75. Synthesis and Evaluation as Irreversible Glycosidase Inhibitors of Mono- and Oligo(glycosylthio)benzoquinones

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(27.I.94)

The mono(glucosylthio)hydroquinone **2** was prepared by *S*-glycosidation of 2-mercaptobenzene-1,4-diol and by addition of the acetylated 1-thioglucose **3** to benzo-1,4-quinone (*Scheme 1*). The second, higher yielding procedure was adopted for the preparation of a range of (glucosylthio)hydroquinones. Addition of **3** to 2-chlorobenzo-1,4-quinone, followed by oxidation gave the 1-thioglucosides **7** and **12** (1.3:1), while addition of HCl to the (glucosylthio)quinone **4** and oxidation gave mainly **12** (*Scheme 1*). Similarly, the bis(glucosylthio)hydroquinone **33** was obtained from **3** and **4** (*Scheme 4*), and the (cellobiosylthio)hydroquinone **18** from the thiol **16** and benzo-1,4-quinone (*Scheme 2*). Addition of the 4-thioglucoside **21** to benzo-1,4-quinone (→ **22**) and to **4** was followed by oxidation to yield the mono(glucosylthio)quinone **23** and the disubstituted quinones **24** and **25**, respectively (*Scheme 3*). A mixture **24**/**25** was also obtained from the addition of **3** to **23**. The tris(glucosylthio)hydroquinone **36** was obtained by addition/elimination to the dichloroquinone **29** or the dimesylate **31**, which was prepared in a simplified way (*Scheme 4*). The tetrakis(glucosylthio)hydroquinone **37** was obtained from **3** and chloranil, followed by reduction. The acylated hydroquinones were deprotected (→ **5**, **9**, **14**, **19**, **27**, **34**, and **38**), and oxidized to the corresponding quinones (**6**, **10**, **15**, **20**, **28**, **35**, and **40**). The (glucosylthio)quinones **6**, **15**, **20**, **28**, and **35** were tested as time-dependent inactivators of a retaining β-1,4-glucosidase from *Agrobacterium faecalis* (*Abg*), which has a strong exo-glucosidase action (*Table 1*). Similarly, compounds **20**, **28**, and **35** were tested with a cellulase from *Cellulomonas fimi* (*Cex*) which degrades cellulose and cellooligosaccharides by hydrolysis of a cellobiose unit from the nonreducing terminus. The most effective inactivators for *Abg* were **6**, **15**, and **35**, which inactivated this enzyme with similar second-order rate constants. (Glycosylthio)quinone **28** was the worst inactivator and did not show normal saturation behaviour. Inactivation of *Cex* by the (glycosylthio)quinones was 3–500 times slower than that of *Abg*. The three inactivators **20**, **28**, and **35** had approximately the same efficacy with *Cex*, suggesting that they bind to this enzyme in a similar mode. Further, the K_i values observed are very similar to K_m values measured for aryl cellobiosides, implying that they bind at the active site.

Introduction. – Irreversible inhibitors of glycosidases, which react specifically at the active site of the enzyme, are tools for structural and mechanistic studies of glycosidases [1] [2]. Such inhibitors are most often substrate analogues which possess a functional group of suitable reactivity towards the amino-acid residues at the active site of the glycosidase. As a rule, an electrophilic functionality is required to form a covalent enzyme-inhibitor bond and to thereby inactivate the enzyme. Examples of such active site-directed inactivators include *N*-(bromoacetyl)glycopyranosylamines [3–6], glycopyranosyl isothiocyanates [7], and epoxyalkyl glycosides [2].

In this context we became interested in quinone glycosides. Quinones readily add nucleophiles to form aromatic hydroquinone derivatives [8] [9]. The 2-methylbenzo-1,4-

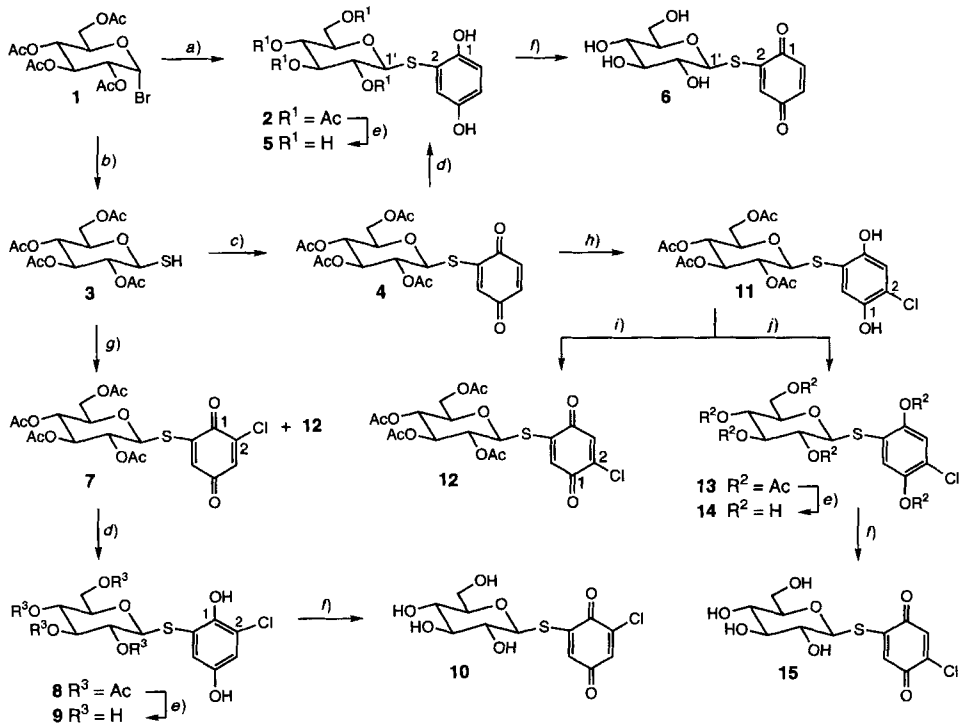
quinone and its 3-glutathion-*S*-yl derivative are potent inhibitors of NADP-linked 15-hydroxyprostaglandin dehydrogenases [10], and chlorinated benzo-1,4-quinones irreversibly inhibit glutathione S-transferases [11]. Many quinone glycosides (= *O*-glycosides) are natural products, most notably (glycosyloxy)anthracyclinones [12] or -anthraquinones [13]. A number of *O*- and *S*-glycosides of naphtho-1,4-quinones possess antitumor [14] and antifungal [15] [16] activity. *S*-Glycosides (= 1-thioglycosides) and *O*,*S*-bisglycosides of mercaptophenols were also synthesised [17]. Benzoquinone glycosides, however, are apparently not known. Benzoquinone 1-thioglycosides appeared to be particularly well suited for our purpose, as alkyl and aryl 1-thioglycosides are more stable to hydrolysis by acids or enzymes than the corresponding glycosides [18].

We report the synthesis of 1-thio-glucosides of benzo-1,4-quinone, 2-chlorobenzo-1,4-quinone, and of the corresponding hydroquinones. We have also prepared three types of quinone bis(1-thioglycosides) representing 'quinologous' trisaccharides. Two of them are cellotriose analogs, where a glucosyl unit at the reducing end or in the central position of cellotriose is replaced by a quinone moiety. In a further analog of a trisaccharide, two glucose units were attached to the quinone *via* their anomeric positions (C(1)–S). Considering that these compounds represent a new class of oligosaccharide analogs, we have also prepared tris- and tetrakis(glucosylthio)benzoquinones and -hydroquinones. We also report the testing of a number of these compounds as irreversible inactivators of two enzymes which cleave β-1,4-glucosidic linkages. One of these, *Agrobacterium faecalis* β-glucosidase (*Abg*), hydrolyses a range of β-glucosidic linkages and has a strong exo-glucosidase action on cello-oligosaccharides [19]. Hydrolysis is effected with retention of the anomeric configuration, and the enzyme follows a double-displacement mechanism involving a covalent glycosyl-enzyme intermediate which is formed and hydrolyzed *via* oxycarbenium-ion-like transition states [20]. The other enzyme is a cellulase from *Cellulomonas fimi* (*Cex*) which degrades cellulose and cello-oligosaccharides *via* hydrolysis of a cellobiose unit from the nonreducing terminus [21] according to a similar mechanism.

Results and Discussion. – *Quinone 1-Thioglycosides.* We evaluated two routes for the preparation of quinone mono-(1-thioglucosides) (*Scheme 1*). The classical procedure for the synthesis of 1-thioglycosides is based on the reaction of a glycosyl halide with a thiol under alkaline conditions [22]. In this way, acetobromoglucose **1** reacted with 2-mercaptobenzene-1,4-diol [23] [24] in the presence of KOH to afford 54% of the crystalline 2,5-dihydroxyphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**2**). No *O*-glucosidation was observed. The scope of this method is, however, limited by the availability of more highly substituted mercaptohydroquinones.

Various (alkylthio)- and (arylthio)quinones were prepared by the nucleophilic addition of alkanethiols or arenethiols to quinones, followed by oxidation [25–29], but this sequence was never used to prepare (glycosylthio)quinones or -hydroquinones. We realized an efficient synthesis of 3,6-dioxocyclohexa-1,4-dienyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**4**) by adding the easily available 1-thioglucose **3** [30] [31] to benzo-1,4-quinone (**17**). A spontaneous addition, indicated by decolorization, led to the hydroquinone **2**, which was oxidized *in situ* by adding a further equivalent of benzo-1,4-quinone to give 64% of crystallized yellow 1-thioglucoside **4**. A yield of 81% of **4** was realized by performing the oxidation with (diacetoxyiodo)benzene instead of benzo-1,4-quinone.

Scheme 1



a) 2-Mercaptobenzene-1,4-diol, KOH, acetone, 24 h, r.t.; 54%. *b*) 1. $NH_2C(S)NH_2$, acetone, 15 min, reflux [30]; 2. $Na_2S_2O_5$, CCl_4/H_2O, 15 min, reflux [31]; 70%. *c*) Benzo-1,4-quinone (**17**; 2 equiv.), MeOH, 1 h, r.t.; 64%; or 1. **17** (1 equiv.), MeOH, 1 h, r.t.; 2. $PhI(OAc)_2$, 15 min, r.t.; 81%. *d*) $Na_2S_2O_4$, $CHCl_3/H_2O$, 5 min, r.t.; 96% (**2**), 93% (**8**). *e*) NaOMe, MeOH, 45 min, r.t.; 93% (**5**), 86% (**9**), 86% (**14**). *f*) $PhI(OAc)_2$, MeOH; 15 min, r.t.; 80% (**6**), 57% (**10**), 73%) (**15**). *g*) 1. 2-Chlorobenzo-1,4-quinone, MeOH, 1 h, r.t.; 2. $PhI(OAc)_2$, 15 min, r.t.; 65% (**7**/**12** 1.3:1). *h*) HCl, $CHCl_3$, 45 min, r.t.; 79%. *i*) Ag_2O, Na_2SO_4, CH_2Cl_2, 30 min, r.t.; 71%. *j*) Ac_2O/Py, 15 h, r.t.; 86%.

The direct deacetylation of the thioglucoside **4** in the presence of basic catalysts (*e.g.* NaOMe, K_2CO_3, DBU, NH_3) failed due to the lability of the quinone moiety towards bases. Acidic conditions induced glycoside cleavage before the deacetylation was complete. Thus, **4** was first transformed in almost quantitative yield into the corresponding hydroquinone **2** by reduction with $Na_2S_2O_4$ in a two-phase system. Deacetylation of **2** with 2 equiv. of NaOMe in MeOH then afforded **5** in 93% yield. Oxidation of **5** was best performed with 1.5 equiv. of (diacetoxyiodo)benzene in MeOH[1]). The quinone **6** precipitated from the reaction mixture, either directly or upon addition of CH_2Cl_2, and was obtained nearly pure in a yield of 80%. Crystallization gave the analytically pure quinone as small orange needles.

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[1]) Other oxidizing agents tested were H_2O_2, 3-chloroperbenzoic acid, 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (= 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile), cerium(IV) ammonium nitrate, HgO, MnO_2, and PbO_2. (Diacetoxyiodo)benzene gave the best results with regard to selectivity, yield, and ease of workup.

The structure of **4** is confirmed by the CI-MS which shows the typical quinone $[M + 2 + NH_4]^+$ peak at m/z 490 and by a strong IR band at 1632 cm^{-1}. In the ^{1}H-NMR spectrum (see *Exper. Part, Tables 2* and *3*), the β-D-configuration of **4** and **2** is evident from $J(1',2')$ of 9.9 and 10.1 Hz, respectively. H–C(1') of **2** resonates at 4.61 ppm; the H–C(1') signal of **4** is shifted downfield to 4.88 ppm. The 3 aromatic H of **2** give rise to a *m* at 6.91–6.86 ppm, and the phenolic OH resonate at 6.59 and 5.35 ppm as *s*, which are exchangeable with D_2O. The quinonoid H of **4** resonate at 6.83 (*d*, J = 10.1 Hz), 6.75 (*dd*, J = 2.4, 10.1 Hz), and 6.69 (*d*, J = 2.3 Hz) ppm, consistent with a mono-substituted quinone ring. In the ^{13}C-NMR spectra of **4** and **2** (see *Exper. Part, Table 4*), the C(1') *d*'s appear at 80.73 and 85.91 ppm, and thus characteristically at a higher field as compared to *O*-glucosides. The signals for the carbonyl C-atom of **4** are observed at 184.16 and 183.24 ppm.

The ^{1}H-NMR spectrum of **5** in (D_6)DMSO shows 3 *d*'s at 5.30, 5.05, and 4.94 ppm and a *t* at 4.44 ppm, all exchangeable with D_2O, evidencing the OH groups at C(2'), C(3'), C(4'), and C(6'). The quinone structure of **6** is confirmed by the $[M + 2 + NH_4]^+$ peak at m/z 322 in the CI-MS, two strong IR bands at 1644 and 1662 cm^{-1}, and the 2 *s*'s for the carbonyl groups at 189.07 and 187.84 ppm in the ^{13}C-NMR spectrum (see *Exper. Part, Table 5*). In the ^{1}H-NMR spectrum ((D$_6$)DMSO), the 4 D_2O-exchangeable OH signals appear at 5.61 (*d*, J = 5.7 Hz), 5.20 (*d*, J = 4.6 Hz), 5.07 (*d*, J = 5.3 Hz), and 4.57 ppm (*dd*, '*t*', J = 5.4 Hz). H–C(1') resonates at 4.78 ppm and is shifted downfield, as compared to the corresponding signal for **5** (4.46 ppm). The UV spectrum of **6** is characterized by the π–π^* and the n–π^* transitions at 251 (lg ε = 3.8) and 407 nm (lg ε = 3.2).

The structure of **2** and **4** was established by X-ray analysis (*Figs. 1–3*). The crystal structure of the hydroquinone **2** shows an intramolecular H-bond between one phenolic OH group and O–C(5') (= O1), characterized by a O,O distance of 2.86 Å. This correlates with a relative orientation of the aromatic and the pyranoside ring characterized by the dihedral angles O1–C2–S–C8 = –87.2 and C2–S–C8–C9 of 68.6° (arbitrary numbering) and a *gt* arrangement of the AcO–C(6') group. This orientation is quite different in the quinone **4**; it is characterized by corresponding values of –82.5 and –171.9° and a *gg* orientation of the AcO–C(6') group, *i.e.* by a combined rotation around the C8–S and the C(5')–C(6') bonds, as compared to the hydroquinone **2**. The other phenolic group of **2** forms an intermolecular H-bond to the carbonyl O-atom of a neighbouring AcO–C(4') group, linking the molecule into infinite one-dimensional chains.

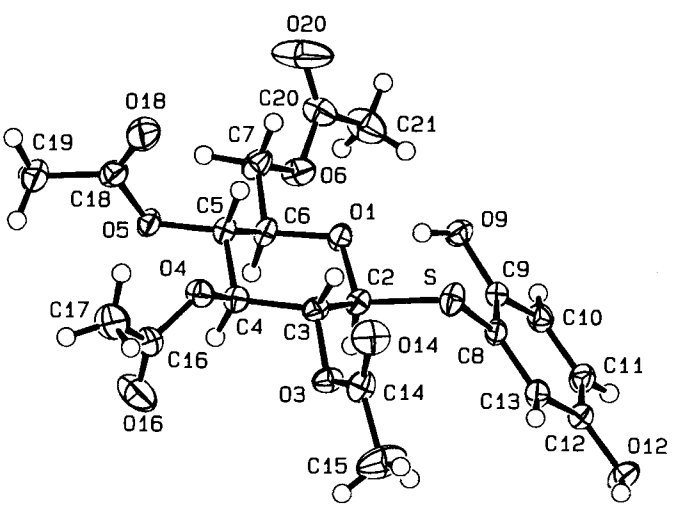


Fig. 1. *X-Ray structure of* **2**. Arbitrary numbering.

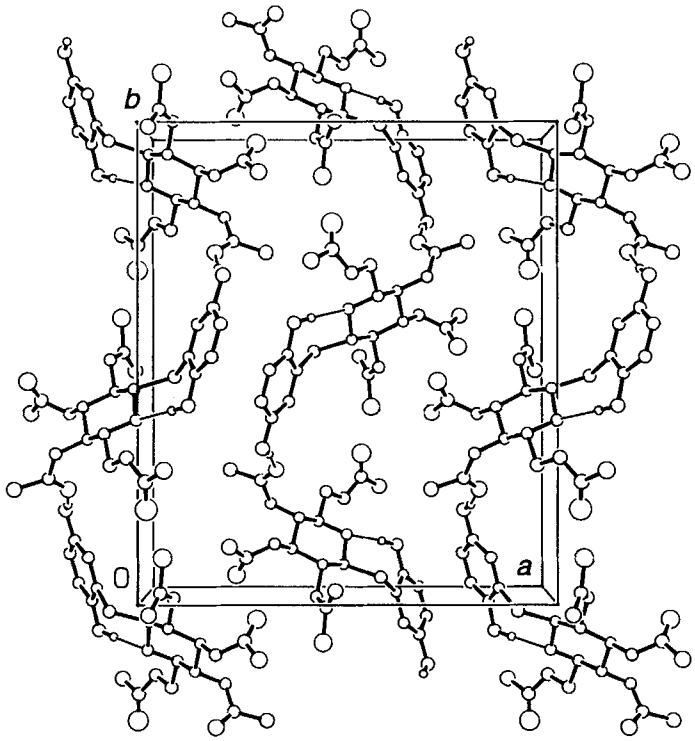


Fig. 2. *Packing diagram for* **2**. The intermolecular H-bonds link the molecules into one-dimensional chains running parallel to the crystallographic *b* axis.

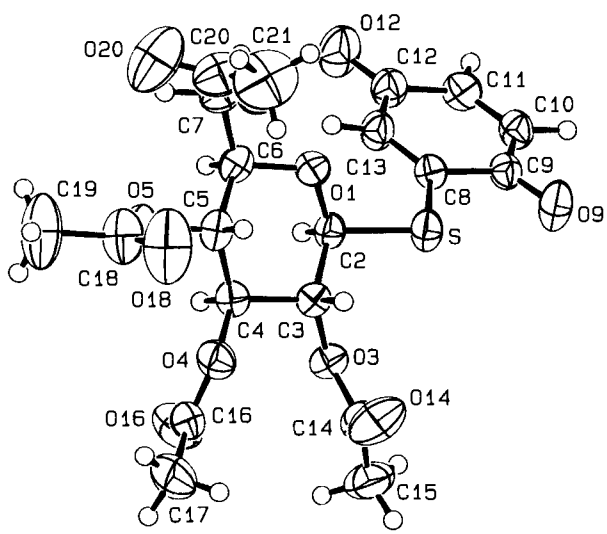


Fig. 3. *X-Ray structure of* **4**. Arbitrary numbering.

For the synthesis of the 2-chlorobenzo-1,4-quinone 1-thioglucosides we added 2-chlorobenzo-1,4-quinone to **3** in MeOH and oxidized the product with (diacetoxyiodo)benzene (*Scheme 1*) to obtain 65% of a 1.3:1 mixture of the 2,6- and the 2,5-disubstituted chloro-(glucopyranosylthio)quinones **7** and **12**. The regioisomers were separated by preparative HPLC. The 2,6-disubstituted quinone **7** was also purified by repeated recrystallizations in hexane/acetone. Reduction with $Na_2S_2O_4$ afforded the chloro-hydroquinone **8** (93%), which was deacetylated to **9** (86%) and oxidized to the deprotected chloroquinone 1-thioglucoside **10** (57%). The isomeric 2,5-disubstituted quinone **15** was synthesized more efficiently from **4**. Addition of HCl to **4** afforded mainly the hydroquinone **11** (79%). It was oxidized to the benzoquinone **12** (71%) and acetylated to the hydroquinone acetate **13** (86%). Both **12** and **13** were easily purified by crystallization. Deacetylation of **13** led to **14** (86%) which was oxidized with (diacetoxyiodo)benzene to **15** (73%).

The ^{1}H-NMR spectra of **7** and **12** in $CDCl_3$ (see *Exper. Part, Tables 2* and *3*) show 2 *d*'s at 6.98 and 6.73 ppm (J = 2.4 Hz) for the quinonoid H of **7**, and 2 *s*'s at 7.07 and 6.92 ppm for those of **12** indicating the 2,6-, and the 2,5-disubstitution, respectively. Analogous signals are observed in the spectra of the unprotected derivatives **10** and **15**. The UV spectra of **10** and **15** are characterized by two bands at 293 and 288 nm and 424 and 425 nm, respectively. Thus, as reported before [32] [33], the chloro substituents cause a bathochromic shift of the bands for the π–π^* transition.

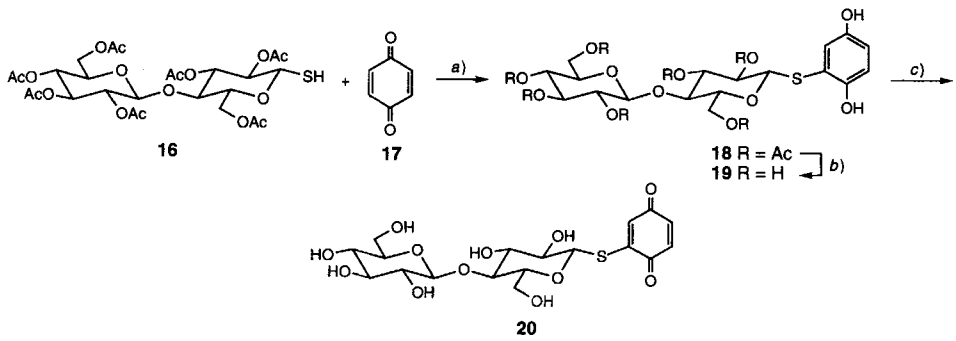
It was stated that the introduction of a second substituent into mono-substituted quinones by nucleophilic addition is mainly determined by the nature of the first substituent [8] [9] [34]. Benzo-1,4-quinones with a strong acceptor substituent add a nucleophile preferentially in the '*ortho*'-position to yield 1,2,3,4-tetrasubstituted benzenes [35], whereas strongly electron-donating groups favour '*para*'-addition, affording 1,2,4,5-tetrasubstituted benzenes [36]. In both cases, the formation of the '*meta*' (= 1,2,3,5-tetrasubstituted)-products is also observed. Depending on steric hindrance, the strength of the donor or acceptor properties of the first substituent, and on reaction conditions, the '*meta*'-product may predominate [37] [38]. There are indications that weak donor or acceptor substituents tend to form '*meta*'-substituted products [36]. The low regioselectivity of the addition of the 1-thioglucose **3** to chlorobenzoquinone is in keeping with these guidelines (*cf.* below), considering that the Cl-substituent is both a σ-acceptor and a π-donor, and that the '*ortho*'-position is sterically hindered. The relatively high regioselectivity observed for the addition of gaseous HCl to the quinone 1-thioglucoside **4** is best rationalized by assuming a regioselective protonation of the quinone carbonyl group, directed by the vicinal glucosylthio substituent.

2. *Quinone 1-Thiocellobiosides.* The addition of 1 equiv. of benzo-1,4-quinone (**17**) to the 1-thiocellobiose **16** [39] in MeOH/THF (*Scheme 2*) afforded the crystalline hydroquinone 1-thiocellobioside **18** (82%), which was deacetylated (NaOMe) to give **19** (70%) and then oxidized with (diacetoxyiodo)benzene to yield the desired quinone 1-thiocellobioside **20** (75%).

The structure of **20** is evidenced by the IR absorptions at 1664 and 1646 cm^{-1}, the UV bands at 250 (lg ε = 3.7) and 407 nm (lg ε = 3.2), and the $[M + Na]^+$ peak at m/z 487 in the ESI-MS. In the ^{13}C-NMR spectrum, the carbonyl C resonate at 184.47 and 184.19 ppm.

3. *Quinones with a 1-Thioglucose and a 4-Thioglucose Moiety.* We explored two routes for the synthesis of quinone derivatives carrying both a 1- and a 4-thioglucosyl sub-

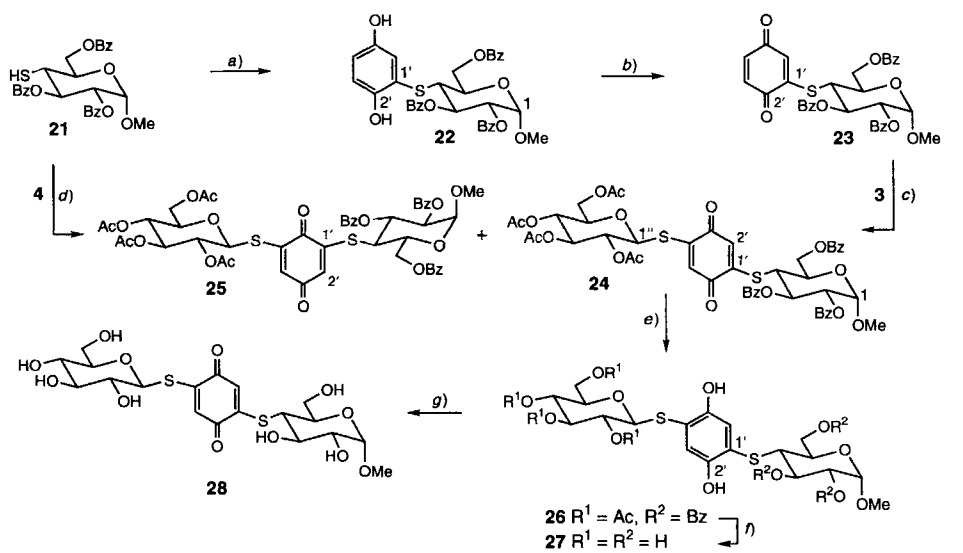
Scheme 2



a) 1.2 Equiv. of **17**, MeOH/THF, 1 h, r.t.; 2. $Na_2S_2O_4$, $CHCl_3/H_2O$, 5 min, r.t.; 82%. *b*) NaOMe, MeOH; 3 h, r.t., followed by FC; 70%. *c*) $PhI(OAc)_2$, MeOH, 20 min, r.t.; 75%.

stituent, one attached to the quinone *via* its anomeric position and the other one *via* its 4-position (*Scheme 3*). The hydroquinone **22** was prepared in 81% yield by addition of the 4-thioglucose **21** [40] [41] to **17**. Oxidation with Ag_2O afforded the quinone **23** (93%). The 1-thioglucose **3** was then added to quinone **23** and the product oxidized to give a 2.5:1 mixture (80%) of the 2,5-disubstituted quinone **24** and the 2,6-disubstituted regioisomer **25**, which were separated by preparative HPLC.

Scheme 3



a) 1. **17**, MeOH, 30 min, r.t.; 2. $Na_2S_2O_4$, $CHCl_3/H_2O$, 5 min, r.t.; 81%. *b*) Ag_2O, CH_2Cl_2, 30 min, r.t.; 93%. *c*) 1. **3** (1 equiv.), MeOH, 30 min, r.t.; 2. $PhI(OAc)_2$, 30 min, r.t.; 66% (**24**/**25** 2.5:1). *d*) 1. **4** (1 equiv.), MeOH, 30 min, r.t.; 2. $PhI(OAc)_2$, 30 min, r.t.; 83% (**24**/**25** 10:1); after recrystallization from C_6H_6 44% of pure **24**. *e*) $Na_2S_2O_4$, $CHCl_3/H_2O$, 5 min, r.t.; 100%. *f*) NaOMe, MeOH; 10 h, r.t.; 86%. *g*) $PhI(OAc)_2$, 20 min, r.t.; 58%.

We also examined the converse route *viz.* the addition of the 4-thioglucose **21** to the quinone **4** (see *Scheme 3*) using the same conditions as before. We obtained a 10:1 mixture of **24** and **25** (83%). From this mixture, **24** was isolated by repeated crystallization from benzene. The unprotected quinone **28** was prepared in the usual manner *via* the hydroquinone **26** (98%), followed by deacetylation to **27** (86%) and by oxidation of **27** to **28** (76%).

The regioselectivity differences of the two routes are surprising. As discussed above for the regioselectivity of the formation of the chlorobenzoquinone 1-thioglucosides, one expects the predominant formation of **24** for both the addition of **3** to **23** and of **21** to **4**. The higher regioselectivity observed for the addition of **21** to **4** correlates with the expected higher nucleophilicity of **21** *vs.* **3** and the stronger σ-acceptor properties of the 1-thioglucose moiety in **4** as compared to the 4-thioglucose moiety in **23**, suggesting that not only the substituent of the quinone, but also the nucleophilicity of the attacking species contribute to the regioselectivity[2]).

The ^{1}H-NMR data of **22**–**27** are summarized in *Tables 6* and *7* (see *Exper. Part*). The signals of the quinoid H of **23** in 3- and 4-position relative to the glucosylthio substituent appear at 6.59 (*d*, J = 10.0 Hz) and 6.46 ppm (*dd*, J = 2.3, 10.1 Hz), at higher field than those of the corresponding signals of **4**, whereas the *d* of the quinoid H in position 6 is shifted somewhat downfield to 6.80 ppm (J = 2.3 Hz). The type of substitution of **24** and **25** is obvious from the ^{1}H-NMR signals of the quinonoid H. The ^{1}H-NMR spectrum of the 2,5('*para*')-disubstituted quinone **24** is characterized by 2 *s*'s at 6.82 and 6.42 ppm, whereas the quinonoid H of the 2,6('*meta*')-disubstituted quinone **25** give rise to 2 *d*'s at 6.78 (J = 2.2 Hz) and 6.33 ppm (J = 2.2 Hz).

4. *Bis- and Tetrakis(glucosylthio)quinones.* The crystalline, bisglucosylated quinone **32** (*Scheme 4*) was prepared in 32% yield by addition of the 1-thioglucose **3** to the quinone 1-thioglucose **4** and subsequent oxidation with benzo-1,4-quinone. It was reduced with $Na_2S_2O_4$ to the hydroquinone **33** (92%) which was also obtained directly from **3** and **4** (40%). Deacetylation of **33** gave **34** (62%), which was again oxidized with (diacetoxyiodo)benzene, yielding 68% of the deprotected bisglucosylated quinone **35**.

Tolkach et al. prepared naphthoquinone 1-thioglucosides in 65–95% yields by treating halogenated naphthoquinones with the thiol **3** in the presence of K_2CO_3 [15]. We intended to simplify the access to **32** by treating 2,5-dichlorobenzo-1,4-quinone (**29**) [42] and 2,5-bis(mesyloxy)benzo-1,4-quinone (**31**) with **3**. The latter was prepared previously from 2,5-dihydroxybenzo-1,4-quinone (**30**) [43] in four steps and an overall yield of 39% [44]. We developed a new procedure which gave **31** in one step and in a slightly better yield (41%) by mesylating **30** with methanesulfonic anhydride/pyridine in THF (*Scheme 4*). Both the K_2CO_3-promoted reactions of **3** with **29** or with **31** gave a 1.3:1 mixture of **36** and **32** (57 and 55%, resp.). The electrophilic character of the initially formed quinone **32** is markedly increased by the glucosylthio substituents, and the nucleophilic addition of a thiol is competing with substitution. Attempts to avoid the addition by varying the reaction conditions were not successful.

The tetrasubstituted hydroquinone **37** was synthesized by treating **3** with 2,3,5,6-tetrachlorobenzo-1,4-quinone (= chloranil) in the presence of K_2CO_3 (54%). Oxidation of **37** with (diacetoxyiodo)benzene afforded 88% of the brown quinone **39** by crystallization

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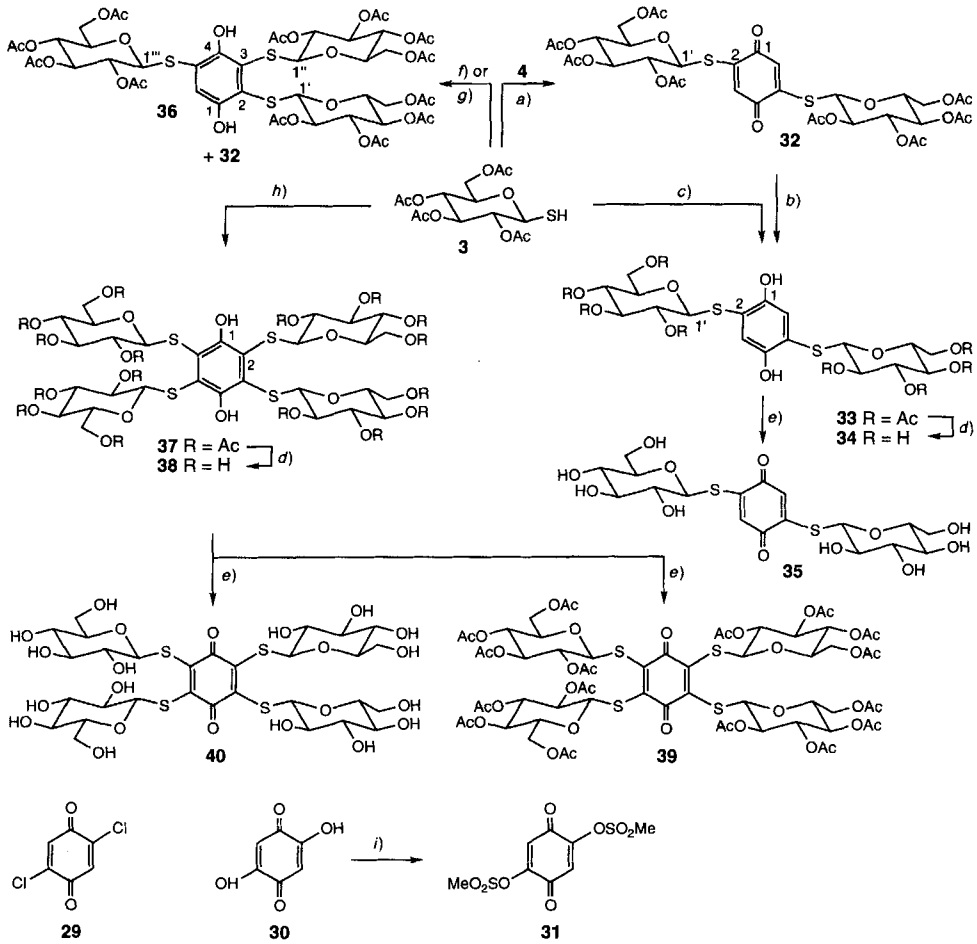
[2]) The addition of **3** to **4** (see below) gave **32** as a readily crystallizing material (32% yield). The ^{1}H-NMR spectrum of the crude addition product indicates that the regioselectivity is distinctly lower than the one observed for the addition of **21** to **4**; the regioisomeric addition products of **3** and **4** could, however, not be separated by analytical HPLC.

Scheme 4



a) **4**, followed by **17** (1 equiv.), MeOH/THF, 1 h, r.t.; 32%. *b*) $Na_2S_2O_4$, $CHCl_3/H_2O$, 5 min, r.t.; 92%. *c*) **4**, acetone/MeOH, 30 min, r.t.; 40%. *d*) NaOMe, MeOH, 45 min, r.t.; 62% (**34**; after crystallization from i-PrOH), 93% (**38**). *e*) $PhI(OAc)_2$, 20 min, r.t.; 68% (**35**), 88% (**39**), 77% (**40**). *f*) **29**, K_2CO_3, acetone/H_2O, 1 h, r.t., FC; 57% (**36**/**32** 1.3:1). *g*) **31**, K_2CO_3, acetone/H_2O, 1 h, r.t., FC; 55% (**36**/**32** 1.3:1). *h*) Chloranil, K_2CO_3, acetone/H_2O, 1 h, r.t., FC; 54%. *i*) $(MeSO_2)_2O$/Py, THF, 6 h, r.t.; 41%.

from MeOH. The deprotected hydroquinone **38** was prepared in 93% yield after deacetylation of 37 with NaOMe. Subsequent oxidation gave 77% of the quinone **40**.

The ^1H- and ^{13}C-NMR spectra of **32**–**35** (see *Exper. Part, Tables 2–5*) show 1 set of signals for the 2 glucosyl residues, the 2 quinonoid H-atoms, and the 3 pairs of homotopic C-atoms of the quinone unit. The signals for H–C(1′) of **32** and **35** appear at 4.87 (D_2O) and 4.80 ppm ((D$_6$)DMSO), resp., with the same chemical-shift values as for the monosubstituted derivatives **3** and **6**. The β-D-configuration is evident by $J(1',2')$ of 9.8 (**32**) and 9.1 Hz (**35**). The structure of **35** is confirmed by the $[M + Na]^+$ peak at m/z 519.5 in the ESI-MS and the IR band at 1640 cm^{-1}. In the ^{13}C-NMR spectrum, the resonance of the carbonyl groups at 184.20 ppm shows an upfield shift of *ca.* 4 ppm, as compared to the monosubstituted quinone **6**.

The structure of **36** was evidenced by elemental analysis, MS, and NMR spectroscopy. The ^{1}H-NMR spectrum displays 3 sets of signals, corresponding to the 3 glucosyl residues. The *d*'s of the anomeric H appear at 4.88 (J = 10.0 Hz), 4.69 (J = 10.2 Hz), and 4.60 ppm (J = 10.2 Hz), revealing the β-D-configuration.

Similar to **32**–**35**, ^{1}H-NMR spectra of **37**–**40** show only 1 set of signals for the glucosyl residues. H–C(1') of **39** and **40** resonates at 5.46 (J = 10.1 Hz), and 5.09 ppm (J = 9.0 Hz), resp., showing a downfield shift of *ca.* 0.6 and 0.3 ppm, as compared to the corresponding mono- (**4**, **6**) and disubstituted quinones (**32**, **35**). The ^{13}C-signal of the carbonyl groups at 178.32 ppm of **40** (*Table 5*) is shifted further upfield by *ca.* 10 ppm, as compared to **6**, and by *ca.* 6 ppm, as compared to **35**. The UV spectra of **39** and **40** are characterized by bands at 374 (lg ε = 3.6), and 371 nm (lg ε = 3.7), respectively. Conceivably, this tetrasubstitution of benzoquinone causes a bathochromic shift of the band for the π–π^* transition and a hypsochromic shift for the n–π^* transition resulting in an overlapping of the two bands [45].

Inactivation Studies. (Glycosylthio)quinones **6**, **15**, **20**, **28**, and **35** were tested as time-dependent inactivators of *Abg* and/or *Cex* (*Table 1*). Inactivation was found to conform to the simple scheme where the inactivator (I) first binds reversibly to the enzyme (E), with a dissociation constant K_i, then reacts covalently, with a rate constant k_i:

$$E + I \overset{K_i}{\rightleftharpoons} E \cdot I \overset{k_i}{\rightarrow} E - I$$

The (glycosylthio)quinones were reasonably stable in aqueous solution, decomposition occurring over a time period of hours as judged by TLC analysis of incubation mixtures.

Table 1. *Inactivation of Glycosidases by Quinone Thioglycosides: Kinetic Parameters*

Inhibitor	Enzyme	k_i [min^{-1}]	K_i [mM]	k_i/K_i [min^{-1} mM^{-1}]
6	*Abg*	0.03	0.06	0.5
15	*Abg*	0.08	0.4	0.2
20	*Cex*	0.0014	1.2	0.001
28	*Abg*	–	–	0.009
28	*Cex*	0.004	1.2	0.003
35	*Abg*	0.014	0.04	0.35
35	*Cex*	0.0012	0.7	0.002

Their decomposition was, however, accelerated by the presence of buffers in the reaction mixture, presumably due to general acid/base catalysis. A range of buffers was tested, but buffers containing tris(hydroxymethyl)aminomethane (= 2-amino-2-(hydroxymethyl)propane-1,3-diol; *Tris*), 2,2',2''-nitrilotris(ethanol), 1*H*-imidazole, 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES), and phosphate were all found to cause this unwanted degradation. Fortunately, one of the enzymes (*Cex*) is quite stable in deionised H_2O at the relatively high concentrations of enzyme employed for the inactivation mixtures; thus, *Cex* could be studied in the absence of added buffer. The other enzyme, *Abg*, requires a buffer, but fortunately this enzyme was also the most rapidly inactivated, so lengthy incubations were not required. These problems with stability decreased the accuracy with which the kinetic parameters could be determined since it was frequently not possible to study the first-order reactions for more than one half-life. Nonetheless, error limits in all cases were $< \pm 30\%$.

The most effective inactivators (based upon k_i/K_i values) for *Abg* were **6** and **15**, the simple β-D-glucosylthio derivatives, and **35**, the bis(β-D-glucosylthio) derivative, which all inactivated with similar second-order rate constants. Surprisingly, the (glycosylthio)-quinone with the second sugar moiety linked *via* its 4-position, **28**, which might have been

expected to be the best inactivator based upon its greater resemblance to the cello-oligosaccharide substrates for this enzyme, was the worst inactivator tested with this enzyme. In addition, the kinetic behaviour was unusual, not showing the normal saturation behaviour at the inactivator concentrations tested. As a consequence, only the k_i/K_i value could be determined, from the slope of the plot of k_{obs} *vs.* inhibitor concentration. The most likely explanation is that this compound does indeed bind more tightly in a specific orientation at the active site, but that when bound in this manner, it is not able to react with the active site residue which interacts with the other, less constrained derivatives. Inactivation requires binding in a second, less favourable binding mode, in competition with the non-productive binding mode.

Inactivation of *Cex* by (glycosylthio)quinones was found to be 3–500 times slower than that seen with *Abg*, again based upon k_i/K_i values. This likely simply reflects differences in active-site architecture which fortuitously result in the placement of a suitable nucleophile closer to the bound (glycosylthio)quinone moiety in *Abg* than in *Cex*. All three inactivators tested had approximately the same efficacy, suggesting that they are all bound in a similar mode. Indeed, the K_i values observed are very similar to K_m values measured for aryl cellobiosides [21], implying that this binding is, indeed, at the active site.

These (glycosylthio)quinone derivatives, therefore, represent a new class of active-site-directed inactivators for glycosidases which bind covalently to the enzyme. These (glycosylthio)quinones have considerable potential for identification of active-site residues, but their lability in buffered solution does limit their usefulness for some other applications.

We thank the *Swiss National Science Foundation*, *F. Hoffmann-La Roche AG*, Basle, the *Natural Sciences and Engineering Research Council of Canada*, and the *Protein Engineering Network* for financial support of this work.

Experimental Part

General. MeOH was dried over Mg, CH_2Cl_2 over $CaCl_2$, acetone over K_2CO_3, and THF over Na. All other solvents were simply distilled. Benzo-1,4-quinone (**17**) and 2-chlorobenzo-1,4-quinone were purified by sublimation *i.v.* Solvents were evaporated under reduced pressure below 40°. Products were dried at r.t./0.05–0.01 mbar. TLC: 0.25-mm precoated silica-gel plates (*Merck*, silica gel *60* F_{254}); detection by spraying the plates with 2.5% anisaldehyde soln. in EtOH/AcOH/H_2SO_4 80:1:3 followed by heating at *ca.* 200°. Flash chromatography (FC): silica gel (*Merck 60*, 0.040–0.063 mm). High-performance liquid chromatography (HPLC): anal. *Spherisorb*-silica 250 × 4.0 mm or *Zorbax-Sil* 250 × 4.6 mm column; prep. *Spherisorb-Si60* 250 × 20 mm column. M.p.: uncorrected. Optical rotations: 1-dm cell at 25° and 589 nm; values were determined from a regression curve. UV Spectra (λ_{max} in nm (ε)): 1-cm quartz cell. IR Spectra: KBr or 3% $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR Spectra: chemical shifts δ in ppm rel. to $SiMe_4$ as internal standard; coupling constants J in Hz. Mass spectra: chemical ionization (CI; NH_3) at 70 eV, electron-spray ionisation (ESI), or fast-atom bombardment (FAB).

Inactivation Studies, Materials and Methods. All buffers and substrates were obtained from *Sigma*. *Abg* and *Cex* were isolated from their *E. coli* clones as previously described [20] [46] and assayed as follows. *Abg* was assayed by measuring the rate of release of 4-nitrophenol from 4-nitrophenyl β-D-glucopyranoside by following changes in absorbance at 400 nm. Assays were performed at 37° in 50 mM sodium phosphate buffer, pH 7.0, containing 0.1% BSA (bovine serum albumin). *Cex* was assayed in an identical manner, except that 4-nitrophenyl cellobioside was employed as substrate. Time courses for inactivation at each inactivator concentration were determined by incubating a small volume of the enzyme in the presence of inactivator, then removing 10-µl aliquots at time intervals and assaying these as described above. Incubation conditions employed were: *Abg* (0.005 mg·ml^{-1}) in 50 mM sodium phosphate buffer containing 0.1% BSA, pH 7.0, 37°: *Cex* (0.07 mg·ml^{-1}) in deionised H_2O containing

Table 2. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *for the S-Glucosides* **2**, **4**, **7**, **8**, **12**, **32**, **33**, **38** (300 MHz, $CDCl_3$), *and* **5**, **9**, **10**, **14**, **34**, **35** (300 MHz, D_2O)[a][b])

Compound	**2**	**4**[c])	**5**	**7**	**8**	**9**	**10**[d])	**12**	**14**	**32**	**33**	**34**	**35**	**38**
H–C(3)	6.89[e])	6.69	7.04	6.73	6.99[f])	6.92[f])	6.77	6.82	7.07[f])	6.70	7.06	7.06	6.75	–
H–C(5)	6.89[e])	6.75	–	6.98	6.85[f])	6.87[f])	7.11	–	–	–	–	–	–	–
H–C(6)	6.89[e])	6.83	6.87	–	–	–	–	7.07	6.92[f])	6.70	7.06	7.06	6.75	–
H–C(1′)	4.61	4.88	4.69	4.88	4.66	4.66	4.98	4.89	4.63	4.87	4.67	4.71	4.95	5.47
H–C(2′)	4.94	5.24	3.30	5.23	4.95	3.28	3.48	5.24	3.26	5.23	4.96	3.30	3.46	5.07
H–C(3′)	5.20	5.31	3.50	5.31	5.21	3.47	3.57	5.31	3.46	5.31	5.21	3.48	3.55	5.27
H–C(4′)	5.01	5.09	3.36	5.08	5.02	3.31	3.60	5.09	3.32	5.08	5.07	3.35	3.48	5.11
H–C(5′)	3.73	3.85	3.46	3.85	3.76	3.43	3.63	3.87	3.42	3.85	3.76	3.46	3.62	3.75
H_A–C(6′)	4.22	4.21	3.87	4.22	4.25	3.84	3.92	4.23	3.84	4.22	4.19	3.86	3.89	4.08
H_B–C(6′)	4.16	4.13	3.68	4.12	4.17	3.66	3.70	4.12	3.65	4.11	4.19	3.66	3.68	4.23

[a]) Resonances for AcO and *H*OAr: see *Exper. Part.*

[b]) Assignment based upon selective mononuclear-decoupling experiments; the quinonoid and aromatic H-atoms were assigned in accordance with [45] and [48].

[c]) Recorded at 400 MHz.

[d]) Recorded at 500 MHz.

[e]) *Multiplet.*

[f]) Assignments may be reversed.

Table 3. *^{1}H-NMR Coupling Constants* J [Hz] *for the S-Glucosides* **2**, **4**, **7**, **8**, **12**, **32**, **33**, **38** (300 MHz, $CDCl_3$), *and* **5**, **9**, **10**, **14**, **34**, **35** (300 MHz, D_2O)

Compound	**2**	**4**[a])	**5**	**7**	**8**	**9**	**10**[b])	**12**	**14**	**32**	**33**	**34**	**35**	**38**
J(3,5)	–	2.3	2.8	2.4	3.1	2.9	[c])	–	–	–	–	–	–	–
J(5,6)	–	10.1	8.7	–	–	–	–	–	–	–	–	–	–	–
J(1′,2′)	9.9	9.9	9.8	9.7	10.0	9.9	9.4	9.7	9.8	9.8	10.1	9.8	9.3	10.1
J(2′,3′)	9.2	9.1	8.9	9.2	9.2	9.0	9.2	9.2	8.8	9.2	9.2	9.2	8.7	9.3
J(3′,4′)	9.3	9.2	9.0	9.1	9.3	9.0	8.8	9.1	8.9	9.2	9.4	9.0	8.7	9.2
J(4′,5′)	10.0	10.0	9.7	10.1	10.0	9.6	9.7	10.1	9.7	10.0	10.0	9.6	9.6	10.0
J(5′,6′)	2.7	2.2	2.1	2.3	2.6	2.2	2.2	2.3	2.1	2.2	3.7	2.1	[e])	2.3
	4.9	6.5	5.5	6.4	4.9	5.5	6.0	6.4	5.6	6.8	–	5.7	5.9	4.5
J(6′,6′)	12.4	12.4	12.4	12.4	12.5	12.4	12.5	12.4	12.4	12.3	–	12.4	12.1	12.5

[a]) Recorded at 400 MHz.

[b]) Recorded at 500 MHz.

[c]) *Doublet* appears as br. *singlet.*

[e]) Signal not resolved.

0.1% BSA, 37°. The following inactivator-concentration ranges were studied. Inactivations of *Abg*: **6**, 0.016–0.16 mM; **15**, 0.01–0.1 mM **28**, 1.1–5 mM; **35**, 0.08–4.3 mM. Inactivations of *Cex*: **20**, 0.2–3.0 mM; **28**, 0.2–2 mM; **35**, 0.2–3 mM. Control experiments were performed in each case in which no inactivator was included, and rate constants were corrected for the small amount of nonspecific inactivation observed. Pseudo-first-order rate constants for inactivation at each concentration (k_{obs}) were extracted by fitting the plot of residual rate *vs.* inactivator concentration ([I]) to a first-order curve by nonlinear regression using the program GraFit [47]. Values of the quilibrium binding constant, K_i, and the inactivation rate constant, k_i, were derived from these values of k_{obs} by direct fit to the following expression using GraFit [47]: $k_{obs} = k_i[I]/(K_i + [I])$.

*2-(2',3',4',6'-Tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzene-1,4-diol* (**2**). *a*) A soln. of KOH (2.06 g, 37.0 mmol) in H_2O (50 ml) was added to **1** (15.2 g, 37.0 mmol) and 2-mercaptobenzene-1,4-diol [23] [24] (5.27 g, 37.0 mmol) in acetone (150 ml). The mixture was stirred for 24 h at r.t. Acetone was distilled off, the residue dissolved in $CHCl_3$, the soln. washed 3× with H_2O, dried (Na_2SO_4), and evaporated. Crystallization from pentane/CH_2Cl_2 gave **2** (9.5 g, 54%).

b) A soln. of **4** (8.3 g, 17.66 mmol) in $CHCl_3$ (100 ml) was vigorously shaken at r.t. with 100 ml of an aq. soln. of 16.0 g (91.95 mmol) of $Na_2S_2O_4$ until the yellow colour of the org. layer had disappeared (*ca.* 5 min). The org. layer was separated, washed with H_2O, dried (Na_2SO_4), and evaporated: nearly pure **2** (8.03 g, 96%). A sample was crystallized from pentane/CH_2Cl_2. Colourless needles. M.p. 154°. R_f (hexane/AcOEt 1:1) 0.29. $[\alpha]_D^{25} = -34.09$ ($c = 0.52$, $CHCl_3$). UV (CH_2Cl_2). 231 (6300), 307 (5200). UV (MeOH): 207 (22000), 307 (5900). IR (KBr): 3600–3250*s* (br.), 2945*w*, 1748*s*, 1605*w*, 1492*m*, 1455*w*, 1370*w*, 1229*s*, 1125*w*, 1082*w*, 1065*m*, 1039*s*, 915*w*, 828*w*, 781*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*; ArO*H*: 6.59 (*s*, exchange with D_2O); 5.35 (*s*, exchange with D_2O); AcO: 2.13 (*s*); 2.11 (*s*); 2.02 (*s*); 1.99 (*s*). ^{13}C-NMR: *Table 4*. CI-MS: 490 (67, $[M + NH_4]^+$), 393 (25), 392 (100), 213 (17), 102 (10). Anal. calc. for $C_{20}H_{24}O_{11}S$ (472.45): C 50.84, H 5.12, S. 6.79; found: C 50.60, H 5.36, S 6.95.

*2-(2',3',4',6'-Tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzo-1,4-quinone* (**4**). *a*) A soln. of **17** (6.0 g, 55.55 mmol) in MeOH (80 ml) was added dropwise at r.t. with stirring to **3** [31] (10.0 g, 27.47 mmol) in MeOH (120 ml). Stirring was continued for 1 h, half of the MeOH evaporated, and the yellow precipitate filtered off and immediately dissolved in $CHCl_3$ (*ca.* 100 ml). Removal of the solvent and crystallization from hexane/acetone gave **4** (8.3 g, 64%).

Table 4. *^{13}C-NMR Chemical Shifts* [ppm] (75 MHz, $CDCl_3$) *for the Protected 1-Thioglucosides* **2**, **4**, **7**, **8**, **12**, **32**, **33**, **37**, *and* **38**[a])

	2	**4**	**7**	**8**	**12**	**32**	**33**	**37**	**38**
C(1)	152.30	183.24	176.35	148.17	176.42	180.06	151.16	152.79	174.57
C(2)	114.07	149.41	143.35	121.54	145.13	150.98	118.80	124.55	145.08
C(3)	123.17	128.09	134.07	120.22	133.22	127.02	122.91	–	–
C(4)	149.09	184.16	182.01	148.79	181.22	–	–	–	–
C(5)	119.97	137.20	128.43	122.10	150.45	–	–	–	–
C(6)	116.83	136.12	149.11	115.93	127.22	–	–	–	–
C(1')	85.91	80.73	81.18	85.61	80.81	80.53	86.21	85.29	82.55
C(2')	69.87	69.27	69.18	69.81	69.21	69.30	69.64	70.49	71.16
C(3')	73.77	73.48	73.41	73.71	73.39	73.38	73.54	73.54	73.64
C(4')	67.85	67.99	67.93	67.80	67.91	67.94	67.76	68.38	68.01
C(5')	76.03	76.39	76.57	76.13	76.62	76.44	76.01	75.43	75.97
C(6')	61.71	62.14	62.12	61.65	62.14	62.12	61.64	61.81	61.68
AcO	171.02	170.63	170.64	171.20	170.66	170.54	170.47	170.58	170.52
	170.28	169.99	170.01	170.27	170.00	169.91	169.93	169.98	170.09
	169.61	169.33	169.34	169.67	169.35	169.24	169.12	169.53	169.28
	169.44	169.12	169.17	169.43	169.15	168.98	168.95	169.34	169.20
	20.79	20.54	20.54	20.78	20.66	20.52	20.56	20.72	20.64
	20.69	20.49		20.71	20.54	20.43	20.52	20.54	20.56
	20.56			20.56			20.40		

[a]) The assignment of the sugar C-atoms is based upon a ^{1}H,^{13}C-HMQC (^{1}H, 500 MHz) of **3**; the quinonoid and aromatic C-atoms were assigned according to [48–50].

b) A soln. of **17** (741 mg, 6.86 mmol) in MeOH (40 ml) was added dropwise at r.t. with stirring to a soln. of **3** (2.5 g, 6.87 mmol) in MeOH (40 ml), and the mixture was stirred for 30 min. (Diacetoxyiodo)benzene (3.31 g, 10.29 mmol) was added in small portions. Stirring was continued for 30 min and the precipitate collected by filtration. Concentration of the filtrate to half of its volume gave additional product. Washing of the combined precipitates and drying yielded nearly pure **4** (2.6 g, 81%). Yellow needles. M.p. 166°. R_f (hexane/AcOEt 1:1) 0.47.

Table 5. *^{13}C-NMR Chemical Shifts* [ppm] (75 MHz, D_2O) *for the 1-Thioglucosides* **5**, **6**, **9**, **10**, **14**, **15**, **34**, **35**, *and* **40**[a])

	5[b])	**6**	**9**	**10**[b])	**14**	**15**	**34**	**35**	**40**
C(1)	151.78[c])	187.84	147.68	180.67	147.68	180.82	151.53	184.20	178.32
C(2)	120.43	152.41	124.05[c])	146.03	124.35	147.40	121.97	154.21	148.59
C(3)	123.11	130.47	120.17	136.88	119.36[c])	136.35	122.28	129.58	–
C(4)	151.90[c])	189.07	151.68	186.81	152.09	185.72	–	–	–
C(5)	120.11	140.07	121.86	130.62	119.24	153.30	–	–	–
C(6)	119.37	139.34	122.65[c])	152.26	124.00[c])	129.61	–	–	–
C(1′)	89.29	84.85	89.48	85.23	89.38	84.87	89.00	84.81	87.54
C(2′)	74.41	74.19	74.43	74.20	74.43	74.17	74.47	74.27	76.19
C(3′)	79.72	79.79	79.76	79.81	79.72	79.77	79.75	79.85	79.82
C(4′)	71.91	71.88	71.84	71.89	71.90	71.84	71.94	71.86	71.91
C(5′)	82.59	82.73	82.62	82.80	82.58	82.76	82.55	82.80	82.97
C(6′)	63.43	63.29	63.41	63.31	63.45	63.27	63.50	63.35	63.35

[a]) The assignment of the sugar C-atoms is based upon a ^{1}H,^{13}C-HMQC (^{1}H, 500 MHz) of **5**; the quinonoid and aromatic C-atoms were assigned according to [48–50].

[b]) Recorded at 125 MHz.

[c]) Assignments may be reversed.

Table 6. *Selected ^{1}H-NMR Chemical Shifts* [ppm] (300 MHz, $CDCl_3$) *for the Hydroquinones* **22**, **26**, *and* **27**, *and the Quinones* **23**–**25**[a])

	22	**23**[b])	**24**	**25**	**26**	**27**[c])
H–C(1)	5.18	5.24	5.23	5.22	5.17	4.68
H–C(2)	5.23	5.28	5.29	5.26	5.23	3.44
H–C(3)	6.02	6.10	6.08	6.11	6.03	3.57
H–C(4)	3.45	3.84	3.85	3.86	3.55	2.67
H–C(5)	4.25	4.34	4.33	4.32	4.27	3.67
H_A–C(6)	4.81	4.75	4.70	4.86	4.75	4.02
H_B–C(6)	4.75	4.70	4.70	4.67	4.75	3.90
H–C(2′)	–	6.80	6.42	6.33	–	–
H–C(3′)	6.59	–	–	–	7.07	7.06
H–C(4′)	6.47	6.46	–	6.78	–	–
H–C(5′)	–	6.59	6.82	–	–	–
H–C(6′)	6.93	–	–	–	6.75	6.98
H–C(1″)	–	–	4.60	4.69	4.39	4.53
H–C(2″)	–	–	5.17	5.17	4.86	3.19
H–C(3″)	–	–	5.26	5.27	5.13	3.38
H–C(4″)	–	–	5.04	5.04	4.98	3.26
H–C(5″)	–	–	3.75	3.76	3.61	3.34
H_A–C(6″)	–	–	4.19	4.15	4.12	4.02
H_B–C(6″)	–	–	4.08	4.07	4.12	3.66
ArO*H*	6.14	–	–	–	6.39	
	5.18	–	–	–	6.09	
MeO	3.43	3.48	3.48	3.48	3.44	3.35

[a]) Resonances for AcO and BzO, see *Exper. Part.* [b]) Recorded at 400 MHz. [c]) In CD_3OD.

Table 7. *^{1}H-NMR Coupling Constants* J [Hz] (300 MHz, $CDCl_3$) *for the Hydroquinones* **22**, **26**, *and* **27**, *and the Quinones* **23–25**[a])

	22	**23**[a])	**24**	**25**	**26**	**27**[b])
J(1,2)	3.5	3.5	3.5	3.5	3.6	3.6
J(2,3)	9.8	9.9	9.9	9.9	9.8	9.4
J(3,4)	11.1	11.0	11.0	11.0	11.2	10.6
J(4,5)	11.0	11.0	11.0	11.0	11.1	10.8
J(5,6)	2.1	2.3	[c])	2.2	[c])	2.2
	3.6	4.0	[c])	4.3	[c])	5.1
J(6,6)	12.4	12.2	[c])	12.2	[c])	11.8
J(2′,4′)	–	–	–	2.2	–	–
J(3′,4′)	8.8	10.0	–	–	–	–
J(4′,6′)	2.9	2.3	–	–	–	–
J(1″,2″)	–	–	9.8	9.9	10.1	9.7
J(2″,3″)	–	–	9.2	9.2	9.2	8.6
J(3″,4″)	–	–	9.2	9.2	9.4	8.6
J(4″,5″)	–	–	10.0	10.2	10.0	9.5
J(5″,6″)	–	–	2.1	2.5	3.8	2.1
	–	–	6.8	6.3	3.8	[c])
J(6″,6″)	–	–	12.4	12.4	–	[c])

[a]) Recorded at 400 MHz. [b]) In CD_3OD. [c]) Not determined.

$[\alpha]_D^{25} = -66.15$ ($c = 0.52$, $CHCl_3$). UV (CH_2Cl_2): 231 (8000), 253 (8200), 309 (1500), 396 (2000). IR ($CHCl_3$): 2950*w*, 2868*w*, 1756*s*, 1669*s*, 1612*m*, 1570*m*, 1374*s*, 1322*w*, 1283*m*, 1087*m*, 1061*s*, 1046*s*, 998*m*, 910*m*, 883*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Tables 2* and *3*; AcO: 2.13 (*s*); 2.07 (*s*); 2.05 (*s*); 2.02 (*s*). ^{13}C-NMR: *Table 4*. CI-MS: 491 (23), 490 (99, $[M + 2 + NH_4]^+$), 382 (11), 350 (31), 331 (25), 307 (12), 230 (12), 214 (10), 213 (100), 153 (14). ESI-MS: 493 (100, $[M + Na]^+$). Anal. calc. for $C_{20}H_{22}O_{11}S$ (470.44): C 51.06, H 4.71, S 6.81; found: C 51.12, H 4.53, S. 7.02.

2-(β-D-Glucopyranosylthio)benzene-1,4-diol (**5**). A soln. of Na (49 mg, 2.12 mmol) in MeOH (5 ml) was added under N_2 at r.t. to a stirred soln. of **2** (500 mg, 1.06 mmol) in MeOH (5 ml). According to TLC (AcOEt/MeOH/H_2O 50:6:1), the reaction was completed after 45 min. *Amberlite IR-120* (H^+) was added until the soln. was neutral (test paper), the resin filtered off, and the solvent evaporated. Crystallization of the residue from AcOEt/EtOH gave **5** (300 mg, 93%). Colourless needles. M.p. 103°. R_f (AcOEt/MeOH/H_2O 50:6:1) 0.44. $[\alpha]_D^{25} = -27.65$ ($c = 0.51$, MeOH). UV (MeOH): 209 (11000), 307 (880). IR (KBr): 3600–3100*s*, 2930*w*, 1610*w*, 1492*s*, 1453*m*, 1360*m*, 1270*m*, 1206*s*, 1100*m* (sh), 1035*s*, 907*m*, 873*m*, 819*m*, 780*s*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.76 (*s*, exchange with D_2O, ArO*H*); 8.71 (br. *s*, exchange with D_2O, ArOH); 6.79 (*d*, $J = 2.9$, H–C(3)); 6.62 (*d*, $J = 8.6$, H–C(6)); 6.49 (*dd*, $J = 2.9$, 8.6, H–C(5)); 5.30 (*d*, '*s*', exchange with D_2O, OH); 5.05 (*d*, $J = 4.9$, exchange with D_2O, OH); 4.94 (*d*, $J = 5.2$, exchange with D_2O, OH); 4.46 (*d*, $J = 9.7$, H–C(1′)); 4.44 (*ddd*, '*t*', $J = 5.5$, exchange with D_2O, OH–C(6′)); 3.66 (*ddd*, $J = 1.8$, 5.3, 11.7, H_A–C(6′)); 3.45 (*ddd*, '*m*', $J = 5.4$, 11.9, H_B–C(6′)); 3.20 (*m*, $J = 4.9$, 8.6, 8.8, H–C(3′), H–C(5′)); 3.10 (*m*, $J = 5.2$, 8.9, H–C(4′)); 3.02 (*ddd*, '*t*', $J = 8.9$, H–(C(2′)). ^{1}H-NMR (D_2O, 300 MHz): *Tables 2* and *3*. ^{13}C-NMR: *Table 5*. CI-MS: 322 (100, $[M + NH_4]^+$), 214 (9). Anal. calc. for $C_{12}H_{16}O_7S$ (304.31); C 47.36, H 5.30, S 10.54; found: C 47.62, H 5.56, S 10.30.

(β-D-Glucopyranosylthio)benzo-1,4-quinone (**6**). (Diacetoxyiodo)benzene (159 mg, 0.49 mmol) was added in small portions at r.t. to a stirred soln. of **5** (100 mg, 0.33 mmol) in MeOH (10 ml). Stirring was continued for 30 min. CH_2Cl_2 (*ca.* 80 ml) was added to the mixture and the precipitate collected by filtration and washed several times with CH_2Cl_2. Drying gave nearly pure **6** (80 mg, 80%). A sample was crystallized from i-PrOH. Orange crystals. M.p. 202° (dec.). R_f (AcOEt/MeOH/H_2O 50:6:1) 0.48. $[\alpha]_D^{25} = -135.55$ ($c = 0.045$, MeOH). UV (MeOH): 205 (16000), 251 (8500), 407 (2500). IR (KBr): 3600–3150*s*, 3060*w*, 2977*w*, 2925*w*, 2895*m*, 2868*w*, 1662*s*, 1644*s*, 1611*m*, 1571*m*, 1453*w*, 1416*w*, 1356*m*, 1330*m*, 1314*m*, 1293*s*, 1274*m*, 1252*w*, 1227*w*, 1110*s*, 1087*s*, 1061*s*, 1027*s*, 998*s*, 910*w*, 881*s*, 858*w*, 815*w*, 720*w*, 696*w*, 655*w*, 614*w*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 6.94 (*d*, $J = 10.2$, H–C(6)); 6.82 (*dd*, $J = 2.4$, 10.1, H–C(5)); 6.72 (*d*, $J = 2.4$, H–C(3)); 5.61 $J = 5.7$, exchange with D_2O, OH); 5.20 (*d*, $J = 4.6$, exchange with D_2O, OH); 5.07 (*d*, $J = 5.3$, exchange with D_2O, OH); 4.78 (*d*, $J = 9.30$, H–C(1′)); 4.57 (*dd*, '*t*', $J = 5.4$, exchange with D_2O, OH–C(6′)); 3.66 (*ddd*, '*dd*', $J = 5.4$, 10.5, H_A–C(6′)); 3.40 (*ddd*, '*m*', $J = 6.0$, 11.7, H_B–C(6′)); 3.27–3.07 (*m*, H–C(5′), H–C(4′), H–C(3′), H–C(2′)). ^{13}C-NMR: *Table 5*. CI-MS: 323 (13), 322 (100,

$[M + 2 + NH_4]^+$), 320 (56, $[M + NH_4]^+$), 296 (10), 295 (58), 180 (30). Anal. calc. for $C_{12}H_{14}O_7S$ (302.29): C 47.68, H 4.67, S 10.60; found: C 47.75, H 4.80, S 10.51.

*2-Chloro-6-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzo-1,4-quinone* (**7**). A soln. of 2-chlorobenzo-1,4-quinone (196 mg, 1.37 mmol) in MeOH (5 ml) was added to **3** (500 mg, 1.37 mmol) in MeOH (5 ml). The soln. was stirred for 30 min at r.t. and treated with (diacetoxyiodo)benzene (660 mg, 2.05 mmol). The mixture was stirred for further 30 min and evaporated. FC (hexane/AcOEt 1:1) gave **7**/**12** 1.3:1 (454 mg, 65%), which was separated by prep. HPLC (hexane/CH_2Cl_2/AcOEt 9:9:2, 15 ml/min). A pure sample of **7** was also obtained after 3 crystallizations in hexane/acetone.

Data of **7**: Yellow needles. M.p. 180°. Anal. HPLC (hexane/AcOEt 7:3, 2 ml/min): t_R 5.9 min. R_f (hexane/AcOEt 1:1) 0.50. $[\alpha]_D^{25} = -70.58$ ($c = 0.52$, $CHCl_3$). UV (MeOH): 207 (23000), 302 (6300), 408 (1600). IR (KBr): 3055*w*, 2960*w*, 1750*s*, 1688*s*, 1640*s*, 1568*s*, 1432*w*, 1370*s*, 1282*m*, 1230*s*, 1091*m*, 1048*s*, 981*w*, 908*m*, 832*w*, 796*m*, 772*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*; AcO: 2.12 (*s*); 2.06 (*s*, 6 H); 2.03 (*s*). ^{13}C-NMR: *Table 4*. CI-MS: 526 (39), 525 (23), 524 (100, $[M + 2 + NH_4]^+$), 522 (17), 230 (6), 213 (6). Anal. calc. for $C_{20}H_{21}ClO_{11}S$ (504.88): C 47.58, H 4.19, Cl 7.02, S 6.35; found: C 47.55, H 4.18, Cl 7.14, S 6.49.

Data of **12**: Yellow needles. M.p. 204° (dec.). Anal. HPLC (hexane/AcOEt 7:3, 2 ml/min): t_R 5.0 min. R_f (hexane/AcOEt 1:1) 0.53. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.06 (*s*, H–C(6)); 6.82 (*s*, H–C(3)); 5.31 (*dd*, '*t*', $J = 9.1$, H–C(3')); 5.23 (*dd*, '*t*', $J = 9.2, 9.7$, H–C(2')); 5.09 (*dd*, $J = 9.1, 10.1$, H–C(4')); 4.89 (*d*, $J = 9.7$, H–C(1')); 4.23 (*dd*, $J = 2.1, 12.4$, H_A–C(6')); 4.12 (*dd*, $J = 6.7, 12.4$, H_B–C(6')); 3.87 (*ddd*, $J = 2.1, 6.6, 10.1$, H–C(5')); 2.14, 2.07, 2.06, 2.04 (4*s*, 4 Ac).

*2-Chloro-6-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzene-1,4-diol* (**8**). A soln. of **7** (144 mg, 0.285 mmol) in $CHCl_3$ (4 ml) was treated with $Na_2S_2O_4$ (298 mg, 1.71 mmol) in H_2O (4 ml) as described for **2** (procedure *b*), yielding nearly pure **8** (134 mg, 93%). This product was used in the next step. White foam. R_f (hexane/AcOEt 1:1) 0.45. UV ($CHCl_3$): 241 (3600), 313 (5300). IR ($CHCl_3$): 3458*w*, 2958*w*, 1756*s*, 1604*w*, 1470*m*,1435*m*, 1375*m*, 1330*m*, 1170*m*, 1088*m*, 1040*s*, 948*w*, 914*w*, 861*w*, 822*w*, 598*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*; ArOH: 6.85 (*s*, exchange with CD_3OD); 5.54 (*s*, exchange with CD_3OD); AcO: 2.14 (*s*); 2.13 (*s*); 2.03 (*s*); 2.00 (*s*). ^{13}C-NMR: *Table 4*.

*2-Chloro-6-(β-*D*-glucopyranosylthio)benzene-1,4-diol* (**9**). A soln. of **8** (100 mg, 0.197 mmol) in MeOH (10 ml) was deacetylated with 0.04M NaOMe in MeOH (10 ml) as described for **5**. FC (AcOEt/MeOH/H_2O 50:6:1) of the crude material and lyophilization gave **9** (57.4 mg, 86%). R_f (AcOEt/MeOH/H_2O 50:6:1) 0.45. UV (MeOH): 210 (18000), 311 (4700). IR (KBr): 3348*s* (br.), 2922*m*, 1603*m*, 1581*m*, 1438*s*, 1321*s*, 1222*s*, 1070*s*, 947*m*, 860*m*, 790*s*, 714*m*. ^{1}H-NMR: *Tables 2* and *3*. ^{13}C-NMR: *Table 5*. FAB-MS: 361 (9, $[M + Na]^+$), 338 (15, M^+).

*2-Chloro-6-(β-*D*-glucopyranosylthio)-benzo-1,4-quinone* (**10**). A soln. of **9** (90 mg, 0.266 mmol) in MeOH (5 ml) was treated with (diacetoxyiodo)benzene (128 mg, 0.399 mmmol) as described for **6**. The precipitate was collected by filtration, washed with CH_2Cl_2, and dried: **10** (51.4 mg, 57%). Orange solid. M.p. 124° (dec.). R_f (AcOEt/MeOH/H_2O 50:6:1) 0.53. UV (MeOH): 209 (11000), 293 (4400), 424 (1400). IR (KBr): 3406*s*, 2888*m*, 1678*s*, 1634, 1562*s*, 1412*m*, 1366*m*, 1292*s*, 1224*m*, 1082*s*, 1044*s*, 902*m*, 824*w*, 798*s*, 784*m*, 618*m*, 580*m*. ^{1}H-NMR: *Tables 2* and *3*. ^{13}C-NMR: *Table 5*.

*2-Chloro-5-(2',3'4',6-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzene-1,4-diol* (**11**). Dry HCl was bubbled into a soln. of **3** (1.3 g, 2.76 mmol) in $CHCl_3$ (40 ml, treated with $CaCl_2$) at r.t. until the yellow colour of the quinone had disappeared (*ca.* 45 min). The mixture was washed with H_2O, dried (Na_2SO_4), and evaporated. FC (hexane/AcOEt 3:2) of the crude material gave 1.1 g (79%) of **7** in a purity of *ca.* 90% (by ^{1}H-NMR). It was used without further purification for the following transformations.

*2-Chloro-5-(2',3',4',6'-tetra-*O*-acetyl-*D*-glucopyranosylthio)benzo-1,4-quinone* (**12**). A mixture of **11** (100 mg, 0.197 mmol) in CH_2Cl_2 (10 ml), anh. Na_2SO_4 (1.0 g), and Ag_2O (137 mg, 0.592 mmol) was stirred for 30 min at r.t. The mixture was filtered through *Celite* and the filtrate evaporated. Crystallization of the residue from petroleum ether/CH_2Cl_2 gave pure **12** (71 mg, 71%). Yellow needles. M.p. 205° (dec.). R_f (hexane/AcOEt 1:1) 0.53. $[\alpha]_D^{25} = -57.60$ ($c = 0.5$, $CHCl_3$). UV (MeOH): 205 (17000), 292 (8800), 409 (1800). IR (KBr): 3060*w*, 2950*w*, 2880*w*, 1744*s*, 1658*s*, 1567*m*, 1430*m*, 1376*m*, 1328*w*, 1301*w*, 1222*s*, 1092*m*, 1062*s*, 1046*s*, 1032*s*, 1021*s*, 982*w*, 900*m*, 805*w*, 682*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*; AcO: 2.15 (*s*); 2.07 (*s*); 2.06 (*s*); 2.03 (*s*). ^{13}C-NMR: *Table 4*. CI-MS: 526 (39), 525 (25), 524 (100, $[M + 2 + NH_4]^+$), 522 (23), 290 (11), 230 (28), 213 (23). Anal. calc. for $C_{20}H_{21}ClO_{11}$ (504.88): C 47.58, H 4.19, Cl 7.02, S 6.35; found: C 47.42, H 4.24, Cl 7.13, S 6.21.

*2-Chloro-5-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzene-1,4-diyl Diacetate* (**13**). A soln. of **11** (2.15 g, 4.24 mmol) in Ac_2O/pyridine 1:1 (20.0 ml) was stirred for 15 h at. r.t. The mixture was poured onto ice/H_2O. The precipitate was dissolved in CH_2Cl_2, the soln. washed several times with H_2O, dried ($MgSO_4$), and evaporated. Crystallization of the residue from MeOH gave pure **8** (2.15 g, 86%). Colourless needles. M.p. 184°. R_f (hexane/AcOEt 1:1) 0.42. $[\alpha]_D^{25} = -33.80$ ($c = 0.5$, $CHCl_3$). UV (MeOH): 207 (26000), 252 (9900). IR (KBr):

3025*w*, 2950*w*, 2895*w*, 1771*s*, 1746*s*, 1640*w*, 1472*s*, 1435*m*, 1372*s*, 1300*m*, 1260*s*, 1228*s*, 1196*s*, 1162*s*, 1092*s*, 1051*s*, 1012*s*, 984*m*, 923*s*, 883*m*, 827*w*, 808*w*, 690*w*, 674*w*, 647*w*, 617*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47 (*s*, arom. H); 7.22 (*s*, arom. H); 5.21 (*dd*, '*t*', $J \approx 9.2$, H–C(3')); 5.09 (*dd*, '*t*', $J = 9.4, 9.9$, H–C(4')); 5.09 (*dd*, $J = 9.1, 10.1$, H–C(2')); 4.66 (*d*, $J = 10.0$, H–C(1')); 4.23 (*dd*, $J = 2.5, 12.4$, H_A–C(6')); 4.16 (*dd*, $J = 4.8, 12.4$, H_B–C(6')); 3.69 (*ddd*, $J = 2.5, 4.8, 10.0$, H–C(5')); 2.36, 2.31, 2.10, 2.08, 2.03, 2.01 (6*s*, 6 Ac). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.54, 170.09, 169.36, 169.18, 168.44, 168.05 (6*s*, 6 CO); 148.51 (*s*); 144.84 (*s*); 129.16 (*d*); 128.01 (*s*); 129.59 (*s*); 124.37 (*d*); 85.44 (*d*, C(1')); 75.85 (*d*, C(5')); 73.80 (*d*, C(3')); 70.05 (*d*, C(2')); 68.03 (*d*, C(4')); 61.87 (*t*, C(6')); 20.64 (*q*, Me). CI-MS: 611 (10), 610 (42), 609 (28), 608 (100, $[M + NH_4]^+$), 566 (19), 290 (17), 278 (23), 230 (32), 213 (18). Anal. calc. for $C_{24}H_{27}ClO_{13}S$ (590.97): C 48.77, H 4.60, Cl 6.00, S 5.42; found: C 48.97, H 4.56, Cl 6.22, S 5.44.

*2-Chloro-5-(β-*D*-glucopyranosylthio)benzene-1,4-diol* (**14**). A soln. of **13** (1.60 g, 2.71 mmol) in MeOH (30 ml) was deacetylated with 0.54M NaOMe in MeOH (10 ml) as described for **5**. FC (AcOEt/MeOH/H_2O 50:6:1) of the crude gave **14** (0.79 g, 86%). White solid. M.p. 151°. R_f (AcOEt/MeOH/H_2O 50:6:1) 0.48. UV (MeOH): 209 (20000), 310 (5500). IR (KBr): 3650–3100*s*, 2890*w*, 1635*m*, 1558*w*, 1542*w*, 1478*m*, 1425*m*, 1310*m*, 1200*s*, 1068*s*, 1040*s*, 875*m*, 810*m*. ^{1}H-NMR: *Tables 2* and *3*. ^{13}C-NMR: *Table 5*. CI-MS: 358 (41), 357 (18), 356 (100, $[M + NH_4]^+$), 322 (11).

*2-Chloro-5-(β-*D*-glucopyranosylthio)benzo-1,4-quinone* (**15**). A soln. of **14** (500 mg, 1.48 mmol) in MeOH (10 ml) was oxidized with (diacetoxyiodo)benzene (715 mg, 2.22 mmol) as described for **6**. CH_2Cl_2 was added to the mixture until all of the quinone had precipitated (*ca.* 150 ml). The orange precipitate was collected on a fritted funnel, washed 3× with CH_2Cl_2, and dried. The quinone was dissolved in a small quantity of H_2O and freeze-dried. Subsequent drying under high vacuum (10^{-5} mbar) for 48 h yielded pure **15** (363 mg, 73%). Orange fluffy solid. R_f (AcOEt/MeOH/H_2O 50:6:1) 0.43. $[\alpha]_D^{25} = -137.69$ ($c = 0.065$, MeOH). UV (MeOH): 209 (12000), 288 (6900), 425 (1700). IR (KBr): 3650–3100*s*, 3055*w*, 2910*w*, 2875*w*, 1600*s*, 1562*s*, 1404*m*, 1355*m*, 1320*m*, 1271*m*, 1214*s*, 1045*m* (sh), 1020*s*, 886*m*, 804*m*, 683*w*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.36 (*s*, H–C(6)); 6.83 (*s*, H–C(3)); 5.65 (*d*, $J = 5.6$, exchange with D_2O, OH); 5.23 (*d*, $J = 4.5$, exchange with D_2O, OH); 5.08 (*d*, $J = 5.3$, exchange with D_2O, OH); 4.82 (*d*, $J = 9.2$, H–C(1')); 4.56 (*dd*, '*t*', $J = 5.2$, exchange with D_2O, OH–C(6')); 3.65 (*m*, H_A–C(6')); 3.39 (*m*, H_B–C(6'), H–C(3')); 3.22–3.08 (*m*, H–C(5'), H–C(4'), H–C(2')). ^{13}C-NMR: *Table 5*. CI-MS: 358 (34), 357 (14), 356 (100, $[M + 2 + NH_4]^+$), 354 (30, $[M + NH_4]^+$), 180 (13). Anal. calc. for $C_{12}H_{13}ClO_7S$ (336.73): C 42.80, H 3.89, Cl 10.53, S 9.52; found: C 43.02, H 4.03, Cl 10.60, S 9.71.

*2-(2',2'',3',3'',4'',6',6''-Hepta-O-acetyl-β-*D*-cellobiosylthio)benzene-1,4-diol* (**18**). A soln. of **17** (2.77 g, 25.68 mmol) in MeOH (40 ml) was added with stirring at r.t. to 2,2',3,3',4',6,6'-hepta-*O*-acetyl-1-thio-β-D-cellobiose [39] (**16**, 8.38 g, 12.84 mmol) in MeOH (300 ml) and THF (25 ml). After 1 h, the precipitate was filtered off and the remaining filtrate concentrated to half of its volume to obtain a second fraction of crude material. Both fractions were immediately dissolved in $CHCl_3$ (*ca.* 60 ml). After evaporation of the $CHCl_3$, the crude product was again dissolved in $CHCl_3$ (150 ml) and treated with $Na_2S_2O_4$ (10.49 g, 60.29 mmol) in H_2O (150 ml), as described above. Evaporation gave nearly pure **18** (8.0 g, 82%). An anal. pure sample was obtained by FC (hexane/AcOEt 5:7). White solid. M.p. 192°. R_f (hexane/AcOEt 5:7) 0.27. $[\alpha]_D^{25} = -17.22$ ($c = 0.54$, $CHCl_3$). UV (MeOH): 206 (33000), 307 (7200). IR (KBr): 3650–3200*s*, 3015*w*, 2965*w*, 2880*w*, 1750*s*, 1645*w*, 1494*s*, 1454*m*, 1375*s*, 1240*s*, 1169*s*, 1134*m*, 1044*s*, 964*w*, 909*m*, 876*w*, 821*w*, 778*m*, 675*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.87 (*m*, 3 arom. H); 6.56 (*s*, exchange with CD_3OD, ArO*H*); 5.23 (*s*, exchange with CD_3OD, ArOH); 5.15 (2*dd*, '*m*', $J \approx 9.1, 9.4$, H–C(3'), H–C(3'')); 5.06 (*dd*, '*t*', $J = 9.6$, H–C(4'')); 4.91 (*dd*, $J = 8.0, 9.2$, H–C(2'')); 4.85 (*dd*, '*t*', $J = 9.4, 9.8$, H–C(2')); 4.61 (*dd*, $J = 2.1, 12.1$, H_A–C(6')); 4.55 (*d*, $J = 10.0$, H–C(1')); 4.49 (*d*, $J = 8.0$, H–C(1'')); 4.38 (*dd*, $J = 4.2, 12.5$, H_A–C(6'')); 4.07 (*dd*, $J = 5.1, 12.1$, H_B–C(6')); 4.02 (*dd*, $J = 2.3, 12.6$, H_B–C(6'')); 3.69 (*dd*, '*t*', $J = 9.1, 9.9$, H–C(4')); 3.63 (*m*, H–C(5'), H–C(5'')); 2.14, 2.12, 2.06, 2.02, 2.00, 2.00, 1.98 (7*s*, 7 Ac). ^{13}C-NMR (50.6 MHz, $CDCl_3$): 170.52, 170.44, 170.13, 169.75, 169.55, 169.25, 168.98 (7*s*, 7 CO); 151.94 (*s*, C(1)); 149.13 (*s*, C(4)); 122.98 (*d*, C(3)); 119.62 (*d*, C(5)); 116.55 (*d*, C(6)); 114.15 (*s*, C(2)); 100.50 (*d*, C(1'')); 85.58 (*d*, C(1')); 76.36 (*d*); 75.84 (*d*); 73.29 (*d*); 72.72 (*d*); 71.77 (*d*); 71.43 (*d*); 69.85 (*d*); 67.61 (*d*); 61.37 (*t*, C(6'), C(6'')); 20.58, 20.44, 20.33 (3*q*, 3 Me). ESI-MS: 783.1 (100, $[M + Na]^+$). Anal. calc. for $C_{32}H_{40}O_{19}S$ (760.70): C 50.52, H 5.30, S 4.21; found: C 50.28, H 5.38, S 4.15.

*2-(β-*D*-Cellobiosylthio)benzene-1,4-diol* (**19**). A soln. of **18** (2.0 g, 2.62 mmol) in MeOH (20 ml) was deacetylated with 0.52M NaOMe in MeOH (10 ml) within 3 h, as described above. FC (AcOEt/MeOH/H_2O 13:2:1) of the crude material gave 0.86 g (70%) of **19**. White lyophilisate. R_f (AcOEt/MeOH/H_2O 13:2:1) 0.25. UV (MeOH): 205 (22000), 307 (4900). IR (KBr): 3650–3100*s*, 2930*w*, 1640*w*, 1495*w*, 1456*w*, 1210*m*, 1170*m*, 1077*s*, 1025*s*, 995*m* (sh), 820*w*, 782*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.79 (*s*, exchange with D_2O, ArOH); 8.73 (br. *s*, exchange with D_2O, ArO*H*); 6.78 (*d*, $J = 2.9$, H–C(3)); 6.62 (*d*, $J = 8.6$, H–C(6)); 6.49 (*dd*, $J = 2.9, 8.6$, H–C(5)); 5.48 (br. *d*, exchange with D_2O, OH); 5.22 (*d*, $J = 4.8$, exchange with D_2O, OH); 4.99 (*d*, $J = 4.9$, exchange with D_2O, OH); 4.96 (*d*, $J = 5.4$, exchange with D_2O, OH); 4.75 (*s*, exchange with D_2O, OH); 4.55 (*m*, after exchange with D_2O *d*,

J = 9.9, 2 OH, H–C(1′)); 4.28 (*d*, J = 7.9, H–C(1″)); 7.73–3.65 (*m*, H_A–C(6′), H_A–C(6″), H_B–C(6′)); 3.40 (*m*, H_B–C(6″), H–C(3′), H–C(4′), H–C(5′)); 3.20–2.96 (*m*, after exchange with D_2O *m* for H–C(3″), H–C(4″), H–C(5″), *dd* 't', J = 9.2, for H–C(2′), *dd*, J = 8.0, 9.0 for H–C(3′)). ^{13}C-NMR (50.6 MHz, (D_6)DMSO): aglycon: 150.04 (*s*); 148.14 (*s*); 119.91 (*s*); 117.54 (*d*); 115.59 (*d*); 114.77 (*d*); glycon: 102.84 (*d*, C(1″)); 85.91 (*d*, C(1′)); 79.36, 78.65, 76.66, 76.33, 76.04, 73.17, 72.22, 69.91 (8*d*); 60.92, 60.10 (2*t*).

*2-(β-*D*-Cellobiosylthio)benzo-1,4-quinone* (**20**). A soln. of **19** (300 mg, 0.64 mmol) in MeOH (10 ml) was treated with (diacetoxyiodo)benzene (309 mg, 0.96 mmol) as described for **6**. The precipitate was lyophilized to afford **20** (223 mg, 75%). Orange fluffy solid. R_f (AcOEt/MeOH/H_2O 13:2:1) 0.26. $[\alpha]_D^{25} = -132.73$ (c = 0.055, MeOH). UV (MeOH): 207 (13000), 250 (7100), 407 (2100). IR (KBr): 3650–3050*s*, 2930*w*, 2890*w*, 1664*s*, 1646*s*, 1611*w*, 1570*m*, 1500*m* (sh), 1375*m*, 1328*m*, 1294*m*, 1172*m*, 1070*s*, 1035*s*, 1000*s*, 885*m*, 823*w*, 653*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 6.93 (*d*, J = 10.0, H–C(6)); 6.82 (*dd*, J = 2.3, 10.0, H–C(5)); 6.71 (*d*, J = 2.4, H–C(3)); 5.80 (*d*, J = 5.9, OH); 5.24 (*d*, J = 4.8, OH); 5.04 (*d*, J = 4.8, OH): 5.00 (*d*, J = 5.3, OH); 4.90 (*d*, J = 10.0, H–C(1′)); 4.87 (*d*, J = 2.0, OH); 4.62 (*m*, 2 OH); 4.27 (*d*, J = 7.8, H–C(1″)); 3.72 (*m*, H_A–C(6′), H_A–C(6″)); 3.55 (*m*, H_B–C(6′), H_B–C(6″)); 3.44–3.37 (*m*, H–C(3′), H–C(4′), H–C(5′)); 3.27 (*m*, H–C(5″)); 3.22–3.11 (*m*, H–C(3″), H–C(4″)); 3.07–2.96 (*m*, H–C(2′), H–C(2″)). ^{13}C-NMR (50.6 MHz, (D_6)DMSO): aglycon: 184.47, 184.19 (2*s*, 2 CO); 149.75 (*s*, C(2)); 137.34, 136.25, 127.18 (3*d*); glycon: 103.06 (*d*, C(1″)); 81.73 (*d*, C(1′)); 79.70, 78.90, 76.84, 76.51, 76.05, 73.31, 72.13, 70.08 (8*d*); 61.08. 60.13 (2*t*). ESI-MS: 487.2 (100, $[M + Na]^+$). Anal. calc. for $C_{18}H_{24}O_{12}S$ (464.43): C 46.55, H 5.21, S 6.90; found: C 46.65, H 5.25, S 6.73.

*Methyl 2,3,6-Tri-*O*-benzoyl-4-deoxy-4-(2′,5′-dihydroxyphenylthio)-α-*D*-glucopyranoside* (**22**). A soln. of **17** (0.93 g, 8.60 mmol) in MeOH (10 ml) was added dropwise to a stirred soln. of methyl 2,3,6-tri-*O*-benzoyl-4-thio-α-D-glucopyranoside [41] (**21**, 3.60 g, 6.89 mmol) in MeOH (50 ml). The mixture was stirred for 30 min at r.t. and evaporated. A soln. of the residue in $CHCl_3$ (*ca.* 30 ml) was vigorously shaken with $Na_2S_2O_4$ (6 g) in H_2O (30 ml) until the yellow colour of the org. layer had disappeared (*ca.* 5 min). The org. layer was separated, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 2:1) gave **22** (3.52 g, 81%). White solid. M.p. 93°. R_f (hexane/AcOEt 2:1) 0.20. UV (MeOH): 240 (26000), 308 (5100). IR (KBr): 3600–3200*s*, 2940*w*, 1720*s*, 1598*m*, 1487*m*, 1448*m*, 1312*m*, 1269*s*, 1192*m*, 1173*m*, 1107*m*, 1090*m*, 1065*m*, 1023*m*, 773*w*, 606*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 6* and *7*; BzO: 8.04–7.91 (*m*, 6 H); 7.62–7.35 (*m*, 9 H). ^{13}C-NMR (50 MHz, (D_6)DMSO): 165.35, 165.27, 164.95, (3*s*, 3 CO); 150.00, 149.73 (2*s*); 133.31, 133.25, 129.40, 129.25, 129.17, 129.00, 128.88, 128.72, 128.63, 128.50, 120.01 (11*d*); 117.45 (*s*); 116.26, 116.12 (2*d*); 96.39 (*d*, C(1)); 72.86, 70.21, 69.64 (3*d*); 64.24 (*t*, C(6)); 54.80 (*q*, MeO); 47.69 (*d*, C(4)). CI-MS: 648 (23, $[M + NH_4]^+$), 544 (17), 540 (11), 509 (29), 508 (100), 459 (19), 404 (11), 387 (10), 386 (32), 337 (30).

*Methyl 2,3,6-Tri-*O*-benzoyl-4-deoxy-4-(3′,6′-dioxocyclohexa-1′,4′-dienylthio)-α-*D*-glucopyranoside* (**23**). A soln. of **22** (3.52 g, 5.58 mmol) in CH_2Cl_2 (100 ml) was treated with Ag_2O (7.77 g, 33.5 mmol) and anh. Na_2SO_4 (10.0 g) as described for **12**. Evaporation gave **23** (3.28 g, 93%), which was used for the next step. A sample was recrystallized from hexane/acetone. Orange needles. M.p. 163°. R_f (hexane/acetone 2:1) 0.37. $[\alpha]_D^{25} = +291.8$ (c = 0.5, $CHCl_3$). UV ($CHCl_3$): 242 (2800), 414 (2900). IR (KBr): 3055*w*, 2985*w*, 2950*w*, 2833*w*, 1712*w*, 1663*s*, 1641*s*, 1610*m*, 1581*m*, 1564*m*, 1547*m*, 1491*w*, 1450*m*, 1400*w*, 1370*m*, 1357*m*, 1342*m*, 1314*s*, 1270*s*, 1216*m*, 1192*m*, 1178*m*, 1141*s*, 1107*s*, 1067*s*, 1054*s*, 1025*s*, 996*s*, 973*m*, 932*w*, 916*m*, 882*s*, 862*w*, 814*w*, 798*w*, 731*w*, 709*s*, 685*m*, 662*w*, 646*w*, 612*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Tables 6* and *7*; BzO: 8.06–7.87 (*m*, 6 H); 7.63–7.29 (*m*, 9 H). ^{13}C-NMR (50 MHz, (D_6)DMSO): 184.23, 183.44, 165.38, 164.91, 164,88 (5*s*, 5 CO); 148.60 (*s*); 136.60, 136.08 (2*d*, 2 quinonoid C); 133.69, 133.54, 133.39, 129.37, 129.20, 129.11, 128.94, 128.91, 128.87, 128.84, 128.70, 128.59, 128.54 (13*d*); 127.29 (*d*, quinonoid C); 96.54 (*d*, C(1)); 72.10, 71.09, 68.23 (3*d*); 63.85 (*t*, C(6)); 54.91 (*q*, MeO); 43.25 (*d*, C(4)). CI-MS: 649 (28), 648 (80, $[M + 2 + NH_4]^+$), 647 (39), 646 (100, $[M + NH_4]^+$), 599 (22), 598 (10), 597 (27), 337 (10). Anal. calc. for $C_{34}H_{28}O_{10}S$ (628.62): C 64.96, H 4.49, S 5.10; found: C 65.09, H 4.32, S 5.39.

*Methyl 2,3,6-Tri-*O*-benzoyl-4-deoxy-4-[3′,6′-dioxo-4′-(2″,3″,4″,6″-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)-cyclohexa-1′,4′-dienylthio]-α-*D*-glucopyranoside* (**24**) *and Methyl 2,3,6-Tri-*O*-benzoyl-4-deoxy-4-[3′,6′-dioxo-5′-(2″,3″,4″,6″-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)cyclohexa-1′,4′-dienylthio]-α-*D*-glucopyranoside* (**25**). *a*) A soln. of **23** (2.40 g, 3.82 mmol) in acetone (50 ml) was added at r.t. to a stirred soln. of **3** (1.39 g, 3.82 mmol) in MeOH (40 ml). The mixture was stirred for 30 min and evaporated. FC (toluene/AcOEt 3:1) gave the hydroquinones (3.00 g, 79%; R_f 0.33), which were dissolved in MeOH (40 ml) and treated with (diacetoxyiodo)benzene (1.17 g, 3.62 mmol) for 30 min at r.t. The precipitate was collected by filtration and dried to afford **24**/**25** 2.5:1 (2.49 g, 66%), which were separated by prep. HPLC (hexane/CH_2Cl_2/AcOEt 3:5:2).

b) A soln. of **4** (2.0 g, 4.25 mmol) in acetone (20 ml) and MeOH (40 ml) was added dropwise at r.t. to a stirred soln. of **21** (2.22 g, 4.25 mmol) in MeOH (100 ml). The mixture was stirred for 30 min at r.t. and (diacetoxyiodo)benzene (2.05 g, 6.36 mmol) added in small portions. Stirring was continued for 30 min and the precipitate collected by filtration. Concentration of the mixture of its volume gave a further portion of product.

Drying of the combined precipitates yielded **24**/**25** 10:1 (3.5 g, 83%), which was recrystallized twice in benzene to afford isomerically pure **24** (1.86 g, 44%).

Data of **24**: Orange crystals. M.p. 252°. R_f (hexane/acetone 1:1) 0.46. Anal. HPLC (hexane/CH_2Cl_2/AcOEt 5:3:2): t_R 5.8 min. $[\alpha]_D^{25} = +213.2$ ($c = 0.5$, $CHCl_3$). UV ($CHCl_3$): 243 (23000), 357 (11000). IR ($CHCl_3$): 3042*w*, 2960*w*, 1756*s*, 1732*s*, 1654*s*, 1602*m*, 1585*w*, 1558*s*, 1492*m*, 1452*m*, 1374*m*, 1316*m*, 1268*s*, 1092*s*, 1068*s*, 1025*s*, 916*w*, 875*w*, 602*w*, 583*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 6* and *7*; BzO: 8.06–7.88 (*m*, 6 H); 7.67–7.29 (*m*, 9 H); AcO: 2.12, 2.06, 2.04, 2.02 (4*s*). ^{13}C-NMR (75 MHz, $CDCl_3$): 179.63, 170.68, 170.01, 169.34, 169.02, 165.85, 165.77, 165.15 (8*s*, CO); 150.55, 150.39 (2*s*); 133.48, 133.31, 129.92, 129.78, 129.68, 129.43, 128.84, 128.74 (8*d*); 128.46 (*s*); 128.12, 127.62, 127.17 (3*d*); 97.37 (*d*, C(1)); 80.59 (*d*, C(1″)); 76.45 (*d*, C(5″)); 73.49 (*d*, C(3″)); 72.79, 70.49 (2*d*); 69.34 (*d*, C(2″)); 68.76 (*d*); 67.99 (*d*, C(4″)); 63.61 (*t*, C(6)); 62.19 (*t*, C(6″)); 55.86 (*q*, MeO); 45.84 (*d*, C(4)); 20.66, 20.53 (2*q*, 2 Me). FAB-MS: 992 (100, $[M + 1]^+$), 961 (71), 871 (44), 839 (18), 613 (33). Anal. calc. for $C_{48}H_{46}O_{19}S_2$ (991.01): C 58.18, H 4.68, S 6.47; found: C 57.95, H 4.80, S 6.43.

Data of **25**: Orange crystals. M.p. 232°. R_f (hexane/acetone 1:1) 0.46. Anal. HPLC (hexane/CH_2Cl_2/AcOEt 5:3:2): t_R 7.8 min. $[\alpha]_D^{25} = +145.5$ ($c = 0.53$, $CHCl_3$). UV ($CHCl_3$): 243 (22541), 361 (5423), 453 (2041). IR ($CHCl_3$): 2960*w*, 2840*w*, 1755*s*, 1711*s*, 1672*m*, 1633*m*, 1556*m*, 1452*m*, 1418*m*, 1365*s*, 1316*m*, 1262*s*, 1092*s*, 1069*s*, 1017*s*, 915*w*, 864*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 6* and *7*; BzO: 8.08–7.86 (*m*, 6 H); 7.66–7.25 (*m*, 9 H); AcO: 2.07, 2.06, 2.05, 2.02 (4*s*). ^{13}C-NMR (75 MHz, $CDCl_3$): 180.94, 179.52, 170.60, 170.03, 169.32, 169.10, 166.04, 165.81, 165.08, (9*s*, 9 CO); 149.06, 147.90 (2*s*); 133.46, 133.38, 129.93, 129.79, 129.71 (5*d*); 129.45 (*s*); 129.27 (*d*); 128.83 (*s*); 128.64, 128.46, 128.12 (3*d*); 97.31 (*d*, C(1)); 81.11 (*d*, C(1″)); 76.34 (*d*, C(5″)); 73.49 (*d*, C(3″)); 72.76, 70.76 (2*d*); 69.26 (*d*, C(2″)); 68.52 (*d*); 67.96 (*d*, C(4″)); 63.74 (*t*, C(6)); 62.10 (*t*, C(6″)); 55.83 (*q*, MeO); 45.95 (*d*, C(4)); 20.56 (*q*, Me).

*Methyl 2,3,6,-Tri-*O*-benzoyl-4-deoxy-4-[4′-(2″,3″,4″,6″-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)-2′,5′-dihydroxyphenylthio]-α-*D*-glucopyranoside* (**26**). A soln. of **24** (1.0 g, 1.01 mmol) in $CHCl_3$ (50 ml) was treated with $Na_2S_2O_4$ (1.8 g, 10.34 mmol) in H_2O (50 ml) as described for **2** (procedure *b*). Evaporation and drying yielded **26** (1.0 g, 100%). White foam. R_f (hexane/AcOEt 1:1) 0.30. UV ($CHCl_3$): 244 (16000), 267 (8300), 324 (6700). IR ($CHCl_3$): 3464*m*, 3042*w*, 2843*w*, 1756*s*, 1730*s*, 1602*w*, 1585*w*, 1467*s*, 1452*m*, 1368*m*, 1270*s*, 1093*s*, 1069*s*, 1039*s*, 916*w*, 881*w*, 599*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 6* and *7*; BzO: 7.98–7.90 (*m*, 6 H); 7.73–7.34 (*m*, 9 H); AcO: 2.08, 2.05, 2.00, 1.97 (4*s*). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.68, 170.05, 169.23, 169.15, 165.93, 165.83, 165.56 (7*s*, 7 CO); 151.42, 149.56 (2*s*); 133.43, 133.24, 129.88, 129.76, 129.60 (5*d*); 129.39, 128.91 (2*s*); 128.42, 122.30 (2*d*); 121.37 (*s*); 121.28 (*d*); 118.23 (*s*); 97.26 (*d*, C(1)); 86.58 (*d*, C(1″)); 76.00 (*d*, C(5″)); 73.57 (*d*, C(3″)); 73.15, 70.49 (2*d*); 69.91 (*d*, C(2″)); 69.68 (*d*); 67.86 (*d*, C(4″)); 63.97 (*t*, C(6)); 61.68 (*t*, C(6″)); 55.73 (*q*, MeO); 50.73 (*d*, C(4)); 20.54 (*q*, Me). FAB-MS: 992.5 (4, $M + 1]^+$), 961.5 (7), 331 (38), 169 (79), 105 (100).

*Methyl 4-Deoxy-4-[4′-(β-*D*-glucopyranosylthio)-2′,5′-dihydroxyphenylthio]-α-*D*-glucopyranoside* (**27**). A soln. of **26** (337 mg, 0.339 mmol) in MeOH (15 ml) was treated for 10 h with 0.2M NaOMe in MeOH (10 ml) as described above, neutralized with *Amberlite*, and evaporated. The residue was partitioned between H_2O and $CHCl_3$ and extracted twice with $CHCl_3$. Lyophilization of the aq. layer gave **27** (149 mg, 86%). White fluffy solid. R_f (AcOEt/i-PrOH/H_2O 1:7:2) 0.76. UV (MeOH): 211 (28000), 262 (7700), 320 (8200). IR (KBr): 3382*s* (br.), 2926*m*, 1636*m*, 1468*m*, 1414*s*, 1360*m*, 1312*m*, 1198*s*, 1140*s*, 1066*s*, 1036*s*, 896*m*, 878*m*, 806*m*, 704*m*, 668*m*, 584*m*. ^{1}H-NMR: *Tables 6* and *7*. ^{13}C-NMR (75 MHz, D_2O): 153.15, 151.04 (2*s*); 124.97 (*d*); 123.61 (*s*); 122.04 (*d*); 120.74 (*s*); 101.84 (*d*, C(1)); 88.83 (*d*, C(1″)); 82.60, 79.75, 75.00, 74.44, 74.31, 72.70, 71.96 (7*d*); 64.18, 63.50 (2*t*); 57.69 (*q*, MeO); 53.66 (*d*, C(4)). FAB-MS: 535 (13, $[M + Na]^+$), 512 (21, M^+).

*Methyl 4-Deoxy-4-[3′,6′-dioxo-4′-(β-*D*-glucopyranosylthio)cyclohexa-1′,4′-dienylthio]-α-*D*-glucopyranoside* (**28**). A soln. of **27** (138 mg, 0.269 mmol) in MeOH (5 ml) was oxidized with (diacetoxyiodo)benzene (130 mg, 0.404 mmol) as described for **6**. Washing of the precipitate with CH_2Cl_2 and drying afforded pure **28** (80 mg, 58%). Orange-red crystals. M.p. 280° (dec.). R_f (AcOEt/i-PrOH/H_2O 1:7:2) 0.78. $[\alpha]_D^{25} = +43.4$ ($c = 0.175$, H_2O). UV (H_2O): 217 (17000), 361 (12000). IR (KBr): 3406*s* (br.), 3012*m*, 2976*m*, 2930*s*, 2884*m*, 2844*m*, 1638*s*, 1624*s*, 1560*s*, 1542*m*, 1464*m*, 1450*m*, 1398*m*, 1364*m*, 1348*m*, 1334*m*, 1286*m*, 1230*s*, 1182*m*, 1138*s*, 1128*s*, 1114*s*, 1086*s*, 1058*s*, 1040*s*, 1023*s*, 992*s*, 898*m*, 880*s*, 870*m*, 856*w*, 842*w*, 822*w*, 798*m*, 764*w*, 744*w*, 688*m*, 656*m*, 606*s*, 582*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 6.94, 6.72 (2*s*, 2 quinonoid H); 5.61 (*d*, $J = 5.8$, exchange with D_2O, OH); 5.36 (*d*, $J = 6.3$, exchange with D_2O, OH); 5.20 (*d*, $J = 4.7$, exchange with D_2O, OH); 5.07 (*d*, $J = 6.3$, exchange with D_2O, OH); 5.06 (*d*, $J = 5.3$, exchange with D_2O, OH); 4.82 (*m*, 2 H, after exchange with D_2O *d*, $J = 9.3$, H–C(1″), OH); 4.65 (*d*, $J = 3.4$, H–C(1)); 4.55 (*dd*, '*t*', $J \approx 5.3$, 5.6, OH); 3.68–3.46 (*m*, H_A–C(6), H_B–C(6), H_A–C(6″), H_B–C(6″), H–C(5)); 3.43–3.07 (*m*, H–C(5″), H–C(3), H–C(3″), H–C(2), H–C(4″), H–C(2″), H–C(4)); 3.29 (*s*, MeO). ^{13}C-NMR (75 MHz, (D_6)DMSO): 180.58, 180.35 (2*s*, 2 CO); 152.87, 151.35 (2*s*); 126.34, 124.94 (2*d*); 99.79 (*d*, C(1)); 81.86 (*d*, C(1″)); 81.04, 77.69, 72.79, 72.19, 71.22, 70.92, 69.60 (7*d*); 60.74, 60.66 (2*t*); 54.61 (*q*, Me); 46.78 (*d*, C(4)). FAB-MS: 512 (79, $[M + 2]^+$). Anal. calc. for $C_{19}H_{26}O_{12}S_2$ (510.54): C 44.70, H 5.13; found: C 44.42, H 5.38.

2,5-Bis(methylsulfonyloxy)benzo-1,4-quinone (**31**). Pyridine (227 mg, 2.87 mmol) was added at r.t. to a stirred soln. of methanesulfonic anhydride (500 mg, 2.87 mmol) in THF (20 ml). After 15 min, the mixture was evaporated and the residue dissolved in THF (20 ml). This soln. was dropped with stirring at 0° to **30** (100 mg, 0.71 mmol) in THF (10 ml). The mixture was stirred for 6 h at r.t., filtered, and evaporated. The residue was washed with ice-cold H_2O and dried. Crystallization from acetone gave **31** (86 mg, 41%). Yellow crystals. M.p. 182° ([44]: 182–183°). IR (KBr): 3080*m*, 3030*m*, 2940*m*, 1680*s*, 1622*s*, 1422*m*, 1375*s*, 1338*s*, 1290*w*, 1239*m*, 1190*s*, 1120*s*, 974*s*, 919*s*, 860*s*, 804*s*, 764*m*, 636*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.06 (*s*, quinonoid H); 3.59 (*s*, MeO). Anal. calc. for $C_8H_8O_8S_2$ (296.92): C 32.43, H 2.72, S 21.64; found: C 32.48, H 2.80, S 21.58.

*2,5-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzo-1,4-quinone* (**32**). A soln. of **4** (1.29 g, 2.75 mmol) in MeOH (20 ml) and THF (20 ml) was added at r.t. to a stirred soln. of **3** (1.0 g, 2.75 mmol) in MeOH (20 ml), followed by addition of **17** (0.3 g, 2.78 mmol) in MeOH (5 ml). The mixture was stirred for 1 h and half of the solvent evaporated. The yellow crystals were filtered off and immediately dissolved in 50 ml of $CHCl_3$. Evaporation and crystallization of the crude gave pure **32** (0.73, 32%). Yellow needles. M.p. 257°. R_f (hexane/AcOEt 1:3) 0.79. $[\alpha]_D^{25} = -66.27$ ($c = 0.51$, $CHCl_3$). UV ($CHCl_3$): 240 (11000), 345 (11000). IR (KBr): 3060*w*, 2950*w*, 2880*w*, 1744*s*, 1646*s*, 1510*s*, 1434*m*, 1379*s*, 1322*m*, 1300*s*, 1247*s*, 1223*s*, 1145*w*, 1129*w*, 1093*s*, 1050*s*, 1021*s*, 984*m*, 915*s*, 891*s*, 806*m*, 682*w*, 643*w*, 618*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*; AcO: 2.12 (*s*); 2.06 (*s*, 6H); 2.03 (*s*). ^{13}C-NMR: *Table 4*. CI-MS: 854 (21), 853 (40), 852 (100, $[M + 2 + NH_4]^+$), 391 (38), 382 (25), 366 (11), 364 (44), 350 (10), 331 (20), 304 (23), 271 (11), 230 (11), 213 (54), 133 (65). Anal. calc. for $C_{34}H_{40}O_{20}S_2$ (832.78): C 49.03, H 4.84, S 7.70; found: C 49.31, H 4.61, S 7.92.

*2,5-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzene-1,4-diol* (**33**). *a*) A soln. of **4** (4.2 g, 8.94 mmol) in acetone (50 ml) was added at r.t. to a stirred soln. of **3** (3.25 g, 8.94 mmol) in MeOH (80 ml). Stirring was continued for 30 min and the soln. concentrated to *ca.* 30 ml. The precipitate was collected and dried. Crystallization from hexane/acetone gave **33** (3.0 g, 40%).

b) A soln. of **32** (1.69 g, 2.03 mmol) in $CHCl_3$ (40 ml) was treated with $Na_2S_2O_4$ (1.8 g, 10.34 mmol) in H_2O (20 ml) as described for **2**. Crystallization of the crude material gave pure **17** (1.56 g, 92%). M.p. 211°. R_f (hexane/AcOEt 1:3) 0.62. $[\alpha]_D^{25} = -43.88$ ($c = 0.515$, $CHCl_3$). UV (MeOH): 208 (39000), 260 (13000), 319 (11000). IR (KBr): 3650–3200*m*, 3020*w*, 2945*w*, 1755*s*, 1599*w*, 1484*m*, 1470*m*, 1432*m*, 1374*s*, 1240*s*, 1088*m*, 1040*s*, 980*w*, 913*m*, 804*w*, 754*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*; ArO*H*: 6.65 (*s*, exchange with D_2O); AcO: 2.13 (*s*, 6H); 2.03 (*s*); 2.00 (*s*). ^{13}C-NMR (50.6 MHz, $CDCl_3$): *Table 4*. CI-MS: 854 (21), 853 (41), 852 (100, $[M + NH_4]^+$), 522 (39), 382 (15), 350 (22), 331 (17), 230 (21), 214 (11), 213 (98), 210 (34), 153 (20). Anal. calc. for $C_{34}H_{42}O_{20}S_2$ (834.80): C 48.91, H 5.07, S 7.68; found: C 49.20, H 4.90, S 7.85.

*2,5-Bis(β-*D*-glucopyranosylthio)benzene-1,4-diol* (**34**). A soln. of **33** (2.52 g, 3.02 mmol) in MeOH (50 ml) was deacetylated with 0.6M NaOMe in MeOH (10 ml) as described for **5**. Crystallization of the yellow-brownish residue from i-PrOH gave **34** (0.97 g, 62%) containing traces of i-PrOH which could not be removed by drying at 10^{-7} mbar. A nearly pure product was obtained by lyophilization of an aq. soln. White solid. M.p. (lyophilisate) 159–161°. R_f (AcOEt/i-PrOH/H_2O 1:7:2) 0.81. UV (MeOH): 210 (5400), 261 (1800), 319 (1800). IR (KBr): 3650–3000*s*, 2880*w*, 1630*w*, 1555*w*, 1466*m*, 1410*m*, 1307*m*, 1275*m*, 1195*m*, 1095*s* (sh), 1060*s* (sh), 1030*s*, 872*m*, 803*m*. ^{1}H-NMR: *Tables 2* and *3*. ^{13}C-NMR: *Table 5*. ESI-MS: 521.4 (100, $[M + Na]^+$).

*2,5-Bis(β-*D*-glucopyranosylthio)benzo-1,4-quinone* (**35**). A soln. of **34** (500 mg, 1.0 mmol) in MeOH (10 ml) was treated with (diacetoxyiodo)benzene (483 mg, 1.5 mmol), similarly as described for **6**. Lyophilization of an aq. soln. of the crude yielded **35** (339 mg, 68%). Orange fluffy solid. R_f (AcOEt/i-PrOH/H_2O 1:7:2) 0.74. $[\alpha]_D^{25} = -211.0$ ($c = 0.155$, MeOH). UV (MeOH): 211 (17000), 352 (11000). IR (KBr): 3650–3000*s*, 2880*w*, 1640*s*, 1552*s*, 1408*w*, 1326*m*, 1270*w*, 1224*m*, 1102*m* (sh), 1043*s*, 1018*s*, 872*m*, 808*m*. ^{1}H-NMR: *Tables 2* and *3*. ^{13}C-NMR: *Table 5*. ESI-MS: 519.5 (100, $[M + Na]^+$). Anal. calc. for $C_{18}H_{24}O_{12}S_2 \cdot H_2O$ (514.51): C 42.02, H 5.09, S 12.46; found: C 41.86, H 5.22, S 12.10.

*2,3,5-Tris(2′,3′,4′,6′-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzene-1,4-diol* (**36**). *a*) A mixture of **3** (204 mg, 0.56 mmol) in acetone (10 ml) and K_2CO_3 (78 mg, 0.56 mmol) in H_2O (2 ml) was added at r.t. to a stirred soln. of 2,5-dichlorobenzo-1,4-quinone (**29**; 50 mg, 0.28 mmol) in acetone (10 ml). Stirring was continued for 1 h and the mixture evaporated. FC (hexane/AcOEt 1:2) of the crude gave **36** (R_f 0.29; 107 mg, 32%) and **32** (R_f 0.52; 58 mg, 25%). A sample of **36** was recrystallized from MeOH.

b) As described in *a*), but with **31** (83 mg, 0.28 mmol) instead of **29**. FC (hexane/AcOEt 1:2) of the crude gave **36** (104 mg, 31%) and **32** (57 mg, 24%).

Data of **36**: White crystals. M.p. 167°. R_f (hexane/AcOEt 1:2) 0.29. $[\alpha]_D^{25} = -34.9$ ($c = 0.495$, $CHCl_3$). UV ($CHCl_3$): 243 (12000), 337 (10000). IR ($CHCl_3$): 3403*w*, 2961*w*, 1755*s*, 1430*w*, 1376*m*, 1091*m*, 1040*s*, 915*w*, 866*w*, 599*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.20 (*s*, arom. H); 7.16 (*s*, exchange with D_2O, ArO*H*); 7.01 (*s*, exchange with D_2O, ArO*H*); 5.28, 5.20, 5.19 (*3dd*, '*t*', $J = 9.2, 9.3$, H–C(3′), H–C(3″), H–C(3‴)); 5.13–4.96 (*m*, *dd*, '*t*', $J = 9.2$,

10.2, *dd*, '*t*', *J* = 9.1, 10.1, H–C(4'), H–C(4''), H–C(4'''), H–C(2'), H–C(2''), H–C(2''')); 4.88, 4.69, 4.59 (3*d*, *J* = 10.0, 10.2, 10.2, H–C(1'), H–C(1''), H–C(1''')); 4.28–4.09 (*m*, *J* = 2.3, 12.4, 2 H–C(6'), 2 H–C(6''), 2 H–C(6''')); 3.85, 3.72 (2*m*, H–C(5'), H–C(5''), H–C(5''')); 2.16, 2.13, 2.11, 2.10, 2.09, 2.05, 2.02, 2.01, 2.00 (9*s*, 12 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.69, 170.46, 170.06, 169.99, 169.91, 169.59, 169.37, 169.33, 169.27, 169.21 (10*s*, 12 CO); 152.39, 150.17, (2*s*, C(1), C(4)); 124.01, 121.92 (2*s*); 120.59 (*s*, *d*); 87.50, 86.74, 83.73, 75.98, 73.85, 73.58, 70.16, 69.80, 69.53, 68.11, 67.78, (15*d*); 62.01 (2*t*); 61.64 (*t*); 20.70, 20.65, 20.53 (3*q*, 3 Me). FAB-MS: 1197 (1.4, M^+), 391 (7), 331 (53), 169 (100), 109 (68). Anal. calc. for $C_{48}H_{60}O_{29}S_3$ (1197.18): C 48.16, H 5.05, S 8.04; found: C 48.12, H 4.78, S 7.89.

Identification of **32**: ^{1}H-NMR (300 MHz, $CDCl_3$): 6.68 (*s*, H–C(3)); 5.29 (*dd*, '*t*', *J* = 9.1, H–C(3')); 5.21 (*dd*, '*t*', *J* = 9.2, 9.7, H–C(2')); 5.06 (*dd*, '*t*', *J* = 9.2, 10.1, H–C(4')); 4.86 (*d*, *J* = 9.8, H–C(1')); 4.20 (*dd*, *J* = 2.2, 12.4, H_A–C(6')); 4.09 (*dd*, *J* = 6.8, 12.4, H_B–C(6')); 3.85 (*ddd*, *J* = 2.2, 6.8, 10.0, H–C(5')); 2.10, 2.04, 203, 2.01 (4*s*, 4 AcO).

*2,3,5,6-Tetrakis(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzene-1,4-diol* (**37**). A mixture of **3** (1.2 g, 3.297 mmol) in acetone (50 ml) and K_2CO_3 (479 mg, 3.47 mmol) in H_2O (5 ml) was added at r.t. to a stirred soln. of tetrachlorobenzo-1,4-quinone (203 mg, 0.824 mmol) in acetone (50 ml). Stirring was continued for 1 h. The mixture was neutralized with AcOH and evaporated. A soln. of the crude mixture in $CHCl_3$ (50 ml) was washed with H_2O and shaken with a soln. of $Na_2S_2O_4$ (2.0 g) in H_2O (20 ml) until the red colour of the org. layer had disappeared. The org. layer was washed with H_2O, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 1:2) of the crude gave **37** (700 mg, 54%). White solid. R_f (hexane/AcOEt 1:3) 0.36. UV ($CHCl_3$): 244 (13000), 294 (4200), 356 (11000). IR ($CHCl_3$): 3416*w*, 2959*w*, 1756*s*, 1440*m*, 1420*m*, 1374*s*, 1090*s*, 1040*s*, 915*m*, 849*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42 (*s*, exchange with D_2O, ArOH); 5.30 (*m*, *J* = 1.9, 9.2, H–C(3')); 5.13 (*d*, *J* = 9.9, H–C(1')); 5.06 (*m*, *J* = 10.1, H–C(4'), H–C(2')); 4.23 (*dd*, *J* = 4.8, 12.4, H_B–C(6')); 4.13 (*m*, *J* = 2.8, 12.3, H_A–C(6')); 3.76 (*m*, *J* = 2.8, 4.8, 10.0, H–C(5)); 2.12, 2.08, 2.03, 2.02 (4*s*, 4 AcO). ^{13}C-NMR: *Table 4*. FAB-MS: 1559.5 (3, M^+), 331 (47), 169 (100), 109 (68).

*2,3,5,6-Tetrakis(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosylthio)benzo-1,4-quinone* (**39**). A soln. of **37** (200 mg, 0.128 mmol) in MeOH (5 ml) was stirred with (diacetoxyiodo)benzene (62 mg, 0.192 mmol) at r.t. for 20 min. The precipitate was collected by filtration and washed with ice-cold MeOH. Drying afforded **39** (176 mg, 88%). A sample was recrystallized from MeOH. Red-brown crystals. M.p. 201°. R_f (hexane/AcOEt 1:3) 0.38. $[\alpha]_D^{25} = -17.6$ (*c* = 0.051, $CHCl_3$). UV ($CHCl_3$): 245 (16000), 373 (6500). IR ($CHCl_3$): 2958*w*, 1757*s*, 1665*m*, 1499*w*, 1431*w*, 1368*s*, 1090*s*, 1061*s*, 914*m*, 598*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): *Tables 2* and *3*; 2.09, 2.07, 2.03, 2.02 (4*s*, 4 AcO). ^{13}C-NMR: *Table 4*. FAB-MS: 1888.5 (4), 1558.7 (4, $[M + 1]^+$), 229 (7), 331 (55), 169 (100), 109 (74). Anal. calc. for $C_{62}H_{76}O_{38}S_4$ (1557.53): C 47.81, H 4.92, S 8.24; found: C 47.59, H 5.14, S 8.37.

*2,3,5,6-Tetrakis(β-*D*-glucopyranosylthio)benzene-1,4-diol* (**38**). A soln. of **37** (700 mg, 0.449 mmol) in MeOH (30 ml) was treated with 0.18M NaOMe in MeOH (5 ml) for 3 h at r.t. H_2O (5 ml) was added and the soln. neutralized with *Amberlite IR-120* (H^+) and evaporated. Lyophilization of an aq. soln. of the residue yielded **38** (372 mg, 93%). A sample was recrystallized from MeOH/H_2O. White solid. M.p. 227° (dec.). R_f (AcOEt/EtOH/H_2O) 0.18. UV (H_2O): 212 (10000), 349 (4800). IR (KBr): 3344*s*, 2894*m*, 1624*m*, 1458*m*, 1386*s*, 1272*m*, 1184*s*, 1100*s*, 1084*s*, 1046*s*, 990*s*, 866*m*, 814*m*, 668*m*, 620*m*, 576*m*, 538*m*. ^{1}H-NMR (300 MHz, D_2O): 4.79 (*d*, *J* = 9.6, H–C(1')); 3.73 (*dd*, H_A–C(6')); 3.63 (*dd*, *J* = 4.9, 12.7, H_B–C(6')); 3.48–3.26 (*m*, 4 H, H–C(2'), H–C(3'), H–C(4'), H–C(5')). ^{13}C-NMR (75 MHz, D_2O): 155.45 (*s*, C(1)); 127.90 (*s*, C(2)); 90.09 (*d*, C(1')); 82.67 (*d*, C(5')); 79.77 (*d*, C(3')); 75.65 (*d*, C(2')); 71.78 (*d*, C(4')); 63.30 (*t*, C(6')). FAB-MS: 886.9 (M^+), 724, 425, 241 (22), 149 (40), 117 (18).

*2,3,5,6-Tetrakis(β-*D*-glucopyranosylthio)benzo-1,4-quinone* (**40**). A mixture of **38** (160 mg, 0.18 mmol), (diacetoxyiodo)benzene (90 mg, 0.28 mmol), and MeOH (100 ml) was stirred for 20 min at r.t. The mixture was filtered and concentrated to *ca.* 5 ml. CH_2Cl_2 (*ca.* 70 ml) was added and the precipitate collected by filtration. Drying gave **40** (123 mg, 77%). Brown solid. UV (MeOH): 219 (13000), 371 (6600). IR (KBr): 3372*s*, 2922*m*, 1654*s*, 1506*m*, 1418*m*, 1362*m*, 1270*m*, 1216*m*, 1048*s*, 878*m*, 808*m*, 780*m*, 720*m*, 668*m*, 618*m*, 580*m*. ^{1}H-NMR (300 MHz, D_2O): 5.09 (*d*, *J* = 9.0, H–C(1')); 3.81 (*dd*, '*t*', *J* = 12.2, H_A–C(6')); 3.63 (*dd*, '*t*', H_B–C(6')); 3.48–3.30 (*m*, H–C(5'), H–C(4'), H–C(3'), H–C(2')). ^{13}C-NMR: *Table 5*.

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