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High yielding diastereoselective *syn*-dihydroxylation of protected HBO: an access to D-(+)-ribo-1,4-lactone and 5-O-protected analogues

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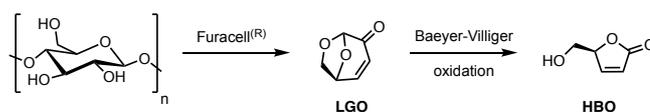
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Abstract: A diastereoselective chemo-enzymatic synthetic pathway to D-(+)-ribo-1,4-lactone, a versatile chiral sugar derivative widely used for the synthesis of various natural products, has been designed from cellulose-based levoglucosenone (**LGO**). This route involves a sustainable Baeyer-Villiger oxidation of **LGO** to produce enantiopure (S)- γ -hydroxymethyl- α,β -butenolide (**HBO**) that is further functionalized with various protecting groups to provide 5-O-protected D-(+)-ribo-1,4-lactones. The resulting 5-O-protected lactones then undergo a diastereoselective and high yielding *syn*-dihydroxylation of the α,β -unsaturated lactone moiety followed by a deprotection step to give D-(+)-ribo-1,4-lactone. Through this 4-step synthetic route from **LGO**, D-(+)-ribo-1,4-lactone is obtained with d.r. varying from 82:18 to 97:3 and in overall yields between 32 and 41% depending on the protecting group used. Moreover, valuable synthetic intermediates 5-O-*tert*-butyldimethylsilyl-, 5-O-*tert*-butyldiphenylsilyl- as well as 5-O-benzyl-ribo-1,4-lactones are obtained in 3 steps from **LGO** in 58, 61 and 40%, respectively.

Introduction

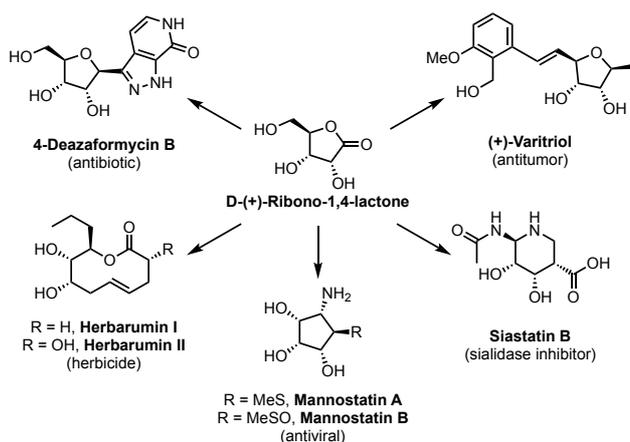
In a context of increasing scarcity and price of fossil resources, and also more drastic regulations such as the REACH regulation, the use of alternative renewable resources has raised a growing interest in the scientific community. The production of valuable chemicals from renewable biomass has been largely developed in the last decades, with the aim of offering new sustainable efficient procedures as alternative routes to traditional synthetic pathways.¹ In this context, an interesting alternative is the valorization of lignocellulose, which is the most abundant and bio-renewable biomass on earth.² The catalytic fast pyrolysis (CFP) of lignocelluloses has already been deeply studied for the production of target products in high yields.³ Levoglucosenone (**LGO**) is one of the products that can be produced from lignocellulose CFP (Scheme 1). The structure of this synthon is particularly interesting, due to the presence of one natural chiral center preserved from cellulose, and the presence of two functionalisable moieties (α,β -unsaturated ketone and protected aldehyde functionality). According to these properties, **LGO** constituted a synthon of choice for the production of several valuable products such as natural products, nucleosides, anticancer drugs and building blocks.⁴⁻⁸

Among the compounds obtained from **LGO**, the unsaturated chiral γ -lactone (S)- γ -hydroxymethyl- α,β -butenolide (**HBO**, Scheme 1) has found numerous applications as a key intermediate for the synthesis of drugs (such as Burseran or Isostegane),^{9,10} flavors^{11,12} and antiviral agents against HIV or hepatitis B virus.¹³⁻¹⁵ Our team recently developed cost-efficient, low toxicity and green syntheses of optically pure **HBO** from **LGO** using Baeyer-Villiger oxidations.¹⁶⁻¹⁹ Dedicated to the development of valuable applications of this platform molecule, our team then designed and optimized the chemo-enzymatic synthesis of (S)-dairy lactone,¹² a flavor used in food applications for its fruity odor and creamy dairy-like taste.



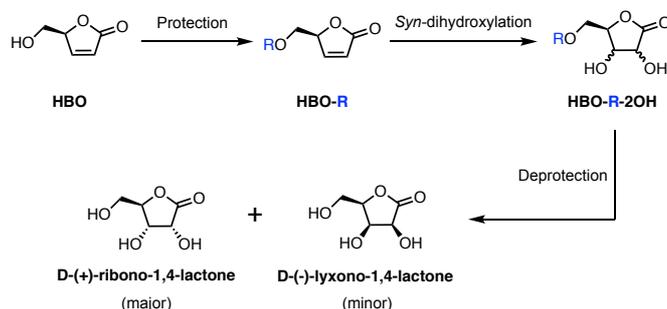
Scheme 1. Synthesis¹⁶⁻¹⁹ of **HBO** from cellulose-based levoglucosenone (**LGO**).

D-(+)-ribo-1,4-lactone, a rather costly rare sugar (ca. 50€/g) present in leaves of *Listea japonica*, displays an interesting vicinal 1,2-*cis*-diol and has been used for the synthesis of various natural or synthetic bioactive molecules²⁰ - such as Herbarumin I²¹ or (+)-Varitriol²² (Scheme 2).



Scheme 2. Some molecules of interest accessible from D-(+)-ribo-1,4-lactone

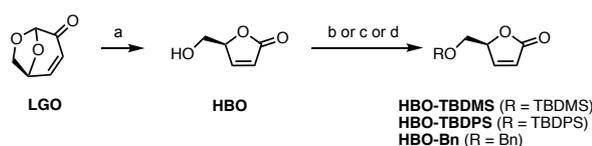
D-(+)-ribo-1,4-lactone can be prepared in ca. 65% yield through the molecular bromine-mediated oxidation of D-ribose,²³ a costly sugar (ca. 400€/kg). Another route consists in first protecting the primary alcohol of **HBO** with bulky groups to hinder the upper face of the molecule, then performing the asymmetric *syn*-dihydroxylation of the α,β -unsaturation in presence of KMnO_4 (1.25 eq) and dicyclohexano-18-crown-6 ether (10 mol%) in CH_2Cl_2 at -42°C .²⁴ Although this procedure provides 5-*O*-protected D-(+)-ribo-1,4-lactone in d.r. between 12:1 and 50:1 depending on the protecting group used, the oxidizing agent is used in stoichiometric amount, the yields remain low to average (<66%) - due to overoxidation of the resulting diol - and energy-demanding low temperature control is required. In this paper, we will describe a high yielding *syn*-dihydroxylation of 5-*O*-protected **HBO**, and discuss the influence of the protecting group on its diastereoselectivity, as well as the final deprotection steps required to access D-(+)-ribo-1,4-lactone (Scheme 3).



Scheme 3. Synthetic strategy to convert **HBO** into (+)-D-ribo-1,4-lactone

Results and Discussion

The first step of the synthetic route to D-(+)-ribo-1,4-lactone consisted in the efficient and straightforward H_2O_2 -mediated Baeyer-Villiger oxidation of **LGO** into **HBO** (Scheme 4).¹⁹ Validated at the kilo scale, this sustainable synthetic procedure provides **HBO** in 84% yield. Protection of **HBO** was performed using benzyl (Bn), *tert*-butyldimethylsilyl (TBDMS), as well as *tert*-butyldiphenylsilyl (TBDPS) protecting groups. Silyl ethers **HBO-TBDMS** and **HBO-TBDPS** were obtained under classical conditions (silyl chloride, imidazole, DMF) in 78 and 82% yields, respectively. For the benzyl ether **HBO-Bn**, acidic conditions using benzyl 2,2,2-trichloroacetimidate as benzyl donor²⁵ were applied and lead to **HBO-Bn** in 53% yield.



a: 30% aq. H_2O_2 , H_2O , 84%; b: (**HBO-TBDMS**): imidazole, TBDMSCl, Et_3N , DMAP, DCM, 78%; c: (**HBO-TBDPS**): imidazole, TBDPSCl, DMF, rt, 82%; d: (**HBO-Bn**): benzyl 2,2,2-trichloroacetimidate, TFOH, DCM-cyclohexane, 0°C , 53%

Scheme 4. Protection of **HBO** with TBDMS, TBDPS and Bn protecting groups

Olefin dihydroxylation is a common reaction in the synthesis of pharmaceuticals and natural products. The Sharpless asymmetric dihydroxylation,^{26,27} involving osmium catalyst, has been widely used due to its high stereospecificity and enantioselectivity.

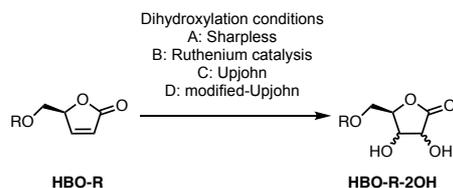


Table 1. *syn*-Dihydroxylation using Sharpless conditions, RuCl₃ catalysis, Upjohn and modified-Upjohn conditions.

Entry	Substrate (HBO-R)	Meth. ^[b]	Yield (%) ^[b]	d.r. (%) NMR ^[c, d]	d.r. (%) HPLC ^[c, e]
1	HBO-TBDMS	A	0	-	-
2		B	60	94:6	97:3
3		C	50	91:9	91:9
4		D	88	93:7	95:5
5	HBO-TBDPS	A	0	-	-
6		B	62	94:6	94:6
7		C	55	95:5	92:8
8		D	89	97:3	94:6
9	HBO-Bn	A	0	-	-
10		B	60	80:20	88:12
11		C	12	78:22	86:14
12		D	75	82:18	83:17

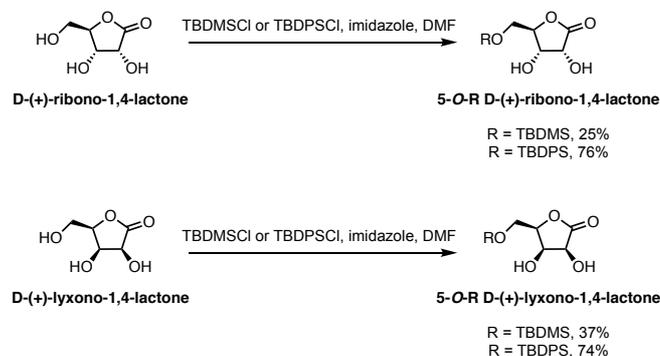
A: AD-mix- β (K₂OsO₄ or OsO₄, K₃Fe(CN)₆, chiral ligand (DHQD)₂PHAL) and basic buffer K₂CO₃. **B:** RuCl₃ (5 mol%), NaIO₄ (1.5 eq), CeCl₃ (10 mol%), CH₃CN/AcOEt/water (3/3/1), rt, 30 min. **C:** K₂OsO₄ (5 mol%), NMO (1.28 eq), acetone/water (4/1), rt, 18h. **D:** K₂OsO₄ (0.6 mol%), NMO (1.1 eq), EtOH/H₂O (1/1), citric acid (0.75 eq), rt, 18h.

[a] Determined by ¹H NMR of crude reaction mixture. [b] Isolated as a pure mixture of diastereomers. [c] Major diastereomer being the D-ribo-1,4-lactone derivative. [d] Determined by ¹H NMR of crude reaction mixture. [e] Determined by HPLC of crude reaction mixture.

Classical Sharpless conditions were first applied (Table 1, entries 1, 5 and 9) with the commercially available AD-mix β (K₂OsO₄ or OsO₄, K₃Fe(CN)₆, chiral ligand (DHQD)₂PHAL) and basic buffer K₂CO₃. Nevertheless, under such conditions no dihydroxylation was observed. Ruthenium-catalyzed *syn*-dihydroxylation using an *in situ* generation of the oxidant specie RuO₄²⁸ (RuCl₃·5H₂O, NaIO₄, CeCl₃, CH₃CN-AcOEt-water (3/3/1)) was also investigated (Table 1, entries 2, 6 and 10). Under these conditions, **HBO-TBDMS-2OH**, **HBO-TBDPS-2OH** and **HBO-Bn-2OH** were obtained in 60, 62 and 60% yields, respectively, comparable to that obtained with KMnO₄/dicyclohexano-18-crown-6 ether²⁴. Upjohn dihydroxylation conditions,²⁹⁻³¹ involving osmium tetroxide as catalyst and *N*-methylmorpholine-*N*-oxide (NMO) as oxidant, were then investigated (Table 1, entries 3, 7 and 11). Among the different solvent mixtures tested (*i.e.*, methanol, acetone-water and acetone-water-butanol), acetone/water proved the most relevant one and gave access to dihydroxylated derivatives of **HBO-TBDMS** (**HBO-TBDMS-2OH**), **HBO-TBDPS** (**HBO-TBDPS-2OH**), and **HBO-Bn** (**HBO-Bn-2OH**) in moderate yields, 50, 55 and 12% respectively. As classical Upjohn conditions did not lead to higher yields, modified-Upjohn conditions were applied as the addition of citric acid had been proven beneficial.³¹ After being optimized, this room temperature procedure provided the corresponding 5-*O*-protected dihydroxylactones in excellent yields (**HBO-TBDMS-2OH**: 88%, overall yield from **LGO**: 58%; **HBO-TBDPS-2OH**: 89%, overall yield from **LGO**: 61%; **HBO-Bn-2OH**: 89%, overall yield from **LGO**: 40%) (Table 2, entries 4, 8 and 12). The diastereomeric excesses were first evaluated by performing ¹H NMR spectroscopy of the crude reaction mixtures by looking at the signal of the protons of the CH₂ at the γ position. Calculations showed that the *syn*-dihydroxylation proceeds with d.r. between 82:18 and 97:3 depending on the protecting group used, demonstrating the average to high diastereoselectivity of the *syn*-dihydroxylation.

As expected, the higher steric hindrance of *tert*-butyldimethyl silyl and *tert*-butyldiphenyl silyl groups provides the highest d.r. compared to the less bulky “flat” benzyl group. Nevertheless, because of partial overlapping of signals in ¹H NMR spectroscopy, d.r. needed to be confirmed by another technique.

To confirm the diastereoisomeric ratios measured by ¹H NMR spectroscopy, HPLC analysis of the crude dihydroxylation mixtures was carried out. To do so, the two pure diastereomers (*i.e.*, protected D-ribo-1,4-lactone and D-lyxono-1,4-lactone) were required for every single protected **HBO-R**. As these compounds were not commercially available, we first dedicated ourselves to their synthesis starting from readily available commercial D-ribo-1,4-lactone, D-lyxono-1,4-lactone and D-gulonolactone.

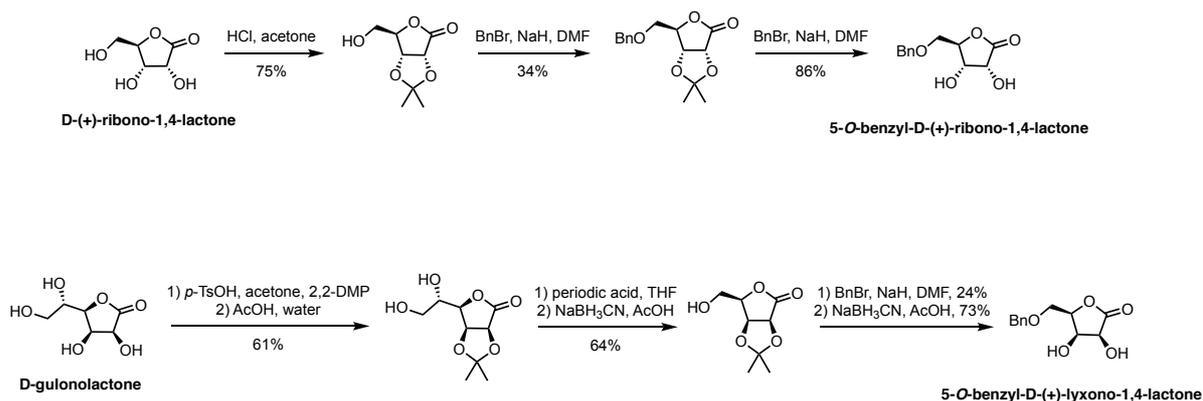


Scheme 5. Preparation of the silylated standards for HPLC

5-*O-tert*-butyldimethylsilyl-D-ribonolactone and 5-*O-tert*-butyldimethylsilyl-D-lyxono-1,4-lactone were readily obtained in one step through the silylation of D-ribo-1,4-lactone and D-lyxono-1,4-lactone, respectively (TDMSCl, imidazole, DMF, 25% yield for ribono-1,4-lactone and 37% for lyxono-1,4-lactone) (Scheme 5). The same strategy was applied for the synthesis of the TBDPS derivatives and provided 5-*O-tert*-butyldiphenylsilyl-D-ribonolactone and 5-*O-tert*-butyldiphenylsilyl-D-lyxono-1,4-lactone in 76 and 74% yield, respectively. The synthesis of the benzylated standards proved less straightforward and required multi-step pathways. The three-step preparation of 5-*O*-benzyl-D-ribo-1,4-lactone started with the selective acetalization of D-ribo-1,4-lactone into 2,3-*O*-isopropylidene-D-ribo-1,4-lactone (HCl, acetone, 75%) (Scheme 6). The latter was then benzylated (BnBr, NaH, DMF, 34%)³² and the resulting intermediate was hydrolyzed (Montmorillonite K10, EtOH, 86%) to provide 5-*O*-benzyl-D-ribonolactone. The preparation of 5-*O*-benzyl-D-lyxono-1,4-lactone was even more tedious and required a six-step pathway. L-gulonolactone was first bis-acetalized (acetone, *p*-TsOH, 2,2-DMP) to provide crude 2,3-5,6-di-*O*-isopropylidene-L-gulonolactone which then underwent a selective hydrolysis of the ketal at the 5,6-positions (AcOH/water) giving access to 2,3-*O*-isopropylidene-L-gulonolactone (61% from L-gulonolactone). The 5,6-diol moiety of the latter was then submitted to an oxidative cleavage (periodic acid, THF)³³ and the resulting crude aldehyde was readily reduced (NaBH₃CN, AcOH) to provide 2,3-*O*-isopropylidene-D-lyxono-1,4-lactone (64% over the two steps). Finally, the benzylation of the primary alcohol at C-6 (BnBr, NaH, DMF, 24%) followed by the hydrolysis of the ketal (AcOH, water, 73%) led to 5-*O*-benzyl-D-lyxono-1,4-lactone (7% overall yield from L-gulonolactone).

With all the standards in hand, HPLC analyses of the crude reaction mixture were performed. The d.r. calculated from the chromatograms and reported in Table 1 were similar to those obtained by ¹H NMR spectroscopy with values between 82:18 and 97:3, thus undoubtedly confirming the protecting group-dependency of the *syn*-dihydroxylation diastereoselectivity toward D-ribo-1,4-lactone scaffold. When compared to the previously reported procedure involving K₂O₈ and DCH-18-crown-6 ether,²⁴ RuO₄-catalyzed and modified-Upjohn *syn*-dihydroxylation prove as diastereoselective, the latter is nevertheless more efficient with regards to yields.

The fourth and final step of this novel chemo-enzymatic route to D-(+)-ribo-1,4-lactone from **LGO** consisted in the removal of the protecting groups at the 5-*O* position of the **HBO-R-2OH** compounds. It is noteworthy to mention that the cleavage procedures have been performed on the mixtures of diastereomers and not on isolated protected D-ribo-1,4-lactones. Deprotection of the benzyl group of **HBO-Bn-2OH** was readily performed using palladium-catalyzed hydrogenation providing **HBO-2OH** in 92% yield (Table 2, entry 1). Silyl ethers cleavage was first attempted under classical deprotection conditions in presence of fluoride anions. Among the various reagents used, KF proved efficient on **HBO-TBDPS-2OH**, providing D-(+)-ribo-1,4-lactone in 52% yield (Table 2, entry 2), while tetra-*n*-butylammonium fluoride (TBAF) allowed the deprotection of **HBO-TBDMS-2OH** in 68% yield (Table 2, entry 6).



Scheme 6. Preparation of the benzylated standards for HPLC

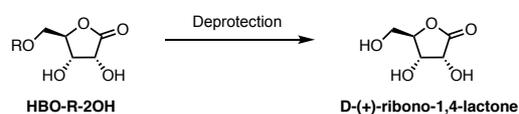


Table 2. Deprotection of **HBO-R-2OH**

Entry	Substrate (HBO-R-2OH)	Procedure	Yield (%) ^[a]	Overall yield from LGO (%)
1	HBO-Bn-2OH	H ₂ , Pd/C, EtOH	92	31
2	HBO-TBDPS-2OH	KF, DMF	52	32
3		CH ₃ COCl, MeOH	51	31
4		TfOH-SiO ₂ , MeCN	62	38
5		Montmorillonite K10, MeOH/water	<10	-
6	HBO-TBDMS-2OH	TBAF, THF, DOWEX 50W	68	39
7		CH ₃ COCl, MeOH	37	21
8		Montmorillonite K10, MeOH/water	77	44

[a] Isolated

In the latter case, it is worth noting that the resulting D-ribo-1,4-lactone being highly water-soluble, resin-based post-treatment was used instead of classical aqueous treatment to remove the excess of reagent. Assays using acetyl chloride³⁴ and triflic acid supported on silica³⁵ as acid catalyst on **HBO-TBDPS-2OH** resulted in 51 and 62% yields, respectively (Table 2, entry 3). Successful deprotection of **HBO-TBDMS-2OH** in 37% was also observed with acetyl chloride (Table 2, entry 7). Finally, we were pleased to observe that the use of a sustainable and mild procedure³⁶ involving Montmorillonite K10 in a methanol/water mixture allowed the deprotection of **HBO-TBDMS-2OH** in 77% (Table 2, entry 8). Unfortunately, the implementation of this procedure on **HBO-TBDPS-2OH** did not prove successful with only <10% yield (Table 2, entry 5). Indeed, TBDPS being considerably more stable (ca. 100 times) than TBDMS towards acidic hydrolysis, its removal requires harsher acidic conditions.³⁷

Conclusion

This four-step synthetic route from cellulose-based levoglucosenone (**LGO**) involving (i) H₂O₂-mediated Baeyer-Villiger oxidation and (ii) diastereoselective and high yielding modified-Upjohn *syn*-dihydroxylation as key steps allows to access D-(+)-ribo-1,4-lactone with good to excellent diastereoselectivity and in good overall yields using TBDMS (44% yield, d.r. ca. 94:6), TBDPS (38%, d.r. ca. 94:6) and Bn (31%, d.r. ca. 80:20) protecting group, respectively. Although this new route does not compete with the one-step oxidation of D-ribose into D-(+)-ribo-1,4-lactone (ca. 65%) in terms of yield, diastereoselectivity and number of steps, not only it uses **LGO**, a cheaper renewable starting material, but it also allows the straightforward synthesis of 5-O-silylated and benzylated ribono-1,4-lactones which are valuable intermediates for the synthesis of high value added chemicals such as bioactive compounds and functional additives for drugs, food, feed or cosmetics.

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Keywords: Chiral pool • Oxidation • Asymmetric synthesis • Dihydroxylation • Substituent effects

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