# THE FACILE CONVERSION OF PYRANOID GLYCALS INTO 2-DEOXY-GLYCOSIDIC ORTHOESTERS

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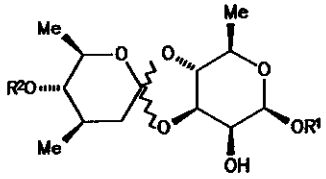
Abstract-The formation of 2-deoxy-glycosidic orthoesters involving the palladium(II) catalysed reaction of pyranoid glycals with alcohols in the presence of sodium hydrogen carbonate is described.

The known methods for the synthesis of orthoesters[1] are limited and most of these are not applicable for the construction of multifunctional compounds containing 2-deoxy-glycosidic orthoester moieties such as flambamycin (1, $R^1$,$R^2$=carbohydrate derived substituents) and everninomicin-2, members of the orthosomycin[2] group of antibiotics. Jaurand[3] described the conversion of pyranoid glycals into 2-deoxy-glycosidic spiro-orthoesters in moderate yields using a method based on a glycosyloxyselenation procedure. We now report the efficient preparation of a number of 2-deoxy-glycosidic orthoesters by the palladium(II) mediated reaction of pyranoid glycals with alcohols.

Dunkerton[4] reported that the reaction of tri-O-acetyl-D-glucal (2) with methanol and 0.5 mol equivalent of palladium(II) chloride followed by the reduction with $NaCNBH_3$ furnished 3 and 4. However, in our hands, the reaction carried out under a wide spectrum of reaction conditions and different amounts of palladium(II) chloride, furnished the same products with or without the addition of $NaCNBH_3$. This result is contrary to Dunkerton's

suggestion that the products resulted from hydride reduction of an intermediate organopalladium-complex. Futhermore, complete reaction of the starting material required the use of one mol equivalent of palladium(II) chloride. The reaction products which were identified[5] included 3, 5 and 6. However, the presence of 4 could not be detected in the reaction mixture. A more detailed study of the reaction revealed that compounds 5 and 6 arose by acid-catalysed reactions of 3, the initial product of the reaction. The addition of finely powdered $NaHCO_3$ to the reaction mixture, in the hope of preventing the above mentioned acid-catalysed decomposition of 3, had a surprising result. Under these reaction conditions the glucal 2 was converted mainly into the 2-deoxy cyclic orthoester 7. The treatment of 2 with methanol and one mol equivalent of palladium(II) acetate also furnished 7 as the main product, but at a considerably reduced rate. Finely divided palladium separated from the reaction mixture in both cases. The quantitative conversion of 2 and 8 into 7 and 9, respectively, was obtained by the reaction of the glucals with the appropriate alcohol in the presence of one mol equivalent of $(CH_3CN)_2PdCl_2$ or $(BnCN)_2PdCl_2$ and finely powdered $NaHCO_3$. Orthoester formation in these cases was considerably faster than in the case of the corresponding reactions with palladium(II) chloride. In the absence of $NaHCO_3$, the reaction of 2 with methanol and $(CH_3CN)_2PdCl_2$ furnished 3 in a quantitative yield.

The reaction of 2 with ethanol, 2-propanol or ethane-1,2-diol in the presence of $(CH_3CN)_2PdCl_2$ and $NaHCO_3$ furnished the cyclic orthoesters 10, 11 and 12 , respectively, in good to average yields. Similarly the reaction of the galactal 13 with methanol and $(CH_3CN)_2PdCl_2$ furnished the orthoester 14. The orthoester formation can be rationalised (cf. scheme 1) in terms of the cis-elimination[6] of HPdCl from an intermediate organopalladium-compmlex followed by addition of alcohol to the resulting ketene acetal. The facile addition of alcohols to ketene acetals is a well known process.[7] It is of interest to note that the reaction of the adducts, obtained by the reaction of simple alkenes with $Hg(OAc)_2$ in alcohols with



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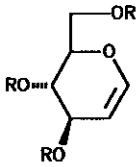
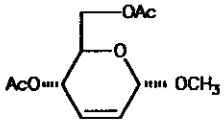


2 R = Ac
8 R = Bz
19 R = $CH_3$



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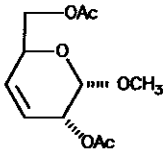

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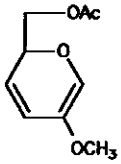

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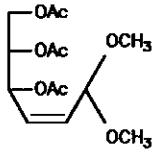

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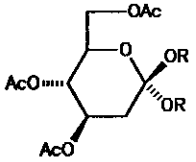
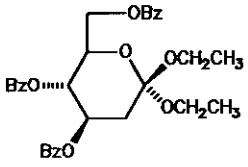


7 R = $CH_3$
10 R = $CH_2CH_3$
11 R = $CH(CH_3)_2$



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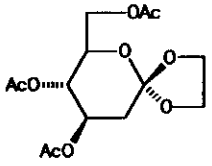

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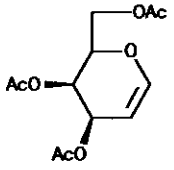

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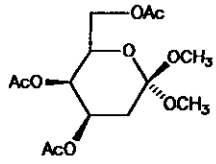

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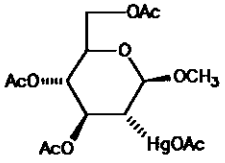

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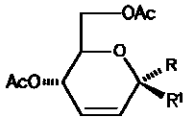
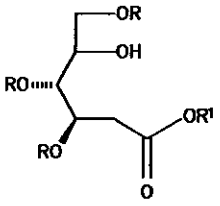
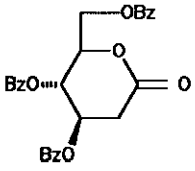


16a R = H, $R^1$ = $O^tC_4H_9$
16b R = $O^tC_4H_9$, $R^1$ = H



17 R = Bz, $R^1$ = $CH_2CH_3$



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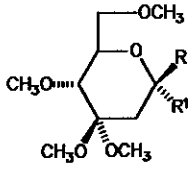
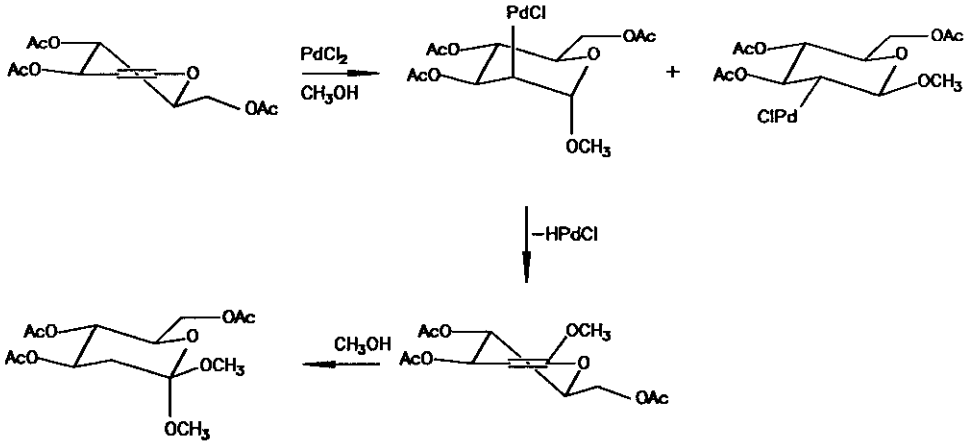


20 R = $OCH_3$, $R^1$ = H
21 R = H, $R^1$ = $OCH_3$

$Li_2PdCl_4$ is thought to involve the elimination of HPdCl from an intermediate organopalladium-complex, resulting in the formation of enol ethers.[8] However, we found[5] that treatment of Hg-substituted carbohydrate 15 (obtained[9] by the reaction of 2 with $Hg(OAc)_2$ in methanol) with this palladium reagent furnished 3 as the only product. This conversion probably involves the chloride-ion catalysed trans-elimination[10] of Pd(OAc)Cl from the organopalladium compound formed by transmetallation of 15.

The role of the $NaHCO_3$ in the orthoester reaction is uncertain. The replacement of $NaHCO_3$ by a weak organic base such as pyridine results in the complete suppression of orthoester formation. The low solubility of $NaHCO_3$




Scheme 1

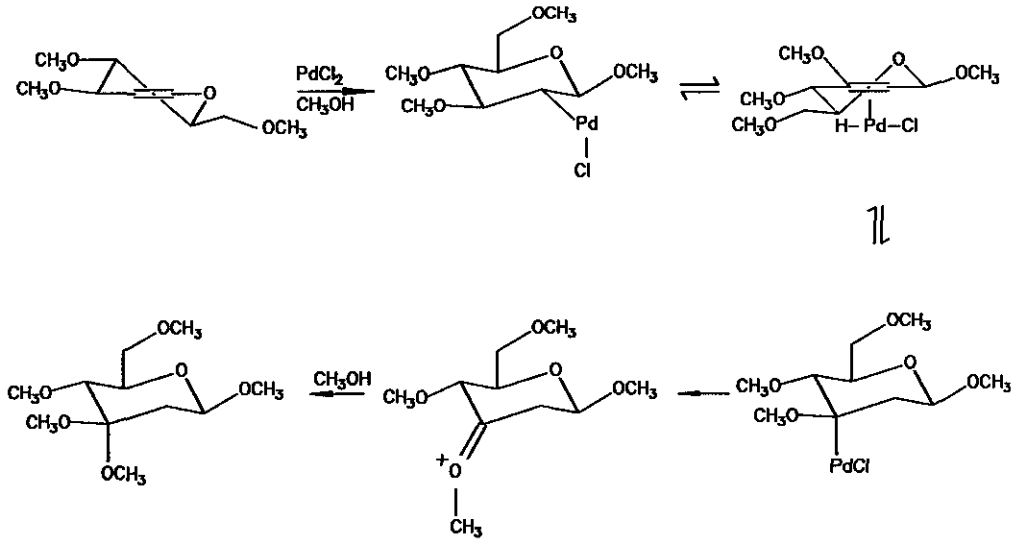
in alcohols may result in a low but replenishable (acid-base exchange reaction) concentration of alkoxide ions which, by ligand exchange, reduces the Lewis-acidity of the palladium(II)-reagent, thereby preventing competing reactions such as conversion of 2 into 3. The latter conversion may involve a Lewis acid-catalysed reaction similar to that effected by the treatment of solutions of 2 in alcohols with boron trifluoride etherate.[11] Alternatively it may involve the elimination of ClPdOAc from an organopalladium intermediate of the type shown in scheme 1. If this is the case, it must be assumed that the competition between HPdCl and ClPdOAc elimination

is entirely dependant on the reaction conditions. Structural factors may also play a significant role. This is illustrated by the finding[5] that the palladium(II) mediated reaction of 2 with t-butanol in the presence of $NaHCO_3$ furnished only the pseudoglycals 16. In this case β-elimination of HPdCl from the organopalladium intermediate may be disfavoured due to destabilising $A^{(1,2)}$-strain[12] in the transition state involving the bulky t-butoxy group.

The orthoester reaction described above requires the use of one mol equivalent of the palladium(II)-reagents. Attempts to carry out the reaction with a catalytic quantity of palladium(II)-reagent in the presence of an appropriate oxidising agent[13] were only partially successful. The reaction of 2 with methanol and 0.25 mol equivalent of $(CH_3CN)_2PdCl_2$ in the presence of 1 mol equivalent of p-quinone furnished the expected orthoester 7 in a significantly reduced yield. The use of $Na_2S_2O_8$ as oxidizing agent resulted in the formation of a complex mixture of products. The reaction of 8 with 0.1 mol equivalent of $(CH_3CN)_2PdCl_2$ and ethanol in the presence of one mol equivalent of copper(II) chloride furnished the hydroxy-ester 17. It is of interest to note that copper(II) salts also interfere in the palladium(II) mediated reaction of alkenes with alcohols to give acetals and stoichiometric amounts of palladium(II) chloride give rise to the best results.[14] Compound 17 probably resulted from copper(II)-catalysed hydrolysis of the intermediate orthoester 9. This result is in line with the finding that the acid-catalysed hydrolysis furnished 17 rather than the lactone 18. The preferred formation of 17 can be rationalised in terms of the stereoelectronic effects operating in the hydrolysis of closely related cyclic orthoesters.[15] The acid catalysed hydrolysis of 7 and 10 also resulted in ring opening.

Interestingly the reaction of tri-O-methyl-D-glucal (19) with methanol and $(CH_3CN)_2PdCl_2$ in the presence of $NaHCO_3$ furnished the protected 2-deoxy-alduloses 20 and 21 as major products. The conversion of 19 into eg. 20 can be rationalised in terms of the mechanism involving the elimination-readdi-

tion[16] of hydridopalladium chloride shown in scheme 2. However, comparison of these results with those described above indicates that the nature of the C-3 substituent (i.e. methoxy or acetoxy) directly or indirectly determines which hydrogen (H-1 or H-3) is involved in the elimination reaction. The facile conversion of 19 into 20 and 21 suggests a possible short route to 2-deoxy-alduloses, important γ-radiolysis products of carbohydrates.[16] The facile conversion of the glucal 2 into the spiro-orthoester 12 suggests that the palladium(II)-mediated reaction of glycals with 1,2-diols may provide a route to the 2-deoxy spiro-orthoester carbohydrate derived moieties of the orthosomycins. This possibility is presently under investigation.




Scheme 2

EXPERIMENTAL

All reactions were performed under positive nitrogen pressure in flamed out glass apparatus, using anhydrous solvents. Column chromatography was performed on silica gel [Kieselgel 60 (0.07-0.23 mm particle size)]. Solvent

and liquid reagent mixtures have been expressed throughout on a v/v basis. Nmr spectra were recorded on a Varian VXR 200 spectrometer with deuteriochloroform as solvent and tetramethylsilane as internal standard. Infrared spectra (chloroform solutions) were obtained using a Perkin-Elmer model 297 spectrophotometer, and optical rotations using a Perkin-Elmer model 141 polarimeter with chloroform as solvent at 20°C. Mass spectra were recorded with a Finnigan-Matt 8200 instrument at an ionisation energy of 70 eV. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. All solvent extracts and reaction mixtures were dried over sodium sulphate. Solvent extracts and reaction mixtures were filtered through celite and evaporated to dryness in vacuo below 50°C. The products obtained could be stored indefinitely at -20°C without decomposition. Dichlorobis(benzonitrile)palladium(II) and dichlorobis(acetonitrile)palladium(II) were prepared using the method described by Rockow.[17] 3,4,6-Tri-O-methyl-D-glucal (19) was prepared by hydrolysis of tri-O-acetyl-D-glucal (2) followed by alkylation with methyl iodide to furnish the pure 19 as a colourless liquid with bp 46°C at 0.01 mm Hg (Lit.,[18] 45°C at 0.03 mm Hg). 3,4,6-Tri-O-benzoyl-D-glucal (8) was prepared by hydrolysis of 2 followed by benzoylation with benzoyl chloride in the presence of pyridine to furnish the pure 8 as a colourless oil with $[\alpha]_D$ -8.1° (c=4.77).

1,5-Anhydro-3,4,6-tri-O-acetyl-2-deoxy-1,1-dimethoxy-D-glucitol (7). Tri-O-acetyl-D-glucal (100 mg, 0.367 mmol) was dissolved in methanol (1 ml). $Pd(NCCH_3)_2Cl_2$ (1 eq., 95 mg) and $NaHCO_3$ (3 eq., 123 mg) were added to the solution. After completion of the reaction (15 min) the mixture was filtered through celite and the solvent was removed in vacuo. Chromatography of the crude product (2:1-hexane:ethyl acetate) furnished the pure orthoester 7 (111 mg, 95%) as a colourless oil that crystallises spontaneously. It had mp 53-56°C; $[\alpha]_D$ +55.0° (c=3.8); $\nu_{max}$ 1740 (ester), 1230 (ether) $cm^{-1}$; $^{13}C$-nmr $\delta$ 20.76 (2xq, 2x$\underline{C}H_3COO$), 20.94 (q, $\underline{C}H_3COO$), 34.87 (t, C-2), 48.00 and 50.21 (2xq, 2x$OCH_3$), 62.26 (t, C-6), 68.80 (d, C-5), 70.10 and 70.29 (2xd, C-3 and C-4), 112.27 (s, C-1),

169.81, 170.21 and 170.79 (3xs, 3x$CH_3\underline{C}OO$); $^1$H-nmr δ 1.73 (dd, 1H, $J_{2a,2b}$=12.4 and $J_{2a,3}$=5.2 Hz, H-2a), 1.99, 2.01 and 2.05 (3xs, 9H, 3x$CH_3COO$), 2.48 (dd, 1H, $J_{2a,2b}$=12.4 and $J_{2b,3}$=11.4 Hz, H-2b), 3.22 and 3.30 (2xs, 6H, 2x$OCH_3$), 3.78-3.87 (m, 1H, H-5), 4.06 (dd, 1H, $J_{5,6b}$=2.2 and $J_{6a,6b}$=12.2 Hz, H-6b), 4.22 (dd, 1H, $J_{5,6a}$=5.2 and $J_{6a,6b}$=12.2 Hz, H-6a), 4.95-5.20 (m, 2H, H-3 and H-4); m/z 334 ($M^+$, 6), 304 ($M^+$-$CH_3OH$, 29), 261 ($M^+$-$CH_3CO$, 31). [Found $M^+$, 334.1256. Calc. for $C_{14}H_{22}O_9$, 334.1263]

Under the same conditions as described above but substituting the methanol with a) ethanol, b) isopropanol and c) ethane-1,2-diol (50% in tetrahydrofuran) the following orthoesters were prepared:

1,5-Anhydro-3,4,6-tri-O-acetyl-2-deoxy-1,1-diethoxy-D-glucitol (10). Yield 70% after 24 h. It had mp 45-48°; $[\alpha]_D$ +38.3° (c=1.8); $\nu_{max}$ 1740 (ester), 1240 (ether) $cm^{-1}$; $^{13}$C-nmr δ 14.79 and 15.06 (2xq, 2x$\underline{C}H_3CH_2O$), 20.67, 20.70 and 20.87 (3xq, 3x$\underline{C}H_3COO$), 35.91 (t, C-2), 56.05 and 58.33 (2xt, 2x$CH_3\underline{C}H_2O$), 62.35 (t, C-6), 69.03 (d, C-5), 70.15 and 70.22 (2xd, C-3 and C-4), 111.94 (s, C-1), 169.77, 170.16 and 170.73 (3xs, 3x$CH_3\underline{C}OO$); $^1$H-nmr δ 1.17 (t, 6H, J=7.1 Hz, 2x$C\underline{H}_3CH_2O$), 1.73 (dd, 1H, $J_{2a,2b}$=12.3 and $J_{2b,3}$=11.5 Hz, H-2b), 1.97, 1.99 and 2.02 (3xs, 9H, 3x$CH_3COO$), 2.45 (dd, 1H, $J_{2a,2b}$=12.3 and $J_{2a,3}$=5.2 Hz, H-2a), 3.36-3.41 (m, 4H, 2x$CH_3C\underline{H}_2O$), 3.81 (ddd, 1H, $J_{4,5}$=9.7, $J_{5,6a}$=5.0 and $J_{5,6b}$=2.4 Hz, H-5), 4.03 (dd, 1H, $J_{5,6b}$=2.4 and $J_{6a,6b}$=12.1 Hz, H-6b), 4.20 (dd, 1H, $J_{5,6a}$=5.0 and $J_{6a,6b}$=12.1 Hz, H-6a), 4.98 (dd, 1H, $J_{3,4}$=9.6 and $J_{4,5}$=9.7 Hz, H-4), 5.13 (ddd, 1H, $J_{2a,3}$=5.2, $J_{2b,3}$=11.5 and $J_{3,4}$=9.6 Hz, H-3); m/z 362 ($M^+$, 8), 317 ($M^+$-OEt, 20). [Found: $M^+$, 362.1583. Calc. for $C_{16}H_{26}O_9$, 362.1576]

1,5-Anhydro-3,4,6-tri-O-acetyl-2-deoxy-1,1-di-isopropoxy-D-glucitol (11). Yield 60% after 72 h. The compound, a colourless oil, had $[\alpha]_D$ +67.8° (c=1.7); $\nu_{max}$ 1740 (ester), 1270 (ether) $cm^{-1}$; $^{13}$C-nmr δ 20.72, 20.77 and 20.95 (3xq, 3x$\underline{C}H_3COO$), 23.54, 23.93, 24.01 and 24.10 (4xq, 2x$CH(CH_3)_2$), 37.63 (t, C-2), 62.42 (t, C-6), 66.30, 69.47, 69.97 and 70.35 (4xd, C-3, C-4, C-5 and 2xCH), 112.84 (s, C-1), 170.01, 170.14 and 170.73 (3xs, 3x$CH_3\underline{C}OO$); $^1$H-nmr δ 1.71 (d, 12H, J=6.4 Hz, 2x$CH(\underline{C}H_3)_2$), 1.83 (dd, 1H,

$J_{2a,2b}$=12.2 and $J_{2b,3}$=11.6 Hz, H-2b), 1.99, 2.02 and 2.04 (3xs, 9H, 3x$CH_3COO$), 2.28 (dd, 1H, $J_{2a,2b}$=12.2 and $J_{2a,3}$=5.4 Hz, H-2a), 3.92 (ddd, 1H, $J_{4,5}$=9.8, $J_{5,6a}$=4.9 and $J_{5,6b}$=3.0 Hz, H-5), 4.03-4.25 (m, 2H, H-6a and H-6b), 4.95 (dd, 1H, $J_{3,4}$=9.6 and $J_{4,5}$=9.8 Hz, H-4), 5.18 (ddd, $J_{2a,3}$=5.4, $J_{2b,3}$=11.4 and $J_{3,4}$=9.6 Hz, H-3); m/z 390 ($M^+$, 6), 331 ($M^+$-$OCH(CH_3)_2$, 53). [Found: $M^+$, 390.1898. Calc. for $C_{18}H_{30}O_9$, 390.1889]

1,2-O-(3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)ethanediol (12). Yield 45% after 48 h. It had mp 134-138°C; $[\alpha]_D$ +56.0° (c=0.6); $\nu_{max}$ 1700 (ester), 1240 (ether) $cm^{-1}$; $^{13}$C-nmr δ 20.72, 20.77 and 20.90 (3xq, 3x$\underline{C}H_3COO$), 36.20 (t, C-2), 62.12, 63.97 and 64.97 (3xt, $OCH_2CH_2O$ and C-6), 68.62, 70.21 and 70.33 (3xd, C-3, C-4 and C-5), 118.40 (s, C-1), 169.00, 169.50 and 170.00 (3xs, 3x$CH_3\underline{C}OO$); $^1$H-nmr δ 1.99, 2.00 and 2.04 (3xs, 9H, 3x$CH_3COO$), 2.10 (dd, 1H, $J_{2a,2b}$=12.1 and $J_{2b,3}$=11.6 Hz, H-2b), 2.27 (dd, 1H, $J_{2a,2b}$=12.1 and $J_{2a,3}$=5.5 Hz, H-2a), 3.81-4.24 (m, 7H, H-5, H-6a, H-6b and $OCH_2CH_2O$), 5.03 (dd, 1H, $J_{3,4}$=9.4 and $J_{4,5}$=9.6 Hz, H-4), 5.24 (ddd, 1H, $J_{2a,3}$=5.5, $J_{2b,3}$=11.6 and $J_{3,4}$=9.4 Hz, H-3); m/z 303 ($M^+$-CHO, 4), 289 ($M^+$-$CH_3CO$, 5), 259 ($M^+$-$CH_3CO$-$CH_2O$, 15). [Found: $M^+$-$CH_3CO$, 289.0916. Calc. for $C_{12}H_{17}O_8$, 289.0923]

1,5-Anhydro-3,4,6-tri-O-benzoyl-2-deoxy-1,1-diethoxy-D-glucitol (9). Under the same conditions as described for the preparation of 7 tri-O-benzoyl-D-glucal (8) was treated with $Pd(NCCH_3)_2Cl_2$ and $NaHCO_3$ in the presence of ethanol to give the orthoester 9 (80%) as a colourless oil with $[\alpha]_D$ +7.8° (c=1.0); $\nu_{max}$ 1725 (ester), 1275 (ether) $cm^{-1}$; $^{13}$C-nmr δ 15.00 and 15.19 (2xq, 2x$\underline{C}H_3CH_2O$), 36.31 (t, C-2), 56.35 and 58.50 (2xt, 2x$CH_3\underline{C}H_2O$), 63.59 (t, C-6), 70.02, 70.52 and 71.25 (3xd, C-3, C-4 and C-5), 112.20 (s, C-1), 128.38, 129.68, 129.79, 132.98, 133.18 and 133.33 (arom. C), 165.56, 165.80 and 166.20 (3xs, 3x$C_6H_5\underline{C}OO$); $^1$H-nmr δ 1.23 (t, 6H, J=7.1 Hz, $C\underline{H}_3CH_2O$), 1.99 (dd, 1H, $J_{2a,2b}$=11.9 and $J_{2b,3}$=10.5 Hz, H-2b), 2.08 (dd, 1H, $J_{2a,2b}$=11.9 and $J_{2a,3}$=4.7 Hz, H-2a), 3.59-3.76 (m, 4H, 2x$CH_3C\underline{H}_2O$), 4.24-4.31 (m, 1H, H-5), 4.45 (dd, 1H, $J_{5,6b}$=5.4 and $J_{6a,6b}$=12.0 Hz, H-6b), 4.58 (dd, 1H, $J_{5,6a}$=3.1 and $J_{6a,6b}$=12.0 Hz, H-6a), 5.56-5.63 (m, 2H, H-3 and H-

4), 7.30-8.03 (m, 15H, arom. H); m/z 548 ($M^+$, 4), 503 ($M^+$-$OCH_2CH_3$, 92), 426 ($M^+$-$OCOC_6H_5$, 22). [Found: $M^+$, 548.2035. Calc. for $C_{31}H_{32}O_9$, 548.2046]

1,5-Anhydro-3,4,6-tri-O-acetyl-2-deoxy-1,1-dimethoxy-D-galactol (14). Under the same conditions as described for the preparation of 7 tri-O-acetyl-D-galactal (13) was converted to the corresponding orthoester 14 (90% yield). The compound, a colourless oil, had $[\alpha]_D$ +24° (c=1.0); $\nu_{max}$ 1746 (ester) $cm^{-1}$; $^{13}$C-nmr δ 21.48 (2xq, 2x$\underline{C}H_3COO$), 21.60 (q, $\underline{C}H_3COO$), 31.52 (t, C-2), 48.83 and 50.79 (2xq, 2x$OCH_3$), 62.87 (t, C-6), 66.45, 68.80 and 70.52 (3xd, C-3, C-4 and C-5), 113.59 (s, C-1), 170.77, 171.08 and 171.27 (3xs, 3x$CH_3\underline{C}OO$); $^1$H-nmr δ 1.95, 2.09 and 2.10 (3xs, 9H, 3x$CH_3COO$), 1.89-2.17 (m, 2H, H-2a and H-2b), 3.20 and 3.32 (2xs, 6H, 2x$OCH_3$), 3.96-4.21 (m, 3H, H-5, H-6a and H-6b), 5.11 (ddd, 1H, $J_{3,4}$=3.0, $J_{2a,3}$=5.2 and $J_{2b,3}$=12.2 Hz, H-3), 5.26 (d, 1H, $J_{3,4}$=3.0 Hz, H-4); m/z 334 ($M^+$, 10), 303 ($M^+$-$OCH_3$, 100). [Found: $M^+$, 334.1255. Calc. for $C_{14}H_{22}O_9$, 334.1263]

Ethyl 3,4,6-tri-O-benzoyl-2-deoxy-D-gluconate (17). The orthoester 9 was dissolved in THF. Water (20%) and trifluoroacetic acid (0.5%) were added to the solution at 0°C. The reaction mixture was stirred for 4h. The reaction mixture was diluted with water and extracted with chloroform. Chromatography (2:1-hexane:ethyl acetate) afforded the pure 17 in a yield of 80%. The compound, a colourless oil, had $[\alpha]_D$ +56.0° (c=1.0); $\nu_{max}$ 3620 (hydroxy), 1724 (ester) $cm^{-1}$; $^{13}$C-nmr δ14.01 (q, $OCH_2\underline{C}H_3$), 36.70 (t, C-2), 61.05 and 65.24 (2xt, C-6 and $O\underline{C}H_2CH_3$), 67.67, 69.66 and 73.33 (3xd, C-3, C-4 and C-5), 128.30-133.81 (arom. C), 165.48, 166.56, 167.37 and 169.55 (4xs, 4xcarbonyl); $^1$H-nmr δ 1.13 (t, 3H, J=7.2 Hz, $OCH_2\underline{C}H_3$), 1.63 (s, 1H, OH), 2.78 (dd, 1H, $J_{2a,2b}$=16.6 and $J_{2b,3}$=5.0 Hz, H-2b), 2.88 (dd, 1H, $J_{2a,2b}$=16.6 and $J_{2a,3}$=8.7 Hz, H-2a), 4.0-4.13 (m, 3H, H-5 and $CH_3\underline{C}H_2O$), 4.32 (dd, 1H, $J_{5,6b}$=5.3 and $J_{6a,6b}$=11.7 Hz, H-6b), 4.55 (dd, 1H, $J_{5,6a}$=2.6 and $J_{6a,6b}$=11.7 Hz, H-6a), 5.56 (dd, 1H, $J_{3,4}$=9.0 and $J_{4,5}$=1.7 Hz, H-4), 6.13 (ddd, 1H, $J_{2a,3}$=8.7, $J_{2b,3}$=5.0 and $J_{3,4}$=9.0 Hz, H-3), 7.25-8.11 (m, 15H, arom. H); m/z 520 ($M^+$, 1), 475 ($M^+$-$OCH_2CH_3$, 4). [Found: $M^+$-OEt, 475.1385. Calc. for $C_{27}H_{23}O_8$, 475.1392]

Compound 17 was also obtained in quantitative yield by the reaction of 8 with ethanol in the presence of 1 eq. copper(II) triflate, 0.1 eq. of $Pd(NCCH_3)_2Cl_2$ and finely powdered $NaHCO_3$.

The conversion of tri-O-methyl-D-glucal (19) into 2-deoxy-heksos-3-uloside derivatives.

Treatment of 19 in methanol with 1 eq. of $Pd(NCCH_3)_2Cl_2$ in the presence of $NaHCO_3$ followed by chromatography of the product (1:1-hexane:ethyl acetate) furnished a ca. 1:1 mixture of two ketals in a total yield of 60%. The compounds were identified as:

a) Methyl 2-deoxy-4,6-di-O-methyl-β-D-erythro-heksos-3-ulisode dimethyl ketal (20). The compound had $[\alpha]_D$ 110.5° (c=1.5); $^{13}$C-nmr δ 38.65 (t, C-2), 48.96, 50.04, 56.52, 59.17 and 60.50 (5xq, 5x$OCH_3$), 71.57 (d, C-5), 73.81 (t, C-6), 81.79 (d, C-4), 98.94 (d, C-1), 100.11 (s, C-3); $^1$H-nmr δ 1.44 (dd, 1H, $J_{1,2b}$=9.4 and $J_{2a,2b}$=13.2 Hz, H-2b), 2.11 (dd, 1H, $J_{1,2a}$=2.2 and $J_{2a,2b}$=13.2 Hz, H-2a), 3.22, 3.29, 3.30, 3.37 and 3.41 (5xs, 5x$OCH_3$), 3.20-3.55(m, 4H, H-4, H-5, H-6a and H-6b), 4.40 (dd, 1H, $J_{1,2a}$=2.2 and $J_{1,2b}$=9.2 Hz, H-1); m/z 250 ($M^+$, 3), 219 ($M^+$-$CH_3OH$, 2).

b) Methyl 2-deoxy-4,6-di-O-methyl-α-D-erythro-heksos-3-uloside dimethyl ketal (21). The compound had $[\alpha]_D$ -7.6° (c=1.2); $^{13}$C-nmr δ 36.27 (t, C-2), 49.17, 50.19, 55.20, 58.90 and 60.03 (5xq, 5x$OCH_3$), 69.55 (d, C-5), 71.07 (t, C-6), 81.43 (d, C-4), 97.94 (d, C-1), 98.85 (s, C-3); $^1$H-nmr δ 1.74 (dd, 1H, $J_{1,2b}$=4.4 and $J_{2a,2b}$=14.4 Hz, H-2b), 2.19 (dd, 1H, $J_{1,2a}$=2.0 and $J_{2a,2b}$=14.5 Hz, H-2a), 3.30, 3.31, 3.33, 3.37 and 3.47 (5xs, 5x$OCH_3$), 3.24-3.64 (m, 3H, H-4, H-6a and H-6b), 3.92 (m, 1H, H-5), 4.73 (dd, 1H, $J_{1,2a}$=2.0 and $J_{1,2b}$=4.4 Hz, H-1); m/z 250 ($M^+$, 3), 219 ($M^+$-$CH_3OH$, 2). [Found: $M^+$, 250.1412. Calc. for $C_{11}H_{22}O_6$, 250.1416]

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