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Note

Photooxygenation of alditol-1-*C*-yl derivatives of furan with singlet oxygen

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The last two decades have witnessed much interest in the development and analysis of organic substrates which behave as chemical systems capable of selective and catalytic oxygenation with molecular oxygen [1]. Singlet oxygen ($^1O_2$) has been used frequently to carry out such oxidations [2]. Furan and its derivatives, whose synthesis is basically achieved either through reaction of α-hydroxyaldehydes with 1,3-dicarbonyl compounds or through acid-catalyzed dehydration of carbohydrates [3] as substrates, can be used as acceptors of singlet oxygen to study either reaction kinetics or biological roles [4].

As 1,3-dienes, furans can undergo $^1O_2$ cycloadditions, i.e. selective *cis*-1,4-dioxygenations, which produces bicyclic endoperoxides whose decomposition yields useful products. Depending on the substituents, the reaction conditions, and the solvents used, furan endoperoxides may be precursors of substituted hydroperoxides or dioxiranes [5]. Furan endoperoxides are of interest in the elucidation of oxidation mechanism such as epoxidation, anomalous ozonolysis, and oxidative decarbonylation [6].

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Interest on sensitized photooxygenation of furan and its derivatives has increased due to recent research on reaction models imitating biological oxygenases [7,8]. Several examples of the usefulness of furan derivatives in this field of research are found in the literature including the synthesis of monosaccharides through 2,5-addition to the furan nucleus, the synthesis of unsaturated pyranuloses which are transformed into monosaccharides, and the synthesis of aminodeoxy derivatives of monosaccharides of biological importance [9,10].

This paper studies sensitized photooxygenation as a means of converting alditol-1-*C*-ylfurans into 4-(alditol-1-*C*-yl)-4-oxo-2-butenals, a process which extends the chain of polyhydroxyaldehydes by four carbon atoms.

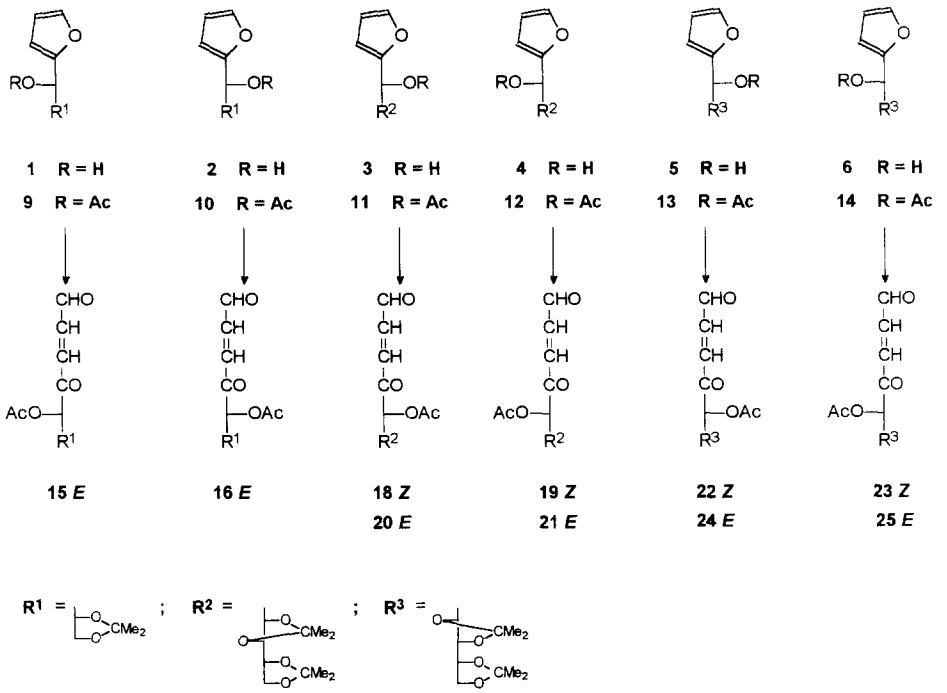
Different compounds can be formed from these products: *C*-alditol heterocycles are obtainable by aromatization of the 4-oxo-2-butenal system; long-chain polyhydroxyaldehydes can be synthesized by a combination of the stereocontrolled reduction of the ketones and hydroxylation of the double bonds. Glyceraldehyde, D-xylose, D-arabinose, and 2,5-anhydro-D-mannose were employed as starting carbonyl compounds.

Prior research [11,12] has shown that the presence of free hydroxyl groups in molecules to be photooxygenated can alter their reactions: an alkoxyhydroperoxide is formed either when sensitized photooxygenation occurs in the presence of an alcohol, or, when the photooxygenated molecule contains a free hydroxyl group. To avoid this transformation, the starting carbonyl compounds used for synthesizing the alditol-1-*C*-ylfurans should not have free hydroxyl groups. Hence, the initial compounds were first transformed into the following derivatives: 2,3-*O*-isopropylidene-D-glyceraldehyde [13], 2,3:4,5-di-*O*-isopropylidene-D-xylose, 2,3:4,5-di-*O*-isopropylidene-D-arabinose and 3,4,6-tri-*O*-benzyl-2,5-anhydro-D-mannose [14,15,21]. Condensation of these derivatives with furan then led respectively to pairs of diastereoisomers, 2-[(1*S* and 1*R*, 2*R*)-1-hydroxy-2,3-dimethylmethylenedioxypropyl]furan (**1** and **2**), 2-[(1*R* and 1*S*)-2,3:4,5-di-*O*-isopropylidene-D-xylitol-1-*C*-yl]furan (**3** and **4**), 2-[(1*R* and 1*S*)-2,3:4,5-di-*O*-isopropylidene-D-arabinitol-1-*C*-yl]furan (**5** and **6**) (Scheme 1), and 2-[(1*R* and 1*S*)-2,5-anhydro-3,4,6-tri-*O*-benzyl-D-mannitol-1-*C*-yl]furan [16] (**7** and **8**) (Scheme 2).

The alcohols **1**–**6** were conventionally acetylated [17] in order to inactivate the hydroxyl group during sensitized photooxygenation (Scheme 1). The hexit-1-yl derivatives **7** and **8** have thus far not been acetylated.

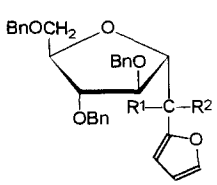
Sensitized photooxygenation reactions of the furan nucleus in the aforementioned derivatives gives unstable endoperoxides which may suffer rearrangements involving loss of the carbohydrate chain [18,19], thus vitiating the main objectives of this research. To avoid this, the endoperoxides were therefore reduced immediately with dimethyl sulfide [11] after completion of the photooxygenation, for which acetone was used as solvent.

When photooxygenation of the D-*threo* isomer **9**, was carried out for 4 min at −60 °C and the subsequent reduction initially performed at −60 °C for 30 min, and then at −4 °C for 20 days, (*E*)-5-*O*-acetyl-2,3-dideoxy-6,7-*O*-isopropylidene-D-*threo*-hept-2-enos-4-ulose, **15**, was obtained quantitatively as indicated by spectroscopic data and elemental analysis. Similarly, the D-*erythro* isomer **10**, treated under the same conditions, furnished quantitatively the stereoisomer (*E*)-5-*O*-acetyl-2,3-dideoxy-6,7-*O*-isopropylidene-D-*erythro*-hept-2-enos-4-ulose, **16**.



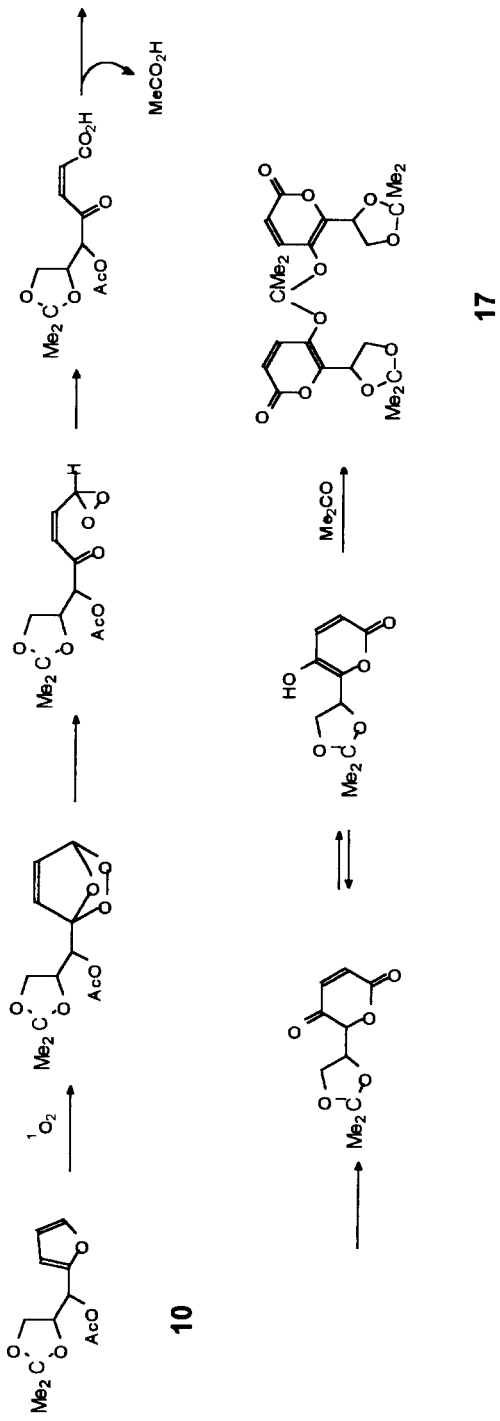
Scheme 1.

The prolonged time allowed for reduction (20 days at −4 °C) was crucial in these experiments. For instance, initial reduction at −60 °C followed by an extension at room temperature, but only for 3 h, gave **15** and **16** in yields of only 11.5 and 14% respectively. A slightly shorter time of photooxygenation (3 min at −60 °C), followed by treatment with the reductant for 90 min at −60 °C, led to complete recovery of unchanged starting compounds, **9** and **10**, perhaps owing to retrocyclo addition in the intermediate endoperoxide [19,20] under these conditions. However, when **10** was photooxygenated at 0 °C (12 min) and reduction subsequently attempted at room temperature (30 min), the endoperoxide rearranged before reduction to give a 68% yield of 2,2-bis[5-(3,3-dimethyl-2,4-dioxacyclopentyl)-2,4-pentadiene-5-olid-4-yloxy]-propane (**17**) as indicated by spectroscopic data and elemental analysis. This result is consistent with an endoperoxide rearrangement [6], in which a dioxirane (Scheme 3) or a



	R1	R2
7	OH	H
8	H	OH

Scheme 2.



Scheme 3.

Baeyer–Villiger-like rearrangement results in a carboxylic acid. A transesterification and a solvent-assistance yields **17**.

For transformations of the furan derivatives **11–14**, the most favourable reaction conditions were photooxygenation at −60 °C for 20 min, followed by dimethyl sulfide reduction for 3.5 h at −60 °C and 1 h at room temperature. Under these conditions, **11–14** quantitatively gave the (*Z*)-5-*O*-acetyl-2,3-dideoxy-6,7:8,9-di-*O*-isopropylidene-non-2-enos-4-uloses having the D-*gulo*- (**18**), D-*ido*- (**19**), D-*gluco*- (**22**), and D-*manno*- (**23**) configurations. These 2-*Z* alkenals isomerized spontaneously to the corresponding 2-*E* alkenals **20**, **21**, **24**, and **25** in the course of a few days. The ^{1}H NMR data pertaining to the terminal alkenal system are given in the Experimental section.

Photooxygenation of compounds **7** and **8** derived from 2,5-anhydro-D-mannose, which possess a free hydroxyl group in the α-position of the side chain, was also performed under similar conditions. Complex mixtures of substances resulted and no single product could be isolated or identified, although it was observed that the furan ring had disappeared and aldehyde as well as alkenic functions were present in the products. Similar negative results were obtained on photooxygenation of the non-acetylated compounds **1–6**, and it appears obvious that a free hydroxyl group in the molecule interferes with the desired product development.

In summary, it can be stated that sensitized photooxygenations of the kind here described should be performed with substrates that are fully hydroxyl-protected; they should be carried out during brief spans of time (4–5 min) at low temperature (−60 °C), and reductive cleavage of the primary oxidation products with dimethyl sulfide should be started at −60 °C, and completed at room temperature.

Under these conditions, the original aldehydo-sugars were transformed into the chain-extended α,β-unsaturated aldehydes **15**, **16**, and **18–25**, with overall yields varying from 12.4 to 43.2% for isomers with *syn* configuration, and from 40.5 to 51.1% for isomers with *anti* configuration.

1. Experimental

General methods.—Furan was distilled over sodium and benzophenone under an argon atmosphere immediately before use. The other solvents used were dried over anhyd sodium or magnesium sulfate, and evaporated under reduced pressure at temperature below 40 °C. TLC was performed on glass plates coated with Silica Gel G (E. Merck), spots being detected with iodine vapour or by charring with H_2SO_4 in EtOH (10%). Column chromatography was performed using Silica Gel Merck 60 (70–230 mesh). Melting points were determined with a Gallenkamp MFB-57 instrument. ^{1}H NMR spectra for solutions in $CDCl_3$ were measured using an Bruker AM-300 spectrometer. Chemical shift values are expressed in ppm (δ), relative to Me_4Si as the internal reference. ^{13}C NMR spectra were recorded with a Bruker AM-300 spectrometer. IR spectra were measured using a Nicolet FTIR-20-SX spectrometer and mass spectra were obtained with a Hewlett–Packard HP-5 spectrometer. Elemental analyses were determined with a Carlo Erba Elemental analyzer 1106.

2-[(1*S* and 1*R*, 2*R*)-1-Hydroxy-2,3-dimethylmethylenedioxypropyl]furan (**1** and **2**),

2-[(1*R* and 1*S*)-2,3:4,5-di-*O*-isopropylidene-D-xylitol-1-*C*-yl]furan (**3** and **4**), 2-[(1*R* and 1*S*)-2,3:4,5-di-*O*-isopropylidene-D-arabinitol-1-*C*-yl]furan (**5** and **6**), and 2-[(1*R* and 1*S*)-2,5-anhydro-3,4,6-tri-*O*-benzyl-D-mannitol-1-*C*-yl]furan (**7** and **8**), were synthesized from commercial D-mannitol, D-arabinose, D-xylose, and 2-amino-2-deoxy-D-glucose hydrochloride, respectively, as described previously [15,21].

*Synthesis of 1-acetoxy-1-furylalkanepolyol derivatives [17], **9–14**, from **1–6**. General procedure.*—Acetic anhydride (4 mL, 39 mmol) and freshly distilled pyridine (2 mL, 25 mmol) were added to the partially protected 1-*C*-(2-furyl) alditol derivatives (4.2 mmol). The reaction mixtures were stirred for 12 h in the dark at room temperature (20 °C), with control of the progress of reaction by TLC. At the end of the reactions, ice was added and the stirring was continued for 30 min. The mixtures were then extracted with chloroform, and the organic layers were washed with water, dried, and evaporated. The resulting syrups were purified by column chromatography, using CH_2Cl_2–Et_2O mixtures as eluents, to give the acetates **9–14** in nearly quantitative yields.

2-[(1*S*,2*R*)-1-Acetoxy-2,3-dimethylmethylenedioxypropyl]furan (**9**) (978 mg, 97%), obtained from **1** (832 mg), was a white solid: mp 78 °C (from hexane–EtOAc); IR (KBr): ν 3108, 1749, 1512, 1460, 1434, 1382, 1222, 1160, 1088, and 1062 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.38, 1.42 (6 H, 2 s, CMe_2), 2.10 (3 H, s, O–CO–CH_3), 3.67 (1 H, dd, $J_{2',3'}$ 5.60, $J_{3',3''}$ 8.84 Hz, H-3'), 3.96 (1 H, dd, $J_{2',3''}$ 6.44 Hz, H-3''), 4.59 (1 H, ddd, $J_{1',2'}$ 8.14 Hz, H-2'), 5.87 (1 H, d, H-1'), 6.32–6.42 (2 H, m, H-3 and 4), 7.35–7.41 (1 H, m, H-5); ^{13}C NMR ($CDCl_3$): δ 20.38 (O–CO–*C*H_3), 25.13, 26.01 (C*Me*$_2$), 66.01 (C-3'), 76.31 (C-2'), 77.38 (C-1'), 109.76 (C-3, *C*Me_2), 110.55 (C-4), 143.67 (C-5), 149.63 (C-2), 169.13 (–OCO–). Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.91; H, 6.74.

2-[(1*R*,2*R*)-1-Acetoxy-2,3-dimethylmethylenedioxypropyl]furan (**10**) (937 mg, 93%), obtained from **2** (832 mg), was a white solid: mp 71 °C (from hexane–EtOAc); IR (KBr): ν 3106, 1750, 1510, 1460, 1430, 1385, 1220, 1160, 1090, and 1060 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.35, 1.37 (6 H, 2 s, CMe_2), 2.08 (3 H, s, O–CO–CH_3), 4.00 (1 H, dd, $J_{2',3'}$ 6.52, $J_{3',3''}$ 8.46 Hz, H-3'), 4.14 (1 H, dd, $J_{2',3''}$ 6.00 Hz, H-3''), 4.49 (1 H, ddd, $J_{1',2'}$ 5.30 Hz, H-2'), 5.95 (1 H, d, H-1'), 6.30–6.38 (2 H, m, H-3 and 4), 7.35–7.41 (1 H, m, H-5); ^{13}C NMR ($CDCl_3$): δ 20.77 (O–CO–*C*H_3), 25.26, 26.31 (C*Me*$_2$), 65.82 (C-3'), 67.96 (C-2'), 75.49 (C-1'), 109.84 (C-3, *C*Me_2), 110.32 (C-4), 142.79 (C-5), 149.56 (C-2), 169.56 (–OCO–). Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.04; H, 6.73.

2-[(1*R*)-1-*O*-Acetyl-2,3:4,5-di-*O*-isopropylidene-D-xylitol-1-*C*-yl]furan (**11**) (1.356 g, 95%), obtained from **3** (1.252 g), was a clear syrupy liquid: IR (KBr): ν 3110, 3040, 2980, 1747, 1610, 1560, 1520, 1450, 1430, 1370, 1229, 1151, 1100, 1069, 1012, 870, and 740 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.32, 1.35, 1.42, 1.57 (12 H, 4 s, 2 CMe_2), 2.10 (3 H, s, O–CO–CH_3), 3.70–4.10 (4 H, m, H-3',4',5', and 5''), 4.45 (1 H, dd, $J_{1',2'}$ 5.50, $J_{2',3'}$ 6.80 Hz, H-2'), 5.98 (1 H, d, H-1'), 6.36 (1 H, dd, $J_{3,4}$ 3.30, $J_{4,5}$ 1.80 Hz, H-4), 6.45 (1 H, d, H-3), 7.40 (1 H, d, H-5); ^{13}C NMR ($CDCl_3$): δ 21.50 (O–CO–*C*H_3), 25.46, 25.50, 26.10, 27.02 (2 C*Me*$_2$), 65.55 (C-5'), 68.65 (C-4'), 78.55 (2 *C*Me_2), 75.10 (C-3'), 77.03 (C-2'), 77.60 (C-1'), 109.69 (C-4), 110.34 (C-3), 142.52 (C-5), 149.50 (C-2), 169.00 (–OCO–). Anal. Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 59.85; H, 7.14.

2-[(1*S*)-1-*O*-Acetyl-2,3:4,5-di-*O*-isopropylidene-D-xylitol-1-*C*-yl]furan (**12**) (1.371 g, 96%), obtained from **4** (1.252 g), was a clear syrupy liquid: IR (KBr): ν 3120, 2990, 1750, 1490, 1450, 1380, 1220, 1160, 1080, 1010, 880, and 720 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.24, 1.34, 1.38, 1.43 (12 H, 4 s, 2 CMe_2), 2.15 (3 H, s, O–CO–CH_3), 3.46 (1 H, dd, $J_{5',5''}$ 3.80, $J_{4',5'}$ 6.90 Hz, H-5'), 3.76–4.44 (3 H, m, H-3',4', and 5''), 4.70 (1 H, dd, $J_{1',2'}$ 7.00, $J_{2',3'}$ 0.80 Hz, H-2'), 5.79 (1 H, d, H-1'), 6.45 (1 H, dd, $J_{3,4}$ 3.20, $J_{4,5}$ 1.80 Hz, H-4), 6.56 (1 H, d, H-3), 7.40 (1 H, d, H-5); ^{13}C NMR ($CDCl_3$): δ 21.08 (O–CO–CH_3), 25.96, 26.31, 26.76, 27.21 (2 CMe_2), 65.93 (C-5'), 75.51 (C-4'), 76.04 (C-3'), 77.03 (C-2'), 78.68 (2 CMe_2), 94.30 (C-1'), 109.53 (C-4), 110.51 (C-3), 143.35 (C-5), 149.75 (C-2), 170.47 (–OCO–). Anal. Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 59.86; H, 7.08.

2-[(1*R*)-1-*O*-Acetyl-2,3:4,5-di-*O*-isopropylidene-D-arabinitol-1-*C*-yl]furan (**13**) (1.299 g, 91%), obtained from **5** (1.252 g), was a clear syrupy liquid: IR (KBr): ν 3040, 1747, 1450, 1370, 1229, 1151, 1100, 1069, 1012, 880, and 860 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.34, 1.37, 1.40, 1.43 (12 H, 4 s, 2 CMe_2), 2.10 (3 H, s, O–CO–CH_3), 3.69–4.13 (4 H, m, H-3',4',5', and 5''), 4.34 (1 H, dd, $J_{1',2'}$ 4.56, $J_{2',3'}$ 6.71 Hz, H-2'), 6.04 (1 H, d, H-1'), 6.34 (1 H, dd, $J_{3,4}$ 3.30, $J_{4,5}$ 1.68 Hz, H-4), 6.42 (1 H, dd, $J_{3,5}$ 0.79 Hz, H-3), 7.39 (1 H, dd, H-5); ^{13}C NMR ($CDCl_3$): δ 20.80 (O–CO–CH_3), 25.11, 26.40, 26.42, 27.30 (2 CMe_2), 67.10 (C-5'), 68.78 (C-4'), 76.68 (C-3'), 78.57 (C-2'), 80.14 (C-1'), 109.72, 109.73 (C-3 and 4), 109.95, 110.20 (2 CMe_2), 142.45 (C-5), 149.49 (C-2), 169.33 (–OCO–). Anal. Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 60.11; H, 7.10.

2-[(1*S*)-1-*O*-Acetyl-2,3:4,5-di-*O*-isopropylidene-D-arabinitol-1-*C*-yl]furan (**14**) (1.342 g, 94%), obtained from **6** (1.252 g), was a clear syrupy liquid: IR (KBr): ν 3048, 1745, 1453, 1372, 1230, 1100, 1155, 1070, and 1010 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.16, 1.25, 1.33, 1.39 (12 H, 4 s, 2 CMe_2), 2.10 (3 H, s, O–CO–CH_3), 3.85–4.35 (4 H, m, H-3',4',5', and 5''), 4.80 (1 H, d, $J_{1',2'}$ 5.65 Hz, H-2'), 5.83 (1 H, d, H-1'), 6.30–6.40 (1 H, m, H-4), 6.48–6.50 (1 H, m, H-3), 7.45–7.55 (1 H, m, H-5); ^{13}C NMR ($CDCl_3$): δ 20.90 (O–CO–CH_3), 25.11, 26.40, 26.42, 27.62 (2 CMe_2), 66.42 (C-5'), 74.00, 75.39, 76.60, 79.14 (C-1',2',3', and 4'), 109.45, 110.40 (C-3 and 4), 110.40, 111.53 (2 CMe_2), 143.07 (C-5), 149.60 (C-2), 170.00 (–OCO–). Anal. Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 59.87; H, 7.13.

Sensitized photooxygenation of 1-acetoxy-1-furylalkanepolyol derivatives: General procedure.—A 0.2 M solution of the substrate (**9**–**14**) in acetone with methylene blue (0.01%) as photosensitizer, was placed in a flask adapted to pass through an oxygen stream. The flask was immersed in a cooling bath and illuminated with a Sylvania L2248 (500 W) or FDG (1000 W) lamp. Progress of the reaction was followed by TLC and when the reactant had disappeared, the irradiation was stopped and dimethyl sulfide (1.5 equiv) was added as reducting agent. After a span of time, the solvent was evaporated and the residue chromatographed. Temperature and reaction time for oxidation and reduction are indicated for each experiment.

(E)-5-O-Acetyl-2,3-dideoxy-6,7-O-isopropylidene-D-threo-*hept-2-enos-4-ulose* (**15**). —Photooxygenation of **9** (36 mg, 0.15 mmol) was performed at −60 °C for 4 min, and reduction at the same temperature for 30 min and additionally at −4 °C for 20 days to give **15** (36 mg, 94%) as a clear syrupy liquid: IR (KBr): ν 1763, 1745, 1705, 1621, 1450, 1160, 1055, and 839 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.39, 1.44 (6 H, 2 s, CMe_2),

2.20 (3 H, s, O–CO–CH_3), 3.95–4.36 (3 H, m, H-6,7, and 7′), 5.56 (1 H, d, $J_{5,6}$ 8.1 Hz, H-5), 6.88 (1 H, dd, $J_{1,2}$ 6.7, $J_{2,3}$ 15.3 Hz, H-2), 7.19 (1 H, d, H-3), 9.77 (1 H, d, H-1). Anal. Calcd for $C_{12}H_{16}O_6$: C, 56.25; H, 6.29. Found: C, 56.34; H, 6.31.

(E)-5-O-Acetyl-2,3-dideoxy-6,7-O-isopropylidene-D-erythro-*hept-2-enos-4-ulose* (**16**).—The reaction conditions of **10** (41 mg, 0.17 mmol) and yields were the same as for **9**, to give **16** (41 mg, 95%) as a clear syrupy liquid: IR (KBr): ν 1765, 1740, 1700, 1630, 1470, 1377, 1150, 1120, 1060, and 843 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.34, 1.37 (6 H, 2 s, CMe_2), 2.15 (3 H, s, O–CO–CH_3), 4.14 (1 H, dd, $J_{6,7}$ 4.7, $J_{7,7'}$ 6.9 Hz, H-7), 4.21 (1 H, dd, $J_{6,7'}$ 4.1 Hz, H-7′), 4.33 (1 H, ddd, $J_{5,6}$ 3.8 Hz, H-6), 5.68 (1 H, d, H-5), 6.86 (1 H, dd, $J_{1,2}$ 6.7, $J_{2,3}$ 15.5 Hz, H-2), 7.17 (1 H, d, H-3), 9.77 (1 H, d, H-1). Anal. Calcd for $C_{12}H_{16}O_6$: C, 56.25; H, 6.29. Found: C, 56.42; H, 6.26.

2,2-Bis [5(3,3-dimethyl-2,4-dioxacyclopentyl)-2,4-pentadiene-5-olid-4-yloxy]-propane (**17**).—When the photooxygenation of **10** (40 mg, 0.17 mmol) was carried out for 12 min at 0 °C followed by reduction with dimethyl sulfide at room temperature for 30 min, was obtained **17** (28 mg, 68%) as a clear syrupy liquid: IR (KBr): ν 1730, 1670, 1380, 1270, and 1120 cm^{-1}; UV: 287.6 nm (Abs = 0.448); ^1H NMR ($CDCl_3$): δ 0.83, 0.86, 0.88, 0.90 (12 H, 4 s, 2 CMe_2), 1.26 (6 H, s, CMe_2), 4.20–4.36 (6 H, m, H of dioxolane rings), 7.45–7.78 (4 H, m, H of α-pyrone rings); MS (EI): 418 $[M-46]^+$, 293, 149, 127, 43. Anal. Calcd for $C_{23}H_{28}O_{10}$: C, 59.47; H, 6.08. Found: C, 59.36; H, 6.06.

(Z)-5-O-Acetyl-2,3-dideoxy-6,7:8,9-di-O-isopropylidene-D-gulo-*non-2-enos-4-ulose* (**18**).—Photooxygenation of **11** (39 mg, 0.12 mmol) was performed at −60 °C for 20 min and reduction with dimethyl sulfide at −60 °C for 3.5 h and at room temperature for 1 h, to give **18** (43 mg, 100%) as a clear syrupy liquid: ^1H NMR ($CDCl_3$): δ 1.17, 1.25, 1.38, 1.42 (12 H, 4 s, 2 CMe_2), 2.19 (3 H, s, O–CO–CH_3), 3.80–4.50 (5 H, m, H-6,7,8,9, and 9′), 5.09 (1 H, d, $J_{5,6}$ 4.7 Hz, H-5), 6.24 (1 H, dd, $J_{1,2}$ 7.3, $J_{2,3}$ 12.0 Hz, H-2), 7.18 (1 H, d, H-3), 10.12 (1 H, d, H-1). Anal. Calcd for $C_{17}H_{24}O_8$: C, 57.29; H, 6.79. Found: C, 57.09; H, 6.82.

When compound **18** was re-examined after a few days (20–30), it had isomerized quantitatively to *(E)*-5-*O*-acetyl-2,3-dideoxy-6,7:8,9-di-*O*-isopropylidene-D-*gulo*-non-2-enos-4-ulose (**20**), which was a clear syrupy liquid: ^1H NMR ($CDCl_3$): δ 1.17, 1.25, 1.47, 1.58 (12 H, 4 s, 2 CMe_2), 2.17 (3 H, s, O–CO–CH_3), 3.80–4.50 (5 H, m, H-6,7,8,9, and 9′), 5.20 (1 H, d, $J_{5,6}$ 4.8 Hz, H-5), 6.86 (1 H, dd, $J_{1,2}$ 6.6, $J_{2,3}$ 16.1 Hz, H-2), 7.18 (1 H, d, H-3), 9.78 (1 H, d, H-1). Anal. Calcd for $C_{17}H_{24}O_8$: C, 57.29; H, 6.79. Found: C, 57.50; H, 6.76.

(Z)-5-O-Acetyl-2,3-dideoxy-6,7:8,9-di-O-isopropylidene-D-ido-*non-2-enos-4-ulose* (**19**).—The reaction conditions of **12** (47 mg, 0.14 mmol) were the same as for **11**. Compound **19** (48 mg, 97%) was obtained as a clear syrupy liquid: ^1H NMR ($CDCl_3$): δ 1.26, 1.37, 1.40, 1.42 (12 H, 4 s, CMe_2), 2.12 (3 H, s, O–CO–CH_3), 3.70–4.60 (5 H, m, H-6,7,8,9, and 9′), 5.78 (1 H, d, $J_{5,6}$ 4.2 Hz, H-5), 6.25 (1 H, dd, $J_{1,2}$ 7.0, $J_{2,3}$ 11.8 Hz, H-2), 7.20 (1 H, d, H-3), 10.20 (1 H, d, H-1). Anal. Calcd for $C_{17}H_{24}O_8$: C, 57.29; H, 6.79. Found: C, 57.17; H, 6.82.

Compound **19** isomerized quantitatively, as described for **18**, to give *(E)*-5-*O*-acetyl-2,3-dideoxy-6,7:8,9-di-*O*-isopropylidene-D-*ido*-non-2-enos-4-ulose (**21**) as a clear syrupy liquid: ^1H NMR ($CDCl_3$): δ 1.26, 1.37, 1.40, 1.42 (12 H, 4 s, 2 CMe_2), 2.15 (3 H, s,

O–CO–CH_3), 3.70–4.60 (5 H, m, H-6,7,8,9, and 9′), 5.90 (1 H, d, $J_{5,6}$ 4.1 Hz, H-5), 6.87 (1 H, dd, $J_{1,2}$ 6.8, $J_{2,3}$ 16.0 Hz, H-2), 7.20 (1 H, d, H-3), 9.78 (1 H, d, H-1). Anal. Calcd for $C_{17}H_{24}O_8$: C, 57.29; H, 6.79. Found: C, 57.14; H, 6.81.

*(Z)-5-O-Acetyl-2,3-dideoxy-6,7:8,9-di-O-isopropylidene-*D-gluco*-non-2-enos-4-ulose* (**22**).—The reaction conditions of **13** (31 mg, 0.09 mmol) were the same as for **11**. Compound **22** (30 mg, 94%) was obtained as a clear syrupy liquid: ^{1}H NMR ($CDCl_3$): δ 1.25, 1.33, 1.35, 1.40 (12 H, 4 s, 2 CMe_2), 2.10 (3 H, s, O–CO–CH_3), 3.90–4.40 (5 H, m, H-6,7,8,9, and 9′), 5.29 (1 H, d, $J_{5,6}$ 3.0 Hz, H-5), 6.21 (1 H, dd, $J_{1,2}$ 7.2, $J_{2,3}$ 12.0 Hz, H-2), 7.14 (1 H, d, H-3), 10.14 (1 H, d, H-1). Anal. Calcd for $C_{17}H_{24}O_8$: C, 57.29; H, 6.79. Found: C, 57.37; H, 6.82.

Compound **22** isomerized, as described for **18**, to give (*E*)-5-*O*-acetyl-2,3-dideoxy-6,7:8,9-di-*O*-isopropylidene-D-*gluco*-non-2-enos-4-ulose, **24**, as a clear syrupy liquid: ^{1}H NMR ($CDCl_3$): δ 1.29, 1.34, 1.37, 1.41 (12 H, 4 s, 2 CMe_2), 2.11 (3 H, s, O–CO–CH_3), 3.80–4.40 (5 H, m, H-6,7,8,9, and 9′), 5.37 (1 H, d, $J_{5,6}$ 3.0 Hz, H-5), 6.82 (1 H, dd, $J_{1,2}$ 6.6, $J_{2,3}$ 18.3 Hz, H-2), 7.15 (1 H, d, H-3), 9.76 (1 H, d, H-1). Anal. Calcd for $C_{17}H_{24}O_8$: C, 57.29; H, 6.79. Found: C, 57.20; H, 6.76.

*(Z)-5-O-Acetyl-2,3-dideoxy-6,7:8,9-di-O-isopropylidene-*D-manno*-non-2-enos-4-ulose* (**23**).—The reaction conditions of **14** (44 mg, 0.13 mmol) were the same as for **13**. Compound **23** (44 mg, 95%) was obtained as a clear liquid: ^{1}H NMR ($CDCl_3$): 1.25, 1.34, 1.35, 1.40 (12 H, 4 s, 2 CMe_2), 2.10 (3 H, s, O–CO–CH_3), 3.80–4.20 (4 H, m, H-7,8,9, and 9′), 4.57 (1 H, m, H-6), 5.90–6.05 (1 H, m, H-5), 6.22 (1 H, dd, $J_{1,2}$ 7.1, $J_{2,3}$ 12.0 Hz, H-2), 7.32 (1 H, d, H-3), 10.20 (1 H, d, H-1). Anal. Calcd for $C_{17}H_{24}O_8$: C, 57.29; H, 6.71. Found: C, 57.48; H, 6.77.

Compound **23** isomerized quantitatively, as described for **18**, to give (*E*)-5-*O*-acetyl-2,3-dideoxy-6,7:8,9-di-*O*-isopropylidene-D-*manno*-non-2-*enos*-4-*ulose* (**25**) as a clear syrupy liquid: ^{1}H NMR ($CDCl_3$): δ 1.26, 1.33, 1.39, 1.40 (12 H, 4 s, 2 CMe_2), 2.10 (3 H, s, O–CO–CH_3), 3.85–4.20 (4 H, m, H-7,8,9, and 9′), 4.50–4.65 (1 H, m, H-6), 5.90–6.00 (1 H, m, H-5), 6.80 (1 H, dd, $J_{1,2}$ 7.4, $J_{2,3}$ 16.0 Hz, H-2), 7.40 (1 H, d, H-3), 9.76 (1 H, d, H-1). Anal. Calcd for $C_{17}H_{24}O_8$: C, 57.29; H, 6.79. Found: C, 57.44; H, 6.82.

Sensitized photooxygenations of 1-hydroxyl-1-furylalkanepolyol derivatives. (**1**–**8**).—Photooxygenations of **7** and **8** were carried out with 68 mg (0.14 mmol) and 76 mg (0.15 mmol) respectively of substrate at −60 °C for 40 min. Dimethyl sulfide (14 mg) was added and the mixture maintained at −60 °C for 6 h, and at room temperature for another 2 h. The solvent was eliminated and the residue could not be identified through IR or ^{1}H NMR spectroscopy, although disappearance of the furan ring was observed as well as the presence of aldehydic and olefinic absorptions.

The same negative results, as for **7** and **8**, were found when compounds **1**–**6** were photooxygenated under the same operating conditions.

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