CYCLOADDITION REACTIONS LEADING TO CARBOHYDRATE DERIVATIVES. PART II. HETERO DIELS-ALDER REACTIONS OF MONOSACCHARIDE 1,1-DITHIOOXALATES AND O-THIOFORMATES. A COMPARATIVE STUDY[+]

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Abstract - A series of chiral dihydrothiopyran derivatives has been obtained in hetero Diels-Alder reactions of monosaccharide O-thioformates and 1,1-dithiooxalates with several butadienes. Diastereo- and regioselectivities of the reactions were studied.

Recently we have published a preliminary report[1] on Diels-Alder reactions of sugar O-thioformates. In the present paper these results will be described in detail in comparison with the data of similar studies on 1,1-dithiooxalates.

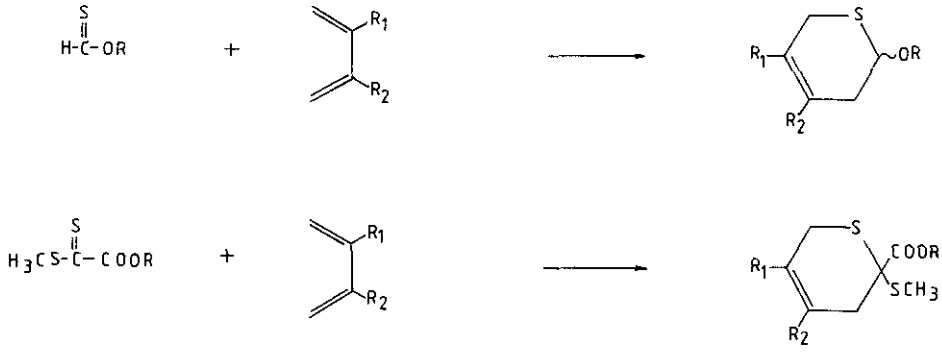
The 3,6-dihydro-2H-thiopyran skeleton can be used for the synthesis of 5-thiopyranose sugar analogs. Hetero Diels-Alder reaction of thiocarbonyl compounds[2] with dienes is regarded to be one of the simplest modes of preparing dihydrothiopyrans.

Vyas and Hay[3-6] employed [$4_\pi + 2_\pi$] cycloadditions of cyanodithioformates for the synthesis of (±)-6-thiodeoxyulopyranosidonic nitriles.

Diels-Alder reactions applied on chiral carrier molecules often exhibit diastereoselectivity and regioselectivity enabling their use in construction of chiral compounds[7]. David et al.[8] for example, synthesized disaccharides by means of cycloadditions of glycosyloxybutadienes with aldehydes. Albeit several examples are known for the application of dithio- or thionocarboxylates in [$4_\pi + 2_\pi$] cycloadditions[9-11], to the best of our knowledge, no attempt has been done to use them on chiral substrates.

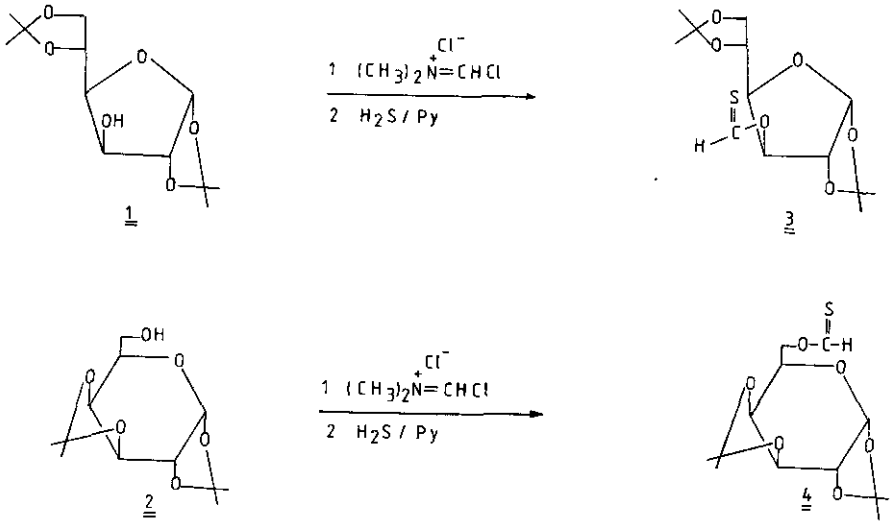
O-Thioformates and 1,1-dithiooxalates seem to be a suitable precursors for "sugar-like" dihydrothiopyrans as in Diels-Alder reactions with dienes the former type can lead to "glycosides", whereas the latter to "ketosides" of 6-thio-2-ulosonic acid-like compounds.

[+]Dedicated to Professor Sir D. H. R. Barton on the occassion of his 70th birthday.

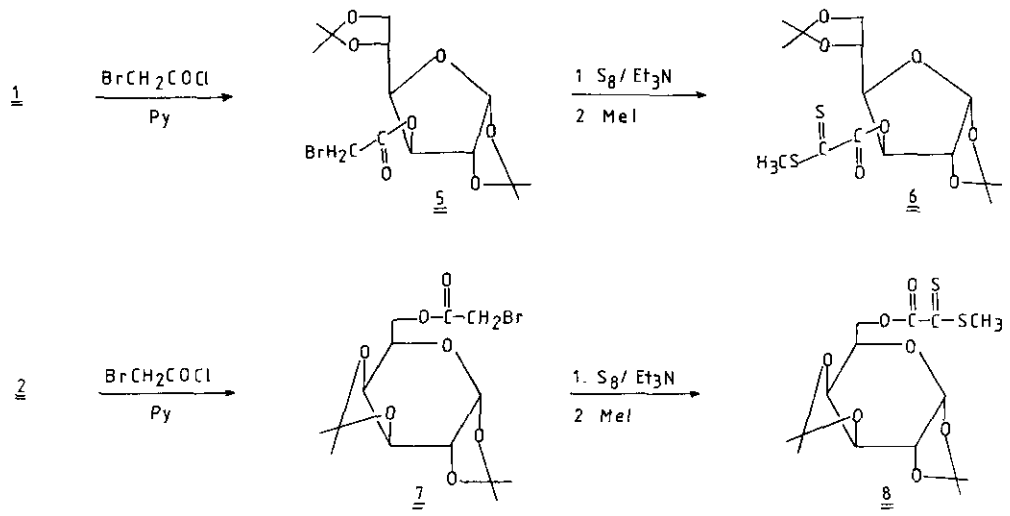


Since at least one new chiral center originates from the reactions it can be assumed that the application of a proper chiral alcohol as the R grouping would have directing influence on the stereochemical outcome of the reaction. For this reason simple sugar derivatives such as 1[12] and 2[13] were applied in the present experiments.

O-Thioformates were prepared according to the method of Barton and McCombie[14]:



1,1-Dithiooxalates can be obtained from bromoacetates by thiolation with elementary sulphur[15] or from dithiolanium ylides by cycloreversion[9]. For their Diels-Alder reaction only one example is known[9]. Sugar dithiooxalates 6 and 8 were prepared from 1 and 2 by the use of the method of Thiel et al.[15]



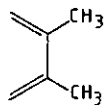
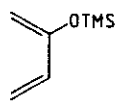
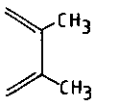
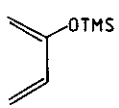
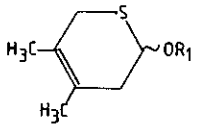
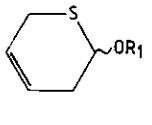
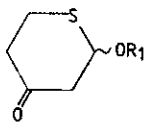
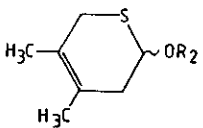
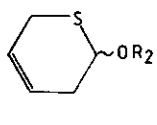
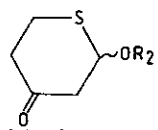
3 and 4 were allowed to react with butadiene, 2,3-dimethylbutadiene and 2-trimethylsilyloxybutadiene, respectively, under thermal conditions (160°C) to give diastereomeric mixtures of three types of thiopyran derivatives in excellent yields (Table 1.).

Although minor diastereoselection was observed in these cases, all of the stereoisomers in the glucose series 9a,b - 11a,b could be separeted easily using column chromatography. Analysis of the ^{1}H-nmr spectra (Table 2.) of 9a,b, 10a,b, 12a,b and 13a,b, respectively, clearly demonstrated the half-chair conformation of the dihydrothiopyran ring. In the case of 11a,b and 14a,b a complex nmr study was necessary to exclude the presence of the other regioisomer B.

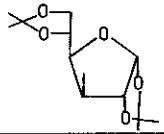
That fact was demonstrated by the evidences of spin-decouplings and COSY spectra[16] showing that H-2 and H-3 and H-3' protons were coupled only with each other, therefore an isolating group (>C=O) should be found in position 4. Similar information could be extracted from 2D ^{1}H/^{13}C shift-correlation maps and from the data of selective INEPT experiments[17]. With the use of the latter selective long-range couplings could be observed between H-2 and C-3 ($^{2}J_{C,H}$); H-2 and C-4 ($^{3}J_{C,H}$) and H-2 and C-6 ($^{3}J_{C,H}$), respectively, corroborating the fact that the keto group in 11a,b and 14a,b was located in position 4 of the thiopyran ring.

Table 1.

Diels-Alder reaction of compounds 3 and 4

	3 + 	3 + 	3 + 	4 + 	4 + 	4 + 
	 9a,b	 10a,b	 11a,b	 12a,b	 13a,b	 14a,b
Reaction time (h)	16	16	30	16	16	31
Ratio of diastereomers	1:1 (2:5)*	3:4	2:3	4:7	5:6	6:7
mp (°C)	a syrup / b 86-87	35-38 / syrup	92-94 / 76-78			
$[\alpha]_D^{20}$ ($CHCl_3$)	+7.71 (c 1.09) / -12.3 (0.73)	+5.83 (0.89) / -9.41 (1.35)	+7.13 (0.78) / -10.52 (1.07)			
Ir (cm^{-1})			1713.6 ($\nu_{C=O}$)			1712 ($\nu_{C=O}$)
Ms (m/z)	386 (M^+)	358 (M^+)	375 (M^+)	386 (M^+)	358 (M^+)	375 (M^+)
Anal. (Calcd.) C	59.47 (59.04) / 58.96	57.24 (56.96) / 56.85	54.26 (54.40) / 54.40	59.36	57.16	54.32
H	7.87 (7.82) / 7.58	7.40 (7.31) / 7.12	6.71 (6.95) / 7.01	7.83	7.42	6.72
S	8.61 (8.28) / 7.97	8.48 (8.93) / 8.68	8.58 (8.55) / 8.28	8.46	8.59	8.54

* Under 2.5 kbar

R_1 = 

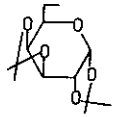
R_2 = 

Table 2.

^{1}H-Nmr. data of compounds 9a,b - 14a,b

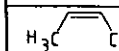
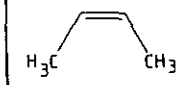
	9a	9b	10a	10b	11a	11b	12a,b	13a,b	14a,b
Glucose/ Galactose part	δ 5.86 (H-1); 4.30 (H-2); 4.58 (H-3); 4.09 (H-4); 4.11 (H-5); 4.18 (H-6); 3.97 (H-6') ppm. $J_{1,2}$=3.9 Hz; $J_{2,3}$=0 Hz; $J_{3,4}$=3.2 Hz; $J_{4,5}$=8.5 Hz; $J_{5,6}$=5.6 Hz; $J_{6,6'}$=8.5 Hz						δ 5.40 (H-1); 4.30 (H-2); 4.49 (H-3); 3.94 (H-4); 4.24 (H-5); 3.90 (H-6); 3.58 (H-6') ppm.		
Thiopyran δ (ppm)									
H-2	4.95	4.77	4.96	4.78	5.30	5.14	4.80	4.80	5.02
H-3e	2.57	2.57	2.63	2.65	2.90	2.91	2.64	2.66	2.90
H-3a	2.59	2.21	2.41	2.30		2.76	2.32	2.45	
H-4e	-	-	5.70	5.66	-	-	-	5.70	-
H-4a	-	-			-	-	-		-
H-5e	-	-	5.88	5.81	3.22	3.65	-	5.85	2.72
H-5a	-	-				3.45	-		
H-6e	3.27	3.40	3.35	3.51	2.75	2.65	3.30	3.35	3.20
H-6a	2.75	2.61	2.96	2.77			2.64	2.86	2.72
J (Hz)	2,3e=4.0	2,3e=3.7	2,3e=4.0	2,3e=3.5		2,3e=3.3			
	2,3a=2.6	2,3a=2.4	2,3a=3.0	2,3a=3.0		2,3a=3.5			
	3e,3a=17.0	3e,3a=17.5	2,6 =0.5	3e,3a=18.0		2,6 =1.5			
	6e,6a=16.5	6e,6a=17.0	3e,3a=18.0	3,6 =2.5		2e,2a=14.0			
	2,6e=0.8	2,6e=0.7	3,6 =2.5	3,4 =4.8					
			3,4=5.0	4,5 =11.0					
			4,5=11.0	5,6 =5.5					
			5,6=5.5	6e,6a=17.0					
			6e,6a=17.0						
	1.65; 1.75 1.64; 1.69						1.68; 1.73		
	Isopropylidene: 1.30-1.50								

Table 3.

^{13}C-Nmr shifts of compounds 9a - 11b

	9a	9b	10a	10b	11a	11b
Glucose part C-1	105.28	105.22	105.31	105.22	105.13	105.26
C-2	84.54	81.72	84.72	81.73	84.16	81.26
C-3	81.36	79.09	81.40	80.94	81.17	78.07
C-4	80.89	77.72	80.96	77.65	83.34	80.90
C-5	79.38	75.38	78.42	74.45	72.11	71.80
C-6	72.57	72.42	72.60	72.32	67.94	67.63
Thiane part						
C-2	67.82	66.87	67.90	67.07	81.48	79.77
C-3	39.00	39.09	32.49	32.54	49.70	49.77
C-4	122.06	122.26	123.11	123.07	205.04	204.97
C-5	122.94	123.06	124.73	123.94	42.81	42.66
C-6	25.41	25.39	22.34	21.34	24.30	23.82
Other Isopropylidene CH_3	25.2 - 27.40					
C_q	109.0 - 111.81					
	19.65; 20.05	19.47; 20.11				

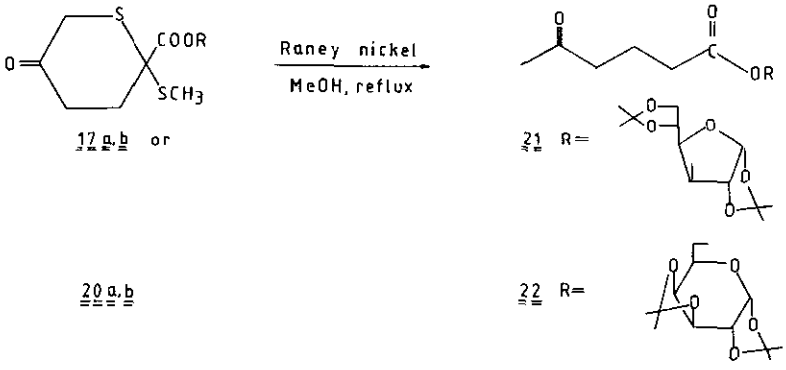
Comparing optical rotations of diastereomeric pairs 9a,b; 10a,b and 11a,b, respectively with the ^{1}H- and ^{13}C-nmr shifts at C-2 of the dihydrothiopyran ring one can establish that they are upfield shifted for the levorotatory isomer comparing with that of the dextrorotatory one. In the lack of any information about the most stable conformations of the thiopyran ring it could not be concluded for the absolute configuration of the new chirality center.

One attempt was done for the preparation of 9a,b under 2.5 kbar pressure. A promising, enhanced (2:5) stereoselectivity was observed. Experiments in these direction are under way.

Dithiooxalates 6 and 8 exhibited much higher dienophilic reactivity than O-thioformates. At room temperature reaction of the former with butadienes resulted in diastereomeric mixtures of compounds 15a,b - 20a,b (Table 4.). Due to the lower reaction temperatures slightly higher diastereoselection could be observed for the cycloadditions of 6 and 8 than that for the O-thioformates 3 and 4.

Configurations of C-2 in the thiopyran part 15a,b - 20a,b could not be deduced from the nmr spectra. Large homoallylic couplings ($^{5}J_{H,H}$) were observed between H-3,3' and H-6,6'. The ^{1}H chemical shifts (Table 5.) are very similar in the diastereomeric pairs a and b with the exception of glucose H-5 in both 15a,b and 16a,b. This may indicate the existence of distinct, preferred rotamer populations in the isomers resulting in differential shielding effects by virtue of the diamagnetic anisotropy of the >C=O group.

In order to verify the structures of compounds 17a,b and 20a,b they were desulphurized by Raney nickel to give the expected hexan-5-onoate esters 21 and 22, respectively.



17 a,b or 20 a,b

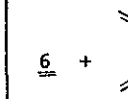
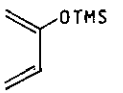
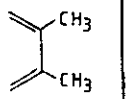
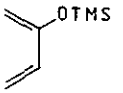
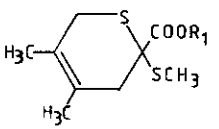
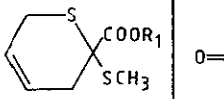
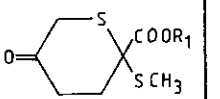
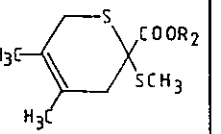
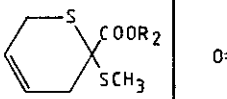
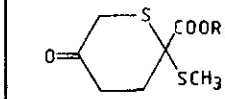
21 R=

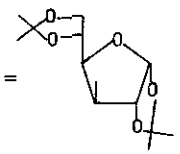
22 R=

In conclusion it can be established that ($4_{\pi}+2_{\pi}$) cycloaddition reactions of sugar O-thioformates and 1,1-dithiooxalates exhibit minor diastereoselectivity in general but for several examples they can lead to useful chiral dihydrothiopyran derivatives in good yields. The reason of the opposite regioselectivity of the thioformates and ditiooxalates in the reaction with an asymmetric diene is under investigation.

Table 4.

Reaction of 6 and 8 with dienes

	6 + 	6 + 	6 + 	8 + 	8 +	8 + 
						
	15a,b	16a,b	17a,b	18a,b	19a,b	20a,b
Reaction time (h)	1.5	8.0	16.0	1.5	6.0	16.0
Yield (%)	87.0	97.0	73.3	94.6	70.0	89.8
Ratio of isomers	1:2	1.6:4	7:10	9:13	1:1	1:9 (separable)
$[\alpha]_D^{20}$ ($CHCl_3$)						-46.79 (c 1.56) / -77.18 (c 1.63)
Ir (cm^{-1})	1734 (ν_{-COO})	1735 (ν_{-COO})	1720 (ν_{-CO}) 1730 (ν_{-COO})	1723 (ν_{-COO})	1723 (ν_{-COO})	1725 (ν_{-CO}) 1720 / 1730 (ν_{-COO}) 1735
Ms (m/z)	461 (M^+)	433 (M^+)	448 (M^+)	461 (M^+)	433 (M^+)	448 (M^+) / 448 (M^+)
Anal. (Calcd.) C	54.65 (54.76)	52.90 (52.75)	50.82 (50.87)	54.80	52.70	50.96 / 51.00
H	6.90 (7.00)	6.60 (6.52)	6.22 (6.29)	7.10	6.45	6.35 / 6.40
S	13.85 (13.92)	14.91 (14.82)	14.20 (14.29)	14.00	14.76	14.32 / 14.21

R_1 = 

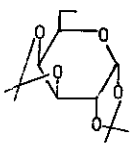
R_2 = 

Table 5.

^{1}H-Nmr spectral data of compounds 15a,b - 20a,b (200 MHz, $CDCl_3$)

δ (ppm)

	15a,b a	(b)	16a,b		17a,b	18a,b	19a,b		20a,b
Glucose/ Galactose part H-1	5.88	(5.86)	5.86	(5.84)			5.50	(5.51)	
H-2	4.43	(4.42)	4.42	(4.41)			4.32	(4.22)	
H-3	5.29	(5.32)	5.30	(5.28)			4.60	(4.61)	
H-4	4.18	(4.18)	4.17	(4.17)			4.22	(4.32)	
H-5	4.21	(4.33)	4.31	(4.19)			4.03	(4.06)	
H-6	4.13	(4.14)	4.12	(4.10)			4.43	(4.38)	
H-6'	3.98	(3.97)	3.96	(3.95)			4.23	(4.23)	
Thiane part									
H-3	2.88	(2.94)	2.88	(2.92)		2.45	2.95	(2.95)	
H-3'	2.47	(2.55)	2.57	(2.54)	2.44-2.96	2.88	2.57	(2.57)	2.40-2.70
H-4	-					-			2.67
H-5	-		5.73-5.81		2.44-2.96	-	5.75-5.81		2.86
H-6	3.24	(3.21)	3.31	(3.27)	2.99	3.26	3.34	(3.33)	3.02
H-6'	2.86	(2.83)	3.07	(3.01)	3.65	2.88	3.06	(3.02)	3.60
Other Isopropylidenes CH_3	1.30-1.53								
SCH_3	2.20								
H_3C CH_3	1.73; 1.76					1.72; 1.76			

EXPERIMENTAL

General methods: Melting points were determined on a Kofler block and are uncorrected. Solutions were concentrated at 40°C (bath) under diminished pressure. Chromatography was performed on Kieselgel 60. Optical rotations were measured with a Bendix automatic polarimeter. Ir spectra (KBr discs) were recorded with a Perkin-Elmer spectrophotometer, 200 MHz ^{1}H-nmr and 50.3 MHz ^{13}C-nmr spectra with a Bruker WP-200 SY spectrometer for solutions $CDCl_3$. Mass spectra were obatined by using a VG-7035 GC/MS/DS instrument.

3 and 4 were prepared by the use of the procedure of Barton and McCombie[14].

1,2:5,6-Di-O-isopropylidene-3-O-thioformyl-α-D-glucofuranose (3). Yield: 63.5 %. mp 77-78 °C. $[\alpha]_D^{20}$ -26.1° (c 2.18, $CHCl_3$). Ms (m/z): 304 (M^+). ^{1}H-Nmr ($CDCl_3$) δ 9.69 (s, 1H, -C(=S)-H); 6.00 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1); 4.18 (m, 2H, H-6,6'); 1.63; 1.50; 1.40 (singlets, 12H, $4CH_3$) ppm. Anal. Calcd for $C_{13}H_{20}O_6S$: C, 51.32; H, 6.58; S, 10.53. Found: C, 50.85; H, 6.39; S, 10.86.

1,2:3,4-Di-O-isopropylidene-6-O-thioformyl-α-D-galactopyranose (4). Yield: 95.0 %. mp 86-87°C. $[\alpha]_D^{20}$ -56.7° (c 1.64, $CHCl_3$). Ms (m/z): 304 (M^+). ^{1}H-Nmr ($CDCl_3$) δ 9.74 (s, 1H, -C(=S)-H); 5.58 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1) ppm. Anal. Calcd for $C_{13}H_{20}O_6S$: Found: C, 51.67; H, 7.00; S, 11.00.

Diels-Alder reaction of 3 and 4 were performed in toluene in a closed autoclave with an excess of the dienes. After completion of the reaction (tlc) in the case of 11a,b and 14a,b methanol was added to remove the trimethysilyl group. After evaporation the mixtures were chromatographed on silica gel using hexane -Et_2O (8:2) mixture as eluent.

1 and 2 were bromoacetylated according to the Ref. 18. to give 5 and 7, respectively. 5 has been described in Ref. 18.

6-O-Bromoacetyl-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (7). Obtained as a syrup. Yield: 61 %. $[\alpha]_D^{20}$ -24.55° (c 2.22, $CHCl_3$). Ms (m/z): 381 (M^+). Anal. Calcd for $C_{14}H_{21}O_7Br$: C, 44.11; H, 5.55; Br, 20.96. Found: C, 44.31; H, 5.62; Br, 21.10.

Preparation of 6 and 8:
Finely powdered sulphur (19 mmol) was suspended in a mixture of dry dimethylformamide (12 ml) and triethylamine (28 mmol) then 5 or 7 was added drop by drop to the stirred solution. After 2-3 h stirring the mixture was treated with methyl iodide (10.4 mmol) and after another 30 min of agitation it was poured in water, extracted with chloroform. The organic layer was washed with dilute citric acid, aqueous $NaHCO_3$, successively, and dried ($MgSO_4$). The product was purified by chromatography on silica gel using hexane -EtOAc (8:2) mixture as eluent.

1,2:5,6-Di-O-isopropylidene-3-O-(methylthio-thioxoacetyl)-α-D-glucofuranose (6). Reddish-violet crystals. Yield: 47.0 %. mp 78-79°C. $[\alpha]_D^{20}$ +8.65°(c 1.04, $CHCl_3$). Ir: 1720 cm^{-1} ($\nu_{C=O}$). Ms (m/z): 378 (M^+). Anal. Calcd for $C_{15}H_{22}O_7S_2$: C, 47.60; H, 5.86; S, 16.94. Found: C, 47.49; H, 5.80; S, 16.72.

1,2:3,4-Di-O-isopropylidene-6-O-(methylthio-thioxoacetyl)-α-D-galactopyranose (8). Red crystals. Yield: 61.9 %. mp 73-74°C. $[\alpha]_D^{20}$ -38.0° (c 1.50, $CHCl_3$). Ir: 1730 cm^{-1} ($\nu_{C=O}$). Ms (m/z): 378 (M^+). Anal. Calcd for $C_{15}H_{22}O_7S_2$: Found: C, 47.72; H, 5.86; S, 16.96.

Hetero Diels-Alder reaction of 6 and 8:
6 or 8 was allowed to react with a 20 % excess of the appropriate dienes in benzene at room temperature. After the reaction was complete the solution was evaporated and purified on a silica gel column using hexane -EtOAc (8:2) mixture as eluent. In the case of 17a,b and 20a,b the trimethylsilyloxy substituent was removed by methanolysis (r.t.) prior to purification.

Desulphurization of 17a,b and 20a,b:
The compounds were treated with a 15-fold excess of Raney nickel in boiling methanol for 5 h. After filtration the residue was chromatographed using $CHCl_3$-EtOAc (8:2) mixture as eluent.

1,2:5,6-Di-O-isopropylidene-3-O-(hexan-5'-onoyl)-α-D-glucofuranose (21): Yield: 31.7 %. $[\alpha]_D^{20}$ -25.90 (c 2.78, $CHCl_3$). Ir: 1710-1740 cm^{-1} ($\nu_{C=O}$). Ms (m/z): 372 (M^+). ^{1}H-Nmr data ($CDCl_3$): δ 5.88 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1); 4.19 (m, 2H, H-6,6'); 2.54 (t, 2H, $J_{2'-CH_2,3'-CH_2}$ = 7.5 Hz, 2'-CH_2); 2.40 (t, 2H, $J_{3'-CH_2,4'-CH_2}$ = 7.5 Hz, 4'-CH_2); 2.18 (s, 3H, 6'-CH_3); 1.91 (quintett, 2H, 3'-CH_2) ppm. Anal. Calcd for $C_{18}H_{28}O_8$: C, 58.05; H, 7.58. Found: C, 57.90; H, 7.50.

1,2:3,4-Di-O-isopropylidene-6-O-(hexan-5'-onoyl)-α-D-galactopyranose (22). Yield: 43.0 %. $[\alpha]_D^{20}$ -37.87° (c 2.93, $CHCl_3$). Ir: 1715-1740 cm^{-1} ($\nu_{C=O}$). Ms (m/z): 372 (M^+). ^{1}H-Nmr data ($CDCl_3$): δ 5.53 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1); 2.54 (t, 2H, $J_{2'-CH_2,3'-CH_2}$ = 7.5 Hz, 2'-CH_2); 2.39 (t, 2H, $J_{3'-CH_2,4'-CH_2}$ = 7.5 Hz, 4'-CH_2); 2.15 (s, 3H, 6'-CH_3); 1.90 (quintett, 2H, 3'-CH_2) ppm. Anal. Calcd for $C_{18}H_{28}O_8$. Found: C, 58.10; H, 7.62.

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