Synthesis of Chiral Spiroacetals from Carbohydrates

Angeles Martín, José A. Salazar, and Ernesto Suárez*

Instituto de Productos Naturales y Agrobiología del C.S.I.C., Carretera de La Esperanza 3, 38206-La Laguna, Tenerife, Spain

Received January 9, 1996[⊗]

Chiral spiroacetals of the 1,7-dioxaspiro[5.5]undecane, 1,6-dioxaspiro[4.5]decane, and 1,6-dioxaspiro-[4.4]nonane types have been prepared from carbohydrates in pyranose or furanose forms. The spirocyclization reaction has been accomplished from a conveniently homologated carbohydrate by an intramolecular hydrogen abstraction reaction promoted by alkoxy radicals. Thus, 2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-(3′-hydroxypropyl)-α-D-glucopyranose (**2**) was photolyzed with visible light in the presence of (diacetoxyiodo)benzene and iodine to give a mixture of (1*R*)-(**3**) and (1*S*)-2,3,4,6-tetra-*O*-benzyl-1-deoxy-D-glucopyranose-1-spiro-2′-tetrahydrofuran (**4**). The photolysis of methyl 6-deoxy-6-(2′-hydroxyethyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (**8**) gave the isomeric spiroacetals methyl (5*S*)- (**9**) and (5*R*)-6-deoxy-5,2′-epoxy-6-ethyl-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (**10**) in which the spirocenter is now located at C-5. The spiroacetals of the [5.5]undecane series: methyl (5*R*)- (**19**) and (5*S*)-6-deoxy-5,3′-epoxy-2,3,4-tri-*O*-methyl-6-propyl-*β*-D-glucopyranoside (**20**) have been prepared starting from methyl 6-deoxy-6-(3′-hydroxypropyl)-2,3,4-tri-*O*-methyl-*β*-D-glucopyranoside (**18**). The reaction has also been applied to hexofuranoses and 1-deoxy-1-(3′-hydroxypropyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**21**) gave rise to (1*S*)- (**22**) and (1*R*)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-tetrahydrofuran (**23**); and 1-deoxy-1-(4′-hydroxybutyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**28**) to (1*R*)- (**30**) and (1*S*)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-tetrahydropyran (**32**). Both spiroacetal enantiomers are formally available from the same carbohydrate.

The characterization of many important natural products which exhibit a spiroacetal ring system in their structures has stimulated the development of several methodologies for the synthesis of this substructural unit.[1] These metabolites isolated from a large variety of natural sources can have very simple structures such as the 1,7-dioxaspiro[5.5]undecane itself which is the major component of the pheromone of the olive fruit fly (*Dacus oleae*)[2] or can be very complex antiparasitic agents (avermectins and milbemycins)[3] or polyether antibiotics[4] of the monensin[5] and lonomycin[6] type.

Most common routes to spiroacetals are based on the preparation of the dihydroxy ketone, the typical method for the ring closure being the usual acid-promoted spirocyclization. This may be inconvenient in complex molecules bearing acid-sensitive protective groups. We wish to report here on a convenient methodology for the synthesis of optically active spiroacetals from carbohydrates in which the spirocyclization is achieved by an intramolecular hydrogen abstraction reaction promoted by alkoxy radicals.[7,8] Thus, chiral 1,7-dioxaspiro[5.5]-undecane, 1,6-dioxaspiro[4.5]decane, and 1,6-dioxaspiro-[4.4]nonane derivatives can be prepared in good yields. Most natural products having a spiroacetal moiety in their structures fall into one of these three categories. Racemic spiroacetals have been previously prepared using a radical methodology[9] and different approaches to these compounds from carbohydrates have recently been reported.[10]

As depicted in Scheme 1, the first step is the formation of a C-glycopyranoside if the spirocenter is going to be generated at C-1 (**A**) or a homologation of the carbohydrate side chain if it is at C-5 (**B**). The second step is a remote functionalization of the C-1 or C-5 carbon atom from an alkoxy radical generated from the corresponding alcohol by photolysis in presence of (diacetoxyiodo)-benzene (DIB) and iodine. In previous papers from this laboratory we have developed hypervalent iodine re-

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

(1) For reviews of spiroacetals see: (a) Vaillancourt, V.; Praft, N. E.; Perron, F.; Albizati, K. F. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1992; Vol. 8, pp 533−691. (b) Perron, F.; Albizati, K. F. *Chem. Rev.* **1989**, *89*, 1617−1661. (c) Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309. (d) Kluge, A. F. *Heterocycles* **1986**, *24*, 1699−1740.

(2) Davies, H. G.; Green, R. H. *Chem. Soc. Rev.* **1991**, *20*, 211−269, 271−339.

(3) (a) Baker, R.; Herbert, R.; Howse, P. E.; Jones, O. T.; Francke, W.; Reith, W. *J. Chem. Soc., Chem. Commun.* **1980**, 52−53. For a review on pheromone spiroacetals see: (b) Mori, K. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1992; Vol. 9, pp 1−534.

(4) For reviews on polyether antibiotics see: (a) *Polyethers Antibiotics: Naturally Occurring Acid Ionophores*; Westley, J. W., Ed.; Marcel Dekker: New York, 1982; Vols. 1 and 2. (b) Wierenga, W. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1992; Vol. 4, pp 533−691.

(5) For recent synthesis of monensin see: (a) Ireland, R. E.; Armstrong, J. D., III; Leberton, J.; Meissner, R. S.; Rizzacasa, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7152−7156. (b) Ireland, R. E.; Meissner, R. S.; Rizzacasa, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7166−7172.

(6) For recent synthesis of lonomycin A see: Evans, D. A.; Ratz, A. M.; Huff, B. E.; Sheppard, G. S. *J. Am. Chem. Soc.* **1995**, *117*, 3448−3467.

(7) For a recent review on intramolecular free radical functionalizations see: Majetich, G.; Wheless, K. *Tetrahedron* **1995**, *51*, 7095−7129.

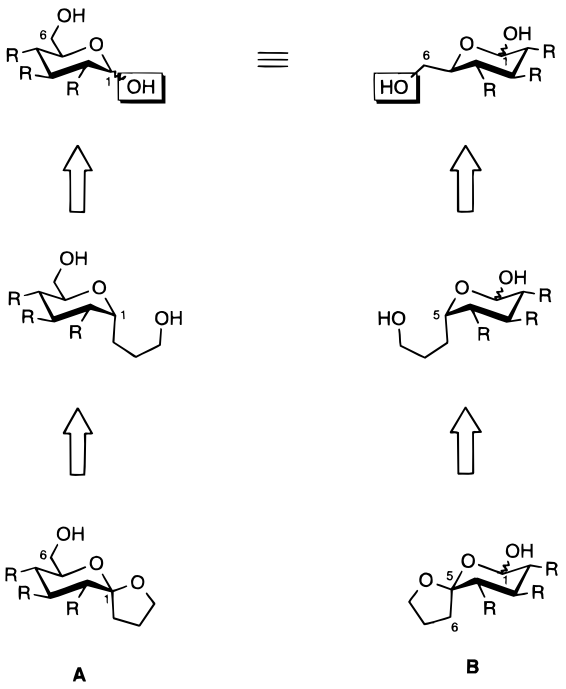
(8) For a preliminary communication see: Martín, A.; Salazar, J. A.; Suárez, E. *Tetrahedron Lett.* **1995**, *36*, 4489−4492.

(9) (a) Kay, I. T.; Williams, E. G. *Tetrahedron Lett.* **1983**, *24*, 5915−5918. (b) Kay, I. T.; Bartholomew, D. *Tetrahedron Lett.* **1984**, *25*, 2035−2038. (c) Baker, R.; Brimble, M. A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 125−131. (d) Wincott, F. E.; Danishefsky, S. J.; Schulte, G. *Tetrahedron Lett.* **1987**, *28*, 4951−4954.

(10) (a) Cubero, I. I.; López Espinosa, M. T. P.; Richardson, A. C.; Aamlid, K. H. *Carbohydr. Res.* **1993**, *242*, 281−296. (b) Cubero, I. I.; López Espinosa, M. T. P.; Kari, N. *Carbohydr. Res.* **1994**, *261*, 231−242. (c) Cubero, I. I.; López Espinosa, M. T. P.; Kari, N. *Carbohydr. Res.* **1995**, *268*, 187−200. (d) Preuss, R.; Karl-Heinz, J.; Schmidt, R. R. *Liebigs Ann. Chem.* **1992**, 377−382. (e) Grondin, R.; Leblanc, Y.; Hoogsteen, K. *Tetrahedron Lett.* **1991**, *32*, 5021−5024. (f) Remy, G.; Cottier, L.; Descotes, G. *Can. J. Chem.* **1983**, *61*, 434. (g) Bernasconi, C.; Cottier, L.; Descotes, G. *Carbohydr. Res.* **1983**, *2*, 159. (h) Remy, G.; Cottier, L.; Descotes, G. *J. Carbohydr. Chem.* **1983**, *1*, 37.

S0022-3263(96)00060-6 CCC: $12.00

Scheme 1



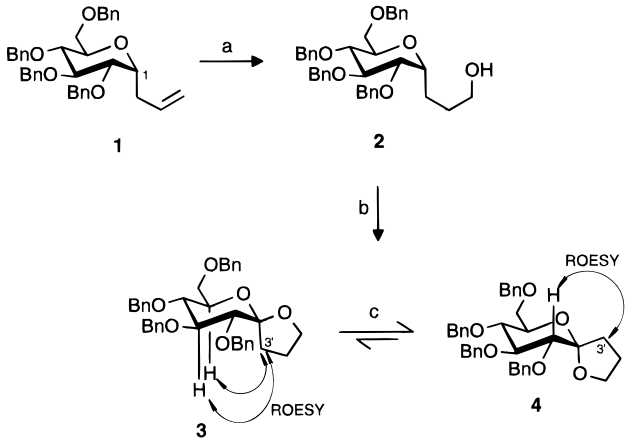
agents as mild oxidizing agents for the generation of alkoxy radicals from alcohols.[11]

This methodology allows both spiroacetal enantiomers to be formally obtained from the same carbohydrate depending on the carbon atom (C-1 or C-6) in which the additional side chain si formed, since a hydroxymethylenation[12] of the anomeric carbon of **B** gives rise to the optical isomer of **A**. Taking into account the relatively limited variety in Nature of carbohydrates,[13] particularly hexoses, this feature is synthetically interesting because it allows the required absolute configuration of the stereogenic centers in natural spiroacetals to be achieved.

Results and Discussion

Allyl derivative **1** was prepared following Kishi methodology.[14] Treatment of *p*-nitrobenzoyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside with allyltrimethylsilane and $BF_3{\cdot}Et_2O$ gave a (α:*β*, 9:1) mixture of allylglucopyrans from which the α-isomer **1** was separated by chromatography (Scheme 2). Hydroboration−oxidation of the major stereoisomer **1** gave rise to alcohol **2** which underwent intramolecular hydrogen abstraction when submitted to reaction with (diacetoxyiodo)benzene (DIB) and iodine under the conditions summarized in Table 1 (entry 1). Two C-1 isomeric dioxaspiro[4.5]decanyl derivatives **3** and **4** were formed in 68% overall yield in a ratio of 3:1. By HETCOR and ROESY experiments[15] both diastereomeric spiroacetals were found to possess the C-1 stereochemistry illustrated in Scheme 2 in which the most

Scheme 2[a]



[a] (a) $BH_3{\cdot}THF$, 0 °C → rt, 5 h; NaOH, H_2O_2, 40 °C, 0.5 h; (b) see Table 1; (c) HCl, AcOH, 50 °C, 6 h.

informative interactions with the C-3′ protons are illustrated by arrows in the structures of **3** and **4**.

The minor compound **4** is the thermodynamically more stable, as indicated by the acid-catalyzed isomerization of **3** to **4**. The equilibrium (**3:4**, 1:4) is reached after 6 h at 50 °C in AcOH containing traces of HCl. Since all the sugar substituents are in equatorial positions, the preferred configuration of the spirocenter of this dioxaspiro-[4.5]decanyl ring system is then determined primarily by the anomeric effect as occurs in the [5.5] variety.[16]

In order to prepare a 1,6-dioxaspiro[4.5]decane derivative with the spirocenter at C-5 the necessary two-carbons homologation of the carbohydrate side chain was accomplished from commercially available methyl α-D-glucopyranoside as shown in Scheme 3. The tosylate **6** was prepared from alcohol **5** which in turn was obtained by a three-step protocol from the above-mentioned glucopyranose in 60% overall yield.[17] Compound **6** was converted into allyl derivative **7** using freshly prepared allylmagnesium bromide in ether (88%).[18] The required alcohol **8** was obtained by ozonolysis of **7** in a mixture of CH_2Cl_2−MeOH followed by *in situ* reduction with $NaBH_4$. The hydrogen abstraction reaction was then carried out by treating **8** with the DIB/iodine system, as shown in Table 1 (entry 2) to yield the spiroacetal isomers **9** and **10** in a ratio of 1.7:1. The reaction proceeded in good overall yield (75%), and the expected 1,3-diaxial steric interaction by the 1α-methoxy group did not seem to influence the six-membered transition state necessary for the hydrogen abstraction. Assignment of the C-5 stereochemistry was by examination of NOE difference experiments as shown in Scheme 3. Reaction of the minor isomer **10** with TsOH in AcOH gave after 7 h at rt an approximately equimolecular mixture of **9** and **10**.

(11) (a) Concepción, J. J.; Francisco, C. G.; Hernández, R.; Salazar, J. A.; Suárez, E. *Tetrahedron Lett.* **1984**, *25*, 1953−1956. (b) Armas, P.; Concepción, J. J.; Francisco, C. G.; Hernández, R.; Salazar, J. A.; Suárez, E. *J. Chem. Soc., Perkin Trans. 1* **1989**, 405−411. (c) Dorta, R. L.; Francisco, C. G.; Hernández, R.; Salazar, J. A.; Suárez, E. *J. Chem. Res.* **1990**, 240−241.

(12) Chatani, N.; Ikeda, T.; Sano, T.; Sonoda, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Org. Chem.* **1988**, *53*, 3387−3389.

(13) Lichtenthaler, F. W.; Cuny, E.; Martin, D.; Rönninger, S.; Weber, T. In *Carbohydrates as Organic Raw Materials*; Lichtenthaler, F. W., Ed.; VCH: Weinhein, 1991; pp 207−246.

(14) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976−4978.

(15) (a) Bothner-By, A. A.; Stephens, R. L.; Lee, J.; Warren, C. D.; Jeanloz, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 811−813. (b) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207−213. (c) Kessler, H.; Griesinger, C.; Kerssebaum, R.; Wagner, K.; Ernst, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 607−609.

(16) (a) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: New York, 1983. (b) Deslongchamps, P.; Rowan, D. D.; Pothier, N.; Sauvé, T.; Saunders, J. K. *Can. J. Chem.* **1981**, *59*, 1105. (c) Pothier, N.; Rowan, D. D.; Deslongchamps, P.; Saunders, J. K. *Can. J. Chem.* **1981**, *59*, 1132.

(17) (a) Bernet, B.; Vasella, A. *Helv. Chim. Acta* **1979**, *62*, 1990. (b) Hirst, E. L.; Percival, E. In *Methods in Carbohydrate Chemistry*; Vol. 2; Whistler, R. L.; Wolfrom, M. L.; Eds.; Academic Press: New York, 1963; p 147.

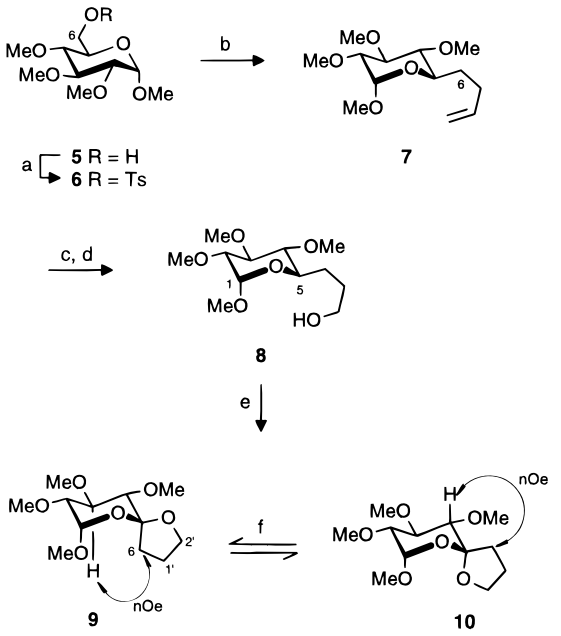
(18) Aged solutions of allylmagnesium bromide, addition of CuI, or changing the solvent to tetrahydrofuran, lead to complex mixtures.

Table 1. Synthesis of Chiral Spiroacetals[a]

entry	substrate	reagents[b] (mmol)	time (h)	*T* (°C)	products (yield, %)
1	**2**	DIB/I_2(1.1/1)	1	40	**3**(51); **4**(17)
2	**8**	DIB/I_2(1.1/1)	0.6	40	**9**(47); **10**(28)
3	**11**	DHSA/I_2(2.5/1)	6	80	**12**(7); **13**(12); **14**(8)
4	**11**	DIB/I_2(1.1/1)	3	40	complex mixture
5	**11**	HgO/I_2(1.5/1.5)	9	20	complex mixture
6	**18**	DIB/I_2(1.1/1)	0.5	40	**19**(53); **20**(33)
7	**18**	DHSA/I_2(2.3/1.1)	5	80	**19**(33); **20**(24)
8	**18**	HgO/I_2(2.5/2.5)	5	20	**19**(18); **20**(33)
9	**21**	DIB/I_2(1.2/1)	3	40	**22**(42); **23**(25)
10	**28**+**29**	DIB/I_2(1.8/1)	2.5	40	**30**(16); **31**(9); **32**(17); **33**(7)

[a] All reactions were performed in cyclohexane by irradiation with two 100 W tungsten-filament lamps. [b] Per mmol of substrate; DIB = (diacetoxyiodo)benzene; DHSA = diphenylhydroxyselenium acetate [$Ph_2Se(OH)(OAc)$].

Scheme 3[a]

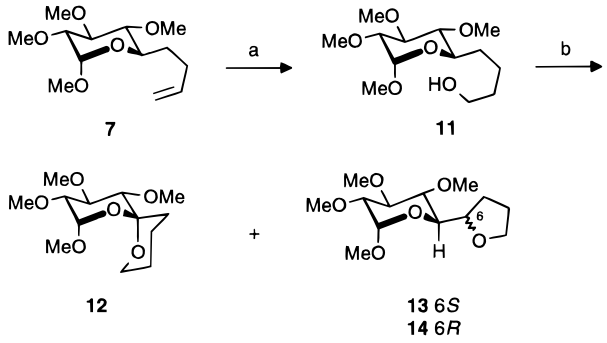


[a] (a) TsCl, Py, rt, 7 h; (b) CH_2=$CHCH_2MgBr$, Et_2O, 0 °C → rt, 3 h; (c) O_3, $MeOH/CH_2Cl_2$, −78 °C; (d) $NaBH_4$, 0 °C → rt, 2.25 h; (e) see Table 1; (f) TsOH, AcOH, rt, 7 h.

A study by molecular mechanics using the MMX force field[19] is in accord with the stability observed for the pair of stereoisomers of the dioxaspiro[4.5]decanyl series **3** and **4** (**4** is favored over **3** by 2.89 kcal/mol of MMX steric energy) and also with the similar stability of stereoisomers **9** and **10** (**9** favored over **10** only by 0.4 kcal/mol).

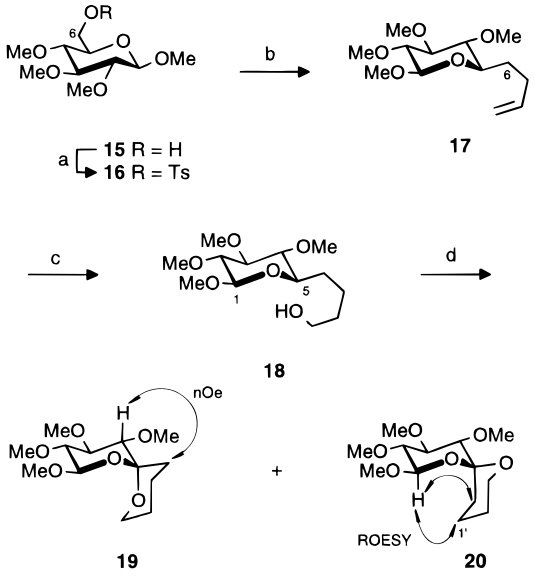
With compound **7** at hand we decided to study the formation of spiroacetals of the [5.5]undecane series. Hydroboration−oxidation of olefin **7** afforded the alcohol **11** in 90% yield (Scheme 4). The photolysis of **11** in presence of DIB/I_2 or HgO/I_2 led to complex mixtures that were not studied (Table 1, entries 4 and 5). Nevertheless, the use of diphenylhydroxyselenium acetate (DHSA) as oxidant[20] gave three compounds in low yield (entry 3) for which we propose structures **12**−**14**. By studies of molecular mechanics and ROESY experiments the stereochemistries were tentatively assigned as shown in Scheme 4. The formation of compounds **13** and **14**, through a six-membered transition state, seems to indicate difficulties for the radical abstraction of the C-5 proton, very probably due to 1,3-diaxial steric interactions with the methoxyl group at C-1.

Scheme 4[a]



[a] (a) BH_3·THF; NaOH, H_2O_2; (b) see Table 1.

Scheme 5[a]



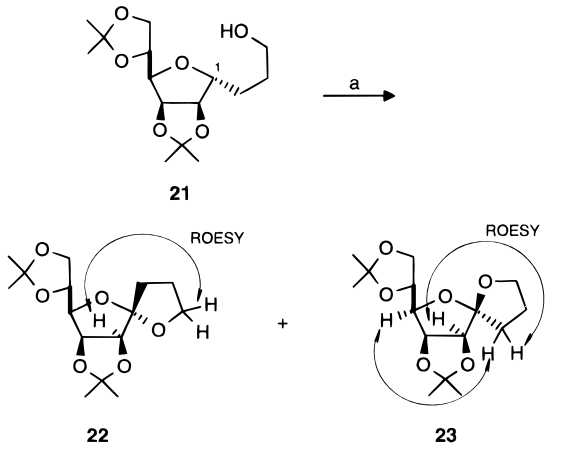
[a] (a) TsCl, Py, rt, 16 h; (b) CH_2=$CHCH_2MgBr$, Et_2O, rt, 4 h; (c) BH_3·THF; NaOH, H_2O_2; 0 °C → rt, 4 h (d) see Table 1.

In an effort to avoid **13** and **14** we have prepared the alcohol **18** in three steps from methyl 2,3,4-tri-*O*-methyl-*β*-D-glucopyranoside (**15**) (Scheme 5), following an identical methodology with that used to obtain **8** (Scheme 3).[17] The photolysis of **18** with DIB/I_2 gave a good overall yield (86%) of isomeric 1,7-dioxaspiro[5.5]undecane derivatives **19** and **20** (Table 1, entry 6). The use of other oxidant systems DHSA and HgO led to poorer yields (entries 7 and 8). The C-5 sterochemistries were determined using

(19) MMX force field as implemented in PCMODEL (v. 4.0), Serena Software, Bloomington IN, 47402-3076. See: Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Advances in Molecular Modelling*; JAI Press: Greenwich, CT, 1992; Vol. 2.

(20) (a) Dorta, R. L.; Francisco, C. G.; Freire, R.; Suárez, E. *Tetrahedron Lett*. **1988**, *29*, 5429−5432. (b) Dorta, R. L.; Francisco, C. G.; Suárez, E. *Tetrahedron Lett*. **1994**, *35*, 1083−1086. (c) Dorta, R. L.; Francisco, C. G.; Suárez, E. *Tetrahedron Lett*. **1994**, *35*, 2049−2052.

Scheme 6 [a]



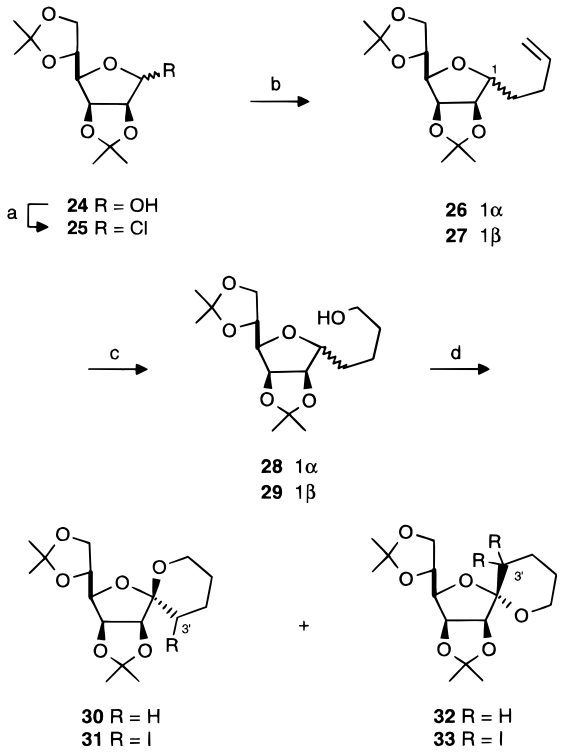
[a] (a) See Table 1.

difference NOE and ROESY experiments in combination with DEPT and HETCOR spectra to assign carbons and protons as shown in Scheme 5. The major compound **19** is now the thermodynamically more stable by 2.7 kcal/mol as established by molecular mechanics. It is also clear from these calculations that the new ring adopts the chair conformation that has a maximum number of anomeric effects. We have not isolated, in this case, any compound coming from a hydrogen abstraction through a six-membered transition state as it occurred in the photolysis of compound **11**. As observed 1,3-diaxial interactions seem to be critical for the synthesis of these dioxaspiro[5.5]undecane derivatives using this methodology (compare entries 3, 4 and 5 to 6). Contrarily, these steric interactions have little effect on the synthesis of dioxaspiro[4.5]decanes **9** and **10** (compare entries 1 and 2).

1-Allyl-1-deoxy-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose, prepared by radical allylation of the corresponding 1-chloro-mannose derivative following the Keck and Yates procedure,[21] was transformed via hydroboration−oxidation into the desired alcohol **21**. Photolysis of **21** with the DIB/I_2 system gave a mixture of the 1,6-dioxaspiro[4.4]nonane derivatives **22** and **23** (entry 9). The stereochemistries at C-1 were clearly assigned on the basis of the ROESY spectra (principal correlations shown by arrows in Scheme 6). As may be expected compound **22** is the more stable (by 5 kcal/mol) as well as being the major component of the C-1 isomeric mixture.

The synthesis of spiroacetals of the [4.5]decane type in which the tetrahydropyran ring is formed during the radical reaction was accomplished from the mannofuranosyl chloride **25**. Treatment of **25** with 3-butenylmagnesium bromide gave the mixture of isomers **26** and **27** which could only be partially resolved by careful chromatography (Scheme 7).[22] The mixture of alcohols **28** and **29**, obtained by hydroboration of olefins **26** and **27**, was then submitted to the radical cyclization reaction conditions (entry 10). In this case two iodine compounds **31** and **33** were formed besides the expected spiroacetals **30** and **32**. The proposed C-1 stereochemistry for compound **30** was confirmed by the observed ROESY interactions of the proton at C-3′ with protons at C-2, C-3, and C-4. The reduction of iodine derivatives **31** and **32** with Bu_3SnH to give, respectively, compounds **30** and **32** in good yields established the C-1 stereochemistry of those compounds.

Scheme 7[a]



[a] (a) CCl_4, Ph_3P, reflux, 4.5 h; (b) CH_2═$CHCH_2CH_2MgBr$, Et_2O, 0 °C, 22 h; (c) BH_3·THF, 0 °C → rt, 5 h; NaOH, H_2O_2, 40 °C, 1 h; (d) see Table 1.

The iodine compounds are probably formed by hydrogen abstraction at C-3′ through a more favorable six-membered cyclic transition state before the abstraction and spirocyclization at C-1 takes place.

Experimental Section

General. Melting points were determined with a hot-stage apparatus and are uncorrected. Optical rotation measurements were recorded at room temperature in $CHCl_3$. IR spectra were recorded in $CHCl_3$ solutions. NMR spectra were determined at 200 or 400 MHz for ^1H and 50.3 MHz for ^{13}C for $CDCl_3$ solutions unless otherwise stated in the presence of TMS as internal standard. Phase sensitive ROESY spectra were measured with a mixing time of 700 ms. Mass spectra were determined at 70 eV unless otherwise specified. Merck silica gel 60 PF_{254} and 60 (0.063−0.2 mm) were used for preparative thin-layer chromatography (TLC) and column chromatography, respectively. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a chromatotron for centrifugally assisted chromatography. Commercial reagents and solvents were analytical grade or were purified by standard procedures prior to use.[23] All reactions involving air- or moisture-sensitive materials were carried out under an argon atmosphere. The spray reagent for TLC was vanillin (1 g) in H_2SO_4−EtOH (4:1; 200 mL). (Diacetoxyiodo)benzene (DIB) 98% was purchased from Aldrich. Diphenylhydroxyselenium acetate (DHSA) [$Ph_2Se(OH)(OAc)$] has been previously prepared in this laboratory.[20a]

(21) (a) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829−5831. (b) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079−4094.

(22) François, P.; Perilleux, D.; Kempener, Y.; Sonveaux, E. *Tetrahedron Lett.* **1990**, *31*, 6347−6350.

(23) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(3′-hydroxypropyl)-α-D-glucopyranose (2). To a solution of compound **1**[14] (455 mg, 0.807 mmol) in dry THF (40 mL) at 0 °C and under Ar was added dropwise a 1 M solution of BH_3−THF complex (4.4 mL, 4.4 mmol) and stirred at rt for 5 h. The mixture was then cooled to 0 °C and treated with a 3 M aqueous solution of NaOH (25 mL). The oxidation was carried out by slow dropwise addition of 30% H_2O_2 (25 mL), the temperature being maintained below 40 °C. After stirring for an additional 0.5 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography of the residue (*n*-hexane−EtOAc, 75:25) gave compound **2** (345 mg, 73%) as a crystalline solid: mp 91.5−92.5 °C (from acetone−*n*-hexane); $[\alpha]_D$ +21.3° (*c* = 0.474); IR 3650, 3500 cm^{-1}; ^1H NMR 1.63−1.82 (4H, m), 3.57−3.80 (8H, m), 4.03 (1H, m), 4.45 (1H, d, *J* = 10.7 Hz), 4.48 (1H, d, *J* = 11.9 Hz), 4.57 (1H, s), 4.63 (1H, s), 4.70 (1H, d, *J* = 11.9 Hz), 4.79 (1H, d, *J* = 10.9 Hz), 4.81 (1H, d, *J* = 10.7 Hz), 4.92 (1H, d, *J* = 10.9 Hz), 7.11−7.36 (20H, m); ^{13}C NMR 20.84 (t), 29.01 (t), 62.15 (t), 69.02 (t), 71.00 (d), 72.98 (t), 73.37 (t), 74.20 (d), 74.90 (t), 75.33 (t), 78.11 (d), 80.07 (d), 82.27 (d), 127.48−128.30 (20 × d), 137.78 (s), 138.03 (s), 138.14 (s), 138.59 (s); MS (EI) *m*/*z* (rel intensity) 583 ($[M + H]^+$, 1), 491 (3), 385 (29), 277 (12), 259 (14), 253 (31), 181 (100); HRMS calcd for $C_{30}H_{35}O_6$ 491.2434, found 491.2424.

Photolysis of 2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(3′-hydroxypropyl)-α-D-glucopyranose (2). A solution of compound **2** (33 mg, 0.06 mmol) in cyclohexane (7 mL) containing DIB (22 mg, 0.066 mmol) and iodine (15 mg, 0.06 mmol) under Ar was irradiated with two 100 W tungsten-filament lamps at 40 °C for 1 h. The reaction mixture was then poured into aqueous saturated $Na_2S_2O_3$ and extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Chromatotron chromatography of the residue (*n*-hexane−EtOAc, 90:10) gave (1*R*)-2,3,4,6-tetra-*O*-benzyl-1-deoxy-D-glucopyranose-1-spiro-2′-tetrahydrofuran (**3**) (16.8 mg, 0.029 mmol, 51%) and (1*S*)-2,3,4,6-tetra-*O*-benzyl-1-deoxy-D-glucopyranose-1-spiro-2′-tetrahydrofuran (**4**) (5.6 mg, 0.01 mmol, 17%). Compound **3**: mp 69.8−71.3 °C (from acetone−*n*-hexane); $[\alpha]_D$ +29.8° (*c* = 0.416); IR 2990, 1355, 1060, 1022 cm^{-1}; ^1H NMR 1.93−2.00 (2H, m), 2.04 (1H, m), 2.19 (1H, m), 3.47 (1H, m), 3.54−3.63 (2H, m), 3.66−3.74 (3H, m), 3.95 (1H, dd, *J* = 6.8, 13.6 Hz), 4.10 (1H, dd, *J* = 7.5, 13.6 Hz), 4.52 (1H, d, *J* = 10.7 Hz), 4.55 (1H, d, *J* = 11.9 Hz), 4.61 (1H, d, *J* = 11.9 Hz), 4.74 (1H, d, *J* = 11.1 Hz), 4.78 (1H, d, *J* = 10.9 Hz), 4.83 (1H, d, *J* = 10.7 Hz), 4.86 (1H, d, *J* = 11.1 Hz), 4.92 (1H, d, *J* = 10.9 Hz), 7.14−7.36 (20H, m); ^{13}C NMR 25.02 (t), 27.73 (t), 68.20 (t), 69.46 (t), 73.41 (t), 73.83 (d), 75.08 (t), 75.08 (t), 75.63 (t), 78.13 (d), 82.28 (d), 84.40 (d), 109.88 (s), 127.52−128.50 (20 × d), 138.10 (s), 138.22 (s), 138.66 (s), 138.73 (s); MS (EI) *m*/*z* (rel intensity) 580 (M^+, 1), 489 (2), 459 (1), 397 (3), 383 (4), 365 (2), 273 (1), 240 (100); HRMS calcd for $C_{37}H_{40}O_6$ 580.2825, found 580.2827. Compound **4**: IR 2980, 1355, 1070, 1020 cm^{-1}; ^1H NMR 1.78−1.98 (4H, m), 3.55 (1H, d, *J* = 9.5 Hz), 3.62 (1H, dd, *J* = 1.9, 10.8 Hz), 3.68 (1H, t, *J* = 9.5 Hz), 3.72 (1H, dd, *J* = 3.7, 10.8 Hz), 3.82−3.89 (2H, m), 3.99 (1H, m), 4.02 (1H, t, *J* = 9.5 Hz), 4.52 (1H, d, *J* = 12.2 Hz), 4.54 (1H, d, *J* = 10.9 Hz), 4.58 (1H, d, *J* = 12.2 Hz), 4.68 (1H, d, *J* = 11.4 Hz), 4.83 (1H, d, *J* = 10.9 Hz), 4.88 (1H, d, *J* = 11 Hz), 4.91 (1H, d, *J* = 11 Hz), 4.95 (1H, d, *J* = 11.4 Hz), 7.15−7.34 (20H, m); ^{13}C NMR 24.02 (t), 33.44 (t), 68.13 (t), 68.74 (t), 71.24 (d), 73.31 (t), 74.73 (t), 75.46 (t), 75.55 (t), 78.50 (d), 80.05 (d), 84.52 (d), 107.34 (s), 127.52−128.80 (20 × d), 138.04 (s), 138.15 (s), 138.36 (s), 138.68 (s); MS (EI) *m*/*z* (rel intensity) 580 (M^+, 1), 489 (4), 397 (5), 365 (2), 291 (5), 274 (5), 253 (40); HRMS calcd for $C_{37}H_{40}O_6$ 580.2825, found 580.2826.

Isomerization of (1*R*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-D-glucopyranose-1-spiro-2′-tetrahydrofuran (3). To a solution of spiro compound **3** (15 mg, 0.026 mmol) in acetic acid (1 mL) was added a solution of HCl (2 μL) in acetic acid (0.075 mL). The mixture was stirred at 50 °C for 6 h, poured into an aqueous solution of KOH (0.5%), and extracted with CH_2Cl_2. The combined extracts weredried over Na_2SO_4 and concentrated under reduced pressure. Chromatotron chromatography of the residue (*n*-hexane−EtOAc, 92:8) gave the spiroacetals **4** (12 mg, 0.021 mmol, 80%) and **3** (3 mg, 0.005 mmol, 20%).

Methyl 2,3,4-Tri-*O*-methyl-6-*O*-tosyl-α-D-glucopyranoside (6). To a solution of alcohol **5**[17] (3.71 g, 15.7 mmol) in dry pyridine (70 mL) was added, under Ar, tosyl chloride (9 g, 47.1 mmol), and the solution was stirred at rt for 16 h. The reaction mixture was then poured into ice−water and extracted with $CHCl_3$. The organic extracts were washed with dilute HCl and water, dried over Na_2SO_4, and concentrated under reduced pressure to give the title compound **6** (6 g, 15 mmol, 98%): IR 1364, 1177 cm^{-1}; ^1H NMR 2.45 (3H, s), 3.05 (1H, dd, *J* = 8.8, 10 Hz), 3.11 (1H, dd, *J* = 3.5, 9.5 Hz), 3.34 (3H, s), 3.46 (3H, s), 3.47 (1H, dd, *J* = 9.5, 10 Hz), 3.48 (3H, s), 3.59 (3H, s), 3.62 (1H, ddd, *J* = 2.4, 4.1, 8.5 Hz), 4.20 (1H, dd, *J* = 2.4, 10.7 Hz), 4.25 (1H, dd, *J* = 4.1, 10.7 Hz), 4.72 (1H, d, *J* = 3.5 Hz), 7.35 (2H, d, *J* = 8.2 Hz), 7.81 (2H, d, *J* = 8.3 Hz); ^{13}C NMR 21.56 (q), 55.22 (q), 58.92 (q), 60.40 (q), 60.72 (q), 68.42 (d), 68.66 (t), 78.75 (d), 81.45 (d), 83.33 (d), 97.31 (d), 127.92 (2 × d), 129.76 (2 × d), 132.99 (s), 144.79 (s); MS (CI, CH_4) *m*/*z* (rel intensity) 389 ($[M - H]^+$, 1), 359 (8), 327 (100), 295 (23), 219 (6), 187 (47), 155 (100).

Methyl 6-Allyl-6-deoxy-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (7). To a solution of *p*-toluenesulfonate **6** (615 mg, 1.577 mmol) in dry Et_2O (30 mL) was added, under Ar at 0 °C, allylmagnesium bromide in Et_2O (6.5 mL, 6.31 mmol). The mixture was stirred at rt for 4 h, poured into brine, and extracted with Et_2O. The organic layer was washed with aqueous saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography (*n*-hexane−EtOAc, 85:15) of the residue gave the title compound **7** (361 mg, 1.39 mmol, 88%): IR 3079, 1640 cm^{-1}; ^1H NMR 1.45 (1H, m), 1.86 (1H, m), 2.05 (1H, m), 2.22 (1H, m), 2.75 (1H, t, *J* = 9.4 Hz), 3.12 (1H, dd, *J* = 3.6, 9.5 Hz), 3.32−3.55 (2H, m), 3.34 (3H, s), 3.46 (3H, s), 3.50 (3H, s), 3.57 (3H, s), 4.71 (1H, d, *J* = 3.6 Hz), 4.93 (1H, dd, *J* = 1.5, 10.3 Hz), 5.00 (1H, dd, *J* = 1.5, 17.4 Hz), 5.78 (1H, dddd, *J* = 6.6, 6.6, 10.2, 17.0 Hz); ^{13}C NMR 29.74 (t), 30.88 (t), 54.87 (q), 58.79 (q), 60.56 (q), 60.68 (q), 69.38 (d), 81.98 (d), 83.44 (d), 84.06 (d), 97.06 (d), 114.69 (t), 138.23 (d); MS (CI, CH_4) *m*/*z* (rel intensity) 260 (M^+, 1), 259 (5), 229 (100), 197 (98), 173 (9), 165 (29), 145 (63); HRMS calcd for $C_{12}H_{21}O_4$ 229.1440, found 229.1439.

Methyl 6-Deoxy-6-(2′-hydroxyethyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (8). A solution of compound **7** (200 mg, 0.769 mmol) in CH_2Cl_2/MeOH (51 mL, 1:1) was cooled to −78 °C, and ozone was introduced into the solution until it became blue. Then Ar was bubbled through the solution to expel excess of ozone, and the mixture was heated to 0 °C. $NaBH_4$ (73 mg, 1.92 mmol) was added and the solution stirred for 2.25 h at rt. The reaction mixture was then poured into water and extracted with $CHCl_3$, dried over Na_2SO_4, and concentrated. Chromatotron chromatography of the residue (first *n*-hexane−EtOAc, 45:55 and then 30:70) gave compound **8** (174 mg, 0.66 mmol, 86%): mp 59.8−60.6 °C (from *n*-hexane); $[\alpha]_D$ +141.5° (*c* = 0.260); IR 3622, 3464 cm^{-1}; ^1H NMR 1.39−1.98 (4H, m), 2.81 (1H, dd, *J* = 8.9, 9.6 Hz), 3.16 (1H, dd, *J* = 3.6, 9.7 Hz), 3.39 (3H, s), 3.47 (1H, t, *J* = 9.5 Hz), 3.49 (1H, m), 3.50 (3H, s), 3.55 (3H, s), 3.61 (3H, s), 3.67 (2H, t, *J* = 6.2 Hz), 4.76 (1H, d, *J* = 3.6 Hz); ^{13}C NMR 27.92 (t), 28.86 (t), 55.01 (q), 58.84 (q), 60.64 (q), 60.75 (q), 62.54 (t), 69.98 (d), 81.90 (d), 83.43 (d), 83.94 (d), 97.12 (d); MS (EI) *m*/*z* (rel intensity) 247 ($[M - OH]^+$, 2), 233 (2), 201 (5), 169 (8), 145 (4), 131 (22), 101 (78), 88 (100); HRMS calcd for $C_{11}H_{21}O_5$ 233.1389, found 233.1375.

Photolysis of Methyl 6-Deoxy-6-(2′-hydroxyethyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (8). A solution of alcohol **8** (117 mg, 0.443 mmol) in cyclohexane (8 mL) containing DIB (158 mg, 0.487 mmol) and iodine (111 mg, 0.443 mmol) under Ar was irradiated at 40 °C for 0.5 h in a similar manner to that described above for the photolysis of **2**. Chromatotron chromatography of the reaction residue (*n*-hexane−EtOAc, 60:40) gave methyl (5*S*)-6-deoxy-5,2′-epoxy-6-ethyl-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (**9**) (55 mg, 0.21 mmol, 47%) and methyl (5*R*)-6-deoxy-5,2′-epoxy-6-ethyl-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (**10**) (32 mg, 0.122 mmol, 28%). Compound **9**: IR 2838, 1446, 1375, 1167, 1077 cm^{-1}; ^1H NMR 1.96−2.12 (4H, m), 3.20 (1H, d, *J* = 9.2 Hz), 3.28 (1H, dd, *J* = 4, 9.1 Hz),

3.34 (1H, t, $J = 9.2$ Hz), 3.45 (3H, s), 3.49 (3H, s), 3.51 (3H, s), 3.59 (3H, s), 3.82 (1H, m), 4.01 (1H, m), 4.79 (1H, d, $J = 3.9$ Hz), irradiation at δ 1.96−2.12 (6-H_2) gave rise to a NOE enhancement of the 3-H signal (δ 3.34, 10%); ^{13}C NMR 24.85 (t), 31.07 (t), 56.26 (q), 58.97 (q), 60.76 (q), 60.80 (q), 67.80 (t), 80.42 (d), 81.07 (d), 83.91 (d), 98.09 (d), 110.29 (s); MS (EI) *m*/*z* (rel intensity) 261 ([M − H]$^+$, 3), 231 (90), 199 (41), 171 (13), 167 (9), 145 (8), 101 (67), 88 (100); HRMS calcd for $C_{11}H_{19}O_5$ 231.1232, found 231.1206. Compound **10**: IR 2836, 1445, 1376, 1171, 1089 cm^{-1}; ^{1}H NMR 1.86−2.16 (4H, m), 3.12 (1H, d, $J = 9.6$ Hz), 3.22 (1H, dd, $J = 4.0$, 9.7 Hz), 3.42 (3H, s), 3.51 (3H, s), 3.61 (3H, s), 3.64 (3H, s), 3.80 (1H, t, $J = 9.7$ Hz), 3.98−4.08 (2H, m), 4.79 (1H, d, $J = 4.0$ Hz), irradiation at δ 1.86−2.16 (6-H_2) gave rise to a NOE enhancement of the 4-H signal (δ 3.12, 6.5%); ^{13}C NMR 24.09 (t), 36.07 (t), 55.49 (q), 58.92 (q), 60.75 (q), 61.40 (q), 70.25 (t), 80.30 (d), 82.14 (d), 83.11 (d), 98.14 (d), 108.50 (s); MS (EI) *m*/*z* (rel intensity) 231 ([M − OMe]$^+$, 6), 199 (3), 167 (2), 159 (3), 114 (98), 101 (44), 88 (100); HRMS calcd for $C_{11}H_{19}O_5$ 231.1232, found 231.1264.

Isomerization of Methyl 5(*R*)-6-Deoxy-5,2′-epoxy-6-ethyl-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (10). To a solution of spiro compound **10** (4 mg, 0.015 mmol) in acetic acid (0.4 mL) was added a 0.1 M solution of TsOH in acetic acid (0.015 mL). The mixture was stirred at rt for 7 h, poured into an aqueous solution of NaOH (10%), and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Chromatotron chromatography of the residue (*n*-hexane−EtOAc, 92:8) gave the spiroacetals **10** (1.6 mg, 0.006 mmol, 40%) and **9** (1.4 mg, 0.005 mmol, 35%).

Methyl 6-Deoxy-6-(3′-hydroxypropyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (11). To a solution of compound **7** (328 mg, 1.26 mmol) in dry THF (20 mL) at 0 °C and under Ar was added dropwise a 1 M solution of BH_3−THF complex (5 mL) and stirred at rt for 4 h. The mixture was then cooled to 0 °C and treated with a 3 M aqueous solution of NaOH (52 mL). The oxidation was carried out by slow dropwise addition of 30% H_2O_2 (52 mL), the temperature being maintained below 40 °C. After stirring for an additional 1 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography of the residue (*n*-hexane−EtOAc, 40:60) gave compound **11** (315 mg, 1.13 mmol, 90%): IR 3623, 3475 cm^{-1}; ^{1}H NMR 1.36−1.50 (2H, m), 1.52−1.71 (2H, m), 1.78−1.86 (2H, m), 2.78 (1H, t, $J = 9.2$ Hz), 3.15 (1H, dd, $J = 3.7$, 9.6 Hz), 3.36−3.59 (2H, m), 3.37 (3H, s), 3.49 (3H, s), 3.52 (3H, s), 3.60 (3H, s), 3.64 (2H, t, $J = 6.3$ Hz), 4.73 (1H, d, $J = 3.6$ Hz); ^{13}C NMR 21.77 (t), 31.15 (t), 32.59 (t), 54.89 (q), 58.78 (q), 60.57 (q), 60.72 (q), 62.41 (t), 69.95 (d), 81.94 (d), 83.45 (d), 83.97 (d), 97.02 (d); MS (CI, CH_4) *m*/*z* (rel intensity) 277 ([M + H]$^+$, 2), 261 (52), 247 (80), 229 (36), 215 (100), 183 (98). HRMS calcd for $C_{11}H_{19}O_4$ 215.1283, found 215.1279.

Photolysis of Methyl 6-Deoxy-6-(3′-hydroxypropyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (11). A solution of compound **11** (102 mg, 0.367 mmol) in cyclohexane (6 mL) containing DHSA (205 mg, 0.66 mmol) and iodine (92 mg, 0.367 mmol) under Ar was irradiated with two 100 W tungsten-filament lamps at reflux temperature for 3 h. Furthermore DHSA (79 mg, 0.257 mmol) was added and the reflux continued for 3 h. The reaction mixture was then poured into aqueous saturated $Na_2S_2O_3$ and extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Chromatotron chromatography (*n*-hexane−EtOAc, 85:15) of the residue afforded methyl (5*R*)-6-deoxy-5,3′-epoxy-2,3,4-tri-*O*-methyl-6-propyl-α-D-glucopyranoside (**12**) (7 mg, 0.025 mmol, 7%) and a mixture of two compounds **13** and **14** which was separated by flash chromatography over neutral alumina (benzene−EtOAc, 97.5:2.5) to afford: methyl (6*S*)-6-deoxy-6,3′-epoxy-2,3,4-tri-*O*-methyl-6-propyl-α-D-glucopyranoside (**13**) (12 mg, 0.043 mmol, 12%) and methyl (6*R*)-6-deoxy-6,3′-epoxy-2,3,4-tri-*O*-methyl-6-propyl-α-D-glucopyranoside (**14**) (8 mg, 0.027 mmol, 8%). Compound **12**: IR 2935, 2840, 1081, 1045 cm^{-1}; ^{1}H NMR 1.63−1.69 (3H, m), 1.79−1.91 (3H, m), 3.03 (1H, d, $J = 8$ Hz), 3.39 (1H, dd, $J = 3.6$, 8 Hz), 3.42 (1H, t, $J = 8$ Hz), 3.52 (3H, s), 3.53 (3H, s), 3.54 (3H, s), 3.57 (3H, s), 3.73 (1H, m), 3.96 (1H, ddd, $J = 2.8$, 11.2, 12.4 Hz), 4.87 (1H, d, $J = 3.6$ Hz); ^{13}C NMR 18.43 (t), 25.15 (t), 29.21 (t), 56.99 (q), 59.09 (q), 60.09 (q), 60.23 (q), 61.91 (t), 79.47 (d), 80.69 (d), 86.02 (d), 97.61 (d), 100.67 (s); MS (CI, CH_4) *m*/*z* (rel intensity) 276 (M$^+$, 1), 275 (7), 245 (100), 213 (83), 181 (49), 153 (100), 88 (100); HRMS calcd for $C_{12}H_{21}O_5$ 245.1389, found 245.1377. Compound **13**: IR 2934, 2830, 1160, 1097, 1050 cm^{-1}; ^{1}H NMR 1.86−1.97 (4H, m), 3.23 (1H, dd, $J = 3.6$, 9.6 Hz), 3.28 (1H, dd, $J = 8.8$, 10 Hz), 3.39 (3H, s), 3.46 (1H, dd, $J = 8.8$, 9.6 Hz), 3.50 (3H, s), 3.58 (3H, s), 3.61 (1H, m), 3.62 (3H, s), 3.75 (1H, m), 3.91 (1H, m), 4.15 (1H, m), 4.82 (1H, d, $J = 3.6$ Hz); ^{13}C NMR 25.97 (t), 26.70 (t), 55.03 (q), 58.95 (q), 60.63 (q), 60.81 (q), 68.73 (t), 70.95 (d), 75.90 (d), 80.48 (d), 81.62 (d), 83.78 (d), 97.52 (d); MS (CI, CH_4) *m*/*z* (rel intensity) 275 ([M − H]$^+$, 7), 245 (95), 213 (100), 185 (12), 181 (29), 153 (11), 88 (95); HRMS calcd for $C_{12}H_{21}O_5$ 245.1389, found 245.1400. Compound **14**: IR 2933, 2835, 1158, 1096, 1055 cm^{-1}; ^{1}H NMR 1.82−1.97 (4H, m), 2.96 (1H, t, $J = 9.6$ Hz), 3.16 (1H, dd, $J = 3.6$, 9.6 Hz), 3.40 (3H, s), 3.51 (3H, s), 3.52 (3H, s), 3.55 (1H, t, $J = 9.6$ Hz), 3.62 (3H, s), 3.76 (1H, dd, $J = 2.2$, 10 Hz), 3.77 (1H, m), 3.90 (1H, dd, $J = 6.4$, 13.6 Hz), 4.16 (1H, ddd, $J = 2.2$, 6.4, 6.4 Hz), 4.79 (1H, d, $J = 3.6$ Hz); ^{13}C NMR 25.14 (t), 25.96 (t), 54.86 (q), 58.89 (q), 60.23 (q), 60.90 (q), 68.44 (t), 70.84 (d), 78.10 (d), 81.54 (d), 81.93 (d), 83.65 (d), 96.94 (d); MS (CI, CH_4) *m*/*z* (rel intensity) 277 ([M + H]$^+$, 13), 275 (7), 245 (47), 213 (100), 205 (2), 181 (37), 88 (100); HRMS calcd for $C_{11}H_{17}O_4$ 213.1127, found 213.1107. Photolysis was also performed with DIB/I_2 (Table 1, entry 4) and with HgO/I_2 (Table 1, entry 5) but complex mixtures were obtained in both cases.

Methyl 2,3,4-tri-*O*-methyl-6-*O*-tosyl-β-D-glucopyranoside (16). To a solution of alcohol **15**[17] (2.95 g, 12.5 mmol) in dry pyridine (60 mL) was added, under Ar, tosyl chloride (7.14 g, 37.5 mmol), and the solution was stirred at rt for 7 h. The reaction mixture was then poured into ice−water and extracted with CH_2Cl_2. The organic extracts were washed with dilute HCl and water, dried over Na_2SO_4, and concentrated under reduced pressure to give the title compound **16** (4.8 g, 12.3 mmol, 98%): mp 72.5−74.1 °C (from *n*-hexane−EtOAc); $[\alpha]_D$ −13.3° (*c* = 0.346); IR 1599, 1448, 1364, 1176 cm^{-1}; ^{1}H NMR 2.45 (3H, s), 2.91 (1H, dd, $J = 7.7$, 8.5 Hz), 3.02 (1H, t, $J = 9.0$ Hz), 3.13 (1H, t, $J = 8.6$ Hz), 3.34 (1H, ddd, $J = 2.2$, 4.9, 9.5 Hz), 3.43 (3H, s), 3.48 (3H, s), 3.54 (3H, s), 3.59 (3H, s), 4.08 (1H, d, $J = 7.6$ Hz), 4.18 (1H, dd, $J = 4.9$, 10.4 Hz), 4.27 (1H, dd, $J = 2.2$, 10.4 Hz), 7.34 (2H, d, $J = 8.2$ Hz), 7.81 (2H, d, $J = 8.3$ Hz); ^{13}C NMR 21.5 (q), 56.67 (q), 60.24 (q), 60.29 (q), 60.57 (q), 68.56 (t), 72.36 (d), 78.62 (d), 83.31 (d), 86.19 (d), 103.8 (d), 127.89 (2 × d), 129.67 (2 × d), 132.79 (s), 144.72 (s); MS (EI) *m*/*z* (rel intensity) 389 ([M − H]$^+$, <1), 359 (<1), 327 (10), 295 (2), 219 (1), 187 (5), 88 (100); HRMS calcd for $C_{15}H_{19}O_6S$ 327.0902, found 327.0901.

Methyl 6-Allyl-6-deoxy-2,3,4-tri-*O*-methyl-β-D-glucopyranoside (17). To a solution of *p*-toluenesulfonate **16** (4.5 g, 11.5 mmol) in dry Et_2O (200 mL) was added, under Ar at 0 °C, allylmagnesium bromide in Et_2O (48.6 mL, 46 mmol). The mixture was stirred at rt for 3 h, poured into brine, and extracted with Et_2O. The organic layer was washed with aqueous saturated $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated under reduced pressure. Dry column chromatography (*n*-hexane−EtOAc, 90:10) of the residue gave the title compound **17** (2.38 g, 9.15 mmol, 79%): IR 3078, 1640, 1086, 1061 cm^{-1}; ^{1}H NMR 1.53 (1H, m), 1.88 (1H, m), 2.06−2.30 (2H, m), 2.81 (1H, t, $J = 9.1$ Hz), 2.93 (1H, dd, $J = 7.7$, 9.2 Hz), 3.09 (1H, ddd, $J = 2.4$, 9.5, 9.5 Hz), 3.11 (1H, t, $J = 8.9$ Hz), 3.50 (3H, s), 3.52 (3H, s), 3.54 (3H, s), 3.59 (3H, s), 4.06 (1H, d, $J = 7.7$ Hz), 4.95 (1H, dddd, $J = 1.7$, 1.7, 1.7, 10.0 Hz), 5.01 (1H, dddd, $J = 1.6$, 1.6, 1.6, 17.0 Hz), 5.80 (1H, dddd, $J = 7.0$, 7.0, 10.1, 17.0 Hz); ^{13}C NMR 29.68 (t), 30.79 (t), 56.73 (q), 60.33 (q), 60.60 (q), 60.68 (q), 73.67 (d), 83.87 (d), 83.95 (d), 86.58 (d), 104.08 (d), 114.82 (t), 138.12 (d); MS (CI, CH_4) *m*/*z* (rel intensity) 259 ([M − H]$^+$, 2), 229 (5), 197 (9), 173 (4), 165 (13), 101 (31), 88 (100); HRMS calcd for $C_{12}H_{21}O_4$ 229.1440, found 229.1430.

Methyl 6-Deoxy-6-(3′hydroxypropyl)-2,3,4-tri-*O*-methyl-β-D-glucopyranoside (18). To a solution of compound **17** (200 mg, 0.77 mmol) in dry THF (12 mL) at 0 °C and under

Ar was added dropwise a 1 M solution of BH_3−THF complex (4.62 mL) and stirred at rt for 5 h. The mixture was then cooled to 0 °C and treated with a 3 M aqueous solution of NaOH (32 mL). The oxidation was carried out by slow dropwise addition of 30% H_2O_2 (32 mL), the temperature being maintained below 40 °C. After stirring for an additional 1 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography of the residue (*n*-hexane−EtOAc, 1:1) gave the compound **18** (196 mg, 0.7 mmol, 92%): mp 56.5−58.5 °C (from acetone−*n*-hexane); $[\alpha]_D$ −4.5° (c = 0.334); IR 3620, 3450 cm^{-1}; ^{1}H NMR 1.39−1.89 (6H, m), 2.87 (1H, t, J = 9 Hz), 2.95 (1H, dd, J = 7.7, 9 Hz), 3.09 (1H, m), 3.13 (1H, t, J = 9 Hz), 3.51 (3H, s), 3.54 (3H, s), 3.56 (3H, s), 3.61 (3H, s), 3.65 (2H, t, J = 6.3 Hz), 4.10 (1H, d, J = 7.7 Hz); ^{13}C NMR 21.66 (t), 31.11 (t), 32.39 (t), 56.65 (q), 60.23 (q), 60.50 (q), 60.58 (q), 62.32 (t), 74.40 (d), 83.68 (d), 83.79 (d), 86.42 (d), 103.97 (d); MS (EI) m/z (rel intensity) 261 ([M − OH]$^+$, 6), 247 (3), 229 (3), 215 (7), 187 (5), 183 (14), 145 (23), 101 (100), 88 (100); HRMS calcd for $C_{13}H_{25}O_5$ 261.1702, found 261.1700.

Photolysis of Methyl 6-Deoxy-6-(3′hydroxypropyl)-2,3,4-tri-*O*-methyl-*β*-D-glucopyranoside (18). A solution of compound **18** (50 mg, 0.18 mmol) in cyclohexane (5 mL) containing DIB (64 mg, 0.198 mmol) and iodine (45 mg, 0.18 mmol) under Ar was irradiated at 40 °C for 0.5 h in a similar manner to that described above for the photolysis of **2**. Chromatotron chromatography of the reaction residue (*n*-hexane−EtOAc, 85:15) gave methyl (5*R*)-6-deoxy-5,3′-epoxy-2,3,4-tri-*O*-methyl-6-propyl-*β*-D-glucopyranoside (**19**) (16.5 mg, 0.059 mmol, 53%) and methyl (5*S*)-6-deoxy-5,3′-epoxy-2,3,4-tri-*O*-methyl-6-propyl-*β*-D-glucopyranoside (**20**) (26.5 mg, 0.095 mmol, 33%). Compound **19**: IR 2836, 1128, 1086, 1049 cm^{-1}; ^{1}H NMR 1.50−1.53 (2H, m), 1.66−1.71 (2H, m), 1.81−1.93 (2H, m), 2.83 (1H, d, J = 9.6 Hz), 2.99 (1H, t, J = 8.6 Hz), 3.50 (1H, t, J = 9.4 Hz), 3.56 (3H, s), 3.57 (3H, s), 3.58 (3H, s), 3.60 (3H, s), 3.66−3.77 (2H, m), 4.42 (1H, d, J = 8 Hz), irradiation at δ 2.83 (4-H) gave rise to a NOE enhancement of the 6-H_2 signal (9.5%); ^{13}C NMR 18.11 (t), 24.41 (t), 30.05 (t), 56.86 (q), 60.35 (q), 60.83 (q), 61.15 (t), 61.53 (q), 82.65 (d), 84.10 (d), 85.17 (d), 97.25 (s), 98.99 (d); MS (EI) m/z (rel intensity) 275 ([M − H]$^+$, 3), 245 (71), 213 (21), 181 (13), 153 (18), 128 (100), 101 (31), 88 (100); HRMS calcd for $C_{12}H_{21}O_5$ 245.1389, found 245.1389. Compound **20**: IR 2837, 1446, 1089, 1008 cm^{-1}; ^{1}H NMR 1.53−1.76 (6H, m), 3.12 (1H, d, J = 7.1 Hz), 3.16 (1H, t, J = 7.2 Hz), 3.32 (1H, t, J = 7.2 Hz), 3.52 (3H, s), 3.54 (3H, s), 3.54 (3H, s), 3.56 (3H, s), 3.71 (1H, m), 4.02 (1H, ddd, J = 2.6, 11.7, 11.7 Hz), 4.38 (1H, d, J = 6.9 Hz); ^{13}C NMR 17.88 (t), 25.11 (t), 27.07 (t), 56.15 (q), 59.66 (q), 59.70 (q), 59.83 (q), 61.72 (t), 82.96 (d), 83.37 (d), 85.75 (d), 98.99 (s), 100.57 (d); MS (EI) m/z (rel intensity) 245 ([M − OMe]$^+$, 6), 213 (4), 181 (5), 153 (7), 128 (100), 101 (20), 88 (94); HRMS calcd for $C_{12}H_{21}O_5$ 245.1389, found 245.1391. Photolysis was also performed with DHSA/I_2 (Table 1, entry 7) and with HgO/I_2 (Table 1, entry 8).

1-Deoxy-1-(3′-hydroxypropyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (21). To a solution of 1-allyl-1-deoxy-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose[21] (443 mg, 1.56 mmol) in dry THF (50 mL) at 0 °C and under Ar was added dropwise a 1 M solution of BH_3−THF complex (4.7 mL, 4.7 mmol) and stirred at rt for 4 h. The mixture was then cooled to 0 °C and treated with a 3 M aqueous solution of NaOH (50 mL). The oxidation was carried out by slow dropwise addition of 30% H_2O_2 (50 mL), the temperature being maintained below 40 °C. After stirring for an additional 1 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography of the residue (*n*-hexane-EtOAc, 60:40) gave compound **21** (310 mg, 70%): IR 3660, 3500 cm^{-1}; ^{1}H NMR 1.32 (3H, s), 1.36 (3H, s), 1.43 (3H, s), 1.48 (3H, s), 1.39−1.66 (4H, m), 3.66 (2H, t, J = 5.9 Hz), 3.77 (1H, dd, J = 3.7, 7.4 Hz), 4.02 (1H, dd, J = 4.8, 8.6 Hz), 4.07 (1H, t, J = 7.2 Hz), 4.09 (1H, dd, J = 6, 8.6 Hz), 4.39 (1H, ddd, J = 4.9, 6.0, 7.3 Hz), 4.49 (1H, d, J = 6.3 Hz), 4.75 (1H, dd, J = 3.7, 6.1 Hz); ^{13}C NMR 24.52 (q), 25.05 (q), 25.99 (q), 26.78 (q), 27.04 (t), 29.03 (t), 62.08 (t), 66.77 (t), 73.36 (d), 79.77 (d), 80.57 (d), 84.10 (d), 85.28 (d), 109.02 (s), 112.51 (s); MS (EI) m/z (rel intensity) 287 ([M − CH_3]$^+$, 73), 229 (4), 211 (3), 201 (4), 187 (4), 169 (10), 101 (100); HRMS calcd for $C_{14}H_{23}O_6$ 287.1495, found 287.1488.

Photolysis of 1-Deoxy-1-(3′-hydroxypropyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (21). A solution of compound **21** (50 mg, 0.165 mmol) in cyclohexane (10 mL) containing DIB (95 mg, 0.29 mmol) and iodine (42 mg, 0.165 mmol) under Ar was irradiated at 40 °C for 3 h in a similar manner to that described above for the photolysis of **2**. Chromatotron chromatography of the reaction residue (*n*-hexane-EtOAc, 85:15) gave (1*S*)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-tetrahydrofuran (**22**) (20 mg, 0.067 mmol, 42%) and (1*R*)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-tetrahydrofuran (**23**) (12.5 mg, 0.042 mmol, 25%). Compound **22**: IR 3015, 1388, 1378, 1070 cm^{-1}; ^{1}H NMR 1.34 (3H, s), 1.37 (3H, s), 1.44 (3H, s), 1.46 (3H, s), 1.88 (1H, m), 1.94−2.01 (2H, m), 2.14 (1H, m), 3.85 (1H, dd, J = 3.7, 8.2 Hz), 3.91 (2H, t, J = 6.6 Hz), 4.01 (1H, dd, J = 4.4, 8.8 Hz), 4.08 (1H, dd, J = 6.4, 8.8 Hz), 4.35 (1H, ddd, J = 4.4, 6.4, 8.4 Hz), 4.52 (1H, d, J = 6 Hz), 4.81 (1H, dd, J = 3.7, 6 Hz); ^{13}C NMR 23.53 (t), 24.69 (q), 25.23 (q), 25.95 (q), 26.67 (q), 31.01 (t), 67.01 (t), 67.91 (t), 73.12 (d), 78.99 (d), 80.08 (d), 84.98 (d), 109.19 (s), 112.51 (s), 115.08 (s); MS (EI) m/z (rel intensity) 285 ([M − CH_3]$^+$, 100), 242 (7), 199 (53), 184 (4), 167 (82), 141 (52), 101 (99); HRMS calcd for $C_{14}H_{21}O_6$ 285.1338, found 285.1333. Compound **23**: IR 3010, 1388, 1377, 1072 cm^{-1}; ^{1}H NMR 1.33 (6H, s), 1.41 (3H, s), 1.43 (3H, s), 1.74 (1H, m), 1.94−2.06 (3H, m), 3.48 (1H, dd, J = 4, 8 Hz), 3.95 (1H, ddd, J = 0.8, 7, 15 Hz), 4.02 (1H, dd, J = 4.2, 8.8 Hz), 4.07 (1H, dd, J = 6, 8.8 Hz), 4.08 (1H, m), 4.43 (1H, ddd, J = 4.4, 6.2, 8.2 Hz), 4.48 (1H, d, J = 6 Hz), 4.75 (1H, dd, J = 4, 6 Hz); ^{13}C NMR 24.20 (t), 24.77 (q), 25.15 (q), 25.77 (q), 27.06 (q), 34.08 (t), 67.09 (t), 69.18 (t), 73.28 (d), 77.04 (d), 79.20 (d), 83.01 (d), 109.26 (s), 112.55 (s), 113.48 (s); MS (EI) m/z (rel intensity) 285 ([M − CH_3]$^+$, 51), 243 (6), 199 (22), 167 (15), 141 (38), 101 (65); HRMS calcd for $C_{14}H_{21}O_6$ 285.1338, found 285.1350.

1-(3′-Butenyl)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (26) and 1-(3′-Butenyl)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-*β*-D-mannofuranose (27). To a solution of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (**24**) (1 g, 3.85 mmol) in dry THF (18 mL) were added under Ar CCl_4 (2.7 mL, 28 mmol) and Ph_3P (2.52 g, 9.6 mmol). The mixture was heated at reflux for 4.5 h, cooled at rt, filtered over Celite 545, and concentrated under reduced pressure. To a solution of the crude residue containing compound **25** (3.2 g) in dry Et_2O (40 mL) was added freshly prepared 3-butenylmagnesium bromide in Et_2O (49 mL, 53.9 mmol) under Ar at 0 °C and the reaction kept at rt for 22 h. The reaction mixture was then poured into brine and extracted with Et_2O, dried over Na_2SO_4, and concentrated. Dry column chromatography (*n*-hexane−EtOAc, 93:7) gave a mixture of compounds **26** and **27** (825 mg, 2.77 mmol, 72%, **26**:**27** = 65:35). The mixture could be partially resolved by careful chromatotron chromatography. Compound **26**: IR 3080, 1640 cm^{-1}; ^{1}H NMR 1.34 (3H, s), 1.38 (3H, s), 1.40−1.65 (2H, m), 1.46 (3H, s), 1.50 (3H, s), 2.13 (2H, m), 3.72 (1H, dd, J = 3.7, 7.6 Hz), 4.04 (1H, dd, J = 4.7, 8.7 Hz), 4.07 (1H, m), 4.11 (1H, dd, J = 6.1, 8.7 Hz), 4.40 (1H, ddd, J = 4.8, 6.0, 7.6 Hz), 4.51 (1H, d, J = 6.2 Hz), 4.77 (1H, dd, J = 3.7, 6.1 Hz), 5.00 (1H, dddd, J = 1.6, 1.6, 1.6, 10.2 Hz), 5.05 (1H, dddd, J = 1.7, 1.7, 1.7, 17.0 Hz), 5.82 (1H, dddd, J = 6.5, 6.5, 10.2, 16.9 Hz); ^{13}C NMR 24.61 (q), 25.31 (q), 26.07 (q), 26.94 (q), 29.68 (t), 29.80 (t), 67.03 (t), 73.43 (d), 79.93 (d), 80.71 (d), 83.56 (d), 85.28 (d), 109.14 (s), 112.52 (s), 115.26 (t), 137.43 (d); MS (EI) m/z (rel intensity) 299 ([M + H]$^+$, 16), 283 (100), 241 (44), 225 (29), 197 (7), 181 (17), 123 (98), 101 (100); HRMS calcd for $C_{16}H_{26}O_5$ 298.1780, found 298.1782. Compound **27**: mp 35.7−37.3 °C (from *n*-hexane); $[\alpha]_D$ −5.6° (c = 0.250): IR 3079, 1640 cm^{-1}; ^{1}H NMR 1.33 (3H, s), 1.38 (3H, s), 1.45 (3H, s), 1.47 (3H, s), 1.70−1.86 (2H, m), 2.18 (2H, m), 3.45 (1H, dd, J = 3.6, 7.6 Hz), 3.48 (1H, ddd, J = 3.6, 6.7, 6.7 Hz), 4.05 (1H, dd, J = 5.1, 8.7 Hz), 4.10 (1H, dd, J = 5.8, 8.7 Hz), 4.40 (1H, ddd, J = 5.3, 5.3, 7.6 Hz), 4.60 (1H, dd, J = 3.6, 6.2 Hz), 4.73 (1H, dd, J = 3.6, 6.2 Hz), 4.98

(1H, dddd, J = 1.6, 1.6, 1.6, 10.2 Hz), 5.04 (1H, dddd, J = 1.7, 1.7, 1.7, 17.1 Hz), 5.82 (1H, dddd, J = 6.6, 6.6, 10.2, 16.9 Hz); ^{13}C NMR 24.71 (q), 25.32 (q), 25.78 (q), 26.90 (q), 27.35 (t), 30.22 (t), 66.97 (t), 73.23 (d), 80.83 (d), 81.35 (d), 81.50 (d), 81.55 (d), 108.98 (s), 112.24 (s), 114.74 (t), 138.20 (d); MS (EI) *m*/*z* (rel intensity) 299 ([M + H]$^+$, 3), 298 (M$^+$, 1), 283 (100), 241 (10), 225 (5), 197 (3), 165 (10), 123 (91), 101 (98); HRMS calcd for $C_{16}H_{26}O_5$ 298.1780, found 298.1761.

1-Deoxy-1-(4′-hydroxybutyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (28) and 1-Deoxy-1-(4′-hydroxybutyl)-2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranose (29). To a solution of compounds **26** and **27** (514 mg, 1.72 mmol) in dry THF (17 mL) at 0 °C and under Ar was added dropwise a 1 M solution of BH_3−THF complex (10.3 mL) and stirred at rt for 5 h. The mixture was then cooled to 0 °C and treated with a 3 M aqueous solution of NaOH (35 mL). The oxidation was carried out by slow dropwise addition of 30% H_2O_2 (35 mL), the temperature being maintained below 40 °C. After stirring for an additional 1 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Dry column chromatography of the residue (*n*-hexane-EtOAc, 1:1) gave compounds **28** and **29** (480 mg, 1.52 mmol, 88%). An aliquot of the mixture could be partially resolved by careful chromatotron chromatography. Compound **28**: IR 3620, 3488 cm^{-1}; ^{1}H NMR 1.34 (3H, s), 1.38 (3H, s), 1.41−1.69 (6H, m), 1.46 (3H, s), 1.50 (3H, s), 3.66 (1H, t, J = 6.3 Hz), 3.73 (1H, dd, J = 3.7, 7.7 Hz), 4.04 (1H, dd, J = 4.6, 8.7 Hz), 4.06 (1H, m), 4.11 (1H, dd, J = 6.1, 8.7 Hz), 4.40 (1H, ddd, J = 4.6, 6.0, 7.7 Hz), 4.51 (1H, d, J = 6.4 Hz), 4.77 (1H, dd, J = 3.7, 6.1 Hz); ^{13}C NMR 22.01 (t), 24.64 (q), 25.14 (q), 26.10 (q), 26.94 (q), 30.29 (t), 32.22 (t), 62.69 (t), 67.01 (t), 73.46 (d), 79.98 (d), 80.75 (d), 84.08 (d), 85.29 (d), 109.14 (s), 112.56 (s); MS (EI) *m*/*z* (rel intensity) 317 ([M+H]$^+$, 8), 301 (100), 259 (81), 243 (9), 215 (6), 200 (10), 183 (22), 165 (43), 101 (97); HRMS calcd for $C_{15}H_{25}O_6$ 301.1651, found 301.1647. Compound **29**: IR 3620, 3496 cm^{-1}; ^{1}H NMR 1.26−1.79 (6H, m); 1.34 (3H, s), 1.38 (3H, s), 1.45 (3H, s), 1.48 (3H, s), 3.47 (1H, dd, J = 3.6, 7.3 Hz), 3.47 (1H, ddd, J = 3.6, 6.8, 6.8 Hz), 3.67 (1H, t, J = 6.2 Hz), 4.05 (1H, dd, J = 5.1, 8.6 Hz), 4.10 (1H, dd, J = 5.8, 8.6 Hz), 4.40 (1H, ddd, J = 5.2, 5.2, 7.4 Hz), 4.62 (1H, dd, J = 3.6, 6.2 Hz), 4.74 (1H, dd, J = 3.6, 6.2 Hz); ^{13}C NMR 22.22 (t), 24.70 (q), 25.30 (q), 25.76 (q), 26.92 (q), 27.76 (t), 32.59 (t), 62.59 (t), 66.97 (t), 73.22 (d), 80.78 (d), 81.42 (d), 81.60 (d), 82.16 (d), 109.00 (s), 112.32 (s); MS (EI) *m*/*z* (rel intensity) 317 ([M + H]$^+$, 8), 301 (100), 259 (58), 243 (6), 215 (5), 183 (21), 165 (45), 101 (96); HRMS calcd for $C_{15}H_{25}O_6$ 301.1651, found 301.1658.

Photolysis of 1-Deoxy-1-(4′-hydroxybutyl)-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (28+29). A solution of the mixture of alcohols **28** and **29** (40 mg, 0.126 mmol) in cyclohexane (4 mL) containing DIB (73 mg, 0.227 mmol) and iodine (32 mg, 0.126 mmol) under Ar was irradiated at 40 °C for 2.5 h in a similar manner to that described above for the photolysis of **2**. Chromatotron chromatography of the reaction residue (*n*-hexane-EtOAc, 93:7) gave (1*R*)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-tetrahydropyran (**30**) (6.4 mg, 0.02 mmol, 16%), (1*S*,3′*R*)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-(3′-iodotetrahydropyran) (**31**) (5.1 mg, 0.011 mmol, 9%), (1*S*)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-tetrahydropyran (**32**) (6.8 mg, 0.022 mmol, 17%), (1*R*)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-(3′,3′-diiodotetrahydropyran) (**33**) (5.1 mg, 0.009 mmol, 7%). Compound **30**: IR 2942, 1373, 1236, 1066 cm^{-1}; ^{1}H NMR 1.36 (3H, s), 1.38 (3H, s), 1.46 (3H, s), 1.50−1.79 (6H, m), 1.56 (3H, s), 3.73 (1H, dd, J = 4.4, 7.9 Hz), 3.85−3.88 (2H, m), 4.11 (2H, d, J = 5.3 Hz), 4.35 (1H, d, J = 6.1 Hz), 4.45 (1H, ddd, J = 5.3, 5.3, 7.9 Hz), 4.77 (1H, dd, J = 4.4, 6.1 Hz); ^{13}C NMR 19.18 (t), 24.80 (t), 25.26 (q), 25.42 (q), 25.73 (q), 27.00 (q), 31.65 (t), 63.67 (t), 66.96 (t), 73.69 (d), 77.80 (d), 79.67 (d), 84.87 (d), 102.96 (s), 109.23 (s), 114.05 (s); MS (EI) *m*/*z* (rel intensity) 315 ([M + H]$^+$, 3), 299 (30), 257 (9), 239 (6), 213 (22), 181 (12), 141 (52), 101 (100); HRMS calcd for $C_{15}H_{23}O_6$ 299.1495, found 299.1487. Compound **31**: IR 2992, 1373, 1075, 994 cm^{-1}; ^{1}H NMR 1.36 (3H, s), 1.39 (3H, s), 1.48 (3H, s), 1.55 (3H, s), 1.73 (1H, m), 1.88 (1H, m), 2.35 (1H, m), 2.51 (1H, dddd, J = 4.1, 12.8, 12.8, 12.8 Hz), 3.85 (1H, m), 3.97 (1H, ddd, J = 2.5, 11.3, 11.3 Hz), 4.10 (1H, dd, J = 6.4, 8.6 Hz), 4.14 (1H, dd, J = 4.8, 8.6 Hz), 4.27 (1H, dd, J = 4.5, 12.4 Hz), 4.31 (1H, dd, J = 4.6, 6.9 Hz), 4.41 (1H, ddd, J = 4.9, 6.5, 6.5 Hz), 4.86 (1H, dd, J = 4.6, 6.2 Hz), 4.90 (1H, d, J = 6.2 Hz); ^{13}C NMR 25.32 (q), 25.56 (q), 25.56 (q), 26.91 (q), 28.44 (t), 34.16 (t), 34.34 (d), 61.97 (t), 66.57 (t), 74.15 (d), 79.86 (d), 81.64 (d), 85.80 (d), 101.74 (s), 109.23 (s), 114.72 (s); MS (EI) *m*/*z* (rel intensity) 441 ([M + H]$^+$, 8), 425 (69), 397 (9), 383 (20), 339 (13), 313 (89), 255 (23), 141 (35), 101 (100); HRMS calcd for $C_{15}H_{22}O_6I$ 425.0461, found 425.0463. Compound **32**: IR 2945, 1373, 1162, 1085 cm^{-1}; ^{1}H NMR 1.32 (3H, s), 1.39 (3H, s), 1.46 (6H, s), 1.54−1.80 (6H, m), 3.58 (1H, m), 3.72 (1H, ddd, J = 2.7, 11.5, 11.5 Hz), 3.83 (1H, dd, J = 3.7, 8.0 Hz), 4.05 (1H, dd, J = 4.4, 8.6 Hz), 4.13 (1H, dd, J = 6.2, 8.6 Hz), 4.34 (1H, d, J = 6.0 Hz), 4.40 (1H, ddd, J = 4.4, 6.2, 8.0 Hz), 4.78 (1H, dd, J = 3.7, 6.0 Hz); ^{13}C NMR 19.25 (t), 24.55 (q), 25.19 (t), 25.29 (q), 25.91 (q), 26.89 (q), 28.50 (t), 61.28 (t), 67.17 (t), 73.17 (d), 78.81 (d), 80.02 (d), 85.85 (d), 105.71 (s), 109.16 (s), 112.43 (s); MS (EI) *m*/*z* (rel intensity) 315 ([M + H]$^+$, 9), 313 (3), 299 (94), 257 (18), 241 (12), 213 (29), 181 (43), 141 (65), 101 (100); HRMS calcd for $C_{16}H_{25}O_6$ 313.1651, found 313.1658. Compound **33**: IR 2934, 1375, 1099, 1065 cm^{-1}; ^{1}H NMR 1.12 (1H, brd, J = 13.8 Hz), 1.35 (3H, s), 1.41 (3H, s), 1.47 (3H, s), 1.73 (3H, s), 2.18 (1H, m), 2.69 (1H, ddd, J = 2.8, 2.8, 14.6 Hz), 2.98 (1H, ddd, J = 4.1, 12.5, 14.6 Hz), 3.69−3.81 (2H, m), 3.99 (1H, dd, J = 4.2, 5.6 Hz), 4.16 (1H, dd, J = 6.5, 8.7 Hz), 4.25 (1H, dd, J = 5.4, 8.7 Hz), 4.47 (1H, d, J = 6.1 Hz), 4.47 (1H, ddd, J = 5.5, 5.5, 6.5 Hz), 4.72 (1H, dd, J = 4.2, 6.1 Hz); ^{13}C NMR 24.04 (q), 25.36 (q), 25.60 (q), 26.59 (q), 26.97 (t), 50.45 (t), 60.03 (t), 66.34 (t), 73.53 (d), 79.10 (d), 80.48 (d), 87.96 (d), 103.16 (s), 108.85 (s), 113.63 (s), the C-3′(s) could not be observed; MS (EI) *m*/*z* (rel intensity) 567 ([M + H]$^+$, 3), 551 (49), 509 (16), 439 (28), 424 (10), 381 (11), 323 (6), 312 (100), 196 (29), 101 (100); HRMS calcd for $C_{15}H_{21}O_6I_2$ 550.9428, found 550.9432.

Reduction of (1*S*,3′*R*)-1-Deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-(3′-iodotetrahydropyran) (31). To a solution of compound **31** (4 mg, 0.009 mmol) in dry benzene (1 mL) were added Bu_3SnH (0.012 mL, 0.045 mmol) and AIBN (1 mg, 0.006 mmol) and stirred at reflux temperature for 40 min. The reaction mixture was then poured into water, extracted with Et_2O, dried over Na_2SO_4, and concentrated. The residue was purified by chromatotron chromatography (*n*-hexane-EtOAc, 87:13) to give compound **30** (2.3 mg, 0.007 mmol, 80%).

Reduction of (1*R*)-1-Deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose-1-spiro-2′-(3′,3′-diiodotetrahydropyran) (33). To a solution of compound **33** (5 mg, 0.009 mmol) in dry benzene (1 mL) were added Bu_3SnH (0.024 mL, 0.09 mmol) and AIBN (1 mg, 0.006 mmol) and stirred at reflux temperature for 0.5 h. The reaction mixture was then poured into water, extracted with Et_2O, dried over Na_2SO_4, and concentrated. The residue was purified by chromatotron chromatography (*n*-hexane-EtOAc, 93:7) to give compound **32** (2.5 mg, 0.008 mmol, 90%).

Acknowledgment. This work was supported by the Investigation Programme no. PB93-0171 of the Dirección General de Investigación Científica y Técnica and Programmes no. 93/030 and 93/014 of the Dirección General de Universidades e Investigación del Gobierno de Canarias. A.M. thanks the Ministerio de Educación y Ciencia, Spain, for a fellowship.

Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds **2**−**4**, **6**−**14**, **16**−**23**, and **26**−**33** (56 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960060G