Pergamon

Tetrahedron Vol. 51, No. 3, pp. 871-908, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)00978-3

The Reaction of Acetyliron [(η^5-C_5H_5)Fe(CO)(PPh_3)($COCH_3$)] with Sugar Aldehydes. New Synthesis of Deoxysugars

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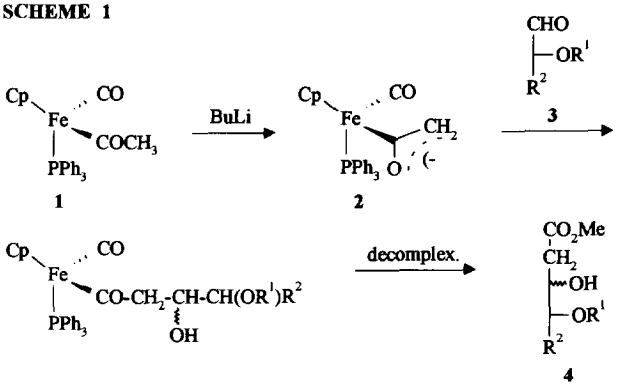
Abstract: *Aldol reactions of sugar aldehydes (**5** - **13**) with enolate **2** of racemic and both enantiomeric forms of acetyliron were investigated. The steric course of reactions depended strongly on the counterions used. High stereocontrol was achieved with the following cations: tin(II), diethylaluminum(I), zirconium(IV) and the triethylaluminum-containing cation. Matched pairs, particularly with the pentose- and hexose-derived aldehydes, yielded the corresponding aldol products with very high stereoselectivities.Products of aldol reactions were decomplexed with N-bromosuccinimide in methanol. From aldols **14a-d** - **18a-d** stereoisomeric methyl 2-deoxypentonates and 2-deoxyhexonates were obtained and their configuration was determined. Aldols obtained from acetyliron anion (**2**) and pentose- and hexose-derived aldehydes **8** - **13** led after decomplexation to pairs of stereoisomeric methyl 6-deoxy(7-deoxy)-hept(oct)uronates. These products were separated and their configuration was assigned on the basis of chemical transformations to free 6-deoxyheptoses. In case of D- and L-arabino aldehydes (**9** and **10**) - because of low stability of products - the configuration was assigned by the synthesis of a model compound. A regularity was found in the ^1H NMR spectra of methyl 6-deoxy-hepturonates connecting coupling constants $J_{\alpha,\beta}$ and $J_{\alpha',\beta}$ of the methylene protons with the configuration of the β-carbon atom.*

INTRODUCTION

Numerous stereoselective syntheses of natural products with the help of iron(II) complex: cyclopentadienyl-carbonyl-triphenylphosphine-acetyliron [**1**, (η^5-C_5H_5)Fe(CO)(PPh_3)($COCH_3$)], performed in the laboratory of Professor Davies,[1-8] demonstrated clearly the value of this organometallic auxiliary in organic synthesis. In a recent paper[9] the synthesis of (3R,4S)-statine, a diastereoisomer of naturally occurring component of pepstatin, was presented.

In this work we demonstrate that complex **1** (acetyliron) is a practical reagent in carbohydrate chemistry enabling the synthesis of several useful monosaccharide derivatives (**4**). The reaction of enantiomeric forms of acetyliron with optically active sugar aldehydes **3** ("matched" and "mismatched" pairs[10]) permitted also to draw conclusions regarding the probable stereochemistry of the transition state of the reactions.

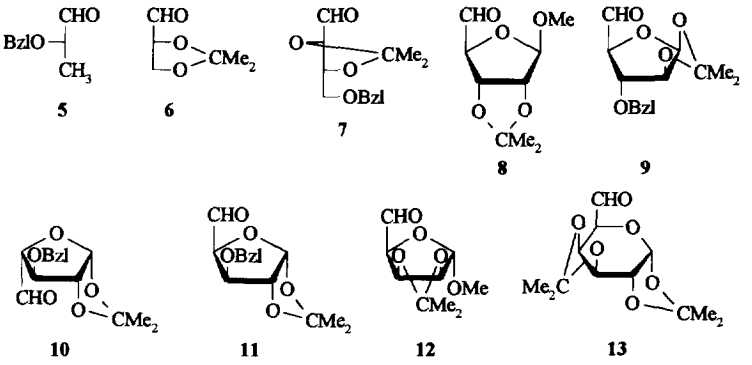
SCHEME 1



RESULTS

For the reaction with the enolate **2** of acetyliron (**1**) a series of aldehydes was chosen comprising three-carbon [O-benzyl-L-lactaldehyde (**5**), 2,3-O-isopropylidene-D-glyceraldehyde (**6**)], tetra-carbon [4-O-benzyl-2,3-O-isopropylidene-D-threose (**7**)], penta-carbon [methyl 2,3-O-isopropylidene-β-D-ribo-dialdo-1,4-furanoside (**8**), 3-O-benzyl-1,2-O-isopropylidene-β-D- and L-arabino-dialdo-1,4-furanoses (**9** and **10**), 3-O-benzyl-1,2-O-isopropylidene-α-D-xylo-dialdo-1,4-furanose (**11**) and methyl 2,3-O-isopropylidene-α-D-lyxo-dialdo-1,4-furanoside (**12**)] and a single hexa-carbon aldehyde [1,2:3,4-di-O-isopropylidene-α-D-galacto-dialdo-1,5-pyranose (**13**)](**Chart 1**).#

CHART 1



Racemic as well as **R** and **S** enantiomeric forms of **1** were employed. Enolate **2** was generated from **1** with n-butyllithium at -78° for 15 min. In order to increase the stereoselectivity of aldol reactions[11,12], a series of metal cations replacing Li^+ was investigated. Besides the well-proven counterions: diethylaluminum(I)

#Carbohydrate configurational assignments are used here in order to preserve the uniformity of description. However, in the discussion of the stereochemical results we had to resort to CIP designations.

and tin(II), several other metallic salts and organometallic compounds have been checked: Cp_2ZrCl_2, $(i\text{-}PrO)_3TiCl$, and $MgBr_2$ - all of them investigated earlier[12], and Et_3Al, $CeCl_3$, $NiCl_2$, $LaCl_3$, Cp_2TiCl_2, $TiCl_4$, and $ZrCl_4$. Exchange of lithium for another metal cations was performed at the same temperature by adding a suitable salt (2.5 mol. equiv.). After 1 h the aldehyde was added and the reaction mixture was stirred at -78°. The aldehyde component was usually taken in ca 20% molar excess because sugar aldehydes are not very stable under strongly basic conditions and undergo slight decomposition. When the reaction was complete (ca. 45 min) methanol was added and the work-up followed (see **Experimental**).

Distinct influence on the stereochemistry of the aldol reactions exerted Et_2Al^+, Et_3Al, Sn^{2+}, $(i\text{-}PrO)_3Ti^+$, and Zr^{4+}. Titanium tetrachloride caused decomposition of **2**. The remaining salts had little influence on the reaction and the stereochemical results were essentially similar to those achieved with Li^+.

Two series of experiments have been performed. In the first, preparative scale (10 mM) series, performed with racemic acetyliron (**1**)[##], decomplexation experiments were made leading to mixtures of stereoisomeric aldol products (**4**). These products were separated and their structure and stereochemistry was determined. In the second series, analytical scale reactions of aldehydes **3** with enantiomeric forms of acetyliron were performed and the ratios of products formed were determined with HPLC. As it turned out, the proportions of stereoisomeric products obtained from racemic form and from enantiomers of **1** were practically the same.

O-Benzyl-L-lactaldehyde (5)

The yields and proportions of stereoisomers **14a-14d** are collected in **Table 1**. Decomplexation of **14a - 14d** with N-bromosuccinimide in methanol led to two diastereoisomeric methyl 4-O-benzyl-2,5-dideoxy-L-pentonates (**15** and **16**) which were separated and their configuration was determined as 3R,4S (*erythro*) and 3S,4S (*threo*, respectively (**Scheme 2**) (*vide infra*).

Aldol reactions of **R-2** with **5** and Li^+, $(i\text{-}PrO)_3Ti^+$, Et_2Al^+, or Et_3Al as cations are practically non-stereoselective. Under similar conditions **S-2** demonstrated a weak stereoselectivity (1.8 - 2.3 : 1) in favor of the *"erythro"* product **14c** (SRS). In contrast, when tin(II) was employed as the cation, enolate **R-2** gave aldol **14a** in a distinct predominance over the stereoisomeric **14b** (**Table 1**, entry 5). Enolate **S-2** yielded with the same counterion **14d** as the main product (entry 10). The yields of both reactions were low.

2,3-O-Isopropylidene-D-glyceraldehyde (6)

Aldol reactions of **6** are summarized in **Table 2**. The configuration of all stereoisomeric products **17a-17d** was deduced from: 1. analytical-scale aldol reactions with **R-** and **S-2**, and 2. *via* decomplexation of products to the known methyl 2-deoxy-4,5-O-isopropylidene-D-*erythro*- and *threo*-pentonates.

Condensation of **R-2** with **6** in the presence of Li^+ was non-stereoselective and provided both stereoisomeric products **17a** and **17b** in equal amounts. Moderate stereoselectivity (1.5 - 2.6 : 1 in favor of **17a**) was achieved with $(i\text{-}PrO)_3Ti^+$, Et_2Al^+ and Et_3Al (**Table 2**, entries 2, 3, and 5). The reactions with **S-2** were even less stereoselective favoring slightly **17c** over **17d**. Triethylaluminum behaved here differently yielding **17c** in a 3.8 : 1 predominance over **17d** (entry 11).

[##]In these experiments the molar proportion **RS-1** : **3** was 1 : 1.2 in order to achieve full consumption of the substrates and to avoid kinetic resolution of racemic **1**.

TABLE 1
Reactions with O-benzyl-L-lactaldehyde (**5**)

1	Entry	MX	Yield %	**14a** (RRS)	**14b** (RSS)	**14c** (SRS)	**14d** (SSS)
R	1	BuLi	50	50	50	-	-
	2	$(iPrO)_3TiCl$	70	56	44	-	-
	3	Et_2AlCl[a]	60	56	44	-	-
	4	Et_3Al	35	50	50	-	-
	5	$SnCl_2$[b]	20	92	8	-	-
S	6	BuLi	45	-	-	67	33
	7	$(iPrO)_3TiCl$	65	-	-	68	32
	8	Et_2AlCl[b]	60	-	-	70	30
	9	Et_3Al	40	-	-	65	35
	10	$SnCl_2$[a]	25	-	-	20	80

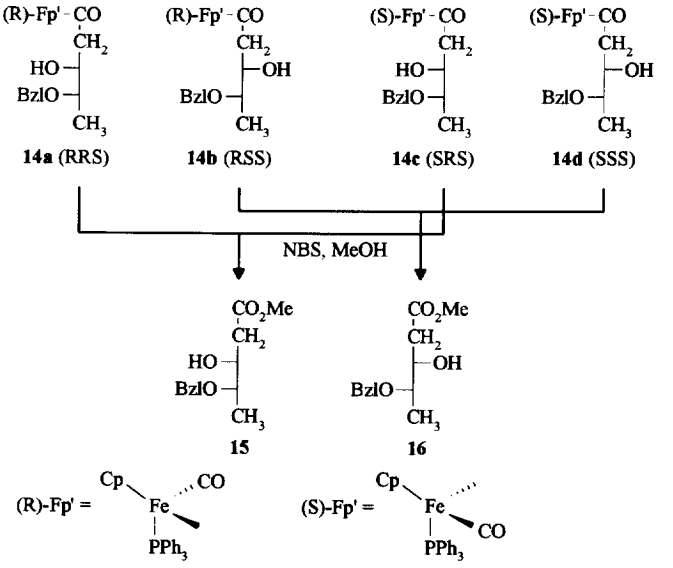
[a]Mismatched pair. [b]Matched pair.

TABLE 2
Reactions with 2,3-O-isopropylidene-D-glyceraldehyde (**6**)

1	Entry	MX	Yield %	**17a** (RSR)	**17b** (RRR)	**17c** (SSR)	**17d** (SRR)
R	1	BuLi[a]	40	50	50	-	-
	2	$(iPrO)_3TiCl$	45	64	36	-	-
	3	$ZrCl_4$	20	54	46	-	-
	4	Et_2AlCl[e]	60	72	28	-	-
	5	Et_3Al	45	60	40	-	-
	6	$SnCl_2$[b,f]	30	35	65	-	-
S	7	BuLi[c]	50	-	-	54	46
	8	$(iPrO)_3TiCl$	50	-	-	58	42
	9	$ZrCl_4$	25	-	-	86	14
	10	Et_2AlCl[f]	50	-	-	60	40
	11	Et_3Al	50	-	-	79	21
	12	$SnCl_2$[d,e]	40	-	-	90	10

[a]Ref.[13]: RSR : RRR = 58 : 42 (-78°C); [b]Ref.[13]: 5 : 95 (-78°C); [c]Ref.[13]: SSR : SRR = 59 : 41 (-78°C); [d]Ref.[13]: 96 : 4 (-78°C); [e]Matched pair; [f]Mismatched pair.

SCHEME 2

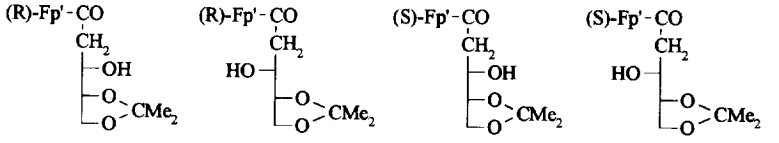


RRR = $R_{Fe}R_{\beta\text{-}C}S_{\gamma\text{-}C}$ (first letter denotes configuration at the iron atom, the second - at the β-carbon atom, and the third - at the γ-carbon atom).

Tin(II) cation gave **17c** and **17d** in a 9 : 1 proportion when **S-2** was employed; with **R-2** both stereoisomeric products **17a** and **17b** were obtained in 1 : 1.8 proportion. Zirconium(IV) cation behaved similarly although the selectivities were lower than with the tin(II) cation (cf. entries 4 and 10).

The stereoselectivities obtained here resemble those observed by Davies[13] for aldol reactions of **6** performed at -78°. An exception is the reaction between R-**2** and **6** in the presence of tin(II) cation; proportion of products **17a** and **17b** we found was 35 : 65 (entry 6) compared to 5 : 95 found by Davies[13].

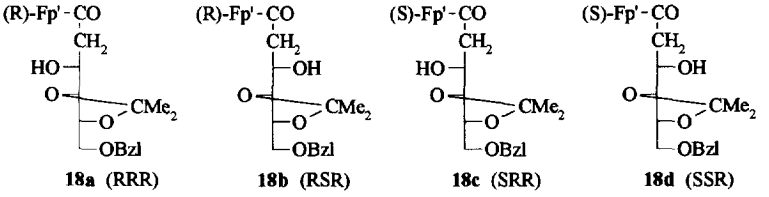
CHART 2



4-O-Benzyl-2,3-O-isopropylidene-D-tetrose (7)

The reaction of **R-2** or **S-2** with **7** leading to aldol products **18a**, **18b** and **18c**, **18d**, respectively, favors clearly those having *erythro* configurational arrangement of β and γ carbon atoms (**18a** and **18c**, **Chart 3** and **Table 3**). This observation is actual for practically all counterions investigated.

CHART 3



18a (RRR) **18b** (RSR) **18c** (SRR) **18d** (SSR)

TABLE 3

Reactions with 4-O-benzyl-2,3-O-isopropylidene-D-tetrose (**7**)

1	Entry	MX	Yield %	**18a** (RRR)	**18b** (RSR)	**18c** (SRR)	**18d** (SSR)
R	1	BuLi	50	82	18	-	-
	2	$(iPrO)_3TiCl$	40	76	24	-	-
	3	$ZrCl_4$	20	82	18	-	-
	4	Et_2AlCl[a]	50	69	31	-	-
	5	Et_3Al	40	79	21	-	-
	6	$SnCl_2$[b]	25	94	6	-	-
S	7	BuLi	50	-	-	65	35
	8	$(iPrO)_3TiCl$	40	-	-	83	17
	9	$ZrCl_4$	30	-	-	67	33
	10	Et_2AlCl[b]	50	-	-	70	30
	11	Et_3Al	40	-	-	63	37
	12	$SnCl_2$[a]	25	-	-	77	23

[a]Mismatched pair; [b]Matched pair.

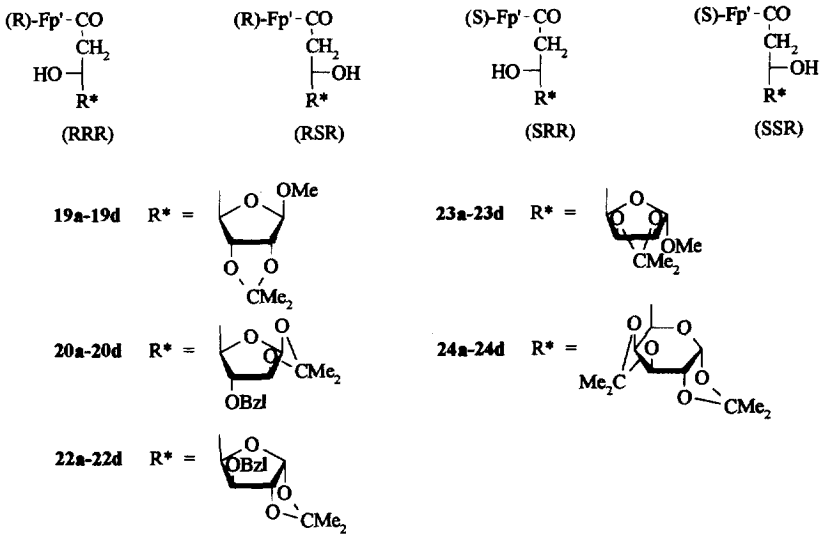
Pentose aldehydes (8 - 12)

Aldol reactions of enolate **2** with pentose aldehydes **8 - 12** displayed similarities making convenient a joint description of the results achieved.

As in other cases described above, the aldol products obtained from **8**, **9**, **11**, and **12** are arranged in the same order: RRR, RSR, SRR, and SSR (**Chart 4**) referring to the configuration at the iron atom and β and γ carbon atoms of the acyl ligand. For aldehyde **10** (L-*arabino* configuration) enantiomeric forms of those obtained with **9** (D-*arabino*) are discussed.

The configuration of all aldol products was deduced - as in the previous cases - from products of decomplexation and from experiments with optically active forms of acetyliron.

CHART 4



Most extensively were studied the reactions of **1** with methyl 2,3-O-isopropylidene-β-D-ribo-dialdo-1,4-furanoside (**8**). This aldehyde can be easily purified and can be stored for several months without visible decomposition. The results of aldol reactions of **8**, leading to stereoisomeric products **19a** - **19d** are presented in **Table 4**.

Lithium cation promoted the formation of $C_\beta C_\gamma$-*erythro* products from both, **R-** and **S-2** (entries 1 and 12). Very similar results were also obtained with caesium(III), nickel(II), lantanum(III), Cp_2Ti^{2+}, and magnesium(II) cations (entries 7-11 and 18-22). Diethylaluminum cation showed high stereoselectivity in reaction with **S-2** (matched pair, cf. **Discussion**) and no stereoselectivity with **R-2** (mismatched pair). As expected, a reversed stereoselectivity was observed for the tin(II) cation (entries 6 and 17). A similar behaviour of Et_3Al, forming probably a complex cation Et_3AlLi^+, is rather surprizing (entries 5 and 16). Zirconium(IV) cation behaved here rather neutrally furnishing with **R-** and **S-2** similar proportions of aldol products with the *erythro* stereoisomers in preference (entries 3 and 14).

Table 5 shows the results of aldol reactions of the D-*arabino* aldehyde **9**.

Here also, lithium cation promoted the formation of *erythro* aldols **20a** and **20c** from **R-** and **S-2**, respectively (**Table 5**, entries 1 and 7). Tin(II) and diethylaluminum(I) cations displayed the expected high stereoselectivities (entries 6, 12, and 4, 10). Triethylaluminum was in this case essentially "neutral" and gave similar proportions of aldol products as the lithium cation (entries 5 and 11). In contrast, zirconium(IV) cation gave in the reaction with **S-2** the $C_\beta C_\gamma$-*threo* product **20d** in a 2 : 1 predominance over the *erythro* aldol **20c** (entries 3 and 9).

TABLE 4
Reactions with methyl 2,3-O-isopropylidene-β-D-ribo-dialdo-1,4-furanoside (**8**)

1	Entry	MX	Yield %	**19a** (RRR)	**19b** (RSR)	**19c** (SRR)	**19d** (SSR)
R	1	BuLi	50	85	15	-	-
	2	$(iPrO)_3TiCl$	64	73	27	-	-
	3	$ZrCl_4$	63	79	21	-	-
	4	Et_2AlCl[a]	55	50	50	-	-
	5	Et_3Al	46	94	6	-	-
	6	$SnCl_2$[b]	14	95	5	-	-
	7	$CeCl_3$	56	84	16	-	-
	8	$NiCl_2$	59	84	16	-	-
	9	$LaCl_3$	52	87	13	-	-
	10	Cp_2TiCl_2	39	86	14	-	-
	11	$MgBr_2$	12	83	17	-	-
S	12	BuLi	50	-	-	70	30
	13	$(iPrO)_3TiCl$	68	-	-	83	17
	14	$ZrCl_4$	65	-	-	76	24
	15	Et_2AlCl[b]	75	-	-	97	3
	16	Et_3Al	25	-	-	71	29
	17	$SnCl_2$[a]	6.5	-	-	66	34
	18	$CeCl_3$	54	-	-	71	29
	19	$NiCl_2$	57	-	-	71	29
	20	$LaCl_3$	48	-	-	73	27
	21	Cp_2TiCl_2	41	-	-	76	24
	22	$MgBr_2$	12	-	-	73	27

[a]Mismatched pair. [b]Matched pair.

In **Table 6** the results of aldol reactions performed with the enantiomer of **9**, aldehyde **10**, are collected. The proportion of stereoisomeric products **21a-21d** (being enantiomers of **20a-20d**) match very closely the figures obtained with **9** what confirmed, to some extent, the figures recorded in **Table 5**.

TABLE 5
Reactions with 3-O-benzyl-1,2-O-isopropylidene-β-D-arabino-dialdo-1,4-furanose (**9**)

1	Entry	MX	Yield %	**20a** (RRR)	**20b** (RSR)	**20c** (SRR)	**20d** (SSR)
R	1	BuLi	67	79	21	-	-
	2	$(iPrO)_3TiCl$	67	75	25	-	-
	3	$ZrCl_4$	45	82	18	-	-
	4	Et_2AlCl[a]	45	55	45	-	-
	5	Et_3Al	61	79	21	-	-
	6	$SnCl_2$[b]	18	>99	<1	-	-
S	7	BuLi	71	-	-	84	16
	8	$(iPrO)_3TiCl$	71	-	-	80	20
	9	$ZrCl_4$	45	-	-	32	68
	10	Et_2AlCl[b]	67	-	-	97	3
	11	Et_3Al	64	-	-	84	16
	12	$SnCl_2$[a]	12	-	-	72	28

[a]Mismatched pair. [b]Matched pair.

TABLE 6
Reactions with 3-O-benzyl-1,2-O-isopropylidene-β-L-arabino-dialdo-1,4-furanose (**10**)

1	Entry	MX	Yield %	**21a** (SSS)	**21b** (SRS)	**21c** (RSS)	**21d** (RRS)
R	1	BuLi	65	78	22	-	-
	2	$(iPrO)_3TiCl$	47	76	24	-	-
	3	$ZrCl_4$	18	79	21	-	-
	4	Et_2AlCl[a]	46	57	43	-	-
	5	Et_3Al	34	86	14	-	-
	6	$SnCl_2$[b]	28	>99	<1	-	-
S	7	BuLi	65	-	-	78	22
	8	$(iPrO)_3TiCl$	53	-	-	79	21
	9	$ZrCl_4$	23	-	-	32	68
	10	Et_2AlCl[b]	64	-	-	97	3
	11	Et_3Al	26	-	-	87	13
	12	$SnCl_2$[a]	23	-	-	71	29

[a]Mismatched pair. [b]Matched pair.

The results of aldol reactions of the *xylo* aldehyde **11** are shown in **Table 7**. As previously, lithium and triisopropoxytitanium cations promoted the formation of *erythro* products **22a** and **22c** from both enantiomeric forms of acetyliron, respectively (**Table 7**, entries 1, 2 and 7, 8). Surprizing is the low stereoselectivity achieved in reaction with **S-2** having diethylaluminum(I) as the counterion (entry 10), and - in contrast - the very high "reversed" stereoselectivity obtained with triethylaluminum (entries 5 and 11). As in the case of aldehyde **9**, zirconium(IV) cation promoted here also the formation of the SSR (*threo*) stereoisomeric aldol in predominance (entry 9).

TABLE 7
Reactions with 3-O-benzyl-1,2-O-isopropylidene-α-D-xylo-dialdo-1,4-furanose (**11**)

1	Entry	MX	Yield %	**22a** (RRR)	**22b** (RSR)	**22c** (SRR)	**22d** (SSR)
R	1	BuLi	47	79	21	-	-
	2	$(iPrO)_3TiCl$	33	73	27	-	-
	3	$ZrCl_4$	41	65	35	-	-
	4	Et_2AlCl[a]	35	33	67	-	-
	5	Et_3Al	48	20	80	-	-
	6	$SnCl_2$[b]	13	97	3	-	-
S	7	BuLi	53	-	-	66	34
	8	$(iPrO)_3TiCl$	41	-	-	71	29
	9	$ZrCl_4$	49	-	-	35	65
	10	Et_2AlCl[b]	52	-	-	72	28
	11	Et_3Al	62	-	-	7	93
	12	$SnCl_2$[a]	7	-	-	47	53

[a]Mismatched pair. [b]Matched pair.

Aldol reactions of the last pentose aldehyde **12**, of the *lyxo* configuration, are presented in **Table 8**.

The triisopropoxytitanium cation is in this case a stronger "*erythro*-promoter" than the lithium cation, what led to **23a** and **23c** as major products from **R-** and **S-2**, respectively (entries 1, 2 and 7, 8). Tin(II) and diethylaluminum cations displayed here their "normal" stereoselectivities (entries 4, 6 and 10, 12). And again, zirconium(IV) cation showed in reaction with **S-2** a distinct preference for the *threo* product **23d** (entry 9). Triethylaluminum promoted the formation of *erythro* aldols (entries 5 and 11).

*1,2:3,4-Di-O-isopropylidene-α-D-galacto-dialdo-1,5-pyranose (**13**)*

The results of aldol reactions of **13** with **R-** and **S-2** are recorded in **Table 9**. The stereochemical results are essentially similar to those achieved with **12**. Remarkably different is the behaviour of **R-** and **S-2** with triethylaluminum as the counterion: in both cases the *threo* products, **24b** and **24d**, were formed in predominance. Tin(II) cation furnished with **R-2** exclusively aldol of the RRR configuration **24a** (entry 5);

the reaction with **S-2** was slow and yielded the aldol products in trace amount only (entry 10).

TABLE 8
Reactions with methyl 2,3-O-isopropylidene-α-D-lyxo-dialdo-1,4-furanoside (**12**)

1	Entry	MX	Yield %	**23a** (RRR)	**23b** (RSR)	**23c** (SRR)	**23d** (SSR)
R	1	BuLi	60	67	33	-	-
	2	$(iPrO)_3TiCl$	75	77	23	-	-
	3	$ZrCl_4$	50	89	11	-	-
	4	Et_2AlCl[a]	13	61	39	-	-
	5	Et_3Al	44	63	37	-	-
	6	$SnCl_2$[b]	25	98	2	-	-
S	7	BuLi	60	-	-	68	32
	8	$(iPrO)_3TiCl$	70	-	-	89	11
	9	$ZrCl_4$	35	-	-	28	72
	10	Et_2AlCl[b]	63	-	-	93	7
	11	Et_3Al	54	-	-	79	21
	12	$SnCl_2$[a]	20	-	-	70	30

[a]Mismatched pair. [b]Matched pair.

TABLE 9
Reactions with 1,2;3,4-di-O-isopropylidene-α-D-galacto-dialdo-1,5-pyranose (**13**)

1	Entry	MX	Yield %	**24a** (RRR)	**24b** (RSR)	**24c** (SRR)	**24d** (SSR)
R	1	BuLi	38	79	21	-	-
	2	$(iPrO)_3TiCl$	45	64	36	-	-
	3	Et_2AlCl[a]	58	42	58	-	-
	4	Et_3Al	66	21	79	-	-
	5	$SnCl_2$[b]	19	100	0	-	-
S	6	BuLi	42	-	-	75	25
	7	$(iPrO)_3TiCl$	55	-	-	89	11
	8	Et_2AlCl[b]	62	-	-	93	7
	9	Et_3Al	44	-	-	32	68
	10	$SnCl_2$[a]	1	-	-	33	67

[a]Mismatched pair. [b]Matched pair.

DECOMPLEXATION OF ALDOLS. SYNTHESIS OF DEOXYSUGARS

For decomplexation of all aldols N-bromosuccinimide (NBS) in dichloromethane - methanol solution proved to be most effective. The reactions were clean and the work-up was uncomplicated to yield the resulting methyl esters in good overall yield. The use of bromine in methanol, a reagent often employed by Davies[14] for a similar purpose, led to low yield of esters contaminated with side products making the purification difficult.

Methyl 2-deoxypentonates and 2-deoxyhexonates

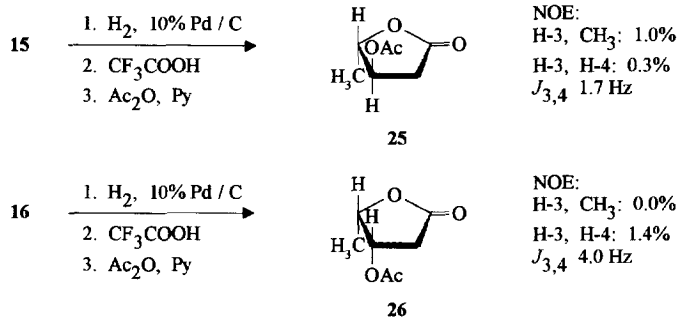
Decomplexation of aldols obtained from **2** and aldehydes **5** - **7** and isolation of the expanded acyl ligand in form of methyl esters presents a new route to 2-deoxyaldonic acids derivatives.

Aldols **14a-d** obtained from **5** and the anion formed from racemic acetyliron are only partially separable (two peaks, HPLC). Therefore enantiomeric complexes **1** had to be employed. From reactions of **R-1** and **S-1** with **5** pairs of diastereoisomeric aldols were obtained and separated by HPLC. **R-1** furnished aldols **14a** and **14b**, and **S-1** yielded **14c** and **14d**, all in pure form. Decomplexation of **14a** and **14c** led to the same methyl 4-O-benzyl-2,5-dideoxy-L-pentonate (**15**) in 71%. Similarly, from **14b** and **14d** the other stereoisomeric methyl pentonate **16** was obtained in the same yield (**Scheme 2**).

Although both esters have been mentioned in literature[15,16], the lack of specific rotation data on one hand, and similarity of their ^{1}H NMR spectra on the other, made the configurational assignment impossible. Therefore both compounds were debenzylated, hydrolyzed and subsequently acetylated to furnish the acetylated γ-lactones **25** and **26**, respectively, in 70% each (**Scheme 3**).

The NOE experiments with both lactones have clearly shown that **25** (and **15**) had the *erythro*, and **26** (and **16**) the *threo* configuration. These conclusions were supported by the $J_{3,4}$ coupling constants in the ^{1}H NMR spectra of both γ-lactones: small value for the 3,4-*trans* arrangement in **13** and larger value for the *cis* arrangement[17,18].

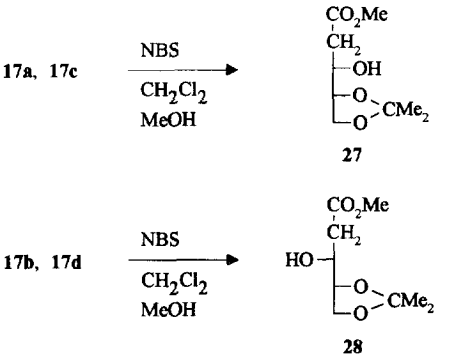
SCHEME 3



A similar experimental route was employed also in case of aldols **17a** - **17d** obtained from **R-1** and **S-1** and aldehyde **6**. Direct decomplexation of each two-component mixture led to two stereoisomeric methyl 2-deoxy-D-pentonates which were difficult to separate. Therefore it was more convenient to separate first the mixture of aldols into pairs **17a**, **17c** and **17b**, **17d** and to perform the decomplexation leading to pure

stereoisomeric methyl 2-deoxy-4,5-O-isopropylidene-D-pentonates **27** (73% yield) and **28** (90%), respectively (**Scheme 4**).

SCHEME 4



The *erythro* and *threo* configurations could be easily assigned to **27** and **28** because both compounds are described in literature and their $[\alpha]_D$ values are known[19] (cf. **Experimental**).

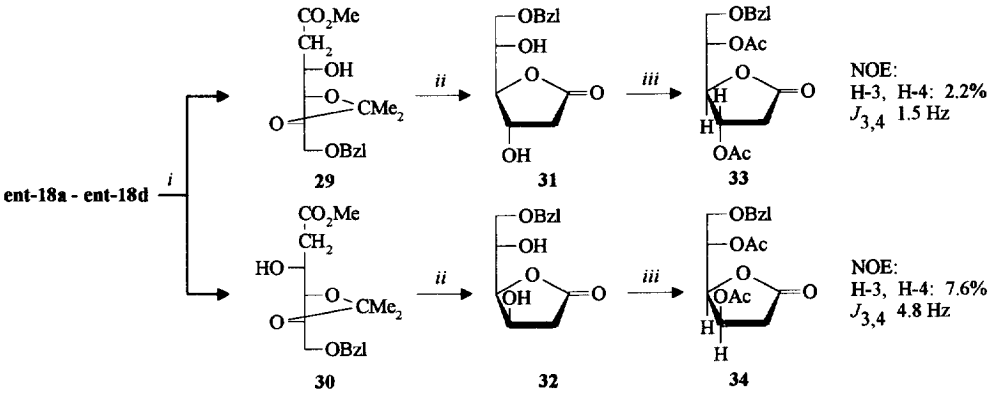
Configurational deduction of aldols **18a-d** was made by performing the reaction of **R-1** and **S-1** with the enantiomer of **7**, aldehyde **ent-7** to form pairs of diastereoisomeric aldols **ent-18a**, **ent-18b** and **ent-18c**, **ent-18d**, respectively. Here also decomplexation of **ent-18a** and **ent-18c** furnished one methyl 2-deoxy-L-hexonate (**29**) and decomplexation of **ent-18b** and **ent-18d** led to the other stereoisomer **30**. In the preparative scale it was convenient to perform the reaction of **ent-7** with the anion generated from racemic acetyliron. Decomplexation of the mixture **ent-18a** - **ent-18d** gave **29** and **30** which could be readily separated by simple column chromatography in 36 and 20% yield. Both compounds have not been described in literature yet. Therefore the samples were hydrolyzed with trifluoroacetic acid to yield lactones **31** and **32**. The lactones were acetylated to 3,5-di-O-acetyl derivatives **33** and **34**. Here again the NOE experiments helped to assign L-*lyxo* configuration to **33** (and, consequently, to **29** and **31**), and L-*xylo* configuration to **34** (and also to **30** and **32**) (**Scheme 5**).

A similar sequence of reactions was performed also with **7**. As the result methyl 6-O-benzyl-2-deoxy-4,5-O-isopropylidene-D-*lyxo*- and -D-*xylo*-hexonates (**35** and **36**) have been obtained in 24 and 17% isolated yields. Hydrolysis of both products with trifluoroacetic acid, as described above, led to the γ-lactones **37** and **38** in good yields (**Scheme 6**).

6-Deoxyheptoses

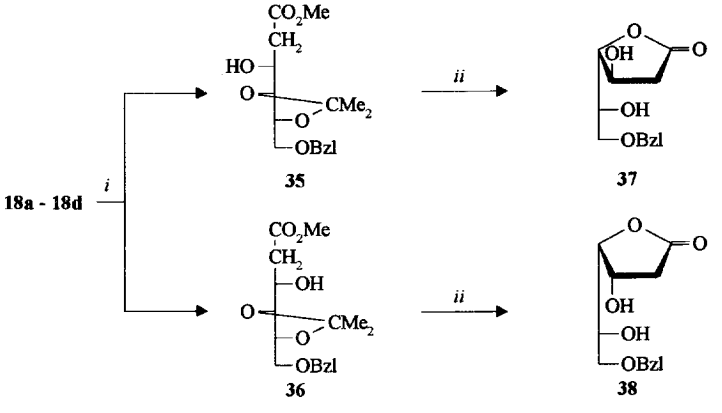
All aldol reactions with aldehydes **8** - **13** were performed separately with enantiomeric complexes, **R-1** and **S-1**. From each reaction pairs of stereoisomeric products **19a,b** - **24a,b** and **19c,d** - **24c,d** were obtained, separated, and decomplexed with N-bromosuccinimide and methanol. This permitted to identify stereoisomeric methyl esters differing in configuration at the β-carbon atom.

SCHEME 5



i. NBS, MeOH; *ii*. CF_3COOH; *iii*. Ac_2O, Py

SCHEME 6



i. NBS, MeOH; *ii*. CF_3COOH

The proportion of aldol products formed in reactions of **2** and aldehydes **8** - **13** in the presence of various counterions could be determined with racemic acetyliron; four aldols formed could be readily separated by means of HPLC. **Figure 1** demonstrates the separation of aldols obtained from the D-*arabino* aldehyde **9** and **RS-2**. The only exception was the D-*lyxo* aldehyde **12**; in this case for all reactions optically complexes had to be used because of insufficient separation of aldols.

For the preparative scale synthesis of methyl esters all aldol reactions were performed with racemic acetyliron. Mixtures of aldols were decomplexed without prior separation and the mixtures of methyl 6-deoxyhepturonates were separated without difficulties by simple column chromatography.

From the D-*ribo* aldehyde **8** two stereoisomeric esters **39** and **40** were obtained in 22 and 67% yield, respectively. Both products were reduced with diisobutylaluminum hydride (DIBAH) to diols **41** and **42**. Hydrolysis of the methyl glycoside and of the isopropylidene grouping followed by acetylation led to peracetylated 6-deoxyheptoses **43** and **44**. From the ^1H NMR spectrum of **44** it was evident that a single β-

anomer with $J_{1,2}$ 8.6 Hz was obtained. The coupling constant $J_{4,5}$ 10.1 Hz indicated the axial-axial orientation of H-4 and H-5. This confirmed the D-*allo* configuration of **44**, as well as of **40** and **42**. The ^{1}H NMR spectrum of **43** indicated the presence of α and β anomers in 1.5 : 1 proportion. Coupling constant $J_{4,5}$ 1.3 Hz found in the spectrum of the β anomer confirmed the alternative, L-*talo* configuration of **43**, as well as of **39** and **41**.

FIGURE 1

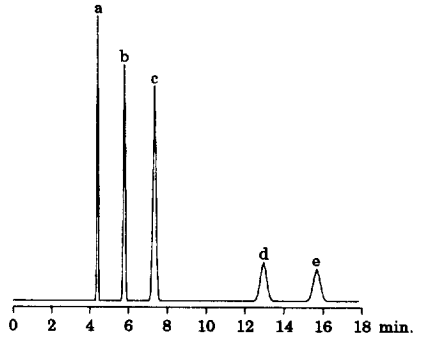


FIGURE 1. HPLC - chromatogram of aldols obtained from **RS-2** and 3-O-benzyl-1,2-O-isopropylidene-β-D-arabino-dialdo-1,4-furanose (**9**).
a. Acetyliron; b. RRR - aldol; c. SRR; d. SSR; e. RSR.
First letter denotes configuration at the iron atom, second - at the β-carbon atom, and the third - at the γ-carbon atom.

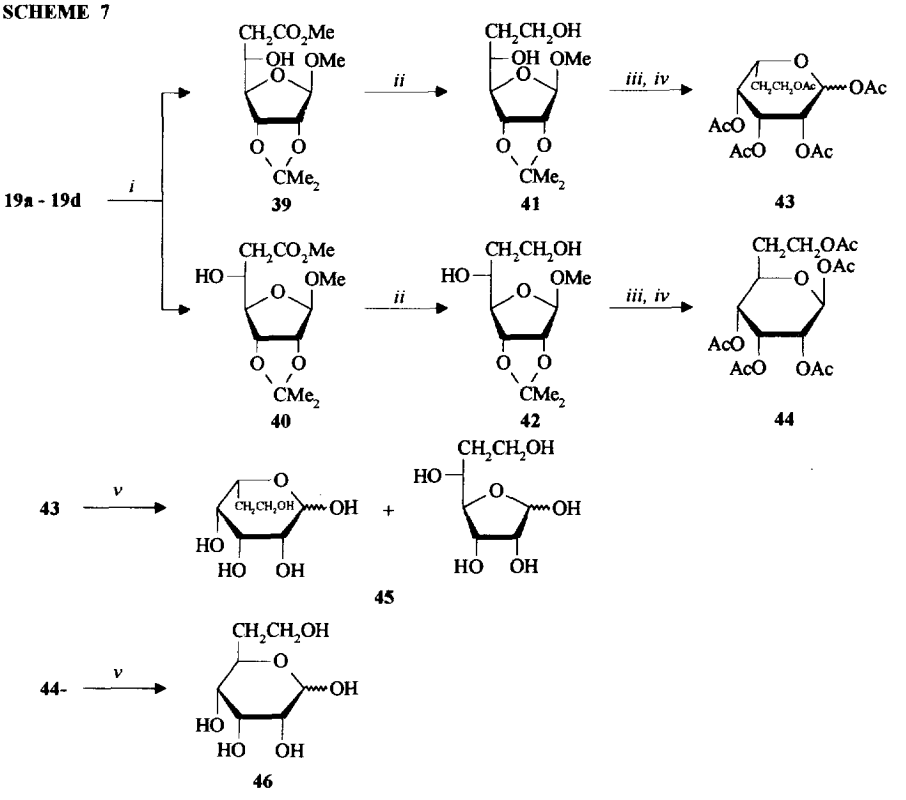
Deacetylation of **43** and **44** with IRA-400 (OH^- form) resin in methanol - water solution afforded free 6-deoxy-L-*talo*- and -D-*allo*-heptoses (**45** and **46**). Sugar **45** occurs in methanol solution - according to its ^{13}C NMR spectrum - as a mixture of four components (both anomeric furanose and pyranose forms). ^{13}C NMR spectrum of **46** points at a single (probably β-pyranose) form (**Scheme 7**).

Decomplexation of aldols obtained from the D-*arabino* aldehyde **9** and **RS-2** (**Fig. 1**) led to two stereoisomeric methyl esters **47** and **48** in 37 and 12% yield. Both esters were unstable; they decomposed gradually within a few days even when kept at the fridge temperatures (2 - 5°C). DIBAH reduction furnished diols **49** and **50**, respectively (**Scheme 8**). Unexpectedly, attempts at debenzylation of **49** and **50** failed; instead of free triols, mixtures of several unidentified products were formed. Both products were therefore converted to the stable 5,7-di-O-methyl derivatives **51** and **52** (**Scheme 8**).

The same sequence of reactions was also realized with the enantiomeric L-*arabino* aldehyde **10** and the analogous decomplexation products were obtained: methyl esters **ent-47** and **ent-48**, diols **ent-49** and **ent-50**, and 5,7-di-O-methyl derivatives **ent-51** and **ent-52**.

In order to assign configuration to these products it was necessary to synthesize one of the dimethylated products on an unambiguous way. Starting from the known 3-O-benzyl-1,2-O-isopropylidene-6-O-trityl-α-D-galactofuranose (**53**)[20] *via* aldehyde **54**, the 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-5,7-di-O-methyl-α-D-galactoheptofuranose was obtained (**55**)[21] and proved to be identical with **ent-52**. This confirmed unequivocally configurations D-*altro* and L-*galacto* of **51** and **52**, L-*altro* and D-*galacto* of **ent-51** and **ent-52**, and of the corresponding parent compounds (**Scheme 8**).

SCHEME 7

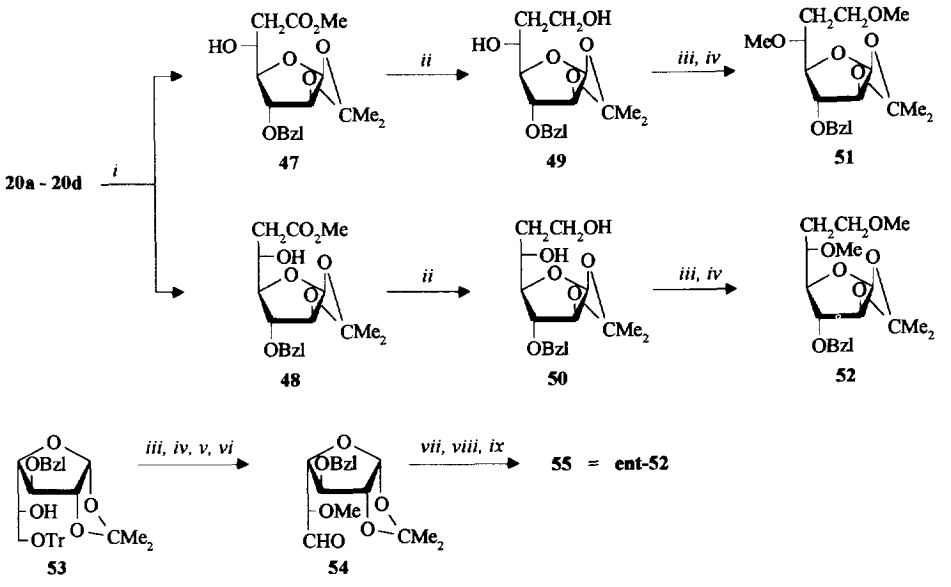


i. NBS, MeOH; *ii*. DIBAH; *iii*. 70% AcOH, 80 - 90°C; *iv*. Ac_2O, Py; *v*. IRA-400.

Decomplexation of the aldols obtained from the D-*xylo* aldehyde **11** furnished methyl esters **56** and **57** in 46 and 18% yield (**Scheme 9**). DIBAH reduction yielded diols **58** and **59**. Debenzylation of both products occurred smoothly and yielded the corresponding triols **60** and **61** in a quantitative yield. De-isopropylidenation with hot 70% acetic acid and acetylation of the products formed led in case of **60** to two anomeric peracetylated 6-deoxy-D-*gluco*-heptopyranoses (**62**). Deacetylation of **62** afforded free 6-deoxy-αβ-D-*gluco*-heptose (**63**). Analogous steps with **61** led to a mixture of peracetylated 6-deoxy-L-*ido*-heptoses (**64**) in the pyranose and furanose forms (^{1}H NMR). Deacetylation yielded the free sugar (**65**) also as a mixture of pyranose and furanose forms (^{13}C NMR) (**Scheme 9**).

Decomplexation of aldols obtained from the D-*lyxo* aldehyde **12** led to stereoisomeric methyl esters **66** and **67**[22]. Further steps, analogous to those performed for the products obtained from the *ribo* aldehyde **8** (**Scheme 7**) are shown in **Scheme 10**. D-*Manno* configuration of **68** was unambiguously determined by an X-ray structural analysis[22]. The ^{13}C NMR spectrum of **72** was identical with that of 6-deoxy-D-*manno*-heptose published[23].

SCHEME 8



i. NBS, MeOH; *ii*. DIBAH; *iii*. NaH; *iv*. MeI; *v*. 85% HCOOH; *vi*. Swern ox.; *vii*. CH_3OCH_2MgCl; *viii*. NaH, MeI, CS_2; *ix*. n-Bu_3SnH.

The last series of transformations was performed with the aldols obtained from the D-*galacto* aldehyde **13**. Decomplexation led to two stereoisomeric methyl esters **74** and **75** (**Scheme 11**). Their configuration was assigned on the basis on ^1H NMR data (*vide infra*).

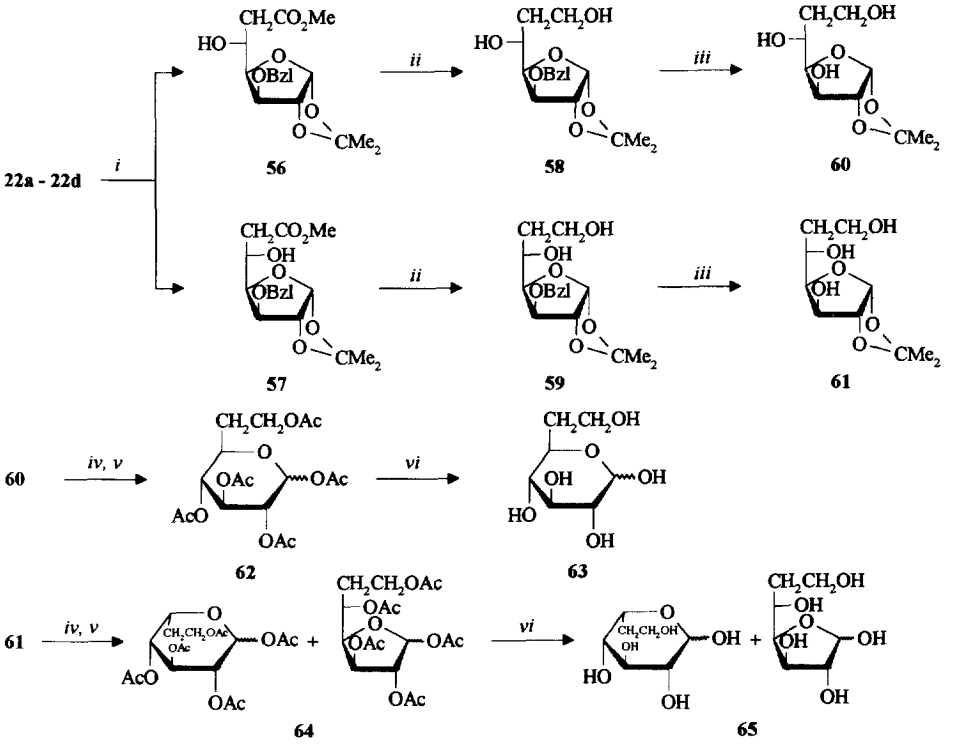
Configuration of stereoisomers by the ^1H NMR data

For the assignment of relative configuration (at the Fe atom and β-carbon atom in the acyl ligand) to the aldols obtained from acetyliron and aldehydes Liebeskind's[12,24] observation can be used. According to this observation, in the ^1H NMR spectra (taken in C_6D_6) methylene protons show the absorption of the RS/SR stereoisomer (obtained from benzaldehyde) resonating *between* the signals of the methylene hydrogens of the RR/SS isomer.

The application of this regularity to the aldols described in this work was uncertain. In the spectra of several aldols the signals of methylene protons were not resolved or were outside of the expected regions. Only in a few cases the methylene proton signals fitted to the rule.

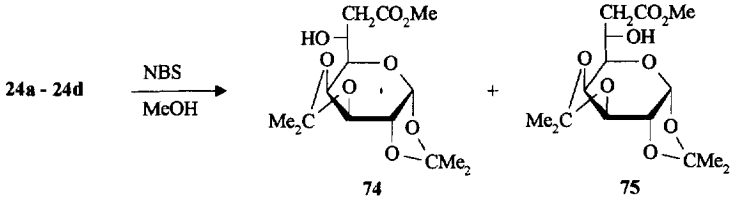
We have found another practical regularity in the ^1H NMR spectra of the decomplexation products, i. e. methyl esters of deoxyuronic and deoxyaldonic acids. In the spectra of two stereoisomeric esters of β,γ-dioxy acids the coupling constant $J_{\alpha,\beta}$ of the lower-field methylene proton (H_α) is distinctly smaller than of that ($J_{\alpha',\beta}$) of the higher-field proton $H_{\alpha'}$ in the *erythro* stereoisomer. In the spectrum of the *threo* stereoisomer - if both methylene proton signals are resolved - $J_{\alpha,\beta}$ becomes larger and $J_{\alpha',\beta}$ becomes smaller in comparison with the *erythro* stereoisomer.

SCHEME 9



i. NBS, MeOH; *ii*. DIBAH; *iii*. 10% Pd / C; *iv*. 70% AcOH, 80 - 90°C; *v*. Ac_2O, Py; *vi*. IRA-400.

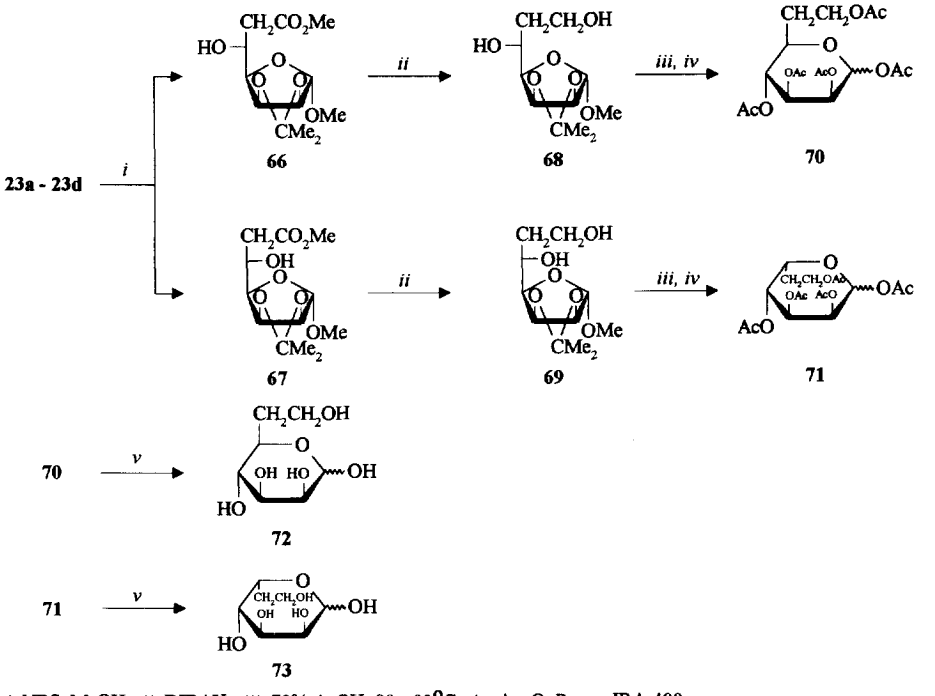
SCHEME 11



This regularity can be best seen from the **Table 10**. It served for the configurational assignment of the esters **74** and **75**.

It should be mentioned here that configuration of methyl deoxyuronates as well as diols obtained from them was studied by the circular dichroism methods[25].

SCHEME 10



i. NBS, MeOH; *ii*. DIBAH; *iii*. 70% AcOH, 80 - 90°C; *iv*. Ac_2O, Py; *v*. IRA-400.

DISCUSSION

The stereoselectivity of addition of nucleophiles to α-chiral α-alkoxyaldehydes is considered to be dependent on several factors including reactive conformation of the aldehyde[15] ("Felkin-Anh model"[26]), steric effects and σ^*-orbital energies[27], and chelation in the transition state[28]. An important theoretical study, permitting a deeper insight into these factors, was recently presented by Frenking, Köhler and Reetz.[29,30] Acording to these authors, the stereochemistry of the energetically lowest lying transition state (with inclusion of the participating cation) is determined by a combination of Coulombic interactions, electronic, steric as well as conformational factors.

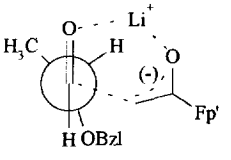
In starting the discussion of our results it is tempting to invoke the Frenking-Reetz consideration as their modelling was performed on O-methyl-L-lactaldehyde.[29,30] For the addition of lithium hydride to this aldehyde thirteen low-energy transition states have been calculated, eight of them leading to *"threo"* and five to *"erythro"* products. The lowest energy transition states must be under chelation control.[30]

The results of addition of **R-** and **S-2** to O-benzyl-L-lactaldehyde (**5**) clearly show (**Table 1**) that the reactions with Li^+, $(i\text{-}PrO)_3Ti^+$, Et_2Al^+, and Et_3Al as counterions - with the exception of tin(II) cation - are either non-stereoselective (with **R-2**) or exhibit moderate $C_\beta C_\gamma$-*erythro* selectivity (with **S-2**). We assume therefore that these results can be interpreted in terms of Frenking-Reetz non-chelated models **78** and **79** (corresponding to models **d** and **e** in Ref. 30) which anticipate a slight predominance of the *erythro* product.

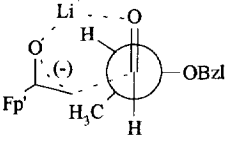
TABLE 10
Absorption of the methylene protons in the ^1H NMR spectra (in $CDCl_3$) and their vicinal coupling constants with proton at C_β-carbon atom.

Ester	δ (ppm)	J_{vic}	Configuration at $C_\beta C_\gamma$	Ester	δ (ppm)	J_{vic}	Configuration at $C_\beta C_\gamma$
39	2.62 2.54	3.9 8.6	*erythro*	**76****	2.78 2.64	3.1 9.3	*erythro*
40	2.56*	-	*threo*	**77****	2.84 2.64	8.4 4.5	*threo*
47,ent-47	2.82 2.50	3.0 8.9	*erythro*	**15**	2.62 2.51	4.1 2.51	*erythro*
48,ent-48	2.55 2.47	8.6 4.1	*threo*	**16**	2.53*	-	*threo*
56	2.80 2.53	3.0 9.1	*erythro*	**27**	2.73 2.48	2.8 8.4	*erythro*
57	2.55 2.43	8.4 4.3	*threo*	**28**	2.57 2.49	7.5 4.5	*threo*
66	2.82 2.60	3.2 9.0	*erythro*	**29**	2.76 2.50	3.1 9.0	*erythro*
67	2.71 2.66	4.5 8.1	*threo*	**30**	2.58*	-	*threo*
74	2.86 2.52	3.1 8.4	*erythro*	**35**	2.76 2.50	3.1 9.0	*erythro*
75	2.73 2.62	6.2 6.7	*threo*	**36**	2.58*	-	*threo*

* Methylene proton signals are not resolved.
** Methyl 6-deoxy-1,2-O-isopropylidene-α-D-*gluco*-heptofuranuronate (**76**) and methyl 6-deoxy-1,2-O-isopropylidene-β-L-*ido*-heptofuranuronate (**77**) were prepared by debenzylation of **56** and **57**, respectively (see **Experimental**).



78 (*erythro*)



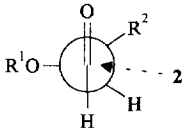
79 (*threo*)

However, a further extension of the Frenking-Reetz models appears to be difficult as the transition states with another α-alkoxyaldehydes and another counterions have not been calculated yet. In further discussion the following observations appear to be most important:

1. There is a general tendency (with a few exceptions only) for the dominant formation of the $C_\beta C_\gamma$-*erythro* aldols.

2. In the reactions between acetyliron and aldehydes dialkylaluminum cations[11,12] promote the formation of $R_{Fe}R_\beta$ ($S_{Fe}S_\beta$)### aldols as the major products. Our results point at a similar property of the (i-PrO)$_3$Ti$^+$ cation (**Tables 1 - 9**).

3. In the same reactions, tin(II) cation favors the formation of $R_{Fe}S_\beta$ ($S_{Fe}R_\beta$)### aldols. According to our data (**Tables 1 - 9**) a similar preference - although somewhat weaker - is exhibited also by the zirconium(IV) cation.



80

Preferred formation of the *erythro* products points at the Felkin-Anh type, non-chelated model **80** as the reactive conformation of the sugar aldehydes **3** for the reactions summarized in **Tables 1 - 9**.

The question arises now of matched and mismatched pairs of reagents, i.e. of dominant and non-dominant aldols in reaction of **R-** and **S-2** with aldehydes **5 - 13** in the presence of suitable counterions. On the basis of the above observations, matched and mismatched pairs and configuration of the preferred aldols for diethylaluminum(I) and tin(II) as counterions are indicated in **Tables 1 - 9**. It is remarkable that for pentose and hexose-derived aldehydes (**8 - 13**) the matched pairs exhibited stereoselectivities equal or better than 13:1 whereas for lower aldehydes the corresponding figures are far less impressive [except the tin(II)-promoted reactions].

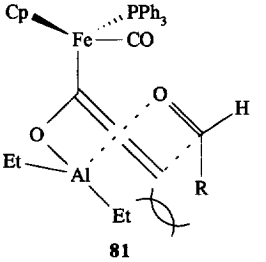
The origin of diastereoselectivity induced by R_2Al^+ cations was discussed earlier by Davies[14] and Liebeskind[24] in terms of a six-membered, boat-like transition state. For *re*- and *si*-attacks of **R-2** and **S-2** on the carbonyl group four transition states **81 - 84** (rather of the skew-boat type) can be depicted showing that *re*-attack on **S-2** (or *si*-attack on **R-2**) will avoid unfavorable steric interactions. Therefore, for the majority of aldehydes investigated (of the D configuration, pentose - derived aldehydes), transition state **83** will represent the matched pair. Similar transition states can be proposed also for the (i-PrO)$_3$Ti$^+$-mediated reactions as well as even for reactions with the lithium cation.

Distinctly different must be the transition state of the reactions occurring in the presence of tin(II) cation. Liebeskind[24] proposed a four-membered transition state with the tin atom forming a covalent bond with the C-atom. For the reactions of R-**2** with sugar aldehydes of the D configuration two transition states, **85** and **86**, can be proposed. *re*-Attack (transition state **85**) must be certainly favored; in **86** a severe interaction would occur between R-part of the aldehyde and cyclopentadienyl ligand of the complex. We assume that analogous transition states may be considered also for the zirconium(IV) - mediated reactions.

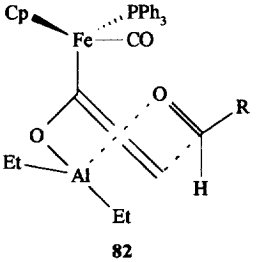
A special effect of triethylaluminum and of zirconium(IV) chloride must be additionally mentioned. In reactions of **1** with aldehydes **11** and **13** the former compound, and with **9 - 12** the latter, exhibited a pronounced *threo* directing effect. We assume that chelation must be responsible for the *si*-attack, leading to *threo* products. The question arises, why only in these cases chelation becomes apprehensible while - according to Frenking and Reetz[30] - this effect involving carbonyl and α-oxygen atoms should lower very

With RCHO, where R is an alkyl group. When R contains an α-oxygen atom, the configurational designation will be changed to $R_{Fe}S_\beta$ ($S_{Fe}R_\beta$) or $R_{Fe}R_\beta$ ($S_{Fe}S_\beta$).

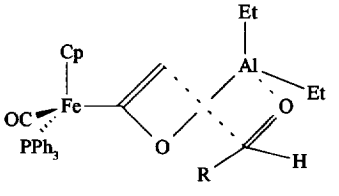
significantly the energy of the transition states. The answer is, we suppose, that cations are involved, in the first place, in bonding to oxygen atom of the enolate **2** and to aldehydic oxygen atom neglecting the intramolecular chelation within the aldehyde. However, this statement may be not entirely correct. If we compare the stereochemical results of Et_2Al-mediated reaction of **2** with propionaldehyde [>100 : 1 in favor of the $R_{Fe}R_{\beta}$ ($S_{Fe}S_{\beta}$) stereoisomer[14]] and with 2-benzyloxypropionaldehyde (O-benzyl-L-lactaldehyde, **5**) (only 2.3 : 1 in favor of the analogous stereoisomer **14c**) then some participation of an intramolecularly chelated transition state leading eventually to the alternative stereoisomer (**14d**) appears to be probable.



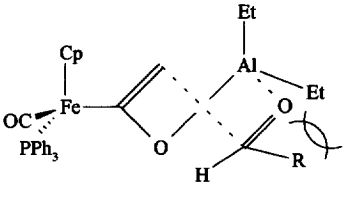
81
"erythro" attack (R_{Fe})



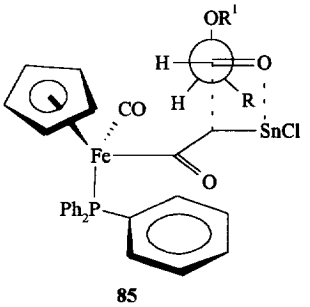
82
"threo" attack (R_{Fe})



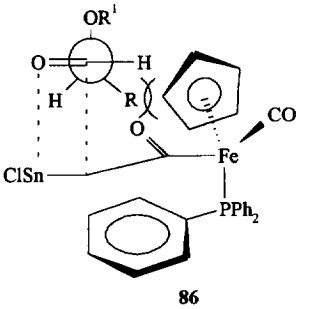
83
"erythro" attack (S_{Fe})



84
"threo" attack (S_{Fe})



85
"erythro" attack



86
"threo" attack

Decomplexation of aldols leads to new monosaccharide derivatives elongated with the CH_2CO_2Me or - after reduction of the ester grouping - with the CH_2CH_2OH moiety. If the elongation occurs at C-1 of the sugar substrate, 2-deoxyaldonic acid esters are obtained. If at the terminal carbon atom - 6-deoxyheptoses or 7-deoxyoctose are the products.

Although the routes to 2-deoxy-aldonates described here require the use of acetyliron complex **1**, a reagent not common presently in organic chemistry laboratories, they permit to obtain the carbohydrate derivatives in pure diastereoisomeric forms. The synthesis of eight compounds of this type was reported here. There can be little doubt that the synthesis of other stereoisomers of 2-deoxy-pentonic and 2-deoxy-hexonic acids can be performed equally well. Decomplexation and isolation of the elaborated acyl ligands in form of uronic acid esters opened the synthetic access to the family of 6-deoxy-D- and L-heptoses which are - in many cases - difficult to obtain on another ways. Several sugars of this type can be obtained as practically single compounds if proper counterions are used for the aldol reactions.

6-Deoxyheptoses occur as components in bacterial polysaccharides. D-*Manno* stereoisomer was found in lipopolysaccharides isolated from *Yersinia (Pasteurella) pseudotuberculosis* type IIA[31] and *Pseudomonas pseudomallei*[23], D-*altro* stereoisomer was found in LPS of *Eubacterium saburreum*[32] and *Camphylobacter jejuni*[33], and D-*talo* - in *Camphylobacter coli*[34]. 6-Deoxyheptoses of the D-*manno*[35,36,37], D-*galacto*[21,38], D-*altro*[36,39] and D-*talo*[36] configuration have been synthesized.

It is evident that an analogous approach can be used for the synthesis of 7-deoxyoctoses by application of another hexose-derived aldehydes.

CONCLUSIONS

The results of aldol reactions of sugar aldehydes with both enantiomeric forms of acetyliron permit to draw some conclusions regarding the stereochemical course of the reactions (for convenience, the conclusions below are actual for aldehydes of D configuration):

1. The configuration of the α-carbon atom of the aldehyde directs the attack of the enolate **2** (of **R**- or **S**-configuration) - in accord with the Felkin-Anh model - on the *re* side of the formyl group what leads to the $C_\beta C_\gamma$-*erythro* aldols. Undoubtedly, this is one of the major factors determining the stereochemical course of the reactions.

2. With diethylaluminum(I) as the counterion, **S-2** enolate forms a matched pair with the result that SRR aldol is formed in >90% stereoselectivity. In the mismatched pair, the stereochemical influences of acetyliron and of the aldehyde oppose each other resulting in a seriously decreased stereoselectivity. Nevertheless, it seems that Felkin-Anh directing effect appears to more strongly influence the stereochemical outcome of the reactions.

3. With tin(II) cation the matched pair is realized with the **R-2** enolate producing the RRR aldol with very high stereoselectivity as the main product in all investigated cases. The drawback of these reactions is their low yield, rarely exceeding 20%.

The reactions described here present a contribution towards understanding the preparative and stereochemical value of the acetyliron complex. On the other hand, the products obtained possess a value in carbohydrate synthesis. Wider exploitation of this route in carbohydrate synthesis depends - in our opinion - on commercial availability of non-expensive organoiron reagents and (at least to some extent) on overcoming the prejudice against more complex organometallic reagents.

EXPERIMENTAL

General methods. All manipulations on organometallic complexes were performed under argon. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a stream of argon prior to use. Other solvents were purified and dried accordingly to literature methods. Butyllithium was used as a 1.6 M solution in hexane, triisopropoxytitanium chloride as a 1.0 M solution in hexane, diethylaluminum chloride as a 1.8 M solution in toluene, triethylaluminium as 1.0 M solution in hexane, tin (II) chloride as freshly prepared solution in THF (*ca.* 1 M), and other salts as solids. TLC was performed on Silica Gel HF-254 and column chromatography on Silica Gel 230 - 400 mesh (Merck) using mixtures of hexane - ethyl acetate (**A**, 8 : 3; **B**, 4 : 1; **C**, 7 : 1; **D**, 5 : 1; **E**, 7 : 3; **F**, 2 : 1; **G**, 1 : 1) and hexane - acetone (**H**, 2 : 1; **I**, 3 : 1; **J**, 4 : 1; **K**, 6 : 1) as eluents. The ratio of iron complexes obtained was determined by HPLC (Shimadzu C-R4A chromatograph equipped with Nucleosil 100-7 Macherey - Nagel analytical column) using mixtures **A**, **B**, and **C** as eluents. Preparative separations of iron complexes were executed with HPLC using Macherey - Nagel preparative column (Nucleosil 100-7). ^1H NMR spectra were recorded with a Bruker AM-500 (500 MHz) spectrometer in deuterobenzene (C_6D_6), deuterochloroform ($CDCl_3$), and deuteromethanol (CD_3OD) with Me_4Si as internal standard. High resolution mass spectra (HR-MS) were measured with AMD-604 mass spectrometer. IR spectra were recorded on a Perkin -Elmer 1640 FT-IR spectrophotometer.
Compounds **1**[40], **5**[41], **6** and **11**[42], **7**[43], **12**[22], and **13**[44] were prepared according to literature methods. **R-1** and **S-1** were of commercial origin (Fluka).

3-O-Benzyl-1,2-O-isopropylidene-5-O-(tert-butyldiphenylsilyl)-β-D-arabinofuranose

To a solution of 1,2-O-isopropylidene-5-O-(tert-butyldiphenylsilyl)-β-D-arabinofuranose[45] (1.39 g, 3.24 mM) in DMF (10 mL) cooled to -20°C sodium hydride (85 mg, 3.57 mM) was added and the mixture was stirred for 30 min. Benzyl chloride (450 mg, 3.55 mM) was added at -20°C. After 15 min. the mixture was allowed to attain room temperature and stirring was continued for 2.5 h. Water (20 mL) was slowly added and the product was extracted with ether (5 × 20 mL). Combined organic extracts were washed with water (20 mL), dried over Na_2SO_4, and concentrated to dryness. Column chromatography of the residue (eluent **D**) gave 3-O-benzyl-1,2-O-isopropylidene-5-O-(tert-butyldiphenylsilyl)-β-D-arabinofuranose (1.08 g, 64%) as a colourless oil, $[\alpha]_D^{20}$ +1.0° (*c* 1.0, chloroform); ^1H NMR ($CDCl_3$): δ 5.88 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1), 4.67 (d, 1H, H-2), 4.62 (s, 2H, CH_2Ph), 4.22 (m, 2H, H-3,4), 3.80 (m, 2H, H-5,5'), 1.34 and 1.30 (2s, 6H, CMe_2), 1.04 (s, 9H, ^tBu). *Anal.*: $C_{31}H_{38}O_5Si$ (518.72). Calc.: C 71.78; H 7.38. Found: C 71.71; H 7.26.

3-O-Benzyl-1,2-O-isopropylidene-5-O-(tert-butyldiphenylsilyl)-β-L-arabinofuranose

Starting from 1,2-O-isopropylidene-5-O-(tert-butyldiphenylsilyl)-β-L-arabinofuranose[45], according to procedure described above, 3-O-benzyl-1,2-O-isopropylidene-5-O-(tert-butyldiphenylsilyl)-β-L-arabinofuranose (1.29 g, 77%) was obtained; $[\alpha]_D^{20}$ -1.5° (*c* 1.3, chloroform). *Anal.*: $C_{31}H_{38}O_5Si$ (518.72). Calc.: C 71.78; H 7.38. Found: C 71.60; H 7.25.

3-O-Benzyl-1,2-O-isopropylidene-β-D-arabinofuranose

To a solution of 3-O-benzyl-1,2-O-isopropylidene-5-O-(tert-butyldiphenylsilyl)-β-D-arabinofuranose (830 mg, 1.60 mM) in THF (10 mL), tetrabutylammonium fluoride (760 mg, 2.40 mM) was added, and the mixture was stirred at room temperature for 1.5 h. The solvents were evaporated. Column chromatography (eluent **F**) of the residue gave 3-O-benzyl-1,2-O-isopropylidene-β-D-arabinofuranose (341 mg, 76%); m.p.: 77 - 78°C; lit.[46] : 79 - 80°C; $[\alpha]_D^{22}$ +20.6° (*c* 1.1, chloroform); lit.[46] : $[\alpha]_D^{25}$ +23.2° (*c* 0.5, chloroform); ^1H NMR ($CDCl_3$): δ 5.92 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1), 4.68 (dd, 1H, $J_{2,3}$ 0.9 Hz, H-2), 4.65 and 4.57 (ABq, 2H, *J* 11.7 Hz, CH_2Ph), 4.20 (m, 1H, H-4), 3.98 (dd, 1H, $J_{3,4}$ 3.4 Hz, H-3), 3.74 (m, 2H, H-5,5'), 2.08 (1H, OH), 1.53 and 1.35 (2s, 6H, CMe_2). *Anal.*: $C_{15}H_{20}O_5$ (280.32). Calc.: C 64.27; H 7.19. Found: C 64.00; H 7.17.

3-O-Benzyl-1,2-O-isopropylidene-β-L-arabinofuranose

Starting from 3-O-benzyl-1,2-O-isopropylidene-5-O-(tert-butyldiphenylsilyl)-β-L-arabinofuranose, according to procedure described above, 3-O-benzyl-1,2-O-isopropylidene-β-L-arabinofuranose (360 mg, 80%) was obtained; m.p.: 77 - 78°C; lit.[47] 74 - 75°C; $[\alpha]_D^{20}$ -19.2° (*c* 1.7, chloroform); lit.[47]: $[\alpha]_D^{26}$ -22.5° (*c* 1.2,

chloroform). *Anal.*: $C_{15}H_{20}O_5$ (280.32). Calc.: C 64.27; H 7.19. Found: C 64.26; H 7.30.

*Preparation of sugar aldehydes (***8***,* **9**, and **10***) by Swern oxidation. General procedure.*

To a cooled (-78°C) solution of oxalyl chloride (3.17 g, 25.0 mM) in dichloromethane (60 mL) was slowly added a solution of DMSO (3.90 g, 50 mM) in dichlorometane (50 mL) followed by addition of alkohol (20.0 mM) in dichlorometane (50 mL). After 15 min. of stirring, triethylamine (14.0 mL, 100 mM) was added. After attaining room temperature, water (100 mL) was added, and the product was extracted with dichlorometane (3 × 100 mL). Combined organic extracts were washed with 1 M aqueous hydrochloric acid (100 mL), saturated aqueous $NaHCO_3$ (100 mL), water (100 mL), and dried over Na_2SO_4. The solvents were evaporated. Column chromatography of the residue gave pure aldehydes.

Methyl 2,3-O-isopropylidene-β-D-ribo-dialdo-1,4-furanoside (**8**, 94%) was obtained from methyl 2,3-O-isopropylidene-β-D-ribofuranoside[48] (eluent **H**).

3-O-Benzyl-1,2-O-isopropylidene-β-D-arabino-dialdo-1,4-furanose (**9**, 92%) was obtained from 3-O-benzyl-1,2-O-isopropylidene-β-D-arabinofuranose (eluent **G**).

3-O-Benzyl-1,2-O-isopropylidene-β-L-arabino-dialdo-1,4-furanose (**10**, 84%) was obtained from 3-O-benzyl-1,2-O-isopropylidene-β-L-arabinofuranose (eluent **G**).

Reaction of the acetyliron complex with sugar aldehydes on the preparative scale. General procedure.

A solution of the acetyliron (**1**, 4.54 g, 10.0 mM) in THF (100 mL) was cooled to -78°C and butyllithium (7.8 mL, 12.5 mM) was added. After 15 min., a solution of aldehyde (12.0 mM) in THF (20 mL) was added and the mixture was stirred at -78°C for 45 min. Methanol (10 mL) was added and the mixture was allowed to attain room temperature. The solution was filtered through a short silica gel column and concentrated to dryness. Mixture of the starting complex and diastereoisomeric products was used for the decomplexation step without further purification. Analytical samples of the mixtures were separated by preparative HPLC.

Reaction of the acetyliron complex with sugar aldehydes in the presence of metal cation other than lithium. General procedure.

A solution of acetyliron complex (**R-1** or **S-1** enantiomer, 91 mg, 0.2 mM) in THF (2 mL) was cooled to -78°C and butyllithium (0.25 mL, 0.4 mM) was added. After 15 min. a solution of diethylaluminium chloride (0.5 mM) was added, and the mixture was stirred at -78°C for 1 h. A solution of aldehyde (0.25 mM) in THF (1 mL) was added. After 45 min., methanol (0.1 mL) and water (0.1 mL) were added and the mixture was allowed to attain room temperature. Product ratios were determined by HPLC.

With O-benzyl-L-lactaldehyde (5). Products were eluted with eluent **C**.

(RRS)-[CpFe(CO)(PPh$_3$)COC$_{11}$H$_{15}$O$_2$] (**14a**)

^{1}H NMR (C_6D_6): δ 4.52 and 4.38 (ABq, 2H, *J* 11 Hz, CH_2Ph), 4.19 (bs, 5H, Cp), 3.79 (m, 1H), 3.57 (m, 1H), 3.35 (m, 2H), 2.90 (m, 1H), 1.26 (bs, 3H, CH_3). HR-MS / LSIMS: $C_{36}H_{36}FeO_4P$ $(M+H)^+$. Calc.: 619.1701. Found: 619.1697. MS / LSIMS: 1259 $(2M+Na)^+$, 739 $(M+CpFe)^+$, 641 $(M+Na)^+$, 619 $(M+H)^+$.

(RSS)-[CpFe(CO)(PPh$_3$)COC$_{11}$H$_{15}$O$_2$] (**14b**)

^{1}H NMR (C_6D_6): δ 4.46 and 4.38 (ABq, 2H, *J* 12.0 Hz, CH_2Ph), 4.20 (s, 5H, Cp), 3.81 (m, 1H), 3.56 (m, 1H), 3.39 (m, 1H, H-4), 3.28 (m, 2H), 1.16 (d, 3H, $J_{5,4}$ 6.3 Hz, CH_3). MS / LSIMS: 1259 $(2M+Na)^+$, 739 $(M+CpFe)^+$, 641 $(M+Na)^+$, 619 $(M+H)^+$.

(SRS)-[CpFe(CO)(PPh$_3$)COC$_{11}$H$_{15}$O$_2$] (**14c**)

^{1}H NMR (C_6D_6): δ 4.51 and 4.42 (ABq, 2H, *J* 11.9 Hz, CH_2Ph), 4.18 (s, 5H, Cp), 3.72 (m, 1H), 3.57 (m, 1H), 3.52 (bd, 1H, $J_{2,2'}$ 17 Hz, H-2), 3.38 (m, 1H), 3.27 (dd, 1H, $J_{2',3}$ 9 Hz, H-2'), 1.20 (d, 3H, $J_{5,4}$ 6.1 Hz, CH_3). HR-MS / LSIMS: $C_{36}H_{36}FeO_4P$ $(M+H)^+$. Calc.: 619.1701. Found: 619.1697. MS / LSIMS: 1259 $(2M+Na)^+$, 641 $(M+Na)^+$, 619 $(M+H)^+$.

(SSS)-[CpFe(CO)(PPh_3)$COC_{11}H_{15}O_2$] **(14d)**

^{1}H NMR (C_6D_6): δ 4.46 and 4.33 (ABq, 2H, *J* 12.0 Hz, CH_2Ph), 4.20 (s, 5H, Cp), 3.58 (m, 3H), 3.07 (m, 1H), 2.93 (dd, 1H, $J_{2,3}$ 9.4, $J_{2,2'}$ 16.6 Hz, H-2), 1.18 (d, 3H, $J_{5,4}$ 6.3 Hz, CH_3). MS / LSIMS: 1259 $(2M+Na)^+$, 739 $(M+CpFe)^+$, 641 $(M+Na)^+$, 619 $(M+H)^+$.

With 2,3-O-isopropylidene-D-glyceraldehyde (6). Products were eluted with eluent **B**.

(RSR)-[CpFe(CO)(PPh_3)$COC_7H_{13}O_3$] **(17a)**

^{1}H NMR (C_6D_6): δ 4.19 (d, 5H, $J_{Cp,P}$ 1.0 Hz, Cp), 3.98 - 4.05 (m, 2H), 3.77 (m, 1H), 3.57 (m, 2H), 3.48 (dd, 1H, $J_{2,3}$ 2.7, $J_{2,2'}$ 17.3 Hz, H-2), 3.31 (dd, 1H, $J_{2',3}$ 7.9 Hz, H-2'), 1.40 and 1.29 (2s, 6H, CMe_2). HR-MS / LSIMS: $C_{32}H_{34}FeO_5P$ $(M+H)^+$. Calc.: 585.1493. Found: 585.1487. MS / LSIMS: 1191 $(2M+Na)^+$, 607 $(M+Na)^+$, 585 $(M+H)^+$.

(RRR)-[CpFe(CO)(PPh_3)$COC_7H_{13}O_3$] **(17b)**

^{1}H NMR (C_6D_6): δ 4.21 (d, 5H, $J_{Cp,P}$ 1.0 Hz, Cp), 4.13 (m, 1H), 3.88 (dd, 1H, $J_{5,4}$ 6.3, $J_{5,5'}$ 8.1 Hz, H-5), 3.79 (dd, 1H, $J_{5',4}$ 6.6 Hz, H-5'), 3.57 (m, 1H), 3.47 (dd, 1H, $J_{2,3}$ 3.1, $J_{2,2'}$ 16.7 Hz, H-2), 3.05 (m, 1H), 2.91 (dd, 1H, $J_{2',3}$ 8.5 Hz, H-2'), 1.49 and 1.29 (2s, 6H, CMe_2). MS / LSIMS: 607 $(M+Na)^+$, 585 $(M+H)^+$.

(SSR)-[CpFe(CO)(PPh_3)$COC_7H_{13}O_3$] **(17c)**

^{1}H NMR (C_6D_6): δ 4.14 (d, 5H, $J_{Cp,P}$ 1.0 Hz, Cp), 3.98 - 4.08 (m, 2H), 3.78 (dd, 1H, $J_{2,3}$ 2.0, $J_{2,2'}$ 17.2 Hz, H-2), 3.57 (m, 2H), 3.34 (m, 1H), 3.01 (dd, 1H, $J_{2',3}$ 9.3 Hz, H-2'), 1.42 and 1.29 (2s, 6H, CMe_2). HR-MS / LSIMS: $C_{32}H_{34}FeO_5P$ $(M+H)^+$. Calc.: 585.1493. Found: 585.1487. MS / LSIMS: 607 $(M+Na)^+$, 585 $(M+H)^+$.

(SRR)-[CpFe(CO)(PPh_3)$COC_7H_{13}O_3$] **(17d)**

^{1}H NMR (C_6D_6): δ 4.18 (bs, 5H, Cp), 3.94 (m, 1H, H-5), 3.86 (m, 1H), 3.72 (m, 1H, H-5'), 3.55 - 3.65 (m, 2H), 3.34 (dd, 1H, $J_{2,3}$ 9.5, $J_{2,2'}$ 17.2 Hz, H-2), 3.17 (dd, 1H, $J_{2',3}$ 1.3 Hz, H-2'), 1.52 and 1.32 (2s, 6H, CMe_2). MS / LSIMS: 607 $(M+Na)^+$, 585 $(M+H)^+$.

With 4-O-benzyl-2,3-O-isopropylidene-D-tetrose (7). Products were eluted with eluent **B**.

(RRR)-[CpFe(CO)(PPh_3)$COC_{15}H_{21}O_4$] **(18a)**

^{1}H NMR (C_6D_6): δ 4.47 and 4.44 (ABq, 2H, *J* 12.3 Hz, CH_2Ph), 4.41 (m, 1H, $J_{5,6}$ 2.5, $J_{5,6'}$ 5.8, $J_{5,4}$ 7.8 Hz, H-5), 4.13 (m, 6H, $J_{Cp,P}$ 1.2 Hz, Cp, H-3), 3.87 (dd, 1H, $J_{6,6'}$ 10.6 Hz, H-6), 3.82 (dd, 1H, $J_{2,3}$ 1.9, $J_{2,2'}$ 17.2 Hz, H-2), 3.73 (t, 1H, $J_{4,3}$ 7.9 Hz, H-4), 3.66 (dd, 1H, H-6'), 3.05 (dd, 1H, $J_{2',3}$ 9.5 Hz, H-2'), 1.45 and 1.42 (2s, 6H, CMe_2). HR-MS / LSIMS: $C_{40}H_{42}FeO_6P$ $(M+H)^+$. Calc.: 705.2068. Found: 705.2070. MS / LSIMS: 727 $(M+Na)^+$, 705 $(M+H)^+$, 676 $(M - CO)^+$, 648 $(M - 2CO)^+$.

(RSR)-[CpFe(CO)(PPh_3)$COC_{15}H_{21}O_4$] **(18b)**

^{1}H NMR (C_6D_6): δ 4.61 (m, 1H, H-5), 4.44 (s, 2H, CH_2Ph), 4.16 (d, 5H, $J_{Cp,P}$ 1.1 Hz, Cp), 3.80 (m, 1H, H-3), 3.66 (dd, 1H, $J_{4,5}$ 8.0, $J_{4,3}$ 2.2 Hz, H-4), 3.50 - 3.60 (m, 3H, H-2,6,OH), 3.35 (dd, 1H, $J_{6',5}$ 6.0, $J_{6',6}$ 9.9 Hz, H-6'), 3.24 (dd, 1H, $J_{2',3}$ 1.1, $J_{2',2}$ 17.2 Hz, H-2'), 1.60 and 1.50 (2s, 6H, CMe_2). MS / LSIMS: 727 $(M+Na)^+$, 705 $(M+H)^+$, 648 $(M - 2CO)^+$.

(SRR)-[CpFe(CO)(PPh_3)$COC_{15}H_{21}O_4$] **(18c)**

^{1}H NMR (C_6D_6): δ 4.47 and 4.43 (ABq, 2H, *J* 12.4 Hz, CH_2Ph), 4.27 (m, 1H, $J_{5,6}$ 2.6, $J_{5,6'}$ 5.5 Hz, H-5), 4.20 (d, 5H, $J_{Cp,P}$ 1.2 Hz, Cp), 3.96 (t, 1H, $J_{4,3}$ 7.8 Hz, H-4), 3.85 (dd, 1H, $J_{6,6'}$ 10.5 Hz, H-6), 3.68 (dd, 1H, H-6'), 3.59 (m, 1H, H-3), 3.49 (dd, 1H, $J_{2,3}$ 2.3, $J_{2,2'}$ 17.3 Hz, H-2), 3.37 (dd, 1H, $J_{2',3}$ 8.0 Hz, H-2'), 1.46 and 1.40 (2s, 6H, CMe_2). HR-MS / LSIMS: $C_{40}H_{42}FeO_6P$ $(M+H)^+$. Calc.: 705.2068. Found: 705.2063. MS / LSIMS: 727 $(M+Na)^+$, 705 $(M+H)^+$, 648 $(M - 2CO)^+$.

(SSR)-[CpFe(CO)(PPh_3)$COC_{15}H_{21}O_4$] **(18d)**

^{1}H NMR (C_6D_6): δ 4.51 (m, 1H, $J_{5,6}$ 4.1, $J_{5,6'}$ 5.1, $J_{5,4}$ 8.1 Hz, H-5), 4.40 (s, 2H, CH_2Ph), 4.25 (m, 1H, H-3), 4.21 (d, 5H, $J_{Cp,P}$ 1.2 Hz, Cp), 4.05 (dd, 1H, $J_{4,3}$ 2.8 Hz, H-4), 3.63 (dd, 1H, $J_{6,6'}$ 10.4 Hz, H-6), 3.56 (dd, 1H, $J_{2,3}$ 3.6 Hz, H-2), 3.55 (dd, 1H, H-6'), 3.09 (dd, 1H, $J_{2',3}$ 9.2, $J_{2,2'}$ 16.7 Hz, H-2'), 1.50 and 1.45 (2s, 6H, CMe_2). MS / LSIMS: 727 $(M+Na)^+$, 705 $(M+H)^+$, 648 $(M - 2CO)^+$.

With methyl 2,3-O-isopropylidene-β-D-ribo-dialdo-1,4-furanoside (8). Products were eluted with eluent **A**.

(RRR)-[CpFe(CO)(PPh_3)$COC_{10}H_{17}O_5$] **(19a)**

^{1}H NMR (C_6D_6): δ 5.08 (d, 1H, $J_{2,3}$ 5.8 Hz, H-2), 5.04 (s, 1H, H-1), 4.59 (d, 1H, H-3), 4.21 (d, 5H, $J_{Cp,P}$ 1.0

Hz, Cp), 4.03 (m, 1H, H-5), 3.73 (dd, 1H, $J_{6,5}$ 3.6, $J_{6,6'}$ 17.3 Hz, H-6), 3.62 (m, 1H, H-4), 3.18 (dd, 1H, $J_{6',5}$ 7.7 Hz, H-6'), 3.08 (s, 3H, OCH_3), 1.46 and 1.14 (2s, 6H, CMe_2). HR-MS / LSIMS: $C_{35}H_{38}FeO_7P$ $(M+H)^+$. Calc.: 657.1705. Found: 657.1705. MS / LSIMS: 679 $(M+Na)^+$, 657 $(M+H)^+$, 625 $(M - OCH_3)^+$, 600 $(M - 2CO)^+$.

(RSR)-[CpFe(CO)(PPh_3)$COC_{10}H_{17}O_5$] **(19b)**

^1H NMR (C_6D_6): δ 5.00 (s, 1H, H-1), 4.66 (d, 1H, $J_{2,3}$ 6.7 Hz, H-2), 4.59 (d, 1H, H-3), 4.25 (d, 6H, $J_{Cp,P}$ 1.0 Hz, H-4, Cp), 4.01 (m, 1H, H-5), 3.47 (dd, 1H, $J_{6,5}$ 6.5, $J_{6,6'}$ 16.5 Hz, H-6), 3.27 (dd, 1H, $J_{6',5}$ 4.6 Hz, H-6'), 3.15 (s, 3H, OCH_3), 1.44 and 1.12 (2s, 6H, CMe_2). MS / LSIMS: 679 $(M+Na)^+$, 657 $(M+H)^+$, 625 $(M - OCH_3)^+$, 600 $(M - 2CO)^+$.

(SRR)-[CpFe(CO)(PPh_3)$COC_{10}H_{17}O_5$] **(19c)**

^1H NMR (C_6D_6): δ 5.06 (s, 1H, H-1), 5.03 (d, 1H, $J_{2,3}$ 6.0 Hz, H-2), 4.59 (d, 1H, H-3), 4.40 (d, 1H, $J_{4,5}$ 8.3 Hz, H-4), 4.22 (d, 5H, $J_{Cp,P}$ 0.6 Hz, Cp), 3.83 (m, 1H, H-5), 3.49 (dd, 1H, $J_{6,5}$ 6.7, $J_{6,6'}$ 16.8 Hz, H-6), 3.43 (dd, 1H, $J_{6',5}$ 2.9 Hz, H-6'), 3.13 (s, 3H, OCH_3), 1.48 and 1.14 (2s, 6H, CMe_2). MS / LSIMS: 679 $(M+Na)^+$, 657 $(M+H)^+$, 625 $(M - OCH_3)^+$, 600 $(M - 2CO)^+$.

(SSR)-[CpFe(CO)(PPh_3)$COC_{10}H_{17}O_5$] **(19d)**

^1H NMR (C_6D_6): δ 4.98 (s, 1H, H-1), 4.89 (bs, 1H, H-4), 4.85 (d, 1H, $J_{2,3}$ 5.9 Hz, H-2), 4.61 (d, 1H, H-3), 4.34 (d, 5H, $J_{Cp,P}$ 1.0 Hz, Cp), 4.05 (m, 1H, H-5), 3.55 (dd, 1H, $J_{6,5}$ 7.5, $J_{6,6'}$ 16.5 Hz, H-6), 3.19 (dd, 1H, $J_{6',5}$ 5.5 Hz, H-6'), 3.05 (s, 3H, OCH_3), 1.44 and 1.10 (2s, 6H, CMe_2). MS / LSIMS: 679 $(M+Na)^+$, 657 $(M+H)^+$, 625 $(M - OCH_3)^+$, 600 $(M - 2CO)^+$.

With 3-O-benzyl-1,2-O-isopropylidene-β-D-arabino-dialdo-1,4-furanose ***(9)***. Products were eluted with eluent **B**.

(RRR)-[CpFe(CO)(PPh_3)$COC_{16}H_{21}O_5$] **(20a)**

^1H NMR (C_6D_6): δ 5.87 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 4.53 (d, 1H, H-2), 4.48 (d, 1H, $J_{3,4}$ 1.2 Hz, H-3), 4.44 and 4.35 (ABq, 2H, *J* 11.8 Hz, CH_2Ph), 4.43 (m, 1H, H-5), 4.21 (d, 5H, $J_{Cp,P}$ 1.2 Hz, Cp), 4.08 (dd, 1H, $J_{4,5}$ 10.0 Hz, H-4), 4.03 (dd, 1H, $J_{6,5}$ 2.2, $J_{6,6'}$ 17.6 Hz, H-6), 3.19 (dd, 1H, $J_{6',5}$ 9.2 Hz, H-6'), 1.48 and 1.07 (2s, 6H, CMe_2). HR-MS / LSIMS: $C_{41}H_{42}FeO_7P$ $(M+H)^+$. Calc.: 733.2018. Found: 733.2014. MS / LSIMS: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

(RSR)-[CpFe(CO)(PPh_3)$COC_{16}H_{21}O_5$] **(20b)**

^1H NMR (C_6D_6): δ 5.68 (bs, 1H, H-1), 4.18 (bs, 5H, Cp), 1.70 and 1.29 (2s, 6H, CMe_2). MS / LSIMS: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

(SRR)-[CpFe(CO)(PPh_3)$COC_{16}H_{21}O_5$] **(20c)**

^1H NMR (C_6D_6): δ 5.85 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.27 (bs, 5H, Cp), 3.80 (dd, 1H, $J_{6,5}$ 5.8, $J_{6,6'}$ 17.5 Hz, H-6), 3.45 (dd, 1H, $J_{6',5}$ 2.0 Hz, H-6'), 1.38 and 1.08 (2s, 6H, CMe_2). MS / LSIMS: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

(SSR)-[CpFe(CO)(PPh_3)$COC_{16}H_{21}O_5$] **(20d)**

^1H NMR (C_6D_6): δ 5.70 (d, 1H, $J_{1,2}$ 4.2 Hz, H-1), 4.23 (bs, 5H, Cp), 3.51 (dd, 1H, $J_{6,5}$ 3.9, $J_{6,6'}$ 16.7 Hz, H-6), 3.20 (dd, 1H, $J_{6',5}$ 8.6 Hz, H-6'), 1.25 (s, 6H, CMe_2). MS / LSIMS: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

With 3-O-benzyl-1,2-O-isopropylidene-β-L-arabino-dialdo-1,4-furanose ***(10)***. Products were eluted with eluent **B**.

(SSS)-[CpFe(CO)(PPh_3)$COC_{16}H_{21}O_5$] **(21a)**

HR-MS / LSIMS: $C_{41}H_{42}FeO_7P$ $(M+H)^+$. Calc.: 733.2018. Found: 733.2014. MS / LSIMS: 853 $(M + CpFe)^+$, 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

(SRS)-[CpFe(CO)(PPh_3)$COC_{16}H_{21}O_5$] **(21b)**

MS / LSIMS - NBA: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

(RSS)-[CpFe(CO)(PPh_3)$COC_{16}H_{21}O_5$] **(21c)**

MS / LSIMS - NBA: 853 $(M + CpFe)^+$, 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

(RRS)-[CpFe(CO)(PPh_3)$COC_{16}H_{21}O_5$] **(21d)**

MS / LSIMS - NBA: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

With 3-O-benzyl-1,2-O-isopropylidene-α-D-xylo-dialdo-1,4-furanose (11). Products were eluted with eluent **B**.

*(RRR)-[CpFe(CO)(PPh$_3$)COC$_{16}$H$_{21}$O$_5$] (**22a**)*

^{1}H NMR (C_6D_6): δ 5.93 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1), 4.74 (m, 1H, H-5), 4.61 and 4.43 (ABq, 2H, J 11.6 Hz, CH_2Ph), 4.38 (d, 1H, H-2), 4.33 (d, 1H, $J_{3,4}$ 1.6 Hz, H-3), 4.25 (dd, 1H, $J_{4,5}$ 9.0 Hz, H-4), 4.09 (s, 5H, Cp), 4.05 (d, 1H, $J_{6,6'}$ 17.3 Hz, H-6), 3.22 (dd, 1H, $J_{6',5}$ 9.8 Hz, H-6'), 1.35 and 1.09 (2s, 6H, CMe_2). HR-MS / LSIMS: $C_{41}H_{42}FeO_7P$ $(M+H)^+$. Calc.: 733.2018. Found: 733.2014. MS / LSIMS: 1488 $(2M + Na + H)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

*(RSR)-[CpFe(CO)(PPh$_3$)COC$_{16}$H$_{21}$O$_5$] (**22b**)*

^{1}H NMR (C_6D_6): δ 5.97 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 4.50 (m, 1H, H-5), 4.40 (dd, 1H, $J_{2,3}$ 0.7 Hz, H-2), 4.28 (d, 5H, $J_{Cp,P}$ 1.2 Hz, Cp), 4.25 and 4.20 (ABq, 2H, J 12.0 Hz, CH_2Ph), 4.18 (dd, 1H, $J_{4,3}$ 4.1, $J_{4,5}$ 5.3 Hz, H-4), 3.87 (d, 1H, H-3), 3.75 (dd, 1H, $J_{6,5}$ 9.5, $J_{6,6'}$ 16.5 Hz, H-6), 3.11 (dd, 1H, $J_{6',5}$ 2.4 Hz, H-6'), 1.42 and 1.15 (2s, 6H, CMe_2). MS / LSIMS: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

*(SRR)-[CpFe(CO)(PPh$_3$)COC$_{16}$H$_{21}$O$_5$] (**22c**)*

^{1}H NMR (C_6D_6): δ 5.90 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.54 and 4.41 (ABq, 2H, J 11.9 Hz, CH_2Ph), 4.48 (dd, 1H, $J_{4,3}$ 2.4, $J_{4,5}$ 9.0 Hz, H-4), 4.40 (d, 1H, H-2), 4.31 (s, 5H, Cp), 4.22 (d, 1H, H-3), 4.15 (m, 1H, H-5), 3.70 (dd, 1H, $J_{6,5}$ 5.9, $J_{6,6'}$ 17.4 Hz, H-6), 3.48 (dd, 1H, $J_{6',5}$ 2.8 Hz, H-6'), 1.44 and 1.09 (2s, 6H, CMe_2). MS / LSIMS: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

*(SSR)-[CpFe(CO)(PPh$_3$)COC$_{16}$H$_{21}$O$_5$] (**22d**)*

^{1}H NMR (C_6D_6): δ 5.97 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.58 (m, 1H, H-5), 4.44 (dd, 1H, $J_{4,3}$ 3.8, $J_{4,5}$ 4.3 Hz, H-4), 4.36 (d, 1H, H-2), 4.30 and 4.18 (ABq, 2H, J 11.8 Hz, CH_2Ph), 4.21 (d, 5H, $J_{Cp,P}$ 1.1 Hz, Cp), 3.91 (d, 1H, H-3), 3.76 (dd, 1H, $J_{6,5}$ 4.7, $J_{6,6'}$ 16.7 Hz, H-6), 3.22 (dd, 1H, $J_{6',5}$ 7.8 Hz, H-6'), 1.41 and 1.15 (2s, 6H, CMe_2). MS / LSIMS: 755 $(M+Na)^+$, 733 $(M+H)^+$, 676 $(M - 2CO)^+$.

With methyl 2,3-O-isopropylidene-α-D-lyxo-dialdo-1,4-furanoside (12). Products were eluted with eluent **A**.

*(RRR)-[CpFe(CO)(PPh$_3$)COC$_{10}$H$_{17}$O$_5$] (**23a**)*

^{1}H NMR (C_6D_6): δ 4.98 (s, 1H, H-1), 4.78 (m, 1H, H-5), 4.74 (dd, 1H, $J_{3,2}$ 5.8, $J_{3,4}$ 3.3 Hz, H-3), 4.52 (d, 1H, H-2), 4.16 (d, 5H, $J_{Cp,P}$ 1.0 Hz, Cp), 3.95 (dd, 1H, $J_{6,5}$ 1.7, $J_{6,6'}$ 17.2 Hz, H-6), 3.85 (dd, 1H, $J_{4,5}$ 8.4 Hz, H-4), 3.15 (dd, 1H, $J_{6',5}$ 9.9 Hz, H-6'), 3.07 (s, 3H, OCH_3), 1.47 and 1.11 (2s, 6H, CMe_2). MS / LSIMS: 679 $(M+Na)^+$, 657 $(M+H)^+$, 600 $(M - 2CO)^+$.

*(RSR)-[CpFe(CO)(PPh$_3$)COC$_{10}$H$_{17}$O$_5$] (**23b**)*

^{1}H NMR (C_6D_6): δ 4.99 (s, 1H, H-1), 4.52 (d, 1H, $J_{2,3}$ 5.9 Hz, H-2), 4.46 (m, 1H, H-5), 4.28 (m, 6H, $J_{Cp,P}$ 1.1 Hz, H-4, Cp), 3.83 (dd, 1H, $J_{3,4}$ 3.4 Hz, H-3), 3.55 (dd, 1H, $J_{6,5}$ 9.0, $J_{6,6'}$ 16.5 Hz, H-6), 3.34 (dd, 1H, $J_{6,5}$ 2.5 Hz, H-6'), 3.10 (s, 3H, OCH_3), 1.39 and 1.10 (2s, 6H, CMe_2). HR-MS / LSIMS: $C_{35}H_{38}FeO_7P$ $(M+H)^+$. Calc.: 657.1704. Found: 657.1704. MS / LSIMS: 679 $(M+Na)^+$, 657 $(M+H)^+$, 600 $(M - 2CO)^+$.

*(SRR)-[CpFe(CO)(PPh$_3$)COC$_{10}$H$_{17}$O$_5$] (**23c**)*

^{1}H NMR (C_6D_6): δ 4.94 (s, 1H, H-1), 4.66 (dd, 1H, $J_{3,2}$ 5.8, $J_{3,4}$ 3.4 Hz, H-3), 4.52 (d, 1H, H-2), 4.25 (m, 1H, H-5), 4.22 (d, 5H, $J_{Cp,P}$ 0.9 Hz, Cp), 4.00 (dd, 1H, $J_{4,5}$ 7.7 Hz, H-4), 3.69 (dd, 1H, $J_{6,5}$ 2.5, $J_{6,6'}$ 17.6 Hz, H-6), 3.51 (dd, 1H, $J_{6',5}$ 8.2 Hz, H-6'), 3.09 (s, 3H, OCH_3), 1.45 and 1.14 (2s, 6H, CMe_2). MS / LSIMS: 679 $(M+Na)^+$, 657 $(M+H)^+$, 625 $(M - OCH_3)^+$, 600 $(M - 2CO)^+$.

*(SSR)-[CpFe(CO)(PPh$_3$)COC$_{10}$H$_{17}$O$_5$] (**23d**)*

^{1}H NMR (C_6D_6): δ 5.02 (s, 1H, H-1), 4.53 (m, 1H, H-5), 4.51 (d, 1H, $J_{2,3}$ 5.9 Hz, H-2), 4.25 (d, 5H, $J_{Cp,P}$ 1.0 Hz, Cp), 4.24 (dd, 1H, $J_{4,5}$ 6.0 Hz, H-4), 3.97 (dd, 1H, $J_{3,4}$ 3.4 Hz, H-3), 3.79 (dd, 1H, $J_{6,5}$ 3.2, $J_{6,6'}$ 16.8 Hz, H-6), 3.19 (dd, 1H, $J_{6',5}$ 7.7 Hz, H-6'), 3.09 (s, 3H, OCH_3), 1.42 and 1.12 (2s, 6H, CMe_2). MS / LSIMS: 679 $(M+Na)^+$, 657 $(M+H)^+$, 625 $(M - OCH_3)^+$, 600 $(M - 2CO)^+$.

With 1,2;3,4-di-O-isopropylidene-α-D-galacto-dialdo-1,5-pyranose (13). Products were eluted with eluent **B**.

*(RRR)-[CpFe(CO)(PPh$_3$)COC$_{13}$H$_{21}$O$_6$] (**24a**)*

^{1}H NMR (C_6D_6): δ 5.54 (d, 1H, $J_{1,2}$ 4.9 Hz, H-1), 4.65 (dd, 1H, $J_{4,3}$ 8.1, $J_{4,5}$ 1.2 Hz, H-4), 4.52 (dd, 1H, $J_{3,2}$ 2.1 Hz, H-3), 4.17 (dd, 1H, H-2), 4.11 (d, 5H, $J_{Cp,P}$ 1.1 Hz, Cp), 4.03 (d, 1H, $J_{7,7'}$ 17.6 Hz, H-7), 3.77 (d, 1H,

$J_{OH,6}$ 9.0 Hz, OH), 3.57 (m, 2H, H-5,6), 3.03 (dd, 1H, $J_{7',6}$ 10.0 Hz, H-7'), 1.49, 1.45, 1.16 and 1.06 (4s, 12H, 2 × CMe_2). MS / LSIMS: 735 $(M+Na)^+$, 713 $(M+H)^+$.

(RSR)-[CpFe(CO)(PPh_3)$COC_{13}H_{21}O_6$] **(24b)**

^1H NMR (C_6D_6): δ 5.50 (d, 1H, $J_{1,2}$ 4.9 Hz, H-1), 4.41 (1H), 4.31 (s, 5H, Cp), 4.14 (dd, 1H, *J* 1.6 and 4.3 Hz), 4.04 (m, 1H, *J* 8.0 and 0.8 Hz), 3.83 (d, 1H, *J* 6.2 Hz), 3.69 (dd, 1H, $J_{7,6}$ 8.8, $J_{7,7'}$ 16.6 Hz, H-7), 3.56 (2H), 3.24 (d, 1H, H-7'), 1.12 and 1.04 (2s, 12H, 2 × CMe_2). MS / LSIMS: 735 $(M+Na)^+$, 713 $(M+H)^+$.

(SRR)-[CpFe(CO)(PPh_3)$COC_{13}H_{21}O_6$] **(24c)**

^1H NMR (C_6D_6): δ 5.52 (bs, 1H, H-1), 4.34 (s, 5H, Cp), 1.57, 1.46, 1.16 and 1.05 (4s, 12H, 2 × CMe_2). HR-MS / LSIMS: $C_{38}H_{42}FeO_8P$ $(M+H)^+$. Calc.: 713.1967. Found: 713.1956. MS / LSIMS: 735 $(M+Na)^+$, 713 $(M+H)^+$.

(SSR)-[CpFe(CO)(PPh_3)$COC_{13}H_{21}O_6$] **(24d)**

^1H NMR (C_6D_6): δ 5.58 (d, 1H, $J_{1,2}$ 4.5 Hz, H-1), 4.31 (s, 5H, Cp). MS / LSIMS: 735 $(M+Na)^+$, 713 $(M+H)^+$.

Decomplexation of iron complexes. General procedure.

A solution of the crude product of reaction of acetyliron complex **1** (4.54 g, 10.0 mM) with sugar aldehydes in dichloromethane (100 mL) and methanol (50 mL) was cooled to -78°C and NBS (1.87g, 10.5 mM) was added. The mixture was allowed to attain room temperature slowly. The solvents were evaporated. The residue was extracted with ether (10 × 20 mL) and combined organic extracts were concentrated to dryness. Column chromatography of the residue gave pure products.

Products of reaction of racemic acetyliron complex with aldehyde **5** were separated by preparative HPLC (eluent **C**) and two pairs of complexes (**14a,c** and **14b,d**) were obtained.

Products of reaction of acetyliron complex with aldehyde **6** were separated by column chromatography (eluent **E**) and two pairs of complexes (**17a,c** and **17b,d**) were obtained.

Decomplexation of **14a,c**. Product was eluted with eluent **A**.

*4-O-Benzyl-2,5-dideoxy-L-*erythro*-pentonic acid methyl ester* (**15**). Yield 71%; $[\alpha]_D^{20}$ +31.5° (*c* 2.0, chloroform); ν_{max} (film): 1736 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.63 and 4.49 (ABq, 2H, *J* 11.7 Hz, CH_2Ph), 4.03 (m, 1H, H-3), 3.69 (s, 3H, $COOCH_3$), 3.56 (dq, 1H, $J_{4,5}$ 6.3, $J_{4,3}$ 4.9 Hz, H-4), 2.89 (d, 1H, $J_{OH,3}$ 4.9 Hz, OH), 2.62 (dd, 1H, $J_{2,3}$ 4.1, $J_{2,2'}$ 16.2 Hz, H-2), 2.51 (dd, 1H, $J_{2',3}$ 8.3 Hz, H-2'), 1.22 (d, 3H, H-5,5',5''). HR-MS / LSIMS: $C_{13}H_{19}O_4$ $(M+H)^+$. Calc.: 239.1283. Found: 239.1283.

Decomplexation of **14b,d**. Product was eluted with eluent **A**.

*4-O-Benzyl-2,5-dideoxy-L-*threo*-pentonic acid methyl ester* (**16**). Yield 71%; $[\alpha]_D^{20}$ +14.5° (*c* 2.8, chloroform); ν_{max} (film): 1735 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.66 and 4.45 (ABq, 2H, *J* 11.5 Hz, CH_2Ph), 4.00 (m, 1H, H-3), 3.68 (s, 3H, $COOCH_3$), 3.53 (dq, 1H, $J_{4,5}$ 6.2, $J_{4,3}$ 4.9 Hz, H-4), 2.85 (d, 1H, $J_{OH,3}$ 4.8 Hz, OH), 2.53 (d, 2H, H-2,2'), 1.23 (d, 3H, H-5,5',5''). HR-MS / LSIMS: $C_{13}H_{19}O_4$ $(M+H)^+$. Calc.: 239.1283. Found: 239.1283.

Decomplexation of **17a,c**. Product was eluted with eluent **A**.

*2-Deoxy-4,5-O-isopropylidene-D-*erythro*-pentonic acid methyl ester* (**27**). Yield 73%; $[\alpha]_D^{22}$ -10.6° (*c* 1.0, chloroform); lit.[19] : $[\alpha]_D^{20}$ -11.8° (*c* 0.6, chloroform); ν_{max} (film): 1737 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.90 - 4.15 (m, 4H, H-3,4,5,5'), 3.73 (s, 3H, $COOCH_3$), 3.12 (d, 1H, $J_{OH,3}$ 3.8 Hz, OH), 2.73 (dd, 1H, $J_{2,3}$ 2.8, $J_{2,2'}$ 16.7 Hz, H-2), 2.48 (dd, 1H, $J_{2',3}$ 8.4 Hz, H-2'), 1.41 and 1.35 (2s, 6H, CMe_2). HR-MS / EI: $C_8H_{13}O_5$ $(M-CH_3)^+$. Calc.: 189.0763. Found: 189.0761.

Decomplexation of **17b,d**. Product was eluted with eluent **A**.

*2-Deoxy-4,5-O-isopropylidene-D-*threo*-pentonic acid methyl ester* (**28**). Yield 90%; $[\alpha]_D^{22}$ +16.9° (*c* 1.1, chloroform); lit.[19]: $[\alpha]_D^{20}$ +13.3° (*c* 1.2, chloroform); ν_{max} (film): 1738 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.98 - 4.20 (m, 3H, H-3,4,5), 3.85 (dd, 1H, *J* 5.9 and 8.0 Hz, H-5'), 3.72 (s, 3H, $COOCH_3$), 2.79 (d, 1H, $J_{OH,3}$ 5.6 Hz, OH), 2.57 (dd, 1H, $J_{2,3}$ 7.5, $J_{2,2'}$ 15.9 Hz, H-2), 2.49 (dd, 1H, $J_{2',3}$ 4.5 Hz, H-2'), 1.45 (d, 3H, *J* 0.5 Hz, *Me*CMe), 1.37 (d, 3H, *J* 0.5 Hz, MeC*Me*). HR-MS / EI: $C_8H_{13}O_5$ $(M-CH_3)^+$. Calc.: 189.0763. Found: 189.0765.

Decomplexation of **ent-18a-d**. Products were eluted with eluent **A**.

6-O-Benzyl-2-deoxy-4,5-O-isopropylidene-L-lyxo-*hexonic acid methyl ester* (**29**). Yield 36%; $[\alpha]_D^{22}$ -10.2° (*c* 1.4, chloroform); ν_{max} (film): 1740 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.59 (s, 2H, CH_2Ph), 4.11 (m, 1H, H-5), 4.04 (m, 1H, H-3), 3.70 (dd, 1H, $J_{4,3}$ 7.7, $J_{4,5}$ 7.5 Hz, H-4), 3.71 (s, 3H, $COOCH_3$), 3.67 (dd, 1H, $J_{5,6}$ 5.3, $J_{6,6'}$ 9.8 Hz, H-6), 3.62 (dd, 1H, $J_{6',5}$ 5.5 Hz, H-6'), 3.49 (bs, 1H, OH), 2.76 (dd, 1H, $J_{2,3}$ 3.1, $J_{2,2'}$ 16.3 Hz, H-2), 2.50 (dd, 1H, $J_{2',3}$ 9.0 Hz, H-2'), 1.39 and 1.38 (2s, 6H, CMe_2). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1344.

6-O-Benzyl-2-deoxy-4,5-O-isopropylidene-L-xylo-*hexonic acid methyl ester* (**30**). Yield 20%; $[\alpha]_D^{22}$ +2.7° (*c* 1.3, chloroform); ν_{max} (film): 1735 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.58 (s, 2H, CH_2Ph), 4.21 (m, 1H, H-5), 4.09 (m, 1H, H-3), 3.85 (dd, 1H, $J_{4,3}$ 3.1, $J_{4,5}$ 8.0 Hz, H-4), 3.70 (s, 3H, $COOCH_3$), 3.65 (dd, 1H, $J_{6,5}$ 5.2, $J_{6,6'}$ 10.2 Hz, H-6), 3.58 (dd, 1H, $J_{6',5}$ 5.0 Hz, H-6'), 2.79 (d, 1H, $J_{OH,3}$ 7.5 Hz, OH), 2.58 (m, 2H, H-2,2'), 1.43 and 1.41 (2s, 6H, CMe_2). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1344.

Decomplexation of **18a-d**. Products were eluted with eluent **A**.

6-O-Benzyl-2-deoxy-4,5-O-isopropylidene-D-lyxo-*hexonic acid methyl ester* (**35**). Yield 24%; $[\alpha]_D^{20}$ +13.4° (*c* 1.5, chloroform). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1332.

6-O-Benzyl-2-deoxy-4,5-O-isopropylidene-D-xylo-*hexonic acid methyl ester* (**36**). Yield 17%; $[\alpha]_D^{20}$ -2.4° (*c* 1.7, chloroform). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1335.

Decomplexation of **19a-d**. Products were eluted with eluent **K**.

Methyl (methyl 6-deoxy-2,3-O-isopropylidene-α-L-talo-*heptofuranosid)uronate* (**39**)

Yield 607 mg (22%); $[\alpha]_D^{23}$ -64.3° (*c* 5.3, chloroform); ν_{max} (film): 1745 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.98 (s, 1H, H-1), 4.85 (d, 1H, $J_{3,2}$ 6.0 Hz, H-3), 4.59 (d, 1H, H-2), 4.42 (d, 1H, $J_{4,5}$ 2.6 Hz, H-4), 4.07 (m, 1H, H-5), 3.71 (s, 3H, $COOCH_3$), 3.47 (s, 3H, OCH_3), 2.56 (m, 2H, H-6,6'), 1.48 and 1.32 (2s, 6H, CMe_2). HR-MS / EI: $C_{11}H_{17}O_7$ $(M\text{-}CH_3)^+$. Calc.: 261.0974. Found: 261.0974.

Methyl (methyl 6-deoxy-2,3-O-isopropylidene-β-D-allo-*heptofuranosid)uronate* (**40**)

Yield: 1.85 g (67%); $[\alpha]_D^{24}$ -51.6° (*c* 10.3, chloroform); ν_{max} (film): 1740 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.97 (s, 1H, H-1), 4.87 (d, 1H, $J_{3,2}$ 6.0 Hz, H-3), 4.58 (d, 1H, H-2), 4.18 (d, 1H, $J_{4,5}$ 4.7 Hz, H-4), 4.08 (m, 1H, H-5), 3.73 (s, 3H, $COOCH_3$), 3.41 (s, 3H, OCH_3), 2.62 (dd, 1H, $J_{6,5}$ 3.9, $J_{6,6'}$ 15.9 Hz, H-6), 2.54 (dd, 1H, $J_{6',5}$ 8.6 Hz, H-6'), 1.48 (d, 3H, *J* 0.4 Hz, *Me*CMe), 1.32 (d, 3H, *J* 0.5 Hz, MeC*Me*). HR-MS / EI: $C_{11}H_{17}O_7$ $(M\text{-}CH_3)^+$. Calc.: 261.0974. Found: 261.0969.

Decomplexation of **20a-d**. Products were eluted with eluent **E**.

Methyl 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-β-D-altro-*heptofuranuronate* (**47**)

Yield: 1.30 g (37%); $[\alpha]_D^{20}$ +9.8° (*c* 1.5, chloroform); ν_{max} (film): 1730 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.90 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 4.66 (d, 1H, H-2), 4.61 (ABq, 2H, *J* 11.7 Hz, CH_2Ph), 4.23 (m, 2H, H-3,5), 3.98 (dd, 1H, $J_{4,3}$ 2.1, $J_{4,5}$ 8.6 Hz, H-4), 3.71 (s, 3H, $COOCH_3$), 2.82 (dd, 1H, $J_{6,5}$ 3.0, $J_{6,6'}$ 16.9 Hz, H-6), 2.50 (dd, 1H, $J_{6',5}$ 8.9 Hz, H-6'), 1.49 and 1.31 (2s, 6H, CMe_2). HR-MS / EI: $C_{17}H_{21}O_7$ $(M\text{-}CH_3)^+$. Calc.: 337.1287. Found: 337.1285.

Methyl 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-α-L-galacto-*heptofuranuronate* (**48**)

Yield: 420 mg (12%); $[\alpha]_D^{20}$ +19.3° (*c* 2.5, chloroform); ν_{max} (film): 1740 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.89 (d, 1H, $J_{1,2}$ 4.2 Hz, H-1), 4.69 (dd, 1H, $J_{2,3}$ 1.3 Hz, H-2), 4.67 and 4.55 (ABq, 2H, *J* 11.7 Hz, CH_2Ph), 4.18 (m, 1H, H-5), 4.02 (dd, 1H, $J_{3,4}$ 4.2 Hz, H-3), 3.97 (dd, 1H, $J_{4,5}$ 5.5 Hz, H-4), 3.70 (s, 3H, $COOCH_3$), 2.55 (dd, 1H, $J_{6,5}$ 8.6, $J_{6,6'}$ 15.9 Hz, H-6), 2.47 (dd, 1H, $J_{6',5}$ 4.1 Hz, H-6'), 1.55 and 1.36 (2s, 6H, CMe_2). HR-MS / EI: $C_{17}H_{21}O_7$ $(M\text{-}CH_3)^+$. Calc.: 337.1287. Found: 337.1285.

Decomplexation of **21a-d**. Products were eluted with eluent **E**.

Methyl 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-β-L-altro-*heptofuranuronate* (**ent-47**)

Yield: 1.51 g (43%); $[\alpha]_D^{20}$ -11.3° (*c* 1.1, chloroform). HR-MS / EI: $C_{17}H_{21}O_7$ $(M\text{-}CH_3)^+$. Calc.: 337.1287. Found: 337.1285.

Methyl 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-α-D-galacto-*heptofuranuronate* (**ent-48**)

Yield: 530 mg (15%); $[\alpha]_D^{20}$ -22.1° (*c* 2.5, chloroform). HR-MS / EI: $C_{17}H_{21}O_7$ $(M\text{-}CH_3)^+$. Calc.:

337.1287. Found: 337.1286.

Decomplexation of **22a-d**. Products were eluted with eluent **E**.

*Methyl 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-α-D-*gluco-*heptofuranuronate* (**56**)

Yield: 1.62 g (46%); $[\alpha]_D^{20}$ -17.5° (*c* 0.75, chloroform). ^{1}H NMR ($CDCl_3$): δ 5.90 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.71 and 4.60 (ABq, 2H, *J* 11.8 Hz, CH_2Ph), 4.61 (d, 1H, H-2), 4.37 (m, 1H, H-5), 4.10 (d, 1H, $J_{3,4}$ 3.2 Hz, H-3), 4.05 (dd, 1H, $J_{4,5}$ 8.4 Hz, H-4), 3.71 (s, 3H, $COOCH_3$), 2.80 (dd, 1H, $J_{6,5}$ 3.0, $J_{6,6'}$ 16.6 Hz, H-6), 2.53 (dd, 1H, $J_{6',5}$ 9.1 Hz, H-6'), 1.48 and 1.31 (2s, 6H, CMe_2). HR-MS / EI: $C_{18}H_{25}O_7$ $(M+H)^+$. Calc.: 353.1600. Found: 353.1597.

*Methyl 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-β-L-*ido-*heptofuranuronate* (**57**)

Yield: 634 mg (18%); $[\alpha]_D^{20}$ -44.5° (*c* 0.8, chloroform); ν_{max} (film): 1745 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.00 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.72 and 4.48 (ABq, 2H, *J* 11.8 Hz, CH_2Ph), 4.65 (d, 1H, H-2), 4.43 (m, 1H, H-5), 4.14 (dd, 1H, $J_{4,3}$ 3.8, $J_{4,5}$ 5.0 Hz, H-4), 4.01 (d, 1H, H-3), 3.69 (s, 3H, $COOCH_3$), 2.55 (dd, 1H, $J_{6,5}$ 8.4, $J_{6,6'}$ 15.8 Hz, H-6), 2.43 (dd, 1H, $J_{6',5}$ 4.3 Hz, H-6'), 1.48 and 1.33 (2s, 6H, CMe_2). HR-MS / EI: $C_{18}H_{25}O_7$ $(M+H)^+$. Calc.: 353.1600. Found: 353.1600.

Decomplexation of **24a-d**. Products were eluted with eluent **A**.

*7-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-*glycero-*D-*galacto-*octopyranuronate* (**74**)

Yield: 1.66 g (50%); $[\alpha]_D^{20}$ -48.3° (*c* 1.25, chloroform); ν_{max} (film): 1737 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.50 (d, 1H, $J_{1,2}$ 4.9 Hz, H-1), 4.63 (dd, 1H, $J_{3,2}$ 2.3, $J_{3,4}$ 7.9 Hz, H-3), 4.49 (dd, 1H, $J_{4,5}$ 1.8 Hz, H-4), 4.31 (dd, 1H, H-2), 4.18 (m, 1H, H-6), 3.71 (s, 3H, $COOCH_3$), 3.66 (dd, 1H, $J_{5,6}$ 8.6 Hz, H-5), 3.21 (d, 1H, $J_{OH,6}$ 5.7 Hz, OH), 2.86 (dd, 1H, $J_{7,6}$ 3.1, $J_{7,7'}$ 16.8 Hz, H-7), 2.52 (dd, 1H, $J_{7',6}$ 8.4 Hz, H-7'), 1.51, 1.46, 1.37 and 1.32 (4s, 12H, 2 × CMe_2). HR-MS / EI: $C_{14}H_{21}O_8$ $(M-CH_3)^+$. Calc.: 317.1236. Found: 317.1235.

*7-Deoxy-1,2:3,4-di-O-isopropylidene-α-L-*glycero-*D-*galacto-*octopyranuronate* (**75**)

Yield: 365 mg (11%); mp.: 106-107°C; $[\alpha]_D^{20}$ -54.6° (*c* 0.35, chloroform); ν_{max} (KBr): 1732 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.54 (d, 1H, $J_{1,2}$ 5.1 Hz, H-1), 4.64 (dd, 1H, $J_{3,2}$ 2.4, $J_{3,4}$ 8.0 Hz, H-3), 4.30 - 4.42 (m, 3H, H-2,4,6), 3.79 (dd, 1H, $J_{5,4}$ 1.8, $J_{5,6}$ 4.5 Hz, H-5), 3.70 (s, 3H, $COOCH_3$), 3.34 (bs, 1H, OH), 2.73 (dd, 1H, $J_{7,6}$ 6.2, $J_{7,7'}$ 16.3 Hz, H-7), 2.62 (dd, 1H, $J_{7',6}$ 6.7 Hz, H-7'), 1.49, 1.47, 1.34 and 1.33 (4s, 12H, 2 × CMe_2). HR-MS / EI: $C_{14}H_{21}O_8$ $(M-CH_3)^+$. Calc.: 317.1236. Found: 317.1235.

Preparation of lactones ***25*** *and* ***26***

To a solution of ester **15** or **16** (220 mg, 0.92 mM) in ethanol (3 mL) 10% Pd / C (100 mg) was added and the suspension was hydrogenated at atmospheric pressure for 20 h. The mixture was filtered through a Celite pad, washed with warm methanol, and concentrated to dryness. To the residue THF (2 mL), water (0.5 mL) and trifluoracetic acid (2.5 mL) were added. After stirring for 20 h, the solvents were coevaporated with toluene, and the residue was dissolved in pyridine (2 mL). To this solution acetic anhydride (1 mL) and DMAP (a small crystal) were added. Stirring was continued for 24 h and the solvents were evaporated. Column chromatography (eluent **F**) of the residue gave the pure product.

*3-O-Acetyl-2,5-dideoxy-L-*erythro-*pentonic acid γ-lactone* (**25**). Yield 102 mg (70%); $[\alpha]_D^{22}$ +19.6° (*c* 0.8, chloroform); ν_{max} (film): 1786, 1740 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.45 (m, 1H, H-3), 4.16 (dq, 1H, $J_{4,5}$ 6.6, $J_{4,3}$ 1.7 Hz, H-4), 2.24 (dd, 1H, $J_{2,3}$ 6.2, $J_{2,2'}$ 18.4 Hz, H-2), 2.12 (dd, 1H, $J_{2',3}$ 2.8 Hz, H-2'), 1.54 (s, 3H, OAc), 0.83 (d, 3H, H-5,5',5''). HR-MS / EI: $C_7H_{10}O_4$ $(M)^+$. Calc.: 158.0579. Found: 158.0581.

*3-O-Acetyl-2,5-dideoxy-L-*threo-*pentonic acid γ-lactone* (**26**). Yield 102 mg (70%); $[\alpha]_D^{24}$ -32.4° (*c*, 1.3, chloroform); ν_{max} (film): 1786, 1742 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.72 (m, 1H, H-3), 3.80 (dq, 1H, $J_{4,5}$ 6.5, $J_{4,3}$ 4.0 Hz, H-4), 2.16 (dd, 1H, $J_{2,3}$ 1.7, $J_{2,2'}$ 18.0 Hz, H-2), 2.03 (dd, 1H, $J_{2',3}$ 5.6 Hz, H-2'), 1.53 (s, 3H, OAc), 1.00 (d, 3H, H-5,5',5''). HR-MS / EI: $C_7H_{10}O_4$ $(M)^+$. Calc.: 158.0579. Found: 158.0581.

Preparation of lactones ***31, 32, 37*** *and* ***38****. General procedure.*

To a solution of ester **29**, **30**, **35** or **36** (820 mg, 2.53 mM) in THF (5 mL) water (1 mL) and

trifluoracetic acid (10 mL) were added. Stirring was continued for 3 h. The solvents were evaporated. Column chromatography of the residue (dichloromethane - methanol, 95 : 5) gave the pure product.

6-O-Benzyl-2-deoxy-L-lyxo-*hexonic acid γ-lactone* (**31**). Yield 523 mg (82%); mp. 61 - 62°C; $[\alpha]_D^{20}$ +34.7° (*c* 1.6, chloroform); ν_{max} (film): 1770 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.53 - 4.59 (m, 3H, *J* 11.7 Hz, CH_2Ph, H-3), 4.32 (t, 1H, $J_{4,3} = J_{4,5} = 3.2$ Hz, H-4), 4.00 (m, 1H, $J_{5,6}$ 5.7, $J_{5,6'}$ 7.0 Hz, H-5), 3.62 (m, 2H, H-6,6'), 2.95 (dd, 1H, $J_{2,3}$ 7.1, $J_{2,2'}$ 17.9 Hz, H-2), 2.47 (dd, 1H, $J_{2',3}$ 4.0 Hz, H-2'). HR-MS / EI: $C_{13}H_{16}O_5$ $(M)^+$. Calc.: 252.0998. Found: 252.0995.

6-O-Benzyl-2-deoxy-L-xylo-*hexonic acid γ-lactone* (**32**). Yield 363 mg (57%); mp. 95 - 97°C; $[\alpha]_D^{25}$ +42.8° (*c* 1.95, chloroform); ν_{max} (film): 1777 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.57 (m, 3H, CH_2Ph, H-3), 4.35 (t, 1H, $J_{4,3} = J_{4,5} = 5.5$ Hz, H-4), 4.28 (dt, 1H, H-5), 3.71 (dd, 1H, $J_{6,5}$ 5.4, $J_{6,6'}$ 9.5 Hz, H-6), 3.60 (dd, 1H, $J_{6',5}$ 7.3 Hz, H-6'), 2.77 (dd, 1H, $J_{2,3}$ 6.5, $J_{2,2'}$ 17.8 Hz, H-2), 2.60 (dd, 1H, $J_{2',3}$ 2.3 Hz, H-2').

6-O-Benzyl-2-deoxy-D-lyxo-*hexonic acid γ-lactone* (**37**). Yield 542 mg (85%); mp. 62 - 64°C; $[\alpha]_D^{20}$ -34.4° (*c* 1.15, chloroform); ν_{max} (film): 1770 cm^{-1}. HR-MS / EI: $C_{13}H_{16}O_5$ $(M)^+$. Calc.: 252.0998. Found: 252.1000.

6-O-Benzyl-2-deoxy-D-xylo-*hexonic acid γ-lactone* (**38**). Yield 382 mg (60%); mp. 96 - 98°C; $[\alpha]_D^{20}$ -51.1° (*c* 1.1, chloroform). HR-MS / EI: $C_{13}H_{16}O_5$ $(M)^+$. Calc.: 252.0998. Found: 252.0998.

*Acetylation of **31** and **32***

To a solution of lactone **31** or **32** (370 mg, 1.46 mM) in pyridine (5 mL) acetic anhydride (1.5 mL) and DMAP (a small crystal) were added. The mixture was stirred overnight at room temperature. The solvents were evaporated. Column chromatography (eluent **H**) gave the pure product.

3,5-Di-O-acetyl-6-O-benzyl-2-deoxy-L-lyxo-*hexonic acid γ-lactone* (**33**). Yield 437 mg (89%); $[\alpha]_D^{20}$ +18.6° (*c* 0.6, chloroform); ν_{max} (film): 1790, 1747 cm^{-1}. ^1H NMR (C_6D_6): δ 5.29 (m, 1H, H-5), 4.96 (dt, 1H, H-3), 4.62 (dd, 1H, $J_{4,3}$ 1.5, $J_{4,5}$ 3.4 Hz, H-4), 4.20 (ABq, 2H, *J* 12.1 Hz, CH_2Ph), 3.46 (dd, 1H, $J_{6,5}$ 5.7, $J_{6,6'}$ 9.8 Hz, H-6), 3.42 (dd, 1H, $J_{6',5}$ 6.7 Hz, H-6'), 2.45 (dd, 1H, $J_{2,3}$ 7.4, $J_{2,2'}$ 18.6 Hz, H-2), 2.13 (dd, 1H, $J_{2',3}$ 1.8 Hz, H-2'), 1.52 and 1.43 (2s, 6H, 2 × OAc). HR-MS / EI: $C_{17}H_{20}O_7$ $(M)^+$. Calc.: 336.1209. Found: 336.1210.

3,5-Di-O-acetyl-6-O-benzyl-2-deoxy-L-xylo-*hexonic acid γ-lactone* (**34**). Yield 417 mg (85%); $[\alpha]_D^{20}$ +21.6° (*c* 1.1, chloroform); ν_{max} (film): 1792, 1744 cm^{-1}. ^1H NMR (C_6D_6): δ 5.41 (m, 1H, H-5), 4.94 (m, 1H, H-3), 4.50 (dd, 1H, $J_{4,3}$ 4.8, $J_{4,5}$ 5.9 Hz, H-4), 4.19 (ABq, 2H, *J* 11.9 Hz, CH_2Ph), 3.44 (dd, 1H, $J_{6,5}$ 5.6, $J_{6,6'}$ 10.2 Hz, H-6), 3.41 (dd, 1H, $J_{6',5}$ 5.4 Hz, H-6'), 2.20 (dd, 1H, $J_{2,3}$ 4.8, $J_{2,2'}$ 17.9 Hz, H-2), 2.13 (dd, 1H, $J_{2',3}$ 7.4 Hz, H-2'). HR-MS / EI: $C_{17}H_{20}O_7$ $(M)^+$. Calc.: 336.1209. Found: 336.1210.

*Reduction of uronic esters **39**, **40**, **47**, **48**, **ent-47**, **ent-48**, **56**, **57** and **67**. General procedure.*

To a solution of ester (2.5 mM) in dichloromethane (25 mL) cooled to -20°C, DIBAH (1.2 M solution in toluene, 12.5 mL, 15.0 mM) was slowly added, the mixture was stirred for 3 h, and allowed to attain room temperature. Methanol (5 mL) and water (1 mL) were very slowly added. Stirring was continued for 1 h. To the mixture was added silica gel (5 - 10 g) and the solvents were evaporated. Column chromatography (eluent **H**) of the residue gave the pure product.

Methyl 6-deoxy-1,2-O-isopropylidene-α-L-talo-*heptofuranoside* (**41**)

Yield: 366 mg (59%); mp.: 52 - 53°C; $[\alpha]_D^{24}$ -43.8° (*c* 1.1, chloroform). ^1H NMR ($CDCl_3$): δ 4.98 (s, 1H, H-1), 4.81 (d, 1H, $J_{3,2}$ 6.0 Hz, H-3), 4.58 (d, 1H, H-2), 4.33 (d, 1H, $J_{4,5}$ 3.2 Hz, H-4), 3.83 (m, 2H, H-7,7'), 3.78 (m, 1H, H-5), 3.47 (s, 3H, OCH_3), 1.70 - 1.83 (m, 2H, H-6,6'), 1.48 (d, 3H, *J* 0.4 Hz, *Me*CMe), 1.32 (d, 3H, *J* 0.5 Hz, MeC*Me*). HR-MS / EI: $C_{10}H_{17}O_6$ $(M\text{-}CH_3)^+$. Calc.: 233.1025. Found: 233.1017.

*Methyl 6-deoxy-1,2-O-isopropylidene-β-D-*allo-*heptofuranoside* (**42**)

Yield: 570 mg (92%); $[\alpha]_D^{20}$ -52.3° (*c* 8.5, chloroform). ^{1}H NMR ($CDCl_3$): δ 4.98 (s, 1H, H-1), 4.88 (d, 1H, $J_{3,2}$ 6.0 Hz, H-3), 4.58 (d, 1H, H-2), 4.23 (d, 1H, $J_{4,5}$ 2.2 Hz, H-4), 3.93 (m, 1H, H-5), 3.85 (m, 2H, H-7,7'), 3.45 (s, 3H, OCH_3), 1.72 - 1.83 (m, 2H, H-6,6'), 1.48 (d, 3H, *J* 0.5 Hz, *Me*CMe), 1.33 (d, 3H, *J* 0.5 Hz, MeC*Me*). HR-MS / EI: $C_{10}H_{17}O_6$ $(M\text{-}CH_3)^+$. Calc.: 233.1025. Found: 233.1022.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-β-D-*altro-*heptofuranose* (**49**)

Yield: 486 mg (60%); $[\alpha]_D^{20}$ +10.3° (*c* 1.1, chloroform). ^{1}H NMR ($CDCl_3$): δ 5.90 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1), 4.68 (dd, 1H, $J_{2,3}$ 1.0 Hz, H-2), 4.65 and 4.59 (ABq, 2H, *J* 11.6 Hz, CH_2Ph), 4.21 (dd, 1H, $J_{3,4}$ 3.3 Hz, H-3), 4.07 (m, 1H, H-5), 4.00 (dd, 1H, $J_{4,5}$ 6.3 Hz, H-4), 3.89 (m, 2H, H-7,7'), 1.88 (m, 1H, H-6), 1.70 (m, 1H, H-6'), 1.53 and 1.34 (2s, 6H, CMe_2). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1339.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-α-L-*galacto-*heptofuranose* (**50**)

Yield: 390 mg (48%); $[\alpha]_D^{20}$ +21.8° (*c* 3.1, chloroform). ^{1}H NMR ($CDCl_3$): δ 5.92 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1), 4.68 (dd, 1H, $J_{2,3}$ 0.8 Hz, H-2), 4.65 and 4.54 (ABq, 2H, *J* 11.8 Hz, CH_2Ph), 3.96 (dd, 1H, $J_{4,3}$ 3.0, $J_{4,5}$ 7.1 Hz, H-4), 3.93 (m, 2H, H-3,5), 3.81 (m, 2H, H-7,7'), 1.66 (m, 2H, H-6,6'), 1.53 and 1.34 (2s, 6H, CMe_2). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1261.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-β-L-*altro-*heptofuranose* (**ent-49**)

Yield: 470 mg (58%); $[\alpha]_D^{20}$ -10.8° (*c* 1.3, chloroform). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1339.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-α-D-*galacto-*heptofuranose* (**ent-50**)

Yield: 300 mg (37%); $[\alpha]_D^{20}$ -25.0° (*c* 1.1, chloroform). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1327.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-α-D-*gluco-*heptofuranose* (**58**)

Yield: 413 mg (51%); mp.: 51 - 52°C; $[\alpha]_D^{20}$ -52.5° (*c* 1.1, chloroform). ^{1}H NMR ($CDCl_3$): δ 5.95 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.74 and 4.55 (ABq, 2H, *J* 11.8 Hz, CH_2Ph), 4.64 (d, 1H, H-2), 4.16 (m, 1H, H-5), 4.11 (d, 1H, $J_{3,4}$ 3.3 Hz, H-3), 4.04 (dd, 1H, $J_{4,5}$ 7.7 Hz, H-4), 3.87 (m, 2H, H-7,7'), 1.92 (m, 1H, H-6), 1.75 (m, 1H, H-6'), 1.49 and 1.32 (2s, 6H, CMe_2). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1338.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-β-L-*ido-*heptofuranose* (**59**)

Yield: 455 mg (56%); mp.: 68 - 69°C; $[\alpha]_D^{20}$ -62.2° (*c* 0.36, chloroform). ^{1}H NMR ($CDCl_3$): δ 6.00 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.72 and 4.46 (ABq, 2H, *J* 11.8 Hz, CH_2Ph), 4.66 (d, 1H, H-2), 4.20 (m, 1H, H-5), 4.07 (dd, 1H, $J_{4,3}$ 3.5, $J_{4,5}$ 5.4 Hz, H-4), 3.98 (d, 1H, H-3), 3.80 (m, 2H, H-7,7'), 1.80 (m, 1H, H-6), 1.58 (m, 1H, H-6'), 1.49 and 1.33 (2s, 6H, CMe_2). HR-MS / EI: $C_{16}H_{21}O_6$ $(M\text{-}CH_3)^+$. Calc.: 309.1338. Found: 309.1338.

*Methyl 6-deoxy-2,3-O-isopropylidene-β-L-*gulo-*heptofuranoside* (**69**)

Yield: 410 mg (66%); mp.: 55 - 57°C; $[\alpha]_D^{20}$ +67.6° (*c* 1.4, chloroform). ^{1}H NMR ($CDCl_3$): δ 4.95 (s, 1H, H-1), 4.74 (dd, 1H, $J_{3,2}$ 5.9, $J_{3,4}$ 3.6 Hz, H-3), 4.58 (d, 1H, H-2), 4.26 (m, 1H, H-5), 3.88 (m, 2H, H-7,7'), 3.83 (dd, 1H, $J_{4,5}$ 5.6 Hz, H-4), 3.34 (s, 3H, OCH_3), 1.88 (m, 2H, H-6,6'), 1.47 and 1.30 (2s, 6H, CMe_2). HR-MS / EI: $C_{10}H_{17}O_6$ $(M\text{-}CH_3)^+$. Calc.: 233.1025. Found: 233.1026.

Debenzylation of ***56*** *-* ***59****. General procedure.*

To a solution of benzyl ether **58** or **59** (1.5 mM) in ethanol (10 mL) 10% Pd / C was added (300 mg) and the suspension was hydrogenated at atmospheric pressure for 1 h. The mixture was filtered through a Celite pad, washed with warm methanol, and the filtrate was concentrated to dryness. The product, which is sufficiently pure for the next reaction step, was obtained in a quantitative yield.

Debenzylation of **56** or **57** (0.5 mM) needed longer (16 h) reaction time. After filtration through a short silica gel column (eluent: ethyl acetate) the pure product was obtained.

*6-Deoxy-1,2-O-isopropylidene-α-D-*gluco*-heptofuranose* (**60**)
$[\alpha]_D^{20}$ -3.5° (*c* 1.4, etanol). ^{1}H NMR ($CDCl_3$): δ 5.96 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.53 (d, 1H, H-2), 4.35 (m, 1H, H-3), 3.98 (dd, 1H, $J_{4,3}$ 2.8, $J_{4,5}$ 5.4 Hz, H-4), 3.85 - 3.97 (m, 3H, H-5,7,7'), 1.89 (m, 2H, H-6,6'), 1.48 and 1.32 (2s, 6H, CMe_2). HR-MS / EI: $C_9H_{15}O_6$ $(M\text{-}CH_3)^+$. Calc.: 219.0868. Found: 219.0869.

*6-Deoxy-1,2-O-isopropylidene-β-L-*ido*-heptofuranose* (**61**)
Mp.: 98 - 101°C; $[\alpha]_D^{20}$ -32.9° (*c* 1.2, methanol). ^{1}H NMR ($CDCl_3$): δ 5.99 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.52 (dd, 1H, $J_{2,3}$ 0.5 Hz, H-2), 4.30 (m, 2H, H-3,5), 4.05 (t, 1H, $J_{4,3} = J_{4,5} = 3.0$ Hz, H-4), 3.94 (m, 1H, H-7), 3.87 (m, 1H, H-7'), 1.97 (m, 1H, H-6), 1.85 (m, 1H, H-6'), 1.49 and 1.33 (2s, 6H, CMe_2). HR-MS / EI: $C_9H_{15}O_6$ $(M\text{-}CH_3)^+$. Calc.: 219.0868. Found: 219.0868.

*Methyl 6-deoxy-1,2-O-isopropylidene-α-D-*gluco*-heptofuranuronate* (**76**)
Yield: 88 mg (67%); $[\alpha]_D^{20}$ -10.3° (*c* 4.8, methanol); lit.[49] $[\alpha]_D^{22}$ -5° (*c* 3.5, chloroform); ν_{max} (film): 1730 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.95 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.54 (d, 1H, H-2), 4.40 (m, 1H, H-5), 4.36 (d, 1H, $J_{3,4}$ 2.8 Hz, H-3), 4.01 (dd, 1H, $J_{4,5}$ 6.8 Hz, H-4), 3.73 (s, 3H, $COOCH_3$), 2.78 (dd, 1H, $J_{6,5}$ 3.1, $J_{6,6'}$ 16.7 Hz, H-6), 2.64 (dd, 1H, $J_{6',5}$ 9.3 Hz, H-6'), 1.48 and 1.32 (2s, 6H, CMe_2). HR-MS / EI: $C_{10}H_{15}O_7$ $(M\text{-}CH_3)^+$. Calc.: 247.0818. Found: 247.0816.

*Methyl 6-deoxy-1,2-O-isopropylidene-β-L-*ido*-heptofuranuronate* (**77**)
Yield: 106 mg (81%); $[\alpha]_D^{20}$ -28.9° (*c* 3.3, methanol); ν_{max} (film): 1729 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.99 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.53 (dd, 1H, $J_{2,3}$ 0.6 Hz, H-2), 4.50 (m, 1H, H-5), 4.27 (dd, 1H, $J_{3,4}$ 2.8 Hz, H-3), 4.03 (t, 1H, H-4), 3.73 (s, 3H, $COOCH_3$), 2.84 (dd, 1H, $J_{6,5}$ 8.4, $J_{6,6'}$ 16.7 Hz, H-6), 2.64 (dd, 1H, $J_{6',5}$ 4.5 Hz, H-6'), 1.48 and 1.32 (2s, 6H, CMe_2). HR-MS / EI: $C_{10}H_{15}O_7$ $(M\text{-}CH_3)^+$. Calc.: 247.0818. Found: 247.0816.

*Methylation of diols **49**, **50**, **ent-49** and **ent-50**. General procedure.*
To a solution of diol (32 mg, 0.1 mM) in DMF (2 mL) sodium hydride (0.4 mM) was added and the mixture was stirred for 1 h. Iodomethane (32 μL, 0.5 mM) was added and the stirring was continued overnight. Water (2 drops) was added and the solvents were evaporated. Column chromatography (eluent **H**) of the residue gave the pure product.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-5,7-di-O-methyl-β-D-*altro*-heptofuranose* (**51**)
Yield: 25 mg (71%); $[\alpha]_D^{20}$ +14.8° (*c* 2.7, chloroform). ^{1}H NMR ($CDCl_3$): δ 5.87 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1), 4.63 (d, 1H, H-2), 4.59 (s, 2H, CH_2Ph), 4.07 (d, 1H, $J_{3,4}$ 2.8 Hz, H-3), 3.94 (dd, 1H, $J_{4,5}$ 7.8 Hz, H-4), 3.46 - 3.57 (m, 3H, H-5,7,7'), 3.39 and 3.32 (2s, 6H, 2 × OCH_3), 2.00 (m, 1H, H-6), 1.73 (m, 1H, H-6'), 1.54 and 1.33 (2s, 6H, CMe_2). HR-MS / EI: $C_{18}H_{25}O_6$ $(M\text{-}CH_3)^+$. Calc.: 337.1651. Found: 337.1652.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-5,7-di-O-methyl-α-L-*galacto*-heptofuranose* (**52**)
Yield: 32 mg (91%); $[\alpha]_D^{20}$ +22.6° (*c* 3.0, chloroform). ^{1}H NMR ($CDCl_3$): δ 5.84 (d, 1H, $J_{1,2}$ 4.2 Hz, H-1), 4.64 (dd, 1H, $J_{2,3}$ 0.5 Hz, H-2), 4.66 and 4.54 (ABq, 2H, *J* 11.6 Hz, CH_2Ph), 3.90 (m, 2H, H-3,4), 3.42 - 3.52 (m, 3H, H-5,7,7'), 3.43 and 3.31 (2s, 6H, 2 × OCH_3), 1.79 (m, 1H, H-6), 1.68 (m, 1H, H-6'), 1.56 and 1.37 (2s, 6H, CMe_2). HR-MS / EI: $C_{18}H_{25}O_6$ $(M\text{-}CH_3)^+$. Calc.: 337.1651. Found: 337.1649.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-5,7-di-O-methyl-β-L-*altro*-heptofuranose* (**ent-51**)
Yield: 24 mg (69%); $[\alpha]_D^{20}$ -14.0° (*c* 2.9, chloroform). HR-MS / EI: $C_{18}H_{25}O_6$ $(M\text{-}CH_3)^+$. Calc.: 337.1651. Found: 337.1646.

*3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-5,7-di-O-methyl-α-D-*galacto*-heptofuranose* (**ent-52**)
Yield: 19 mg (54%); $[\alpha]_D^{20}$ -21.2° (*c* 2.2, chloroform); lit.[21]: $[\alpha]_D^{20}$ -23.6° (*c* 4.3, chloroform). ^{1}H NMR ($CDCl_3$): identical as for **34**[4]. HR-MS / EI: $C_{18}H_{25}O_6$ $(M\text{-}CH_3)^+$. Calc.: 337.1651. Found: 337.1656.

*Hydrolysis and acetylation of **41**, **42**, **60**, **61**, **68**[22] and **69**. General procedure.*

A solution of protected heptofuranose(side) (0.5 mM) in 70% acetic acid (20 mL) was heated at 80-90°C for 24 h. The solvents were coevaporated with toluene, and the residue was dissolved in pyridine (3 mL). Acetic anhydride (1.5 mL) and DMAP (a small crystal) were added. Stirring was continued overnight, the solvents were evaporated, and the product was isolated by column chromatography.

*6-Deoxy-1,2,3,4,7-penta-O-acetyl-αβ-L-*talo*-heptopyranose* (**43**)

Eluent **H**; yield: 148 mg (73%). An analytical sample was separated by HPLC (eluent **I**) to give pure α and β anomers in a proportion of 1.5 : 1.0.

*6-Deoxy-1,2,3,4,7-penta-O-acetyl-α-L-*talo*-heptopyranose* (**43α**): $[\alpha]_D^{27}$ -75.3° (*c* 7.3, chloroform). ^{1}H NMR ($CDCl_3$): δ 6.13 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1), 5.33 (t, 1H, $J_{3,4}$ 3.6 Hz, H-3), 5.25 (m, 1H, H-4), 5.10 (m, 1H, $J_{2,3}$ 3.9, $J_{2,4}$ 1.0 Hz, H-2), 4.19 (m, 2H, H-7,7'), 4.15 (m, 1H, H-5), 2.16, 2.15, 2.14, 2.03 and 2.01 (5s, 15H, 5 × OAc), 2.00 (m, 1H, H-6), 1.77 (m, 1H, H-6'). HR-MS / EI: $C_{15}H_{21}O_9$ $(M\text{-}OAc)^+$. Calc.: 345.1186. Found: 345.1170.

*6-Deoxy-1,2,3,4,7-penta-O-acetyl-β-L-*talo*-heptopyranose* (**43β**): $[\alpha]_D^{27}$ -15.2° (*c* 3.8, chloroform). ^{1}H NMR ($CDCl_3$): δ 5.81 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 5.40 (m, 1H, $J_{2,3}$ 3.6, $J_{2,4}$ 0.9 Hz, H-2), 5.23 (m, 1H, $J_{4,3}$ 3.7, $J_{4,5}$ 1.3 Hz, H-4), 5.15 (t, 1H, H-3), 4.20 (m, 1H, H-7), 4.13 (m, 1H, H-7'), 3.91 (m, 1H, $J_{5,6}$ 4.1, $J_{5,6'}$ 9.0 Hz, H-5), 2.20, 2.15, 2.11, 2.05 and 2.00 (5s, 15H, 5 × OAc), 2.05 (m, 1H, H-6), 1.83 (m, 1H, H-6'). HR-MS / EI: $C_{15}H_{21}O_9$ $(M\text{-}OAc)^+$. Calc.: 345.1186. Found: 345.1170.

*6-Deoxy-1,2,3,4,7-penta-O-acetyl-α-D-*allo*-heptopyranose* (**44**)

Eluent **J**; yield: 164 mg (81%); $[\alpha]_D^{20}$ +8.4° (*c* 6.2, chloroform). ^{1}H NMR ($CDCl_3$): δ 5.95 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 5.67 (t, 1H, $J_{3,2} = J_{3,4}$ = 3.0 Hz, H-3), 4.96 (dd, 1H, H-2), 4.80 (dd, 1H, $J_{4,5}$ 10.1 Hz, H-4), 4.18 (m, 2H, H-7,7'), 4.08 (m, 1H, $J_{5,6}$ 3.0, $J_{5,6'}$ 9.0 Hz, H-5), 2.17, 2.11, 2.05, 2.03 and 2.01 (5s, 15H, 5 OAc), 1.93 (m, 1H, H-6), 1.77 (m, 1H, H-6'). HR-MS / EI: $C_{15}H_{21}O_9$ $(M\text{-}OAc)^+$. Calc.: 345.1186. Found: 345.1177.

*6-Deoxy-1,2,3,4,7-penta-O-acetyl-αβ-D-*gluco*-heptopyranose* (**62**)

Eluent **G**; yield: 180 mg (89%); mp.: 83 - 85°C. ^{1}H NMR ($CDCl_3$): δ 6.28 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1α), 5.67 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1β), 5.44 (t, 1H, $J_{3,2} = J_{3,4}$ = 10.3 Hz, H-3α), 5.22 (t, 1H, $J_{3,2}$ 9.6 Hz, H-3β), 5.10 (dd, 1H, H-2β), 5.07 (dd, 1H, H-2α), 4.93 (t, 2H, H-4α,4β), 4.19 (m, 2H, H-7α,7β), 4.12 (m, 2H, H-7'α,7'β), 4.01 (m, 1H, $J_{5,4}$ 9.7, $J_{5,6}$ 2.8, $J_{5,6'}$ 9.7 Hz, H-5α), 3.72 (m, 1H, $J_{5,4} = J_{5,6}$ = 9.3, $J_{5,6'}$ 2.9 Hz, H-5β), 1.90 (m, 2H, H-6α,6β), 1.80 (m, 2H, H-6'α,6'β). *Anal.*: $C_{17}H_{24}O_{11}$ (404.37). Calc.: C 50.49, H 5.98. Found: C 50.39, H 6.05.

*6-Deoxy-penta-O-acetyl-L-*ido*-heptose* (**64**)

Eluent **G**; yield: 156 mg (77%) as a mixture of pyranose and furanose forms in a proportion of 9.4 : 5.2 : 1.2 : 1.0. ^{1}H NMR ($CDCl_3$): δ (for two major products) 6.03 (m, H-1a,1b), 5.18 (t, *J* 3.8 Hz, H-3a), 5.05 (m, *J* 0.9, 4.7 Hz, H-3b), 5.00 (m, *J* 0.7, 1.9 and 4.0 Hz, H-2a), 4.93 (m, *J* 0.6, 2.7 and 4.7 Hz, H-2b), 4.89 (m, H-4b), 4.81 (m, *J* 0.6, 2.4 and 3.4 Hz, H-4a), 4.32 (m, *J* 2.7, 3.5 and 9.7 Hz, H-5b), 4.03 - 4.25 (m, H-5a,7a,7'a,7b,7'b), 1.74 - 2.10 (m, H-6a,6'a,6b,6'b), 2.04 - 2.15 (OAc). HR-MS / EI: $C_{15}H_{21}O_9$ $(M\text{-}OAc)^+$. Calc.: 345.1186. Found: 345.1184.

*6-Deoxy-1,2,3,4,7-penta-O-acetyl-αβ-D-*manno*-heptopyranose* (**70**)

Eluent **H**; yield: 170 mg (84%). ^{1}H NMR ($CDCl_3$): δ 6.02 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1α), 5.82 (d, 1H, $J_{1,2}$ 1.2 Hz, H-1β), 5.48 (dd, 1H, $J_{2,3}$ 3.0 Hz, H-2β), 5.32 (dd, 1H, $J_{3,2}$ 3.5, $J_{3,4}$ 10.0 Hz, H-3α), 5.25 (dd, 1H, H-2α), 5.18 (t, 1H, $J_{4,5}$ 10.0 Hz, H-4α), 5.13 (m, 1H, $J_{4,3}$ 9.9, $J_{4,5}$ 9.2 Hz, H-4β), 5.10 (dd, 1H, H-3β), 4.23 (m, 2H, H-7α,7'α), 4.12 (m, 2H, H-7β,7'β), 3.93 (m, 1H, H-5α), 3.67 (m, 1H, H-5β), 1.90 (m, 4H, H-6α,6'α,6β,6'β). *Anal.*: $C_{17}H_{24}O_{11}$ (404.37). Calc.: C 50.49, H 5.98. Found: C 50.62, H 6.14.

*6-Deoxy-1,2,3,4,7-penta-O-acetyl-αβ-L-*gulo*-heptopyranose* (**71**)

Eluent **G**; yield: 174 mg (86%). ^{1}H NMR ($CDCl_3$): δ 5.97 (d, 1H, $J_{1,2}$ 8.7 Hz, H-1α), 5.55 (t, 1H, $J_{3,2} = J_{3,4}$ = 5.6 Hz, H-3β), 5.43 (m, 1H, $J_{3,2}$ 3.4, $J_{3,4}$ 3.6 Hz, H-3α), 5.31 (m, 1H, H-5β), 5.20 (dd, 1H, $J_{2,1}$ 2.4

Hz, H-2β), 5.10 (dd, 1H, H-2α), 5.01 (d, 1H, H-1β), 4.92 (dd, 1H, $J_{4,5}$ 1.4 Hz, H-4α), 4.30 (t, 1H, $J_{4,5}$ 5.6 Hz, H-4β), 4.19 (m, 1H, H-5α), 4.10 (m, 4H, H-7α,7'α,7β,7'β), 1.75 - 1.98 (m, 4H, H-6α,6'α,6β,6'β). HR-MS / LSIMS: $C_{17}H_{25}O_{11}$ $(M+H)^+$. Calc.: 405.1397. Found: 405.1380.

*Deacetylation of **43**, **44**, **62**, **64**, **70** and **71**. General procedure.*

To a solution of peracetylated 6-deoxyheptose (1.0 mM) in methanol (10 mL) water (0.1 mL) and IRA-400 resin were added. Stirring was continued for 24 h. The suspension was filtered through Celite pad and washed with warm methanol. The filtrate was evaporated to dryness and dried under vacuum to give pure 6-deoxyheptose as free sugar.

*6-Deoxy-L-*talo*-heptose* (**45**)

Yield: 170 mg (87%) as a mixture of pyranose and furanose forms; $[\alpha]_D^{20}$ -31.8° (*c* 1.1, methanol, after 24h). ^{13}C NMR (CD_3OD): δ (major compound): 96.54 (C-1), 73.66, 73.13, 68.73, 67.01, 59.61 (C-7), 35.05 (C-6). HR-MS / LSIMS: $C_7H_{15}O_6$ $(M+H)^+$. Calc.: 195.0869. Found: 195.0869.

*6-Deoxy-D-*allo*-heptose* (**46**)

Yield: 163 mg (84%); mp.: 104 - 106°C; $[\alpha]_D^{20}$ +29.6° (*c* 1.05, methanol, after 24h). ^{13}C NMR (CD_3OD): δ 95.28 (C-1), 73.58, 72.87, 72.80, 71.92, 59.86 (C-7), 35.95 (C-6). HR-MS / LSIMS: $C_7H_{14}O_6Na$ $(M+Na)^+$. Calc.: 217.0688. Found: 217.0695.

*6-Deoxy-D-*gluco*-heptose* (**63**)

Yield: 165 mg (85%); $[\alpha]_D^{20}$ +62.9° (*c* 1.0, methanol, after 24h). ^{13}C NMR (CD_3OD): δ 98.06 (C-1β), 93.76 (C-1α), 77.96 (β), 76.40 (β), 75.90 (α), 75.48 (β), 74.77 (α), 74.28 (β), 73.96 (α), 69.54 (α), 60.03 (C-7α), 59.59 (C-7β), 35.90 (C-6α), 35.82 (C-6β). HR-MS / LSIMS: $C_7H_{15}O_6$ $(M+H)^+$. Calc.: 195.0869. Found: 195.0866.

*6-Deoxy-L-*ido*-heptose* (**65**)

Yield: 117 mg (60%); $[\alpha]_D^{20}$ -9.2° (*c* 1.0, methanol, after 24h). ^{13}C NMR (CD_3OD): δ 95.79, 93.94, 78.72, 72.58, 72.40, 72.16, 72.08, 71.68, 71.39, 67.58, 59.70, 59.57, 34.89, 33.15. HR-MS / LSIMS: $C_7H_{15}O_6$ $(M+H)^+$. Calc.: 195.0869. Found: 195.0866.

*6-Deoxy-D-*manno*-heptose* (**72**)

Yield: 169 mg (87%); $[\alpha]_D^{20}$ +37.0° (*c* 1.4, methanol, after 24h); lit.[35]: $[\alpha]_D^{20}$ +25° (*c* 0.7, water). HR-MS / LSIMS: $C_7H_{15}O_6$ $(M+H)^+$. Calc.: 195.0869. Found: 195.0866.

*6-Deoxy-L-*gulo*-heptose* (**73**)

Yield: 157 mg (81%); $[\alpha]_D^{20}$ -1.1° (*c* 1.4, methanol, after 24h). ^{13}C NMR (CD_3OD): δ 95.73 (C-1α), 95.47 (C-1β), 73.81 (β), 73.35 (α), 73.03 (α), 72.92 (β), 71.20 (α), 70.91 (α), 65.97 (β), 63.54 (β), 59.79 (C-7β), 59.75 (C-7α), 34.41 (C-6α), 34.17 (C-6β). HR-MS / LSIMS: $C_7H_{15}O_6$ $(M+H)^+$. Calc.: 195.0869. Found: 195.0866.

ACKNOWLEDGMENTS

This work was financed from the Grant No. P303 013 05 obtained from the State Committee for Scientific Research (KBN). Z. P. is grateful to the Foundation of the Polish Science (FNP) for a stipend.

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(*Received in UK* 23 *August* 1994; *revised* 31 *October* 1994; *accepted* 4 *November* 1994)