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USE OF 2-METHYL-2-PROPANETHIOL IN THE SYNTHESIS OF *C*-THIOGLYCOSYL DERIVATIVES

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ABSTRACT

The reaction of 3-ethoxycarbonyl-2-methyl-5-(D-*arabino*-tetritol-1-yl)furan with 2-methyl-2-propanethiol in acid media yielded a mixture of 5-(1-*S*-*tert*-butyl-1-thio-D-*arabino*- and -D-*ribo*-tetritol-1-yl)-3-ethoxycarbonyl-2-methylfuran (**2** and **3**). Longer reaction times yielded a mixture of **2** and **3**, and 3-ethoxycarbonyl-2-methyl-5-(4-thio-β-D-erythrofuranosyl)furan. 5-(4-*S*-*tert*-Butyl-4-thio-D-*arabino*-tetritol-1-yl)-3-ethoxycarbonyl-2-methylfuran has been synthesised and, on treatment with acid, underwent ring closure to afford mainly **8** and also the α-anomer **11**.

INTRODUCTION

Acyclic sugar nucleosides have attracted interest as potential antiviral agents and they have been synthesised from active bromo derivatives of *aldehydo* sugars and suitable purine and pyrimidine derivatives[1–6]. Purine and pyrimidine nucleosides of thiopentoses have been synthesised by condensations of 2,3,5-tri-*O*-acetyl-4-thio-α,β-D-ribofuranosyl halides with purines and pyrimidines[7,8].

In order to obtain acyclic 1-alkylthio-*C*-glycoside analogues and *C*-glycosides of thiotetroses, we have studied the reaction in acid media of 3-ethoxycarbonyl-2-methyl-5-(D-*arabino*-tetritol-1-yl)furan (**1**) with 2-methyl-2-propanethiol. The peculiar behaviour of 2-methyl-2-propanethiol in these reactions has been ascribed to the easy formation of the *tert*-butyl cation and release of steric strain in the molecule when the *tert*-butyl cation is lost[9–11].

RESULTS AND DISCUSSION

The reaction of **1** with 2-methyl-2-propanethiol in conc. hydrochloric acid at room temperature for 10 min gave a ~1:2 mixture of the diastereomers **2** and **3**, the structures of which were established on the basis of spectroscopic data together

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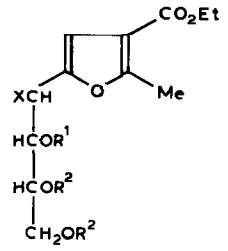
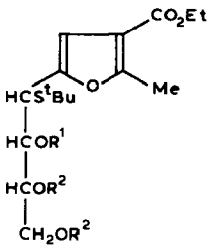
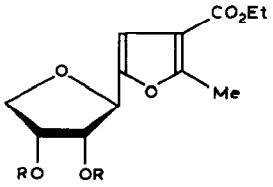


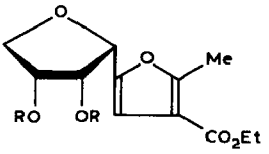
1 X = OH, $R^1 = R^2 = H$
2 X = S-^{t}Bu, $R^1 = R^2 = H$
4 X = S-^{t}Bu, $R^1 = R^2 = Ac$
6 X = S-^{t}Bu, $R^1 = H; R^2, R^2 = CMe_2$



3 $R^1 = R^2 = H$
5 $R^1 = R^2 = Ac$
7 $R^1 = H; R^2, R^2 = CMe_2$



8 R = H
9 R = Ac
10 R, R = CMe_2



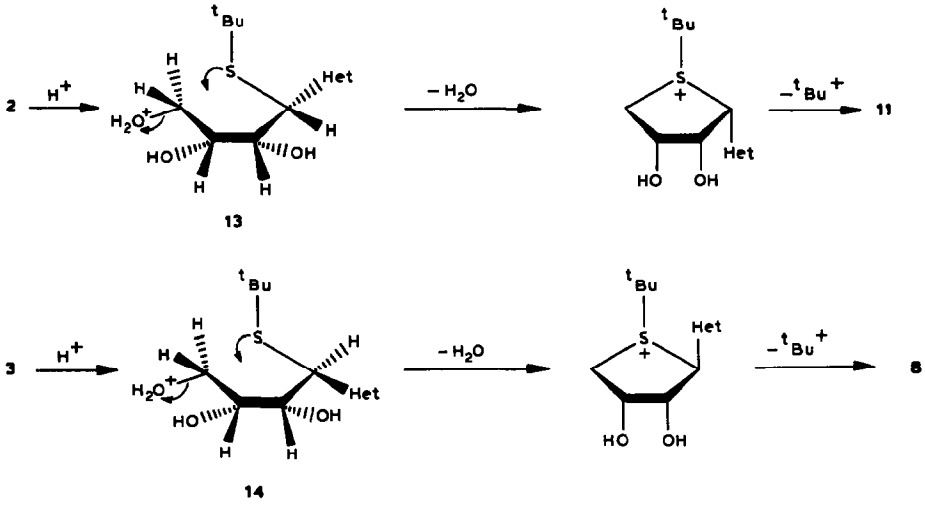
11 R = H
12 R = Ac

with those of the corresponding acetates (**4** and **5**) and 3,4-*O*-isopropylidene derivatives (**6** and **7**).

When **1** was treated with acid for 8 h, column chromatography of the products gave **8** (minor) and a mixture of **2** and **3**. Assignment of structure to the β-anomer **8** was based on spectroscopic data, together with those of the corresponding acetate (**9**) and 2,3-*O*-isopropylidene derivative (**10**). The configurations at C-1 in **9** and **10** were deduced from the $J_{1,2}$ values (6.5 and <1 Hz, respectively), which were similar to those reported[12,13] for the furanose analogues, from the chemical shift of the signals for H-1, and from the $[\alpha]_D$ values (see below). Assignments of the configuration at C-1 of *C*-nucleosides have been based on the n.m.r. data for α,β-pairs[13–20].

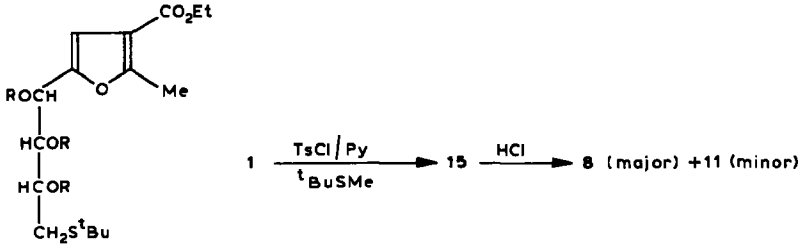
Treatment of the ~1:2 mixture of **2** and **3** with acid for 20 h yielded only one (**8**) of the two possible cyclic isomers, and a ~1:1.2 mixture of **2** and **3** was recovered. The fact that the α-anomer **11** was not detected accords with destabilisation of transition state **13**. Syntheses of furanosides[21] and 1,5-dithiopyranosides[22] by ring closure and loss of benzyl cation from the intermediate oxonium ion and episulfonium ion, respectively, have been reported.

2-(D-*arabino*-Tetritol-1-yl)furans, the condensation products of D-glucose

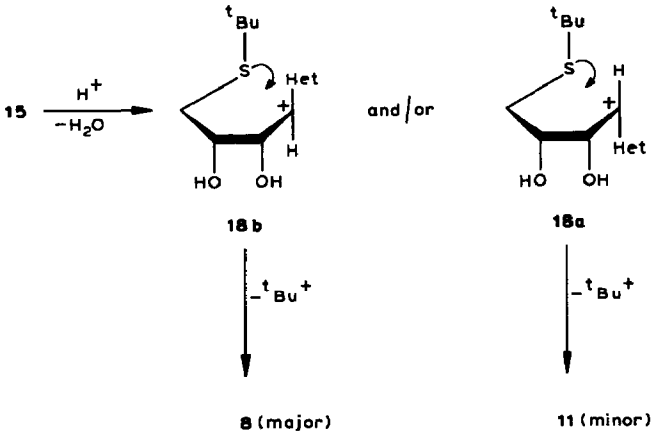


with β-dicarbonyl compounds[23], lose[12] (also Ref. 23, p. 111) a molecule of water when treated with acids, yielding 2-(1,4-anhydrotetrahydroxybutyl)furans. The introduction of a *tert*-butylthio group at C-4 in **15–17** and the subsequent cyclisation in acid media was also studied as a route to the *C*-glycosides of thiotetroses. The structure of **15** was established on the basis of elemental analysis and spectroscopic data, together with those of the corresponding acetate **16** and benzoate **17**. Treatment of **15** with conc. hydrochloric acid for 5 min gave a ~1:6 α,β-mixture, (**11** and **8**). Acetylation of this mixture yielded a mixture of **9** (β-anomer) and **12** (α-anomer), the ^{1}H-n.m.r. spectrum of which contained doublets for H-1 at δ 4.55 ($J_{1,2}$ 6.5 Hz) and 4.72 ($J_{1,2}$ 4.2 Hz) which confirmed the configuration at C-1.

These mixtures were more dextrorotatory than the pure compounds **8** and **9**. In agreement with the values reported for *C*-nucleosides[12] and nucleosides[23], the β-anomer **8** was more strongly levorotatory than the α-anomer **11**, indicating that the reaction of **15** proceeded preferentially with inversion of the configuration at C-1. A possible mechanism for the reaction is shown in the annexed scheme. The



15 R = H
16 R = Ac
17 R = Bz



key intermediate is the resonance-stabilised carbonium ion **18**, which can undergo intramolecular nucleophilic attack to yield thiofuranosides **8** (major) and **11** (minor).

EXPERIMENTAL

The general methods have been described[24]. N.m.r. spectra (^1H 80, ^{13}C 20 MHz) were recorded with a Bruker WP-80-SY spectrometer.

*Reaction between 3-ethoxycarbonyl-2-methyl-5-(*D-arabino-*tetritol-1-yl)furan*[23] (**1**) *and 2-methyl-2-propanethiol in acid media.* — A mixture of **1** (5 g, 18.25 mmol), 2-methyl-2-propanethiol (20 mL), and conc. hydrochloric acid (16 mL) was stirred at room temperature for 10 min, then basified with aqueous 20% K_2CO_3 (100 mL), and extracted with hexane (50 mL) followed by chloroform (4 × 50 mL). The combined chloroform extracts were dried, filtered, and concentrated. Column chromatography (ether) of the crude product yielded a mixture (5.75 g, 91%) of 5-(1-*S*-*tert*-butyl-1-thio-D-*arabino*- and -D-*ribo*-tetritol-1-yl)-3-ethoxycarbonyl-2-methylfuran (**2** and **3**), isolated as a syrup, $[\alpha]_D^{15}$ −10° (*c* 1, chloroform); ν_{max}^{film} 3460–3420, 3130, 1720, 1625, 1586, 1375, 1221, 1075, and 770 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 6.58 and 6.56 (2 s, 1 H, furan H-4), 4.27 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 4.2–3.3 (m, 5 H, H-1,2,3,4,4′), 3.15 (bs, 3 H, exchangeable with D_2O, 3 OH), 2.6 (s, 3 H, furan Me), and 1.4 (m, 12 H, Me_3C and CH_3CH_2O); ^{13}C, δ 164.24 (COO), 158.42 (furan C-2), 153.58 and 151.59 (furan C-5), 114.27 (furan C-3), 109.87 and 108.26 (furan C-4), 75.43, 74.12, 72.21, and 71.62 (C-2,3), 63.75 and 63.34 (C-4), 60.20 (CH_3CH_2O), 44.36 and 44.01 (Me_3C), 43.35 and 42.84 (C-1), 31.25 and 31.14 (Me_3C), 14.30 and 13.81 (CH_3CH_2O and furan Me). Mass spectrum: *m/z* 346 (M^+), 328 ($M^+ - H_2O$), 301 ($M^+ - C_2H_5O$), 289 ($M^+ - C_4H_9$), 271 ($M^+ - C_4H_9, H_2O$), 257 ($M^+ - C_4H_9S$), 255 ($M^+ - C_3H_7O_3$), 199 (100%), and 197.

Anal. Calc. for $C_{16}H_{26}O_6S$: C, 55.47; H, 7.56. Found: C, 55.61; H, 7.42.

A mixture (2.8 g, 8 mmol) of **2** and **3**, 2-methyl-2-propanethiol (18 mL), and

conc. hydrochloric acid (15 mL) was stirred at room temperature for 20 h, then basified, and extracted with ethyl acetate (4 × 50 mL). Column chromatography (1:1 hexane–ether) of the crude product gave, first, **8** (0.61 g, 28%) and then a mixture (0.7 g, 25%) of **2** and **3**.

After reaction for 8 h, column chromatography (1:1 hexane–ether) of the crude product gave, first, 3-ethoxycarbonyl-2-methyl-5-(4-thio-β-D-erythro-furanosyl)furan (**8**; 1.14 g, 23%), isolated as a syrup, $[\alpha]_D^{15}$ −167° (*c* 1, chloroform); ν_{max}^{film} 3450, 3150, 1730, 1624, 1590, 1445–1415, 1305, 1228, 1095, 1040, and 775 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 6.54 (s, 1 H, furan H-4), 4.72–4.22 (m, 3 H, H-1,2,3), 4.25 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 3.22 (dd, 1 H, *J* 11.5 and 4.5 Hz, H-4), 3.30–2.90 (m, 2 H, exchangeable with D_2O, 2 OH), 2.91 (dd, 1 H, *J* 11.5 and 3.5 Hz, H-4′), 2.53 (s, 3 H, furan Me), and 1.32 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O); ^{13}C, δ 164.28 (COO), 159.22 (furan C-2), 150.67 (furan C-5), 114.35 (furan C-3), 108.69 (furan C-4), 79.37 and 74.50 (C-2,3), 60.35 (CH_3CH_2O), 45.6 (C-1), 33.68 (C-4), 14.33 and 13.91 (CH_3CH_2O and furan Me). Mass spectrum: *m/z* 272 (M^+), 254 ($M^+ - H_2O$), 243 ($M^+ - C_2H_5$), 237 ($M^+ - H_2O$, OH), 227 ($M^+ - C_2H_5O$), 225 ($M^+ - C_2H_5$, H_2O), 199, and 167 (100%).

Anal. Calc. for $C_{12}H_{16}O_5S$: C, 52.92; H, 5.92. Found: C, 52.75; H, 5.81.

Eluted second was a mixture (2.27 g, 36%) of **2** and **3**.

Conventional acetylation of the mixture (0.4 g, 1.15 mmol) of **2** and **3** (10-min reaction) with acetic anhydride–pyridine (1:1, 10 mL), with column chromatography (3:1 hexane–ether) of the crude product, gave a mixture (0.5 g, 92%) of 3-ethoxycarbonyl-2-methyl-5-(2,3,4-tri-*O*-acetyl-1-*S*-*tert*-butyl-1-thio-D-*arabino*- and -D-*ribo*-tetritol-1-yl)furan (**4** and **5**), isolated as a syrup, $[\alpha]_D^{15}$ +32° (*c* 1, chloroform); ν_{max}^{film} 3130, 1760, 1720, 1620, 1585, 1375, 1240–1210, 1080, 1050, and 800 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 6.55 (s, 1 H, furan H-4), 5.4–5.0 (m, 1 H, H-3), 4.3–3.95 (m, 3 H, H-1,4,4′), 4.25 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 2.56 and 2.54 (2 s, 3 H, furan Me), 2.1–2.0 (4 s, 9 H, 3 Ac), 1.35 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O), 1.3 and 1.5 (2 s, 9 H, Me_3C); ^{13}C, δ 169.95, 168.96, 168.75, and 163.35 (4 COO), 158.41 and 157.84 (furan C-2), 151.31 and 150.66 (furan C-5), 114.20 and 114.03 (furan C-3), 108.99 and 108.73 (furan C-4), 72.15, 71.65, and 70.38 (C-2,3), 61.42 and 61.10 (C-4), 59.68 (CH_3CH_2O), 43.9 and 43.5 (Me_3C), 40.75 and 40.39 (C-1), 30.62 (Me_3C), 20.53 and 20.24 (3 CH_3COO), 14.0 and 13.36 (CH_3CH_2O and furan Me). Mass spectrum: *m/z* 472 (M^+), 412 ($M^+ - C_2H_4O_2$), 383 ($M^+ - C_4H_9S$), 356 ($M^+ - C_4H_9$, $C_2H_3O_2$), 255 ($M^+ - C_9H_{13}O_6$), 199, and 43 (100%).

Anal. Calc. for $C_{22}H_{32}O_9S$: C, 55.91; H, 6.83. found: C, 56.12; H, 6.66.

Acetonation of the mixture of **2** *and* **3**. — A mixture (1.12 g, 3.25 mmol) of **2** and **3** (10-min reaction), anhydrous acetone (45 mL), 2,2-dimethoxypropane (2.2 mL), and toluene-*p*-sulfonic acid (0.75 g) was kept at room temperature for 1 h, then basified with aqueous 10% K_2CO_3 (20 mL), and extracted with chloroform (4 × 20 mL). The combined extracts were dried, filtered, and concentrated, and column chromatography (5:1 hexane–ether) of the crude product yielded a mixture (1.1 g, 84%) of 5-(1-*S*-*tert*-butyl-3,4-*O*-isopropylidene-1-thio-D-*arabino*- and -D-

ribo-tetritol-1-yl)-3-ethoxycarbonyl-2-methylfuran (**6** and **7**), isolated as a syrup $[\alpha]_D^{17}$ −4° (*c* 1, chloroform); ν_{max}^{film} 3485, 3120, 1720, 1620, 1585, 1370, 1230, 1070, 845, and 765 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 6.85 (s, 1 H, furan H-4), 4.28 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 4.25–3.80 (m, 5 H, H-1,2,3,4,4'), 2.62 (s, 3 H, furan Me), 2.48 and 2.35 (2 d, 1 H, *J* 4.0 and 5.0 Hz, exchangeable with D_2O, OH), and 1.4–1.25 (m, 18 H, Me_3C, Me_2C, and CH_3CH_2O); ^{13}C, 163.62 (COO), 158.0 (furan C-2), 153.46 and 150.8 (furan C-5), 113.98 (furan C-3), 109.02 and 108.10 (furan C-4), 108.90 (Me_2C), 75.9, 75.36, and 73.96 (C-2,3), 66.37 (C-4), 59.74 (CH_3CH_2O), 44.02 and 43.59 (Me_3C), 43.37 and 42.51 (C-1), 30.95 and 30.84 (Me_3C), 26.58 and 26.49 (Me_2C), 14.05 and 13.50 (CH_3CH_2O and furan Me). Mass spectrum: *m/z* 386 (M^+), 371 ($M^+ - CH_3$), 368 ($M^+ - H_2O$), 341 ($M^+ - C_2H_5O$), 329 ($M^+ - C_4H_9$), 315 ($M^+ - C_4H_9$, CH_3), 297 ($M^+ - C_4H_9S$), 255, 199, and 101 (100%).

Anal. Calc. for $C_{19}H_{30}O_6S$: C, 59,04; H, 7.82. Found: C, 58.79; H, 8.05.

Acetonation of the mixture of **2** and **3** obtained in the 8-h reaction gave a mixture of **6** and **7**, $[\alpha]_D^{17}$ −11° (*c* 1, chloroform), the i.r. and n.m.r. spectra of which were superposable on those of the mixture obtained above, except for the different intensities of several ^{13}C-n.m.r. signals.

Acetylation of **8**. — Conventional treatment of **8** (0.15 g, 0.55 mmol) with acetic anhydride–pyridine (1:1, 10 mL), with column chromatography (3:1 hexane–ether) of the crude product, gave 5-(2,3-di-*O*-acetyl-4-thio-β-D-erythrofuranosyl)-3-ethoxycarbonyl-2-methylfuran (**9**; 0.19 g, 97%), isolated as a syrup, $[\alpha]_D^{15}$ −136° (*c* 1, chloroform); ν_{max}^{film} 3110, 1760, 1722, 1620, 1586, 1374, 1250–1220, 1080, 1023, and 770 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 6.54, (s, 1 H, furan H-4), 5.62 (m, 2 H, H-2,3), 4.55 (d, 1 H, *J* 6.5 Hz, H-1), 4.28 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 3.37 (dd, 1 H, *J* 11.5 and 5.0 Hz, H-4), 3.0 (dd, 1 H, *J* 11.5 and 4.0 Hz, H-4'), 2.53 (s, 3 H, furan Me), 2.12 and 2.06 (2 s, 6 H, 2 Ac), and 1.33 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O); ^{13}C, δ 169.93, 169.75, and 163.75 (3 COO), 159.43 (furan C-2), 149.01 (furan C-5), 114.52 (furan C-3), 109.17 (furan C-4), 76.88 and 73.34 (C-2,3), 60.13 (CH_3CH_2O), 43.51 (C-1), 31.45 (C-4), 20.79 and 20.68 (2 *Me*COO), 14.39 and 13.85 (CH_3CH_2O and furan Me). Mass spectrum: *m/z* 356 (M^+), 327 ($M^+ - C_2H_5$), 311 ($M^+ - C_2H_5O$), 296 ($M^+ - C_2H_4O_2$), 267 ($M^+ - C_2H_4O_2$, C_2H_5), 253 ($M^+ - C_2H_3O$, $C_2H_4O_2$), 237 (100%), 209, 199, 191, and 167.

Anal. Calc. for $C_{16}H_{20}O_7S$: C, 53.92; H, 5.66. Found: C, 54.10; H, 5.69.

Acetonation of **8**. — Treatment of **8** (0.25 g, 0.92 mmol) with anhydrous acetone (11 mL), 2,2-dimethoxypropane (0.5 mL), and a catalytic amount (15 mg) of toluene-*p*-sulfonic acid, as described above and with column chromatography (3:1 hexane–ether) of the crude product, gave 3-ethoxycarbonyl-5-(2,3-*O*-isopropylidene-4-thio-β-D-erythrofuranosyl)-2-methylfuran (**10**; 0.23 g, 80%), m.p. 40° (from hexane), $[\alpha]_D^{25}$ −191° (*c* 0.4, methanol); ν_{max}^{film} 3115, 1725, 1620, 1588, 1380, 1235, 1080, 1050, 890, 840, and 770 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 6.40 (s, 1 H, furan H-4), 4.96 (m, 2 H, H-2,3), 4.32 (bs, 1 H, H-1), 4.28 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 3.06 (m, 2 H, H-4,4'), 2.53 (s, 3 H, furan Me), 1.6 and 1.33 (2 s,

6 H, Me_2C), and 1.33 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O); ^{13}C, δ 163.27 (COO), 158.62 (furan C-2), 150.81 (furan C-5), 113.94 (furan C-3), 111.20 (Me_2C), 106.90 (furan C-4), 86.5 and 83.18 (C-2,3), 59.7 (CH_3CH_2O), 50.3 (C-1), 37.74 (C-4), 26.15 and 24.96 (Me_2C), 14.03 and 13.45 (CH_3CH_2O and furan Me). Mass spectrum: *m/z* 312 (M^+), 297 ($M^+ - CH_3$), 267 ($M^+ - C_2H_5O$), 255 ($M^+ - C_3H_5O$), 254 ($M^+ - C_3H_6O$), 237 ($M^+ - C_3H_7O_2$), 198 (100%), 170, and 169.

Anal. Calc. for $C_{15}H_{20}O_5S$: C, 57.67; H, 6.45. Found: C 57.95; H, 6.66.

*5-(4-*S*-tert-Butyl-4-thio-*D*-arabino-tetritol-1-yl)-3-ethoxycarbonyl-2-methylfuran* (**15**). — A solution of **1** (5.3 g, 19.3 mmol) in dry pyridine (25 mL) was treated with tosyl chloride (0.5 g) for 24 h at 3–5°. Water (100 mL) was then added, the mixture was extracted with chloroform (100 mL), and the extract was washed with 5% hydrochloric acid (5 × 50 mL), saturated aqueous sodium hydrogencarbonate (2 × 50 mL), and water (50 mL), then dried, filtered, and concentrated. To a solution of the crude product in ethanol (10 mL) was added a solution of sodium ethoxide (from 0.5 g of sodium) and 2-methyl-2-propanethiol (10 mL) in ethanol (15 mL). The mixture was stirred and boiled under reflux for 30 h, then cooled, concentrated, diluted with water (30 mL), and extracted with chloroform (3 × 30 mL). The combined extracts were dried, filtered, and concentrated, and column chromatography (2:1 hexane–ether) of the crude product gave **15** (4.5 g, 67%), m.p. 90° (from chloroform–hexane), $[\alpha]_D^{25}$ +9° (*c* 1, methanol); ν_{max}^{KBr} 3520, 3440, 3330, 1710, 1580, 1220, 1090, 1060, 1024, 824, and 762 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 6.63 (s, 1 H, furan H-4), 4.94 (m, 1 H, H-1), 4.27 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 3.85 (m, 2 H, H-2,3), 3.15–2.63 (m, 4 H, 2 H exchangeable with D_2O, H-4,4′, 2 OH), 2.55 (s, 3 H, furan Me), 1.68 (bs, 1 H, exchangeable with D_2O, OH), and 1.45–1.20 (m, 12 H, Me_3C, CH_3CH_2O); ^{13}C, δ 164.22 (COO), 158.91 (furan C-2), 151.93 (furan C-5), 114.57 (furan C-3), 108.58 (furan C-4), 74.68, 70.57, and 67.11 (C-1,2,3), 60.18 (CH_3CH_2O), 42.77 (Me_3C), 32.73 (C-4), 31.13 (Me_3C), 14.35 and 13.78 (CH_3CH_2O and furan Me) (Found: C, 55.74; H, 7.57. $C_{16}H_{26}O_6S$ calc.: C, 55.47; H, 7.56%).

Conventional acetylation of **15** (0.5 g, 1.44 mmol) and column chromatography (3:1 hexane–ether) of the crude product gave 3-ethoxycarbonyl-2-methyl-5-(1,2,3-tri-*O*-acetyl-4-*S*-*tert*-butyl-4-thio-D-*arabino*-tetritol-1-yl)furan (**16**; 0.68 g, ~100%), isolated as a syrup, $[\alpha]_D^{25}$ −45° (*c* 1, methanol); ν_{max}^{film} 1765, 1730, 1625, 1590, 1375, 1225, 1085, 1060–1020, and 775 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 6.65 (s, 1 H, furan H-4), 6.02 (d, 1 H, *J* 6.0 Hz, H-1), 5.6 (t, 1 H, *J* 6.0 Hz, H-2), 5.08 (q, 1 H, *J* 6.0 Hz, H-3), 4.26 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 2.64 (d, 2 H, *J* 6.0 Hz, H-4,4′), 2.56 (s, 3 H, furan Me), 2.08, 2.06, and 2.04 (3 s, 9 H, 3 Ac), 1.32 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O), and 1.26 (s, 9 H, Me_3C). Mass spectrum: *m/z* 472 (M^+), 457 ($M^+ - CH_3$), 427 ($M^+ - C_2H_5O$), 413 ($M^+ - C_2H_3O_2$), 412 ($M^+ - C_2H_4O_2$), 356, 352, 309, 267, and 43 (100%).

Anal. Calc. for $C_{22}H_{32}O_9S$: C, 55.91; H, 6.83. Found: C, 55.63; H, 6.80.

Conventional benzoylation of **15** (0.3 g, 0.87 mmol) and column chromatography (2:1 hexane–ether) of the crude product gave 3-ethoxycarbonyl-2-methyl-5-

(1,2,3-tri-*O*-benzoyl-4-*S*-*tert*-butyl-4-thio-D-*arabino*-tetritol-1-yl)furan (**17**; 0.44 g, 77%), m.p. 99° (from hexane–ether), $[\alpha]_D^{25}$ −23° (*c* 1, chloroform); ν_{max}^{KBr} 1755–1735, 1612, 1597, 1465, 1440, 1285–1255, 1110, 1030, and 710 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 8.0 and 7.5 (2 m, 15 H, 3 Ph), 6.83 (s, 1 H, furan H-4), 6.53 (d, 1 H, *J* 7.5 Hz, H-1), 6.30 (dd, 1 H, *J* 7.5 and 4.5 Hz, H-2), 5.58 (m, 1 H, H-3), 4.23 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 2.8 (d, 2 H, *J* 6.5 Hz, H-4,4'), 2.5 (s, 3 H, furan Me), 1.28 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O), and 1.28 (s, 9 H, Me_3C) (Found: C, 67.58; H, 5.82. $C_{37}H_{38}O_9S$ calc.: C, 67.46; H, 5.81%).

*3-Ethoxycarbonyl-2-methyl-5-(4-thio-β- and -α-*D*-erythrofuranosyl)furan* (**8** *and* **11**). — Compound **15** (1.2 g, 3.46 mmol was stirred with conc. hydrochloric acid (5 mL) at room temperature for 5 min, and the mixture was then basified and extracted with ethyl acetate (2 × 50 mL). The combined extracts were concentrated and column chromatography (1:2 hexane–ether) of the crude product gave a mixture (0.94 g, 99%) of **8** (major) and **11** (minor), isolated as a syrup, $[\alpha]_D^{25}$ −138° (*c* 1, chloroform), the i.r., ^1H-n.m.r., and mass spectra of which were identical to those of compound **8**, except for the ^1H-n.m.r. signals at δ 6.69 (s, furan H-4, **11**) and 3.1–2.9 (m, H-4,4', **11**).

Conventional treatment of the mixture (0.19 g, 0.7 mmol) of **8** and **11** with acetic anhydride (5 mL) and dry pyridine (5 mL), with column chromatography (3:1 hexane–ether) of the crude product, gave a mixture (0.17 g, 67%) of 5-(2,3-di-*O*-acetyl-4-thio-β- and -α-D-erythrofuranosyl)-3-ethoxycarbonyl-2-methylfuran (**9** and **12**), isolated as a syrup, $[\alpha]_D^{25}$ −132° (*c* 1, chloroform), the i.r., ^1H-n.m.r., and mass spectra of which were superposable on those of **9**, except for the ^1H-n.m.r. signals at δ 6.64 (s, furan H-4, **12**), 4.72 (d, *J* 4.2 Hz, H-1, **12**), and 3.25–3.20 (m, H-4,4', **12**).

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