62. Glyconothio-*O*-lactones

Part I

Preparation and Reactions with Nucleophiles

by **Marianne Hürzeler**[a]), **Bruno Bernet**[b]), and **Andrea Vasella**[b])*[1])

[a])PRPV Bau 15, *F. Hoffmann-La Roche AG*, CH–4002 Basel

[b]) Organisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich

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Furanoid and pyranoid glyconothio-*O*-lactones were prepared by photolysis of *S*-phenacyl thioglycosides or by thermolysis of *S*-glycosyl thiosulfinates, which gave better results than the thionation of glyconolactones with *Lawesson*'s reagent. Thermolysis of the thiosulfinates obtained from the dimannofuranosyl disulfide **7** or the mannofuranosyl methyl disulfide **8** (*Scheme 2*) gave low yields of the thio-*O*-lactone **2**. However, photolysis of the *S*-phenacyl thioglycoside **6** obtained by *in situ* alkylation of the thiolato anion derived from **5** led in 78–89% to **2**. Similarly, the dithiocarbonate **10** was transformed, *via* **11a**, into the *ribo*-thio-*O*-lactone **12** (79%). Thermolysis of the peracetylated thiosulfinates **14** (*Scheme 3*) led to the intermediate thio-*O*-lactone **15**, which underwent facile β-elimination of AcOH ($\rightarrow$ **16**, 75%) during chromatography. The perbenzylated *S*-glucopyranosyl dithiocarbonate **18** (*Scheme 4*) was transformed either into the *S*-phenacyl thioglucoside **19** or into a mixture of the anomeric methyl disulfides **21a/b**. Whereas the photolysis of **19** led in moderate yield to 2-deoxy-thio-*O*-lactone **20**, oxidation of **21b** and thermolysis of resulting thiosulfinates gave the thio-*O*-lactone **4** (79%), which was transformed into **20** (36%) upon photolysis. The pyranoid *manno*-thio-*O*-lactone **26** was prepared in the same way and in good yields from **22** *via* the dithiocarbonate **24b** and the disulfide **25**. The ring conformations of the δ-thio-*O*-lactones, flattened $^4C_1$ for **15** and **4** and $B_{2,5}$ for **26**, are similar to the ones of the O-analogous oxo-glyconolactones. The reaction of **2** (*Scheme 5*) with MeLi and then with MeI gave the thioglycoside **27** (29%) and the dimeric thio-*O*-lactone **29** (47%). The analogous treatment of **2** with lithium dimethylcuprate ($LiCuMe_2$) and MeI led to a 4:1 mixture (47%) of **31** and **27**. The structure of **2** was proven by an X-ray analysis, and the configuration at C(6) and C(5) of **29** was deduced from NOE experiments. Substitution of MeI by CD_3I led to the CD_3S analogues of **27**, **29**, and **31**, *i.e.* **28**, **30**, and **32**, respectively, evidencing carbophilic addition and *'exo'*-attack on **2** by MeLi and the enethiolato anion derived from **2**. The preferred *'endo'*-attack of $LiCuMe_2$ is rationalized by postulating a single-electron transfer and a diastereoselective pyramidalization of the intermediate radical anion.

Introduction. – Preparative usefulness and mechanistic insight associated with the reactivity of new *S*-glycosyl derivatives directed our attention to (glycosylthio)sulfenyl halides, glycosylsulfenyl halides, and glyconothio-*O*-lactones. We have shown that (glycosylthio)sulfenyl halides are useful auxiliaries for the preparation of enantiomerically pure 2-halothiosulfides and thiiranes [1].

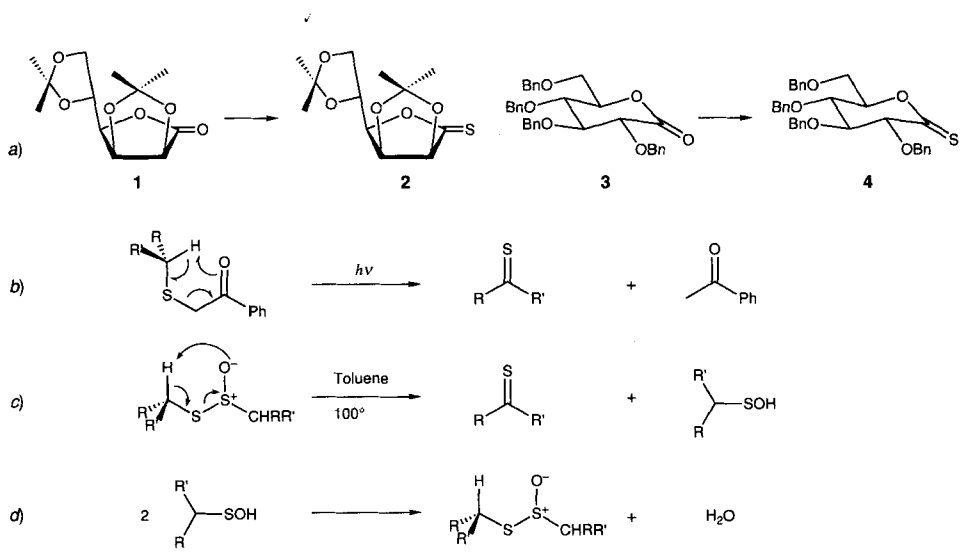
[1]) Present address: Laboratorium für Organische Chemie, ETH-Zentrum, Universitätsstrasse 16, CH–8092 Zürich

We now report our results on the synthesis of glyconothio-*O*-lactones and describe the reaction of a representative member of this class of compounds with MeLi and lithium dimethylcuprate(I) ($LiCuMe_2$).

Glyconothio-*O*-lactones were not known when we started with the project, and we conceived of several methods for their preparation. In the meantime, *Kahne et al.* [2] reported the synthesis of the gluconothio-*O*-lactone **4** (*Scheme 1*) using *Lawesson*'s reagent [3], and *Barrett* and *Lee* [4] reported the synthesis of a benzyl-protected furanoid and a methyl-protected pyranoid aldonothio-*O*-lactone in 80 and 42%, respectively, by using the more highly soluble 4-phenoxy analogue of *Lawesson*'s reagent (*Belleau*'s reagent [5]), which, although not commercially available, is easily prepared.

Results and Discussion. – Attempted thionation of the furanoid mannonolactone **1** (*Scheme 1a*) with bis[tri(cyclohexyl)tin] sulfide and boron trichloride [6] failed. In our hands, the reaction of the pyranoid gluconolactone **3** [7] with *Lawesson*'s reagent led to a complex mixture containing less than 30% of **4**. Similar results were obtained when the reactions were performed according to the experimental indications in [2]. In the analogous reaction with **1**, no trace of the thio-*O*-lactone **2** was found in the reaction mixture. The dependence of the yield upon the substrate [6] [8] [9] and upon small amounts of impurity [6], and the divergent results that *Kahne et al.* and we obtained highlight the desirability of further methods for the preparation of glyconothio-*O*-lactones.

Scheme 1

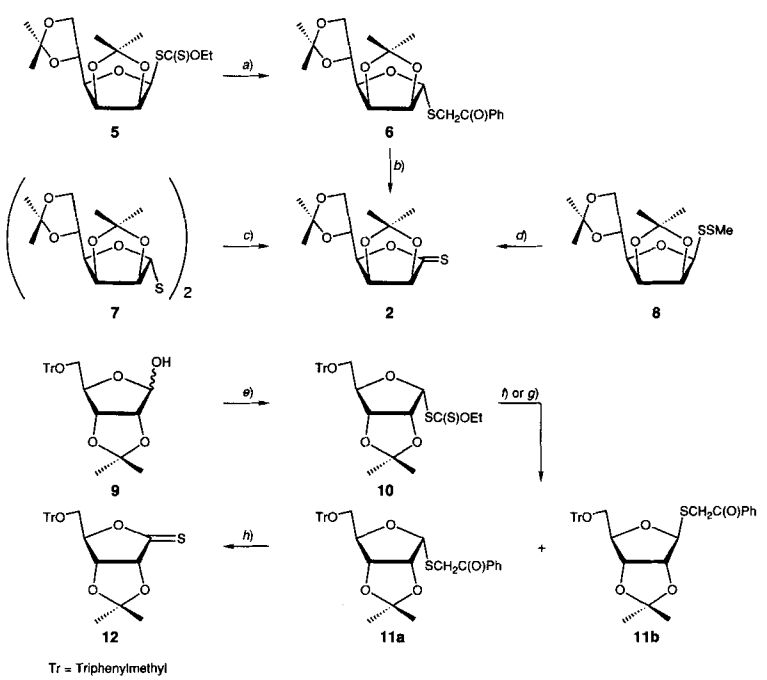


Among the methods for the preparation of the reactive thioaldehydes or thioketones [10] [11], the photochemical *Norrish*-II-type cleavage of phenacyl sulfides of *Vedejs et al.* [12] (*Scheme 1b*) and the thermolysis of *S*-alkyl thiosulfinates [13] [14] [15] (*Scheme 1c*) appeared appropriate for the preparation of glyconothio-*O*-lactones. The unstable thiosulfenic acids which are also produced during the thermolysis of thiosulfinates rapidly

condense and form thiosulfinates again [13] [16] (*Scheme 1d*). Both, thiosulfinates derived from symmetrical diglycosyl disulfides, or from the oxidation of *S*-alkyl-*S'*-glycosyl-disulfides are, therefore, *a priori* suitable starting materials, independently of the regioselectivity of the oxidation. Glycosyl disulfides are known compounds (see [1] and refs. cit. therein). A *S*-phenacyl thioglycoside was prepared by *S*-alkylation of a 1-thio-β-D-glucopyranose with phenacyl chloride [17].

Furanoid Aldonothio-O-lactones. The *S*-phenacyl α-D-thiofuranoside **6** (*Scheme 2*) was obtained in 91% yield by treating **5** [18] [19] with NaOEt in EtOH and then with phenacyl chloride. Photolysis of **6** with Hg high-pressure lamps (see *Exper. Part*) through *Pyrex* or quartz and chromatography of the crude product on silica gel gave the thio-*O*-lactone **2** in 89 and 78% yield, respectively. These yields were only realized for batches > 0.5 g, as chromatography of smaller amounts of crude product led to considerable decomposition. Freshly chromatographed **2** was an odourless, yellow oil. Even the slight degree of decomposition, observed upon keeping the product at –20°, was accompanied by the formation of malodorous secondary products.

Scheme 2



a) NaOEt, EtOH, 10 min at 50°, phenacyl chloride, 1 h at r.t.; 91%. *b*) CH_2Cl_2, *hν*; 78–89%. *c*) 3-Chloroperbenzoic acid, CH_2Cl_2, 1 h at r.t.; toluene, reflux; 11%. *d*) 3-Chloroperbenzoic acid, CH_2Cl_2, 2 h at –78°; toluene, reflux; 29%. e) TsCl, Bu_4NCl, 10% aq. NaOH soln., toluene, 15 min at r.t., KSC(S)OEt, 2 h at r.t.; 85%. *f*) NaOEt, THF, 10 min at 50°, phenacyl chloride, 1 h at r.t.; 83% (**11a**). *g*) As *f*), but in EtOH; 20% (**11a**), 43% (**11b**). *h*) **11a**, CH_2Cl_2, *hν*, 1 h at r.t.; 95%.

Thermolysis of the crude *S*-glycosyl thiosulfinates resulting from the oxidation of **7** [1] [19] and **8** [1] by peracid [20] gave **2** in low yields only, presumably due to the instability of the intermediate thiosulfinates. *S*-Alkyl thiosulfinates easily disproportionate into disulfides and thiosulfonates [21]. Only the disulfide **7** was eluted during an attempt to purify its oxidation product by chromatography.

The *S*-phenacyl thioribofuranosides **11** (*Scheme 2*) were prepared from the dithiocarbonate **10**. The latter was obtained from **9** by a similar procedure (KOH, TsCl, KS(CS)OEt) as that used for the synthesis of **5**. Transesterification of **10** with NaOEt in THF, followed by reaction of the intermediate sulfido anion with phenacyl chloride gave the α-D-thioriboside **11a** (83%). The same sequence in EtOH led to partial anomerization of the intermediate ribofuranosyl anion and resulted in a *ca.* 1:2 mixture of **11a** and **11b** (63%)[2]). Photolysis of **11a** and crystallization of the crude product from petroleum ether gave 95% of the thio-*O*-lactone **12**.

The presence of a phenacyl group in **6** is evidenced by the microanalysis and the mass spectrum with signals for M^+ at *m/z* 394, for $[M - Me]^+$ at *m/z* 379, and $[M - \text{phenacyl}]^+$ at *m/z* 275. In the IR spectrum, the C=O band occurs at 1688 cm^{-1}. The α-D-configuration of **6** is evidenced by the small $J(1,2) \approx 0$ Hz and by the downfield shift of H–C(4) caused by the *cis*-standing alkylthio group [1] (*Table 1*). The *d*'s of CH_2 of the aglycone (J_{gem} = 15.5 Hz) appear at 4.01 and 3.94 ppm. The purity of **2** is indicated by the microanalysis and the mass spectrum (M^+ at *m/z* 274). The UV spectrum shows the characteristic bands for thio-*O*-lactones, at 253 nm ($\varepsilon = 9400$) the band for the π-π* transition and at 380 nm ($\varepsilon \leq 30$) the one for the n-π* transition. The thio-*O*-lactone structure of **2** is corroborated by the absence of H–C(1) and the strong downfield shifts of H–C(4) (4.68 ppm) and C(1) (218.98 ppm).

The α-D-configuration of **10** is revealed by $J(1,2)$ of 5.0 Hz. H–C(1) resonates at low field (6.61 ppm). The anomeric configuration of **11a/b** is again based upon $J(1,2)$ (**11a**: 5.0 Hz; **11b**: 1.8 Hz). In contrast to the 1-thiomannofuranosides, H–C(4) *cis* to the alkylthio group (**11a**) is more shielded than the one of the anomer **11b** (*Table 2*). The $PhCOCH_2$ signals have similar shift values (3.83–4.15 ppm) as the corresponding ones of **6**. The UV spectrum of **12** is similar to the one of **2**. In the ^{1}H-NMR spectrum, H–C(4) of **12** appears at low field (4.96 ppm) and couples only with H–C(5) and H'–C(5) (*Table 2*). $J(3,4)$ of 0 Hz indicates a southern conformation of the furanoid ring. The extreme $J(3,4)$ value fits better with a ^4E than a $^2T_3$ conformation.

*Pyranoid Aldonothio-*O*-lactones.* The sulfinate **14** (*Scheme 3*) is the only known *S,S'*-diglycosyl thiosulfinate [22]. It is a crystalline compound of unknown configuration at the S-atom. We prepared it according to *Bell* and *Horton* by partial hydrolysis of the sulfenyl bromide **13**. Thermolysis of **14** in toluene at 110° and purification of the product by chromatography on silica gel gave the orange, unsaturated thio-*O*-lactone **16** (71%). Chromatography on silanized silica gel, however, afforded the pure, yellow thio-*O*-lactone **15** (20%) and a mixture of **15** with the β-elimination product **16** (*ca.* 40%). Evidently, *O*-acyl protecting groups are not suited for the preparation of saturated, fully substituted glyconothio-*O*-lactones; even the peracetylated gluconolactone **17** undergoes easy β-elimination [23].

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[2]) The reason for the anomerization of the sulfido anion derived from **18** in THF solution is the absence of a favourable intramolecular stabilisation of the cation which prevents partial anomerization of the anions derived from **5** [1], **10**, and **24b**.

Table. 1. *Selected ^{1}H-NMR* ($CDCl_3$) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Hexosyl Part of* **1–8**, **15**, **16**, **19–21**, **24–27**, **29**, *and* **31**

	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H'–C(6)	*J*(1,2)	*J*(2,3)	*J*(3,4)	*J*(4,5)	*J*(5,6)	*J*(5,6')	*J*(6,6')
5	5.63	4.93	4.83	3.59	4.45	4.10	4.10	3.8	5.9	4.4	8.5	4.8	4.8	a)
8	4.88	4.84	4.77	3.57	4.46	4.12	4.12	3.8	5.6	3.4	7.7	5.2	5.2	a)
27[b]	-	4.56	4.83	3.78	4.45	4.11	4.06	-	6.0	4.1	8.0	6.0	4.4	8.8
29[b][c]	-	5.46	4.795	4.29	4.34	4.10	4.07	-	6.2	4.6	7.2	4.9	5.9	8.6
	-	-	5.16	4.82	4.44	4.18	4.18	-	-	3.4	8.6	4.9	4.9	a)
1	-	4.83	4.87	4.37	4.43	4.14	4.06	-	5.2	3.3	8.0	5.8	3.8	9.2
2	-	4.86	4.89	4.68	4.45	4.13	4.08	-	5.1	2.9	6.0	4.2	9.2	10.0
7	5.41	4.79–4.84	4.79–4.84	4.79–4.84	4.42	4.10	4.05	0.5	a)	a)	8.5	6.1	5.1	8.8
6	5.44	4.60	4.78	4.10	4.44	4.06	3.93	0	5.9	3.5	7.8	6.2	4.5	9.0
31[b]	-	4.36	4.80	3.955	4.42	4.09	3.95	-	6.0	3.8	7.9	6.3	4.4	8.6
19	4.53	3.60–3.70	3.60–3.70	3.60–3.70	3.60–3.70	3.40–3.50	3.40–3.50	10.0	a)	a)	a)	a)	a)	a)
21b	4.48	3.64–3.84	3.64–3.84	3.64–3.84	3.47–3.53	3.64–3.84	3.64–3.84	9.0	a)	a)	a)	a)	a)	a)
21a	5.46	3.61–3.87	3.61–3.87	3.61–3.87	4.08–4.15	3.61–3.87	3.61–3.87	4.0	a)	a)	a)	a)	a)	a)
3	-	4.15	3.94	3.99	4.48	3.76	3.70	-	6.6	6.8	8.2	2.4	3.3	11.0
4	-	4.51–4.57	3.85–3.94	3.85–3.94	4.90	3.85–3.94	3.78	-	a)	a)	9.5	2.0	4.0	11.5
15[d]	-	5.60–5.63	5.31–5.41	5.31–5.41	4.69–4.75	4.39	4.46	-	a)	a)	a)	2.8	3.8	13.0
20	-	3.54, 3.18	3.88–3.94	3.88–3.94	4.35–4.38	3.83	3.76	-	e)	a)	a)	3.0	3.5	11.0
16	-	-	6.28	5.65	4.79	4.46	4.38	-	-	4.4	6.0	4.9	4.5	12.0
24b	5.47	4.11	3.71–3.79	3.99	3.60	3.71–3.79	3.71–3.79	1.0	3.0	9.5	9.5	2.5	4.0	a)
25	4.68	4.03	3.61	3.90	3.55	3.77	3.70	0.7	2.5	9.5	9.5	1.9	6.2	10.9
24a	6.34	3.91	3.68–3.84	4.10	3.68–3.84	3.68–3.84	3.68–3.84	2.5	3.0	9.5	9.5	a)	a)	a)
26	-	4.30	3.99	3.88	4.32	3.73	3.73	-	2.5	2.5	8.0	4.3	4.3	a)

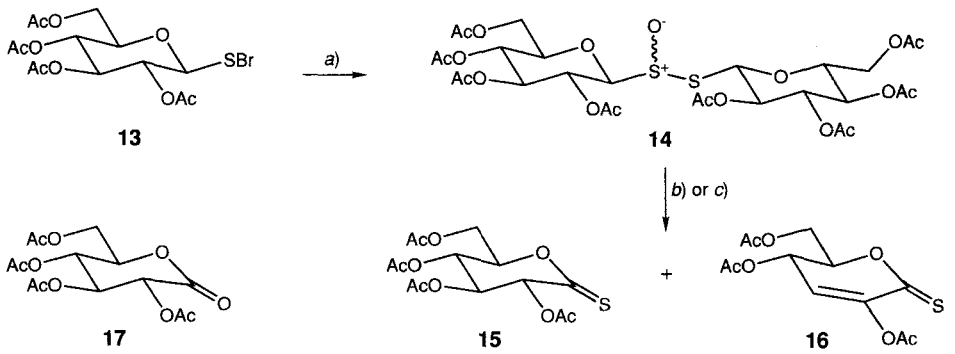
a) Not determined. b) Same numbering as for **2**. c)Values of the thio-*O*-lactone moiety of **29** in the lower row. d)Higher-order spectrum due to virtual couplings. e) $J(2,2') = 16.5$, $J(2,3) = 4.0$, $J(2,4) = 4.0$, $J(2',3) = 3.0$ Hz.

Table. 2. *Selected ^{1}H-NMR* ($CDCl_3$) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Ribosyl Part of* **10–12**

	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H'–C(5)	Me_2C	*J*(1,2)	*J*(2,3)	*J*(3,4)	*J*(4,5)	*J*(4,5')	*J*(5,5')
11b	5.37	4.40–4.59	4.40–4.59	4.40–4.59	3.35	3.29	1.50, 1.29	1.8	a)	a)	7.0	7.0	9.5
12	–	5.14	4.51	4.96	3.80	3.12	1.48, 1.35	–	5.4	0	2.5	1.8	11.0
10	6.61	5.14	4.59–4.79	4.28–4.32	3.56	3.06	1.52, 1.33	5.0	6.3	a)	3.0	3.0	10.5
11a	5.68	4.95	4.61	4.27–4.31	3.39	3.13	1.54, 1.30	5.0	6.5	2.5	3.5	3.5	10.3

a) Not determined.

Scheme 3



a) CCl_4/H_2O 40:3, 30 min at r.t.; 78%. *b*) Toluene, 5 min at 110°; FC (silica gel); 71% (**16a**). *c*) As *b*), but FC (silanized silica gel); 20% (**15**), *ca.* 45% (**15/16**).

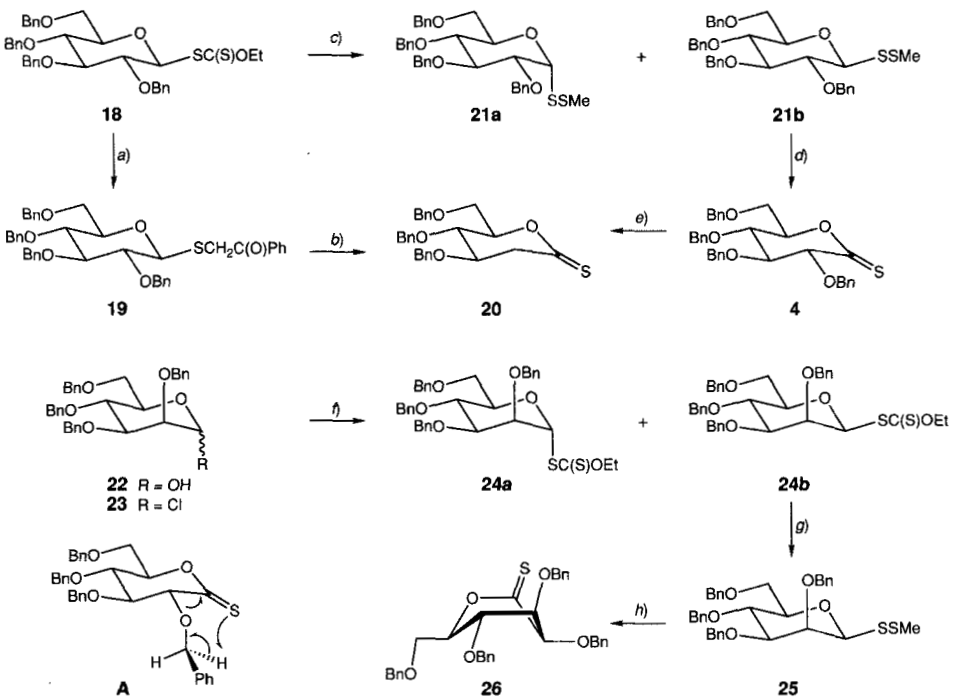
Treatment of the *O*-benzyl-protected dithiocarbonate **18** [1] [18] (*Scheme 4*) with a catalytic amount of NaOMe in MeOH and then with phenacyl chloride gave the *S*-phenacyl glucoside **19**, which, upon irradiation for 1 h, led to 48% of the 2-deoxythio-*O*-lactone **20**. Attempts to obtain **4** by shorter irradiation times failed. Transesterification of **18** with NaOEt in THF [1] gave the corresponding glycosyl-thiolato anion which underwent partial anomerization[1]). The suspension of these sodium thiolates was thiomethylated with dimethyl(methylthio)sulfonium tetrafluoroborate in THF [1] to yield a *ca.* 15:85 mixture **21a/b** (88%) which was separated by flash chromatography. The β-D-anomer **21b** was oxidized with 3-chloroperbenzoic acid. The thiosulfinate(s) were purified by chromatography and heated *in vacuo* for 15 min to 120° [3]) affording 79% of the gluconothio-*O*-lactone **4**. Photolysis of **4** led to 36% of the 2-deoxygluconothio-*O*-lactone **20**.

The thermolysis of thiosulfinates was also successful in the mannopyranose series. *In situ* preparation ($P(Et_2N)_3$ and CCl_4 in CH_2Cl_2 at –40°) of the mannopyranosyl chloride **23** from **22** [24], followed by its reaction with potassium ethyl dithiocarbonate gave a *ca.* 1:9 mixture **24a/b** (88%; *Scheme 4*). The β-D-anomer was transformed into the crystalline β-D-disulfide **25**[2]) (83%) which, upon oxidation and thermolysis, gave 79% of **26**.

The photolytic transformation of the tetrabenzyl ether **4** into **20** indicates that photolysis of **19** leads initially to **4**. H-Abstraction from the γ-position (*Norrish* II type, see **A**) is known for rigid systems [25] [26], and the $CH_2OC(2)$ group of **4** in a flattened $^4C_1$ conformation is in close neighbourhood to the S-atom. The flattened $^4C_1$ conformation, similar to the one of **15** and **17** [27], is suggested by $J(4,5) = 9.5$ Hz in the otherwise poorly resolved ^{1}H-NMR spectrum of **4**.

[3]) Thermolysis in solution gave **4** in lower yields together with decomposition products, evidencing the beneficial effect of removing volatile impurities and reactive by-products *in vacuo*.

Scheme 4



a) NaOMe, MeOH, 30 min at 50°, phenacyl chloride, 1 h at r.t.; 70%. *b*) CH_2Cl_2, *hv*, 1 h at r.t.; 48%. *c*) NaOEt, THF, 30 min at r.t., dimethyl(methylthio)sulfonium tetrafluoroborate, 2 h at r.t.; 10% (**21a**), 7% (**21a/b**), 71% (**21b**). *d*) 3-Chloroperbenzoic acid, CH_2Cl_2, 1 h at 0°; neat, 15 min at 120°/0.05 mbar; 79%. *e*) CH_2Cl_2, *hv*, 15 min at r.t.; 36%. *f*) CCl_4, $P(Et_2N)_3$, 30 min at –40°, KSC(S)OEt, 2 h at –40°; 7% (**24a**), 6% (**24a/b**), 75% (**24b**). *g*) As *c*); 83%. *h*) As *d*); 79%.

The yellow and the orange colour of **15** and **16**, respectively, point towards a thio-*O*-lactone structure which is confirmed by the CI-mass spectra with $[M + 1]^+$ at *m/z* 363 and 303, respectively. The loss of one AcOH in **16** is also reflected in the ^{1}H-NMR spectra (*Table 1*). The *d* (J = 4.4 Hz) of H–C(3) of **16** resonates at 6.28 ppm, indicating the α,β-unsaturated thiocarbonyl moiety which is also revealed by the UV band at 288 nm (ε = 1850) and the IR band at 1650 cm^{-1}. $J(3,4)$ = 4.4 and $J(4,5)$ = 6.0 Hz are compatible with a $^0H_4$ conformation of **16**. Although the signals of the ring H-atoms of **15** are of higher order due to virtual couplings, a rough estimation of $J(2,3)$, $J(3,4)$, and $J(4,5)$ is possible. Their values (*ca.* 8 Hz each) are in agreement with a flattened $^4C_1$ as it is observed for **17**, both in the solid state and in solution [27].

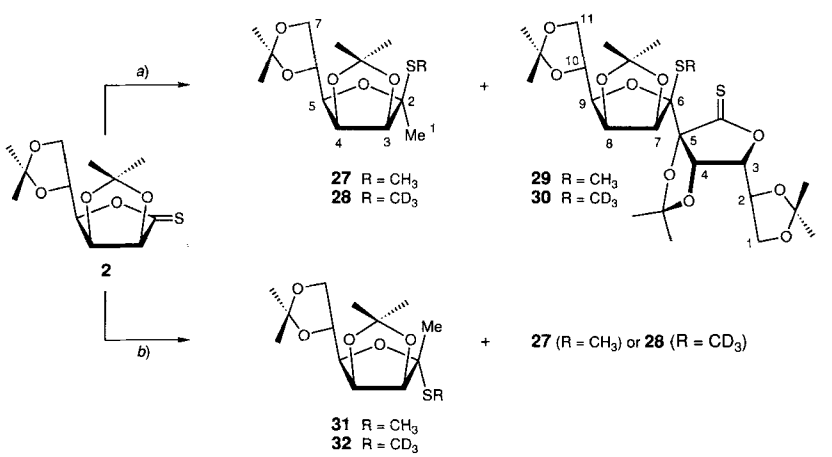
The assignment of the anomeric configuration of **19**, **21b**, and **21a** is based upon $J(1,2)$ (10, 9 and 4 Hz, resp., see *Table 1*). MeS of **21a** (2.43 ppm) resonates at slightly higher field than MeS of **21b** (2.50 ppm), but in the same region as MeS of the analogous mannofuranose derivatives [1]. The UV spectra of **4** and **20** exhibit the characteristic bands for thio-*O*-lactones. The loss of a benzyloxy group in **20** is indicated by signals for 3 benzyloxy groups only, a *ddd* at 3.54 ppm and a *dd* 3.18 ppm for the two H–C(2) showing a large geminal coupling of 16.5 Hz. Again, the poor resolution of signals for H–C(3) and H–C(4) does not allow to determine the conformation of the pyranose ring of **20**.

The anomeric configuration of **24a** and **24b** is indicated by the chemical shift of H–C(1) (**24a**: 6.34 ppm; **24b**: 5.47 ppm) and by $J(1,2)$ [28] (**24a**: 2.5Hz; **24b**: 1.0 Hz). According to the small $J(1,2)$ of 0.7 Hz for **25** and $^1J(C(1),H)$ = 155 Hz [29] [30] with $\delta(C(1))$ 93.88 ppm, the anomeric configuration is retained during thiomethylation. The vicinal coupling constants (*Table 1*) show that **24a**, **24b**, and **25** possess a $^4C_1$ conformation. The thio-*O*-lactone **26**, however, has a different conformation, as indicated by $J(3,4) = 2.5$ Hz. This value and the ones for $J(2,3)$ and $J(4,5)$ (*Table 1*) agree fairly well with those observed for mannono-1,5-lactone in (D_6)DMSO solution [31] ($J(2,3)$ = 3.4, $J(3,4)$ = 1.2, $J(4,5)$ = 8.3 Hz) and evidence that both compounds possess a $B_{2,5}$ conformation.

Addition of Nucleophiles to **2**. The addition of alkyllithium compounds to thio-*O*-esters [32] or thio-*O*-lactones [33] and the alkylation of the intermediate thiolato anions with MeI lead to stable *S*-methyl thioacetals. Similarly, lithium dialkylcuprates undergo carbophilic addition to dithioesters and dithiolactones [34] [35].

The reaction of **2** with MeLi (THF, –78°) and then with MeI gave two main products which could not be separated by flash chromatography (*Scheme 5*). Bulb-to-bulb distillation, however, gave > 97% pure, crystalline methyl heptulofuranoside **27** in the distillate (29%), while the residue consisted mainly of **29** (85%) and **27** (5%). HPLC afforded pure **29** (47%) as a yellow oil. The formation of **29** was not suppressed by changing the reaction conditions (solvent, temperature, order of addition). The reaction of **2** with lithium dimethylcuprate(I) ($LiCuMe_2$), prepared *in situ* by the addition of MeLi to a suspension of CuI in THF, and bulb-to-bulb distillation led to a 4:1 mixture **31/27** (49%) which was separated by prep. HPLC. No **29** was detected in the black residue of the distillation.

Scheme 5



a) MeLi, THF, 2 h at –78°, MeI or CD_3I, 2 h at –78°, then to r.t.; 29% (**27** or **28**), 47% (**29** or **30**). *b*) $LiCuMe_2$ (from MeLi and CuI), THF, 1 h at –30 → –5°, MeI or CD_3I, 10 min at ≤ 0°; 47% (**31/27** or **32/28** 4:1).

Suitable crystals for X-ray analysis were obtained from **27** (*Fig.* and *Table 3*). S(1) and C(5) (arbitrary numbering) are *cis*-oriented, establishing the β-D-configuration of **27**. The furanose ring possesses a $^{O}T_{4}$ conformation with a pseudoequatorial dioxolanyl moiety. The dihedral angle C(14)–S(1)–C(1)–O(1) is 62.8°, in agreement wit an *exo*-anomeric effect which is corroborated by the lengthening of the C(1)–O(1) bond as compared with the C(4)–O(1) bond (*Table 3*).

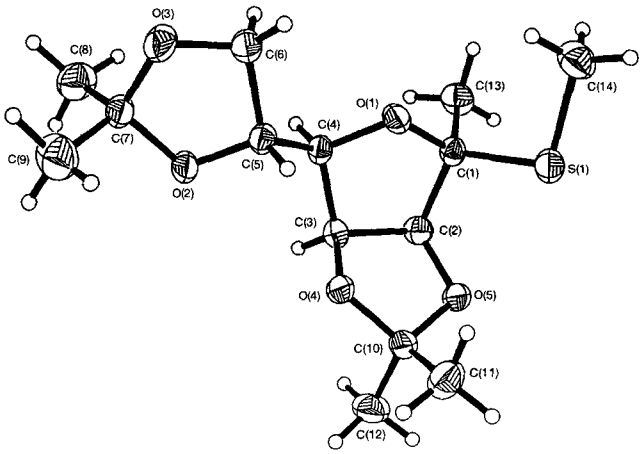


Figure. *X-Ray structure of* **27**. Arbitrary numbering.

Table 3. *Selected Bond Lengths and Bond and Dihedral Angles of the X-Ray Structure of* **27**

Bond lengths [Å]		Bond or dihedral angles [°]		Dihedral angles [°]	
C(1)–C(2)	1.545 (5)	O(1)–C(1)–C(2)	105.4 (3)	O(1)–C(4)–C(5)–O(2)	178.2
C(2)–C(3)	1.523 (7)	C(1)–C(2)–C(3)	104.8 (3)	C(3)–C(4)–C(5)–O(2)	–65.1
C(3)–C(4)	1.516 (5)	C(2)–C(3)–C(4)	104.5 (3)	C(4)–O(1)–C(1)–C(13)	90.0
C(4)–C(5)	1.508 (7)	C(3)–C(4)–O(1)	104.8 (3)	C(4)–O(1)–C(1)–S(1)	–146.4
C(1)–O(1)	1.440 (6)	C(4)–O(1)–C(1)	108.0 (2)	C(3)–C(2)–C(1)–S(1)	125.5
C(2)–O(5)	1.415 (5)	O(1)–C(1)–C(13)	109.7 (3)	O(1)–C(1)–S(1)–C(14)	–62.8
C(3)–O(4)	1.422 (5)	C(13)–C(1)–S(1)	113.2 (3)	C(13)–C(1)–S(1)–C(14)	58.7
C(4)–O(1)	1.425 (6)	C(1)–S(1)–C(14)	99.9 (2)	C(2)–C(1)–S(1)–C(14)	–177.1
C(1)–C(13)	1.516 (7)	C(1)–C(2)–C(3)–C(4)	11.5	H–C(2)–C(3)–H	13.9
C(1)–S(1)	1.810 (5)	C(2)–C(3)–C(4)–O(1)	–29.1	H–C(3)–C(4)–H	–30.4
S(1)–C(14)	1.805 (5)	C(3)–C(4)–O(1)–C(1)	36.9	H–C(4)–C(5)–H	177.7

The anomeric structure of **27** and **31** is evidenced by the ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *4*). As expected, H–C(4) is more shielded for **27** than for **31**, but $\Delta\delta$ is smaller than in the parent aldose analogs [1]. According to the vicinal coupling constants, both anomers possess a $^{O}T_{4}$ conformation, as it is found for **27** in the solid state. MeS resonates at 2.21 (**27**) and 1.98 ppm (**31**), MeC(1) at 1.47 (**27**) and 1.59 ppm (**31**). The latter two signals are easily assigned, since the Me signals of the Me_2C moieties are broadened, due to long-range couplings. In the ^{13}C-NMR spectrum, the anomeric C-atom resonates at 92.9 (**27**) and 90.5 ppm (**31**), whereas the other C-atoms of the furanose ring exhibit the typical shifts of diisopropylidene-mannofuranose derivatives. *Me*–C(1) appears at 21.74 (**27**) and 23.73 ppm (**31**), MeS at 10.02 (**27**) and 11.75 ppm (**31**). In the ^{1}H-NMR spectrum of **29**, signals of two mannose residues are present, the one lacking H–C(1) and the other lacking H–C(1) and H–C(2). The *S*-methyl thioglycoside structure is confirmed in the CI-MS by peaks for $[M + 1]^+$ at *m/z* 563 and for $[M - MeS + NH_3]^+$ at *m/z* 532. In the IR spectra (film or $CHCl_3$ solution), the absence of any band above

1500 cm^{-1} which could be assigned to a double bond, excludes a ene-thiol structure. The yellow colour suggested that **29** is a thio-*O*-lactone. Indeed, the ^{13}C-NMR spectrum shows 3 *s* at 218.97 (C=S), 97.84 (C(5)), and 94.14 ppm (C(6)). The other signals exhibit the expected shift values (*Table 4*). The configuration at C(5) and C(6) was established by NOE experiments (*Table 5*). Upon irradiation of the signal for MeS, the signals of the Me group at 1.59 ppm (3.1%), H–C(10) (1.9%), CH_2(11) (1.6%), H–C(4) (1.2%), and H–C(3) (0.8%) showed intensity enhancements (systematic numbering). This reveals the *'endo'*-position of the MeS group. The NOE's between H–C(4) and H–C(7) suggest the presence of a C(5)–C(6) rotamer similar to the one depicted in *Scheme 5*.

Table. 4. *^{13}C-NMR* (50.6 ppm, $CDCl_3$) *Chemical Shifts* [ppm] *of* **6**, **2**, **27**, **29**, *and* **31**[a]).

	6	**2**	**27**[b])	**29**[b])[c])		**31**[c])
C(1)	88.51	218.98	92.89	94.14	218.97	90.50
C(2)	85.20	86.57[d])	86.45	86.72	97.84	87.82
C(3)	80.08[d])	76.85	80.73	81.69[d])	85.25	80.56[d])
C(4)	79.70[d])	86.50[d])	79.65	81.19[d])	82.45	79.36[d])
C(5)	72.58	72.13	72.86	72.35	73.37	73.27
C(6)	66.74	66.26	67.17	66.67	66.67	67.04
3,4-*O*-Me_2C	112.80, 25.81, 24.52	114.62, 27.13, 25.96	112.66, 25.81, 24.57	113.28, 25.14, 23.68[e])	115.70, 27.64, 26.76[e])	114.45, 25.48, 24.23
5,6-*O*-Me_2C	109.07, 26.70, 25.13	109.78, 26.82, 24.94	109.18, 26.85, 25.21	109.34, 27.09, 25.21[e])	110.02, 27.19, 25.21[e])	109.19, 26.98, 25.21
Me–C(1)	-	-	21.74	-	-	23.73
MeS–C(1)	[f])	-	10.02	12.64	-	11.75

[a]) The assignment is based upon comparison with the spectra of 3,4:5,6-di-*O*-isopropylidene-α-D-mannofuranose [36] and related compounds [1]. [b]) Same numbering as for **2**. [c]) Values of the thio-*O*-lactone moiety of **29** in the right-hand column. [d]) Assignment may be interchanged. [e]) Values for isopropylidene groups may be interchanged. [f]) Signals for $PhCOSCH_2$ at 36.15 (*t*) 193.98 (*s*), 135.36 (*s*), 128.55 (*d*, 2 C), 128.44 (*d*, 2 C), and 133.30 (*d*).

Table. 5. *NOE Experiments on the Dimer* **29**. Systematic numbering.

Irradiated signal [ppm]		NOE [ppm]			
4.52	(MeS)	5.16	(1.2%, H–C(4))	4.09	(1.6%, 2 H–C(11))
		4.82	(0.8%, H–C(3))	1.59	(3.1%, *'endo'*-Me of 7,8-*O*-Me_2C)
		4.34	(1.9%, H–C(10))		
5.46	(H–C(7))	5.16	(5.7%, H–C(4))	1.52	(2.5%, *'exo'*-Me of 4,5-*O*-Me_2C)
		4.795	(8.3%, H–C(8))	1.395	(3.1%, *'exo'*-Me of 7,8-*O*-Me_2C)
5.16	(H–C(4))	5.46	(2.3%, H–C(7))	2.21	(0.7%, MeS)
		4.82	(4.3%, H–C(3))	1.52	(1.0%, *'exo'*-Me of 4,5-*O*-Me_2C)

The thio-*O*-lactone **29** is most probably formed by nucleophilic addition from the less hindered *'exo'*-side of the ene-thiolato anion, resulting from deprotonation of **2** by MeLi, on a second molecule of **2**.

To rationalize the formation of the anomeric thioglycosides **27** and **31**, resulting from the reaction of **2** with MeLi and $LiCuMe_2$, respectively, we checked if both thioglycosides are formed by carbophilic attack. It was reported that aryllithium reagents lead to thiophilic attack on thioketones, dithioesters, and trithiocarbonates [37], while alkyllithium reagents react with thioketones by a thiophilic attack [38], with thio-*O*-ester and thio-*O*-lactones, however, by a carbophilic attack [9] [32] [33]. Carbophilic attack on dithioesters and dithiolactones was also reported for cuprates [34] [35]. Addition of vinylmagnesium bromide to thio-*O*-lactones in the presence of CuI also takes a carbophilic course, for which a mechanism involving a single electron transfer has been proposed [9].

Reaction of **2** with MeLi or $LiCuMe_2$, followed in both cases by the addition of CD_3I, gave the trideuterio analogues of **27**, **29**, and **31**, *i.e.* **28**, **30**, and **32**, respectively, possessing in each case a CD_3S group. The regioselectivity of the additions are easily monitored by ^1H- and ^{13}C-NMR and CI-mass spectroscopy (*Table 6*). Whereas the addition of $LiCuMe_2$ was completely regioselective, the spectra of **28** and **30** show the presence of 4–5% of the undeuteriated species. The absence of the signals for $[M - CH_3S + NH_3]^+$ at *m/z* 277 and for $[M - CH_3S]^+$ at *m/z* 260 in the MS of **28** and **32** establishes the completely carbophilic attacks of MeLi and $LiCuMe_2$. The formation of some undeuteriated products in the reaction with MeLi may be the result of partial Li/I exchange before methylation of the thiolato anions.

Table. 6. *Comparison of the ^1H-NMR, ^{13}C-NMR, and CI-Mass Spectra of the Deuterated with the Ones of the Nondeuterated Addition Products of* **2**

	Signal	**28**	**30**	**32**
^1H-NMR [ppm]	*s* of MeS	2.21 (0.1 H)	2.21 (0.15 H)	1.98 (< 0.03 H)
^{13}C-NMR	*q* of MeS	no signal	no signal	no signal
CI-MS [*m/z*]	$[M + NH_4]^+$	325 (100)	583 (100)	325 (100)
		322 (4, **27**)	580 (5, **29**)	322 (*ca.* 0.5, **31**)
	$[M + 1]^+$	308 (0.5)	566 (40)	308 (60)
			563 (2, **29**)	322 (< 0.5, **31**)
	$[M - CD_3S + NH_3]^+$	274 (80)	532 (50)	274 (93)
	$[M - CD_3S]^+$	257 (33)	566 (5)	257 (100)

Thus, the addition of MeLi or the ene-thiolato anion occurs from the *'exo'*-side of **2**, whereas $LiCuMe_2$ preferentially adds from the *'endo'*-side. Steric hindrance appears to govern the diastereoselectivity of the attack by MeLi . The steric course of the addition of $LiCuMe_2$ is in keeping with an initial single electron transfer. This leads to a radical anion, where the anomeric centre should be pyramidalized, similarly as it was reported for glycosyl nitronate anions [39] to avoid a destabilizing interaction with the lone pairs of the

ring O-atom [40]. The conformation of the furanose ring of the intermediate radical anion is dictated by the preferred pseudoequatorial orientation of the side chain and should be of a ^{O}E type, leading to a preferred pseudoaxial orientation of S–C(1) and, as a consequence, to a pseudoequatorial *'endo'*-attack of the methylating agent. Hence, for this type of bicyclic furanose derivatives, the diastereoselectivity of the reactions of nitronate anions and radical anions differs from the one of neutral radicals [41].

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Experimental Part

General. See [1]. If not stated otherwise, irradiations of *S*-phenacyl thioglycosides were performed with a Hg high-pressure lamp (150 W, *Heraeus*) equipped with a *Pyrex* filter. Prep. HPLC: 250×20 mm column (*Bischoff*) filled with *Si60 Spherisorb* (5 μm), flow rate 14 ml/min, UV detection (254 nm).

*S-Phenacyl 2,3:5,6-Di-*O*-isopropylidene-1-thio-α-*D*-mannofuranoside* (**6**). A soln. of **5** [1] [18] [19] (21.8 g, 60 mmol) and freshly prepared NaOEt [1] (3.83 g, 66 mmol) in EtOH (200 ml) was stirred for 10 min at 50°, cooled to r.t., and added dropwise to a cooled (0°) soln. of phenacyl chloride (10.2 g, 66 mmol) in EtOH (200 ml). After stirring for 1 h at r.t., the soln. was evaporated and the residue dissolved in Et_2O (500 ml). The org. layer was washed with brine (3 x 250 ml), dried ($MgSO_4$), and evaporated. Crystallization of the residue from $(i\text{-}Pr)_2O$ gave **6** (17.73 g, 75%). FC (350 g, hexane/AcOEt 5:1) of the mother liquor gave additional **6** (2.6 g, 16%). M.p. 63°. R_f (hexane/AcOEt 5:1) 0.19. UV (CH_2Cl_2): 244 (12030), 331 (2453). IR (KBr): 2995*m*, 2942*w*, 2888*w*, 1688*s*, 1600*w*, 1580*w*, 1450*w*, 1375*m*, 1300*w*, 1269*m*, 1210*s*, 1162*m*, 1066*s*, 1050*s*, 1001*s*, 979*w*, 841*m*, 758*m*, 692*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.97 (*dd*, *J* = 1.5, 7.0, 2 arom. H); 7.45–7.63 (*m*, 3 arom. H); 5.44 (*s*, H–C(1)); 4.78 (*dd*, *J* = 3.5, 5.9, H–C(3)); 4.60 (br. *d*, *J* = 5.9, H–C(2)); 4.44 (*ddd*, *J* = 4.5, 6.2, 7.8, H–C(5)); 4.10 (*ddd*, *J* = 0.8, 3.5, 7.8, H–C(4)); 4.06 (*dd*, *J* = 6.2, 9.0, H–C(6)); 4.01 (*d*, *J* = 15.5, BzC*H*); 3.94 (*d*, *J* = 15.5, BzC*H*'); 3.93 (*dd*, *J* = 4.5, 9.0, H'–C(6)); 1.47 (*s*, Me); 1.44 (*s*, Me); 1.38 (*s*, Me); 1.32 (*s*, Me). ^{13}C-NMR (50.6 MHz, $CDCl_3$): *Table 4*. EI-MS: 394 (1, M^+), 379 (2, [*M* – Me]$^+$), 275 (20, [*M* – phenacyl]$^+$), 185 (17), 141 (11), 127 (15), 105 (66), 101 (48), 85 (24), 77 (47), 69 (17), 59 (29), 43 (100). Anal. calc. for $C_{20}H_{26}O_6S$ (394.48): C 60.90, H 6.64, S 8.13; found: C 60.91, H 6.73, S 8.05.

*2,3:5,6-Di-*O*-isopropylidene-1-thio-*D*-mannono-1,4-*O*-lactone* (**2**). a) *From* **6** *by Irradiation with a* Heraeus *Lamp*. Irradiation of a soln. of **6** (2 g, 5.68 mmol) in dry CH_2Cl_2 (250 ml) for 1 h at r.t., evaporation, and FC (50 g, hexane/AcOEt 5:1) of the residue gave **2** (1.24 g, 89%).

b) *From* **6** *by Irradiation with a* HPK-125 *Lamp* (*Phillips*). In a original 3-necked quartz irradiation vessel, a soln. of **6** (700 mg, 1.77 mmol) in dry CH_2Cl_2 (250 ml) was treated with molecular sieves (3 Å, *ca.* 0.5 g). After insertion of the H_2O-cooled lamp (125 W), the apparatus was floated with N_2, wrapped with aluminium foil, and irradiated for 3.5 h (TLC: reaction complete). Concentration of the yellow soln. to 5 ml and MPLC (200 g of silica gel, hexane/AcOEt 5:1, flow 4 ml/min for 30 min and then 12 ml/min, UV detector (255 nm)) gave **2** (378 mg, 78%). Yellow, odourless oil. Upon storage for 2 d at –20°, little decomposition to badly smelling secondary products occurred.

c) *From* **7**. A soln. of **7** [1] [19] (550 mg, 1 mmol) and 3-chloroperbenzoic acid (*ca.* 85%, 220 mg, 1.1 mmol) in CH_2Cl_2 (15 ml) was stirred for 1 h at r.t., diluted with CH_2Cl_2 (50 ml), washed with sat. $NaHCO_3$ soln. (50 ml) and brine (3 × 50 ml), dried ($MgSO_4$), and evaporated. Dissolution of the residue (thiosulfinate) in boiling toluene (100 ml), evaporation, and FC (25 g, hexane/AcOEt 4:1) gave **2** (63 mg, 11%).

d) *From* **8**. A soln. of 3-chloroperbenzoic acid (*ca.* 85%, 3.05 g, 15 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cooled (–78°) soln. of **8** [1] (3.22 g, 10 mmol) in CH_2Cl_2 (5 ml). After stirring for 2 h at –78°, the soln. was warmed up to r.t., washed with sat. $NaHCO_3$ soln. (3 × 25 ml) and brine (3 × 25 ml), dried ($MgSO_4$), and evaporated. Dissolution of the residue (thiosulfinate) in boiling toluene (100 ml), evaporation, and FC (350 g, hexane/AcOEt 4:1) gave **2** (795 mg, 29%). R_f (hexane/AcOEt 5:1) 0.19. $[\alpha]_D^{20} = +160.9$ (*c* = 1.0, $CHCl_3$). UV

(MeOH): 253 (9400), 380 (30). IR (KBr): 2995*m*, 2956*w*, 2885*w*, 1455*w*, 1377*m*, 1350*m*, 1330*m*, 1300*m*, 1239*s*, 1208*s*, 1185*m*, 1156*s*, 1117*s*, 1090*s*, 1068*s*, 967*m*, 933*m*, 886*m*, 852*m*, 784*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.89 (*dd*, *J* = 3.0, 5.1, H–C(3)); 4.86 (*d*, *J* = 5.1, H–C(2)); 4.68 (*dd*, *J* = 2.9, 8.0, H–C(4)); 4.45 (*ddd*, *J* = 4.2, 5.9, 8.0, H–C(5)); 4.13 (*dd*, *J* = 6.0, 9.2, H–C(6)); 4.08 (*dd*, *J* = 4.2, 9.2, H'–C(6)); 1.43 (*s*, 2 Me); 1.36 (*s*, Me); 1.34 (*s*, Me). ^{13}C-NMR (50.6 MHz, $CDCl_3$): *See Table 4*. EI-MS: 274 (3, M^+), 259 (22, $[M - Me]^+$), 201 (2), 141 (7), 101 (16), 85 (12), 81 (10), 68 (15), 59 (17), 43 (100), 39 (11), 31 (5). Anal. calc. for $C_{12}H_{18}O_5S$ (274.33): C 52.54, H 6.61, S 11.69; found: C 52.48, H 6.70, S 11.66.

*O-Ethyl S-(2,3-O-Isopropylidene-5-O-trityl-α-*D*-ribofuranosyl) Dithiocarbonate* (**10**). A soln. of **9** [42] (4.32 g, 10 mmol) and Bu_4NCl (100 mg, 0.36 mmol) in toluene (50 ml) was treated with 10% NaOH soln. (20 ml) and TsCl (2.86 g, 15 mmol) and stirred for 15 min at r.t. After addition of potassium ethyl dithiocarbonate (3.21 g, 20 mmol) and stirring for further 2 h at r.t., the org. layer was separated and washed with brine (3 × 25 ml). The aq. layers were extracted with Et_2O (50 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. Filtration of the residue through a pad of silica gel (100 g, 250 ml of hexane/AcOEt 97.5:2.5, 250 ml of hexane/AcOEt 9:1) and crystallization from the filtrate gave **10** (3.6 g, 67%). FC (50 g, hexane/AcOEt 9:1) of the mother liquor gave additional **10** (0.94 g, 18%). ^{1}H-NMR ($CDCl_3$): 7.22–7.50 (*m*, 15 arom. H); 6.61 (*d*, *J* = 5.0, H–C(1)); 5.14 (*dd*, *J* = 5.0, 6.3, H–C(2)); 4.59–4.79 (*m*, H–C(3), CH_2O); 4.28–4.32 (*m*, H–C(4)); 3.56 (*dd*, *J* = 3.0, 10.5, H–C(5)); 3.06 (*dd*, *J* = 3.0, 10.5, H'–C(5)); 1.52 (*s*, Me); 1.38 (*t*, *J* = 7.1, Me); 1.33 (*s*, Me).

*S-Phenacyl 2,3-O-Isopropylidene-5-O-trityl-1-thio-α- and -β-*D*-ribofuranoside* (**11a** and **11b**). A soln. of **10** (5.36 g, 10 mmol) and freshly prepared NaOEt [1] (817 mg, 12 mmol) in dry THF (40 ml) was stirred for 10 min at 50°. The resulting soln. of the thiolate was added dropwise to a cooled (–20°) soln. of phenacyl chloride (1.86 g, 12 mmol) in THF (40 ml). After stirring for 1 h at r.t., the soln. was diluted with Et_2O, washed with brine, dried ($MgSO_4$), and evaporated. FC (350 g, hexane/AcOEt 5:1) of the residue gave **11a** (4.71 mg, 83%).

FC (350 g, hexane/AcOEt 6:1 → 5:1) of the crude product obtained from an analogous reaction in EtOH instead of THF gave **11b** (1.82 g, 32%), **11a/11b** (*ca.* 2:1; 0.92 g, 16%), and **11a** (0.83 g, 15%).

Data of **11a**: R_f (hexane/AcOEt 5:1) 0.18. IR (film): 3061*w*, 3029*w*, 2986*w*, 2935*w*, 1676*m*, 1598*w*, 1490*m*, 1446*s*, 1379*w*, 1319*w*, 1278*m*, 1208*m*, 1158*m*, 1102*m*, 1077*m*, 1011*s*, 914*w*, 892*w*, 863*w*, 760*s*, 700*s*, 638*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.94–7.99 (*m*, 5 arom. H); 7.20–7.62 (*m*, 15 arom. H); 5.68 (*d*, *J* = 5.0, H–C(1)); 4.95 (*dd*, *J* = 5.0, 6.5, H–C(2)); 4.61 (*dd*, *J* = 2.5, 6.5, H–C(3)); 4.27–4.31 (*m*, H–C(4)); 4.15 (*d*, *J* = 14.5, BzC*H*); 4.05 (*d*, *J* = 14.5, BzC*H'*); 3.39 (*dd*, *J* = 3.5, 10.3, H–C(5)); 3.13 (*dd*, *J* = 3.5, 10.3, H'–C(5)); 1.54 (*s*, Me); 1.30 (*s*, Me).

Data of **11b**: R_f (hexane/AcOEt 5:1) 0.22. IR (film): 3066*w*, 3033*w*, 2982*w*, 2942*w*, 1673*m*, 1600*w*, 1485*m*, 1443*s*, 1379*w*, 1317*w*, 1278*m*, 1207*m*, 1155*m*, 1108*m*, 1071*m*, 1012*s*, 918*w*, 892*w*, 864*w*, 761*s*, 700*s*, 638*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.90 (*dd*, *J* = 1.0, 8.0, 2 arom. H); 7.21–7.60 (*m*, 18 arom. H); 5.37 (*d*, *J* = 1.8, H–C(1)); 4.40–4.59 (*m*, H–C(2), H–C(3), H–C(4)); 4.03 (*d*, *J* = 15.0, BzC*H*); 3.83 (*d*, *J* = 15.0, BzC*H'*); 3.35 (*dd*, *J* = 7.0, 9.5 H–C(5)); 3.29 (*dd*, *J* = 7.0, 9.5, H'–C(5)); 1.50 (*s*, Me); 1.29 (*s*, Me).

*2,3-O-Isopropylidene-5-O-trityl-1-thio-*D*-ribono-1,4-O-lactone* (**12**). Irradiation of a soln. of **11a** (2 g, 3.53 mmol) in dry CH_2Cl_2 (250 ml) for 1 h at r.t., evaporation, and crystallization of the residue from petroleum ether (b.p. 50–70°) gave **12** (1.50 g, 95%). $[\alpha]_D^{20} = -71.2$ (*c* = 1.0, $CHCl_3$). UV (MeOH): 252 (5600). IR (KBr): 3062*w*, 2993*w*, 2934*w*, 2878*w*, 1492*w*, 1448*m*, 1374*m*, 1347*m*, 1319*w*, 1285*m*, 1244*m*, 1206*s*, 1173*m*, 1149*m*, 1096*s*, 998*m*, 940*w*, 914*w*, 882*w*, 792*w*, 754*m*, 708*s*, 635*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.24–7.42 (*m*, 15 arom. H); 5.14 (*d*, *J* = 5.4, H–C(2)); 4.96 (*t*, *J* = 2.0, H–C(4)); 4.51 (*d*, 5.4, H–C(3)); 3.80 (*dd*, *J* = 2.5, 11.0, H–C(5)); 3.12 (*dd*, *J* = 1.8, 11.0, H'–C(5)); 1.48 (*s*, Me); 1.35 (*s*, Me). Anal. calc. for $C_{27}H_{26}O_4S$ (446.56): C 72.62, H 5.87, S 7.18; found: C 72.58, H 5.99, S 6.99.

*2,3,4,6-Tetra-*O*-acetyl-1-thio-*D*-glucono-1,5-*O*-lactone* (**15**) *and 2,4,6-Tri-*O*-acetyl-3-deoxy-1-thio-*D*-erythro-hex-2-eno-1,5-*O*-lactone* (**16**). Heating of a soln. of **14** [22] (742 mg, 1 mmol) in toluene (10 ml) for 5 min to 110°, evaporation, and FC (25 g, hexane/AcOEt 2:1) of the residue gave **16** (214 mg, 71%).

FC (60 g of silanized silica gel 60 (*Merck*), hexane/AcOEt 97.5:2.5) of the crude product from an analogous reaction gave **15/16** (153 mg, *ca.* 45%) and pure **15** (72 mg, 20%).

Data of **15**: IR (film): 2960*w*, 1755*s*, 1432*w*, 1371*m*, 1217*s*, 1122*w*, 1049*m*, 959*w*, 908*w*, 599*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.60–5.63 (*m*, H–C(2)); 5.31–5.41 (*m*, H–C(3), H–C(4)); 4.69–4.75 (*m*, H–C(5)); 4.39 (*dd*, *J* = 2.8, 13.0, H–C(6)); 4.46 (*dd*, *J* = 3.8, 13.0, H'–C(6)); 2.19 (*s*, Ac); 2.14 (*s*, Ac); 2.10 (*s*, Ac); 2.09 (*s*, Ac). CI-

MS: 363 (24, $[M+1]^+$), 347 (16), 331 (22), 321 (9), 303 (7), 287 (26), 245 (15), 201 (17), 185 (16), 169 (84), 157 (29), 141 (48), 125 (31), 109 (100), 97 (91).

Data of **16**: R_f (hexane/AcOEt 2:1) 0.21. $[\alpha]_D^{20} = +124.3$ (c = 0.83, $CHCl_3$). UV (MeOH): 220 (3700), 248 (2900), 288 (1850). IR (film): 2950*w*, 1747*s*, 1650*w*, 1435*w*, 1370*m*, 1218*s*, 1157*w*, 1122*m*, 1049*m*, 955*w*, 910*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.28 (*d*, J = 4.4, H–C(3)); 5.65 (*dd*, J = 4.4, 6.0, H–C(4)); 4.79 (br. *td*, $J \approx$ 4.7, 6.0, H–C(5)); 4.46 (*dd*, J = 4.9, 12.0, H–C(6)); 4.38 (*dd*, J = 4.5, 12.0, H'–C(6)); 2.27 (*s*, Ac); 2.14 (*s*, Ac); 2.12 (*s*, Ac). CI-MS: 320 (100, $[M + NH_4]^+$), 303 (10, $[M+1]^+$)), 243 (4), 186 (11), 184 (14), 183 (7), 125 (4), 97 (2), 60 (4). Anal. calc. for $C_{12}H_{14}O_7S$ (302.30): C 47.68, H 4.67, S 10.61; found: C 47.62, H 4.43, S 10.41.

S-*Phenacyl 2,3,4,6-Tetra*-O-*benzyl-1-thio-β*-D-*glucopyranoside* (**19**). A soln. of NaOMe (83 mg of Na, 3.6 mmol) in MeOH (50 ml) was treated with **18** [1] [18] (1.93 g, 3 mmol) and stirred for 30 min at 50°. This soln. was cooled to r.t. and added dropwise to a soln. of phenacyl chloride (0.56 g, 3.6 mmol) in MeOH (25 ml). After stirring for 1 h at r.t. and evaporation, FC (50 g, hexane/AcOEt 5:1) of the residue gave **19** (1.42 g, 70%). R_f (hexane/AcOEt 5:1) 0.25. UV (CH_2Cl_2): 245 (12134), 333 (2925). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.13–8.00 (*m*, 25 arom. H); 4.85 (*d*, J = 11.0, PhC*H*); 4.82 (*d*, J = 11.0, 2 PhC*H*); 4.81, 4.70, 4.57, 4.56, 4.47 (5 *d*, J = 11.0, 5 PhC*H*); 4.53 (*d*, J = 10.0, H–C(1)); 4.12 (*d*, J = 14.5, BzC*H*); 4.04 (*d*, J = 14.5, BzC*H'*); 3.60–3.70 (*m*, 4 H); 3.40–3.50 (*m*, 2 H).

3,4,6-Tri-O-*benzyl-2-deoxy-1-thio*-D-arabino-*hexono-1,5*-O-*lactone* (**20**). a) *From* **19**. Irradiation of a soln. of **19** (2 g, 3 mol) in dry CH_2Cl_2 (250 ml) for 1 h at r.t., evaporation, and FC (50 g, hexane/AcOEt 5:1) of the residue gave **20** (638 mg, 48%).

b) *From* **4**. Irradiation of a soln. of **4** (300 mg, 0.54 mmol) in dry CH_2Cl_2 (250 ml) for 15 min at r.t., evaporation, and FC (25 g, hexane/AcOEt 9:1) of the residue gave **20** (87 mg, 36%). R_f (hexane/AcOEt 5:1) 0.31. $[\alpha]_D^{20} = +56.8$ (c = 1.0, $CHCl_3$). UV (CH_2Cl_2): 254 (12000), 370 (440). IR (film): 3085*w*, 3060*m*, 3029*m*, 2867*m*, 1950*w*, 1875*w*, 1810*w*, 1750*w*, 1685*w*, 1605*w*, 1585*w*, 1496*m*, 1454*s*, 1367*m*, 1326*m*, 1278*s*, 1210*m*, 1160*s*, 1102*s*, 1036*s*, 907*w*, 736*s*, 697*s*, 596*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.18–7.36 (*m*, 15 arom. H); 4.67, 4.61, 4.59, 4.54 (4 *d*, J = 12.0, 4 PhC*H*); 4.47 (*d*, J = 12.0, 2 PhC*H*); 4.35–4.38 (*m*, H–C(5)); 3.88–3.94 (*m*, H–C(3), H–C(4)); 3.83 (*dd*, J = 3.0, 11.0, H–C(6)); 3.76 (*dd*, J = 3.5, 11.0, H'–C(6)); 3.54 (*ddd*, J = 1.7, 4.0, 16.5, H–C(2)); 3.18 (*dd*, J = 3.0, 16.5, H'–C(2)). CI-MS: 466 (82, $[M + NH_3 + 1]^+$), 449 (24), 358 (100), 341 (56), 252 (20), 233 (23), 220 (3), 203 (2), 198 (2). Anal. calc. for $C_{27}H_{28}O_4S$ (448.58): C 72.29, H 6.29, S 7.15; found: C 72.53, H 6.35, S 6.89.

Methyl 2,3,4,6-Tetra-O-*benzyl-α- and -β*-D-*glucopyranosyl Disulfide* (**21a** and **21b**, resp.). A freshly prepared soln. of NaOEt [1] (898 mg, 13.2 mmol) in dry THF (70 ml) was treated with **18** (6.65 g, 10 mmol) and stirred for 30 min at r.t. The suspension was cooled to 0°, added dropwise (poly(tetrafluoroethylene) (= PTFE) tube, pressure) to a soln. of dimethyl(methylthio)sulfonium tetrafluoroborate (3.23 g, 16.5 mmol) in THF (70 ml), and stirred for 2 h at r.t. After dilution with Et_2O (500 ml), the org. layer was washed with brine (3 × 100 ml), dried ($MgSO_4$), and evaporated. FC (350 g, hexane/AcOEt 9:1) of the residue gave **21b** (4.28 g, 71%), **21a/21b** (0.22 g, 7%), and **21a** (0.60 g, 10%).

Data of **21a**: R_f (hexane/AcOEt 9:1) 0.15. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.11–7.38 (*m*, 20 arom. H); 5.46 (*d*, J = 4.0, H–C(1)); 4.93, 4.82, 4.76, 4.73, 4.64, 4.61 (6 *d*, J = 11.0, 6 PhC*H*); 4.46 (*d*, J = 11.0, 2 PhC*H*); 4.08–4.15 (*m*, 1 H); 3.61–3.87 (*m*, 5 H); 2.43 (*s*, MeS).

Data of **21b**: R_f (hexane/AcOEt 9:1) 0.18. M.p. 52–54°. IR (KBr): 3090*w*, 3029*w*, 2868*m*, 2835*m*, 2811*w*, 1605*w*, 1498*w*, 1458*m*, 1400*w*, 1361*m*, 1281*w*, 1219*w*, 1138*m*, 1092*s*, 1065*s*, 1004*m*, 912*w*, 736*s*, 698*s*, 659*w*, 619*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.16–7.35 (*m*, 20 arom. H); 4.95, 4.87 (2 *d*, J = 11.0, 2 PhC*H*); 4.84 (*d*, J = 11.0, 2 PhC*H*); 4.76 (*d*, J = 11.0, PhC*H*); 4.59 (*d*, J = 11.0, 2 PhC*H*); 4.52 (*d*, J = 11.0, PhC*H*); 4.48 (*d*, J = 9.0, H–C(1)); 3.64–3.84 (*m*, 5 H); 3.47–3.53 (*m*, H–C(5)); 2.51 (*s*, MeS). Anal. calc. for $C_{35}H_{38}O_5S_2$ (602.80): C 69.74, H 6.35, S 10.64; found: C 69.81, H 6.25, S 10.83.

2,3,4,6-Tetra-O-*benzyl-1-thio*-D-*glucono-1,5*-O-*lactone* (**4**). A cooled (0°) soln. of **21b** (1 g, 1.7 mmol) in CH_2Cl_2 (30 ml) was treated with 3-chloroperbenzoic acid (406 mg, 2 mmol) and stirred for 1 h at 0°. Evaporation of the soln., FC (25 g, hexane/AcOEt 2:1) of the residue, and heating of the main product (R_f (hexane/AcOEt 2:1) 0.25, thiosulfinate) for 15 min at 120°/0.05 mbar gave **4** (745 mg, 79%). R_f (hexane/AcOEt 2:1) 0.17. $[\alpha]_D^{20} = +126.4$ (c = 1.0, $CHCl_3$). UV (MeOH): 205 (31000), 252 (6600). IR (film): 3088*w*, 3060*w*, 3030*w*, 2868*w*, 1950*w*, 1875*w*, 1810*w*, 1750*w*, 1685*w*, 1605*w*, 1585*w*, 1496*w*, 1452*m*, 1368*m*, 1275*w*, 1238*w*, 1210*m*, 1176*s*,

1096*s*, 1030*m*, 915*w*, 738*s*, 698*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.13–7.41 (*m*, 20 arom. H); 4.90 (*ddd*, *J* = 2.0, 4.0, 9.5, H–C(5)); 4.85 (*d*, *J* = 11.7, ArC*H*); 4.64 (*d*, *J* = 12.0, ArC*H*); 4.63 (*d*, *J* = 12.0, ArC*H*); 4.51–4.57 (*m*, H–C(2), 3 ArC*H*); 4.45 (*d*, *J* = 11.5, ArC*H*); 4.34 (*d*, *J* = 11.7, ArC*H*); 3.85–3.94 (*m*, H–C(3), H–C(4), H–C(6)); 3.78 (*dd*, *J* = 4.0, 11.5, H'–C(6)). Anal. calc. for $C_{34}H_{34}O_5S$ (554.70): C 73.62, H 5.18, S 5.78; found: C 73.46, H 5.15. S 5.79.

*O-Ethyl S-(2,3,4,6-Tetra-O-benzyl-α- and -β-*D*-mannopyranosyl) Dithiocarbonate* (**24a** and **24b**, resp.). A cooled (–40°) soln. of **22** [24] (1.08 g, 2 mmol) and CCl_4 (0.386 ml, 4 mmol) in dry CH_2Cl_2 (10 ml) was treated dropwise with $P(Et_2N)_3$ (0.545 ml, 3 mmol) and stirred for 30 min at –40°. After the addition of potassium ethyl dithiocarbonate (561 mg, 3.5 mmol), stirring was continued for further 2 h at –40°. Filtration of the dark soln. through a pad of silica gel (40 g, hexane/AcOEt 1:1), evaporation, and FC (50 g, hexane/AcOEt 9:1 → 7:1) of the residue gave **24a** (93 mg, 7%), **24a/24b** (80 mg, 6%), and **24b** (998 mg, 75%).

Data of **24a:** R_f (hexane/AcOEt 7:1) 0.31. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.14–7.44 (*m*, 20 arom. H); 6.34 (*d*, *J* = 2.5, H–C(1)); 4.49–4.90 (*m*, 10 H); 4.10 (*t*, *J* = 9.5, H–C(4)); 3.91 (*dd*, *J* = 2.5, 3.0, H–C(2)); 3.68–3.84 (*m*, 4 H); 1.41 (*t*, *J* = 7.1, Me).

Data of **24b:** R_f (hexane/AcOEt 2:1) 0.22. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.16–7.43 (*m*, 20 arom. H); 5.47 (*d*, *J* = 1.0, H–C(1)); 4.52–5.05 (*m*, 10 H); 4.11 (*dd*, *J* = 1.0, 3.0, H–C(2)); 3.99 (*t*, *J* = 9.5, H–C(4)); 3.71–3.79 (*m*, 3 H), 3.60 (*ddd*, *J* = 2.5, 4.0, 9.5, H–C(5)); 1.38 (*t*, *J* = 7.2, Me).

*Methyl 2,3,4,6-Tetra-O-benzyl-β-*D*-mannopyranosyl Disulfide* (**25**). As described for **21a/21b**, with NaOEt (408 mg, 6 mmol), THF (100 ml), **24b** (3.22 g, 5 mmol; 30 min at 50°), dimethyl(methylthio)sulfonium tetrafluoroborate (1.47 g, 7.5 mmol), and THF (50 ml; 1 h at r.t). After workup, FC (75 g, hexane/AcOEt 8:1) of the residue gave **25** (8.26 g, 83%). R_f (hexane/AcOEt 8:1) 0.21. M.p. 55–57°. IR (KBr): 3084*w*, 3029*w*, 2900*w*, 2859*w*, 1495*w*, 1452*m*, 1360*m*, 1136*m*, 1110*m*, 1095*m*, 1071*s*, 1031*s*, 996*m*, 958*w*, 750*s*, 734*s*, 698*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.18–7.44 (*m*, 20 arom. H); 4.96 (*d*, *J* = 11.6, PhC*H*); 4.87 (*d*, *J* = 10.8, PhC*H*); 4.78 (*d*, *J* = 11.6, PhC*H*); 4.73 (*d*, *J* = 11.7, PhC*H*); 4.68 (*d*, *J* = 0.7, H–C(1)); 4.68 (*d*, *J* = 11.7, PhC*H*); 4.60 (*d*, *J* = 11.9, PhC*H*); 4.57 (*d*, *J* = 10.8, PhC*H*); 4.53 (*d*, *J* = 11.9, PhC*H*); 4.03 (*dd*, *J* = 0.7, 2.1, H–C(2)); 3.90 (*t*, *J* = 9.5, H–C(4)); 3.77 (*dd*, *J* = 1.9, 10.9, H–C(6)); 3.70 (*dd*, *J* = 6.2, 10.9, H'–C(6)); 3.61 (*dd*, *J* = 2.9, 9.5, H–C(3)); 3.55 (*ddd*, *J* = 1.9, 6.2, 9.5, H–C(5)); 2.51 (*s*, MeS). ^{13}C-NMR (101.2 MHz, $CDCl_3$): 137.95–138.30 (4 *s*); 127.51–128.52 (several *d*); 93.88 (*d*, *J* = 155); 84.25 (*d*); 80.18 (*d*); 76.25, 75.25, 74.77, 73.42, 72.67 (2 *d*, 4 *t*); 69.75 (*t*); 24.55 (*q*). Anal. calc. for $C_{35}H_{38}O_5S_2$ (602.80): C 69.74, H 6.35, S 10.64; found: C 69.66, H 6.50, S 10.76.

*2,3,4,6-Tetra-O-benzyl-1-thio-*D*-mannono-1,5-O-lactone* (**26**). As described for **4**, with **25** (1.2 g, 2 mmol), CH_2Cl_2 (20 ml), 3-chloroperbenzoic acid (487 mg, 2.4 mmol; R_f (hexane/AcOEt 2:1) 0.28, thiosulfinate): **26** (875 mg, 79%). R_f (hexane/AcOEt 7:1) 0.18. $[\alpha]_D^{20} = -10.2$ (*c* = 1.0, $CHCl_3$). UV (MeOH): 208 (29300), 250 (2000). IR (film): 3087*w*, 3060*w*, 3029*m*, 2922*m*, 2867*m*, 1950*w*, 1875*w*, 1810*w*, 1750*w*, 1700*w*, 1605*w*, 1585*w*, 1496*m*, 1459*s*, 1397*w*, 1358*m*, 1310*w*, 1244*s*, 1180*m*, 1149*s*, 1099*s*, 1025*m*, 910*w*, 740*s*, 698*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.08–7.46 (*m*, 20 arom. H); 5.10 (*d*, *J* = 11.5, ArC*H*); 4.83 (*d*, *J* = 12.0, ArC*H*); 4.63 (*d*, *J* = 12.0, ArC*H*); 4.61 (*d*, *J* = 11.5, ArC*H*); 4.60 (*d*, *J* = 12.0, ArC*H*); 4.54 (*d*, *J* = 12.0, ArC*H*); 4.39 (*d*, *J* = 11.0, ArC*H*); 4.32 (*td*, *J* = 4.3, 8.0, H–C(5)); 4.30 (*d*, *J* = 2.5 H–C(2)); 4.28 (*d*, *J* = 11.0, ArC*H*); 3.99 (*t*, *J* = 2.5, H–C(3)); 3.88 (*dd*, *J* = 2.5, 8.0, H–C(4)); 3.73 (*d*, *J* = 4.3, 2 H–C(6)). Anal. calc. for $C_{34}H_{34}O_5S$ (554.70): C 73.62, H 6.18, S 5.78; found: C 73.48, H 6.35, S 5.84.

*S-Methyl 1-Deoxy-3,4:6,7-di-O-isopropylidene-2-thio-β-*D*-*manno*-hept-2-ulofuranoside* (**27**) *and S-Methyl 3,5^1-Anhydro-5-C-[hydroxy(thiocarbonyl)]-1,2:4,5:7,8:10,11-tetra-O-isopropylidene-6-thio-β-*D*-manno-*D*-manno-undec-6-ulo-6,9-O-furanoside* (**29**). A soln. of **2** (548 mg, 2 mmol) in dry THF (20 ml) was cooled to –78° and treated dropwise with MeLi (*ca.* 1.6 M in Et_2O; 1.25 ml, 2 mmol). After stirring for 2 h at –78° and the addition of MeI (0.25 ml, 4 mmol), the soln. was allowed to warm up to r.t., stirred for 5 min at r.t., diluted with Et_2O (100 ml), washed with brine (3 × 100 ml), dried ($MgSO_4$), and evaporated. FC (25 g, hexane/AcOEt 5:1) of the residue gave **27/29** (445 mg). Bulb-to-bulb distillation (150°/0.1 mbar) gave **27** (176 mg , 29%, > 97% pure) which was purified by prep. HPLC (hexane/AcOEt 5:1, t_R *ca.* 15 min). The residue consisted mainly of **29** (85%) and **27** (5%), and was separated by prep. HPLC (hexane/AcOEt 9:1, t_R (**29**) *ca.* 21 min): pure **29** (264 mg, 47%).

Data of **27**. R_f (hexane/AcOEt 5:1) 0.19. M.p. 85. $[\alpha]_D^{20} = -35.6$ (*c* = 0.60, $CHCl_3$). UV (MeOH): 260 (7200). IR ($CHCl_3$): 2990*s*, 2940*m*, 2880*w*, 1450*w* (br.), 1385*s*, 1375*s*, 1155*m* (br.), 1120*s*, 1065*s*, 995*w*, 980*m*, 970*m*, 960*w*, 935*w*, 890*m*, 865*m*, 845*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.83 (*dd*, *J* = 4.1, 6.0, H–C(4)); 4.56 (*d*, *J* = 6.0,

H–C(3)); 4.45 (*ddd*, *J* = 4.4, 6.0, 8.0, H–C(6)); 4.11 (*dd*, *J* = 6.0, 8.8, H–C(7)); 4.06 (*dd*, *J* = 4.4, 8.8, H'–C(7)); 3.78 (*dd*, *J* = 4.1, 8.0, H–C(5)); 2.21 (*s*, MeS); 1.56 (*s*, Me); 1.47 (*s*, 3 H–C(1)); 1.46 (*s*, Me); 1.38 (*s*, Me); 1.35 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): *Table 4*. CI-MS: 322 (11, $[M + NH_4]^+$), 305 (1, $[M + 1]^+$), 275 (13), 274 (97, $[M - MeS + NH_3]^+$), 258 (15), 257 (100, $[M - MeS]^+$). Anal. calc. for $C_{14}H_{24}O_5S$ (304.40): C 55.24, H 7.95, S 10.53; found: C 55.15, H 7.94, S 10.33.

Data of **29**. Yellow oil. R_f (hexane/AcOEt 5:1) 0.19. $[\alpha]_D^{20} \approx 9.8$ (*c* = 1.2, $CHCl_3$). IR (film): 3260*w*, 3083*w*, 2987*s*, 2935*m*, 1717*w*, 1456*w*, 1376*s*, 1336*w*, 1300*w*, 1249*s*, 1211*s*, 1177*m*, 1121*m*, 1073*s*, 961*w*, 890*w*, 843*m*, 755*w*. IR ($CHCl_3$): 3000*s*, 2950*m*, 2890*w*, 1460*w*, 1385*s*, 1375*s*, 1340*m* (br.), 1305*m* , 1180*s*, 1150*s*, 1120*s*, 1075*s*, 1000*m*, 980*m*, 970*m*, 945*m*, 905*m*, 890*m*, 865*m*, 845*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.46 (br. *d*, *J* ≈ 6.2, H–C(7)); 5.16 (*d*, *J* = 3.4, H–C(4)); 4.82 (*dd*, *J* = 3.3, 8.6, H–C(3)); 4.795 (*dd*, *J* = 4.6, 6.3, H–C(8)); 4.44 (*td*, *J* = 4.8, 8.6, H–C(2)); 4.34 (*td*, *J* ≈ 5.5, 7.2, H–C(10)); 4.29 (*dd*, *J* = 4.6, 7.2, H–C(9)); 4.18 (*d*, *J* = 4.9, 2 H–C(1)); 4.10 (*dd*, *J* = 4.9, 8.6, H–C(11)); 4.07 (*dd*, *J* = 5.9, 8.6, H'–C(11)); 2.21 (*s*, MeS); 1.59 (*s*, Me); 1.52 (*s*, Me); 1.48 (*s*, Me); 1.45 (*s*, Me); 1.43 (*s*, Me); 1.395 (*s*, Me); 1.39 (*s*, Me); 1.38 (*s*, Me). NOE Experiments: *Table 5*. ^{13}C-NMR (50 MHz, $CDCl_3$): *Table 4*. CI-MS: 582 (13), 581 (27), 580 (100, $[M + NH_4]^+$), 563 (18, $[M + 1]^+$), 532 (11, $[M - MeS + NH_3]^+$).

S-(*$^2H_3$*)*Methyl 1-Deoxy-3,4:6,7-di*-O-*isopropylidene-2-thio-β*-D-manno-*hept-2-ulofuranoside* (**28**) *and* S-(*$^2H_3$*)*Methyl 3,5'-Anhydro-5*-C-*[hydroxy(thiocarbonyl]-1,2:4,5:7,8:10,11-tetra*-O-*isopropylidene-6-thio-β*-D-manno-D-manno-*undec-6-ulo-6,9*-O-*furanoside* (**30**). As described for **27/29**, with CD_3I (*Fluka purum*, > 99.5 D) instead of MeI.

Data of **28**. IR ($CHCl_3$): 2990*s*, 2940*m*, 2880*w*, 2140*w*, 1450*w* (br.), 1375*s*, 1155*m* (br.), 1120*s*, 1065*s*, 995*w*, 980*m*, 960*w*, 935*w*, 890*m*, 865*m*, 845*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): identical to that of **27**, except 2.21 (*s*, *ca.* 0.1 H, MeS). ^{13}C-NMR (50 MHz, $CDCl_3$): identical to that of **27**, except for the missing MeS signal at 10.02. CI-MS: 326 (14), 325 (100, $[M + NH_4]^+$), 322 (4, $[M + NH_4]^+$ of **27**), 308 (0.5, $[M + 1]^+$), 275 (11), 274 (80, $[M - CD_3S + NH_3]^+$), 257 (33, $[M - CD_3S]^+$).

Data of **30**. IR ($CHCl_3$): 3000*s*, 2950*m*, 2890*w*, 2150*w*, 1460*w*, 1385*s*, 1375*s*, 1340*m* (br.), 1305*m* , 1180*s*, 1150*s*, 1120*s*, 1075*s*, 1000*m*, 970*m*, 945*m*, 905*m*, 890*m*, 865*m*, 845*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): identical to that of **29**, except 2.21 (*s*, 0.15 H, MeS). ^{13}C-NMR (50 MHz, $CDCl_3$): identical to that of **29**, except for the missing MeS signal at 12.64. CI-MS: 584 (22), 583 (100, $[M + NH_4]^+$), 580 (5, $[M + NH_4]^+$ of **29**), 566 (40, $[M + 1]^+$), 563 (2, $[M + 1]^+$), 550 (5, $[M - Me]^+$), 532 (50, $[M - CD_3S + NH_3]^+$), 515 (5, $[M - CD_3S]^+$).

S-*Methyl 1-Deoxy-3,4:6,7-di*-O-*isopropylidene-2-thio-α*-D-manno-*hept-2-ulofuranoside* (**31**). Under N_2, a suspension of CuI (190 mg, 1 mmol) in dry THF (10 ml) was cooled to -20°, treated with MeLi (1.25 ml, 2 mmol; quick addition by syringe)[4]). The clear soln. was stirred for 10 min at 0°, cooled to –30°, and treated dropwise (within 5 min) with a soln. of **2** (274 mg, 1 mmol) in THF (5 ml). The soln. was stirred for 10 min at –30°, 10 min at –20°,15 min at –10°, and 25 min at –5°. After the addition of MeI (0.5 ml, 8 mmol) and stirring for 5 min at –5° and for 5 min at 0°, the soln. was diluted with Et_2O (100 ml) and washed with sat. NH_4Cl soln. and brine. The org. layer was filtered (Et_2O) through a short column of Na_2SO_4 (15 g) and silica gel (10 g). Evaporation of the filtrate and bulb-to-bulb distillation (150°/0.1 mbar) of the residue gave **31/27** 4:1 (147 mg, 49%) which was separated by HPLC (hexane/AcOEt 9:1 → 5:1): pure **31**. Oil. R_f (hexane/AcOEt 9:1) 0.19. t_R (prep. HPLC, hexane/AcOEt 9:1) *ca.* 8 min. $[\alpha]_D^{20} = 110.4$ (*c* = 0.60, $CHCl_3$). IR ($CHCl_3$): 2990*m*, 2940*m*, 2890*w*, 1455*w* (br.), 1385*s*, 1375*s*, 1150*m* (br.), 1135*s*, 1120*m*, 1065*s*, 1010*w*, 995*w*, 980*m*, 975*m*, 965*w* (sh), 940*w*, 910*m*, 895*m*, 870*m*, 845*m*, 830*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.80 (*dd*, *J* = 3.8, 6.0, H–C(4)); 4.42 (*ddd*, *J* = 4.4, 6.3, 7.9, H–C(6)); 4.36 (*d*, *J* = 6.0, H–C(3)); 4.09 (*dd*, *J* = 6.3, 8.6, H–C(7)); 3.955 (*dd*, *J* = 3.8, 7.9, H–C(5)); 3.95 (*dd*, *J* = 4.4, 8.6, H'–C(7)); 1.98 (*s*, MeS); 1.59 (*s*, 3 H–C(1)); 1.47 (*s*, Me); 1.44 (*s*, Me); 1.36 (*s*, Me); 1.32 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): *Table 4*. CI-MS: 323 (17), 322 (100, $[M + NH_4]^+$), 305 (21, $[M + 1]^+$).

S-(*$^2H_3$*)*Methyl 1-Deoxy-3,4:6,7-di*-O-*isopropylidene-2-thio-α*-D-manno-*hept-2-ulofuranoside* (**32**). As described for **31**, with CD_3I instead of MeI. IR ($CHCl_3$): 2990*m*, 2940*m*, 2890*w*, 2140*w*, 1455*w* (br.), 1385*s*, 1375*s*, 1150*m* (br.), 1135*s*, 1120*m*, 1065*s*, 1010*w*, 995*w*, 980*m*, 965*w* (sh), 940*w*, 910*m*, 895*m*, 870*m*, 845*m*, 830*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): identical to that of **31**, except for the missing MeS signal at 1.98. ^{13}C-NMR

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[4]) Slow addition led to partial dissolution of the Cu salt and to brown-red colouration of the solvent.

(50 MHz, $CDCl_3$): Identical to the spectrum of **31**, except for the missing MeS signal at 11.75. CI-MS: 326 (12), 325 (100, $[M + NH_4]^+$), 322 (*ca.* 0.5, $[M + NH_4]^+$ of **31**), 308 (60, $[M + 1]^+$), 292 (9, $[M - Me]^+$), 275 (12), 274 (93, $[M - CD_3S + NH_3]^+$), 258 (13), 257 (99.5, $[M - CD_3S]^+$), 250 (9).

X-Ray Analysis of **27**. Crystals were obtained from Et_2O/hexane. $C_{14}H_{24}O_5S$ (304.4); triclinic P_1; a = 6.758 (2), b = 7.798 (3), c = 8.536 (3) Å, α = 113.98 (3)°, β = 90.61 (3)°, γ = 102.50 (3)°; V = 398.8 (14) Å^3; D_x = 1.268 Mg/m^3; Z = 1. Intensities were measured in the Θ–2Θ scan mode on a *Siemens-R3m* diffractometer (graphite monochromator, MoK_α, λ = 0.71069 Å) at 298 K, variable scan speed from 1.40 to 10.0°/min in Θ. Of the 2070 total collected reflections and 2070 independent reflections, 1744 were observed ($F > 5.0\sigma(F)$). R = 0.0428, R_w = 0.0532. The structures were solved with the direct-methods routine of SHELXS-86 [43], and the refinement was performed with *Siemens* SHELXTL PLUS [44].

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