10 (d, 1 H), 6.27 (d, 1 H), 6.33 (d, 1 H), 6.81–6.85 (m, 6 H), 7.21 (d, 2 H), 7.40 (d, 2 H), 7.43 (d, 2 H), 7.48–7.53 (m, 3 H), 7.63 (d, 1 H), 7.67 (d, 1 H), 7.93 (d, 2 H). FABMS: 856 (M^+, 3%), 825 ($M - OCH_3$, 44%). FABHRMS: 825.1574 (calcd 825.1547 for $C_{43}H_{38}BrO_{12}$, $M - OCH_3$).

Methyl 1,3,4,6-tetra-O-(4-methoxycinnamoyl)-α-D-fructofuranoside (α-CCCC).—^{1}H NMR (400 MHz): δ 3.40 (s, 3 H, OCH_3), 3.76 (s, 3 H, $CinnOCH_3$), 3.79 (s, 3 H, $CinnOCH_3$), 3.81 (s, 3 H, $CinnOCH_3$), 3.82 (s, 3 H, $CinnOCH_3$), 4.25 (d, 1 H, *J* 12.2 Hz, H-1), 4.33 (q, 1 H, H-5), 4.48 (dd, 1 H, *J* 12.1, 4.8 Hz, H-6), 4.70 (dd, 1 H, *J* 12.1, 2.8 Hz, H-6), 4.71 (d, 1 H, *J* 12.1 Hz, H-1), 5.29 (dd, 1 H, *J* 4.9, 1.6 Hz, H-4), 5.59 (d, 1 H, *J* 1.6 Hz, H-3), 6.23 (d, 1 H, *J* 16.0 Hz, alkenic), 6.24 (d, 1 H, *J* 16.0 Hz, alkenic), 6.30 (d, 1 H, *J* 16.0 Hz, alkenic), 6.35 (d, 1 H, *J* 16.0 Hz, alkenic), 6.71 (d, 2 H, *J* 8.8 Hz, aromatic), 6.74 (d, 2 H, *J* 8.8 Hz, aromatic), 6.84 (d, 2 H, *J* 8.8 Hz, aromatic), 6.88 (d, 2 H, *J* 8.8 Hz, aromatic), 7.27 (d, 2 H, *J* 8.8 Hz, aromatic), 7.35 (d, 2 H, *J* 8.8 Hz, aromatic), 7.41 (d, 2 H, *J* 8.8 Hz, aromatic), 7.46 (d, 2 H, *J* 8.8 Hz, aromatic), 7.59 (d, 1 H, *J* 16.0 Hz, alkenic), 7.62 (d, 1 H, *J* 16.0 Hz, alkenic), 7.66 (d, 1 H, *J* 16.0 Hz, alkenic), 7.68 (d, 1 H, *J* 16.0 Hz, alkenic). FABMS: 834 (M^+, 21%), 803 ($M - OCH_3$, 94%). FABHRMS: 834.2961 (calcd 834.2888 for $C_{47}H_{46}O_{14}$).

Methyl 1,3,4,6-tetra-O-(4-methoxycinnamoyl)-β-D-fructofuranoside (β-CCCC).—^{1}H NMR (400 MHz): δ 3.45 (s, 3 H, OCH_3), 3.77 (s, 3 H, $CinnOCH_3$), 3.81 (s, 3 H, $CinnOCH_3$), 3.82 (s, 6 H, $CinnOCH_3$), 4.39–4.46 (m, 2 H), 4.40 (d, 1 H, *J* 12.0 Hz, H-1), 4.48 (d, 1 H, *J* 11.9 Hz, H-1), 4.58 (dd, 1 H, *J* 11.5, 3.6 Hz, H-6), 5.71 (dd, 1 H, *J* 7.2, 5.8 Hz, H-4), 5.84 (d, 1 H, *J* 7.2 Hz, H-3), 6.28 (d, 1 H, *J* 16.0 Hz, alkenic), 6.30 (d, 1 H, *J* 16.0 Hz, alkenic), 6.34 (d, 1 H, *J* 16.0 Hz, alkenic), 6.40 (d, 1 H, *J* 16.0 Hz, alkenic), 6.70 (d, 2 H, *J* 8.8 Hz, aromatic), 6.83–6.87 (m, 6 H, aromatic), 7.32 (d, 2 H, *J* 8.7 Hz, aromatic), 7.39–7.45 (m, 6 H, aromatic), 7.60–7.70 (m, 4 H, alkenic). FABMS: 834 (M^+, 6%), 803 ($M - OCH_3$, 100%). FABHRMS: 834.2849 (calcd 834.2888 for $C_{47}H_{46}O_{14}$).

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