Oxidation of Glycals with Hydrogen Peroxide

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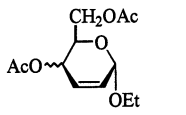
Tri-*O*-acetyl-D-glucal (**8**) treated with a mixture of hydrogen peroxide–molybdenum trioxide undergoes a Ferrier rearrangement to form 2,3-unsaturated anomeric hydroperoxides **14** and **15**.Tri-*O*-acetyl-D-galactal (**10**) and tri-*O*-benzyl-D-glucal (**9**), under the same conditions, afford the hydroperoxides in a low yield, whereas tri-*O*-benzyl-D-galactal (**11**) does not produce any unsaturated hydroperoxide. 2,3-Unsaturated anomeric hydroperoxides of α- and β-D-*erythro*- and α-D-*threo*-**19**, **-20**, and **-24**, respectively, were used for the enantioselective epoxidation of prochiral allylic alcohols **25–27** and oxidation of sulfides **28** and **29** to give stereoselectivities of up to 50% enantiomeric excess.

Recently, we reported on the oxidation of cyclic allylic acetals **1** and **2** with hydrogen peroxide in the presence of a molybdenum trioxide catalyst to the corresponding anomeric hydroperoxides **3** and **4**[1][2].



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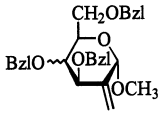

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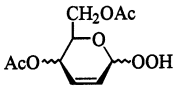

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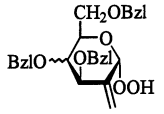

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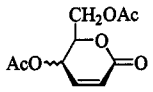
Hydroperoxides **3** and **4** are relatively stable; they can be purified on a silica-gel column and can be stored in a refrigerator without visible decomposition[1][2][3]. The unusual stability of monoperoxyacetals has been noted in the literature[4]. The hydroperoxides **3** (α-D-*threo*) and **4** have been used as chiral oxidants of allylic alcohols and prochiral sulfides with rather moderate enantioselectivities[3][5].

Treatment of **3** and **4** with an acetic anhydride−pyridine mixture leads to dehydratation of substrates affording unsaturated lactones **5** and **6**[2][3]. Lactones **5** can been obtained by an alternative method which consists of a direct oxidation of tri-*O*-acetyl-D-glucal (**8**) and tri-*O*-acetyl-D-galactal (**10**) with *m*-chloroperbenzoic acid in the presence of boron trifluoride−diethyl ether[6].



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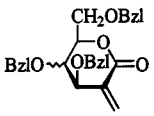

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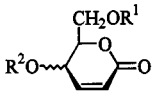

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The one-step oxidation of glycals[6] seems to be superior to stepwise transformation involving the Ferrier rearrangement of acetylated glycals to the respective 2,3-unsaturated glycosides, followed by the anomeric oxidation and dehydratation of anomeric hydroperoxides[1][2]. In the case of lactones **7** bearing different substituents at *O*-4 and *O*-6, however, our method, which uses cheap reagents, offers certain advantages over the commonly used Lichtenthaler's procedure[6]. We have successfully exploited this method in the synthesis of methyl acosaminide and daunosaminide[7].

In 1987, Fehlhaber, Snatzke and Vlahov[8] reported the direct oxidation of tri-*O*-acetyl-D-glucal (**8**) with 85% hydrogen peroxide in dioxane, in the presence of sulfuric acid as the catalyst, to the 2,3-unsaturated α-D-*erythro* hydroxyperoxide **14**. The reaction pathway which should proceed via a Ferrier rearrangement mechanism offered an attractive alternative to our method[1][2][3]. The suggestion of a ^5H_O conformation which was made without justification by the authors for the hydroperoxide **14** ($J_{4,5}$ = 0 Hz in the ^{1}H-NMR spectrum)[8], obviously made the structure assignment doubtful, and prompted us to reinvestigate the oxidation of glycals with hydrogen peroxide in the presence of acid catalysts. It should be stressed that the ^{1}H-NMR spectra of **14** and **15** point to the expected $^OH_5$ conformation for the α anomer **14** ($J_{2,4}$ = 2.0 Hz and $J_{3,4}$ = 1.6

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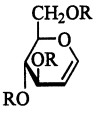
Hz – couplings of olefin protons to the neighbouring pseudoaxial proton; $J_{4,5}$ = 9.6 Hz – a pseudoaxial–axial coupling[9]) and the ^5H_O conformation for the β anomer **15** ($J_{2,4}$ = 1.1, $J_{3,4}$ = 4.1, $J_{4,5}$ = 3.3 Hz[9]). The ^5H_O conformation found for **15** is confirmed by the relatively small $J_{4,5}$ value as well as by relatively large $J_{1,2}$ and $J_{3,4}$ values[9].

Results and Discussion

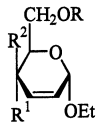
Formation of Hydroperoxides: For the present study we selected glycals **8**–**11** and unsaturated glycosides **12** and **13**. Repetition of the Fehlhaber, Snatzke and Vlahov[8] experiment using, however, only 60% hydrogen peroxide, proved the formation of the anomeric hydroperoxide from glucal **8**. A 4.5:1 mixture of α and β anomers **14** and **15**, however, was obtained. It should be pointed out that we have never observed any dependence of the ratio of α- and β-anomeric hydroperoxides upon the concentration of hydrogen peroxide[1][2][3]. This means that the mixture of **14** and **15** has been erroneously interpreted as a single α anomer in the ^5H_O conformation[8].

The oxidations of compounds **8**, **10**, **12** and **13** were performed using 45% hydrogen peroxide, whereas because of the lypophilicity of **9** and **11**, their oxidation required 60% hydrogen peroxide. All reactions were carried out in the presence of molybdenum trioxide as the acid catalyst.



8: R = Ac
9: R = Bzl

10: R = Ac
11: R = Bzl

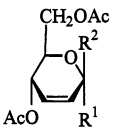


12: R^1 = OBzl, R^2 = H
13: R^1 = H, R^2 = OBzl

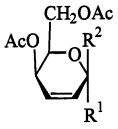
The oxidation of glucal **8** gave a 2:1 mixture of α and β anomers **14** and **15** in 52% yield which was lower than that observed by us for the oxidation of the respective 2,3-unsaturated α-D-*erythro* glycoside **1a**[2]. The mixture of **14** and **15** was separated and the ^{1}H-NMR data of pure anomeric hydroperoxides agreed fully with those previously reported by us[1][2]. Tri-*O*-acetyl-D-galactal (**10**) which is known to give a lower yield for the Ferrier rearrangement[10] under the same conditions, afforded a mixture of three hydroperoxides: α- and β-D-*threo* **16**[2] and **17**[2] and saturated hydroperoxide α-D-*lyxo* **18** in total 28% yield only. The mixture of hydroperoxides **16** and **17** was not separated into pure components.

As a result of the poor leaving-group character of the *C*-3 benzyloxy substituent, the oxidation of glucal **9** gave unsaturated α-D-*erythro* hydroperoxide **19** (45%) and saturated α-D-*arabino* hydroperoxide **21** (24%). Galactal **11** under the same conditions did not produce any unsaturated hydroperoxide, but saturated α-D-*lyxo* hydroperoxide **22** (36%) and hemiacetal **23**[11] (6%) were formed instead.

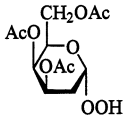
The oxidation of glycoside **12** led to the formation of two anomers **19** and **20** in 60% yield; following chromatographic separation, the ratioof the two anomers was found to be



14: R^1 = OOH, R^2 = H
15: R^1 = H, R^2 = OOH



16: R^1 = OOH, R^2 = H
17: R^1 = H, R^2 = OOH



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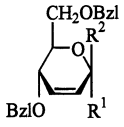
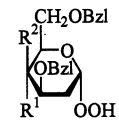
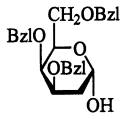


19: R^1 = OOH, R^2 = H
20: R^1 = H, R^2 = OOH

about 4:1, respectively. Glycoside **13** produced only α-D-*threo* anomer **24** (70%). The conformational behaviour of **19**, **20**, and **24** reflects the large anomeric effect operating in 2,3-unsaturated anomeric hydroperoxides[2]. The α-erythro **19** and α-threo **24** hydroperoxides occur exclusively in the $^OH_5$ conformation whereas the β-erythro hydroperoxide **20** occurs in the inverted ^5H_O conformation (relatively large $J_{1,2}$ and $J_{3,4}$, and small $J_{4,5}$ coupling constants).



21: R^1 = OBzl, R^2 = H
22: R^1 = H, R^2 = OBzl



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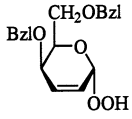

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The dehydratation of the mixture **19** and **20** and hydroperoxide **24** with acetic anhydride–pyridine according to a previously reported procedure[2][3] afforded known lactones **7**[12] (*erythro*, $R^1 = R^2$ = Bzl) and **7**[12] (*threo*, $R^1 = R^2$ = Bzl) in about 80% yield.

Enantioselective Oxidation: Although our previous experiments with the use of anomeric hydroperoxides as chiral oxidants provided moderate enantioselectivities, we decided to examine compounds **19**, **20**, and **24** as oxidants of allylic alcohols **25**–**27** and sulfides **28** and **29**. Having for the first time both anomeric *erythro* hydroperoxides **19** and **20,** we decided that the application of these compounds in the oxidation experiment could be interesting.

Olefins **25**–**27** were epoxidized by **19**, **20** and **24** in the presence of Ti(O*i*Pr)$_4$ in CH_2Cl_2. After a complete conversion of the hydroperoxide, the enantiomeric excess (e. e.) of the epoxy alcohol formed was estimated in the reaction mixture by gas chromatography on cyclodextrin chiral stationary phases[5][13]. The results obtained for three allylic alcohols **25**–**27** are summarized in Table 1.

We found similar optical inductions for all three hydroperoxides. The values of e. e. obtained now are higher than those reported by us in asymmetric oxidations with other glycosyl hydroperoxides[3][5]. The e. e. in the oxidation of **25** with **19** and **24** are particularly interesting because they represent, so far, the best outcome obtained when a chiral hydroperoxide was used as the epoxidation reagent.

Table 1. Enantioselective epoxidation of prochiral allylic alcohols (**25**−**27**) with optically active hydroperoxides **19**, **20** and **24**

Oxidant	Allylic alcohol	Epoxy alcohol		
		T (°C)	e. e.[a] (%)	Absolute configuration
19	3-methyl-2-buten-1-ol (**25**)	0	52	(+)-(*R*)
19	2-methyl-3-buten-2-ol (**26**)	r. t.	5	(+)-(*R*)
19	(*E*)-α-phenylcinnamyl alcohol (**27**)	0	9	(2*R*, 3*S*)
20	3-methyl-2-buten-1-ol (**25**)	0	44	(−)-(*S*)
20	2-methyl-3-buten-2-ol (**26**)	r. t.	13	(−)-(*S*)
20	(*E*)-α-phenylcinnamyl alcohol (**27**)	0	12	(2*S*, 3*R*)
24	3-methyl-2-buten-1-ol (**25**)	−20	50	(+)-(*R*)
24	2-methyl-3-buten-2-ol (**26**)	r. t.	12	(−)-(*S*)
24	(*E*)-α-phenylcinnamyl alcohol (**27**)	−20	12	(2*R*, 3*S*)

[a] Determined by GLC on cyclodextrin phases.

Table 2. Asymmetric oxidation of prochiral sulfides with optically active hydroperoxides **19**, **20** and **24**

Oxidant	Sulfide	Sulfoxide		
		T (°C)	e. e.[a] (%)	Absolute configuration
19	methyl phenyl sulfide (**28**)	0	18	(+)-(*R*)
19	methyl *p*-tolyl sulfide (**29**)	0	14	(+)-(*R*)
20	methyl phenyl sulfide (**28**)	0	40	(−)-(*S*)
20	methyl *p*-tolyl sulfide (**29**)	0	15	(−)-(*S*)
24	methyl phenyl sulfide (**28**)	−20	20	(+)-(*R*)
24	methyl *p*-tolyl sulfide (**29**)	−20	12	(+)-(*R*)

[a] Determined by GLC on cyclodextrin phases.

It is noteworthy that 4,6-di-*O*-benzylated α-D-*threo* hydroperoxide **24** with the olefin **26** displays asymmetric induction in the opposite sense and a lower e. e. than the corresponding 4,6-di-*O*-acetyl derivative **16** in the earlier investigation[5]. As anticipated, the configuration of the anomeric carbon atom to which the hydroperoxy group is bound helps to decide the direction of the asymmetric induction (compare the results found for **19** and **20**).

The asymmetric oxidation of methyl phenyl sulfide **28** and methyl *p*-tolyl sulfide **29** gave the corresponding sulfoxides in lower e. e. than those reported by us for hydroperoxides **4**[3]. The remarkable result is, however, observed for the oxidation of methyl phenyl sulfide with β-D-*erythro* hydroperoxide **20**. As for the epoxidation of olefines **25**−**27**, the oxidation of sulfides **28** and **29** by α and β anomers **19** and **20** leads to the opposite absolute configuration. The results obtained for the oxidation of sulfides **28** and **29** are summarized in Table 2.

In summary, we have demonstrated that not only can 2,3-unsaturated glycosides be oxidized using hydrogen peroxide in the presence of molybdenium trioxide to form anomeric hydroperoxides, but to some extent glycals can, as well. In the case of benzylated galactal, however, a Ferrier rearrangement does not take place and a minute amount of saturated hydroperoxide is formed. Chromatographically pure 2,3-unsaturated glycosyl hydroperoxides used as chiral oxidants gave moderate e. e., although they are better than those observed by us for other glycosyl hydroperoxides[3][5].

Experimental Section

General: All ^{1}H- and ^{13}C-NMR spectra were recorded as solutions in $CDCl_3$ (with TMS as an internal standard) at 25°C with a Varian Gemini 200 and Bruker AM 500 spectrometers. − IR spectra were taken with a Perkin-Elmer FTIR-1600 spectrophotometer. − Optical rotations were measured with a JASCO Dip-360 digital polarimeter at a temperature of 20°C. − Mass spectra were recorded with a AMD 604 mass spectrometer. − Column chromatography was performed on Merck Kieselgel (230−400 mesh). − Melting points: uncorrected values. − Anomeric hydroperoxides obtained by us displayed inconsistent elemental analyses therefore for all of them we provided molecular ion peaks by the LSIMS mass spectrometry technique.

General Procedure for Oxidation of Unsaturated Glycosides with H_2O_2: The suspension of unsaturated glycoside or glycal (**8**−**13**, 8.0 mmol) and molybdenum trioxide (0.12 g) in aqueous 45% hydrogen peroxide (50 ml) for compounds **8**, **10**, **12** and **13**, or in 60% hydrogen peroxide for **9** and **11**, was stirred at room temp. until the substrate disappeared (1 to 7 d); the progress of the reaction was monitored by TLC. Subsequently, water (100 ml) was added and the mixture was extracted with dichloromethane (3 × 60 ml). The combined extracts were washed four times with water, then with brine, dried with $MgSO_4$, and evaporated at room temp. The post-reaction mixture was separated on silica gel by flash chromatography using hexane/*tert*-butyl methyl ether 65:35 v/v as an eluent to afford hydroperoxides **14**−**22** and **24**, respectively.

4,6-Di-O-acetyl-2,3-dideoxy-α- and -β-D-erythro-hex-2-enopyranosyl Hydroperoxide (**14**) *and* (**15**): Compounds **14** and **15**, prepared previously as a mixture[2], were obtained by the oxidation of glucal **8** and separated on silica gel by flash chromatography using hexane/*tert*-butyl methyl ether 65:35 v/v as an eluent in total 52% yield. Compound **14** (35%), m. p. 91−93°C. − $[\alpha]_D$ = +13.7 (*c* = 1.3, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3397 cm^{-1}, 1742, 1660, 1434, 1371 and 1236. − ^{1}H NMR ($CDCl_3$): δ = 2.10 (s, 3 H, Ac) and 2.12 (s, 3 H, Ac), 4.14 (m, 1 H, 5-H), 4.19−4.35 (m, 2 H, 6-H, 6′-H), 5.36 (dq, 1 H, $J_{1,4}$ = 1.4, $J_{2,4}$ = 2.0, $J_{3,4}$ = 1.6, $J_{4,5}$ = 9.6 Hz, 4-H), 5.54 (m, 1-H), 5.78 (ddd, 1 H, $J_{1,2}$ = 2.8, $J_{2,3}$ = 10.2 Hz, 2-H), 6.06 (dt,1 H, $J_{1,3}$ = 1.6 Hz, 3-H), 9.12 (s, 1 H, −OOH). − ^{1}H

NMR (C_6D_6): δ = 1.66, 1.72 (2s, 6 H, 2Ac), 4.14 (ddd, 1 H, $J_{4,5}$ = 9.6, $J_{5,6}$ = 4.2, $J_{5,6'}$ = 2.8 Hz, 5-H), 4.28 (dd, 1 H, $J_{6,6'}$ = 12.2 Hz, 6-H), 4.35 (dd, 1 H, 6′-H), 5.40 (ddd, 1-H, $J_{1,2}$ = 2.8, $J_{2,3}$ = 10.1, $J_{2,4}$ = 2.0 Hz, 2-H), 5.43 (m, 1 H, 1-H), 5.48 (m, 1 H, $J_{1,4}$ = 1.5, $J_{3,4}$ = 1.8 Hz, 4-H), 5.76 (m,1 H, $J_{1,3}$ = 1.3 Hz, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 62.81, 64.94, 67.47, 76.75, 77.00, 77.25, 98.47 (C-1, $J_{C1,H1}$ = 176.1 Hz), 123.04, 132.94. − MS (LSIMS); *m/z*: 269 [M + Na]$^+$. Compound **15** (17%): Oil. − $[\alpha]_D$ = +11.4 (*c* = 1.6, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3379 cm^{-1}, 1738, 1434, 1372 and 1236. − ^{1}H NMR ($CDCl_3$): δ = 2.10 (s, 3 H, Ac) and 2.13 (s, 3 H, Ac), 4.15−4.43 (m, 3 H, 5-H,6-H,6′-H), 5.12 (m, 1 H, $J_{4,5}$ = 3.5 Hz, 4-H), 5.60 (br. s, 1 H, 1-H), 5.98 (ddd, 1 H, $J_{1,2}$ = 2.4, $J_{2,3}$ = 10.3, $J_{2,4}$ = 1.1 Hz, 2-H), 6.15 (ddd, 1 H, $J_{1,3}$ = 1.6, $J_{3.4}$ = 4.1 Hz, 3-H), 9.7 (s, 1 H, −OOH). − ^{1}H NMR (C_6D_6): δ = 1.60, 1.69 (2s, 6 H, 2Ac), 4.13 (m, 1 H, 5-H), 4.18 (dd, 1 H, $J_{5,6}$ = 5.6, $J_{6,6'}$ = 11.4 Hz, 6-H), 4.40 (dd. 1 H, $J_{5,6'}$ = 6.4 Hz, 6′-H), 5.09 (m, 1 H, $J_{1,4}$ = 1.1, $J_{2,4}$ = 1.3, $J_{3,4}$ = 4.2, $J_{4,5}$ = 3.6 Hz, 4-H), 5.48 (ddd, 1 H, $J_{1,2}$ = 2.5, $J_{1,3}$ = 1.8 Hz, 1-H), 5.56 (ddd, 1 H, $J_{2,3}$ = 10.3 Hz, 2-H), 5.76 (m, 1 H, $J_{3,5}$ = 0.4 Hz, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 63.14, 63.89, 73.14, 76.74, 76.99, 77.25, 97.65 (C-1, $J_{C1,H1}$ = 173.9 Hz), 125.80, 128.19. − MS (LSIMS); *m/z*: 269 [M + Na]$^+$.

4,6-Di-O-acetyl-2,3-dideoxy-α- and -β-D-threo-hex-2-enopyranosyl Hydroperoxide (**16**) *and* (**17**), *and 3,4,6-Tri-O-acetyl-2-deoxy-α-D-lyxo-hexopyranosyl Hydroperoxide* (**18**): Compounds **16, 17** and **18** were obtained from galactal **10** according to the procedure described above. The mixture was separated on the silica gel by flash chromatography using hexane/*tert*-butyl methyl ether 65:35 v/v as an eluent to give known 20:1 mixture of **16** and **17** (12%) which was not separated further[2], and **18** (16%). Compound **18**: Oil. − $[\alpha]_D$ = +9.8 (*c* = 1.14, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3396 cm^{-1}, 1746, 1438, 1370, 1240. − ^{1}H NMR ($CDCl_3$): δ = 1.99, 2.0 and 2.15 (3 s, 9 H, 3 Ac), 1.88−2.20 (m, 2 H, 2-H), 4.05−4.35 (m, 3 H, 5-H, 6-H, 6′-H), 5.11 (ddd, 1 H, $J_{3,4}$ = 3.0, $J_{2,3}$ = 5.3, $J_{2',3}$ = 12.5 Hz, 3-H), 5.35 (br. d, 4-H), 5.47 (d, 1 H, $J_{1,2}$ = 4.06 Hz, 1-H), 8.95 (s, 1 H, −OOH). − ^{13}C NMR ($CDCl_3$): δ = 61.91, 62.46, 65.58, 66.06, 66.90, 76.36, 77.0, 77.63, 91.99, 100.96. − MS (LSIMS); *m/z*: 329 [M + Na]$^+$.

4,6-Di-O-benzyl-2,3-dideoxy-α- and -β-D-erythro-hex-2-enopyranosyl Hydroperoxide (**19**) *and* (**20**): Compounds **19** and **20** were obtained from glycoside **12** in 60% yield. Anomers were separated on the silica gel by flash chromatography using hexane/*tert*-butyl methyl ether 65:35 v/v as an eluent.

19 (48%): M. p. 87−88°C. − $[\alpha]_D$ = +115.0 (*c* = 1.36, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3462 cm^{-1}, 3245, 2873, 1659, 1494 and 1453. − ^{1}H NMR ($CDCl_3$): δ = 3.67 (m, 1 H, $J_{6,6'}$ = 10.4 Hz, 6′-H), 3.79 (m, 1 H, 6-H), 4.03 (m, 2 H, 4-H, 5-H), 4.45, 4.60 (2 d, 2 H, *J* = 11.5 Hz, Bzl), 4.56, 4.62 (2 d, 2 H, *J* = 11.9 Hz, Bzl), 4.48 (br. s, 1 H, 1-H), 5.71 (m, 1 H, $J_{2,3}$ = 10.3 Hz, 2-H), 6.20 (d, 1 H, 3-H), 9.75 (s, 1 H, −OOH). − ^{1}H NMR (C_6D_6): δ = 3.59 (dd, 1 H, $J_{5,6}$ = 6.3, $J_{6,6'}$ = 10.5 Hz, 6-H), 3.73 (dd, $J_{5,6'}$ = 1.8 Hz, 1 H, 6′-H), 3.81 (m, 1 H, $J_{1,4}$ = 1.6, $J_{2,4}$ = 1.9, $J_{3,4}$ = 2.0, $J_{4,5}$ = 9.4 Hz, 4-H), 4.13, 4.29 (2 d, 2 H, *J* = 11.8 Hz, Bzl), 4.25 (ddd, 1 H, 5-H), 4.34, 4.42 (2 d, 2 H, *J* = 12.2 Hz, Bzl), 5.45 (ddd, 1 H, $J_{1,2}$ = 2.8, $J_{2,3}$ = 10.3, 2-H), 5.55 (m, 1 H, 1-H), 5.82 (m, 1-H, $J_{1,3}$ = 1.2 Hz, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 69.34, 69.80, 70.22, 71.14, 73.6, 76.74, 76.99, 77.25, 98.66 (C-1), 122.11. − MS (LSIMS); *m/z*: 365 [M + Na]$^+$.

20 (12%): Oil. − $[\alpha]_D$ = +107.6 (*c* = 1.19, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3341 cm^{-1}, 3030, 2868, 1734, 1496 and 1453. − ^{1}H NMR ($CDCl_3$): δ = 3.51 (dd, 1 H, $J_{5,6}$ = 4.7, $J_{6,6'}$ = 10.2 Hz, 6-H), 3.70 (m, 1 H, 4-H), 3.78 (dd, 1 H, $J_{5,6'}$ = 9.4 Hz, 6′-H), 4.35 (m, 1 H, 5-H), 4.54, 4.58 (2 d, 2 H, *J* = 11.7 Hz, Bzl), 4.59 (s, 2 H, Bzl), 5.54 (br. s, 1 H, 1-H), 5.94 (ddd, 1 H, $J_{2,4}$ = 1.3, $J_{1,2}$ = 2.9, $J_{2,3}$ = 10.3 Hz, 2-H), 6.16 (ddq, 1 H, $J_{3,4}$ = 4.3, $J_{2,3}$ = 10.3 Hz, 3-H), 10.07 (s, 1 H, −OOH). − ^{1}H NMR (C_6D_6): δ = 3.52 (dd, 1 H, $J_{5,6}$ = 4.5, $J_{6,6'}$ = 10.2 Hz, 6-H), 3.73 (m, 1-H, 1/2 W = 9.5 Hz, H-4), 3.78 (dd, 1 H, $J_{5,6'}$ = 9.0 Hz, 6′-H), 4.31 (ddd, 1 H, $J_{4,5}$ = 3.0 Hz, 5-H), 5.54 (m, 1 H, 1-H), 5.93 (ddd, 1 H, $J_{1,2}$ = 2.8, $J_{2,4}$ = 1.4, $J_{2,3}$ = 10.3 Hz, 2-H), 6.17 (m, 1-H, $J_{3,4}$ = 4.1 Hz, H-3), 10.07 (s, 1 H, −OOH). − ^{13}C NMR ($CDCl_3$): δ = 67.38, 70.4, 70.49, 73.18, 73.6, 76.74, 76.99, 77.25, 96.89 (C-1), 124.6. − MS (LSIMS); *m/z*: 365 [M + Na]$^+$.

4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl Hydroperoxide (**19**) *and 3,4,6-Tri-O-benzyl-2-deoxy-α-D-arabino-hexopyranosyl Hydroperoxide* (**21**): Compounds **19** and **21** were obtained from glucal **9** and separated on the silica gel by flash chromatography using hexane/*tert*-butyl methyl ether 65:35 v/v as an eluent to afford **19** (45%) and **21** (24%).

21, (24%): Oil. − $[\alpha]_D$ = +65.1 (*c* = 1.7, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3331 cm^{-1}, 3030, 2866, 1496, 1453, 1364. − ^{1}H NMR ($CDCl_3$): δ = 1.78 (ddd, 1 H, $J_{1,2}$ = 4.7, $J_{2,3}$ = 11.5, $J_{2,2'}$ = 13.8 Hz, 2-H), 2.27 (ddd, 1 H, $J_{1,2'}$ = 1.4, $J_{2',3}$ = 5.1, $J_{2,2'}$ = 13.8 Hz, 2′-H), 3.51 (dd, 1 H, $J_{5,6}$ = 8.6, $J_{6,6'}$ = 9.6 Hz, 6-H), 3.63−3.95 (m, 3 H, 4-H, 5-H, 6′-H), 4.51, 4.87 (2 d, 2 H, *J* = 10.9 Hz, Bzl), 4.54, 4.60 (2 d, 2 H, *J* = 12.0 Hz, Bzl), 4.59, 4.62 (2 d, 2 H, *J* = 12.3 Hz, Bzl), 5.36 (br. d, 1 H, 1-H), 9.25 (s, 1 H, −OOH). − ^{13}C NMR ($CDCl_3$): δ = 69.42, 71.48, 71.78, 73.63, 74.84, 76.36, 76.99, 77.63, 101.52, 127.66, 127.9, 128.0. − MS (LSIMS); *m/z*: 473 [M + Na]$^+$.

3,4,6-Tri-O-benzyl-2-deoxy-α-D-lyxo-hexopyranosyl Hydroperoxide (**22**) *and 3,4,6-Tri-O-benzyl-2-deoxy-α-D-lyxo-hexopyranose* (**23**): Compounds **22** and **23** were obtained from galactal **11** according to the procedure described above. The mixture of products was separated on the silica gel by flash chromatography using hexane/*tert*-butyl methyl ether 65:35 v/v as an eluent.

22 (36%): Oil. − $[\alpha]_D$ = + 4.3 (*c* = 1.3, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3346 cm^{-1}, 1605, 1496, 1453, 1362. − ^{1}H NMR ($CDCl_3$): δ = 2.00 (br. dd, 1 H, $J_{1,2}$ = 4.9, $J_{2,2'}$ = 13.4 Hz, 2-H), 2.26 (ddd,1 H, $J_{1,2}$ = 4.7, $J_{2',3}$ = 12.4 Hz, 2′-H), 3.45 (dd, 1 H, $J_{5,6}$ = 5.4, $J_{6,6'}$ = 9.6 Hz, 6-H), 3.64 (dd, 1 H, $J_{5,6'}$ = 6.8 Hz, 6′-H), 3.69 (m, 1 H, 3-H), 3.80 (m, 1 H, 4-H), 3.88 (t, 1 H, 5-H), 4.40, 4.51 (2 d, 2 H, *J* = 11.7 Hz, Bzl), 4.54 (s, 2 H, Bzl), 4.58, 4.90 (2 d, 2 H, *J* = 11.7 Hz, Bzl), 5.36 (d, 1 H, $J_{1,2'}$ = 4.1 Hz, 1-H), 8.95 (s, 1 H, −OOH). − ^{13}C NMR ($CDCl_3$): δ = 70.42, 70.50, 70.84, 72.77, 73.69, 73.91, 74.17, 76.36, 77.00, 77.63, 102.136, 127.28, 127.65. − MS (LSIMS); *m/z*: 473 [M + Na]$^+$.

23 (6%): Spectral and analytical data described in ref.[11].

4,6-Di-O-benzyl-2,3-dideoxy-α-D-threo-hex-2-enopyranosyl Hydroperoxide (**24**): Compound **24** was obtained from glycoside **13** according to the general procedure. The product was isolated on the silica gel by flash chromatography using hexane/*tert*-butyl methyl ether 65:35 v/v as an eluent.

24 (70%): Oil. − $[\alpha]_D$ = −115.9 (*c* = 1.0, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3326 cm^{-1}, 3030, 2870, 1734, 1496 and 1453. − ^{1}H NMR ($CDCl_3$): δ = 3.65 (dd,1 H, $J_{4,5}$ = 2.7, $J_{3,4}$ = 5.3 Hz, 4-H), 3.74 (dd, 2 H, $J_{5,6}$ = 4.9, $J_{6,6'}$ = 10.1 Hz, 6-H), 3.83 (dd, 1 H, $J_{5,6'}$ = 7.2 Hz, 6′-H), 4.27 (m, 1 H, 5-H), 4.49−4.60 (2 d, 2 H, *J* = 11.8 Hz, Bzl), 4.55, 4.64 (2 d, 2 H, *J* = 12.0 Hz, Bzl), 5.53 (dd, 1 H, $J_{1,2}$ = 3.1, $J_{1,3}$ = 1.3 Hz, 1-H), 5.91 (dd, 1 H, $J_{2,3}$ = 10.2 Hz, 2-H), 6.21 (ddd, 1 H, 3-H), 10.38 (s, 1 H, −OOH). − ^{13}C NMR ($CDCl_3$): δ = 66.78, 69.79, 70.25, 70.93, 73.65, 76.36, 77.00, 77.63, 98.27 (C-1), 125.4. − MS (LSIMS); *m/z*: 365 [M + Na]$^+$.

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