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Mendeleev Commun., 1991, **1**(**4**), 133–134

Mendeleev Communications

New Chirones Prepared from 2-Acetoxyglucal

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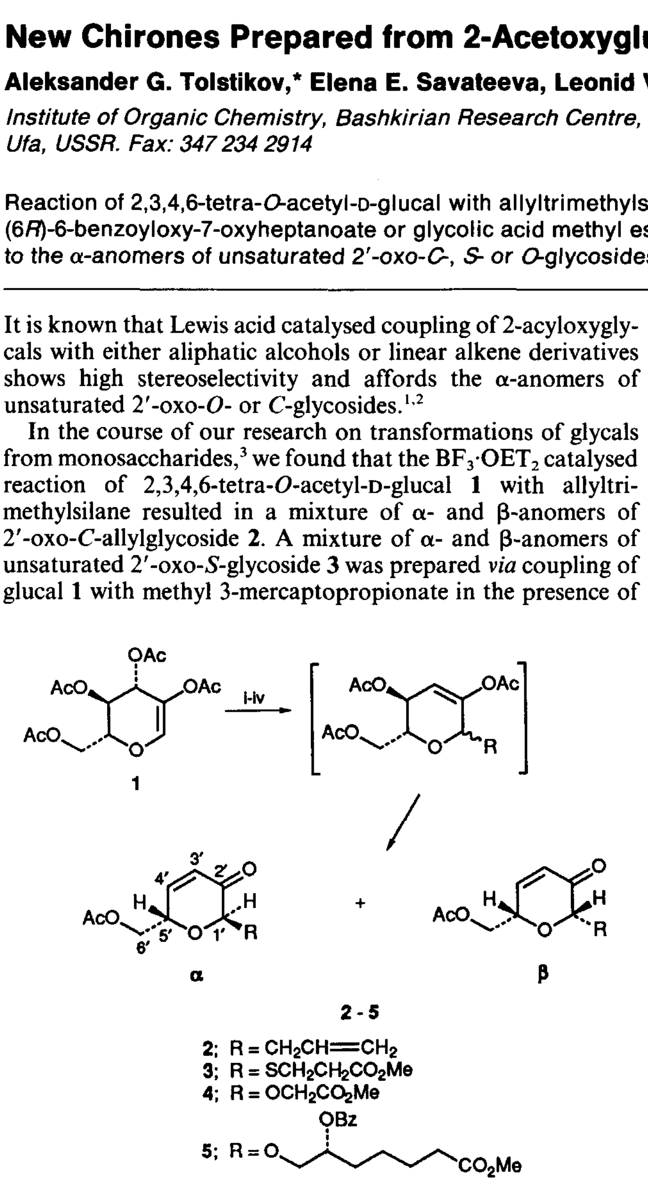
Reaction of 2,3,4,6-tetra-*O*-acetyl-D-glucal with allyltrimethylsilane, methyl 3-mercaptopropionate, methyl (6*R*)-6-benzoyloxy-7-oxyheptanoate or glycolic acid methyl ester, catalysed by boron trifluride etherate, leads preferentially to the α-anomers of unsaturated 2′-oxo-*C*-, *S*- or *O*-glycosides.

It is known that Lewis acid catalysed coupling of 2-acyloxyglycals with either aliphatic alcohols or linear alkene derivatives shows high stereoselectivity and affords the α-anomers of unsaturated 2′-oxo-*O*- or *C*-glycosides.[1,2]

In the course of our research on transformations of glycals from monosaccharides,[3] we found that the $BF_3\cdot OET_2$ catalysed reaction of 2,3,4,6-tetra-*O*-acetyl-D-glucal **1** with allyltrimethylsilane resulted in a mixture of α- and β-anomers of 2′-oxo-*C*-allylglycoside **2**. A mixture of α- and β-anomers of unsaturated 2′-oxo-*S*-glycoside **3** was prepared *via* coupling of glucal **1** with methyl 3-mercaptopropionate in the presence of $BF_3\cdot OEt_2$. Upon catalysis with $BF_3\cdot OEt_2$, reaction of **1** with methyl esters of glycolic or (6*R*)-6-benzoyloxy-7-oxyheptanoic[4] acids gives related derivatives **4** or **5** of 3,4-dideoxyhex-3-enopyranoside-2-ulose as a mixture of α- and β-isomers. In all cases stated here, the reaction proceeds *via* intermediate enol acetates (see Scheme 1). Following treatment of the reaction mixture with sodium hydrogen carbonate, the intermediates are easily hydrolysed give the target products **2–5**.†



Scheme 1 i, CH_2–$CHCH_2\ Si(Me)_3$, $BF_3\cdot OEt_2$, CH_2Cl_2, $-30 \rightarrow 0$°C, 2 h, 80%; ii, $HS\ CH_2CH_2\ CO_2Me$, $BF_3\cdot OEt_2$, PhH, $-5 \rightarrow 20$°C, 4 h, 60% iii, $HOCH_2CO_2Me$ $BF_3\cdot OEt_2$, CH_2Cl_2, $-10 \rightarrow 20$°C, 4 h, 54%; iv, (6*R*)-$HOCH(OBz)(CH_2)_4CO_2Me$, $BF_3\cdot OEt_2$, CH_2Cl_2, $-10 \rightarrow 20$°C, 6 h, 52%

According to HPLC results, the anomeric ratios **2α**:**2β**, **3α**:**3β**, **4α**:**4β** and **5α**:**5β** were 8:1, 5:3, 7:2 and 5:2, respectively. ^{13}C and ^1H NMR spectral assignments and elemental analysis data were as expected for all new compounds. Spectral analysis data for the predominant α-anomers (**2**, **3**, **5**) isolated by HPLC are given below.‡

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† The formation of intermediate enol acetates was supported by ^1H NMR spectral data, and does not conflict with previously reported results.[2]

‡ *Spectral data* for **2α**:$[\alpha]_D^{20}$ -60.1°(*c* 0.’11, $CHCl_3$; ^1H NMR ($CDCl_3$) δ 2.08 (s, 3H, Ac), 2.52 (m, 2H, $3H_2$), 4.17 (dd, 1H, $6'H_{a'}$ J_{gem} -11.74, $J_{6',5'}$ 4.05 Hz), 4.36 (dd, 1H, $6'H_{b'}J_{gem}$ -11.74, $J_{6',5'}$ 6.75 Hz), 4.45 (m, 1H, $1'H_1$), 4.67 (m, 1H, $5'H_1$), 5.12 (m, 2H, $1H_2$), 5.82 (m, 1H, $2H_1$), 6.12 (dd, 1H, $3'H_1$, $J_{3',4'}$ 10.51, $J_{3',5'}$ 2.25 Hz) 6.92 (dd, 1H, $4'H_1$, $J_{4',3'}$ 10.51, $J_{4',5'}$ 2.67 Hz).

For **3α**:$[\alpha]_D^{20}$ 98.2° (*c* 0.68, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.12 (s, 3H, Ac), 2.27 (t, 2H, $2H_2$, *J* 7.1 Hz), 2.95 (m, 2H, $3H_2$), 3.67 (s, 3H, OMe), 4.27 (dd, 1H, $6'H_{a'}$ J_{gem} -11.78, $J_{6',5'}$ 4.08 Hz), 4.38 (dd, 1H, $6'H_b$, J_{gemm} -11.78, $J_{6',5'}$ 5.64 Hz), 4.95 (m, 1H, $5'h_1$), 5.48 (s, 1H, $1'H_1$), 6.15 (dd, 1H, 3′H, $J_{3',4'}$ 10.5, $J_{3',5'}$ 2.62 Hz), 6.98 (dd, 1H, $4'H_1$, $J_{4',3'}$ 10.5, $J_{4',5'}$ 1.63 Hz).

For **5α**:$[\alpha]_D^{20}$ -12.8°(*c* 2.39, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.55–1.80 (m, 4H, $2H_2$, $3H_2$), 2.05 (s, 3H, Ac), 2.10 (m, 2H, $4H_2$), 2.32 (t, 2H, $1H_2$, *J* 6.7 Hz), 2.62 (s, 3H, OMe), 3.97 (dd, 1H $7H_a$, J_{gem} -10.9, $J_{7.6}$ 5.7 Hz), 3.80 (dd, 1H, $7H_b$, J_{gem} -10.9, $J_{7.6}$ 4.2 Hz), 4.12 (dd, 1H, $6'H_{a'}$ J_{gem} -11.7, $J_{6',5'}$ 4.5 Hz), 4.25 (dd, 1H, $6'H_b$, J_{gem} -11.7, $J_{6',5'}$, 5.2 Hz), 4.67 (m, 1H, 5′H), 4.98 (s, 1H, 1′H), 5.30 (m, 1H, $6H_1$), 6.10 (dd, 1H, 4′H, $J_{4',3'}$ 10.95, $J_{4',5'}$ 2.16 Hz, 6.85 (dd, 1H, 3′H, $J_{3',4'}$ 10.95, $J_{3',5'}$, 1.5 Hz), 7.42, 7.55, 8.00 (m, 5H, Bz).

Thus, stereoselective transformations of peracetylated 2-oxyglucal **1** afford chiral structural units of potential usefulness in the synthesis of arachidonic acid metabolites[5] and hetero-analogues thereof.

Received in USSR, 21st June 1991
Received in UK, 9th August 1991; Com. 1/03341G

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