Carbohydrate Research, 53 (1977) 57–66
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SYNTHESIS OF SOME FUROIC AND THENOIC ESTERS OF THE METHYL D-GLUCOPYRANOSIDES, AND THEIR STABILITY TO HIGH-ENERGY RADIATION

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(Received August 13th, 1976; accepted for publication, September 3rd, 1976)

ABSTRACT

The esters obtained by complete esterification of methyl D-glucopyranosides with, respectively, 2-furoyl chloride (β-, **1**; α-, **2**), 2-furanacryloyl chloride (β-, **3**; α-, **4**), 5-bromo-2-furoyl chloride (β-, **5**; α-, **6**), 2-thenoyl chloride (α-, **7**; β-, **8**), 5-methyl-2-thenoyl chloride (α-, **9**; β-, **10**), 5-bromothiopheneacryloyl chloride (α-, **11**; β-, **12**), and 2-thiopheneacryloyl chloride (α-, **13**; β-, **14**) were subjected to irradiation (2.8×10^{19} eV/g/h) in the solid state to a dosage of 7.1×10^{20} eV/g. The e.s.r. spectra of irradiated (irr.) methyl α- and β-D-glucopyranoside and irr. esters **1–14** were examined to determine the nature of the radiation damage; those of the unsubstituted D-glucopyranosides contain one very strong doublet and one very strong singlet, indicating that cleavage of the C-1–O bond (doublet) and dehydrogenation of the C-1–H bond (singlet) had occurred. The e.s.r. spectra of irr. furoates **1** and **2** contain strong doublets, but those of **3–6** have none, showing that the glycosidic bonds in the latter are highly stable to radiation damage, but those in **1** and **2** are stable compared to that in methyl α-D-glucopyranoside. The e.s.r. spectra of the irr. thenoic esters indicated that glycosidic bonds in **11** and **12** are highly stable to radiation-initiated cleavage (absence of doublets), those in **7–10** are fairly stable (weak doublets), and those in **13** and **14** are more stable (strong doublets) than that in methyl α-D-glucopyranoside (very strong doublet). Radiation-initiated, dehydrogenation reactions were decreased for **7** and **8** (very weak singlets), **9** and **10** (very weak, and weak singlets), and **11** and **12** (strong singlets), compared with those of methyl α-D-glucopyranoside, **13**, and **14** (very strong singlets). The radiation stability of these esters may arise from intramolecular transfer of energy to the ester groups, and be followed by dissipation of the energy. The anomeric form of methyl D-glucopyranoside has no influence on the localization of the energy.

INTRODUCTION

We have reported on the synthesis and radiation stability of aromatic esters of D-glucosides[1–4] and of cellulose[5], and used electron spin resonance (e.s.r.) spectrometry to study intramolecular energy-transfer during radiolysis of these esters[4,5]. These investigations were extended to synthesize, and to determine the radiation stability of, cellulose furoates[6] and 2-thenoates[7]. We have now applied these techniques to elucidation of the nature of radiation damage of furoylated and thenoylated methyl D-glucopyranosides.

RESULTS

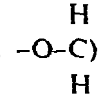
The e.s.r. spectrum of irradiated (irr.) methyl α-D-glucopyranoside contains one very strong doublet (generated by cleavage of the C-1–O bond) and one very strong singlet (generated by dehydrogenation of the C-1–H bond)[4]. The e.s.r. spectrum of irr. methyl β-D-glucopyranoside was the same as that of the irr. α anomer. Irr. methyl tetra-*O*-(2-furoyl)-β- (**1**) and -α- (**2**) D-glucopyranoside respectively give a strong, doublet spectrum and a very weak, five-line spectrum. The doublet spectrum is generated by cleavage of the C-1–O bond, whereas the very weak, five-line spectrum is probably generated by two radicals: a very weak, triplet spectrum (generated by dehydrogenation of the methyl group to yield  $-\mathrm{O}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}$) and a very weak, doublet

TABLE I

ELECTRON-SPIN RESONANCE SPECTRA OF IRRADIATED FUROIC ESTERS OF METHYL D-GLUCOPYRANOSIDES[a]

Methyl D-*glucopyranoside*	*Compound no.*	*No. of lines* (in vacuo)[b]	*Line width* (*mT*)	*g Value*[d]
α-		1 (vs) 2 (vs)	[c]	2.0047
Tetra-*O*-(2-furoyl)-β-	1	2 (s) 5 (vw)	[e]	2.0040
α anomer	2	2 (s) 5 (vw)	[e]	2.0042
Tetra-*O*-(2-furanacryloyl)-β-	3	1 (s) 3 (s)	2.0 0.7	2.0030
α anomer	4	1 (s) 3 (s)	1.9 [e]	2.0030
Tetra-*O*-(5-bromo-2-furoyl)-β-	5	1 (vw)	1.4	2.0045
α anomer	6	1 (vw)	1.4	2.0048

[a] Irradiated in the solid state by ^{60}Co γ-radiation to a dosage of 7.1 × 10^{20} eV/g, except for compound α-, which was irradiated to a dosage of 5.2 × 10^{19} eV/g. [b] Key: s, strong; v, very, w, weak. [c] Main line. [d] Calculated for center of spectrum. [e] Lines overlapped.

spectrum (generated by cleavage of the C-5–O bond). Irr. methyl tetra-*O*-(2-furanacryloyl)-*β*- (**3**) and -*α*- (**4**) D-glucopyranoside respectively give a strong, singlet spectrum and a strong, triplet spectrum. Irr. methyl tetra-*O*-(5-bromo-2-furoyl)-*β*- (**5**) and -*α*- (**6**) D-glucopyranoside give very weak, singlet spectra. For all of the irr. D-glucopyranosides, the g values, calculated for the center of the respective e.s.r. spectrum and recorded in Table I, were almost the same as the free-electron value. The line widths of the clearly resolved, e.s.r. spectra are also recorded in Table I.

Irr. methyl tetra-*O*-(2-thenoyl)-*α*- (**7**) and -*β*- (**8**) D-glucopyranoside respectively give a weak, doublet spectrum and a very weak, singlet spectrum. Irr. methyl tetra *O*-(5-methyl-2-thenoyl)-*α*- (**9**) and -*β*- (**10**) D-glucopyranoside give a weak doublet spectrum and a weak, or very weak, singlet spectrum. Irr. methyl tetra-*O*-(5-bromo-2-thiopheneacryloyl)-*α*- (**11**) and -*β*- (**12**) D-glucopyranoside generate strong, singlet spectra. Irr. methyl tetra-*O*-(2-thiopheneacryloyl)-*α*- (**13**) and -*β*- (**14**) D-glucopyranoside respectively generate a strong, doublet spectrum and a very strong, singlet spectrum. The g values, calculated for the center of the respective e.s.r. spectrum and recorded in Table II, were almost the same as the free-electron value. The line widths of the clearly resolved, e.s.r. spectra are also recorded in Table II.

TABLE II

ELECTRON-SPIN RESONANCE SPECTRA OF IRRADIATED THENOIC ESTERS OF METHYL D-GLUCOPYRANOSIDES[a]

Methyl D-*glucopyranoside*	*Compound no.*	*No. of lines* (in vacuo)[b]	*Line width* (*mT*[c])	*g Value*[d]
α-		1 (vs) 2 (vs)	[e]	2.0047
Tetra-*O*-(2-thenoyl)-*α*-	7	1 (vw) 2 (w)	[e]	2.0033
β anomer	8	1 (vw) 2 (w)	[e]	2.0033
Tetra-*O*-(5-methyl-2-thenoyl)-*α*-	9	1 (vw) 1 (w) 2 (w)	[e]	2.0053
β anomer	10	1 (vw) 1 (w) 2 (w)	[e]	2.0052
Tetra-*O*-(5-bromo-2-thiopheneacryloyl)-*α*-	11	1 (s)	1.2	2.0047
β anomer	12	1 (s)	1.2	2.0048
Tetra-*O*-(2-thiopheneacryloyl)-*α*-	13	1 (vs) 2 (s)	1.2 [e]	2 0030
β anomer	14	1 (vs) 2 (s)	1.2 [e]	2.0030

[a] Irradiated in the solid state by ^{60}Co γ-radiation to a dosage of 7.1 × 10^{20} eV/g, except for compound *α*-, which was irradiated to a dosage of 5.2 × 10^{19} eV/g. [b] Key: s, strong; v, very; w, weak. [c] Main line. [d] Calculated for center of spectrum. [e] Lines overlapped.

DISCUSSION

Stable free-radicals were formed in irradiated, furoic esters of methyl D-glucopyranosides. The mechanism of the loss of energy by the incident, high-energy, γ-radiation to the carbohydrate molecule was, probably, initially random and nonlocalized, followed by generation of high-energy electrons[3]. The localization of the energy of these electrons in methyl α-D-glucopyranoside resulted in formation of stable free-radicals that generated an e.s.r. spectrum indicating cleavage of glycosidic bonds and dehydrogenation (very strong doublet and very strong singlet, respectively).

The presence of substituted furoyl groups on methyl D-glucopyranosides influenced the localization of the energy of the electrons in the methyl D-glucopyranosides, and resulted in cleavage of the glycosidic bond and dehydrogenation. 2-Furoyl groups (compounds **1** and **2**) decreased the radiation-initiated cleavage of glycosidic bonds, and significantly decreased the dehydrogenation (weaker-doublet e.s.r spectrum, and very weak doublet plus triplet e.s r. spectrum, respectively, than that given by irr. methyl α-D-glucopyranoside). 2-Furanacryloyl groups (compounds **3** and **4**) eliminated radiation-initiated cleavage of glycosidic bonds, and decreased the dehydrogenation (absence of doublet e.s.r. spectrum and weaker triplet spectrum, respectively, than that given by irr. methyl α-D-glucopyranoside).

5-Bromo-2-furoyl groups (compounds **5** and **6**) almost totally protected the methyl D-glucopyranosides from radiation degradation (generation of only a very weak, singlet, e s.r. spectrum that indicated a very low extent of dehydrogenation, as compared with irr. methyl α-D-glucopyranoside). The anomeric form of the methyl D-glucopyranoside did not change the influence of these furoyl groups on the localization of the energy of the high-energy electrons in the carbohydrate molecules.

The presence of substituted thenoyl groups on the methyl D-glucopyranosides also influenced the localization of the energy of the secondary electrons on the carbohydrate molecule. 2-Thenoyl groups (compounds **7** and **8**) decreased the radiation-initiated cleavage of glycosidic bonds and dehydrogenation (weaker doublet, and singlet e.s.r. spectrum, respectively, than that given by irr. methyl α-D-glucopyranoside). 5-Methyl-2-thenoyl groups (compounds **9** and **10**) also decreased the radiation-initiated cleavage of glycosidic bonds and dehydrogenation (weaker doublet, and singlet e.s r. spectrum, respectively, than that given by irr. methyl α-D-glucopyranoside).

5-Bromo-2-thiopheneacryloyl groups (compounds **11** and **12**) eliminated the radiation-initiated cleavage of glycosidic bonds and decreased the dehydrogenation (absence of doublet e.s r. spectrum, and a weaker singlet spectrum, respectively, than that given by irr. methyl α-D-glucopyranoside). 2-Thiopheneacryloyl groups (compounds **13** and **14**) decreased the radiation-initiated cleavage of glycosidic bonds (weaker-doublet e.s.r. spectra than that given by irr. methyl α-D-glucopyranoside).

The e.s r. spectra recorded for irr. furoic and thenoic esters of the methyl D-glucopyranosides differ from those for the irr. methyl D-glucopyranosides. The relative intensities of the doublets and singlets in the e.s.r. spectra recorded for the irr. D-glucopyranosides indicate that the presence of furoyl and thenoyl groups decreases the cleavage of the glycosidic bonds and the dehydrogenation reactions of the D-glucopyranosides.

The localization of energy is probably effected through intramolecular transfer of energy, particularly the localization of energy of secondary electrons to the furoyl or thenoyl groups, or selective absorption of energy of the secondary electrons by the furoyl or thenoyl groups, or both. Furoic and thenoic systems should be able to accept the energy, to form well defined, excited states; then, the energy could be dissipated as heat or light, without causing glycosidic bond cleavage and dehydrogenation of the substituted methyl D-glucopyranoside. Similar types of π-electron structures (for example, aromatic groups) have been shown to deactivate the excited state of the group by fluorescence[2,3]. These effects on localization of energy by irradiated substituted carbohydrates appear to be characteristic for groups having π-electron structures[1,4–7]

EXPERIMENTAL

General. — Melting points were determined in a Fisher–Johns apparatus and were not corrected. Infrared (i.r.) spectra were recorded with a Perkin–Elmer Model 621 i.r. spectrophotometer*. Nuclear magnetic resonance (n.m.r.) spectra were determined for solutions in deuteriochloroform at room temperature, with tetramethylsilane as the internal standard, by using a Varian A-60 spectrometer equipped with a V-6040 variable-temperature probe. The substituted D-glucopyranosides were chemically pure, and in the form of solid powders when irradiated. Irradiations were conducted in the SRRC ^{60}Co radiation source[8], which had a dose rate, determined by ferrous–ferric dosimetry[9], of 2.8×10^{10} eV/g/h. The samples were irradiated in air in Pyrex tubes to a total dosage of 7.1×10^{20} eV/g. The irradiated samples were transferred in a dry box from the Pyrex to quartz tubes. The e.s.r. spectra were recorded at ~25° with a Varian 4502-15 EPR spectrometer system, in the form of the first derivative of the absorption line.

Intermediates — 2-Furanacryloyl chloride was prepared by boiling a solution of 2-furanacrylic acid (m.p. 141°; 41 g, 0.30 mole) and thionyl chloride (53 g, 0.45 mole) in dry benzene (120 ml) for 20 h under a reflux condenser (calcium chloride tube). The solution was evaporated to dryness at 25 torr, and the residue was distilled at 78–81°/0.45 torr. The distillate, obtained in 90% yield, solidified on standing, and had m.p. 29–31°.

5-Bromo-2-furoyl chloride was prepared by boiling a solution of 5-bromo-2-furoic acid (30 g, 0.16 mole) and thionyl chloride (26 g, 0.22 mole) in dry benzene (90 ml) for 20 h under reflux, and then evaporating to dryness at 60°/0.5 torr. The

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*Trade names are given as part of the exact experimental conditions, and not as an endorsement of the products over those of other manufacturers.

residue was distilled under vacuum; a fraction having b.p. 78–81°/25 torr was collected in 88% yield; m.p. 58–60°.

5-Methyl-2-thenoyl chloride was prepared by boiling a solution of 5-methyl-2-thiophenecarboxylic acid (20 g, 0.14 mole) and thionyl chloride (25 g, 0.21 mole) in dry benzene (100 ml) for ~17 h under reflux, and then evaporating at 60°/0.5 torr to remove the benzene and the excess of thionyl chloride. The residue was distilled, and a fraction having b.p. 160°/30 torr was collected (21 g, yield 93%); this solidified at 25°.

2-Thenoyl chloride was prepared by boiling a mixture of 2-thiophenecarboxylic acid (25 g, 0.20 mole) and thionyl chloride (35 g, 0.29 mole) in dry benzene (100 ml) for ~17 h under reflux, and then evaporating at 60°/0.5 torr, to remove the benzene and the excess of thionyl chloride. The residue was distilled, and a fraction having b.p. 144–146°/30 torr was collected; this solidified at 25° (24 g, yield 85%).

2-Thiopheneacryloyl chloride was prepared by boiling a mixture of 2-thiopheneacrylic acid (25 g, 0.16 mole) and thionyl chloride (30 g, 0.25 mole) in dry benzene (100 ml) for ~17 h under reflux, and then evaporating at 60°/0.5 torr, to remove the benzene and the excess of thionyl chloride. The residue was distilled, and a fraction having b.p. 100–103°/0.2 torr was collected that solidified at 25° (24 g, yield 85%).

5-Bromo-2-thiopheneacryloyl chloride was prepared by boiling a mixture of 5-bromo-2-thiopheneacrylic acid (28 g, 0.12 mole) and thionyl chloride (21 g, 0.18 mole) in dry benzene (100 ml) for ~24 h under reflux, and then evaporating at 60°/0.5 torr, to remove the benzene and the excess of thionyl chloride. The residue was distilled, and a fraction having b.p. 112–115°/0.1 torr was collected (26 g, yield 87%) that solidified; m.p. 73–74°.

*Methyl 2,3,4,6-tetra-*O*-(2-furoyl)-β-*D*-glucopyranoside* (**1**). — A solution of methyl β-D-glucopyranoside (3 g, 15 mmoles) in chloroform (100 ml) and anhydrous pyridine (15 g, 0.19 mole) was cooled in ice, and a precooled solution (0°) of 2-furoyl chloride (12 g, 92 mmoles) in chloroform (20 ml) was added during 30 min, with stirring, at such a rate that the temperature did not rise above 0°. After about 15 min of stirring, the β-D-glucoside had dissolved; the mixture was kept in the ice-bath and stirred for 2 h at 0°, and for 17 h at 25°. It was then cooled to 0°, ice-cold water (100 ml) was added, and the chloroform layer was successively washed with ice-cold M hydrochloric acid, aqueous sodium hydroxide (1.3M), and water, dried (anhydrous magnesium sulfate), and evaporated at 60°/0.5 torr to a thick syrup from which a solid separated on addition of ethanol. The solid was dissolved in chloroform, ethanol was added and the solution was cooled, whereupon compound **1** crystallized (yield 92%). After two recrystallizations from the same solvent-mixture, it had m.p. 166.5–168°, $[\alpha]_D^{23}$ +34.0° (*c* 6.12, chloroform); ν_{max}^{KBr} 1291 (–OCO–), 1575 (C=C), and 1725 cm^{-1} (CO); n.m.r. data: τ 2.44–3.72 (12 H, ring), 4.30–5.50 (7 H, pyranoside), and 6.46 (3 H, Me).

Anal. Calc. for $C_{27}H_{22}O_{14}$: C, 56.84; H, 3.89. Found: C, 56.65; H, 3.71.

*Methyl 2,3,4,6-tetra-*O*-(2-furoyl)-α-*D*-glucopyranoside* (**2**). — The procedure was the same as for **1**, except that methyl α-D-glucopyranoside was used. Compound **2** was dissolved in chloroform, and on addition of ethanol, a solid separated. On cooling the solution, compound **2** crystallized (yield 81%). After two recrystallizations from the same solvent-mixture, it had m.p. 167–168.5°, $[\alpha]_D^{23}$ +87.4° (*c* 6.17, chloroform); $\nu_{\max}^{\mathrm{KBr}}$ 1291 (–OCO–), 1575 (C=C), and 1719 cm^{-1} (CO); n.m.r. data: τ 2.45–3.74 (12 H, ring), 4.30–5.50 (7 H, pyranoside), and 6.56 (3 H, Me).

Anal. Calc. for $C_{27}H_{22}O_{14}$: C, 56.84; H, 3.89. Found: C, 57.08; H, 3.95.

*Methyl 2,3,4,6-tetra-*O*-(2-furanacryloyl)-β-D-glucopyranoside* (**3**). — A solution of methyl β-D-glucopyranoside (2 g, 10 mmole) in chloroform (100 ml) and anhydrous pyridine (8.4 g, 11 mmoles) was cooled in ice, and a precooled solution (0°) of 2-furanacryloyl chloride (9.6 g, 61 mmoles) in chloroform (20 ml) was added dropwise, under anhydrous conditions, with stirring, during 45 min so that the temperature did not rise above 5°. It was then stirred for 17 h at 5°, ice-cold water (150 ml) was added, and the chloroform layer was successively washed with ice-cold dilute hydrochloric acid (M), aqueous potassium carbonate (0.4M), and water, dried (anhydrous potassium carbonate), and evaporated at 60°/0.5 torr to a thick syrup that was dissolved in petroleum ether (b.p. 40–60°). The compound was purified by chromatography on a column of neutral silica gel (activated for 2 h at 110°), and the product was dissolved in ethyl acetate (100 ml)–petroleum ether (130 ml; b.p. 40–60°). On cooling the solution, compound **3** separated as a solid (yield 25%), m.p. 81–82°, $[\alpha]_D^{23}$ +59.2° (*c* 4.39, chloroform); $\nu_{\max}^{\mathrm{KBr}}$ 1301 (–OCO–), 1553, 1632 (C=C), and 1732 cm^{-1} (CO).

*Methyl 2,3,4,6-tetra-*O*-(2-furanacryloyl)-α-D-glucopyranoside* (**4**). — The procedure was the same as for **3**, except that methyl α-D-glucopyranoside was used. Compound **4** separated as a solid (yield 19%), m.p. 83–85°, $[\alpha]_D^{23}$ +82.4° (*c* 6.33, chloroform); $\nu_{\max}^{\mathrm{KBr}}$ 1300 (–OCO–), 1553, 1632 (C=C), and 1702 cm^{-1} (CO).

*Methyl 2,3,4,6-tetra-*O*-(5-bromo-2-furoyl)-β-D-glucopyranoside* (**5**). — To a solution of methyl β-D-glucopyranoside (1.9 g, 9.8 mmoles) in anhydrous pyridine (93 g, 1.18 moles) at 25° was added 5-bromo-2-furoyl chloride (13.5 g, 65 mmoles), and the mixture was stirred for 24 h. The suspension was filtered, and to the filtrate was added ice-cold water (100 ml); the mixture was made neutral with aqueous potassium hydrogen carbonate (0.5M), and then extracted with dichloromethane. The extract was dried (anhydrous magnesium sulfate) and evaporated at 60°/0.5 torr, to yield a solid which was dissolved in ethyl acetate (10 ml)–hexane (10 ml), and purified by column chromatography as for **3**. The product was eluted from the column by ethyl acetate (100 ml)–hexane (120 ml), and the eluate evaporated at 60°/0.5 torr. Compound **5** was obtained as a tan solid (yield 95%), m.p. 81–82°, $[\alpha]_D^{23}$ +32.0° (*c* 7.59, chloroform); $\nu_{\max}^{\mathrm{KBr}}$ 1290 (–OCO–), 1575 (C=C), and 1730 cm^{-1} (CO); n.m.r. data: τ 2.77–3.65 (8 H, ring), 4.20–5.50 (7 H, pyranoside), and 6.46 (3 H, Me).

Anal. Calc. for $C_{27}H_{18}Br_4O_{14}$: C, 36.60; H, 2.05; Br, 36.08. Found: C, 36.68; H, 1.98; Br, 35.93.

*Methyl 2,3,4,6-tetra-*O*-(5-bromo-2-furoyl)-α-D-glucopyranoside* (**6**). — The procedure was the same as for **5**, except that methyl α-D-glucopyranoside was used. Crude compound **6** was obtained as a gray solid (yield 96%), m.p. 78–79°. A solution of this in ethyl acetate (100 ml)–petroleum ether (100 ml, b.p. 40–60°) was passed through a column of activated aluminum oxide, and the eluate evaporated at 60°/0.5 torr to yield a white solid that had m.p. 83–84°, $[\alpha]_D^{23}$ +52.4° (*c* 7.32, chloroform); ν_{max}^{KBr} 1285 (–OCO–), 1575 (C=C), and 1730 cm^{-1} (CO); n.m.r. data: τ 2.80–3.70 (8 H, ring), 4.10–5.80 (7 H, pyranoside), and 6.53 (3 H, Me).

Anal. Calc. for $C_{27}H_{18}Br_4O_{14}$: C, 36.60; H, 2.05; Br, 36.08. Found: C, 36.74; H, 2.01; Br, 35.95.

*Methyl 2,3,4,6-tetra-*O*-(2-thenoyl)-α-D-glucopyranoside* (**7**). — A solution of methyl α-D-glucopyranoside (2 g, 10 mmoles) in chloroform (130 ml) and anhydrous pyridine (20 g, 0.26 mole) was cooled in ice, and a precooled solution (0°) of 2-thenoyl chloride (9.3 g, 64 mmoles) in chloroform was added, with stirring, at such a rate that the temperature did not rise above 0°. The mixture was kept overnight at 0°, and ice-cold water (100 ml) was added; the chloroform layer was successively washed with ice-cold dilute hydrochloric acid (M), aqueous sodium hydroxide (1.3M), and water, dried (anhydrous magnesium sulfate), and evaporated at 60°/0.5 torr to a thick syrup which was dissolved in ethyl acetate (75 ml)–petroleum ether (150 ml, b.p. 40–60°). The solution was passed through a column of activated aluminum oxide; the product was eluted with ethyl acetate (100 ml), and the eluate was passed through a column of silica gel. On cooling the effluent, compound **7** separated as a white solid (3.2 g, yield 49%), m.p. 71–72°, $[\alpha]_D^{23}$ +90.1° (*c* 6.79, chloroform); ν_{max}^{KBr} 1250 (–OCO–), 1520 (C=C), and 1715 cm^{-1} (CO); n.m.r. data: τ 2.15–3.20 (12 H, ring), 4.00–5.65 (7 H, pyranoside), and 6.54 (3 H, Me)

Anal. Calc. for $C_{27}H_{22}O_{10}S_4$: C, 51.09; H, 3.49; S, 20.21. Found: C, 51.88; H, 3.62; S, 18.52.

*Methyl 2,3,4,6-tetra-*O*-(2-thenoyl)-β-D-glucopyranoside* (**8**). — The procedure was the same as for **7**, except that methyl β-D-glucopyranoside was used. Compound **8** was obtained as a white solid (3.3 g, 50%), m.p. 69–70°, $[\alpha]_D^{23}$ +41.3° (*c* 6.50, chloroform); ν_{max}^{KBr} 1255 (–OCO–), 1520 (C=C), and 1719 cm^{-1} (CO); n.m.r. data: τ 2.05–3.15 (12 H, ring), 4.20–5.65 (7 H, pyranoside), and 6.50 (3 H, Me).

Anal. Calc. for $C_{27}H_{22}O_{10}S_4$: C, 51.09; H, 3.49; S, 20.21. Found: C, 52.39; H, 4.16; S, 17.45.

*Methyl 2,3,4,6-tetra-*O*-(5-methyl-2-thenoyl)-α-D-glucopyranoside* (**9**). — A solution of methyl α-D-glucopyranoside (2 g, 0.01 mole) in chloroform (100 ml) and anhydrous pyridine (15 g, 0.19 mole) was cooled to 25°, and a solution (25°) of 5-methyl-2-thenoyl chloride (10 g, 62 mmoles) in chloroform was added, with stirring, at 25°. The mixture was stirred overnight at 25°, and then cooled in ice to 0°; ice-cold water (100 ml) was added, and the chloroform layer was successively washed with ice-cold dilute hydrochloric acid (M) aqueous sodium hydroxide (1.3M), and water, dried (anhydrous magnesium sulfate), and evaporated at 60°/0.5 torr to a thick syrup which was dissolved in ethyl acetate (100 ml)–petroleum ether (130 ml, b.p. 40–60°).

The solution was passed through a column of activated aluminum oxide, and the product was eluted with ethyl acetate (150 ml), the eluate was passed through a column of silica gel, and the effluent was cooled. Compound **9** separated as a white solid (2.9 g, yield 42%), m.p. 64–65°, $[\alpha]_D^{23}$ +53.2° (*c* 6.36, chloroform); ν_{max}^{KBr} 1249 (-OCO-), 1531 (C=C), and 1715 cm^{-1} (CO); n.m.r. data: τ 2.44–3.60 (8 H, ring), 7.62 (12 H, ring Me), 4.20–5.85 (7 H, pyranoside), and 6.60 (3 H, Me).

Anal. Calc. for $C_{31}H_{30}O_{10}S_4$: C, 53.89; H, 4.38; S, 18.57. Found: C, 54.00; H, 4.26; S, 18.59.

*Methyl 2,3,4,6-tetra-*O*-(5-methyl-2-thenoyl)-β-*D*-glucopyranoside* (**10**). — The procedure was the same as for **9**, except that methyl β-D-glucopyranoside was used. Compound **10** was isolated as a white solid (2.7 g, yield 39%), m.p. 74–75°, $[\alpha]^{23}$ +61.9° (*c* 6.16, chloroform); ν_{max}^{KBr} 1249 (-OCO-), 1530 (C=C), and 1715 cm^{-1} (CO); n.m.r. data, τ 2.35–3.43 (8 H, ring), 7.55 (12 H, ring Me), 4.45–5.70 (7 H, pyranoside), and 6.50 (3 H, Me).

Anal. Calc. for $C_{31}H_{30}O_{10}S_4$: C, 53.89; H, 4.38; S, 18.57. Found: C, 53.70; H, 4.36; S, 18.31.

*Methyl 2,3,4,6-tetra-*O*-(5-bromo-2-thiopheneacryloyl)-α-*D*-glucopyranoside* (**11**). — A solution of methyl α-D-glucopyranoside (1 g, 5.1 mmoles) in chloroform (90 ml) and anhydrous pyridine (20 g, 0.25 mole) was cooled to 25°, a solution (25°) of 5-bromo-2-thiopheneacryloyl chloride (8 g, 32 mmoles) in chloroform was added, with stirring, at 25°, and the mixture was stirred overnight at 25°, and then cooled in ice to 0°. Ice-cold water (100 ml) was added, and the chloroform layer was successively washed with ice-cold, dilute hydrochloric acid (M), aqueous sodium hydroxide (1.3M), and water, dried (anhydrous magnesium sulfate), and evaporated at 60°/0.5 torr to a thick syrup which was dissolved in ethyl acetate (100 ml)–petroleum ether (100 ml, b.p. 40–60°). The solution was passed through a column of activated aluminum oxide, and the product was eluted with ethyl acetate (100 ml). On cooling the eluate, compound **11** separated as a brownish solid (2.8 g, yield 50%), m.p. 88–89° and 93–94°, $[\alpha]_D^{23}$ +94.0° (*c* 6.69, chloroform); ν_{max}^{KBr} 1145 (-OCO-), 1511, 1618 (C=C), and 1725 cm^{-1} (CO); n.m.r. data, τ 2.20–3.15 (12 H, ring), 3.80–4.20 (4 H, chain), 4.40–5.80 (7 H, pyranoside), and 6.55 (3 H, Me).

Anal. Calc. for $C_{35}H_{26}Br_4O_{10}S_4$: C, 39.86; H, 2.48; S, 12.16. Found: C, 40.15; H, 2.59; S, 12.30.

*Methyl 2,3,4,6-tetra-*O*-(5-bromo-2-thiopheneacryloyl)-β-*D*-glucopyranoside* (**12**). — The procedure was the same as for **11**, except that methyl β-D-glucopyranoside was used. Compound **12**, isolated as for **11**, was dissolved in ethyl acetate (80 ml)–petroleum ether (160 ml, b.p. 40–60°), and the solution repassed through a column of activated aluminum oxide, the product being eluted with ethyl acetate (100 ml). On cooling the eluate, compound **12** separated as a brownish solid (3.1 g, yield 55%), m.p. 85–86°, $[\alpha]_D^{23}$ +72.3° (*c* 6.81, chloroform); ν_{max}^{KBr} 1145 (-OCO-), 1511, 1615 (C=C), and 1719 cm^{-1} (CO); n.m.r. data: τ 2.20–3.08 (12 H, ring), 3.75–4.20 (4 H, chain), 4.50–5.65 (7 H, pyranoside), and 6.45 (3 H, Me).

Anal. Calc. for $C_{35}H_{26}Br_4O_{10}S_4$: C, 39.86; H, 2.48; S, 12.16. Found: C, 40.01; H, 2.50; S, 12.30.

Methyl 2,3,4,6-tetra-O-(2-thiopheneacryloyl)-α-D-glucopyranoside (**13**). — To a solution of methyl α-D-glucopyranoside (2 g, 10 mmoles) in anhydrous pyridine (100 g, 1.25 moles) was added solid 2-thiopheneacryloyl chloride (11 g, 64 mmoles), and the mixture was stirred for 100 h at 25°, and cooled in ice to 0°. Potassium carbonate solution (1.2M) was added to neutralize the acid, and the mixture was extracted with chloroform. The extract was successively washed with hydrochloric acid (M) and water, dried (anhydrous sodium sulfate), and evaporated at 60°/0.5 torr to a solid residue (10 g) which was dissolved in ethyl acetate (100 ml)–petroleum ether (100 ml, b.p. 40–60°). The solution was passed through a column of activated aluminum oxide, and the product was eluted with ethyl acetate (100 ml). On cooling the eluate, compound **13** separated as a solid (6.0 g, yield 78%), m.p. 86–87°, $[\alpha]_D^{23}$ +101.8° (*c* 7.17, chloroform); ν_{max}^{KBr} 1141 (–OCO–), 1505, 1616 (C=C), and 1711 cm^{-1} (CO); n.m.r. data: τ 2.10–3.20 (16 H, ring), 3.65–4.10 (4 H, chain), 4.15–5.75 (7 H, pyranoside), and 6.55 (3 H, Me).

Anal. Calc. for $C_{35}H_{30}O_{10}S_4$: C, 56.89; H, 4.09; S, 17.36. Found: C, 56.84; H, 4.22; S, 17.55.

Methyl 2,3,4,6-tetra-O-(2-thiopheneacryloyl)-β-D-glucopyranoside (**14**). — The procedure was the same as for **13**, except that methyl β-D-glucopyranoside was used. Compound **14** was isolated as a solid (6.0 g, yield 78%), m.p. 82–83°, $[\alpha]_D^{23}$ +74.1° (*c* 6.64, chloroform); ν_{max}^{KBr} 1148 (–OCO–), 1510, 1620 (C=C), and 1719 cm^{-1} (CO); n.m.r. data: τ 2.05–3.15 (16 H, ring), 3.64–4.05 (4 H, chain), 4.45–5.65 (7 H, pyranoside), and 6.45 (3 H, Me).

Anal. Calc. for $C_{35}H_{30}O_{10}S_4$: C, 56.89; H, 4.09; S, 17.36. Found: C, 57.07; H, 4.18; S, 17.56.

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