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STUDIES ON D-ERYTHROSE AND ITS ACETATES*

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ABSTRACT

Acetylation of an equilibrated solution of D-erythrose in pyridine yields a mixture containing mainly 1,2,3-tri-*O*-acetyl-α- and -β-D-erythrofuranose. If D-erythrose is dissolved in pyridine and acetic anhydride is added immediately afterwards, acetylated dimers of D-erythrose are formed as well as the triacetates. An investigation of the structure and stereochemistry of these compounds is presented. The dimerization and trimerization of 2,4-*O*-ethylidene-D-erythrose is also studied.

INTRODUCTION

D-Erythrose has not yet been obtained crystalline and the physical data reported by other workers[1–3] are contradictory. This may be because of the ready dimerisation of D-erythrose[1]. As we needed D-erythrose for degradation experiments, and commercial samples were impure, a study on the homogeneity and equilibrium properties of the various forms of this sugar has been undertaken.

RESULTS AND DISCUSSION

When 4,6-*O*-ethylidene-D-glucose is oxidized with sodium metaperiodate[2,4], a crystalline "dimer" of 2,4-*O*-ethylidene-D-erythrose, bis(2,4-*O*-ethylidene-D-erythrose)-1,1′:1′,3-cyclic acetal, is thought to be formed[2]. Various values for the melting point and specific rotation of this compound have been reported[2,4–7]; our preparation showed two components on t.l.c., neither of which was identical with the starting material. The components could not be isolated by chromatography, but acetylation followed by chromatography on silica gel gave two acetylated derivatives. One of these had similar properties (m.p., $[\alpha]_D$) to those reported[2] for the acetate **1** (see Scheme). The ^{1}H-n.m.r. spectrum of this compound revealed the presence of two *O*-acetyl groups and two *O*-ethylidene groups. The protons H-1′, H-2′, H-3′, H-4′ax and H-4′eq formed an approximately first-order system, with H-3′ resonating as a doublet of triplets ($J_{3',4'ax} \approx J_{2',3'}$), H-4′eq as a doublet of doublets, and H-4′ax as a triplet ($J_{4'ax,4'eq} = J_{3',4'ax}$) (Tables I and II). The magnitude of the coupling

*Dedicated to Professor Dexter French on the occasion of his 60th birthday.

TABLE I

CHEMICAL SHIFTS IN δ UNITS FOR COMPOUNDS 1-6[a]

Compound no. (solvent)	**1** ($CDCl_3$)	**1** (C_6D_6)	**2** ($CDCl_3$)	**3** ($CDCl_3$)	**4** ($CDCl_3$)	**4** (C_6D_6)	**5** ($CDCl_3$)	**5** (C_6D_6)	**6** ($CDCl_3$)
H-1	5.86d	6.09d	6.34d	6.17d	5.81d	5.91d	6.40d	6.60d	6.32d
H-2	3.35–3.60m	3.40–3.50m	5.20dd	5.34dd	4.92dd	5.15dd	5.00dd	5.11dd	4.23dd
H-3	3.35–3.70m	3.85–3.95m	5.41o	5.49o	3.81o	3.41o	4.00–4.45m	4.03o[b]	5.12o
H-4_1	3.35–3.70m	3.25–3.40m	4.30dd	4.31dd	4.05–4.45m	4.15dd	4.00–4.45m	4.05–4.20m	4.50dd
H-4_2	3.35–3.70m	3.25–3.40m	4.08dd	3.98dd	4.05–4.45m	4.08dd	4.00–4.45m	4.05–4.20m	4.19dd
H-1′	4.93d	4.82d			4.93d	4.77d	5.20–5.45m	5.30d	5.38–5.42m
H-2′	3.69dd	3.62dd			5.20–5.50m	5.61dd	5.20–5.45m	5.30–5.75m	5.20–5.48m
H-3′	5.00dt	5.30dt			5.20–5.50m	5.73o	5.20–5.45m	5.30–5.75m	5.20–5.48m
H-4_1′	3.38t	3.12t			4.10–4.45m	4.53dd	4.36dd	4.30dd	4.52dd
H-4_2′	4.15dd	4.09dd			4.10–4.45m	4.33dd	4.08–4.30m	4.46dd	4.10–4.30m
OAc (s)	1.99, 2.14	1.58, 1.64	2.07, 2.09, 2.11	2.07 (6H), 2.10	2.10 (6H), 2.12, 2.16, 2.19, 2.23	1.57, 1.60 1.69 (6H), 1.73, 1.75	2.02, 2.05, 2.06, 2.09, 2.10, 2.16	1.56, 1.68, 1.72 (9H), 1.74	2.04, 2.05, 2.06, 2.08, 2.09, 2.14
Ethylidene methyls (d)	1.32, 1.37	1.18, 1.24							
Ethylidene methines (q)	4.65, 4.72	4.30 (2H)							

[a]Numbering of protons refers to the Scheme. Subindices 1 and 2 denote the nonequivalent protons in the methylene groups. Spin-decoupling technique was used; s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, dt = doublet of triplets, o = eight lines centered at noted value, m = multiplet. [b]Probable eight lines, half of which are obscured by protons H-4_1 and H-4_2.

TABLE II

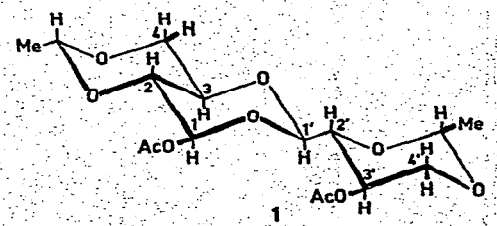
COUPLING CONSTANTS IN Hz FOR COMPOUNDS 1–6

Compound	*Solvent*	$J_{1,2}$	$J_{2,3}$	$J_{3,4_1}$	$J_{3,4_2}$	$J_{4_1,4_2}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4_1'}$	$J_{3',4_2'}$	$J_{4_1',4_2'}$
1[a]	$CDCl_3$	7.5	9.0[b]				3.5	8.5	10.5	5.5	10.5
1[a]	C_6D_6	7.5					3.0	10.0	10.0	5.5	10.5
2	$CDCl_3$	4.5	6.5	5.5	2.9	10.0					
3	$CDCl_3$	1.8	5.3	5.2	4.4	10.0					
4	$CDCl_3$	7.5	10.0	5.0	3.0	12.0	4.0				
4	C_6D_6	7.5	10.0	5.0	3.0	12.0	4.0	4.5	5.5	3.0	12.0
5	$CDCl_3$	3.5	10.0						5.0	3.0	12.5
5	C_6D_6	3.5	10.0				4.0		5.5	2.5	12.0
6	$CDCl_3$	1.5	7.5	5.0	3.0	12.5			6.0	3.0	12.5

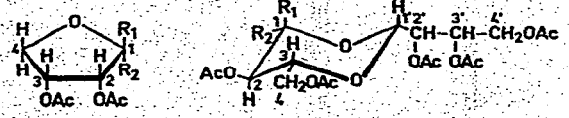
[a] J = 5.0 Hz for ethylidene methyl and methine groups. [b] Observed by addition of $Eu(fod)_3$.

constant between H-2 and H-3, observed by addition of a shift-reagent [$Eu(fod)_3$], indicated a diaxial arrangement[8] between these protons. These ^{1}H-n.m.r. data suggest that **1** has the structure and stereochemistry depicted (see Scheme). The ^{1}H-n.m.r. spectrum of the other compound revealed the presence of three *O*-acetyl groups and three *O*-ethylidene groups, indicating that the compound is an acetylated trimer of D-erythrose.

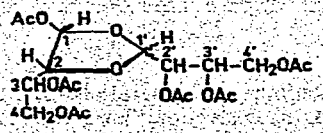
The total number of protons shown by the n.m.r. spectrum, as well as the considerably longer retention-time on g.l.c., is also in agreement with the foregoing



1



2: R_1=H, R_2=OAc **4**: R_1=H, R_2=OAc
3: R_1=OAc, R_2=H **5**: R_1=OAc, R_2=H



6

suggestion. These results explain the varying data, reported for 2,4-*O*-ethylidene-D-erythrose, as being due to a dimer–trimer equilibrium of the compound.

D-Erythrose was synthesised by two methods[5]. When D-erythrose was dissolved in pyridine and treated at once with acetic anhydride, at least four components were observed on g.l.c. (Fig. 1a), irrespective of the mode of synthesis, indicating a mixture of a monomeric and a polymeric group of components. G.l.c. analysis of D-erythrose, obtained from any of the two synthetic methods, did not (after reduction and acetylation) show threitol tetraacetate. This observation proves that no isomerization had taken place. When D-erythrose was dissolved in pyridine and acetylated after 30 min, only the two components thought to be monomeric were observed by g.l.c. (Fig. 1b). The ^{1}H-n.m.r. spectrum of D-erythrose in pyridine-d_5, water, or acetate buffer (pH 4.5) showed signals from the anomeric protons of α- and β-D-erythrofuranose and also signals arising from other types of anomeric proton. In deuterated acetate buffer, the ratio between monomeric and polymeric forms of D-erythrose increased when the sample was heated and then rapidly cooled, indicating that, as expected, the equilibrium is displaced in solution towards the monomers.

D-Erythrose was acetylated under conditions suitable for obtaining good yields of self-addition products. Chromatographic separation afforded five chromato-

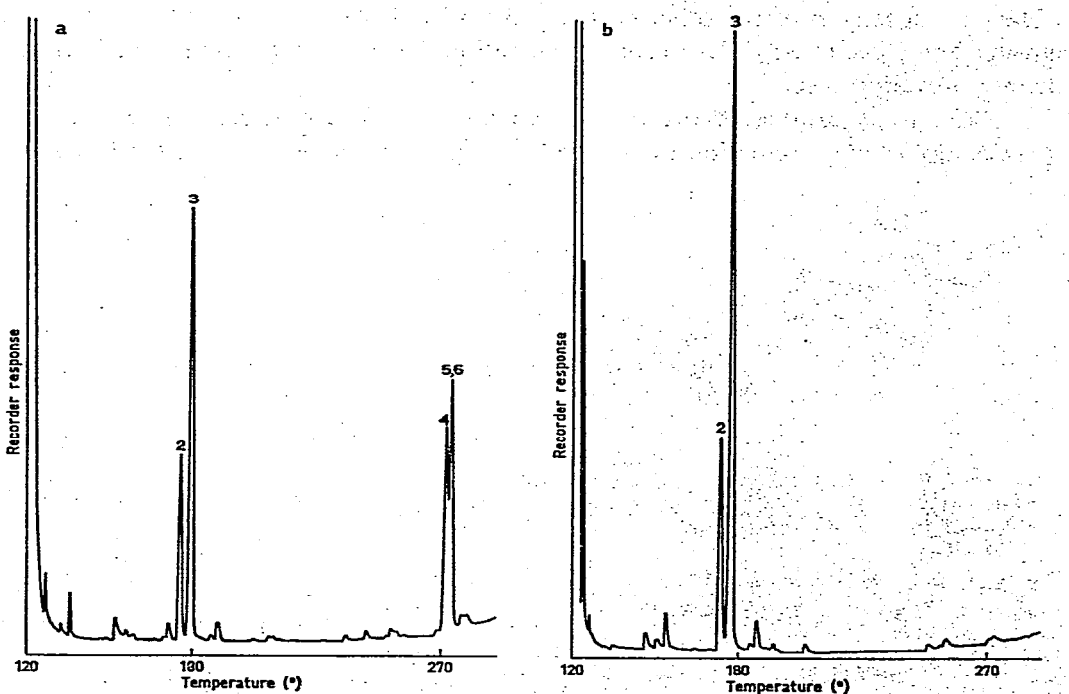


Fig. 1. G.l.c. analysis of D-erythrose (3% OV-1, 35 ml nitrogen/min, program rate 10°/min) acetylated in a solution of pyridine; isolated compounds are numbered. (*a*) Direct addition of acetic anhydride; (*b*) addition after 30 min.

graphically pure compounds (2–6, see Scheme). Deacetylation of 2 and 3 yielded D-erythrose. From ^{1}H-n.m.r. data (Tables I and II), m.s., and high-resolution m.s., it was evident that 2 and 3 were 1,2,3-tri-*O*-acetyl-α- and -β-D-erythrofuranose, respectively. The coupling constant between H-1 and H-2 in 3 was < 2 Hz, indicating a *trans* relationship[9,10], and thus the β configuration for the anomeric centre. In contrast compound 2, having the larger coupling-constant between H-1 and H-2, has the α configuration. An amorphous mixture, most probably consisting of these α and β anomers[11] and a crystalline (but not further characterized) triacetate of D-erythrose[12], have been reported previously.

Compounds 4, 5, and 6 are hexa-acetates of dimers of D-erythrose, according to m.s. and ^{1}H-n.m.r. data (Tables I and II). The structure of 4 was determined as follows. The shifts of H-1 (δ 5.91) and H-2 (δ 5.15) indicate that both C-1 and C-2 carry an acetoxyl group[13]. Proton H-3 exhibited eight lines centered at δ 3.41. The pattern arises from coupling with H-2 and the non-equivalent protons (H-4) of an uncoupled methylene group. These results are analogous to those observed for 2,4-di-*O*-acetyl-1,3-*O*-ethylidene-L-erythritol[14]. The resonance of H-1′ as a doublet at δ 4.77 is in accord with the value expected for a proton in a 1,3-dioxane or 1,3-dioxolane ring[15,16], but the downfield shift of H-2 rules out the latter structure. The resonances of H-2′ and H-3′ at δ 5.61 and δ 5.73, imply that C-2′ and C-3′ carry an acetoxyl group, and the eight line pattern of H-3′ arises in a manner analogous to that of H-3.

The magnitude of the coupling constants for H-1, H-2, and H-3 ($J_{1,2}$ 7.5 and $J_{2,3}$ 10 Hz) is in accord with a 1,3-dioxane ring with diaxial relationships between the protons. Thus, as 4 originates from D-erythrose, it should have the conformation depicted in the Scheme.

By similar reasoning, it was established that 5 was the C-1 epimer of 4. The observation that H-1′ and H-3 in 5 resonate 0.4–0.6 p.p.m. downfield from H-1′ and H-3 in 4 may be attributed to anisotropic deshielding[13] from the acetoxyl group at C-1.

In the ^{1}H-n.m.r. spectrum of compound 6, the signals for H-1, H-2, and H-3 appear at δ 6.32, δ 4.23, and δ 5.12, in accord with the presence of acetoxyl groups at C-1 and C-3 but not at C-2, thus ruling out a 1,3-dioxane ring. Proton H-3 showed the characteristic eight-line pattern arising from coupling with H-2 and the H-4 protons. The chemical shift for H-1′ was in agreement with a proton in a 1,3-dioxolane ring; however, this signal was not resolved into a doublet in any of the solvents used (chloroform-*d*, pyridine-d_5, or benzene-d_6). On the basis of these observations, and as 6 is an isomer of 4 and 5, the structure shown in the Scheme is proposed for 6. The small value of $J_{1,2}$ (< 2 Hz) required that H-1 and H-2 be in the *trans* disposition[9,10].

EXPERIMENTAL

General methods. — Concentration was conducted under diminished pressure below 40°. Melting points are corrected. T.l.c. was performed on Silica gel HF_{254}

(Merck) with solvents (*A*) 3:1:1 ethyl acetate–acetic acid–water, and (*B*) 3:2 ethyl acetate–petroleum ether (b.p. 40–60°). Compounds were detected with the spray reagents *p*-anisidine hydrochloride or 50% sulphuric acid. Column chromatography was performed on silica gel (230–400 mesh, Merck). G.l.c. was effected on a Varian Aerograph 2700 fitted with a flame-ionization detector and a 1.8 m × 2 mm i.d. glass column containing 3% OV-1 on Varaport 30 (100–120 mesh). Acetates were analysed at 120–275° with a program rate of 10°/min, and alditol acetates isothermically at 140°. G.l.c.–m.s. analyses were recorded at 70 eV with a Varian MAT CH 7 instrument equipped with the Spectro System 100 N 100/81 MS and fitted with a Varian Aerograph 1740. G.l.c.–m.s. of compounds **2** and **3** were obtained at 160°, and those of compounds **5** and **6** at 225°. High-resolution mass spectra were obtained with an AEI MS-920 instrument at the Institute of Medical Biochemistry, University of Gothenburg.

I.r. and ^{1}H-n.m.r. spectra were recorded with Perkin–Elmer 337 and Varian HA-100D (100 MHz) spectrometers, respectively. Optical rotation was measured at room temperature on a Perkin–Elmer 141 polarimeter. Preparative, liquid chromatography was performed on a Waters ALC-202 instrument fitted with two steel columns, each one of 30 cm × 0.6 cm i.d. containing Waters' "μ"-Porasil. The solvent used was 86:14 dichloromethane–butanone, the flow rate was 1 ml/min, and the compounds were detected with a refractometer unit connected to a recorder. The samples were injected as 10–15% solutions in chloroform. Injection of 25 μl yielded approximately 2 mg of the desired compound, and each run was complete after 15 min.

*Preparation and characterization of 2,4-*O*-ethylidene-*D*-erythrose and* D*-erythrose.* — *2,4-*O*-Ethylidene-*D*-erythrose.* Periodate oxidation of 4,6-*O*-ethylidene-D-glucose[4] (103 g) afforded 74 g (95%) of 2,4-*O*-ethylidene-D-erythrose as a colourless syrup that was crystallized from about 100 ml of 3:2 pentane-abs. ethanol. The product, an amorphous white solid, had m.p. 117–123°, $[\alpha]_D$ −43.2° (*c* 1.0, water, 2 h) and R_F 0.77 and 0.65 in solvent *A*. (Lit.[5–7] m.p. 149–150°, $[\alpha]_D$ −43.5°; m.p. 145–148°, $[\alpha]_D$ −23.1°; m.p. 65–80°, $[\alpha]_D$ −37.8°, respectively.) In another preparation, the syrup was dissolved in ethyl acetate and the solution kept at room temperature. A solid having identical t.l.c. behaviour as the foregoing product, but with a melting point of 130–135°, was formed.

*1,3-Di-*O*-acetyl-[bis(2,4-*O*-ethylidene-*D*-erythrose) cyclic acetal]* (**1**). 2,4-*O*-Ethylidene-D-erythrose (208 mg, m.p. 117–123°) was acetylated with pyridine (8 ml) and acetic anhydride (3 ml) overnight at room temperature. The solution was poured into ice–water and the mixture was extracted with chloroform. The organic phase was washed successively with M hydrochloric acid (2 × 30 ml), M sodium hydrogencarbonate (2 × 30 ml) and water (2 × 20 ml), and dried (sodium sulphate), filtered, and evaporated. Recrystallization (246 mg) from ethanol gave **1** (130 mg, 46%), m.p. 170–171°, $[\alpha]_D$ −58.0° (*c* 0.8, ethanol) (lit.[2] m.p. 171.5–172°, $[\alpha]_D$ −59°).

*Acetate of a trimer of 2,4-*O*-ethylidene-*D*-erythrose.* The mother liquor from

the crystallization of **1** contained two components (R_F 0.50 and 0.40, solvent *B*). After separation on a column of silica gel with solvent *B* as eluent, the first-eluted compound was found identical with **1**. The other compound obtained (40 mg, amorphous) was chromatographically pure (t.l.c. and g.l.c.) and showed i.r. peaks at $\nu_{max}^{CCl_4}$ 2990, 2930, 2860, 1777, 1755–1740, 1365, 1230, 1118, 1050, and 890 cm^{-1}; n.m.r. data ($CDCl_3$): δ 1.33 (d, 6H, *J* 5.0 Hz, ethylidene methyl groups), 1.41 (d, 3H, *J* 5.0 Hz, ethylidene methyl), 2.07, 2.09 and 2.17 (3 s, 9H, OAc), 4.61, 4.69, 4.79 (3 q, 3H, *J* 5.0 Hz, ethylidene methine groups), 5.97 (d, 1H, *J* 2.2 Hz, anomeric proton), and 5.88–5.95 (m, 1H).

D-*Erythrose*. (*a*) 2,4-*O*-Ethylidene-D-erythrose (3.0 g, m.p. 130–135°) was hydrolysed[2] in sulphuric acid (0.125M, 250 ml) for 45 min at 95° with nitrogen bubbling through the solution, which was kept overnight at room temperature. Neutralisation (barium carbonate), filtration (Celite), and evaporation of the filtrate left an oil (1.75 g, 77%) showing $[\alpha]_D$ −32.5°, (*c* 1.0, water, 72 h) (Lit.[1–3] $[\alpha]_D$ −30°, $[\alpha]_D$ −41°, and $[\alpha]_D$ −18.5°, respectively); n.m.r. data (C_5D_5N): δ 6.98 (d, 1H, *J* 2.1 Hz, β anomer) and 6.66 (d, 1H, *J* 4.3 Hz, α anomer) in the ratio 1:4 (1.5 h).

(*b*) 2,4-*O*-Ethylidene-D-erythrose (55.0 g, m.p. 117–123°) in sulphuric acid (0.125M, 400 ml) was treated as in (*a*), yielding a syrup (41.0 g, 91%) having $[\alpha]_D$ −20.5° (*c* 1.2, water, 72 h).

(*c*) Oxidation of D-glucose with lead tetraacetate[1] (processing as just described) yielded D-erythrose having $[\alpha]_D$ −30.8° (*c* 0.9, water); n.m.r. data (D_2O): δ 5.26 (d, 1H, *J* 4.5 Hz, α anomer) and 5.24 (d, 1H, *J* 3.2 Hz, β anomer) in the ratio 1:3 (72 h).

Preparation and characterization of acetates of D-*erythrose*. — D-Erythrose (1.65 g) was treated with pyridine (10 ml) and acetic anhydride (10 ml), and the mixture processed as described for compound **1**. The dark oil obtained (3.0 g, 90%) was fractionated (2.8 g) on a column (90 × 2.5 cm) of silica gel with 2:1 petroleum ether (b.p. 60–70°)–ethyl acetate as eluent. After elution of compounds **3** and **2** the solvent ratio was changed to 3:2 and combinations of further fractions were based on g.l.c. analysis (3% OV-1 at 225°). Minor fractions (0.36 g) not containing the main components were neglected. The main fractions are listed as follows in order of elution (weight of each and the isolated compounds are given in parentheses). Fraction I (0.63 g, **3**), II (0.06 g, **2** and **3**), III (0.21 g, **2**), IV (0.47 g, **6**), V (0.77 g, **5** and **4**), and VI (0.06 g, **4**). Compounds **2** and **3** were obtained chromatographically pure (t.l.c. and g.l.c.) and **4** crystallized from VI in carbon tetrachloride–cyclohexane. Preparative, liquid chromatography of IV and V gave **6** and **5**, respectively, in essentially pure state. Compounds **2** and **3**, after deacetylation by the Zemplén procedure, showed $[\alpha]_D$ −33.6° (*c* 0.9, water, 48 h) and $[\alpha]_D$ −30.7° (*c* 1.0, water, 48 h), respectively.

1,2,3-Tri-O-*acetyl*-α-D-*erythrofuranose* (**2**). This product was amorphous, $[\alpha]_D$ +56.3° (*c* 1.1, chloroform); R_F 0.50 (solvent *B*); $\nu_{max}^{CCl_4}$ 1747, 1362, 1218, 1110, 1062, 1010, and 932 cm^{-1}; *m/e* 43(100), 55(1), 73(2), 84(2), 85(9), 101(2), 102(2), 103(8), 115(1), 116(1), 144(1), 145(5), and 187 (M − OAc, 2).

Anal. Accurate mass calc. for $C_8H_{11}O_5$ ($M^+ - OAc$): 187.061. Found: 187.061.

1,2,3-Tri-O-acetyl-β-erythrofuranose (3). This product was amorphous, $[\alpha]_D$ −90.4° (*c* 1.1, chloroform); R_F 0.58 (solvent *B*); $\nu_{max}^{CCl_4}$: 1747, 1362, 1215, 1080, and 1005 cm^{-1}; *m/e* 43(100), 55(1), 73(2), 84(2), 85(9), 101(2), 102(3), 103(8), 115(1), 116(1), 127(3), 144(1), 145(6), and 187 ($M - OAc$, 3).

Anal. Accurate mass calc. for $C_8H_{11}O_5$ ($M^+ - OAc$): 187.061. Found: 187.061.

4(S),5(R)-Diacetoxy-6-(R)-acetoxymethyl-2(R)-(1,2,3-triacetoxypropyl)-1,3-dioxane (4). This compound had m.p. 99–100°, $[\alpha]_D$ +17.0° (*c* 0.9, chloroform); R_F 0.25 (solvent *B*); ν_{max}^{KBr}: 1775, 1740, 1425, 1380, 1215, 1160, 1060, and 910 cm^{-1}; *m/e* 43(100), 61(1), 73(2), 85(9), 86(1), 102(1), 103(2), 115(7), 116(4), 127(9), 128(1), 145(2), 158(2), 173(7), 187(14), 188(2), 275(2), 289(3), and 433 ($M^+ - OAc$, 0.2).

Anal. Calc. for $C_{20}H_{28}O_{14}$: C, 48.8; H, 5.7. Found: C, 48.9; H, 5.8.

4(R),5(R)-Diacetoxy-6(R)-acetoxymethyl-2(R)-(1,2,3-triacetoxypropyl)-1,3-dioxane (5). This compound was amorphous, $[\alpha]_D$ +71.3° (*c* 1.5, chloroform) R_F 0.26 (solvent *B*); $\nu_{max}^{CCl_4}$ 1740, 1360, 1220, 1005, and 600 cm^{-1}; *m/e* 43(100), 61(2), 73(3), 85(21), 103(4), 115(11), 116(6), 127(22), 128(2), 145(4), 158(3), 173(11), 187(25), 188(3), 275(2), 289(4), and 433 ($M^+ - OAc$, 0.6).

Anal. Accurate mass calc. for $C_{18}H_{25}O_{16}$ ($M^+ - OAc$): 433.135. Found: 433.135.

4(R)-Acetoxy-5(S)-(1,2-diacetoxyethyl)-2-(1,2,3-triacetoxypropyl)-1,3-dioxolane (6). This compound was amorphous, $[\alpha]_D$ +39.3° (*c* 1.8, chloroform); R_F 0.34 (solvent *B*); $\nu_{max}^{CCl_4}$: 1740, 1360, 1215, 1165, 1050, 1010, and 600 cm^{-1}; *m/e* 43(100), 57(1), 61(2), 71(3), 73(2), 85(8), 86(1), 103(4), 113(2), 115(8), 116(5), 127(5), 128(1), 145(3), 158(3), 173(17), 187(9), 275(8), 276(1), and 433 ($M^+ - OAc$, 0.6).

Anal. Accurate mass calc. for $C_{18}H_{25}O_{16}$ ($M^+ - OAc$): 433.135. Found: 433.135.

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