1997; extension to this code: a) T. J. Lee, J. E. Rice, J. A. P. Rendell, TITAN, a closed shell coupled cluster code, NASA Ames Research Center, Moffet Field, California, 1990; b) pseudopotential code by M. Pelissier, N. Komiha, J. P. Daudey, *J. Comput. Chem.* **1988**, *9*, 298–302.

[15] a) R. Shepard, I. Shavitt, R. M. Pitzer, D. C. Comeau, M. Pepper, H. Lischka, P. G. Szalay, R. Ahlrichs, F. B. Brown, J. G. Zhao, *Int. J. Quantum. Chem.* **1989**, *22*, 149–165; b) Spin–orbit component: R. M.Pitzer, N. W. Winter, COLUMBUS, Ohio State University, Columbus, OH, **1990**.

[16] J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. L. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K.-K. Baeck, H. Sekino, R. J. Bartlett, ACESII, University of Florida, Gainesville, FL, **1995**.

[17] H. Stoll, M. Dolg, H. Preuss, *Pseudopotential Parameters And Basis Sets*, Universität Stuttgart, Stuttgart, **1997**.

[18] For element 114 we used the following basis sets, which were energy optimized at the Dirac–Fock–Coulomb level (DFC): a dual large-component (LC) (26s25p18d12f)/[11s16p11d4f] and a small component (SC) (25s26p25d18f12g)/[10s15p17d11f4g] basis set for the uncorrelated calculations, and an LC (25s25p18d12f)/[10s16p11d5f] and an SC (25s25p25d18f12g(/[10s14p17d11f5g] basis set for the correlated calculations (coupled cluster CCSD(T)). In all DFC calculations the (SS|SS) integrals were neglected, and the Visscher–Coulomb correction was applied instead.[20] The finite extension of the nucleus was described by a Gaussian distribution. For H, LC (7s2p)/[4s2p] and SC (2s7p2d)/[2s4p2d] basis sets were used in the DFC calculations[20] and reduced to LC (5s2p)/[3s2p] and SC (2s5p2d)/[2s3p2d] for the coupled cluster calculations. Similar basis sets were used for the DFC calculations of EH_n molecules (E = C, Si, Ge, Sn, Pb; $n = 2, 4$) and contracted according to the atomic balance scheme. The nonrelativistic all-electron calculations were carried out with a (24s21p17d11f)/[14s13p10d5f] basis set. The nonrelativistic (NR) and relativistic Hartree–Fock (HF) geometries were optimized numerically. In the DFC correlation treatment only the 6d7s7p electrons were correlated, and all virtual orbitals with an energy of > 10 au were ignored. In the all-electron HF calculations, only the 5f6s6p6d7s7p electrons were correlated, and all virtual orbitals were kept active. For the fluorides and chlorides, all-electron calculations were not feasible. The following basis sets were used in all pseudopotential calculations: for H a large (10s3p1d)/[8s3p1d] set;[21, 22] for F and Cl a aug-cc-PVTZ basis set of Dunning.[23] The [1s2s2p] core of the Cl atoms was kept frozen in all correlation treatments. Zero-point vibrational energy corrections were neglected. The uncorrelated HF and DF results for SiH_n, GeH_n, SnH_n and PbH_n are identical to those in ref. [19]. All basis sets are of HF or DF limit quality.

[19] K. G. Dyall, *J. Chem. Phys.* **1992**, *96*, 1210–1217.

[20] L. Visscher, P. J. C. Aerts, O. Visser, W. C. Nieuwpoort, *Int. J. Quantum Chem. Symp.* **1991**, *25*, 131–139.

[21] The exponents are taken from G. C. Lie, E. Clementi, *J. Chem. Phys.* **1974**, *60*, 1275–1287.

[22] The exponents are taken from S. Huzinaga, *J. Chem. Phys.* **1965**, *42*, 1293–1302.

[23] a) T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007–1023; b) R. A. Kendall, T. H. Dunning, R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796–6806.

[24] C. E. Moore, *Atomic Energy Levels*, US GPO, Washington, **1958**.

[25] H. Hotop, W. C. Lineberger, *J. Phys. Chem. Ref. Data* **1985**, *14*, 731–752.

[26] This is also evident from a comparison of atomic DF and HF data.

[27] D. R. Stull, H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS circular no. 37, US GPO, Washington, **1971**.

[28] M. Kaupp, P. von R. Schleyer, *J. Am. Chem. Soc.* **1993**, *115*, 1061–1073.

[29] O. L. Keller, Jr., J. L. Burnett, T. A. Carlson, C. W. Nestor, Jr., *J. Phys. Chem.* **1970**, *74*, 1127–1134.

[30] P. Pyykkö, J. P. Desclaux, *Nature* **1977**, *266*, 336–337.

[31] E. Eliav, U. Kaldor, P. Schwerdtfeger, B. Hess, Y. Ishikawa, *Phys. Rev. Lett.* **1994**, *73*, 3203–3206.

[32] E. Eliav, U. Kaldor, Y. Ishikawa, *Phys. Rev. Lett.* **1995**, *52*, 2765–2769.

[33] E. Eliav, U. Kaldor, Y. Ishikawa, M. Seth, P. Pyykkö, *Phys. Rev. Lett.* **1996**, *53*, 3926–3933.

[34] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563–594.

Perhydroxylated 1,7-Dioxaspiro[5.5]undecanes ("Spiro Sugars"): Synthesis, Stereochemistry, and Structure**

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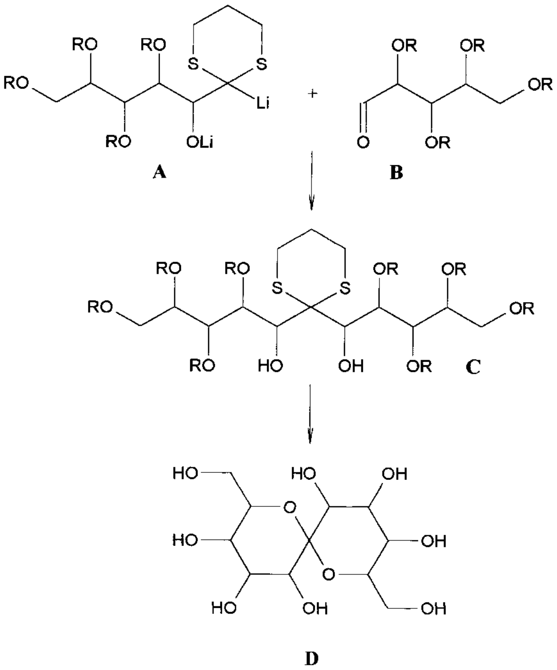
Klaus Schnieders, Sven Thormählen, and
Roland Fröhlich

Dedicated to Professor Dieter Seebach
on the occasion of his 60th birthday

Perhydroxylated 1,7-dioxaspiro[5.5]undecanes (**D**; Scheme 1) – a class of compounds which hitherto has not been identified in nature and whose synthesis is reported herein for the first time – can be formally considered as two hexopyranoses joined together by a spiroacetal center ("spiro sugar").[1]



Scheme 1.

In contrast to perhydroxylated derivatives, spiroacetals are widespread in nature and exhibit a broad range of biological activities, and are found, for example, as insect pheromones, antibiotics, and toxins.[2]

In their synthesis from open-chain precursors – the most common route[2] – structural features such as substituents and their relative arrangement in the acyclic compound need to be taken into consideration. This is particularly evident if the relatively well known properties of monosaccharide hexopyranoses are compared to those of the perhydroxylated 1,7-dioxaspiro[5.5]undecanes (spiro sugars).

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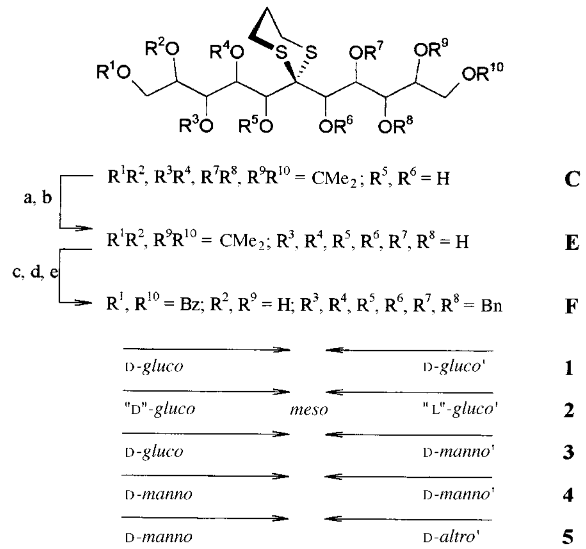
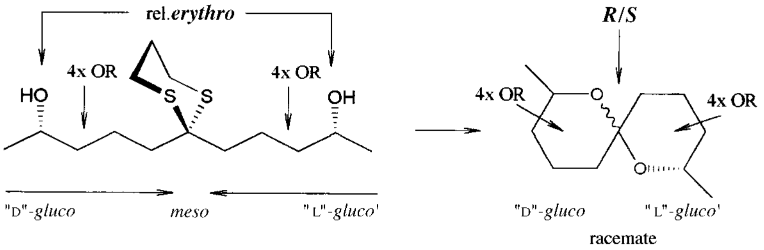
Perhydroxylated 1,7-dioxaspiro[5.5]undecanes can be synthesized efficiently by the "dithiane route"[3] according to the Corey–Seebach procedure.[4] In this reaction an open-chain hexose trimethylene dithioacetal **A** as dianion is coupled with an open-chain aldopentose **B** (Scheme 1). Both precursors are protected as base-stable isopropylidene derivatives,[5] which are available in two or three synthetic steps from the respective sugars.[6, 7] Thus, the chain **C**, which is functionalized at each carbon atom and which according to carbohydrate nomenclature is designated as a substituted undec-6-ulose, is completed in the fourth synthetic step. In this study components **A** and **B** were chosen to cover all relevant combinations of configurations. With respect to the central carbonyl functions (see Table 1, footnote [b]) in the undec-6-uloses these are D-*gluco*/D-*gluco'*, "D"-*gluco*/"L"-*gluco'*, D-*gluco*/D-*manno'*, D-*manno*/D-*manno'*, D-*manno*/D-*altro'* configurated. The data listed in Table 1 reveal that a double stereodifferentiation is applicable to the coupling of components **A** and **B**; the carbonyl components exhibit a marked influence on the Li$^+$ cation which participates in the coupling step as predicted by the "three-point chelation" model[8] (Table 1, entry 4).

A subtly differentiated pattern of protective groups was a prerequisite for obtaining dipyranoid spiroacetals from the open-chain dithanes **C**.[9] This was achieved for all the configurations of the chain **C** studied here[10] (Scheme 2); the simplified protective group strategy was based on fact that the kinetically controlled isopropylidenation[6] of the completely deblocked dithianes **C** leads to the respective terminal 1,2:10,11-diisopropylidene derivatives **E**. The remaining inner free hydroxyl groups were subsequently protected (acid-stable) in the form of benzyl ethers.[11] The cleavage of the isopropylidene groups and subsequent selective benzoylation of the two primary hydroxyl groups[12] furnished the HO-2 and HO-10 unblocked chains **F**. Cleavage of the dithioacetals in compounds **1**–**5** gave solely pyranoid structures.



Scheme 2. a) 2 N HCl/MeOH (1/20), 40 °C, 1 d, > 95 %; b) acetone, concentrated HCl, 25 °C, 5 min, 80 %; c) NaH (80 % in oil, 6.6 equiv), Bu$_4$NI (0.6 equiv), BnBr (6.6 equiv), DMF, 55 °C, 8 h, 54–75 %; d) as a), > 95 %; e) BzCl (10 equiv), pyridine, 25 °C, 30 s, 60–80 %; Bn = benzyl, benzoyl, R^7, R^8 = Me for **1** and **3**.



2

6

Scheme 3.

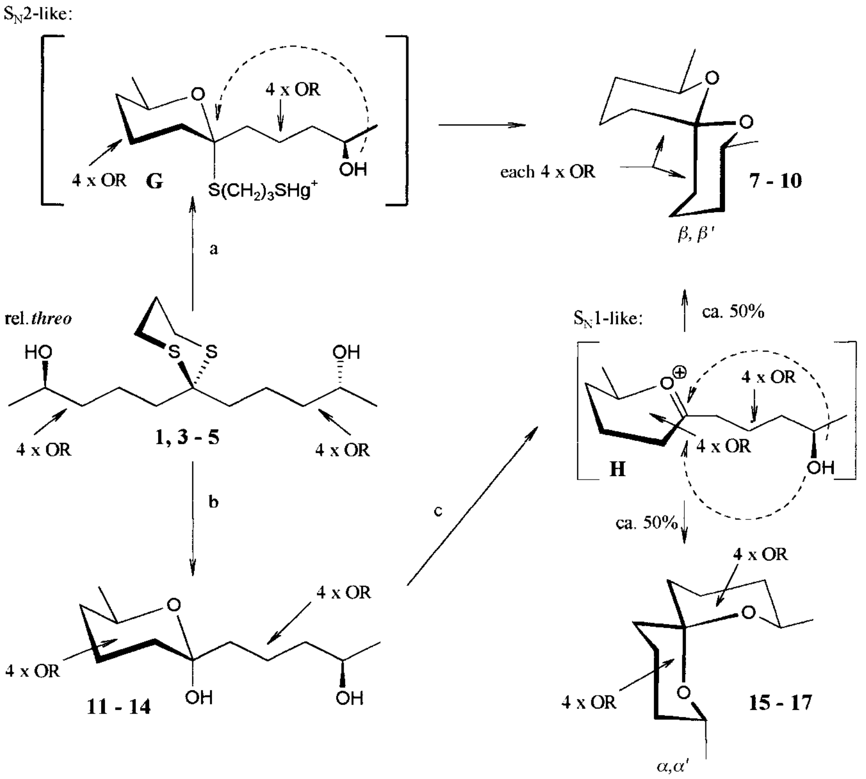
In the intramolecular formation of the spiroacetal a new stereocenter is formed at the spiro carbon atom; thus, the *meso*-compound **2** yielded the racemate **6** (Scheme 3). In contrast, diastereomeric products can be formed for the chiral compounds **1** and **3**–**5**. This study, however, only focuses on those cases in which the unblocked hydroxy groups exhibit a relative *threo* configuration with respect to the central carbonyl group. If the spiroacetal center is considered as an anomeric center, according to carbohydrate nomenclature only the α,α' or β,β' pairs of configurations occur. The above-mentioned *meso*-compound **2** is the prototype for an *erythro* configuration.

Based on the open-chain trimethylene dithioacetals, the two most important mechanisms of spiroacetal formation can now be verified. First the replacement of sulfur atoms in the dithioacetal by hydroxy groups at positions 2 and 10 can proceed with inversion of configuration at the spiro carbon atom in a manner similar to that in a S$_N$2 substitution. This evidently is the case if the conditions mentioned in Scheme 4 are applied for the dithioacetal cleavage (anhydrous acetoni-

Table 1. Couplings of the monosaccharides to carbohydrate chains.[a]

Entry	Dithiane **A**	Aldehyde **B**	Chain **C1**[b]	Chain **C2**[b]	*ds*	Yield [%]
1	D-*gluco*	D-*arabino*	D-*gluco*/D-*gluco'*	D-*gluco*/D-*manno'*	4:1	61
2	D-*gluco*	L-*arabino*	D-*gluco*/L-*gluco'*	D-*gluco*/L-*manno'*	1.5:1	60
3	D-*manno*	D-*arabino*	D-*manno*/D-*gluco'*	D-*manno*/D-*manno'*	1:3	62
4	D-*manno*	D-*ribo*	D-*manno*/D-*altro'*		1:0	65

[a] The 3,4:5,6-di-*O*-isopropylidene-hexosepropane-1,3-diyldithioacetals were treated with 4,5-*O*-isopropylidene-2,3-di-*O*-methyl-pentose in entry 1, in entries 2–4 with the respective 2,3:4,5-di-*O*-isopropylidene-pentose. Dithiane **A** was first metalated with *n*BuLi (2.2 equiv; THF, −30 °C, 5 h), then **B** (0.7 equiv; −78 → 0 °C) was added.[4c] Diastereomers were separated by chromatography on silica gel (cyclohexane/ethyl acetate, 8/1). The yields are based on the amount of **B** employed. [b] The nomenclature used is based on the configuration at position 6 starting from the respective termini. The initial hexose is named first.[1] If the IUPAC rules for carbohydrates were taken into account, the here named D-*gluco*/D-*gluco'* case would translate to D-*gluco*-L-*gulo*.



Scheme 4. a) $HgCl_2$ (3.0 equiv), HgO (4.5 equiv), acetonitrile, reflux, 2 h, 73–95 %; b) $HgCl_2$ (3.0 equiv), HgO (4.5 equiv), acetonitrile/H_2O (4/1), reflux, 5 h, 66 %, (30–35 % of them hemiacetals, 50–60 % β,β' compounds, and 0–5 % α,α' compounds; separation on silica gel, cyclohexane/ethyl acetate, 3/1); c) $BF_3 \cdot Et_2O$, dichloromethane, 25 °C, 5 min, 90 %, ratio of products β,β': α,α' = 1:1 (separation on silica gel, cyclohexane/ethyl acetate, 3/1).

trile, mercury(II) chloride/mercury(II) oxide).[13] Regardless of the symmetry of the chain (C_1 for **3** and **5**, C_2 for **1** and **4**), the relative configuration (*gluco, manno, altro*) and thus the conformation of the segments (*manno*: stretched, *gluco, altro*: both differently banana-shaped),[14] only the β-configurated product (according to carbohydrate nomenclature) is formed. The prerequisite for this strict preference in the reaction sequence *S,S*-acetal → *O,S*-acetal → *O,O*-acetal is that the α-configurated "alkylthioketoside" **G** is always formed first, which in the second step reacts under repeated inversion to give the β,β'-configurated spiroacetals **7**–**10**.

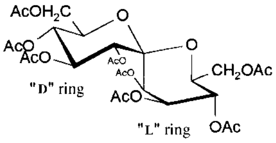
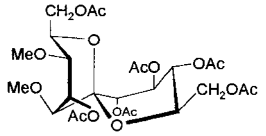
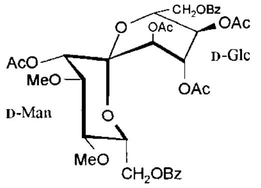
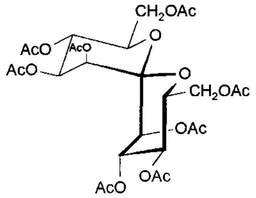
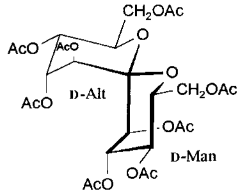
Second the formation of the *O,O*-acetal can proceed via a cyclic oxocarbenium ion intermediate. Experimentally this case may be understood by adding water (20 %) during the cleavage of the dithioacetal (Scheme 4). Although the β,β'-spiroacetal still prevails as the major poduct in all the reactions (50–60 % yield, based on 60–70 % total yield), 30–35 % of α-configurated hemiacetals (**11**–**14**) and up to 5 % of α,α'-configurated spiroacetals are isolated. The hemiacetals **11**–**14**, regardless of the different chain structures, react spontaneously in organic solvents such as dichloromethane or acetonitrile in the presence of catalytic amounts of mineral acids and Lewis acids (HCl, $BF_3 \cdot Et_2O$, F_3CCO_2H) to give 1:1 mixtures of the β,β' derivatives **7**–**10** and the α,α'-configurated compounds **15**–**17**.

This result can be explained under the assumption that the tertiary hydroxy group in hemiacetals **11**–**14** is activated, for example, by protonation, and a cyclic oxocarbenium ion of type **H** is formed as a result. This oxocarbenium ion undergoes extremely rapid intramolecular attack without any facial preference (i.e. as in an S_N1 substitution) by the available hydroxyl groups to furnish the mixture of diastereomeric *O,O*-acetals.

Overall, the stereochemical pathway of the spiroacetal formation can be fully understood—presumably because of the quasi-irreversibility present here, since hitherto, it has not been possible to convert the β,β'-configurated spiroacetals to the respective α,α' isomers, for example, by proton catalysis. S_N2-like processes govern the formation of the first intermediate, the *O,S*-acetal with α configuration, the "alkylthioketoside" **G**. In a second nucleophilic substitution this yields the β,β'-configurated products. In contrast, S_N1-type processes always yield mixtures of products with β,β' or α,α' configurations at the spiroacetal center, since the unusually high reactivity of the intermediate oxocarbenium ion in the intramolecular process will not allow for any facial discrimination with regard to the attack of the second hydroxy group for chains with different configurations. Since two limiting cases are apparent, the results obtained in this study may serve to generalize similar experiments in natural product syntheses—especially if the "dithiane"-route or any comparable synthetic strategies are adopted.

The assignment of the configurations at the spiroacetal centers was initially problematic, because neither the NMR-spectroscopic data nor the determinations of the amount of rotation and their correlation[15] with well-known systems seemed to be acceptable. We assumed (wrongly) that β,β'-configurated spiroacetals would not be formed because, despite the large number of similar systems occurring in nature or prepared synthethically, to our knowledge an arrangement of this kind had not been described;[2] there are only rare reports on α,β'- or β,α'-configurations,[2, 16] which refer to the relative *erythro*-arrangement in the above-mentioned sense and cannot be configurated in another way. In addition, the NMR data in some cases gave indications for the presence of boat conformations, which are extremely unlikely for unfixed hexopyranoses. However, as can be seen in Table 2 the NMR data are clear: for all α-configurations of a hexopyranose segment normal chair conformations are present in solution,[17] in contrast boat conformations occur for all β-*gluco*-configurations. The reason for this is the evidently very high steric demand of an equatorially orientated substituent (the OAc group) at the C2 position of one pyran ring contrasted to that at the other pyran ring, which is eased by a change in conformation (Figure 1). This change of conformation is supported by stereoelectronic effects–

Table 2. Assignment of the conformations by ^{1}H NMR spectroscopy.[a]

	Spiro sugar	Ring A[b]		Ring B[b]	
		J [Hz]	conformation	J [Hz]	conformation
6		$J_{2,3} = 10.2$ $J_{3,4} = 9.2$ $J_{4,5} = 10.2$	C	$J_{2',3'} = 8.8$ $J_{3',4'} = 5.2$ $J_{4',5'} = 8.8$	B
			β-D-*gluco*/α′-L-*gluco* β′-L-*gluco*/α-D-*gluco*	racemate	
7		$J_{2,3} = 2.0$ $J_{3,4} = 8.0$ $J_{4,5} = 10.6$	$^{1,4}B$	$J_{2',3'} = 1.6$ $J_{3',4'} = 6.8$ $J_{4',5'} = 10.8$	$^{1,4}B$
			β-D-*gluco*/β′-D-*gluco*		
8		$J_{2,3} = 3.4$ $J_{3,4} = 7.6$ $J_{4,5} = 10.4$	$^{1,4}B$	$J_{2',3'} = 3.4$ $J_{3',4'} = 8.2$ $J_{4',5'} = 8.8$	$^4C_1$
			β-D-*gluco*/β′-D-*manno*		
9		$J_{2,3} = 2.8$ $J_{3,4} = 9.8$ $J_{4,5} = 9.8$	$^4C_1$	$J_{2',3'} = 2.8$ $J_{3',4'} = 9.8$ $J_{4',5'} = 9.8$	$^4C_1$
			β-D-*manno*/β′-D-*manno*		
10		$J_{2,3} = 3.6$ $J_{3,4} = 9.6$ $J_{4,5} = 9.6$	$^4C_1$	$J_{2',3'} < 1.0$ $J_{3',4'} = 2.8$ $J_{4',5'} = 8.8$	$^4C_1$
			β-D-*manno*/β′-D-*altro*		

[a] The compounds were acetylated with acetanhydride in pyridine after cleavage of the benzoates according to Zemplén and of the benzyl ethers with H_2, Pd/C in methanol (70–75% yield), and then measured in $CDCl_3$ at 300 MHz.[b] Ring A describes the first named, ring B the second named half of the respective dipyranoid system.

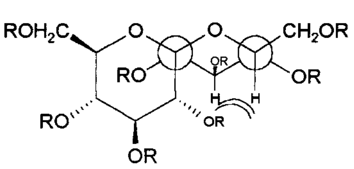


Figure 1. Steric interaction of a substituent at C-2 orientated equatorially relative to the spiroacetal center in β-D-*gluco*/β′-D-*gluco*-configurated spiro sugar. View along: C_{spiro}–C-2.

anomeric and the Δ2 effect.[18, 19] For the "D"-*gluco*/"L"-*gluco′*-configurated racemate **6** these conditions lead to the surprising result that in the case of an identical relative arrangement of the substituents, one ring adopts the chair and the other the boat conformation. On the other hand the strong 1,3-diaxial interaction between O3 of the *altro*-hexose and C2 of the *manno*-pyranose in **10** does not produce a change of the conformation.

In order to verify these interpretations three crystal structure analyses were carried out. The normal case is represented by the *α,α′*-D-*gluco*/D-*gluco′*-configurated spiroacetal **15**,[20a] in which both rings adopt the chair conformation and the C_{spiro}–O distances are almost identical (1.407 and 1.414 Å), which is expected for symmetry reasons (Figure 2). The diasteromeric compound **7** with a *β,β′* configuration crystallizes from methanol with a molecule methanol in the crystal (Figure 3).[20b] The pyran ring which carries the methoxy groups adopts a chair conformation, the peracetylated pyranose adopts a boat conformation. This surprising result may be explained by the slightly different patterns of the protecting groups at the two pyran rings of this otherwise C_2 symmetric compound, but in any case shows that the existence of a boat conformation is probable. Additionally, the C_{spiro}–O distances are clearly different: 1.396 Å in the boat, 1.434 Å in the chair.

The crystal structure of **9** is particularly interesting (Figure 4).[20c] This compound can almost not be distinguished from the corresponding *α,α′*-configurated derivative **17**.[17] The *β,β′* configuration for a chair conformation for both pyran rings can be seen clearly in the crystal structure. The C_{spiro}–O distances differ slightly (1.389 and 1.412 Å) and indicate a distortion of the crystal. In this molecule C6′, O5′, C_{spiro}, O5, and C6 are present in the *all-trans* conformation, an arrangement which shows that this molecule is a pure oxa analogue of the associated carbocyclic compound. This arrangement (C_{2v}

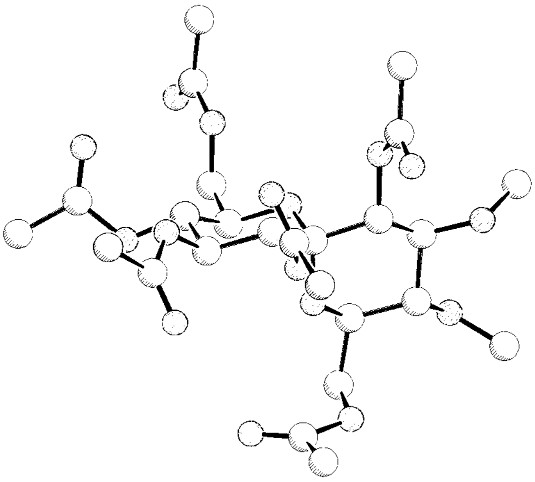


Figure 2. Crystal structure of the α-D-*gluco*/α′-D-*gluco* system **15**.

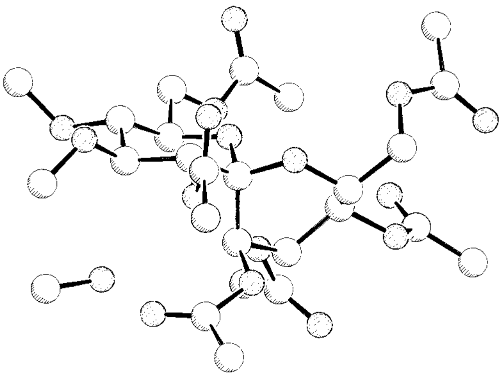


Figure 3. Crystal structure of the β-D-*gluco*/β′-D-*gluco* system **7**.

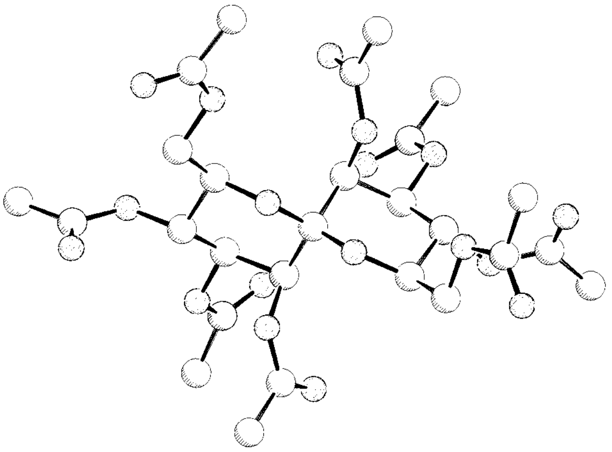


Figure 4. Crystal structure of the β-D-*manno*/β′-D-*manno* system **9**.

symmetry) is the most unfavorable for an acetal segment: alone for formaldehyde hydrate the destabilization compared to an acetal segment with C_2 symmetry is about 9 kcal mol^{-1}.[21]

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[1] H. Redlich, J. B. Lenfers, S. Thormählen, *Synthesis* **1992**, 1112–1118.

[2] Review: F. Perron, K. F. Albizati, *Chem. Rev.* **1989**, *89*, 1617–1661.

[3] D. A. Evans, C. E. Sacks, R. A. Whitney, N. G. Mandel, *Tetrahedron Lett.* **1978**, *8*, 727–730.

[4] a) D. Seebach, *Synthesis* **1969**, 17–36; b) D. Seebach, B. T. Gröbel, *Synthesis* **1977**, 357–402; c) D. Seebach, E. J. Corey, *J. Org. Chem.* **1975**, *40*, 231–237.

[5] In the initial phase of these investigations compounds were used that were partly protected as methyl ethers.

[6] a) H. Redlich, O. Kölln, *Synthesis* **1995**, 1376–1382; b) H. Redlich, O. Kölln, H. Frank, *Synthesis* **1995**, 1383–1388; c) H. Redlich, O. Kölln, *Synthesis* **1996**, 826–832; d) H. Redlich, O. Kölln, *Synthesis* **1996**, 963–969.

[7] M. Fetizon, M. Jurion, *J. Chem. Soc. Chem. Commun.* **1972**, 382–383.

[8] H. Redlich, S. Thormählen, *Tetrahedron Lett.* **1985**, *26*, 3685–3688.

[9] The dithioacetal cleavage at the completely unprotected undeculoses resulted in mixtures of products.

[10] Details on the synthesis and analysis of all the open-chain carbohydrates described here will be published elsewhere.

[11] In addition to the hexabenzyl compounds in some cases also pentabenzyl products were obtained in which one OH group adjacent to the dithiane ring was not protected. As this free hydroxy function has no influence on the subsequent dithioacetal cleavage, these compounds can be used further.

[12] A. Haines, *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 11–51.

[13] E. J. Corey, B. W. Erickson, *J. Org. Chem.* **1971**, *36*, 3553–3560.

[14] P. L. Durette, D. Horton, *Adv. Carbohydr. Chem.* **1971**, *26*, 49–73.

[15] K. Mori, T. Uematsu, K. Yanagi, M. Minobe, *Tetrahedron* **1985**, *41*, 2751–2758.

[16] a) F. E. Ziegler, W. T. Cain, *J. Org. Chem.* **1989**, *54*, 3347–3353; b) M. Kobayashi, S. Aoki, I. Kitagawa, *Tetrahedron Lett.* **1994**, *35*, 1243–1246.

[17] ^{1}H NMR data: **15** (α-D-*gluco*/α′-D-*gluco*), for both rings: $J_{2,3}=10.0$, $J_{3,4}=9.2$, $J_{4,5}=10.2$ Hz; **16** (α-D-*gluco*/α′-D-*manno*), *gluco* ring: $J_{2,3}=9.4$, $J_{3,4}=8.8$, $J_{4,5}=10.0$ Hz, *manno* ring: $J_{2,3}=3.4$, $J_{3,4}=9.2$, $J_{4,5}=9.6$ Hz; **17** (α-D-*manno*/α′-D-*manno*), both rings: $J_{2,3}=3.4$, $J_{3,4}=10.2$, $J_{4,5}=10.2$ Hz.

[18] a) J. T. Edward, *Chem. Ind. (London)* **1955**, 1102–1104; b) P. Deslongchamps, D. D. Rowan, N. Pothier, T. Sauvé, J. K. Saunders, *Can. J. Chem.* **1981**, *59*, 1105–1121; c) P. Deslongchamps, *Stereoelectronic Effects in Organic Chemistry*, Pergamon, New York, **1983**; d) A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer, New York, **1983**; e) *The Anomeric Effect and Associated Stereoelectronic Effects* (Ed.: G. R. Thatcher), American Chemical Society, Washington, DC, **1993** (*ACS Symp. Ser.* **1993**, 539).

[19] R. E. J. Reeves, *J. Am. Chem. Soc.* **1950**, *72*, 1499–1506.

[20] a) Crystal structure data of **15** (single crystals from methanol at $-10\,^{\circ}$C): $C_{25}H_{36}O_{16}$, $M_r=592.54$, crystal dimensions: $0.3\times0.25\times0.2$ mm^3, $a=10.590(1)$, $b=15.029(1)$, $c=19.076(2)$ Å, $V=3036.1(5)$ Å^3, $\rho_{calcd}=1.296$ g cm^{-3}, $\mu=9.4$ cm^{-1}, $Z=4$, orthorhombic, space group $P2_12_12_1$ (no. 19), 6761 measured reflections, $(-h, +k, \pm l)$, $[(\sin\theta)/\lambda]_{max}=0.63$ Å^{-1}, 6189 independent and 5773 bobserved reflections with $I>2\sigma(I)$, 379 refined parameters, $R=0.039$, $wR^2=0.108$, max./min. Residual electron density $0.18/-0.19$ e Å^{-3};[20d] b) crystal structure data of **7** (single crystals from methanol at $-10\,^{\circ}$C): $C_{26}H_{40}O_{17}$, $M_r=624.58$, crystal dimensions: $0.35\times0.2\times0.15$ mm^3, $a=8.1404(5)$, $b=8.8120(6)$, $c=11.7246(8)$ Å, $\alpha=101.239(5)$, $\beta=107.157(6)$, $\gamma=95.688(5)^{\circ}$, $V=777.1(1)$ Å^3, $\rho_{calcd}=1.334$ g cm^{-3}, $\mu=9.7$ cm^{-1}, $Z=1$, triclinic, space group $P1$ (no. 1), 3562 measured reflections, $(\pm h, \pm k, \pm l)$, $[(\sin\theta)/\lambda]_{max}=0.62$ Å^{-1}, 3520 independent and 3392 observed reflections with $I>2\sigma(I)$, 399 refined parameters, $R=0.040$, $wR^2=0.109$, max./min. Residual electron density $0.37/-0.43$ e Å^{-3};[20d] c) crystal structure data of **9** (single crystals from methanol at $-10\,^{\circ}$C): $C_{27}H_{36}O_{18}$, $M_r=648.56$, crystal dimensions: $0.5\times0.25\times0.1$ mm^3, $a=8.929(2)$, $b=9.246(3)$, $c=38.281(2)$ Å, $V=3160.4(13)$ Å^3, $\rho_{calcd}=1.363$ g cm^{-3}, $\mu=10.0$ cm^{-1}, $Z=4$, triclinic, space group $P2_12_12_1$ (no. 19), 3671 measured reflections, $(-h, -k, -l)$, $[(\sin\theta)/\lambda]_{max}=0.62$ Å^{-1}, 3671 independent and 2650 observed reflections with $I>2\sigma(I)$, 414 refined parameters, $R=0.075$, $wR^2=0.194$, max./min. Residual electron density $0.51/-0.36$ e Å^{-3}.[20d] d) Enraf-Nonius-CAD4 diffractometer, $\lambda=1.54178$ Å, $T=223$ K, ω-2θ scan, solution with direct methods, hydrogen aotms in calculated positions, Programs SHELXS-86, SHELXS-93, SCHAKAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100-729. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: (+44)1223–336–033; E-mail: deposit@ccdc.cam.ac.uk).

[21] P. von R. Schleyer, U. Salzner, *J. Am. Chem. Soc.* **1993**, *115*, 10231–10236.