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Glycosyl hydroperoxides

Barbara Szechner, Bartłomiej Furman, Marek Chmielewski *

Institute of Organic Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

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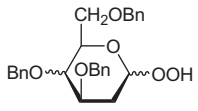
ABSTRACT

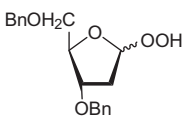
Synthesis of glycosyl hydroperoxides derived from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose and 2,3,4,6-di-*O*-isopropylidene-D-mannofuranose was performed via a Schmidt's imidate intermediate with hydrogen peroxide in an ethyl ether solution in the presence of an acid catalyst. Separation of the α- and β-anomers of the glycosyl hydroperoxides was achieved by chromatography.

1. Introduction

Recently, we have reported that the oxidation of 2-deoxysugars or their glycosides to the corresponding glycosyl hydroperoxides can be performed with hydrogen peroxide in the presence of an acid catalyst using several reaction conditions.[1,2] Glycosyl hydroperoxides derived from 2-deoxysugars 1 and 2,[1,2] similarly to those derived from 2,3-unsaturated sugars **3**,[3] are relatively stable; they can be purified by silica gel chromatography and stored for weeks in the refrigerator without visible decomposition. Easy synthesis of stable hydroperoxides from 2-deoxy- and from 2,3-unsaturated sugars has been rationalized as the readiness of these sugars to form a glycosyl cation which can add the hydrogen peroxide molecule. 2-Deoxy- and 2,3-unsaturated-sugars are known to split off easily an anomeric hydroxy- or alkoxy group.[6,7] The proportion of anomers is controlled by the kinetics of the addition. Epimerization at the anomeric carbon atom has never been observed. It is worth noting that DFT calculation of the conformational behavior of the anomeric peroxy group shows for the α-anomer hydroperoxide higher anomeric effect than for the hydroxy (alkoxy) group.[8]



1



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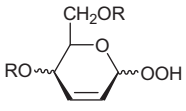

3 R: Bn, Ac, Silyl

Compounds **1**–**3** were used for enantioselective epoxidation of electrophilic olefins. The epoxidation reactions were shown to proceed with high asymmetric induction and the crucial role played by the counter ion was demonstrated.[9]

2. Results and discussion

Contrary to 2-deoxysugars, fully hydroxylated congeners eliminate an alkoxyl or hydroxyl from the anomeric center to form a glycosyl cation under conditions which cause decomposition of the hydroperoxide group, therefore formation of the glycosyl hydroperoxide, according to our standard procedure, cannot be performed. This prompted us to use sugars with an activated anomeric substituent. To this end we employed the well-known Schmidt's trichloroacetimidates **4**–**6** obtained by the known procedures.[10]

Previously used methods based on: 50% hydrogen peroxide and molybdenum trioxide, proposed by Snatzke and co-workers[4] and Taylor and co-workers,[5] hydrogen peroxide in dioxane in the presence of concentrated sulfuric acid or a solution of hydrogen peroxide in *tert*-butanol[2] when applied to imidates **4**–**6** did not provide the expected hydroperoxides. Instead, hydrolysis of the trichloroacetimidate group took place resulting in sugars with the free anomeric hydroxyl group. These results impelled us to apply a method of glycosylation with rigorously anhydrous reaction conditions. This approach proved to be fully successful.

The method based on etheral solution of hydrogen peroxide in the presence of an acid catalyst[2,5,11] led to the formation of the expected hydroperoxides. As acid catalysts we used sulfuric acid or BF_3 etherate. To remove traces of water, molecular sieves were added to the reaction mixture. Compound **4** at −30 °C in the presence of BF_3 etherate provided glucosyl hydroperoxides **7** and **8** in a ratio of about 2.5:1, respectively and in 46.1% yield, whereas in the presence of sulfuric acid, hydroperoxides **7** and **8** were formed in a ratio of about 6:1, respectively and in 40.7% yield. On the other

* Corresponding author.
E-mail address: chmiel@icho.edu.pl (M. Chmielewski).

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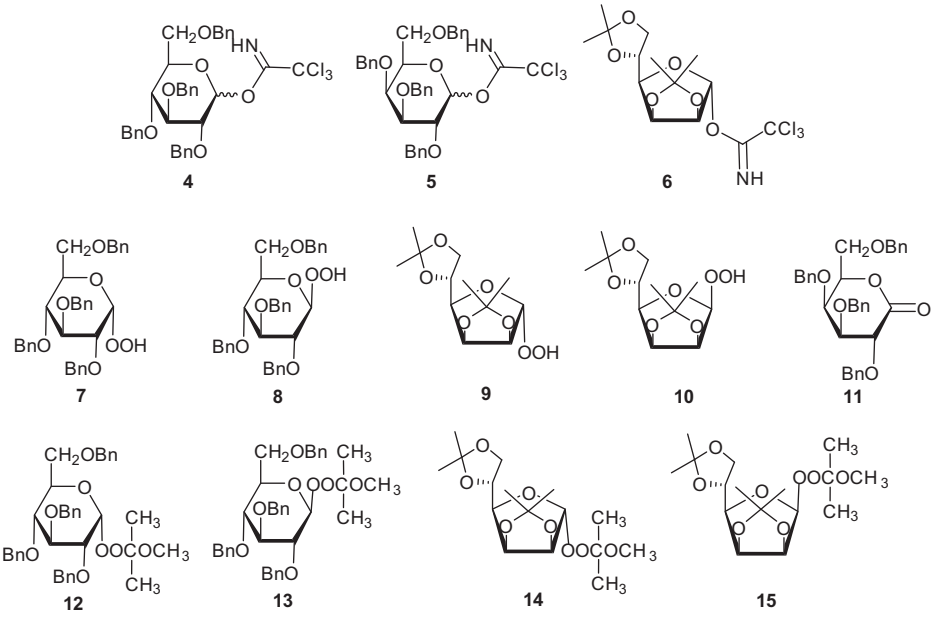

hand compound **6** at −30 °C in the presence of $BF_3{\cdot}Et_2O$ provided hydroperoxides **9** and **10** in the ratio 1:1.6, respectively and in 57.5% yield, whereas in the presence of sulfuric acid, hydroperoxides **9** and **10** were formed in the ratio of about 1:8.5, respectively in 45% yield. α- and β-Glycosyl hydroperoxides can be separated by chromatography. However, since the hydroperoxides thus obtained were contaminated with minute amounts of trichloroacetamide, for the further purification all hydroperoxides were converted into the corresponding peroxides **12**–**15** by treatment with 2-methoxypropene, following the known procedure.[2] Subsequently pure hydroperoxides **7–10** were recovered by acidic hydrolysis.[2]

Galactosyl trichloroacetimidate **5** under both reaction condition gave a complicated mixture of decomposition products in which we succeeded to identify 2,3,4,6-tetra-*O*-benzyl-D-galactonolactone (**11**).[12] This result suggests the initial formation of the glycosyl hydroperoxide which subsequently undergoes elimination of a water molecule to provide the lactone.

Proportion of the α and β anomers of 2,3;5,6-di-*O*-isopropylidenemannofuranosyl hydroperoxides **9** and **10,** with a significant predominance of the β anomer, resulted from the reaction with the use of H_2SO_4. The steric course of the reaction indicates the formation of the glycosyl hydroperoxide with the participation of a glycosyl donor, supporting S_N2-type mechanism, suggested by Schmidt and co-workers.[13]

It should be noted that formation of *tert*-butyl glycosyl peroxides has been achieved in the past from 2,3,4,6-tetra-*O*-acetylmannosyl or rhamnosyl bromides via the cyclic 1,2-peroxyorthoester stage,[14] or from 2,3,4,6-tetra-*O*-benzylglucosyl fluoride via nucleophilic substitution.[15] Other mixed peroxides were formed via the addition of glycosyl hydroperoxides to vinyl ether grouping.[2,16]

Our experiments and previous results[14,15] have shown that, contrary to 2-deoxysugars and 2,3-unsaturated sugars, the formation of glycosyl hydroperoxides derived from fully hydroxylated monosaccharides, requires activation of the anomeric center.

3. Experimental

3.1. General methods

^1H and ^{13}C NMR spectra were recorded on a Brucker DRX 500 Avance Spectrometer, using deuteriated solvents and TMS as an internal standard. Chemical shifts are reported as δ values in ppm and coupling constants are in Hertz. Infrared spectra were recorded on a FT-IR-1600 Perkin–Elmer spectrophotometer. The optical rotations were measured with a JASCO J-2000 digital polarimeter. Thin layer chromatography (TLC) was performed on aluminum sheet Silica Gel 60 F254 (20 × 20 × 0.2) from Merck. Column chromatography was carried out using Merck silica gel (230–400 mesh).

3.2. General procedure of glycosyl hydroperoxides formation

To a solution of sugar trichloroacetimidate (2 mmol) in toluene (10 mL) powdered MS 4 Å (50 mg) and a solution of H_2O_2 in diethyl ether (ca. 2 M, 10 mL) were added. The reaction mixture was cooled to −30 °C and boron trifluoride etherate (0.1 mL) or concentrated sulfuric acid (0.1 mL) was then added and the reaction was monitored by TLC. When the reaction was completed the mixture was diluted with DCM and washed with water until neutral. After drying (Na_2SO_4) and evaporation of solvents the residue was flash-chromatographed affording α- and β-anomers. To remove contamination with trichloroacetamide, products were converted into mixed peroxides (with 2-methoxypropene) from which hydroperoxides were recovered by acidic hydrolysis following our previously reported precedure.[2]

3.3. 2,3,4,6-Tetra-*O*-benzyl-α- and β-D-glucopyranosyl hydroperoxides (7 and 8)

A mixture of glucosyl trichloroacetimidates **4** in the presence of BF_3 etherate provided hydroperoxides **7** and **8** in a ratio 2.5:1 in 46.1% yield, whereas in the presence of H_2SO_4 **7** and **8** were obtained in a ratio 6:1 in 40.7% yield. Contaminated with trichloroacetamide hydroperoxides **7** and **8** were transformed into corresponding peroxides **12** and **13** which after chromatographical purification were deprotected to afford analytically pure **7** and **8**, respectively.

3.4. 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl (1-methoxy-1-methyl)ethyl peroxide (12)

$[\alpha]_D$ +87 (*c* 1.14, CCl_4); ^1H NMR (C_6D_6) δ: 7.31–7.04 (m, 20 H, aromatic), 5.67 (d, 1H, *J* 4.22 Hz, H-1), 4.98–4.90 (m, 2H, 2 PhCH),

4.73–4.66 (m, 1H, PhCH), 4.59 (d, 1H, *J* 11.5 Hz, PhCH), 4.48–4.42 (m, 2H, 2 PhCH), 4.37–4.33 (m, 3H, 2 PhCH, H-5), 4.12 (*ps* t, 1H, *J* 9.7 Hz, H-3), 3.96 (*ps* t, 1H, *J* 9.5 Hz, H-4), 3.85 (dd, 1H, $J_{6,6a}$ 10.8, $J_{5,6}$ 3.2 Hz, H-6), 3.76 (dd, 1H, $J_{6,6a}$ 10.8, $J_{5,6a}$ 1.5 Hz, H-6a), 3.66 (dd, 1H, $J_{2,3}$ 10.0, $J_{1,2}$ 4.3 Hz, H-2), 3.2 (s, 3H, OMe), 1.38 and 1.35 (2 s, 6H, 2 Me); ^{13}C NMR (C_6D_6) δ: 139.7, 139.4, 139.1, 138.7, 128.53, 128.52, 128.42, 128.39, 128.29, 128.06, 127.93, 127.89, 127.87, 127.62, 127.55, 127.44, 105.8, 99.8, 82.3, 80.6, 78.1, 75.5, 75.1, 73.5, 72.8, 71.8, 69.19, 49.20, 23.08, 23.04; IR (CCl_4) *v*: 3033, 2943, 2867, 1102, 1073 cm^{-1}; Anal. calcd for $C_{38}H_{44}O_8$: C,72.59, H, 7.05, found: C, 72.65, H, 7.10.

3.5. 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl (1-methoxy-1-methyl)ethyl peroxide (13)

$[\alpha]_D$ −1.14 (*c* 1.0, CCl_4); ^{1}H NMR (C_6D_6) δ: 7.44–7.0 (m, 20H, aromatic), 5.14 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 5.04–4.94 (m, 2H, 2 PhCH), 4.85–4.76 (m, 2H, 2 PhCH), 4.66 (m, 2H, 2 PhCH), 4.48–4.36 (m, 2H, 2 PhCH), 3.77 (*ps* t, 1H, *J* 9.5 Hz), 3.71–3.65 (m, 3H, H-5, H-6, H-6a), 3.54 (*ps* t, 1H, *J* 8.6 Hz) 3.44–3.40 (dm, $J_{1,2}$ 8.6 Hz, H-2), 3.29 (s, 3H, OMe), 1.43 and 1.35 (2 s, 6H, 2 Me); ^{13}C NMR (C_6D_6) δ: 139.45, 139.23, 139.02, 138.98, 128.52, 128.49, 128.47, 128.44, 128.29, 127.90, 127.85, 127.63, 127.61, 127.54, 106.08, 105.49, 85.36, 80.37, 77.84, 75.58, 75.43, 74.91, 74.88, 73.58, 69.14, 49.12, 23.46, 22.77; IR (CCl_4) *v*: 2904, 2869, 1213, 1072 cm^{-1}; Anal. calcd for $C_{38}H_{44}O_8$: C,72.59, H, 7.05, found: C, 72.64, H, 6.99.

3.6. 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl hydroperoxide (7)

$[\alpha]_D$ +31.3 (*c* 1.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 9.25 (s, 1H, OOH), 7.37–7.24 (m, 18 H, aromatic), 7.15–7.10 (m, 2H, aromatic), 5.32 (d, 1H, *J* 4.1 Hz, H-1), 4.92 (d, 1H, PhCH) and 4.82–4.69 (m, 4 PhCH) and 4.59–4.46 (m, 3 PhCH), 3.96–3.91 (m, 1H, H-4); 3.85 (*ps* t, 1H, *J* 9.5, H-5); 3.72–3.64 (m, 3H, H-2, H-6, H-6a), 3.56 (*ps* t, *J* 9.5, H-3); ^{13}C NMR (125 Hz, $CDCl_3$) δ: 138.5, 138.0, 137.63, 137.58, 128.51, 128.43, 128.39, 128.37, 128.05, 128.02, 127.96, 127.85, 127.74, 127.67, 101.1, 81.6, 79.0, 77.5, 75.7, 75.1, 73.6, 73.4, 71.0, 68.6; IR (film) *v*: 3484, 3282, 2913, 1453, 1047 cm^{-1}; Anal. calcd for $C_{34}H_{36}O_7$: C, 73.36, H, 6.52, found: C, 73.12, H, 6.65.

3.7. 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl hydroperoxide (8)

$[\alpha]_D$ +28 (*c* 1.13, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 9.75 (s, 1H, OOH), 7.37–7.24 (m, 18 H, aromatic), 7.15–7.10 (m, 2H, aromatic), 5.0 (d, 1H, *J* 7.1 Hz, H-1), 4.90–4.80 (m, 2H, 2 PhCH); 4.81–4.73 (m, 2H, 2 PhCH), 4.53–4.45 (m, 2H, 2 PhCH), 3.75 (m, 4H), 3.61–3.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: 138.4, 137.9, 137.8, 137.4, 128.49, 128.39, 128.36, 128.21, 128.02, 127.96, 127.93, 127.81, 127.79, 127.64, 105.9, 84.5, 79.4, 76.7, 75.4, 75.0, 74.6, 74.2, 73.5, 68.6; IR (film) *v*: 3450, 2926, 2869, 1454, 1098 cm^{-1}; Anal. calcd for $C_{34}H_{36}O_7$: C, 73.36, H, 6.52, found: C, 73.14, H, 6.39.

3.8. 2,3;5,6-Di-*O*-isopropylidene-α- and β-D-mannofuranosyl hydroperoxides (9 and 10)

A mixture of glycosyl trichloroimidates **6** in the presence of BF_3 etherate provided hydroperoxides **9** and **10** in a ratio 1:1.6 in 57% yield, whereas in the presence of H_2SO_4 **9** and **10** were obtained in a ratio 1:8.5 in 45% yield. Contaminated with trichloroacetamide hydroperoxides **9** and **10** were transformed into corresponding peroxides **14** and **15** which after chromatographical purification were deprotected to afford analytically pure **9** and **10**, respectively.

3.9. 2,3;5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl (1-methoxy-1-methyl)ethyl peroxide (14)

$[\alpha]_D$ +63.5 (*c* 1.1, CCl_4); ^{1}H NMR (C_6D_6) δ: 5.72 (s, 1 H, H-1), 4.56 (ddd,1H, $J_{4,5}$ 7.7, $J_{5,6}$ 5.7, $J_{5,6a}$ 6.4 Hz, H-5), 4.44 (d, 1H, $J_{2,3}$ 5.9 Hz, H-2), 4.38 (dd, 1H, $J_{2,3}$ 5.9, $J_{3,4}$ 3.4 Hz, H-3), 4.25 (dd, 1H, $J_{4,5}$ 7.7, $J_{3,4}$ 3.7 Hz, H-4), 4.22 (dd, 1H, $J_{6,6a}$ 8.5, $J_{5,6}$ 5.7 Hz, H-6), 4.10 (dd, 1H, $J_{6,6a}$ 8.5, $J_{5,6a}$ 6.4 Hz, H-6a), 3.21 (s, 3H, OMe), 1.43 (s, 3H, Me), 1.33 (s, 3H, Me), 1.30 (s, 6H, 2·Me), 1.27 (s, 3H, Me), 1.04 (s, 3H, Me); ^{13}C NMR (C_6D_6) δ: 112.7, 109.8, 109.0, 105.2, 83.3, 82.1, 79.9, 73.6, 67.2, 49.0, 27.0, 26.1, 25.6, 23.0, 22.9; IR (KBr) *v*: 2994, 2946, 1382, 1265, 1212 cm^{-1}; Anal. calcd for $C_{16}H_{28}O_8$: C, 55.16, H, 8.10, found: C, 55.22, H, 8.07.

3.10. 2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl (1-methoxy-1-methyl)ethyl peroxide (15)

$[\alpha]_D$ −52.5 (*c* 1.2, CCl_4); ^{1}H NMR (C_6D_6) δ: 5.16 (d, 1H, *J* 4.7 Hz, H-1), 4.63 (m, 1H, H-5), 4.26–4.22 (m, 2H, H-6, H-3), 4.17–4.11 (m, 2H, H-2, H-6a), 3.51 (dd, 1H, *J* 7.4, 4.0 Hz, H-4), 3.23 (s, 3H, OMe), 1.54, 1.47, 1.37, 1.32, 1.31, 1.14 (6·s, 18H, 6·Me); ^{13}C NMR (C_6D_6) δ: 114.0, 109.1, 105.4, 104.0, 80.3, 79.2, 78.3, 74.0, 67.3, 49.1, 27.2, 25.8, 25.7, 25.6, 23.1, 23.0; IR (CCl_4) *v*: 2988, 2941, 1381, 1371, 1214 cm^{-1}; Anal calcd for $C_{16}H_{28}O_8$: C, 55.16, H, 8.10, found: C, 55.08, H, 8.13.

3.11. 2,3;5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl hydroperoxide (9)

$[\alpha]_D$ +43 (*c* 1.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 9.19 (s, 1H, OOH), 5.44 (s, 1H, H-1), 4.78 (dd, 1H, $J_{2,3}$ 5.8, $J_{3,4}$ 3.7 Hz, H-3), 4.65 (d, 1H, $J_{2,3}$ 5.9 Hz, H-2), 4.43 (m, 1H, H-5), 4.18 dd, 1H, $J_{4,5}$ 7.0, $J_{3,4}$ 3.6 Hz, H-4), 4.12 (d, 2H, $J_{5,6}$ 5.4 Hz, H-6, H-6a), 1.48, 1.47, 1.39, 1.33 (4·s, 12H, 4·Me), ^{13}C NMR ($CDCl_3$) δ: 113.2, 110.5, 109.3, 82.6, 81.5, 79.4, 73.2, 66.4, 26.8, 25.9, 25.1, 24.5; IR ($CHCl_3$) *v*: 3519, 2940, 1383, 1375, 1069 cm^{-1}; Anal. calcd for $C_{12}H_{20}O_7$: C, 52.17, H, 7.30, found: C, 52.27, H, 7.24.

3.12. 2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl hydroperoxide (10)

$[\alpha]_D$ −19.9 (*c* 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 9.48 (s, 1H, OOH), 5.31 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.84–4.80 (m, 2H, H-6, H-6a), 4.42 (dt, 1H, $J_{5,6} = J_{5,6a}$ 6.3, $J_{4,5}$ 3.6 Hz, H-5), 4.33 (dd, 1H, $J_{2,3}$ 9.1, $J_{3,4}$ 6.3 Hz, H-3), 3.97 (dd, 1H, $J_{4,5}$ 6.2. $J_{3,4}$ 4.2 Hz, H-4), 1.55, 1.49, 1.38, 1.35 (4·s, 16H, 4·Me); ^{13}C NMR ($CDCl_3$) δ: 114.9, 109.4, 104.1, 80.4, 78.9, 78.8, 73.8, 66.7, 26.7, 25,2, 25.1, 24.9; IR ($CHCl_3$) *v*: 3522, 3337, 2991, 2940, 1384, 1374, 1069, 1037 cm^{-1}; Anal. calcd for $C_{12}H_{20}O_7$: C, 52.17, H, 7.30, found: C, 52.03, H, 7.26.

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