Easy and Stereoselective One-Step Incorporation of Two Asymmetric Carbons in Pyranose Derivatives to Acyclic Epoxyamides: New, Potentially Useful Acyclic Chiral Templates

F. J. López-Herrera,* A. M. Heras-López, M. S. Pino-González, and F. Sarabia García

Departamento de Bioquímica, Biología Molecular y Química Orgánica, Facultad de Ciencias, Universidad de Málaga, 29071, Málaga, Spain

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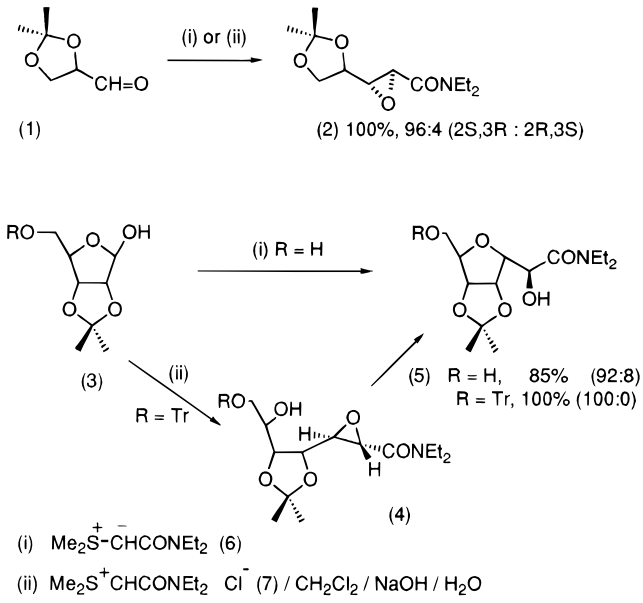
We reacted *N,N*-diethyl-2-(dimethylsulfuranylidene)acetamide with 4,6-*O*-alkylidene-glycopyranoses under several experimental conditions and obtained, stereoselectively, derivatives of acyclic 3-(polyhydroxyalkyl)-α,*β*-epoxyamides. In this way, and in one stage, we introduced, highly stereoselectively, two new chiral carbons with a substituted asymmetric epoxide group that could then be regioselectively transformed and, in addition, obtained highly functionalized acyclic structures starting from easily obtained cyclohemiacetalic monosaccharides. The configuration of the new chiral carbons of the resulting *trans*-epoxyamides was determined by comparing the IR, NMR, and polarimetric data with another epoxyamide of known configuration. We attempted to explain the stereochemistry of the major products by proposing a preferential conformation for the different starting aldehyde sugars in the basic reaction medium that took into account, at first, the principal electrical interactions between the carbonyl group and those unprotected hydroxyl groups with partial hydroxylate character and, secondarily, the preferred equatorial approach (*exo*) of the nucleophile. Finally, we studied the cyclization of the reaction products by an initial Payne transposition of the *γ*-hydroxy-α,*β*-epoxide to α-hydroxy-*β*,*γ*-epoxide, followed by its cyclization to a C-glycofuranoside.

The use of carbohydrate derivatives as chiral templates in the chiron approach to the synthesis of many interesting products is now widely documented.[1] However, there are very few easily prepared carbohydrate derivatives like compound **1**[2] that would serve as comparable versatile synthetic templates. In general, the most frequently employed carbohydrate chiral templates are cyclohemiacetalic monosaccharide derivatives, like, for example, **3**. In these cyclic derivatives, the increase in the number of chiral carbons and their simultaneous transformation into acyclic structures is generally a slow, multistage process which, in addition to needing much time, is often extremely costly. For example, Wittig's reaction is employed to extend the carbonate skeleton of the monosaccharides by two carbon atoms, sometimes with high *E*/*Z* stereoselectivity.[3] The subsequent transformation of the resulting alkenes to allylic alcohols that are later epoxidized by the Sharpless method gives sugar derivatives and other interesting target products.[4]

Our research team recently published[5] a highly stereoselective synthesis of the epoxyamide **2** by reacting 2,3-*O*-isopropylidene-D-glyceraldehyde (**1**) with the amide-stabilized sulfur ylide **6**. More recently,[6] we have described the synthesis of this same compound by using the two-phase method (preparing the ylide in situ from the sulfonium salt **7**) (Scheme 1). Unfortunately, when we extended this reaction to other aldehyde-sugars,[7] although the reaction occurred and gave high yields, we found that, unlike the reaction with **1**, the stereoselectivity of the process was very low. Compound **2** can be considered as a new and useful acyclic chiral template to synthesize interesting chiral compounds. Shortly afterwards, we published[7] the highly stereoselective synthesis of C-glycofuranosides, like **5**, by a similar process, the reaction of the same amide-stabilized sulfur ylide with partially-protected glycofuranoses like **3**. We obtained an analogous result by using the two-phase

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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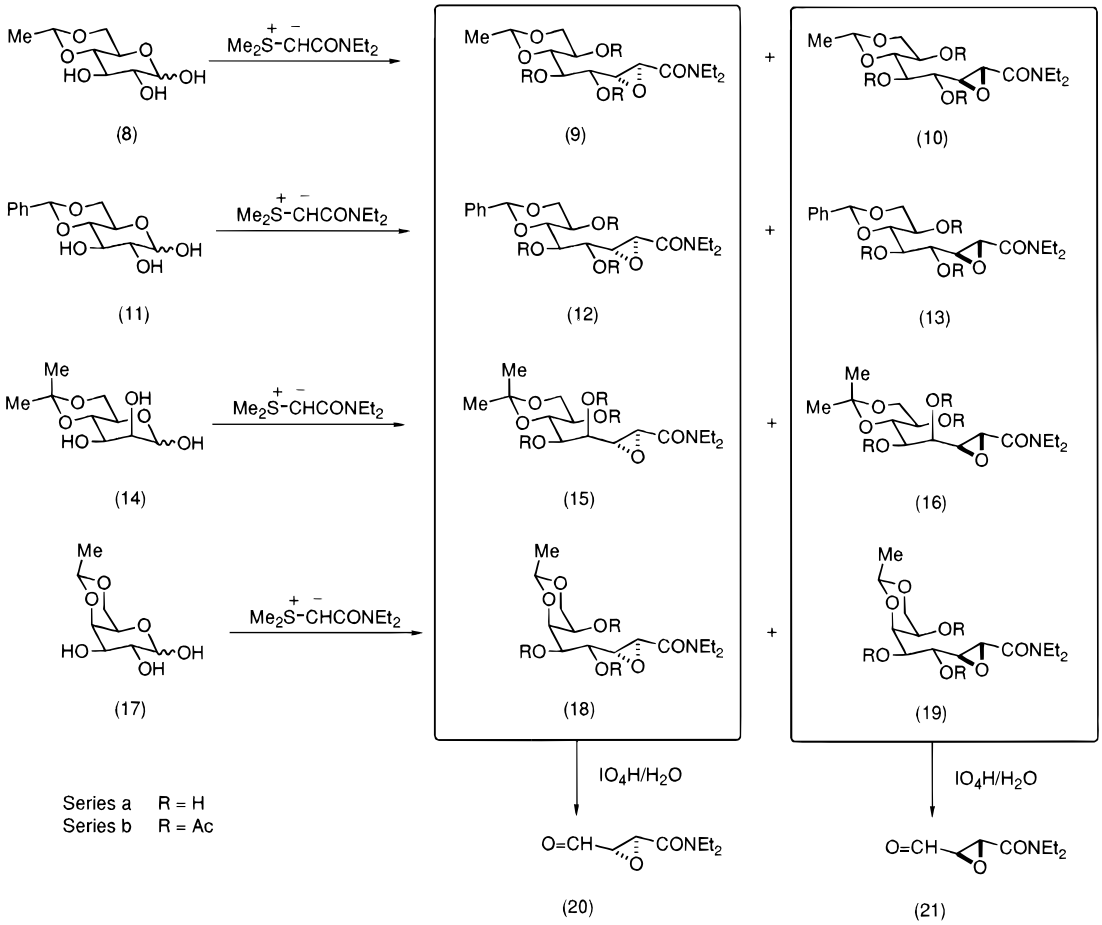
Scheme 2



method.[6] The high stereoselectivity of these processes reflects a high facial diastereoselectivity in the process that adds ylide to the aldehyde forms of the monosaccharide derivatives. We attributed this[7] to (i) the rigidity conferred to the open structure of the starting monosaccharides in the presence of the 2,3-*O*-isopropylidenic group and, moreover, (ii) to the very preferential contribution of one of the rotamers of the C1−C2 bond which is the consequence of the electrical repulsion between the carbonyl group and the alkoxide generated, at least partially, on the OH group in C-4 by the basicity of the medium. The preferential attack on these conformers from the less-hindered α face gives stereoselectively the major epoxyamides. The structures of C-glycofuranosides of the resulting cyclic products are the result of the easy cyclization of the epoxyamides and is the direct consequence of two structural factors: (i) the easy formation of the five-membered rings, and (ii) the presence of the 4,5-*O*-isopropilidenic groups that maintain a *cis* arrangement of the two groups involved in the cyclization (carbon C-3 and the hydroxyl on C-6) which, therefore, are very close in space. These antecedents suggested that we should extend this reaction to simple derivatives of the glycopyranoses with the two following fundamental objectives: (i) to obtain new acyclic epoxyamides, by exploiting their lower tendency to form six-membered rings, and, in view of the stereoselectivity shown in the reactions with cyclohemiacetalic derivatives, this should produce a high stereoselectivity, and (ii) to cyclize these structures to interesting C-glycopyranosides and others like aza-derivatives, etc. With this in mind, we extended this reaction to a series of 4,6-*O*-alkylidene-glycopyranoses in which the protection of the hydroxyl on C-6 of the resultant epoxyamide impedes its intramolecular cyclization to C-glycofuranosides and increases the stability of their acyclic structure. At the same time, the 1,3-dioxane ring introduces a certain conformational rigidity that although less than that of the 2,3-*O*-isopropylidenics, should favor the stereoselectivity of the addition processes.

Results and Discussion

In this way, this present work presents an easy and stereoselective synthesis of new and useful acyclic epoxyamides prepared in only one stage from easily available acyclic monosaccharide derivatives. The first reaction studied was that of 4,6-*O*-ethylidene-D-glucopyranose (**8**) with *N*,*N*-diethyl-2-(dimethylsulfuranylidene)acetamide (**6**) in THF at room temperature. After 48 h of reaction this gave a 85:15 mixture of the epoxyamides **9a** and **10a**, with a total yield of 59%. The same reaction when carried out at 0−5 °C, produced, after 48 h, one product only, **9a**, with a 69% yield and almost total stereoselectivity (Scheme 2). The same reaction in acetonitrile at 0−5 °C, and also after 48 h, gave an increased yield of 85%, but the stereoselectivity was lower (79:21). In this way, and in only one stage, we extended the starting monosaccharide carbon chain by two carbons and introduced simultaneously two new chiral carbons with either complete or high stereoselectivity. Even more, we introduced an asymmetrically substituted epoxy group which has great potential and versatility for subsequent regio- and stereospecific transformation in synthetic reactions. At the same time, we transformed a cyclohemiacetalic monosaccharide derivative into an

Table 1. Reactions of Ylide 6 with Derivatives 8, 11, 14, and 17

compound	solvent	temp (°C)	ylide (equiv)	reaction time (h)	epoxides (%)	stereoselectivity		C-glycosides (%)
8	THF	0−5	2	48	69	100:0	(**9:10**)[a]	16
	THF	rt	2	48	59	85:15	(**9:10**)[a]	16
	MeCN	0−5	2	48	85	79:21	(**9:10**)[a]	0
11	MeCN−THF (5:2)	0−5	2	96	35	63:37	(**12:13**)	0
	THF	rt	4	6	43	84:16	(**12:13**)	0
14	DMSO	rt	2	48	63	52:48	(**15:16**)	0
	MeCN	0−5	2	48	68	88:12	(**15:16**)	<1
17	DMSO	rt	2	48	37	90:10	(**18:19**)	
	MeCN	0−5	2	48	72	70:30	(**18:19**)	10

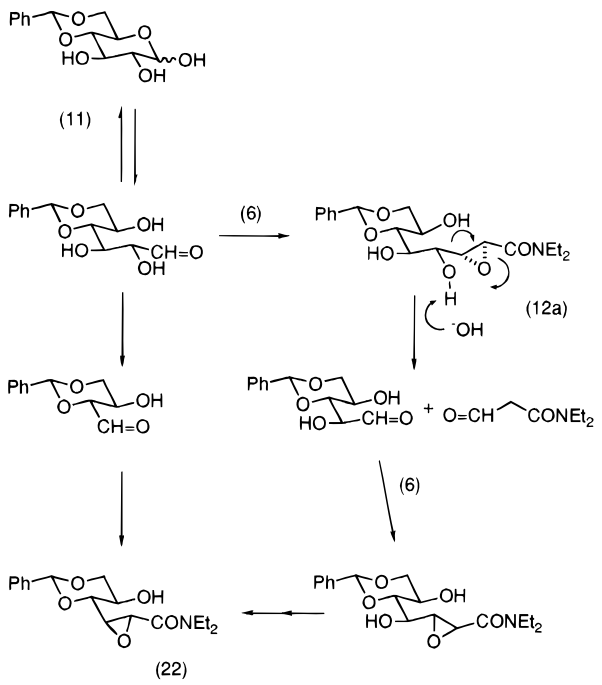
[a] No other diastereomer was detected.

acyclic product. In addition, the obtained epoxyamide was shown to be particularly stable in its open form and this contrasted interestingly with the analogous compounds prepared from glycofuranoses,[7] like **4**, which cyclizes spontaneously to **5**. We extended the reaction to other pyranoses to test the generality of these preliminary results. In this way, we studied the reaction of the ylide **6** with the following pyranose monosaccharide derivatives: 4,6-*O*-benzylidene-D-glucopyranose (**11**), 4,6-*O*-isopropylidene-D-mannopyranose (**14**), and 4,6-*O*-ethylidene-D-galactopyranose (**17**), all very easily obtainable (Scheme 2). The results (Table 1) show similar yields and that these depend on the solvent employed, especially in the case of the D-glucose derivative **8**.

The reactions were carried out using 1:2 or 1:4 molar ratios of monosaccharide/ylide. The reaction times required to consume completely the starting monosaccharide were, respectively, 48 and 6 h. However, the reaction of derivative **11** required 96 h when a molar ratio of 1:2 was used. The presence of free hydroxyl groups on C-2 and C-3 caused simultaneous retroaldolic reactions that degraded the 4,6-*O*-alkylidene-hexopyranoses to 1,3-alkylidene-tetroses and these, in turn, gave rise to secondary products and reduced the reaction yield. Another significant finding was that during long reaction times, the epoxyamides formed initially largely decomposed. In this way, in several of these reactions we detected subproducts, but principally in reaction of **11**, in which **22** was formed, probably the consequence of a previous retroaldolic process on **11**. However, it could be the result of a different reiterative process like that shown in Scheme 3. This latter proposal is supported by the fact that prolonged treatment (96 h) of **12a**, with a certain amount of ylide **6**, under the same conditions as those used for its synthesis was found to cause a partial decomposition. After acetylation and ^{1}H- and ^{13}C-NMR analysis, we found tetrose derivatives that conserved the acetalic group, but had only three carbons of the original polyhydroxylated chain.[8] Thus, in the reaction of **14**, we detected the presence of a minor product (<5%) that could not be separated from one of the principal products, **16**, and subsequent ^{13}C-NMR analysis strongly suggested the structure of a product similar to **22**.[9]

These processes can be minimized by employing short reaction times and even by avoiding an excess of the base used to generate the ylide. We have now simplified and

Scheme 3



perfected the preparation process of these ylides and have used it in many of these reactions, particularly those that used the 1:4 ratio. The ylide is prepared by agitating the sulfonium salt with a 20% solution of NaOH. The resultant ylide **6** was extracted in the organic phase and isolated free of the inorganic residues. After the organic phase was dried and concentrated, the ylide even crystallized out in the refrigerator. We later employed it in the reactions without further purification. Although, in every case, we only obtained *trans* epoxyamides, the yields and the stereoselectivities of the addition processes in some of the reactions with the 4,6-monoacetals of D-glucose (**8** and **11**), D-mannose (**14**), and D-galactose (**17**) were comparatively less than those reached in the reactions with 2,3-isopropylidene-D-ribofuranose[7] (85%, 92:8 of the C-glycosides) and 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (practically quantitative, 87:13). This can be interpreted as the consequence of a larger facial diastereoselection in the aldehyde group of the 2,3-*O*-isopropylidene-glycofuranoses due to a larger impediment to rotation, that lead to a preferential conformation of the C1−C2 bond, by the existence of a greater interaction between the C-1 carbon and the C-4 carbon and its substituents. The latter are found with a *cis* arrangement on the 1,2-dioxolane ring. Comparatively, the 4,6-acetals, together with the free 2-OH and 3-OH groups, present a more flexible carbon chain; however, this increased flexibility is not excessive. If our interpretation

(8) Unknown product (probably **22**) ^{1}H-NMR ($CDCl_3$) δ: 7.6−7.2 (m, 5H, *Ph*CH); 5.48 (s, 1H, PhC*H*), 5.30 (dt, J = 5 and 10 Hz, H-3); 4.48 (dd, J = 5 and 10 Hz, H-8e); 4.2 (m, 1H, H-2); 3.62 (t, J = 10 Hz, H-8a). ^{13}C-NMR ($CDCl_3$) δ: 130.8, 128.8, 128.0, and 126.0 (*Ph*CH); 101.1 (Ph*C*H); 75.8, 67.8, and 61.6 (C-2, C-3, and C-4) and 20.8 (CO_2CH_3).

(9) Unknown product, similar to **22:** ^{13}C-NMR ($CDCl_3$) δ: 167.03 ($CONEt_2$), 76.7 (C-4), 68.2 (C-5), 62.0 (C-6), 57.9 (C-2), 51.5 (C-3). Other signals are similar with that of **16**.

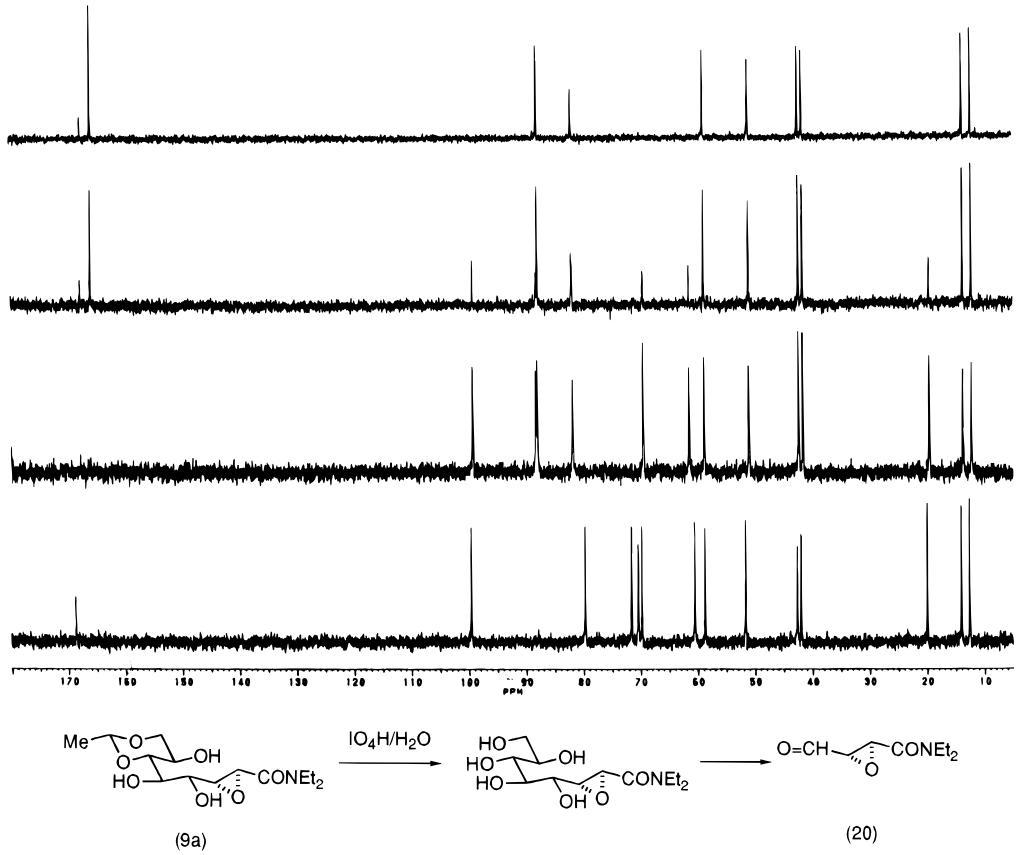


Figure 1. Evolution of the ^{13}C-NMR spectrum of of the periodic oxidation of compound **9a**.

is correct, the stereoselectivity observed for those derivatives of 4,6-*O*-alkylidene-pyranose (maximum for the D-glucopyranoses) (**8** and **11**) should correlate well with the relatively greater or smaller thermodynamic stabilities of these compounds. Thus, the D-glucose, that has its substituents on C-2, C-3, C-4, and C-5 in an equatorial position, should, because of this, have a strong preference for acyclic conformations very similar to that of the initial conformation formed during the opening and closing process of the cyclic hemiacetalic ring. Consequently, the aldehydic carbon and the 5-OH should present a closer proximity and a stronger interaction. This would give greater facial diastereoselection and this, in turn, would confer greater stereoselectivity. The *trans* configuration of the epoxide group of all these compounds was established by the value of the coupling constant $J_{2,3} < 2.2$ Hz and the absolute configuration of the carbons C-2 and C-3, by a polarimetric procedure and the NMR chemical shift correlation with the epoxyamide **2**,[6] the configuration of which is known. Thus, a small amount of **9a** was treated with aqueous periodic acid (in excess, at room temperature and reacted for 12−24 h) to hydrolyze the acetal group and to oxidize the resultant glycol. The sign of the rotatory power of the resulting solution ($[\alpha] = -8.9°$ for the epoxyaldehyde **20**, obtained from **2**) permitted us to assign the structures of **20** or **21**, to the resultant aldehyde-epoxyamide product and from these results we assigned the absolute configuration of the starting epoxyamide. The quantitative transformation of **9a** to **20** was checked by ^{13}C-NMR spectroscopy, carrying out the experiment in D_2O. Figure 1 shows the evolution of the ^{13}C-NMR spectrum during the oxidation process. The lower spectrum corresponds to the starting product **9a**, while the upper corresponds to product **20** formed after 22 h. The latter shows only the signals that correspond to the NEt_2 group (12.2, 13.7, 41.6, and 42.4), the carbons of the epoxide group, C-2 (51.0) and C-3 (58.9), the carbonyl group of the amide *C*ONEt_2 (167.8), and new signals that correspond to the aldehyde group on C-4 (88.2) of compound **20**, together with the signals that correspond to the formaldehyde hydrate (82.0) and the formic acid (166.0), formed during the oxidation. The acetal groups **C**HMe, CH**Me** and the carbons C-4, C-5, C-6, C-7, and C-8 of **9a** had completely disappeared.

Analogously, we confirmed by ^{13}C-NMR spectroscopy that **15a** had been completely transformed into **20**. Moreover, the oxidation spectra of **15a** carried out in D_2O also showed the fastest hydrolysis of the 4,6-*O*-isopropylidenic groups. The reaction was complete after only 5−10 min. Figure 2 shows the evolution of the ^{13}C-NMR spectrum during the oxidation. As before, the lower spectrum corresponds to the starting compound **15a**, while the upper, obtained after 19 h, corresponds to the final product **20**. This latter spectrum is practically identical to the central spectrum that was obtained 5 min after the start of oxidation. Both these spectra show only the signals that correspond to compound **20**, together with those of formaldehyde hydrate (82.0) and formic acid (166.0), formed in the oxidation. As before, the signals of carbons CMe_2 (acetal), C-4, C-5, C-6, C-7, and C-8 of **15a** have completely disappeared.

When we applied this same procedure to these and other polyhydroxy-epoxyamides, we were able to assign the configuration of the carbons of the epoxide group in compounds **9a**, **12a**, **15a**, and **18a** all of which produced compound **20**, while the compounds **10a**, **13a**, **16a**, and **19a** produced **21**. The preferential formation of epoxides with a type **A** structure detected in all cases can be tentatively explained as the result of a strong electrical repulsion between the free carbonyl group and the closest

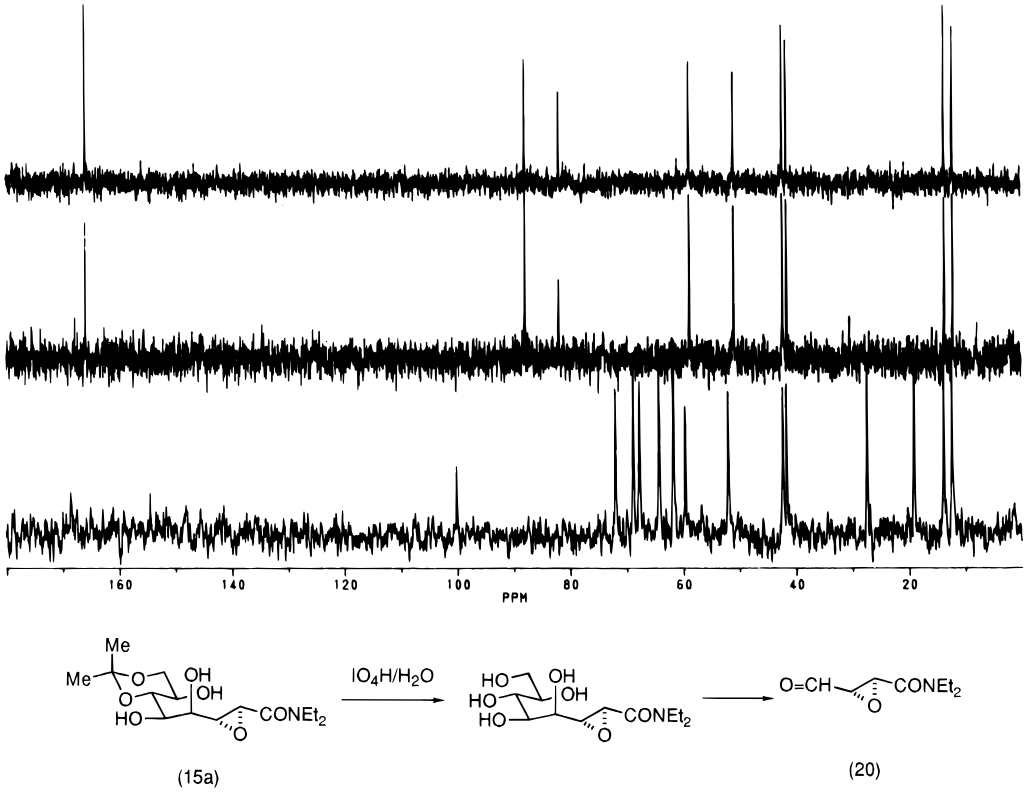
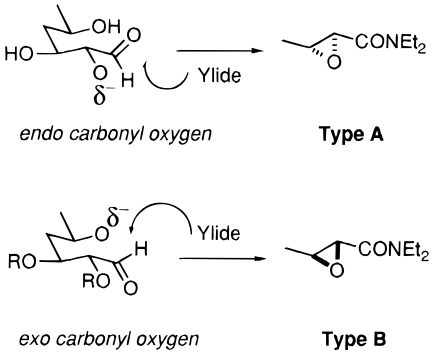


Figure 2. Evolution of the ^{13}C-NMR spectrum of the periodic oxidation of **15a**.



Scheme 4

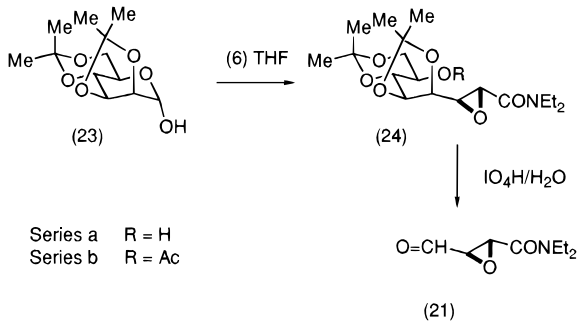
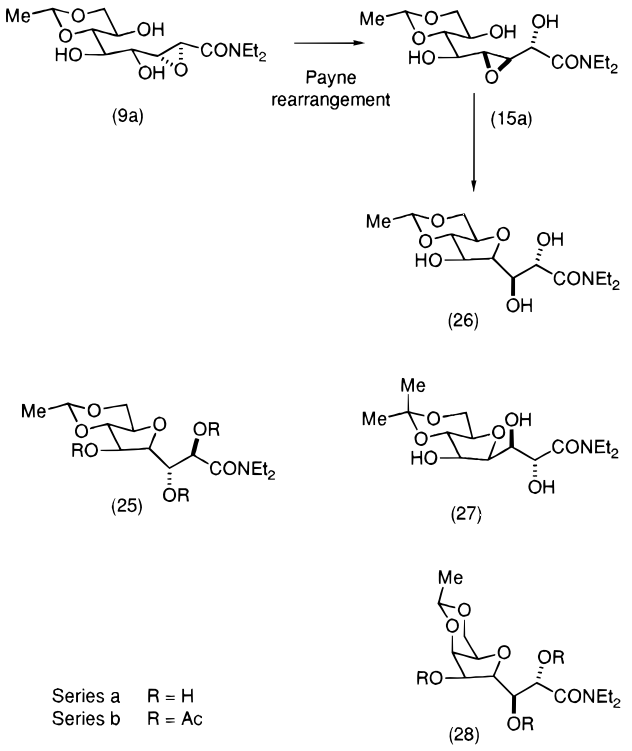


Figure 3.

oxyanion, generated at least partially by the basicity of the medium on OH-2, against the more distant oxyanion on OH-4 of the 2,3-*O*-isopropylidene derivatives (for example, 2,3-*O*-isopropylidene-D-manno or D-ribofuranoses, like **3**[7]). A similar interaction is to be expected between the aldehyde group and the OH-5 of the 4,6-*O*-alkylidene-acetals of the pyranosic structure that are protected on OH-2 and which should produce preferentially a type **B** structure.

This interaction of OH-2 unprotected monosaccharide derivatives, should lead preferentially to an *anti* conformation between the carbonyl group and the oxyanion on C-2, as shown in Figure 3. The *exo* approach of the ylide that should take place preferentially on the *si* face of the carbonyl group leads preferentially, in this way, to the type **A** epoxides. Support for this interpretation about the stereoselectivity of these reactions is given by the result of the study of the reaction of the same ylide with 2,3:4,6-di-*O*-isopropylidene-D-mannopyranose (**23**). The protection of the hydroxyls on C-2 and C-3 avoids the retroaldolic excision processes that decompose the resulting epoxyamides. In addition, the presence of the two ketal groups increases the conformational rigidity of the molecule and this limits the rotation of the C1−C2 bond. Finally, the protection of the OH on C-2 eliminates the effect of the interaction between the carbonyl group and the oxyanion on C-2 to favor the strongest interaction with the oxyanion on C-5 which should favor a preferential *exo* conformation of the carbonyl group, like that which leads to type **B** epoxides (Figure 3). In effect, the reaction at room temperature for 24 h of 2,3:4,6-di-*O*-isopropylidene-D-mannopyranose (**23**) in tetrahydrofuran with 2 equiv of **6** produced 99% of one product only, to which we assigned the structure **24a** (Scheme 4), based on its analytical and spectroscopic data ($J_{2,3}$ = 2.0 Hz). The absolute conformation of the carbons C2 and C3 was determined by treatment with periodic acid in aqueous medium and this produced a dextrorotatory solution that corresponds to **21** and which indicates that we are dealing with a type **A** epoxide. A similar interaction is postulated[7] for the 2,3-*O*-isopropylidene-D-manno- or D-ribofuranoses, like **3**, although, conformational studies[7] confirmed that the preferential attack occurs in these cases on the *si* face to produce type **A** structures.

Scheme 5



The stability of 2,3-*O*-isopropilidene derivatives of monosaccharides with a 2,3-*cis* conformation in the dioxolane ring and even that of the aldehyde sugars that are so easily epimerized, like 2,3-*O*-isopropylidene-D-glyceraldehyde under the above reaction conditions, is recently supported by previous work in our laboratory.[6] This finding, together with the fact that in this present work we obtained in all the cases studied only one, or at most two, epoxide isomers, always with a *trans* configuration, suggested that epimerization on C-2 of the starting monosaccharides had not occurred in these cases. The most unfavorable cases, those which employed long reaction times (96 h for **11**), although they gave smaller yields than when shorter reaction times were employed (6 h for **11**), produced the same epoxides, without being able to detect any products that might derive from a previous epimerization of the starting product to the D-manno isomer. These low yields we attributed to the participation of retroaldolic processes and to the decomposition of the reaction products. Many of these condensation reactions produced smaller amounts of secondary products characterized by their analytical and spectrographic data as C-glycofuranosides **25**, **26**, **27**, and **28**, with a tetrahydrofuran ring. They appear to be the result of a first Payne transposition[10] of the initial 2,3-epoxide that formed a new 3,4-epoxy derivative that finally spontaneously cyclizes to the corresponding C-glycofuranoside (Scheme 5). Some of these C-glycosides were also prepared by cyclization of the corresponding epoxyamides using basic catalysis, and this produced the double process of Payne transposition and intramolecular cyclization that showed complete stereospecificity. This permitted us to make their configurational assignments. The acetylation of all these epoxyamides confirmed the number of free hydroxyl groups and also their positions on the carbon chain. These early results confirm that ring size determines the ease with which these 2,3-epoxyamides are cyclized. Thus, while the 2,3-isopropylidene-glycofuranose derivatives produced mainly cyclic C-glycofuranosides, the pyranosyl derivatives initially produced good yields of acyclic epoxyamides with good stereoselectivity and only under more basic and energetic conditions were these acyclic epoxyamides transformed into C-glycosides.

(10) Payne, G. B. *J. Org. Chem.* **1962**, 3819−3822.

Experimental Section

Melting points are given uncorrected. The ^{1}H-NMR spectra were obtained using $CDCl_3$ as solvent. Microanalyses were performed by the "Servicio de Microanálisis de la Universidad de Málaga". Exact masses (FAB) were recorded at the University of Seville. Column chromatography used Merck silica gel 60 no. 7736. Analytical thin layer chromatography was performed on Merck silica gel 60 no. 7747.

Reaction of 4,6-*O*-Ethylidene-D-glucopyranose (8) with *N,N*-Diethyl-2-(dimethylsulfuranylidene)acetamide (6). Synthesis of *N,N*-Diethyl-2,3-anhydro-6,8-*O*-ethylidene-D-*erythro*-L-*galacto*- and -L-*ido*-octonamides (9a and 10a) and *N,N*-Diethyl-4,7-anhydro-6,8-*O*-ethylidene-D-*erythro*-L-*manno*-octonamide (25a). (a) Reaction in THF at 0−5 °C. To a solution of 0.75 g (3.64 mmol) of 4,6-*O*-ethylidene-D-glucopyranose (**8**) in 25 mL of anhydrous tetrahydrofuran, cooled to 0 °C, while stirring was added slowly 1.27 g (7.27 mmol) of *N,N*-diethyl-2-(dimethylsulfuranylidene)acetamide (**6**). This solution was kept at 0 °C for two days and then at room temperature for one more day. Subsequent ^{13}C-NMR in D_2O revealed that the starting product had disappeared. Chromatography on silica gel (Cl_2CH_2:MeOH:hexane 10:1:7) provided 0.65 g (70%) of **9a** that we crystallized from ethyl acetate, and 0.18 g (16%) of **25a** that we crystallized as white needles from ethyl ether−ethyl acetate.

(b) Reaction in THF at rt. Following the same procedure, but at rt, we obtained a mixture (85:15, 59%) of **9a** and **10a**, and **25a** (16%).

(c) Reaction in Acetonitrile at 0−5 °C. To a solution containing 1.18 g (5.7 mmol) of 4,6-*O*-ethylidene-D-glucopyranose (**8**) in 70 mL of acetonitrile, cooled to 0 °C and stirred, was added slowly 2.0 g (11.43 mmol) of *N,N*-diethyl-2-(dimethylsulfuranylidene)acetamide (**6**). The solution was kept at rt for two days, and ^{13}C-NMR in D_2O revealed that the starting product had disappeared. Excess ylide was destroyed by adding 1 N HCl until the pH was neutral. Chromatography on silica gel (Cl_2CH_2:MeOH:hexane 10:1:7) provided 1.23 g (67%) of **9a** and 0.33 g (18%) of **10a**.

9a: White solid. $[\alpha]^{20}_D = +16.8$ (*c* 3.1, $CHCl_3$). R_f ($CHCl_3$:MeOH:hexane 10:3:4): 0.48. Mp 143−4 °C. IR ν_{max} (cm^{-1}): 3394, 1637. ^{1}H-NMR ($CDCl_3$) δ: 4.73 (c, 1H, $J = 5.0$ Hz); 4.16 (dd, 1H, $J_{7,8e} = 5.3$ Hz, $J_{8a,8e} = 10.7$ Hz); 4.05 (m, 2H); 3.90 (m, 1H); 3.82 (d, 1H, $J_{2,3} = 2.2$ Hz); 3.66 (dd, 1H, $J_{4,5} = 9.3$ Hz, $J_{5,6} = 3.1$ Hz); 3.56−3.38 (m, 4H, $J = 7.2$ Hz); 3.44 (dd, 1H, $J_{7,8a} = 10.5$ Hz, $J_{8a,8e} = 10.9$ Hz); 3.38 (m, 1H); 1.32 (d, 3H, $J = 5.0$ Hz); 1.15 and 1.26 (2t, 6H, $J = 7.1$ and 7.0 Hz); ^{13}C-NMR ($CDCl_3$) δ: 167.0, 98.7, 80.8, 70.5, 70.4, 69.6, 61.0, 57.9, 50.3, 41.5, 20.3, 12.7, 14.5. Mass spectra (*m/e*): 45; 58; 72; 87; 100 (100%); 131; 142; 172. Elemental analysis: Calcd for $C_{14}H_{25}O_7N$: C, 52.64%; H, 7.89%; N, 4.39%. Found: C, 52.46%; H, 7.72%; N, 4.59%. Exact mass: Calcd for $C_{14}H_{25}O_7N$: 319.1631. Found: 319.1654.

10a: Yellowish syrup. R_f ($CHCl_3$:MeOH:hexane 10:3:4): 0.49. IR ν_{max} (cm^{-1}): 3383, 1640. ^{1}H-NMR ($CDCl_3$) δ: 4.69 (c, 1H, $J = 4.9$ Hz); 4.12 (dd, 1H, $J_{7,8e} = 5.3$ Hz, $J_{8a,8e} = 10.7$ Hz); 4.08 (m, 2H); 3.88 (dd, 1H, $J_{7,8a} = 5.2$ Hz, $J_{6,7} = 9.5$ Hz); 3.58−3.34 (m, 5H); 3.80 (d, 1H, $J_{2,3} = 2.2$ Hz); 3.60 (dd, 1H, $J_{4,5} = 2.8$ Hz, $J_{5,6} = 9.1$ Hz); 3.31 (m, 1H); 1.29 (d, 3H, $J = 5.1$ Hz); 1.10 and 1.23 (2t, 6H, $J = 7.2$ and 7.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 166.7, 98.4, 81.4, 70.9, 70.2, 69.6, 60.5, 57.5, 50.8, 41.1, 40.5, 19.9, 14.1 and 12.4. Mass spectra (*m/e*): 58 (15); 72 (54); 100 (100); 131 (28); 142 (15); 160 (16); 172 (12); 201 (7); 232 (2). Elemental analysis: Calcd for $C_{14}H_{25}O_7N$: C, 52.66%; H, 7.83%; N, 4.38%. Found: C, 52.01%; H, 7.79%; N, 4.38%.

25a: White needles. $[\alpha]^{20}_D = +22.8$ (c 1.0, MeOH). R_f ($CHCl_3$:MeOH:hexane 10:3:4): 0.58. Mp 183−4 °C. IR α_{max} (cm^{-1}): 3333, 1600. ^{1}H-NMR ($CDCl_3$) δ: 4.72 (c, 1H, $J = 5.1$ Hz); 4.55 (m, 2H); 4.24 (ddd, 1H, $J = 3.9$ and $J_{6,7} = 9.5$ Hz); 3.92 (dd, 1H, $J_{2,3} = 5.2$ Hz, $J_{3,4} = 7.2$ Hz); 3.82 (dd, 1H, $J_{3,4} = 7.6$ Hz, $J_{4,5} = 6.1$ Hz); 3.66 (dd, 1H, $J_{7,8a} = 9.4$ Hz, $J_{8a,8e} = 9.8$ Hz); 3.62−3.45 (m, 2H); 3.62−3.25 (2 dc, 4H, $J = 7.2$ and 6.6 Hz); 1.40 (d, 3H, $J = 5.0$ Hz); 1.23 and 1.15 (2t, 6H, $J = 7.2$ Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.9 (*C*ONEt$_2$); 100.1, 84.8, 82.2, 74.0, 73.9, 70.8, 68.5, 70.6, 41.6, 40.6, 19.9, 14.2, and 12.6. Mass spectra (*m*/*e*): 58 (16.0); 72 (41.0); 100 (100); 131 (50.5); 160 (66.6); 201 (26.7); 232 (0.3); 273 (0.7); 318 ($M^+ - 1$). Elemental analysis: Calcd for $C_{14}H_{25}O_7N$: C, 52.64%; H, 7.89%; N, 4.39%. Found: C, 52.49%; H, 7.77%; N, 4.53%.

Acetylation of Products 9a, 10a, and 25a. Acetylations with acetic anhydride/pyridine overnight at rt gave the corresponding acetylated products **9b** (86%), **10b** (94%), and **25b** (93%).

9b: Colorless syrup. $[\alpha]^{20}_D = -38.9$ (*c* 2.4, $CHCl_3$). R_f (AcOEt): 0.63. IR ν_{max} (cm^{-1}): 1750 and 1650. ^{1}H-NMR ($CDCl_3$) δ: 5.38 (dd, 1H, $J_{4,5} = 8.3$ Hz, $J_{5,6} = 2.1$ Hz); 5.21 (dd, 1H, $J_{3,4} = 5.1$ Hz, $J_{4,5} = 8.3$ Hz); 4.53 (ddd, 1H, $J_{6,7} = 9.9$ Hz, $J_{7,8a} = 5.3$ Hz); 4.53 (c, 1H, $J = 5.0$ Hz); 4.37 (dd, 1H, $J_{7,8e} = 5.3$ Hz, $J_{8a,8e} = 10.5$ Hz); 4.12 (dd, 1H, $J_{5,6} = 2.1$ Hz, $J_{6,7} = 9.8$ Hz); 3.50−3.30 (m, 1H); 3.48 (d, 1H, $J_{2,3} = 2.1$ Hz); 3.40 (broad c, 4H, $J = 7.1$ Hz); 3.36 (dd, 1H, $J_{2,3} = 2.1$ Hz, $J_{3,4} = 4.9$ Hz); 2.00, 2.04 and 2.06 (3s, 9H); 1.32 (d, 3H, $J = 5.0$ Hz); 1.20 and 1.22 (2t, 6H, $J = 7.1$ Hz). ^{13}C-NMR ($CDCl_3$) δ: 169.7, 169.5, 165.1, 99.2, 76.1, 70.9, 68.4, 67.2, 61.5, 55.6, 51.8, 41.2, 40.5, 20.4, 20.3, 20.2, 14.5 and 12.6. Mass spectra (*m*/*e*): 444 (0.3); 388 (0.9); 316 (6.5); 283 (1.7); 225 (4.8); 183 (8.3); 100 (52.7; 72 (56.9); 58 (8.7); 43 (100). Exact mass calcd for $C_{20}H_{31}O_{10}N$: 445.1948. Found: 445.1945.

10b: Colorless syrup. R_f (AcOEt): 0.60. IR ν_{max} (cm^{-1}): 1754 and 1661. ^{1}H-NMR ($CDCl_3$) δ: 5.39 (dd, 1H, $J_{4,5} = 8.6$ Hz, $J_{5,6} = 1.9$ Hz); 4.96 (dd, 1H, $J_{3,4} = 7.3$ Hz, $J_{4,5} = 8.5$ Hz; 4.69 (c, 1H, $J = 5.0$ Hz); 4.53 (ddd, 1H); 4.17 (dd, 1H, $J_{7,8e} = 5.4$ Hz, $J_{8a,8e} = 10.3$ Hz); 4.04 (dd, 1H, $J_{5,6} = 1.9$ Hz, $J_{6,7} = 9.8$ Hz); 3.69 (d, 1H, $J_{2,3} = 1.8$ Hz); 3.50−3.25 (m, 5H); 3.23 (dd, 1H, $J_{2,3} = 1.9$ Hz, $J_{3,4} = 7.1$ Hz); 2.09, 2.02 and 2.01 (3s, 9H); 1.31 (d, 3H, $J = 5.1$ Hz); 1.19 and 1.11 (2t, 6H, $J = 6.9$ and 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 169.7, 169.6, 165.1, 99.4, 76.3, 70.9, 68.5, 67.3, 61.7, 54.3, 51.9, 41.2, 40.7, 20.5, 20.4, 20.1, 14.6 and 12.7. Mass spectra (*m*/*e*): 386 (2); 316 (17); 283 (5); 225 (13); 183 (21); 142 (57); 115 (38); 100 (100); 72 (78). Elemental analysis: Calcd for $C_{20}H_{31}O_{10}N$: C, 53.93%; H, 6.96%; N, 3.14%. Found: C, 53.68%; H, 6.86%; N, 3.06%.

25b: Colorless syrup. $[\alpha]^{20}_D = +45.8$ (*c* 1.9, $CHCl_3$). R_f (AcOEt): 0.69. IR ν_{max} (cm^{-1}): 1748 and 1654. ^{1}H-NMR ($CDCl_3$) δ: 5.79 (dd, 1H, $J_{4,5} = 5.9$ Hz) 5.46 (d, 1H, $J_{2,3} = 5.4$ Hz); 5.33 (dd, 1H, $J_{2,3} = 5.4$ Hz, $J_{3,4} = 4.3$ Hz); 4.63 (c, 1H, $J = 5.0$ Hz); 4.33 (dd, 1H, $J_{3,4} = 4.2$ Hz, $J_{4,5} = 5.9$ Hz); 4.22 (ddd, 1H); 3.65−3.55 (m, H-6); 3.65−3.00 (2dc, 4H, $J = 7.1$ Hz); 2.12, 2.09 and 2.08 (3s, 9H); 1.35 (d, 3H, $J = 5.0$ Hz); 1.24 and 1.06 (2t, 6H, $J = 7.1$ Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.9, 169.9, 169.5, 164.7, 100.2, 83.6, 78.3, 72.5, 71.7, 71.3, 70.4, 68.6, 41.6 and 40.6, 20.9, 20.8, 20.3, 19.8, 13.8 and 12.6. Mass spectra (*m*/*e*): 444 (0.4, $M^+ - 1$); 373 (0.7); 326 (5.6); 281 (9.5); 243 (22.6); 181 (6.5); 100 (100); 72 (39.0); 58 (4.9); 43 (61.5).

Acid Hydrolysis and Subsequent Glycol Oxidation with Periodic Acid of 9a. An amount of 43 mg (0.13 mmol) of epoxyamide **9a** was treated with a solution of 0.25 g (1.08 mmol) of periodic acid in 2 mL of D_2O and put into the measuring tube of a polarimeter. The reaction was followed to completion by measuring the changes of rotatory power and by ^{13}C-NMR spectroscopy. After 24 h, the rotatory power showed a stable value of $[\alpha]^{20}_D = -21.8$ (*c* 1.15, water), and the next ^{13}C-NMR (D_2O) spectrum, δ: 167.8 (CONEt$_2$); 88.0, 58.9, 51.0, 42.4, 41.6, 13.7, and 12.2, similar to spectrum of **20**.[6]

Treatment of Epoxyamide 9a with KOH/Methanol. Synthesis of *N*,*N*-diethyl-4,7-anhydro-6,8-*O*-ethylidene-D-*erythro*-L-*allo*-octonamide (26). An amount of 0.50 g (1.56 mmol) of epoxyamide **9a** was dissolved into 100 mL of 0.1% w/v potasium hydroxide/methanol. After 30 days, the solution was neutralized with 1 N HCl and methanol was removed. The residue dissolved in warm ethyl acetate, and yielded, after cooling, a mixture of the starting product **9a** and **26**. Both products were separated by crystallization from chloroform. We recovered by concentration of the mother liquor 0.21 g of the starting product **9a** and 0.06 g (12%) of **26** as a white powder. R_f ($CHCl_3$/MeOH/hexane, 10:3:4): 0.58. $[\alpha]^{20}_D$ +16.0 (*c* 0.3, MeOH). IR ν_{max} (cm^{-1}): 1628. ^{1}H-NMR ($CDCl_3$) δ: 4.70 (c, 1H, $J = 5.1$ Hz); 4.42 (d, 1H, $J_{2,3} = 7.7$ Hz); 4.39 (dd, 1H, $J_{4,5} = 6.6$ Hz, $J_{5,6} = 8.6$ Hz); 4.25 (ddd, 1H, $J = 3.1$, 5.9 and 8.3 Hz); 3.97 (dd, 1H, $J_{3,4} = 5.0$ Hz, $J_{4,5} = 6.5$ Hz, $J_{5,6} = 8.6$ Hz); 3.77 (dd, 1H, $J_{2,3} = 7.7$ Hz, $J_{3,4} = 5.0$ Hz); 3.70−3.56 (m, 3H); 3.70−3.15 (m, 4H); 1.35 (d, 3H, $J = 5.1$ Hz); 1.19 and 1.12 (2t, 6H, $J = 7.2$ and 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 172.5, 100.1, 84.3, 82.6, 72.7, 72.3, 71.3, 68.1, 70.8, 42.0, 40.9, 20.0, 14.2, and 12.7. Mass spectra (*m*/*e*): 318 (0.9), 304 (0.2), 239 (0.3), 201 (15.7), 160 (32.3), 131 (50.9), 100 (100), 72 (55.2), 58 (24.3), 43 (23.7). Exact mass calcd for $C_{14}H_{25}O_7N$: 319.1631. Found: 319.1645.

Reaction of 4,6-*O*-Benzylidene-D-*gluco*pyranose (11) with *N*,*N*-diethyl-2-(dimethylsulfuranylidene)acetamide (6). Synthesis of *N*,*N*-Diethyl-2,3-anhydro-6,8-*O*-benzylidene-D-*erythro*-L-*galacto*- and -L-*ido*-octonamides (12a and 13a). Method A. We dissolved 1.02 g (3.81 mmol) of 4,6-*O*-benzylidene-D-glucopyranose (**11**) in 70 mL of acetonitrile:tetrahydrofuran 5:2 v/v at 0−5 °C in a ice-bath. We then added 1.32 g (7.61 mmol) of *N*,*N*-diethyl-2-(dimethylsulfuranylidene)acetamide (**6**) and stirred the reacting solution for 3 days, after which we added 0.66 g (3.81 mmol) of ylide and left the mixture at room temperature for another day (when the reaction was complete we carried out TLC ($CHCl_3$/MeOH/hexane 10:3:4). Excess ylide was neutralized with 0.1 N HCl, and the solvent was removed in vacuo. The residue was crystallized from ethyl acetate (with a little methanol) and the residue, 1.03 g, was recrystallized from water/methanol to give 0.18 g (12%) of practically pure **12a**. The combined mother-liquors were concentrated, and the residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH/hexane 10:1:6) and gave a mixture of **12a** and **13a**, that increases the total yield to 35% (1.7:1 of **12a** and **13a**).

Method B. We dissolved 2 g (3.81 mmol) of **11** and 5.2 g (29.7 mmol) of **6** in 80 mL of anhydrous THF and stirred the reacting solution for 6 h. Excess ylide was neutralized with 0.1 N HCl, and THF was removed in vacuo. From the residual aqueous phase slowly separated 0.86 g (30.3%) of crystalline and practically pure **12a**.

12a: White solid. $[\alpha]^{20}_D = -30.8$ (*c* 0.6, MeOH). R_f ($CHCl_3$/MeOH/hexane 10:3:4): 0.54. Mp 182 °C. IR ν_{max} (cm^{-1}): 1609. ^{1}H-NMR ($CDCl_3$) δ: 7.48−7.36 (m, 5H); 5.55 (s, 1H); 4.35 (dd, 1H, $J_{5,6} = 5.3$ Hz, $J_{6,7} = 10.9$ Hz); 4.11 (m, 2H, $J_{7,8e} = 4.3$ Hz, $J_{8a,8e} = 12.0$); 4.01 (ddd, 1H, $J_{6,7} = 9.9$ Hz, $J_{7,8a} = 9.9$ Hz, $J_{7,8e} = 5.7$ Hz); 3.91 (dd, 1H, $J_{3,4} = 4.2$ Hz, $J_{4,5} = 9.3$ Hz); 3.81 (d, 1H, $J_{2,3} = 2.2$ Hz); 3.67 (dd, 1H, $J_{7,8a} = 10.5$ Hz, $J_{8a,8e} = 10.7$ Hz); 3.55−3.37 (m, 5H); 1.15 and 1.24 (2 t, 6H, $J = 7.2$ and 7.1 Hz). ^{13}C-NMR ($CDCl_3$/CD_3OD 9:1) δ: 168.2, 138.5, 129.5, 128.7, 126.8, 101.8, 81.7, 71.9, 70.9, 61.4, 58.9, 51.7, 42.4, 41.7, 14.7 and 13.1. Mass spectrum: (*m*/*e*): 380 (0.4), 334 (0.3), 263 (3.5), 232 (19.4), 179 (18.1), 172 (28.3), 107 (65.2), 100 (100), 72 (64.7), and 58 (18.7). Elemental analysis: Calcd for $C_{19}H_{27}O_7N$: C, 59.84%; H, 7.08%; N, 3.67%. Found: C, 59.30%; H, 6.87%; N, 3.62%.

13a: Yellowish syrup. $[\alpha]^{20}_D = -32.1$ (*c* 4.6, MeOH). R_f ($CHCl_3$/MeOH/hexane 10:3:4): 0.56. IR ν_{max} (cm^{-1}): 1636. ^{1}H-NMR ($CDCl_3$) δ: 7.44−7.27 (m, 5H); 5.49 (s, 1H); 4.29 (ddd, 1H, $J_{7,8a} = 10.7$ Hz, $J_{7,8e} = 5.1$ Hz); 4.15 (m, 1H); 4.05 (dd, 1H, $J_{7,8e} = 5.1$ Hz, $J_{8a,8e} = 9.8$ Hz); 3.92 (dd, 1H, $J = 5.2$ and 3.1 Hz); 3.85 (dd, 1H, $J_{5,6} = 6.3$ Hz, $J_{6,7} = 9.5$ Hz); 3.70 (d, 1H, $J_{2,3} = 2.2$ Hz); 3.61 (dd, 1H, $J_{7,8a} = 10.4$ Hz, $J_{8a,8e} = 9.9$ Hz); 3.60−3.55 (m, 5H); 1.20 and 1.09 (2 t, 6H, $J = 7.3$ and 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 168.2, 138.5, 129.5, 128.7 and 126.8, 101.8, 82.6, 71.7, 71.2, 61.5, 58.6, 51.6, 42.4, 41.4, 14.7, and 13.1. Mass spectrum (*m*/*e*): 72 (48), 100 (100), 107 (42), 131 (28), 160 (14), 232 (7), and 263 (4).

Acetylation of Products 12a and 13a. Acetylations of a 63:37 mixture of **12a** and **13a** with acetic anhydride/pyridine at rt gave the corresponding acetylated products **12b** (47%)

and **13b** (23%), and these were separated by thin layer chromatography on silica gel (Hex/AcOEt 1:2).

12b: Colorless syrup. $[\alpha]^{20}_D = +12.9$ (*c* 1.1, $CHCl_3$). R_f (AcOEt): 0.69. ^{1}H-NMR ($CDCl_3$) δ: 7.46−7.33 (m, 5H); 5.56 (s, 1H); 5.49 (dd, 1H, $J_{4,5} = 8.5$ Hz, $J_{5,6} = 2.1$ Hz); 5.20 (dd, 1H, $J_{3,4} = 5.7$ Hz, $J_{4,5} = 8.4$ Hz); 4.91 (ddd, 1H, $J_{6,7} = 10.0$ Hz, $J_{7,8a} = 10.0$ Hz, $J_{7,8e} = 5.3$ Hz); 4.38 (dd, 1H, $J_{5,6} = 2.1$ Hz, $J_{6,7} = 9.7$ Hz); 4.36 (dd, 1H, $J_{7,8e} = 5.1$ Hz, $J_{8a,8e} = 15.8$ Hz); 3.67 (dd, 1H, $J_{7,8a} = 10.6$ Hz, $J_{8a,8e} = 10.6$ Hz); 3.41−3.28 (2dc, 4H); 3.44 (d, 1H, $J_{2,3} = 2.0$ Hz); 3.34 (dd, 1H, $J_{2,3} = 1.6$ Hz, $J_{3,4} = 5.5$ Hz); 2.07, 2.03, and 1.99 (3s, 9H); 1.11 (t, 6H, $J = 7.2$ Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.1 and 169.8, 165.3, 136.0, 129.4, 128.4, 126.3, 101.7, 71.5, 68.8, 68.0, 61.7, 55.8, 52.9, 41.4, 40.6, 20.6, 20.5, 14.5 and 12.8. Mass spectrum (*m*/*e*): 72 (60), 100 (100), 105 (58), 115 (52), 142 (40), 172 (19), 224 (8), 326 (7), 388 (2), and 448 (4).

13b: Colorless liquid. R_f (AcOEt): 0.67. $[\alpha]^{20}_D = +27.40$ (*c* 0.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 7.48−7.32 (m, 5H); 5.53 (s, 1H); 5.49 (dd, 1H, $J_{4,5} = 8.6$ Hz, $J_{5,6} = 1.8$ Hz); 4.96 (dd, 1H, $J_{3,4} = 7.5$ Hz, $J_{4,5} = 8.4$ Hz); 4.85 (ddd, 1H, $J_{6,7} = 9.8$ Hz, $J_{7,8a} = 9.9$ Hz, $J_{7,8e} = 5.3$ Hz); 4.37 (dd, 1H, $J_{7,8e} = 5.3$ Hz, $J_{8a,8e} = 10.5$ Hz); 4.30 (dd, 1H, $J_{5,6} = 2.0$ Hz, $J_{6,7} = 9.8$ Hz); 3.71 (d, 1H, $J_{2,3} = 1.9$ Hz); 3.63 (dd, 1H, $J_{7,8a} = 10.3$ Hz, $J_{8a,8e} = 10.3$ Hz); 3.51−3.31 (2 dc, 4H); 3.25 (dd, 1H, $J_{2,3} = 1.9$ Hz, $J_{3,4} = 7.5$ Hz); 2.09, 2.05 and 1.95 (3 s, 9H); 1.18 and 1.11 (2 t, 6H, $J = 7.2$ and 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 169.9, 165.1, 136.9, 129.1, 128.2, 126.2, 101.5, 71.5, 68.8, 68.0, 61.9, 54.5, 52.4, 41.3, 40.9, 20.7, 20.5, 14.8, and 12.8. Mass spectrum (*m*/*e*): 72 (64), 100 (100), 105 (52), 115 (66), 142 (36), 172 (19), 224 (9), 316 (8), 388 (2), and 448 (4).

Acid Hydrolysis and Subsequent Glycol Oxidation with Periodic Acid of 12a. We treated 20 mg (0.05 mmol) of epoxyamide **12a** with a solution of 95 mg (0.42 mmol) of periodic acid in 2 mL of H_2O and introduced it into the measuring tube of a polarimeter and followed the course of the reaction by the noting the variation of rotatory power. After 24 h, the value stabilized at $[\alpha]^{20}_D = -14.0$ (*c* 0.5, water).[6]

Reaction of 4,6-*O*-Isopropylidene-D-mannopyranose (14) with *N*,*N*-Diethyl-2-(dimethylsulfuranylidene)acetamide (6). Syntheses of *N*,*N*-Diethyl-2,3-anhydro-6,8-*O*-isopropylidene-D-*erythro*-L-*gluco*- and L-*altro*-octonamide 15a and 16a) and *N*,*N*-Diethyl-4,7-anhydro-6,8-*O*-isopropylidene-D-*erythro*-L-*talo*-octonamide (27). (a) Reaction in Acetonitrile at 0−5 °C. To a solution containing 0.75 g (3.41 mmol) of 4,6-*O*-isopropylidene-D-mannopyranose (**14**) in 25 mL of acetonitrile, cooled at 0 °C, was slowly added while stirring 1.26 g (7.20 mmol) of *N*,*N*-diethyl-2-(dimethylsulfuranylidene)acetamide (**6**). The solution was kept at rt for two days, it was then analyzed by TLC ($CHCl_3$/MeOH/hexane 10:3:4), and the starting product was seen to have disappeared. Excess ylide was destroyed by adding 1 N HCl until the pH was neutral. Chromatography on silica gel (CH_2Cl_2/MeOH/hexane 10:1:7) provided 0.67 g (59%) of **15a**, 95 mg (8%) of **16a**, and also traces (<1%) of **27**.

(b) Reaction in Dimethyl Sulfoxide at rt. Following the same procedure we reacted compounds **14** and **6** in a ratio of 1:1.3 for two days at room temperature and obtained a 63% yield of a mixture (53:47) of **15a** and **16a**.

15a: White hygroscopic solid. $[\alpha]^{20}_D +5.3$ (*c* 4.3, $CHCl_3$). R_f ($CHCl_3$/MeOH/hexane 10:3:4): 0.54. IR ν_{max} (cm^{-1}): 3401, 1637. ^{1}H-NMR ($CDCl_3$) δ: 4.00−3.32 (m, 11H); 3.82 (d, 1H, $J_{2,3} = 2.2$ Hz); 1.40 and 1.50 (2s, 6H); 1.24 and 1.12 (2t, 6H, $J = 7.0$ and 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 167.3, 98.8, 73.3, 70.8, 69.1, 64.4, 62.1, 58.8, 51.0, 41.6, 40.8, 28.4, 19.4, 14.4, and 12.8. Mass spectrum (*m*/*e*): 59 (92.5), 72 (76.6), 100 (100), 103 (36.1), 131 (39.4), 172 (16.7), 215 (29.7), 232 (27.4), 276 (4.1), 318 (8.3), and 320 (0.07). Exact mass for $C_{15}H_{27}O_7N$: Calcd: 333.1788; Found: 333.1815.

16a: Partially impurified by **15a**. R_f ($CHCl_3$/MeOH/hexane 10:3:4): 0.54. ^{1}H-NMR ($CDCl_3$) δ: 4.00−3.32 (m, 11H); 3.77 (d, 1H, $J_{2,3} = 2.1$ Hz); 1.49 and 1.36 (2s, 6H); 1.24 and 1.12 (2t, 6H). 1.24 and 1.12 (2t, 6H). ^{13}C-NMR ($CDCl_3$) δ: 167.6, 98.7, 72.8, 69.6, 66.7, 63.8, 61.2, 59.0, 50.4; 41.5, d 40.9, 28.6, 19.0, 14.5, and 12.8. Mass spectrum (*m*/*e*): 59 (68), 72 (64), 100 (100), 131 (36), 172 (10), 215 (16), 276 (1), and 318 (3).

27: White solid. R_f ($CHCl_3$/MeOH/hexane 10:3:4): 0.54. IR α_{max} (cm^{-1}): 3416, 1628. ^{1}H-NMR ($CDCl_3$) δ: 4.61 (d, 1H, $J_{2,3} = 8.9$ Hz); 4.50 (dd, 1H, $J_{4,5} = 7.2$ Hz, $J_{5,6} = 7.4$ Hz); 4.04 (dd, 1H, $J_{7,8e} = 4.9$ Hz, $J_{8a,8e} = 9.9$ Hz); 4.02 (dd, 1H, $J_{2,3} = 8.6$ Hz, $J_{3,4} = 4.9$ Hz); 3.96 (dd, 1H, $J_{4,5} = 7.1$ Hz); 3.88 (dd, 1H, $J_{7,8a} = J_{8a,8e} = 10.0$ Hz); 3.72 (dd, 1H, $J_{5,6} = 7.7$ Hz, $J_{6,7} = 10.0$ Hz); 3.60−3.20 (m, 5H, H-7); 1.51 and 1.44 (2s, 6H); 1.20 and 1.23 (2t, 6H, $J = 7.1$ and 7.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 171.1, 101.0, 79.5, 78.7, 74.4, 74.1, 70.9, 69.3, 64.8, 41.6, 40.5, 28.9, 19.5, 14.1, and 12.7. Mass spectrum (*m*/*e*): 59 (35), 72 (61), 100 (100), 131 (77), 160 (19), 190 (13), 215 (42), 258 (1), and 318 (19).

Acetylation of Compound 15a. We treated at room temperature for 12 h 0.23 g (0.68 mmol) of epoxyamide **15a** with 1.2 mL (11.76 mmol) of acetic anhydride in 5 mL of pyridine. This yielded 0.25 g of product **15b** (80%), as a colorless syrup. $[\alpha]^{20}_D = -4.9$ (c 5.6, $CHCl_3$). R_f (AcOEt): 0.67. IR ν_{max} (cm^{-1}): 2996, 2945, 1749, 1653. ^{1}H-NMR ($CDCl_3$) δ: 5.30 (dd, 1H, $J_{4,5} = 8.0$ Hz, $J_{5,6} = 2.2$ Hz); 5.15 (dd, 1H, $J_{3,4} = 4.9$ Hz, $J_{4,5} = 8.0$ Hz); 4.61 (ddd, 1H, $J_{6,7} = 9.8$ Hz, $J_{7,8a} = 8.0$ Hz, $J_{7,8e} = 5.5$ Hz); 3.98 (dd, 1H, $J_{5,6} = 2.5$ Hz, $J_{6,7} = 9.8$ Hz); 3.93 (dd, 1H, $J_{7,8e} = 5.4$ Hz, $J_{8a,8e} = 11.9$ Hz); 3.55 (dd, 1H, $J_{7,8a} = 8.0$ Hz, $J_{8a,8e} = 11.6$ Hz); 3.45−3.20 (2dc, 4H); 3.39 (d, 1H, $J_{2,3} = 2.1$ Hz); 3.39−3.25 (dd, 1H); 2.07, 2.06 and 1.98 (3s, 9H); 1.33 (2s, 6H); 1.05 and 1.16 (2t, 6H, $J = 7.0$ Hz). ^{13}C-NMR ($CDCl_3$) δ: 169.4, 169.3, 168.9, 164.8, 99.3, 68.6, 68.4, 68.0, 63.8, 61.4, 55.7, 51.3, 40.9, 40.2, 27.0, 19.0, 20.2, 20.1, 14.3 and 12.4. Mass spectrum (*m*/*e*): 43 (100), 72 (46.3), 100 (59.8), 115 (31.9), 142 (23.9), 172 (7.4), 239 (12.7), 282 (3.9), 316 (22.4), 402 (1.1), 444 (1.8), and 460 (0.07).

Acid Hydrolisis and Subsequent Glycol Oxidation of 15a with Periodic Acid. We treated 27 mg (0.08 mmol) of epoxyamide **15a** with 70 mg (0.31 mmol) of periodic acid in 2 mL of water and then put it into the measuring tube of a polarimeter. We followed the course of the reaction by noting the variation of the rotatory power. After 19 h the value stabilized at $[\alpha]^{20}_D = -10.23$ (*c* 1.3, water). ^{13}C-NMR (D_2O) δ: 165.9, 58.8, 51.0, 42.3, 41.6, 13.6, and 12.1.[6]

Base-Catalyzed Cyclization of 15a and 16a. Synthesis of *N*,*N*-Diethyl-4,7-anhydro-6,8-*O*-isopropylidene-D-*erythro*-L-*talo*-octonamide (27). An amount of 0.093 g (0.283 mmol) of epoxyamide **16a** was dissolved in 23 mL of 0.1% w/v potasium hydroxide in methanol. The solution was kept at room temperature for 11 days. The course of the reaction was followed by TLC ($CHCl_3$/MeOH/hexane 10:3:4), and we noted the slow formation of a new and less polar product. The solution was then neutralized with 1 N hydrochloric acid, filtered, dried, and concentrated to give 0.080 g of a mixture in which the principal product was identified by ^{13}C-NMR as **27**. Similarly, 0.217 g (0.652 mmol) of epoxyamide **15a** were treated with 50 mL of 0.1% w/v potasium hydroxide in methanol. After 30 days, we recovered 122 mg of the starting product. Longer reaction times (66 days) give the same negative result.

Reaction of 4,6-*O*-Ethylidene-D-galactopyranose (17) with *N*,*N*-Diethyl-2-(dimethylsulfuranylidene)acetamide (6). Synthesis of *N*,*N*-diethyl-2,3-anhydro-6,8-*O*-ethylidene-D-*threo*-L-*galacto*- and -L-*ido*-octonamides (18a and 19a) and *N*,*N*-Diethyl-4,7-anhydro-6,8-*O*-ethylidene-D-*threo*-L-*allo*-octonamide (28a). We added slowly, while stirring, 2.70 g (15.4 mmol) of *N*,*N*-diethyl-2-(dimethylsulfuranylidene)acetamide (**6**) to 1.57 g (7.62 mmol) of 4.6-*O*-ethylidene-D-galactopyranose (**17**) dissolved into 80 mL of acetonitrile at 0−5 °C. After 46 h at rt, TLC ($CHCl_3$/MeOH/hexane 10:3:4) showed that the reaction was complete, and the resulting products were partially resolved by column chromatography on silica gel (CH_2Cl_2/MeOH/hexane 10:1:7). From the resulting mixture, we obtained 1.10 g (45%) of **18a** by crystallization from ethyl acetate. After concentrating the mother liquor (0.90 g), we spectroscopically characterized two new produts, **19a** and **28a**, in addition to residuals of **18a** in a 21:6:10 ratio, to give a total yield of **18a** and **19a** of 72% with a ratio of 7:3.

18a: White solid. $[\alpha]^{20}_D -2.4$ (*c* 0.8, MeOH). R_f ($CHCl_3$/MeOH/hexane 10:3:4): 0.48. Mp 91−92 °C. IR ν_{max} (cm^{-1}): 3411, 1638. ^{1}H-NMR ($CDCl_3$) δ: 4.77 (c, 1H, $J = 5.1$ Hz, 4.12

(dd, 1H, $J_{7,8e}$ = 1.8 Hz, $J_{8a,8e}$ = 12.0 Hz); 4.04 (dd, 1H, $J_{5,6}$ = 7.2 Hz); 3.87 (dd, 1H, $J_{7,8a}$ = 1.3 Hz, $J_{8a,8e}$ = 12.0 Hz); 3.85−3.75 (m, 3H); 3.72 (d, 1H, $J_{2,3}$ = 2.1 Hz); 3.62−3.35 (2dc, 4H, J = 7.5 and 7.3 Hz); 3.33 (dd, 1H, $J_{2,3}$ = 2.2 Hz, $J_{3,4}$ = 5.1 Hz); 1.34 (d, 3H, J = 5.1 Hz); 1.14 and 1.26 (2t, 6H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 167.1, 99.0, 77.2, 71.9, 68.5, 68.4, 62.7, 58.2, 51.7, 41.5, 40.8, 20.8, 14.5 and 12.8. Mass spectrum (*m/e*): 58 (24), 72 (91), 100 (100), 142 (54), 172 (34), 215 (5), 232 (2.1), 272 (0.5) and 304 (0.8). Elemental analysis: Calcd for $C_{14}H_{25}O_7N$: C, 52.65%; H, 7.80%; N, 3.81%. Found: C, 52.66%; H, 7.83%; N, 4.38%.

19a: Data from a mixture of **18a** and **28a**. ^{13}C-NMR ($CDCl_3$) δ: 167.1, 99.0, 77.4, 73.1, 69.3, 66.5, 62.0, 59.4, 48.7, 41.5, 40.9, 20.7, 14.5, and 12.6.

28a: was characterized as the same product resulting from the treatment of **18a** with bases (see below).

Treatment of Epoxyamide 18a with KOH/MeOH. Synthesis of *N,N*-Diethyl-4,7-anhydro-6,8-*O*-ethylidene-D-*threo*-L-*allo*-octonamide (28a). We treated 0.50 g (1.56 mmol) of epoxyamide **18a** with 100 mL of 0.1% w/v potasium hydroxide in methanol. The reaction was followed by TLC ($CHCl_3$/MeOH/hexane 10:1:2), and this showed that the starting epoxide was slowly converted into a less polar product. After 30 days at room temperature, the solution was neutralized, concentrated, and redissolved in ethyl acetate−diethyl ether. It was then cooled to separate the major unreacted product. Concentration of the solution give 0.27 g (54%) of **28a** as practically pure white solid. $[\alpha]^{20}_D$ +24.0 (*c* 1.1, $CHCl_3$). R_f ($CHCl_3$/MeOH/hexane 10:3:4): 0.54. Mp 142 °C. IR ν_{max} (cm^{-1}): 3393, 1625. ^{1}H-NMR ($CDCl_3$) δ: 4.71 (c, 1H, J = 5.0 Hz); 4.55 (d, 1H, $J_{2,3}$ = 6.1 Hz); 4.42 (dd, 1H, $J_{4,5}$ = 8.2 Hz, $J_{5,6}$ = 4.0 Hz); 4.23 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,7}$ = 2.2 Hz); 4.12 (dd, 1H, $J_{3,4}$ = 4.7 Hz, $J_{4,5}$ = 8.2 Hz); 4.06 (dd, 1H, $J_{7,8a}$ = 1.3 Hz, $J_{8a,8e}$ = 10.5 Hz); 3.94 (dd, 1H, $J_{2,3}$ = 5.9 Hz, $J_{3,4}$ = 4.9 Hz); 3.86−3.78 (m, 2H); 3.61−3.32 (2dc, 4H, J = 7.1 Hz); 1.36 (d, 3H, J = 5.0 Hz); 1.21 and 1.14 (2t, 6H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 171.5, 96.8, 82.3, 75.7, 73.4, 72.1, 68.4, 67.3, 40.6, 41.8, 20.8, 12.7, and 14.2. Mass spectrum (*m/e*): 354 (0.1), 319 (0.1), 304 (0.7), 258 (0.3), 219 (1.5), 201 (41.5), 160 (32.8), 131 (74.8), 100 (100), 72 (50.1), and 58 (20.2). Elemental analysis: Calcd for $C_{14}H_{25}O_7N$: C, 52.66%; H, 7.83%; N, 4.38%. Found: C, 52.62%; H, 7.87%; N, 4.02%.

Acetylation of Products 18a, 19a, and 28a. Synthesis of *N,N*-Diethyl-4,5,7-tri-*O*-acetyl-2,3-anhydro-6,8-*O*-ethylidene-D-*threo*-L-*galacto*- and -L-*ido*-octonamides (18b and 19b) and *N,N*-Diethyl-2,3,5-tri-*O*-acetyl-4,7-anhydro-6,8-*O*-ethylidene-D-*threo*-L-*allo*-octonamide (28b). Acetylation of 101 mg (3.16 mmol) of epoxyamide **18a** in 5 mL of pyridine with 1.2 mL (11.76 mmol) of acetic anhydride gave 118 mg (75%) of epoxyamide **18b**. Following the same procedure, we obtained 86 mg (55%) of a mixture of epoxyamides **18b** and **19b** and 99 mg (0.31 mmol) from a mixture of isomers **18a** and **19a**. Finally, we obtained 88 mg (91%) of **28b** from 70 mg (0.22 mmol) of **28a**, 5 mL of pyridine and 0.62 mL (6.58 mmol) of acetic anhydride.

18b: White solid. $[\alpha]^{20}_D$ −7.3 (*c* 1.6, $CHCl_3$). R_f (AcOEt): 0.53. Mp 171−2 °C. ^{1}H-NMR ($CDCl_3$) δ: 5.42 (dd, 1H, $J_{4,5}$ = 2.6 Hz, $J_{5,6}$ = 9.4 Hz; 5.06 (dd, 1H, $J_{3,4}$ = 6.0 Hz, $J_{4,5}$ = 2.6 Hz); 4.65 (ddd, 1H, $J_{6,7}$ = 1.9 Hz); 4.07 (dd, 1H, $J_{7,8a}$ = 1.5 Hz, $J_{8a,8e}$ = 12.9 Hz); 4.05 (c, 1H, J = 5.1 Hz); 3.89 (dd, 1H, $J_{5,6}$ = 9.4 Hz, $J_{6,7}$ = 1.8 Hz); 3.83 (dd, 1H, $J_{7,8e}$ = 1.6 Hz, $J_{8a,8e}$ = 12.7 Hz); 3.62 (d, 1H, $J_{2,3}$ = 1.9 Hz); 3.47−3.28 (2dc, 4H, J = 7.1 and 7.0 Hz); 3.21 (dd, 1H, $J_{2,3}$ = 1.9 Hz, $J_{3,4}$ = 6.0 Hz); 2.10, 2.09, and 2.04 (3s, 9H); 1.31 (d, 3H, J = 5.1 Hz); 1.08 and 1.05 (2t, 6H, J = 7.1 and 7.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.7, 169.3, 168.9, 165.1, 99.1, 74.1, 69.4, 68.7, 67.7, 62.9, 54.2, 52.2, 40.5, 40.1, 20.5, 20.4, 20.3, 14.5, and 12.6. Mass spectrum (*m/e*): 43 (100), 72 (65), 100 (57.8), 115 (18.3), 142 (45.7), 183 (9.8), 283 (3.8), 316 (12.2), 345 (1.4) and 430 (1.2). Elemental analysis for $C_{20}H_{31}O_{10}N$: Calcd: C, 53.93%; H, 6.96%; N, 3.14%. Found: C, 53.70%; H, 6.70%; N, 3.07%.

19b: Data from a mixture with **18b**: R_f (AcOEt): 0.53. ^{1}H-NMR ($CDCl_3$) δ: 5.37 (dd, 1H, $J_{4,5}$ = 2.4 Hz, $J_{5,6}$ = 9.5 Hz); 5.23 (dd, 1H, $J_{3,4}$ = 5.8 Hz, $J_{4,5}$ = 2.5 Hz); 4.70 (ddd, 1H, J = 1.5 Hz); 4.65 (c, 1H, J = 5.0 Hz); 4.07 (dd, 1H, $J_{8a,8e}$ = 13.0 Hz); 3.91 (dd, 1H); 3.82 (dd, 1H, $J_{7,8a}$ = 2.1 Hz, $J_{8a,8e}$ = 12.7 Hz); 3.56−3.26 (2 dc, 4H, J = 7.1 Hz); 3.50−3.25 (m, 2H); 2.13, 2.08, and 2.04 (3s, 9H); 1.32 (d, 1H, J = 5.0 Hz); 1.22 and 1.09 (2 t, 6H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.4, 169.3, 168.9, 164.7, 74.0, 69.4, 69.1, 68.5, 62.8, 56.4, 49.7, 41.1, 40.5, 20.8, 20.2, 14.4, and 12.5.

28b: Colorless syrup. R_f (AcOEt): 0.58. IR ν_{max} (cm^{-1}): 1750 and 1661. ^{1}H-NMR ($CDCl_3$) δ: 5.49 (d, 1H, $J_{2,3}$ = 8.7 Hz); 5.44 (dd, 1H, $J_{3,4}$ = 2.2 Hz); 5.33 (dd, 1H, $J_{4,5}$ = 8.2 Hz, $J_{5,6}$ = 4.2 Hz); 4.60 (c, 1H, J = 5.2 Hz); 4.57 (dd, 1H, $J_{2,3}$ = 8.2 Hz, $J_{3,4}$ = 2.0 Hz); 4.41 (dd, 1H, $J_{5,6}$ = 4.1 Hz, $J_{6,7}$ = 1.9 Hz); 4.12 (dd, 1H, $J_{7,8a}$ = 2.0 Hz, $J_{8a,8e}$ = 13.2 Hz); 3.79 (dd, 1H, $J_{8a,8e}$ = 12.8 Hz, H-8e), 3.73 (ddd, 1H); 3.25−3.05 (2dc, 4H, J = 7.1 and 7.3 Hz); 2.14, 2.07, and 2.02 (3 s, 9H); 1.24 and 1.06 (2t, 6H, J = 7.1 and 7.2 Hz); 1.31 (d, 3H, J = 5.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.6, 169.7, 168.8, 165.1, 96.7, 78.4, 73.8, 73.5, 72.4, 71.2, 67.9, 66.5, 41.5, 40.5, 20.6, 20.3, 13.6, and 12.5. Mass spectrum (*m/e*): 72 (41), 100 (100), 131 (13), 184 (10), 243 (99), 285 (63), 326 (11), 385 (1), and 444 (1).

Acid Hydrolysis and Subsequent Oxidation of Epoxyamide 18a with Periodic Acid. We treated 20 mg (0.06 mmol) of epoxyamide **18a** with 57 mg (0.29 mmol) of periodic acid in 2 mL of water and put it into the measuring tube of a polarimeter. The course of the oxidation was followed by noting the variation of the rotatory power. After 24 h, the value stabilized at $[\alpha]^{20}_D$ = −17.4 (*c* 0.5, water).[6]

Reaction of 2,3:4,6-Di-*O*-isopropylidene-D-mannopyranose (23) with *N,N*-diethyl-2-(dimethylsulfuranylidene)acetamide (6). Syntheses of *N,N*-Diethyl-2,3-anhydro-4,5:6,8-di-*O*-isopropylidene-D-*erithro*-L-*altro*-octonamide (24a). We added slowly, while stirring, 1.30 g (7.42 mmol) of *N,N*-diethyl-2-(dimethylsulfuranylidene)acetamide (**6**) to a solution containing 1.00 g (3.84 mmol) of **23** in 20 mL of THF. The solution was kept at rt for one day, after which TLC ($CHCl_3$/MeOH/hexane 10:1:2) revealed that the starting product had disappeared. Excess ylide was destroyed by adding 0.1 N HCl until the pH was neutral. Chromatography on silica gel (hexane:AcOEt 3:1) provided 1.41 g (99%) of practically pure **24a**.

24a: Colorless syrup. $[\alpha]^{20}_D$ = −58.6 (*c* 7.5, MeOH). IR ν_{max} (cm^{-1}): 3416 and 1653. ^{1}H-NMR ($CDCl_3$) δ: 4.52 (dd, 1H, $J_{4,5}$ = 6.7 Hz, $J_{5,6}$ = 2.9 Hz); 3.98 (t, 1H, $J_{3,4}$ = 6.7 Hz, $J_{4,5}$ = 6.7 Hz); 3.89 (dd, 1H, $J_{5,6}$ = 2.9 Hz, $J_{6,7}$ = 7.2 Hz); 3.64 (ddd, 1H, $J_{6,7}$ = 7.3 Hz, $J_{7,8}$ = 9.9 Hz); 3.56 (d, 1H, $J_{2,3}$ = 2.0 Hz); 3.48 (dd, 1H, $J_{2,3}$ = 2.0 Hz, $J_{3,4}$ = 6.7 Hz); 3.55−3.30 (m, 6H); 1.49, 1.48, 1.37 and 1.34 (4s, 12H); 1.25 and 1.12 (2t, 6H, J = 7.1 and 7.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 168.5, 109.5, 98.8, 76.7, 75.3, 72.0, 64.8, 63.6, 55.7, 52.1, 41.6, 40.9, 28.4, 26.7 25.4, 19.1, 14.7, and 12.3. Mass spectrum (*m/e*): 358 (15, 5), 300 (1.2), 272 (16.6), 214 (7.3), 198 (1.9), 131 (6.6), 100 (100), 72 (36.9), and 59 (58.3). Elemental analysis: Calcd for $C_{18}H_{31}O_7N$: C, 57.90%; H, 8.31%; N, 3.75%. Found: C, 57.60%; H, 8.40%; N, 3.76%.

Periodic Acid Oxidation of Epoxyamide 24a. Synthesis of (2*R*,3*S*)-*N,N*-Diethyl-3-formyl-2,3-epoxypropionamide (21). We treated a solution of 50 mg (0.13 mmol) of the epoxyamide in 2 mL of water with 130 mg (0.57 mmol) of periodic acid. After 24 h, the reaction was complete and produced epoxy-aldehyde **21**, in quantitative yield. The specific rotation of **21** was $[\alpha]^{20}_D$ = +10.3 (*c* 1.2, water).[6]

Treatment of Epoxyamide 24a with Acetic Anhydride. Synthesis of *N,N*-Diethyl-7-*O*-acetyl-2,3-anhydro-4,5:6,8-di-*O*-isopropylidene-D-*erythro*-L-*altro*-octonamide (24b). An amount of 0.50 g (1.34 mmol) of the epoxyamide **24a** was dissolved in 2 mL of anhydrous pyridine, and to the resulting mixture we added 0.4 mL of acetic anhydride at room temperature. After 12 h, the solution was diluted with cold water (4 mL) and extracted with chloroform (5 mL, 3 × 1). The organic phase was then washed once with 2 N HCl (5 mL), saturated sodium bicarbonate (5 mL), and water (5 mL). Finally, it was dried over anhydrous sodium sulfate, filtered, and concentrated to obtain the acetylated product, virtually pure (63% yield of **24b**).

24b: $[\alpha]^{20}_D$ = −4.1° (c 2.1, $CHCl_3$). IR ν_{max} (cm^{-1}): 1751 and 1654. ^{1}H-NMR ($CDCl_3$) δ: 5.0 (ddd, 1H, $J_{6,7}$ = 8.8 Hz, $J_{7,8}$ = 6.0 Hz, $J_{7,8'}$ = 5.0 Hz); 4.31 (dd, 1H, $J_{4,5}$ = 6.8 Hz, $J_{5,6}$ = 1.6 Hz); 4.07 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 6.8 Hz); 4.04 (dd, 1H, $J_{8,8'}$ =

12.1 Hz, $J_{7,8} = 5.3$ Hz); 4.01 (dd, 1H, $J_{5,6} = 1.7$ Hz, $J_{6,7} = 8.8$ Hz); 3.63 (dd, 1H, $J_{8,8'} = 12.1$ Hz, $J_{7,8'} = 6.2$ Hz); 3.49 (d, 1H, $J_{2,3} = 1.9$ Hz); 3.40 (dd, 1H, $J_{2,3} = 1.9$ Hz, $J_{3,4} = 6.8$ Hz); 3.55−3.30 (2dc, 4H); 2.05 (s, 3H, OCOMe); 1.47, 1.35 and 1.31 (3s, 12H); 1.25 and 1.12 (2t, 6H, $J = 7.1$ and 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.1, 165.6, 110.0, 99.7, 76.9, 75.4, 69.0, 67.3, 61.9, 55.3, 52.1, 41.6, 40.9, 26.7, 26.4, 25.4, 20.9, 20.6, 14.8, and 12.9. Mass spectrum (*m*/*e*): 400 (4.5), 342 (1.6), 272 (8.4), 242 (4.4), 214 (3.8), 142 (6.9), 130 (3.9), 100 (100), 58 (7.7), and 43 (98.2).

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Supporting Information Available: Copies of ^{13}C and ^{1}H NMR spectra (16 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.

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