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PHOTO-OXYGENATION OF POLYHYDROXYALKYLFURANS: REARRANGEMENT OF *O*-ACETYL DERIVATIVES*

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ABSTRACT

The photo-oxygenation of ethyl 2-methyl-5-(1,2,3,4-tetra-*O*-acetyl-D-*lyxo*-tetritol-1-yl)-3-furoate, ethyl 2-methyl-5-(1,2,3,4-tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)-3-furoate, 3-acetyl-2-methyl-5-(1,2,3,4-tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)furan, and ethyl 5-(1,4-di-*O*-acetyl-2,3-*O*-isopropylidene-D-*lyxo*-tetritol-1-yl)-2-methyl-3-furoate yielded the corresponding 1,4-*endo*-peroxides (**3a–3d** as pairs of diastereomers). Each diastereomer of the pairs **3a** and **3d** was isolated by fractional crystallisation. The rearrangement of the *endo*-peroxides at room temperature, by dissolution in $CDCl_3$, yielded the corresponding diepoxides and monoepoxides. The reduction of **3a–3d** with methyl sulphide yielded the corresponding γ-diketones, ethyl (*E*)-2-*C*-acetyl-5,6,7,8-tetra-*O*-acetyl-2,3-dideoxy-D-*lyxo*-oct-2-en-4-ulosonate, ethyl (*E*)-2-*C*-acetyl-5,6,7,8-tetra-*O*-acetyl-2,3-dideoxy-D-*arabino*-oct-2-en-4-ulosonate, 3-*C*-acetyl-6,7,8,9-tetra-*O*-acetyl-1,3,4-trideoxy-D-*arabino*-non-3-eno-2,5-diulose, and ethyl (*E*)-2-*C*-acetyl-5,8-di-*O*-acetyl-2,3-dideoxy-6,7-*O*-isopropylidene-D-*lyxo*-oct-2-en-4-ulosonate, which can isomerise into the corresponding *Z* isomers.

INTRODUCTION

The photo-oxygenation of furan derivatives yields 1,4-*endo*-peroxides that can rearrange by various processes to give diepoxides, monoepoxides, or polymers. The *endo*-peroxides can also decompose to give the starting furans[1]. We have reported on the photo-oxygenation of *C*-glycosyl- and polyhydroxyalkyl-furans obtained by the reaction of aldoses with β-dicarbonyl compounds[2]. The resulting *endo*-peroxides underwent[3,4] a C→O rearrangement (similar to a Baeyer–Villiger reaction), the glycosidic moiety being the sole migrating group even when there was a phenyl group in the other α-position[4]. The *C*-glycosyl character of the *endo*-peroxides is lost by this rearrangement. We now report on the photo-oxygenation of *O*-acetylated polyhydroxyalkylfurans, in which the C→O rearrangement was not observed, but mono- and/or di-epoxides were formed.

*Part II. For Part I, see ref. 4a.

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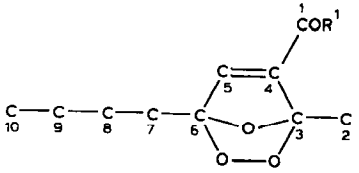
TABLE I

^{13}C-N.M.R. DATA[a] FOR THE *endo*-PEROXIDES **3**



Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*	*R^1*		*AcO and CMe_2*
3a1	161.2	12.6	111.3	137.8	138.1	112.4	68.2	67.7	63.7	61.6	61.3	14.3	170.2, 170.0, 169.2, 168.8; 20.5, 20.4
3a2	161.0	12.7	111.5	137.7	138.0	112.7	67.6	67.4	64.5	61.4	61.1	14.2	170.3, 169.5, 169.2, 168.8; 20.2, 20.0
3b	161.2	12.7 12.8	111.7 111.5	137.9	138.2	112.8	67.9	67.7	65.1 64.7	61.6	61.3	14.1 14.3	170.5, 169.7, 169.3, 168.9; 20.3, 20.2
3c	192.7	12.7	111.4	143.6	136.7 137.0	112.6	67.7	67.6	64.9 64.2	61.4	—	27.1	170.3, 169.5, 169.2, 169.0, 168.8, 168.7; 20.5, 20.2
3d1	161.4	12.9	111.4	138.0	139.1	113.1	76.4	75.3	67.0	64.5	61.3	14.2	170.7, 169.4; 111.0; 27.1 27.0; 20.9, 20.6
3d2	161.3	12.8	111.4	137.6	139.0	112.7	76.5	75.5	66.8	64.4	61.3	14.1	170.5, 169.3; 110.9; 27.1, 26.9; 20.8, 20.6

[a]Values for C-3 and C-6, and C-7 and C-8 may be interchangeable.

RESULTS AND DISCUSSION

The starting products were the furan compounds **1a–c** obtained by the reaction of D-glucose or D-galactose with ethyl acetoacetate or acetylacetone[5]. Treatment of **1a–c** severally with acetic anhydride and pyridine yielded the corresponding tetra-acetates **2a–c**[6]. Compound **2d** was prepared by acetonation of **1a** followed by acetylation (see Experimental).

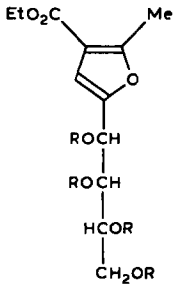
The photo-oxygenations of **2a–d** were carried out severally in methanol and were monitored on the basis of oxygen consumption. The ^{1}H- and ^{13}C-n.m.r. data of the products **3a–d** are given in Table I and the Experimental. A mixture of the two possible diastereomers of **3a–d** was formed in each reaction and they were stable during storage at −20° for several months.

The individual diastereomers **3a1** (the first one crystallising) and **3a2** were obtained by fractional crystallisation of **3a** from methanol. Only one (**3d1**) of the pair of diastereomers **3d** was obtained crystalline and the pair of diastereomers **3b** crystallised as a mixture which was used to study the rearrangement (see below). Neither of the diastereomers **3c** crystallised.

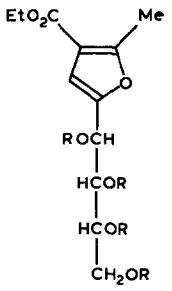
All of the *endo*-peroxides oxidised methyl sulphide to yield, quantitatively, methyl sulphoxide and the corresponding unsaturated γ-diketones **4a–d** (Scheme 1). These reductions were carried out in an aprotic solvent in order to avoid a nucleophilic addition to the double bond in **4**.

Compounds **4a,b,d** could not be purified by chromatography on silica gel or by fractional crystallisation because they isomerised into **5a,b,d**, respectively, but **4c** could be purified.

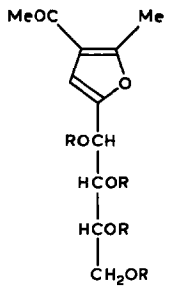
The *endo*-peroxides **3a–d** were fairly stable in solution below −20°, but at room temperature they rearranged quantitatively into **6** and/or **7** in a few days. These rearrangements could be monitored by ^{1}H-n.m.r. spectroscopy. The δ values (1.76–1.80) of the C-Me group signals for the diepoxides **6** accord with the acetal character. The shifts for the signals (δ 2.25–2.36) of the corresponding C-Me groups in the monoepoxides **7** accord with those for acetyl groups. The epoxides **6** and **7** gave no signals for vinylic protons, showing that the double bond of the starting



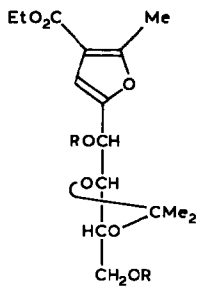
1a R = H
2a R = Ac



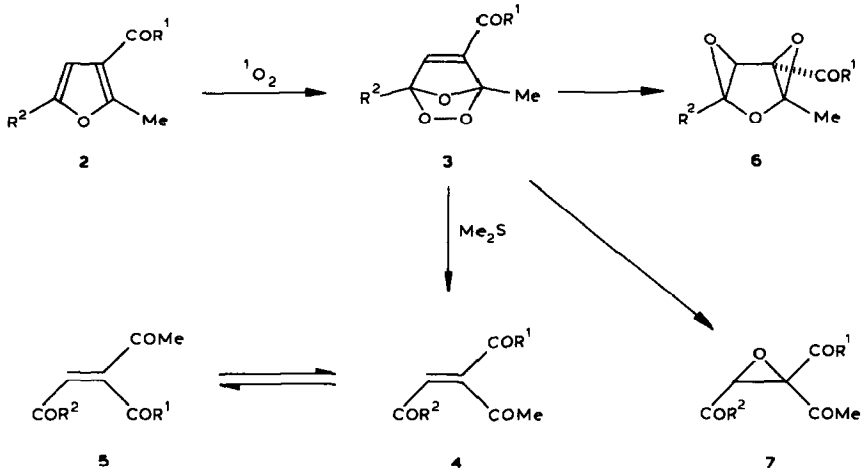
1b R = H
2b R = Ac



1c R = H
2c R = Ac



1d R = H
2d R = Ac



Scheme 1

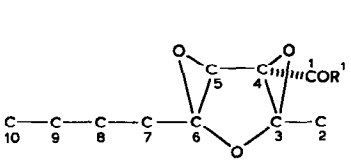
endo-peroxides **3** had disappeared, and the products of a Baeyer–Villiger reaction were not formed[2–4].

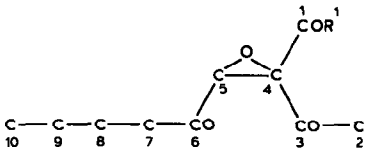
Similarly, the ^{13}C-n.m.r. spectra of **6** and **7** showed that C-4,5 (see Table II) had lost their sp^2 character. The chemical shifts (δ 53.2–60.6 in **6**, and 79.0–86.8 in **7**) of the signals for C-3,4 agree with the proposed structure. The shifts of the signals for C-3 (δ 95.1–96.1) and C-6 (δ 101.0–101.3) in **6** point to their involvement in acetals, whereas these atoms in **7** (δ 201.6–204.1) are attached to carbonyl functions.

On dissolution in chloroform, **3a1** rearranged into **6a1** quantitatively during 32 h at room temperature (1 h at 55°) and during 5 months in the solid state at −20°. The rearrangement of **3a1** in methanol yielded **6a1** together with secondary products. The rearrangement of **3a2** in chloroform yielded **6a2** (diastereomer of **6a1**) and secondary products that were not studied. Similarly, storage of a solution of **3b** in chloroform at room temperature for 32 h gave **6b** (mixture of diastereomers) which rearranged slowly into **7b**. The latter reaction was catalysed by silica gel. In solution in chloroform, **3c** rearranged partially at room temperature during 24 h to give a mixture of **7c** (40%) and **6c** (10%) as estimated by ^{1}H-n.m.r. spectroscopy. When the solution was left for 3 days at room temperature, **3c** slowly disappeared and the only products were **7c** and polymeric material, the proportion of the latter increasing with time. The *endo*-peroxides **3d1** and **3d2** rearranged in chloroform solution into a mixture of the corresponding mono- and di-epoxides **7** and **6**, the proportions depending on concentration, time, and temperature. For a 10% solution at room temperature, the main products were **6d1** and **6d2**, respectively, after 48 h. For a 1% solution and prolonged storage, the corresponding monoepoxides **7d1** and **7d2** were the main products; at 55°, these *endo*-peroxides rearranged during 1 h to give **7d1** and **7d2** with some polymeric material. The epoxides **6d** and **7d** could not be isolated and their abundances were estimated by ^{1}H-n.m.r. spectroscopy.

TABLE II

^{13}C-N.M.R. DATA[a] FOR DIEPOXIDES **6** AND MONOEPOXIDES **7**



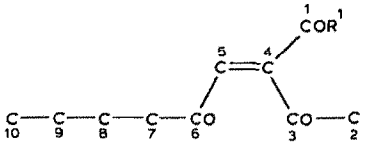


Epoxide	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*[a]	*C-8*[a]	*C-9*[a]	*C-10*	*R*[1]		*AcO and CMe*$_2$
6a	164.9	14.4	95.5	60.5	56.1	101.3	68.3 (68.8)	67.8 (67.9)	67.2 (66.0)	61.5 (62.3)	62.5 (62.3)	14.2	170.3, 170.1, 169.7, 168.9; 20.6
6b	165.1	14.4	95.1	60.6	53.2	101.2	67.8	67.7	63.6	61.8	62.5	14.2	170.5, 169.6, 169.7; 20.8, 20.6, 20.3
6d1	164.5	14.6	96.1	—	55.8	101.0	76.4	75.5	70.0	64.4	62.4	14.1	170.5, 169.3; 110.5; 27.0, 25.6; 20.7, 20.6, 20.2
7b	168.7	25.6 (25.9)	202.6*	86.8	79.0†	201.6*	78.5	74.1 (73.9)	68.7 (68.5)	63.5 (63.7)	62.1	14.0	170.9, 170.6, 170.4, 170.2, 170.0; 20.7, 20.6, 20.3
7d	168.6	25.6	204.1*	86.2	79.3†	202.0*	77.6	76.6	75.0	64.7	62.2	13.9	170.8, 169.9; 111.3; 26.5, 26.9; 20.8, 20.4, 20.1

[a]The values * and † may be interchangeable.

TABLE III

^{13}C-N.M.R. DATA FOR DIKETONES **4**

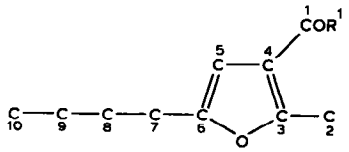


Diketone	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*[a]	*C-9*[a]	*C-10*	*R*[1]		*AcO and CMe*$_2$
4a	162.7	29.6 (27.4)[b]	199.7	146.7	129.4	193.3 (193.5)	74.7	69.3	68.5	61.7	62.6	14.0	169.5, 169.8, 170.3; 20.6, 20.4, 20.3
4b	162.8	29.5 (27.2)	199.5	146.7	129.6 (129.2)	193.0 (193.6)	75.8 (77.8)	68.5 (68.8)	68.2 (68.3)	61.7 (62.1)	62.6 (62.0)	14.0 (14.4)	170.3, 169.7, 169.5, 169.3, (169.9); 20.9, 20.7, 20.6, 20.2
4c	195.4	30.0	201.7	152.1	126.6	192.9	75.6	68.2	67.7	61.4	—	27.0	170.2, 169.6, 169.3; 20.5, 20.1
4d	162.9	29.8	199.9	145.9	130.4	194.5	77.6	76.6	76.4	63.8	62.5	14.0	170.5, 169.7, 111.3; 26.7, 27.0, 20.7, 20.4

[a]These values may be interchangeable. [b]Values in brackets correspond to the diketones **5**.

TABLE IV

^{13}C-N.M.R. DATA FOR THE FURANS **1** AND **2**



Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*[a]	*C-8*[a]	*C-9*[a]	*C-10*	*R*[1]		*AcO and CMe*$_2$
1b	163.4	14.2	157.1	113.5	106.7	155.3	72.7	71.1	66.1	63.4	59.7	13.4	—
1d	164.1	14.3	159.1	114.2	108.7	151.4	79.6	79.0	68.2	62.9	60.3	13.8	109.7; 27.1, 26.9
1e	163.6	14.3	159.5	114.8	110.1	150.5	80.9	76.1	72.6	65.9	60.4	13.5	109.5, 110.5; 27.1, 26.8, 25.2, 25.1
2a	163.5	14.2	159.8	114.9	111.5	146.8	69.6	68.1	67.9	61.9	60.2	13.7	170.4, 170.0, 169.2; 20.5, 20.3
2b	163.7	14.5	159.9	114.7	110.9	147.0	70.2	69.0	66.2	61.9	60.5	13.9	170.6, 169.9, 169.5, 169.4; 20.8
2c	193.4	14.3	158.9	122.1	110.4	146.7	70.0	68.8	65.9	61.6	—	29.0	170.3, 169.6; 20.6
2d	163.7	14.3	159.6	114.5	111.1	147.4	77.0	76.8	68.4	64.7	60.2	13.8	170.6, 169.5; 110.9; 27.1, 26.9; 20.8

[a]These values may be interchangeable.

EXPERIMENTAL

General methods. — Melting points were determinated with a Reichter hotplate microscope and are uncorrected. Solutions were dried over Na_2SO_4 before concentration under diminished pressure. I.r. spectra were recorded with a Pye–Unicam SP 1000 and a Beckman 42-40 spectrometer. N.m.r. spectra (internal Me_4Si) (^1H, 80 MHz; ^{13}C, 20 MHz) were recorded with a Bruker WP-80-SY spectrometer. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. Elemental analyses were performed with a Carlo Erba Elemental Analyzer 1106. Satisfactory analyses could not be obtained for the non-crystalline compounds described below. T.l.c. was performed on Silica Gel G (Merck), with detection by charring with sulfuric acid, and column chromatography was performed on silica gel (Merck, 7734).

Photo-oxygenations were performed at 0° by illumination with a Tunsgram Halogen 60000 T8 R7-s-15 lamp of solutions of the substrate also containing 0.01% of Methylene Blue. Reactions were monitored by measuring the volume of oxygen consumed.

Reaction of D-*galactose with ethyl acetoacetate.* — A mixture of D-galactose (40 g, 0.22 mol), zinc chloride (20 g), ethyl acetoacetate (20 mL), and ethanol (20 mL) was boiled under reflux with vigorous stirring until it became homogeneous. Water (200 mL) was added, and the resulting solution was washed with benzene (5 × 30 mL) and extracted with ethyl acetate (12 × 60 mL). The combined extracts were concentrated *in vacuo* and column chromatography (ethyl acetate) of the resulting pale-yellow syrup yielded, first, syrupy ethyl 2-methyl-5-α,β-D-threofuranosyl-3-furoate (18 g, 31%). Eluted second was ethyl 2-methyl-5-(D-*lyxo*-tetritol-1-yl)-3-furoate (**1a**; 7.5 g, 12%), m.p. 100°; lit.[5] m.p. 98–100°, $[\alpha]_D^{20}$ ~0° (*c* 5, water).

Anal. Calc. for $C_{12}H_{18}O_7$: C, 52.53; H, 6.61. Found: C, 52.31; H, 6.66.

*Ethyl 2-methyl-5-(1,2,3,4-tetra-*O*-acetyl-*D-lyxo-*tetritol-1-yl)-3-furoate* (**2a**). — A solution of **1a** (4.4 g, 16 mmol) in pyridine (20 mL) and acetic anhydride (20 mL) was kept at room temperature for 48 h, and then worked-up in the usual manner. Column chromatography (hexane–ether, 1:1) of the product yielded **2a** (6.04 g, 82%), $[\alpha]_D^{20}$ +1.5° (*c* 1.5, methanol), as a colourless syrup; ν_{max}^{film} 3020, 1760, 1730, 1590, 1380, 1220, 1085, 1055, and 760 cm^{-1}. ^1H-N.m.r. data ($CDCl_3$): δ 6.67 (s, 1 H, H-4), 5.93–5.38 (m, 3 H, H-1′,2′,3′), 4.45–3.85 (m, 4 H, 2 CH_2), 2.58 (s, 3 H, Me-2), 2.10, 2.06, 2.00 (3 s, 12 H, 4 Ac), and 1.33 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table IV.

*Ethyl 5-(1,4-di-*O*-acetyl-2,3-*O*-isopropylidene-*D-lyxo-*tetritol-1-yl)-2-methyl-3-furoate* (**2d**). — A mixture of **1a** (5 g, 22 mmol), conc. H_2SO_4 (0.3 mL), and anhydrous acetone (450 mL) was shaken at room temperature for 20 h. The reaction was monitored by t.l.c. When **1a** had disappeared, the mixture was neutralised with conc. ammonia, filtered, and concentrated *in vacuo*. Column chromatography (hexane–ether, 3:1) of the resulting yellow syrup yielded, first, ethyl 5-(1,2:3,4-di-

O-isopropylidene-D-*lyxo*-tetritol-1-yl)-2-methyl-3-furoate (1.98 g, 30.5%), m.p. 51–52°, $[\alpha]_D^{20}$ −17° (*c* 1, methanol); ν_{max}^{KBr} 2990, 1725, 1625, 1595, 1485, 1395, 1380, 1270, 1175, 1100, 1075, 1040, and 870 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 6.61 (s, 1 H, H-4), 5.19 (d, 1 H, *J* 10 Hz, H-1'), 4.46–3.80 (m, 4 H, 2 CH_2), 3.63–3.45 (m, 2 H, H-2',3'), 2.58 (s, 3 H, Me-2), 1.58, 1.41, 1.35, 1.23 (4 s, 12 H, 2 CMe_2), and 1.32 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table IV.

Anal. Calc. for $C_{18}H_{26}O_7$: C, 61.00; H, 7.70. Found: C, 61.18; H, 7.66.

Eluted second was ethyl 5-(2,3-*O*-isopropylidene-D-*lyxo*-tetritol-1-yl)-2-methyl-3-furoate (**1d**; 3.76 g, 65.5%) as a colourless syrup, $[\alpha]_D^{20}$ +9° (*c* 0.4, methanol); ν_{max}^{film} 3440, 2980, 2930, 1725, 1625, 1595, 1380, 1235, 1095, 905, 855, and 780 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 6.61 (s, 1 H, H-4), 4.76–4.68 (m, 1 H, H-1'), 4.40–4.13 (m, 4 H, 2 CH_2), 3.68–3.30 (m, 2 H, H-2',3'), 2.56 (s, 3 H, Me-2), 2.90–2.80 (bs, 2 H, exchangeable with D_2O, 2 OH), 1.47 (s, 6 H, CMe_2), and 1.35 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table IV.

Conventional acetylation of **1d** (1.95 g, 5.5 mmol), as for **1a** and with crystallisation of the product from ethanol–water, yielded **2d** (1.63 g, 66%), m.p. 45–46°, $[\alpha]_D^{20}$ +40° (*c* 0.1, chloroform); ν_{max}^{KBr} 1760, 1735, 1630, 1595, 1380, 1230, 1215, 1115, 1085, 1020, 835, and 770 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 6.65 (s, 1 H, H-4), 5.83 (d, 1 H, *J* 9 Hz, H-1'), 4.50–3.80 (m, 6 H, H-2',3' and 2 CH_2), 2.54 (s, 3 H, Me-2), 2.09 (s, 6 H, 2 Ac), and 1.45–1.18 (m, 9 H, CMe_2 and CH_3CH_2). For the ^{13}C-n.m.r. data, see Table IV.

Anal. Calc. for $C_{19}H_{26}O_9$: C, 57.29; H, 6.58. Found: C, 57.33; H, 6.27.

Photo-oxygenations. — (*a*) Of **2a**. The photo-oxygenation of a solution of **2a** (1.06 g, 2.4 mmol) in methanol (50 mL) was carried out for 50 min. The solution was cooled to −20° to give 2,5-epidioxy-3-ethoxycarbonyl-2,5-dihydro-2-methyl-5-(1,2,3,4-tetra-*O*-acetyl-D-*lyxo*-tetritol-1-yl)furan (**3a1**; 474 mg, 44.7%), m.p. 120° (from methanol), $[\alpha]_D^{20}$ −28° (*c* 10, chloroform); ν_{max}^{KBr} 1750, 1725, 1615, 1365, 1240, 1215, 1045, 860, and 765 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 7.05 (s, 1 H, HC=), 5.82–5.01 (m, 3 H, H-1',2',3'), 4.39–3.82 (m, 4 H, 2 CH_2), 2.15, 2.10, 2.05 (3 s, 12 H, 4 Ac), 1.98 (s, 3 H, Me-2), and 1.32 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table I.

The mother liquor was concentrated to 2/3 volume and kept at −20° to give **3a2** (145 mg, 13.5%), m.p. 93°, $[\alpha]_D^{20}$ +33° (*c* 1, methanol); ν_{max}^{KBr} 1755, 1725, 1370, 1215, 1060, 880, 840, and 750 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 7.00 (s, 1 H, HC=), 5.68–5.10 (m, 3 H, H-1',2',3'), 4.40–3.84 (m, 4 H, 2 CH_2), 2.12, 2.07, 2.06 (3 s, 12 H, 4 Ac), 2.00 (s, 3 H, Me-2), and 1.30 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{20}H_{26}O_{13}$: C, 50.61; H, 5.53. Found for **3a1**: C, 50.35; H, 5.88. For **3a2**: C, 50.77; H, 5.44.

(*b*) Of **2b**. The photo-oxygenation of **2b** (2 g, 4.2 mmol) in methanol (50 mL) was carried out for 1 h to give 2,5-epidioxy-3-ethoxycarbonyl-2,5-dihydro-2-methyl-5-(1,2,3,4-tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)furan (**3b**; 1.63 g, 79%) as a mixture of diastereomers, m.p. 90°. ^{1}H-N.m.r. data ($CDCl_3$): δ 7.07 (s, 1 H, HC=),

5.88 (d, 1 H, *J* 3 Hz, H-1'), 5.80–5.52 (m, 1 H, H-2'), 5.30–5.03 (m, 1 H, H-3'), 4.43–3.95 (m, 4 H, 2 CH_2), 2.15, 2.07, 2.05 (3 s, 12 H, 4 Ac), 1.99 (s, 3 H, $MeC{=}\overset{O}{\underset{O}{}}$), and 1.30 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{20}H_{26}O_{13}$: C, 50.61; H, 5.53. Found: C, 50.45; H, 5.36.

Ethyl (E)- (**4a**) *and* (Z)-*2-C-acetyl-5,6,7,8-tetra-O-acetyl-2,3-dideoxy-*D-lyxo-*oct-2-en-4-ulosonate* (**5a**). — To a solution of **3a1** (100 mg) in $CDCl_3$ (1 mL) were added two drops of methyl sulphide. The ^{1}H-n.m.r. spectrum of this solution showed a mixture of methyl sulphoxide (δ 2.6; s, 6 H, 2 Me) and **4a**: δ 7.18 (s, 1 H, HC=), 5.63–5.25 (m, 3 H, H-5,6,7), 4.42–3.85 (m, 4 H, 2 CH_2), 2.37 (s, 3 H, MeCO), 2.17, 2.12, 2.10, 2.06 (4 s, 12 H, 4 Ac), and 1.31 (t, 3 H, *J* 7 Hz CH_3CH_2). For the ^{13}C-n.m.r. data, see Table III. Whilst the ^{13}C-n.m.r. spectrum was recorded, **4a** was partially transformed into **5a**. These isomers could not be separated. The new ^{1}H-n.m.r. spectrum showed two new signals: δ 7.12 (s, HC=) and 2.41 (s, MeCO).

Ethyl (E)- (**4b**) *and* (Z)-*2-C-acetyl-5,6,7,8-tetra-O-acetyl-2,3-dideoxy-*D-arabino-*oct-2-en-4-ulosonate* (**5b**). — Compound **3b** (100 mg) was reduced as described for **3a1**. The ^{1}H-n.m.r. spectrum of **4b** contained signals at δ 7.14 (s, 1 H, HC=), 5.80–5.00 (m, 3 H, H-6,7,8), 4.50–4.00 (m, 4 H, 2 CH_2), 2.35 (s, 3 H, MeCO), 2.18, 2.10, 2.06 (3 s, 12 H, 4 Ac), and 1.30 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table III. The two new ^{1}H-n.m.r. signals for **5b** were at δ 7.05 (s, HC=) and 2.39 (s, MeCO).

*1-Ethoxycarbonyl-6-methyl-4-(1,2,3,4-tetra-*O*-acetyl-*D*-lyxo-tetritol-1-yl)-3,5,7-trioxatricyclo[4.1.0.0^{2,4}]heptane* (**6a**). — (*a*) The photo-oxygenation of a solution of **2a** (1 g, 2.3 mmol) in methanol (50 mL) was carried out for 50 min. The solution was kept at room temperature for 3 h and then cooled to −20° to give **6a1** (360 mg, 34%), m.p. 113–114°, $[\alpha]_D^{20}$ +24° (*c* 1, chloroform); ν_{max}^{KBr} 1765, 1730, 1395, 1380, 1235, 1090, 1050, 945, 895, 880, and 840 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.62 (dd, 1 H, *J* 10 and 2 Hz, H-2'), 5.52–5.25 (m, 1 H, H-3'), 5.07 (d, 1 H, *J* 10 Hz, H-1'), 4.50–3.75 (m, 5 H, 2 CH_2 and H-2), 2.17, 2.10, 2.07, 2.04 (4 s, 12 H, 4 Ac), 1.77 (s, 3 H, Me-6), and 1.37 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table II.

Anal. Calc. for $C_{20}H_{26}O_{13}$: C, 50.61; H, 5.53. Found: C, 50.69; H, 5.68.

(*b*) Compound **3a1** (20 mg) dissolved in $CDCl_3$ (1 mL) was transformed (quantitatively) into **6a1** on storage of the solution at room temperature for 48 h, or for 30 min at 55°.

(*c*) A solution of **3a2** (10 mg) in $CDCl_3$ (1 mL) was heated at 55° for 30 min. The ^{1}H-n.m.r. spectrum then indicated a mixture of **6a2** (77%) and several unidentified products. The differences between the ^{1}H-n.m.r. spectra of **6a1** and **6a2** are δ 5.77–5.25 (m, 2 H, H-2',3'), 5.12 (d, 1 H, *J* 7.5 Hz, H-1'), 4.52–3.77 (m, 5 H, 2 CH_2 and H-2), and 1.75 (s, 3 H, Me-6). For the ^{13}C-n.m.r. data, see Table II.

*1-Ethoxycarbonyl-6-methyl-4-(1,2,3,4-tetra-*O*-acetyl-*D*-arabino-tetritol-1-yl)-3,5,7-trioxatricyclo[4.1.0.0.^{2,4}]heptane* (**6b**). — A solution of **3b** (70 mg, 0.2 mmol)

in $CDCl_3$ (1 mL) was kept at room temperature for 32 h and then concentrated *in vacuo*, and the residue was recrystallised from hexane–acetone to give **6b** (54 mg, 77%) as a mixture of diastereomers, m.p. 109–111°; ν_{max}^{KBr} 1760, 1375, 1325, 1230, 1080, 1040, and 840 cm^{-1} ^{1}H-N.m.r. data ($CDCl_3$): δ 5.75–5.50 (m, 2 H, H-1',2'), 5.35–5.00 (m, 1 H, H-3'), 4.60–4.05 (m, 5 H, 2 CH_2 and H-2), 2.16, 2.07, 2.05 (3 s, 12 H, 4 Ac), 1.77 (s, 3 H, MeC=O), and 1.35 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table II.

Anal. Calc. for $C_{20}H_{26}O_{13}$: C, 50.61; H, 5.53. Found: C, 51.03; H, 5.34.

Ethyl (E)-*2-C-acetyl-5,6,7,8-tetra-O-acetyl-2,3-anhydro*-D-arabino-*oct-4-ulosonate* (**7b**). — When solid **3b** (1 g, 4 mmol) was stored at −20° for 5 months, a mixture of **6b** (83%) and **7b** (17%) was formed. Column chromatography (hexane–ethyl acetate, 1:1) of the mixture yielded, first, **6b** (100 mg, 10%), and then **7b** (800 mg, 80%) as a syrupy mixture of diastereomers. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.25–5.00 (m, 3 H, H-5,6,7), 4.50–3.90 (m, 5 H, 2 CH_2 and H-3), 2.32 (s, 3 H, MeCO), 2.15, 2.10, 2.07 (3 s, 12 H, 4 Ac), and 1.30 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table II.

Photo-oxygenation of **2c**. — (*a*) *In acetone.* The photo-oxygenation of **2c** (2 g, 4.8 mmol) in acetone (35 mL) saturated with Methylene Blue was carried out for 45 min. Methyl sulphide (2 mL) was then added and the solvent was removed *in vacuo*, to yield **4c** (1.2 g, 58%), m.p. 110–111° after column chromatography (ether), $[\alpha]_D^{20}$ +37° (*c* 1, chloroform); ν_{max}^{KBr} 1750, 1720, 1680, 1370, 1225, 1200, 1050, 1040, and 970 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 6.88 (s, 1 H, H-4), 5.66 (dd, 1 H, *J* 2 and 9 Hz, H-7), 5.44 (d, 1 H, *J* 2 Hz, H-6), 5.38–5.14 (m, 1 H, H-8), 4.45–4.02 (m, 2 H, H-9,9), 2.37, 2.33 (2 s, 6 H, 2 Ac), 2.20, 2.10, 2.07 (3 s, 12 H, 4 Ac). For the ^{13}C-n.m.r. data, see Table III.

Anal. Calc. for $C_{19}H_{24}O_{11}$: C, 53.27; H, 5.65. Found: C, 52.94; H, 5.48.

(*b*) *In methanol.* The photo-oxygenation of **2c** (1 g, 2.4 mmol) in methanol (35 mL) was carried out for 35 min. The solvent was removed *in vacuo* to give 3-acetyl-2,5-dihydroxy-2,5-epidioxy-2-methyl-5-(1,2,3,4-tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)furan (**3c**; 1.08 g, quantitative) as a syrupy mixture of diastereomers. ^{1}H-N.m.r. data ($CDCl_3$): δ 6.98 (s, 1 H, HC=), 5.90–5.85 (m, 1 H, H-1'), 5.76–5.57 (m, 1 H, H-2'), 5.26–5.07 (m, 1 H, H-3'), 4.40–3.96 (m, 2 H, CH_2), 2.33, 2.32 (2 s, 3 H, MeCO), 2.18, 2.11, 2.08, 2.07, 2.03 (5 s, 12 H, 4 Ac), and 2.01, 1.98 (2 s, 3 H, Me-2). For the ^{13}C-n.m.r. data, see Table I.

Photo-oxygenation of **2d**. — The photo-oxygenation of **2d** (1 g, 2.5 mmol) in methanol (35 mL) was carried out for 35 min. The solution was concentrated to half volume and then kept at −20° to give 5-(1,4-di-*O*-acetyl-2,3-*O*-isopropylidene-D-*lyxo*-tetritol-1-yl)-2,5-epidioxy-3-ethoxycarbonyl-2,5-dihydro-2-methylfuran (**3d1**; 0.5 g, 50%), m.p. 85°, $[\alpha]_D^{20}$ −45° (*c* 1, acetone); ν_{max}^{KBr} 2980, 1765, 1745, 1720, 1365, 1230, 1000, 990, and 845 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 7.11 (s, 1 H, HC=), 5.76 (d, 1 H, *J* 5.4 Hz, H-1'), 4.60–3.98 (m, 4 H, H-2',3',4',4'), 2.20, 2.10 (2 s, 6 H, 2 Ac), 2.03 (s, 3 H, Me-2), 1.43 (s, 6 H, CMe_2), and 1.32 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{19}H_{26}O_{11}$: C, 53.02; H, 6.09. Found: C, 53.00; H, 6.17.

The mother liquor was concentrated *in vacuo,* and a solution of the resulting syrup in ether–light petroleum (2:1, 10 mL) was filtered and concentrated to give **3d2** (500 mg, 50%) as a syrup, $[\alpha]_D^{20}$ +25° (*c* 1, chloroform); ν_{max}^{film} 2990, 1750, 1735, 1610, 1370, 1270, 1230, 1090, 1040, and 790 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 7.15 (s, 1 H, HC=), 5.79 (d, 1 H, *J* 5 Hz, H-1′), 4.57–3.87 (m, 4 H, H-2′,3′,4′,4′), 2.20, 2.12 (2 s, 6 H, 2 Ac), 2.02 (s, 3 H, Me-2), 1.44 (s, 6 H, CMe_2), and 1.32 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table I.

Ethyl (E)- (**4d**) *and* (Z)-*2-C-acetyl-5,8-di-*O*-acetyl-2,3-dideoxy-6,7-*O*-isopropylidene-*D-arabino-*oct-2-en-4-ulosonate* (**5d**). — A solution of **2d** (100 mg, 0.25 mmol) in methanol (25 mL) was photo-oxygenated as described above and then concentrated *in vacuo*. To a solution of the residue in $CDCl_3$ (2 mL) were added two drops of methyl sulphide. The ^{1}H-n.m.r. spectrum of this solution showed a mixture of methyl sulphoxide (δ 2.60) and **4d**: δ 7.21 (s, 1 H, HC=), 5.16 (d, 1 H, *J* 5.5 Hz, H-5), 4.50–3.95 (m, 4 H, H-6,7,8,8), 2.37 (s, 3 H, MeCO), 2.20, 2.10 (2 s, 6 H, 2 Ac), 1.40 (s, 6 H, CMe_2), and 1.31 (t, 3 H, *J* 7 Hz, CH_3CH_2). For the ^{13}C-n.m.r. data, see Table III. When this solution was kept at room temperature for 24 h, the ^{1}H-n.m.r. spectrum showed a new band at δ 7.12 (s), corresponding to **5d**, and the ratio of **4d/5d** was 4:1.

Rearrangement of the endo*-peroxides* **3c, 3d1,** *and* **3d2**. — A solution of each *endo*-peroxide in dry $CDCl_3$ at room temperature was stored under strictly anhydrous condition. Samples were analysed periodically by ^{1}H-n.m.r. spectroscopy.

A solution of **3c** (1%), after 24 h, showed a mixture of **3c** (50%), **7c** (40%), and **6c** (10%). Quantification of **3c** was based on the relative areas of the signals for the olefinic proton and Me-C$\lesssim^{O\text{-}O}_{O}$: δ 6.98 (s, HC= for **3c**), 5.92–5.00 (m, 3 H, for **3c, 6c**, and **7c**), 4.45–3.98 (m, 2 H, for **3c, 7c**, and **6c**), 2.36, 2.34 (2 s, MeCO for **7c1** and **7c2**), 2.20, 2.12, 2.10, 2.05 (4 s, 4 Ac), and 1.80 (s, Me-C$\lesssim^{O\text{-}O}_{O}$ for **6c**). After 3 days, the solution contained a mixture of **7c** and polymeric material.

A solution of **3d1** (1%) after 7 days showed a mixture of **6d1** (77%) and **7d1** (23%): δ 5.56 (d, 1 H, *J* 6 Hz, H-5 for **7d1**), 5.27 (d, 1 H, *J* 6 Hz, H-1′ for **6d1**), 4.52–3.79 (m, 3 H, H-2′,3′,4′,4′ for **6d1** and H-6,7,8,8 for **7d1**), 2.35 (s, 3 H, MeCO for **7d1**), 2.15, 2.10 (2 s, 6 H, 2 Ac for **6d1** and **7d1**), 1.78 (s, 3 H, Me-C$\lesssim^{O}_{O}$ for **6d1**), 1.42 (s, 6 H, CMe_2 for **6d1** and **7d1**), and 1.32 (t, 3 H, *J* 7 Hz, CH_3CH_2 for **6d1** and **7d1**). The composition of this solution did not change for several days.

A solution of **3d1** (10%), after 4 days, showed (^{1}H-n.m.r. spectroscopy) a mixture of **3d1** (10%), **6d1** (16%), and **7d1** (74%). After 7 days, **3d1** was transformed into a mixture of **7d1** and polymeric material.

A solution of **3d2** (1%), after 7 days, showed (^{1}H-n.m.r. spectroscopy) a 1:1 mixture of **7d2** and a polymeric material. The signals for **7d2** are very similar to those for **7d1**, except that at δ 5.43 (d, 1 H, *J* 6 Hz, H-5).

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