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Preparation of di-*O*-triphenylmethyl- (trityl-) cyclomalto-hexaoses and -cyclomaltoheptaoses and characterization of three positional isomers of each by the "hex-5-enose degradation"

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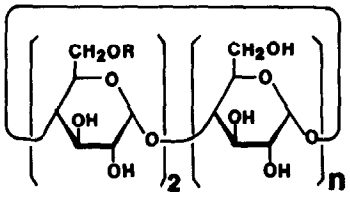
ABSTRACT

Regioisomeric $6^1,6^n$-di-*O*-trityl-cyclomaltohexaoses (cG_6s) or -cyclomaltoheptaoses (cG_7s) were prepared by the reaction of cyclomaltohexaose (**1**, cG_6) or cylomaltoheptaose (**5**, cG_7) with chlorotriphenylmethane in pyridine and isolation by h.p.l.c. The regiochemical determination of each three ditrityl-substituted derivatives has been accomplished by the "hex-5-enose degradation", followed by measurement of their f.a.b.-mass spectra.

INTRODUCTION

It is well known that cyclomalto-oligosaccharides (cG_ns) have the ability to form inclusion compounds with various kinds of inorganic and organic compounds, and that they have become widely used in many fields[1]. Recently, branched cG_ns have been synthesised by enzymatic processes, and these compounds have attracted attention because of their many advantages over the parent cG_ns[2–5]. We have already reported the synthesis of $6^1,6^n$-di-*O*-(*tert*-butyldimethylsilyl)-cG_6 and -cG_7 derivatives[6], and these have been used as intermediates for chemical syntheses of di-*O*-glucosyl-cG_ns[7,8].



	n	R		n	R
1	4	OH	5	5	OH
2($6^1,6^2$)	4	OTr	6($6^1,6^2$)	5	OTr
3($6^1,6^3$)	4	OTr	7($6^1,6^3$)	5	OTr
4($6^1,6^4$)	4	OTr	8($6^1,6^4$)	5	OTr

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In this study, we have attempted regiospecific ditritylation at the primary centers of cyclomaltohexaose (**1**, cG_6) and cyclomaltoheptaose (**5**, cG_7), since these dityrityl-substituted derivatives can also be used as intermediates for chemical syntheses of dibranched cG_ns. We also describe herein the application of the "hex-5-enose degradation"[9] to the regiochemical determination of the ditrityl-substituted cG_ns.

RESULTS AND DISCUSSION

Preparation and Isolation of 6^1,6^n-di-O-trityl-cG$_6$s (**2–4**) *and -cG$_7$s* (**6–8**). — Some research groups have reported[10–14] the preparation of triphenylmethyl (trityl)-substituted cG_ns; however, there are no reports of disubstituted derivatives. Tritylation of **1** or **5**, which had been dried by azeotropic distillation with pyridine, with 3 mol. equiv. of chlorotriphenylmethane for 20 h at 45° gave upon workup a powdery mixture containing disubstituted compounds as the major products. It was observed by monitoring the progress of the reaction by t.l.c. that this reaction proceeded slowly. Ditritylates were separated from monotritylated and over-tritylated compounds by semi-preparative h.p.l.c. on an ODS column (250 × 20 mm i.d., 10 μm), eluting with 83:17 methanol–water. A mixture of **2–4** (46%) and a mixture of **6–8** (41%) were obtained. Each ditritylate was isolated by rechromatography on another ODS column (250 × 20 mm i.d., 5 μm) with 80:20 methanol–water for **2–4** and 75:25 methanol–water for **6–8**, respectively. Fig. 1 (A) and (B) show the elution profiles of each of the regioisomeric mixtures. Relative ratios of A-I, -II, and -III, and of B-I, -II, and -III, as calculated from the peak areas for each chromatogram, were approximately 1:1:2 and 7:1:4, respectively. One might presume from these ratios that B-II may be 6^1,6^2-di-*O*-trityl cG_7 **2** because of the steric hindrance between two bulky trityl groups attached to two

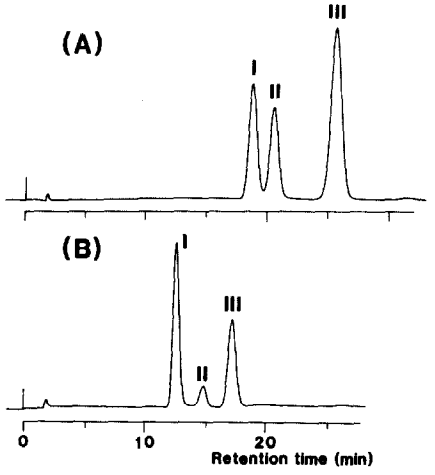


Fig. 1. Elution profiles of each three positional isomers of di-*O*-trityl-cyclomaltohexaose and di-*O*-trityl-cyclomaltoheptaose. Chromatographic conditions: column, YMC-Pack A-312 ODS (150 × 6 mm i.d.); eluent, (A) 78:22 methanol–water, (B) 72:28 methanol–water; flow rate, 1.0 mL/min; wavelength, 241 nm.

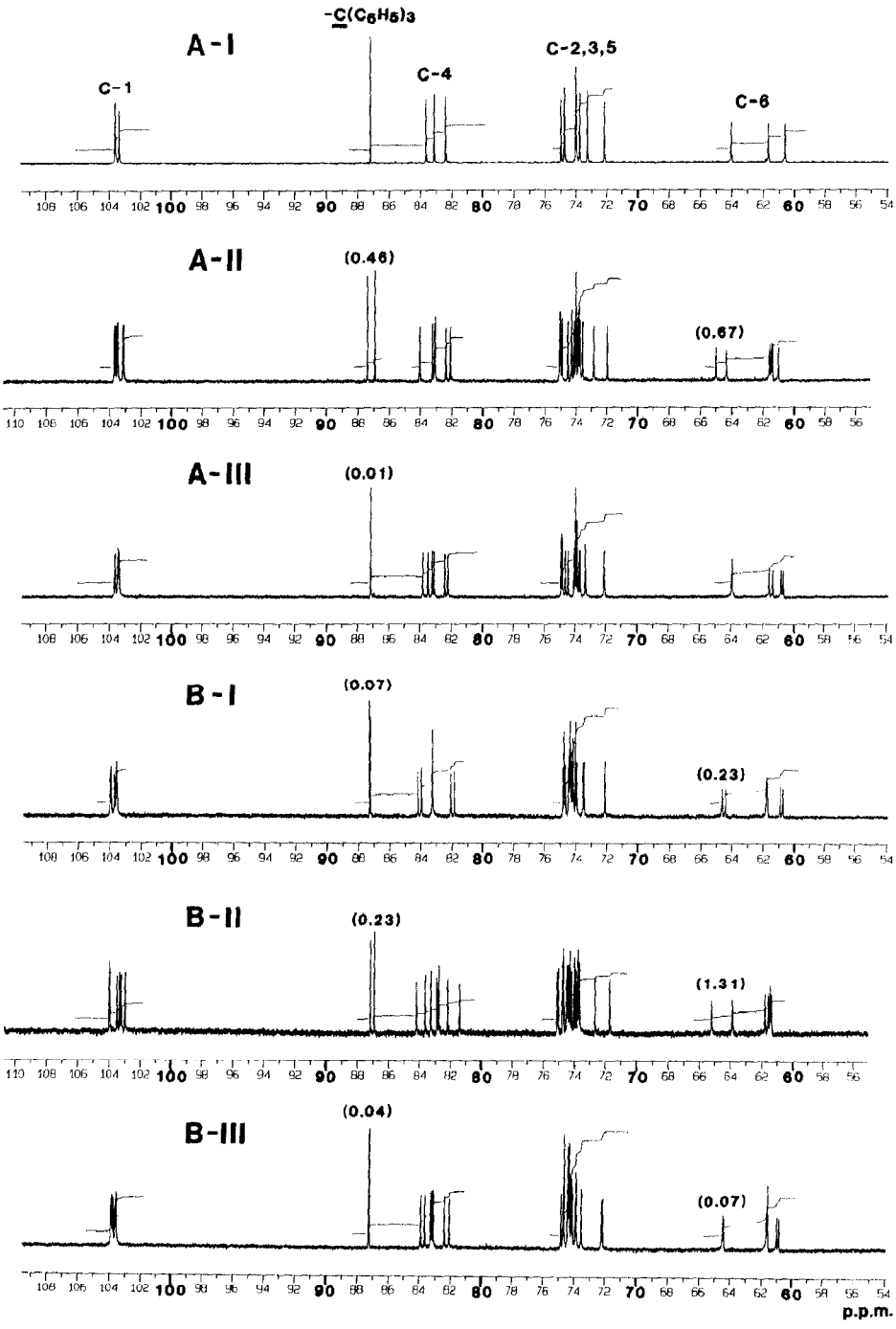


Fig. 2. ^{13}C-N.m.r. spectra of isomeric di-*O*-trityl-cyclomaltohexaoses (A-I, -II, and -III) and -cyclomaltoheptaoses (B-I, -II, and -III) measured in C_5D_5N at 125.65 MHz. The value in parentheses on the signals is the difference ($\Delta\delta$, p.p.m.) of chemical shifts between the two signals.

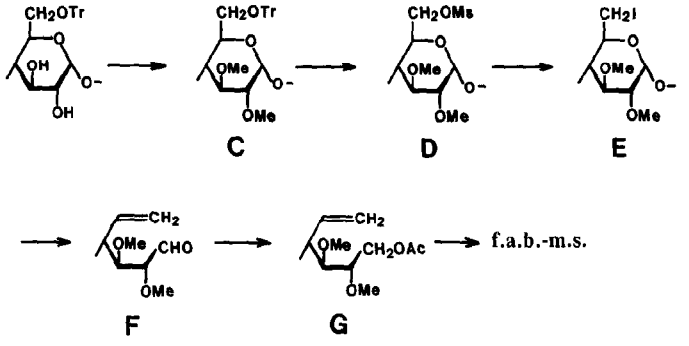
neighboring D-glucose units. On the other hand, it is difficult to specify the regioisomers of ditrityl cG_6 from the ratios produced by the reaction.

^{13}C-N.m.r. spectra. — Fig. 2 shows the ^{13}C-n.m.r. spectra of A-I, -II, and -III and B-I, -II, and -III in C_5D_5N. The signals for C-1, the quaternary carbons of the trityl groups, and the trityl-substituted C-6s, shifted downfield by 2–3 p.p.m. from the other C-6s (δ 60–62), appear at δ 103–104, 87–88, and 64–65 p.p.m., respectively. The relative intensities of these signals were 6:2:2 for A-I, -II, and -III and 7:2:2 for B-I, -II, and -III. The assignment of the C-6 signals was confirmed by the INEPT method. These results proved that all six compounds were indeed di-*O*-trityl-substituted derivatives. From a detailed comparison of the spectra of A-I, -II, and -III, it could be presumed that these were $6^1,6^4$-, $6^1,6^2$- and $6^1,6^3$-di-*O*-trityl cG_6s, respectively. The spectrum of A-I, in contrast to those of A-II and -III, was very simple, as its signals for C-1, -4, and -6 consisted of only two, three, and three lines, respectively. Moreover, the signal for the quaternary carbon of the trityl group and that of the trityloxy-substituted C-6 were coincidental. These facts indicate that the two trityl groups in A-I are located at the most remote position from each other and that A-I is symmetrical. Therefore, A-I is the $6^1,6^4$-disubstituted isomer **4**. On the other hand, the signals in the spectra of A-II and -III as a whole are complex, especially those resonances of the quaternary carbon of the trityl group and trityloxy-substituted C-6 in the spectrum of A-II, which appeared as two signals, each with a relatively large difference of 0.46 and 0.67 p.p.m., respectively. This fact suggests that A-II has two adjacent bulky trityl groups in the molecule and is, therefore, $6^1,6^2$-disubstituted cG_6 **2**; hence A-III is the $6^1,6^3$-disubstituted cG_6 **3**.

Although the data indicate that B-II is the $6^1,6^2$-ditritylated **6**, it cannot be determined whether B-I is the $6^1,6^3$- or the $6^1,6^4$-di-*O*-trityl cG_7.

Characterization of three positional isomers by the "hex-5-enose degradation". — Bernet and Vasella[15] have shown that 6-deoxy-6-halohexopyranosides react with zinc dust under mild conditions with glycoside cleavage and formation of hex-5-enoses. This reaction was subsequently developed by Aspinall *et al.*[9] for the selective cleavage of glycosidic linkages in complex oligo- and poly-saccharides.

Although a method for the determination of substituted positions of disubstituted cG_n had been studied by Fujita *et al.* using Korner's method[16] and taka-amylase-

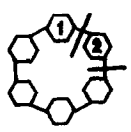
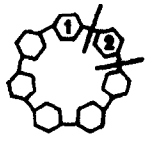
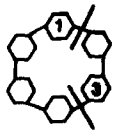
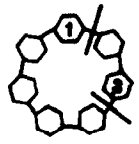
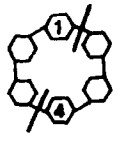
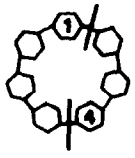


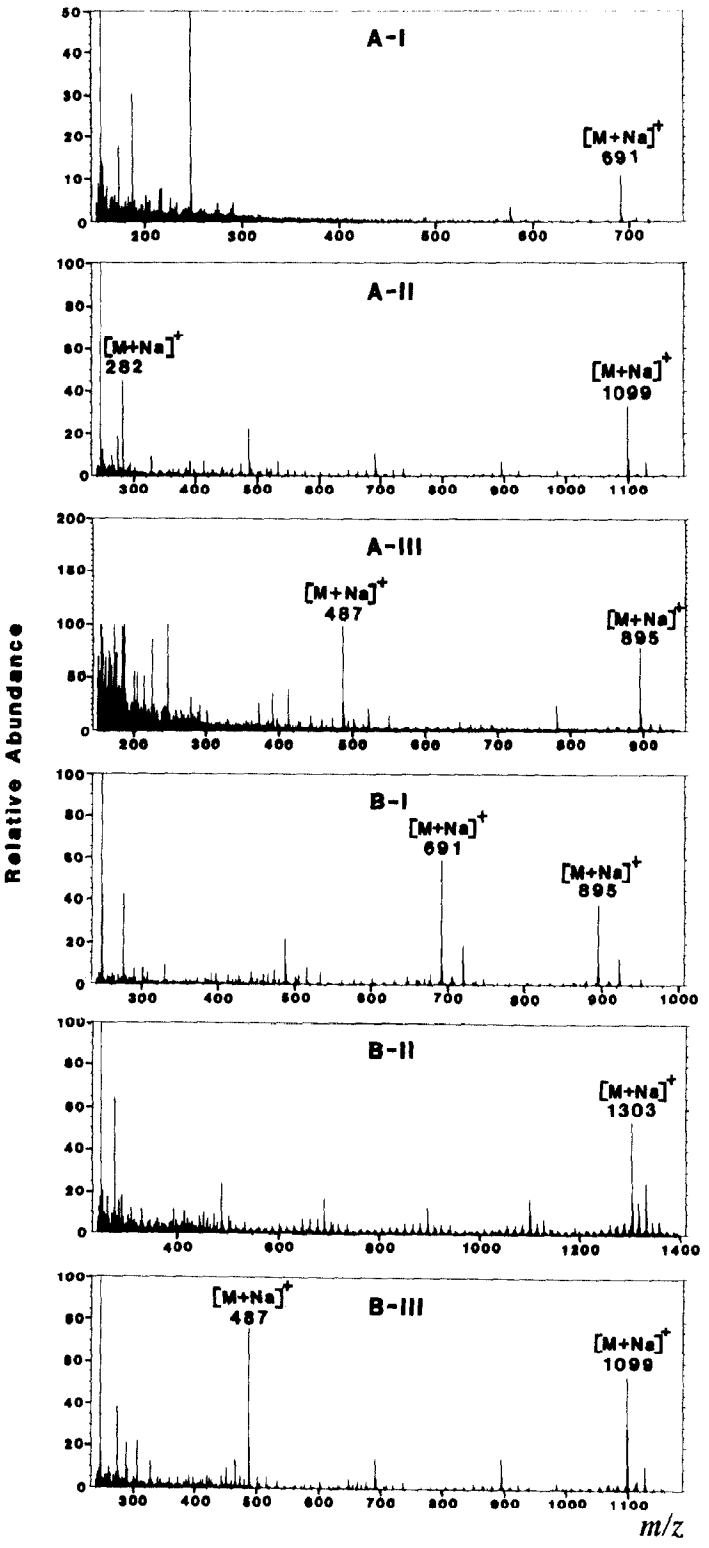
Scheme 1.

catalysed hydrolysis[17], we tried in this work to apply the "hex-5-enose degradation", as confirmed by Aspinall *et al.*[9], to the regiochemical determination (Scheme 1). Methylation[18] of ditrityl derivatives (**2–4, 6–8** → **2–4C, 6–8C**) and subsequent detritylation[19] and methylsulfonylation[20] gave $6^1,6^n$-di-*O*-methylsulfonyl-cG_6 per-*O*-methylates **2–4D** and -cG_7 per-*O*-methylates **6–8D**. Nucleophilic displacement of the methylsulfonyl groups of **2–4D** and **6–8D** with iodide[20] afforded $6^1,6^n$-dideoxy-$6^1,6^n$-diiodo per-*O*-methyl derivatives **2–4E** and **6–8E** as the key intermediates. Next, the "hex-5-enose degradation"[9] was applied to the dideoxydiiodo derivatives. Compounds **2–4E** and **6–8E** were each treated with freshly prepared activated zinc dust and gave the corresponding two types of 5,6-dideoxy-hex-5-enoses **F**. The 5,6-dideoxy-hex-5-enose-terminated derivative was then conveniently characterized by reduction, followed by acetylation, to give 1,2-dideoxy-hex-1-enitol acetates **G**. These two types of partially methylated 1,2-dideoxy-hex-1-enitol acetates produced in each case were identified by f.a.b.-m.s. The predictable molecular ions of the degradation products from **2–4E** and **6–8E** are summarized in Table I. Fig. 3 shows the actual spectra of partially methylated 1,2-dideoxy-hex-1-enitol acetates derived from A-I, -II, and -III, and B-I, -II, and -III. Comparison of the molecular ions shown in Fig. 3 with the predictable molecular ions in Table I made it clear that A-I, -II, and -III, and B-I, -II, and -III are compounds **4**, **2**, and **3**, and **8**, **6**, and **7**, respectively. Thus the substituted positions of disubstituted cG_ns have

TABLE I

The molecular-ions of predictable products from $6^1,6^n$-dideoxy-$6^1,6^n$-diiodo-cG_6 permethylates (**2–4E**) and -cG_7 permethylates (**6–8E**) by the "hex-5-enose degradation"

Dideoxydiiodo permethylates		$[M+Na]^+$ m/z	*Dideoxyiiodo permethylates*		$[M+Na]^+$ m/z
2E		282 1099	**6E**		282 1303
3E		487 895	**7E**		487 1099
4E		691	**8E**		691 895


A-I
[M+Na]+
691
A-II
[M+Na]+
282
[M+Na]+
1099
A-III
[M+Na]+
487
[M+Na]+
895
B-I
[M+Na]+
691
[M+Na]+
895
B-II
[M+Na]+
1303
B-III
[M+Na]+
487
[M+Na]+
1099
Relative Abundance
m/z

been unequivocally determined by the "hex-5-enose degradation", followed by measurement of f.a.b.-mass spectra. About 15 mg of trityl-substituted cG_ns was sufficient to carry out this determination.

EXPERIMENTAL

General. — Melting points were measured with Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a JASCO digital polarimeter, model DIP 360. T.l.c. was performed on Silica Gel 60 (E. Merck) with detection by charring with sulfuric acid. H.p.l.c. was conducted with a JASCO TRI ROTAR SR-1 pump, a Waters U6K universal injector, a Knauer differential refractometer, and a Lab-Quatec CO-1093 column oven. The columns used were (A) YMC-Pack A-312 (150 × 6 mm i.d.), (B) YMC-Pack SH-343-10 (250 × 20 mm i.d.), and (C) YMC-Pack SH-343-5 AQ (250 × 20 mm i.d.). A Shimadzu Chromatopac C-R3A digital integrator was used to quantitate the peak areas. Centrifugal chromatography was performed with a Harrison Centrifugal Thin-Layer Chromatotron, model 7924. ^{13}C-N.m.r. spectra were recorded with JEOL JNM-FX 200 (50.10 MHz) and JEOL GSX-500 (125.65 MHz) spectrometers for solutions in C_5D_5N and $CDCl_3$ (internal Me_4Si). F.a.b.-m.s. was performed with a JEOL JMS-DX 303 mass spectrometer using xenon atoms having a kinetic energy equivalent to 6 kV at an accelerating voltage of 3 kV. Methanol, *m*-nitrobenzyl alcohol, and sodium chloride were used as the solvent, matrix, and additive, respectively.

6^1,6^2- 6^1,6^3-, and 6^1,6^4-Di-O-trityl-cyclomaltohexaoses (**2–4**), *and 6^1,6^2-, 6^1,6^3- and 6^1,6^4-di-O-trityl-cyclomaltoheptaoses* (**6–8**). — Compound **1** or **5** (1 g, dried over phosphorus pentoxide under diminished pressure) was dissolved in dry pyridine (40–50 mL), and the solvent was distilled at atmospheric pressure until the boiling point of the distillate reached 115°. The solution was adjusted to 30–50 mL with dry pyridine, and then chlorotriphenylmethane (3 mol. equiv., 0.86 g for **1**, 0.74 g for **5**) was added and stirred at 45°. The progress of the reaction was monitored by t.l.c. on silica gel plates with 8:4:1 chloroform–methanol–water, and after 20 h the solvent was evaporated, and the residue was poured into a mixture of ice-water (40 mL) and chloroform (40 mL). The precipitate that was deposited between the two phases was collected by filtration and washed successively with water and chloroform. The yields of tritylated cG_6s and cG_7s were 1.37 g and 1.01 g, respectively. Each ditritylated mixture was separated from monotritylated and over-tritylated compounds by semi-preparative h.p.l.c. on column B eluted with 83:17 methanol–water to give a mixture of **2–4** (0.63 g, 46%) and a mixture of **6–8** (0.41 g, 41%). Further, each regioisomer was repeatedly separated on column C with 80:20 methanol–water for **2–4** and 75:25 methanol–water for **6–8**, respectively.

Fig. 3. F.a.b.-m.s. of products from the "hex-5-enose degradation" of 6^1,6^n-dideoxy-6^1,6^n-diiodocyclomaltohexaose permethylates derived from A-I, -II, and III, and -cyclomaltoheptaose permethylates derived from B-I, -II, and -III.

TABLE II

Physico-chemical and analytical data for di-*O*-trityl-cG$_n$s

Compound	*m.p.*	$[\alpha]_D^{26}$		*Elemental analysis found*		*^{13}C-n.m.r. δ (CDCl$_3$)*	
	(°)[a]	(°)	c	*C*	*H*	*CPh$_3$*	*C-6*[b]
2	281	+130.1[c]	1.9	59.23	6.12[e]	87.36	64.97
						86.90	64.30
3	syrup	+126.0[c]	5.7			87.19	63.97
						87.18	63.84
4	280	+120.6[c]	5.1	59.34	6.16[e]	87.19	64.02
6	288	+101.8[d]	2.6	56.54	6.24[f]	87.19	65.22
						86.96	63.91
7	284	+109.1[d]	4.6	57.77	6.27[g]	87.29	64.51
						87.25	64.44
8	285	+97.4[d]	4.0	57.56	6.18[g]	87.32	64.65
						87.25	64.42

[a] Decomposition observed. [b] CPh_3-substituted carbon; [c] Solution in methanol. [d] Solution in 60% methanol. [e] *Anal.* Calc. for $C_{74}H_{88}O_{30}\cdot 2H_2O$: C, 59.51; H, 6.21. [f] *Anal.* Calc. for $C_{80}H_{98}O_{35}\cdot 4H_2O$: C, 56.80; H, 6.32. [g] *Anal.* Calc. for $C_{80}H_{98}O_{35}\cdot 3H_2O$: C, 57.41; H, 6.26.

These compounds, other than **3**, were crystallised from methanol. The physico-chemical and analytical data of these compounds are listed in Table II.

Characterization of three positional isomers. — Each of the three positional isomers was characterized *via* their permethylates **C**, methylated dimethylsulfonyl **D**, and dideoxydiiodo derivatives **E** by the hex-5-enose degradation.

*6^1,6^n-Di-*O*-trityl-cG$_6$ permethylates* (**2–4C**) *and -cG$_7$ permethylates* (**6–8C**). — Compounds **2** (205 mg), **3** (170 mg), **4** (230 mg), **6** (150 mg), **7** (230 mg), and **8** (207 mg) were each methylated with freshly distilled iodomethane (1.8–2.5 mL) and sodium hydride (dry, 97%, 350–500 mg) in freshly distilled *N,N*-dimethylformamide under nitrogen, protecting the mixture from light for 4–5 h at room temperature. The suspension was filtered through a pad of Celite, and the filtrate was concentrated. The residue, dissolved in chloroform, was successively washed with water, dried, and concentrated. Centrifugal chromatography (3:1 hexane–acetone) of the residue gave **2C** (172 mg, 72.7%), **3C** (145 mg, 73.9%), **4C** (162 mg, 61.0%), **6C** (122 mg, 70.3%), **7C** (163 mg, 61.2%), and **8C** (194 mg, 81.0%). ^{13}C-N.m.r. data and specific rotations of these compounds are listed in Table III. Compound **4C** was crystallised from acetone–methanol: m.p. 139–140°.

Anal. Calc. for $C_{90}H_{120}O_{30}\cdot H_2O$: C, 63.59; H, 7.23. Found: C, 63.62; H, 7.29.

*6^1,6^n-Di-*O*-methylsulfonyl-cG$_6$permethylates* (**2–4D**) *and-cG$_7$permethylates* (**6–8D**). — Solutions of **2C** (172 mg), **3C** (122 mg), **4C** (120 mg), **6C** (122 mg), **7C** (130 mg), or **8C** (172 mg) in 70% acetic acid (20–30 mL) were each stirred for 1 h at 75° and then evaporated. The residue was extracted with chloroform, and the extract was washed sequentially with water, aqueous sodium carbonate, and water, dried, and evaporated. Each residue in dry pyridine (4–5 mL) was cooled to −10°, treated with methanesulfonyl

TABLE III

Physico-chemical data for intermediates prepared to characterize the three positional isomers

Compound	$[\alpha]_D$ (in $CHCl_3$) (°)	c	temp. (°)	^{13}*C-n.m.r.* *δ, (CDCl$_3$)*	
				CPh$_3$	*C-6*[a]
2C	+134.3	1.7	28	86.7, 86.3	62.4, 63.8
3C	+151.6	1.2	28	86.7, 86.3	63.3
4C	+147.7	0.4	29	86.6	63.1
6C	+127.0	1.2	27	87.1, 86.3	63.3, 62.4
7C	+133.1	1.3	27	87.2, 86.5	64.1, 63.3
8C	+143.0	1.7	29	86.7, 86.6	63.2, 63.0
				CH$_3$SO$_2$	
2D	+145.3	1.0	28	37.8, 37.5	
3D	+146.0	1.0	28	37.7, 37.5	
4D	+146.7	1.1	28	37.6	
6D	+139.7	1.3	27	37.6, 37.3	
7D	+151.8	1.1	26	37.5, 37.4	
8D	+142.1	1.0	28	37.4	
				CH$_2$I	
2E	+130.7	0.8	26	9.8, 8.4	
3E	+133.3	0.7	27	9.0, 8.4	
4E	+133.2	0.8	26	8.4	
6E	+125.0	1.0	28	9.9, 8.5	
7E	+122.1	1.4	28	8.9, 8.6	
8E	+136.2	1.3	28	8.9, 8.7	

[a] CPh_3-substituted carbon.

chloride (0.4–0.6 mL), and kept overnight at 5°, and then concentrated. The residue, dissolved in chloroform, was washed with water, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. Centrifugal chromatography (2.5:1 benzene–acetone) of the residue afforded **2D** (115 mg, 83.1%), **3D** (83 mg, 86.5%), **4D** (75 mg, 77.6%), **6D** (70 mg, 69.5%), **7D** (84 mg, 78.3%), and **8D** (123 mg, 86.6%). The specific rotations and ^{13}C-n.m.r. data of these compounds are listed in Table III.

6^1,6^n-Dideoxy-6^1,6^n-diiodo-cG$_6$ permethylates (**2–4E**) *and -cG$_7$ permethylates* (**6–8E**). — Solutions of **2D** (95 mg), **3D** (80 mg), **4D** (75 mg), **6D** (63 mg), **7D** (77 mg), or **8D** (95 mg) in *N,N*-dimethylformamide (5 mL) were stirred with sodium hydride (dry, 97%, 500–600 mg) for 3 h at 100°. The mixture was evaporated to dryness, and the residue was extracted with chloroform. The extract was washed with water, aqueous sodium thiosulfate, and water, dried, and evaporated. Centrifugal chromatography (3:1 benzene–acetone) of the residue gave **2E** (70 mg, 70.4%), **3E** (51 mg, 60.9%), **4E** (55 mg, 70.0%), **6E** (52 mg, 79.4 mg), **7E** (70 mg, 87.4%), and **8E** (78 mg, 78.9%). The specific rotations and ^{13}C-n.m.r. data of these compounds are listed in Table III. Compounds **2E** and **4E** were obtained as crystalline precipitates: m.p. 227–228° (from ethanol) and 224–226° (from ethanol–hexane), respectively.

Anal. Calc. for $C_{52}H_{90}I_2O_{28}$: C, 44.07; H, 6.40. Found: C, 44.50; H, 6.72, and C, 44.01; H, 6.62, respectively, for **2E** and **4E**.

The hex-5-enose-degradation. — A solution of **2E** (14 mg) in 14:1 1-propanol–water (6 mL) was boiled with freshly activated zinc dust (0.2 g) under reflux for 1 h. The mixture was filtered through a layer of Celite, and the filtrate was concentrated. The residue in 1:1 methanol–water (4 mL) was treated with sodium borohydride (150 mg) for 3 h at room temperature. The reaction mixture was worked up in the usual manner, and the product was acetylated with acetic anhydride in pyridine. The residue was directly analyzed by f.a.b.-m.s.

Methylated diiodo derivatives **3E**, **4E**, **6E**, **7E**, and **8E** were similarly treated and analyzed by f.a.b.-m.s. (Fig. 3).

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