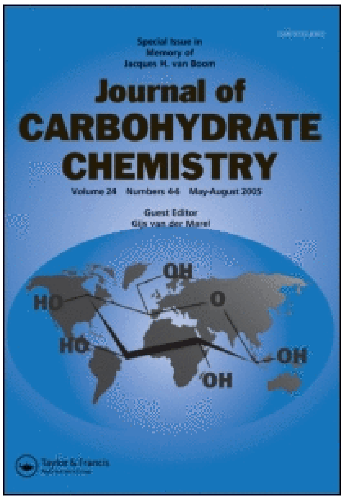

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Stereoselective Transformations Leading to Pentono-1,4-Lactones

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STEREOSELECTIVE TRANSFORMATIONS LEADING TO PENTONO -1, 4-LACTONES [1]

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ABSTRACT

The readily available 2, 3-*O*-isopropylidene-D-erythrose has been stereoselectively transformed into L-ribono and D/L lyxonolactone derivatives via dihydroxylation, iodolactonisation and epoxidation. Also D-ribono-1,4-lactone was converted into L-lyxono-1,4-lactone. These lactones are considered as important starting materials for the synthesis of several chiral compounds. Our observations during these transformations are also presented.

INTRODUCTION

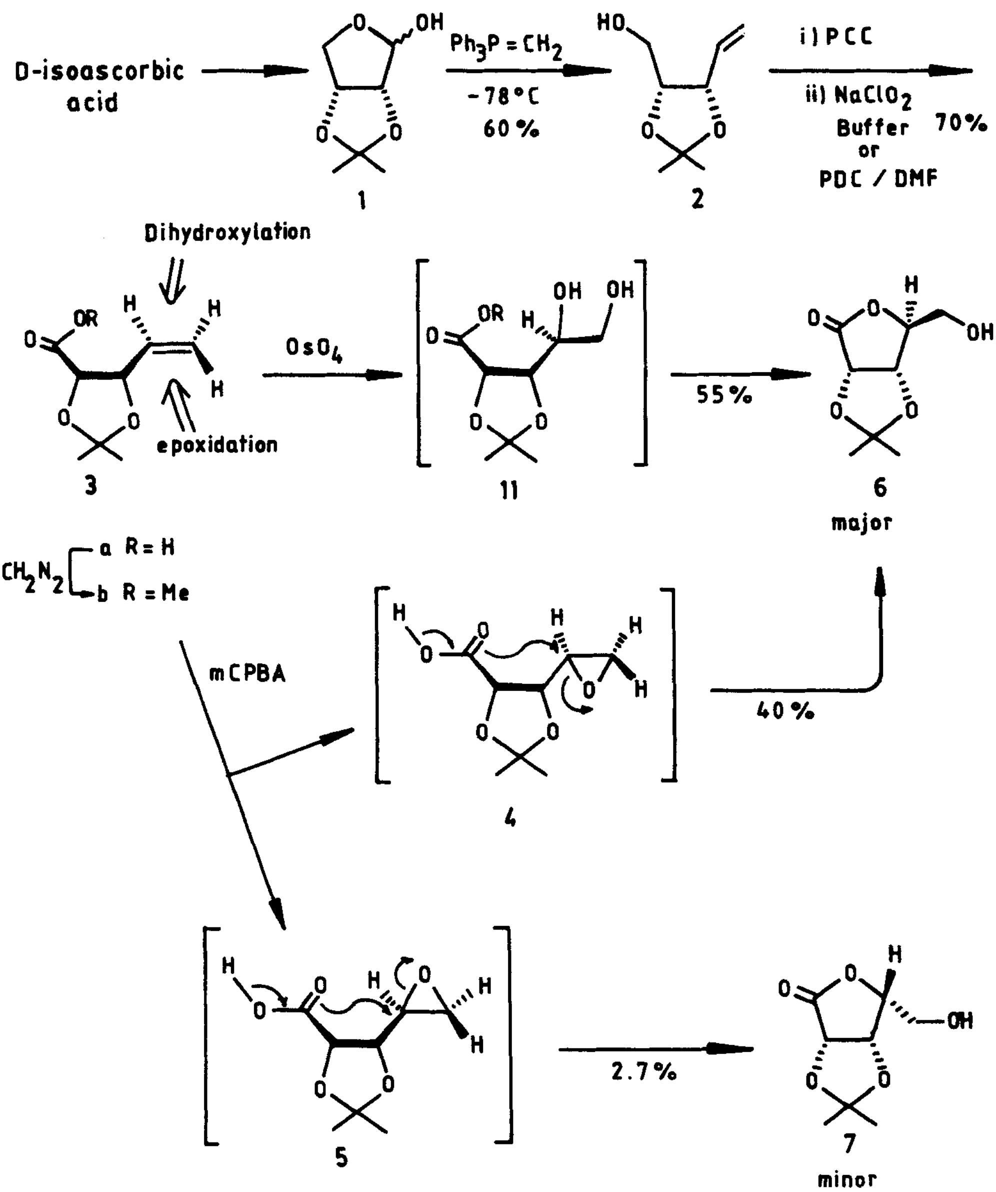
Pentonolactones as chirons have been playing a pivotal role in the synthesis of several classes of chiral compounds.[2] They also constitute part structures of several biologically active natural products. Their availability in pure forms with well defined centres of chirality and easily distinguishable functionalities makes them attractive starting materials.[3] Generally D-pentonolactones are commercially available and affordable whereas L-lactones are very scarce which precludes their use as chiral building blocks. Also L-sugars are playing an increasingly important role in biology, for instance in making L-nucleosides.[4] In this context an easy access to L-lactones will greatly enhance their synthetic potential. Herein we present useful and stereoselective transformations of 2,3-*O*-isopropylidene D-erythrose **1**, which can be obtained in good yields and in just two steps from the inexpensive D-isoascorbic acid[5] to give L-ribonolactone.[6] This methodology was also extended for the synthesis of D and L-lyxonolactone derivatives[7] which are scarcer but very important chiral synthons.[7d,e,f.]

RESULTS AND DISCUSSION

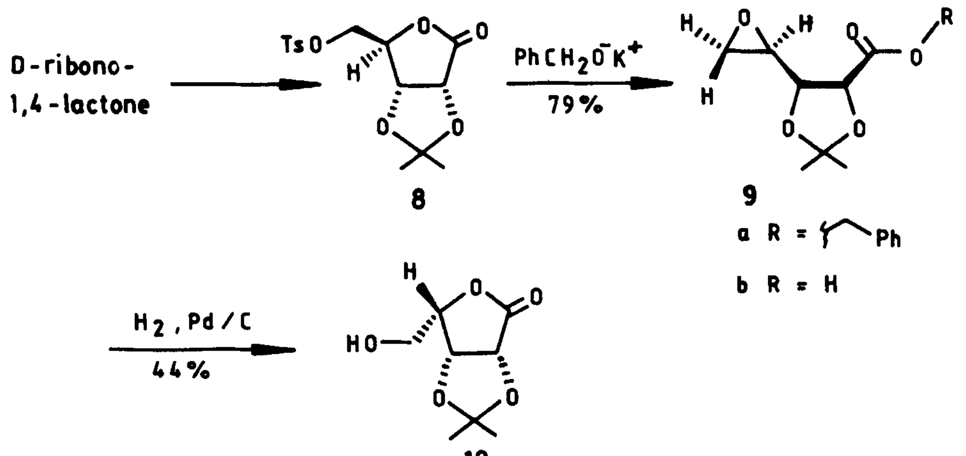
The key intermediate required for our transformations, the olefinic acid **3a**, was obtained from isopropylidene-D-erythrose (**1**) in three simple steps as described below. Wittig olefination of **1** with triphenylmethylene-phosphorane afforded **2**. Stepwise oxidation of **2**, first with PCC to the aldehyde (not shown) and then with sodium chlorite[8] afforded acid **3a**. The oxidation of the alcohol **2** directly to the acid **3a** with PDC in DMF was not as efficient. Three possibilities - epoxidation, dihydroxylation (Scheme 1) and iodolactonisation (Scheme 3) were explored to convert this olefinic acid to the diastereomeric pentonolactones.

Epoxidation of the alkene moiety as the first choice and using MCPBA as the epoxidising agent, the olefinic acid **3a** was converted into the epoxide **4**, which cyclised to give L-ribonolactone (**6**) in 40 % yield during purification on silica gel column. This clearly shows that the epoxide **4**, was formed as a result of *syn* attack of MCPBA with respect to the isopropylidene moiety which later underwent 5-*exo* cyclisation to give **6**. The diastereomeric product D-lyxonolactone (**7**) arising from *anti*-epoxidation was isolated in only 2.7% yield. MCPBA epoxidation of α -alkoxy olefins are reported to be not highly stereoselective.[9] The almost exclusive *syn*-attack observed in our case may be due to the *erythro* nature of the centres of chirality which permits attack from only one face. From this result, it is clear that to obtain **7** as the major product, the epoxy acid should be the C-4 epimer **5** of **4** and to obtain the even more precious and scarce L-lyxonolactone, the epoxy acid **9b** should be the enantiomer of **5**, which can readily be obtained from D-ribonolactone. Thus 5-*O*-tosyl-2,3-*O*-isopropylidene-D-ribonolactone[10] (**8**) on treatment with the potassium salt of benzyl alcohol gave the epoxy benzyl ester[11] **9a** which on hydrogenolytic *O*-debenzylation furnished 2,3-*O*-isopropylidene L-lyxonolactone (**10**) directly (Scheme 2).

We next studied the iodolactonisation of the acid **3a** which should yield either 5-deoxy-5-iodo-2,3-*O*-isopropylidene-L-ribono-1,4-lactone (the thermodynamic product) **11** or 5-deoxy-5-iodo-2,3-*O*-isopropylidene-D-lyxonolactone (the kinetic product) **12**, depending on the reaction conditions.[12a,b,c] These iodolactones are important intermediates in the synthesis of several compounds and this method makes it possible to obtain them in one step from acid **3a** thus avoiding the extra step of making them from corresponding alcohols. To this end, **3a** was subjected to different iodolactonisation conditions. Under thermodynamic control[12c] (I_2, CH_3CN or THF) followed by isopropylidenation with 2,2-dimethoxypropane,


D-isoascorbic acid
$Ph_3P=CH_2$
-78°C
60%
HO
1
2
i) PCC
ii) $NaClO_2$
Buffer
or
PDC / DMF
70%
Dihydroxylation
epoxidation
OR
3
OsO_4
OH OH
11
55%
6
major
CH_2N_2
a R = H
b R = Me
mCPBA
4
40%
5
2.7%
7
minor

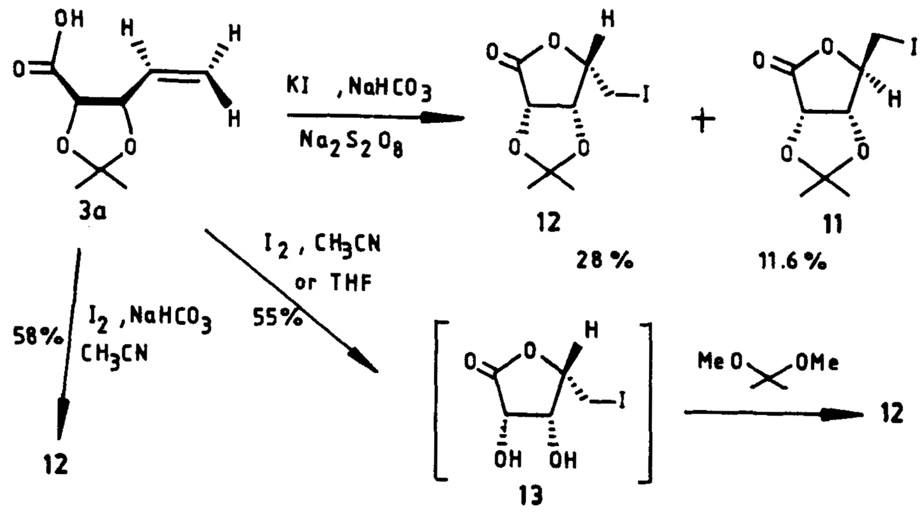
Scheme 1



Scheme 2

we obtained surprisingly 5-deoxy-5-iodo-D-lyxonolactone **12** instead of the expected 5-deoxy-5-iodo-L-ribonolactone derivative **11**. Treatment of **3a** with iodine under kinetic conditions ($NaHCO_3/CH_3CN$) again afforded the lyxonolactone **12** as the major compound. The recently modified iodolactonisation conditions[13] (KI, $NaHCO_3$, $Na_2S_2O_8$) afforded **12** and **11** in 70:30 ratio. Generally, thermodynamic iodolactonisation of α or β substituted 4-pentenoic acid is a reversible reaction and always results in *trans* iodolactone as the major product. But the formation of *cis* product in the case of **3a** is rather surprising and the reason may be that the hydrogen iodide (liberated during the reaction), which is responsible for the reversibility of the reaction,[14] is getting consumed by the isopropylidene group, thus giving the kinetic product, iodo diol **13**, which was later converted back to isopropylidene derivative **12** by treatment with 2,2-dimethoxypropane. The two methods of obtaining 2,3-*O*-isopropylidene lyxonolactone derivatives **12** and **10** have a distinct advantage in contrast to preparing them from isopropylidenation of lyxonolactone where the 3,5-*O*-isopropylidene isomer is always a contaminant[7d] (Scheme 3).

Finally, dihydroxylation of **3a** using OsO_4-NMO resulted in the exclusive *anti*-attack[6c,15] of osmium tetroxide unlike with MCPBA where epoxidation was exclusively *syn* with respect to the isopropylidene group resulted in the formation of L-ribonolactone **6** in 44% yield. However, a better yield for this transformation was realised when the ester **3b** (obtained quantitatively from the acid by reaction with diazomethane) was the substrate for dihydroxylation. Thus these methods of oxidative cyclisation namely epoxidation and dihydroxylation stereochemically complement each other in their mode of attack on olefin (Scheme 1).



Scheme 3

CONCLUSION

The above procedures are useful to obtain L-ribono and L- or D-lyxono lactone derivatives in good yields and in optimum time from a readily available starting material. Using the iodolactonisation route 5-deoxy-5-iodo-L-lyxonolactone derivative can be obtained starting from the antipode of the olefinic acid **3a**,[16] readily obtained from D-ribonolactone. The method to convert D-ribonolactone to L-lyxonolactone can be extended to the conversion of D-arabinolactone to L-xylonolactone and D-xylonolactone to L-arabinolactone. All the intermediates described in these transformations by themselves can be used as chiral synthons.

EXPERIMENTAL

NMR spectra were recorded on Varian Gemini (200 MHz) instrument. Silica gel (60-120 mesh, Acme India) was used for the column chromatography.

1,2,3-Trihydroxy-(2*R*, 3*S*)-2,3-*O* -isopropylidene-pent-4-ene (2). To a mixture of $Ph_3P^+CH_3I^-$ (7.57 g, 18.74 mmol) and *t*-BuO^-K^+ (1.75 g, 15.60 mmol), dry THF (40 mL) was added and the mixture was allowed to stir at room temperature for one h under N_2. Stirring was stopped and solid allowed to settle. The clear supernatant orange-yellow liquid was then decanted into the solution of compound **1** (1.00 g, 6.25 mmol) in dry THF (5 mL) at -78 °C under N_2. The reaction mixture was then slowly allowed to attain the room temperature. After 3 h the reaction mixture was dissolved in ethyl acetate (60 mL) and washed with water (25 mL), dried (Na_2SO_4) and concentrated. Chromatography (EtOAc:Pet. ether, 15:85) yielded **2** (0.592 g, 60%) as an oil : $[\alpha]_D$+40.1 (*c* 2.5, $CHCl_3$), [lit.[17] $[\alpha]_D$-44 (*c* 4.89, $CHCl_3$) for its enantiomer]. ^{1}H NMR ($CDCl_3$) δ 1.4, 1.51 (2S,6H,Me_2C), 3.56 (d,2H,$J_{1,2}$ = 6.0 Hz, H-1a,1b), 4.25 (dt, 1H, $J_{1,2}$ =6.0 Hz, $J_{2,3}$ = 6.0 Hz, H-2), 4.63 (dd, 1H, $J_{2,3}$ = 6.0 Hz, $J_{3,4}$ = 6.0 Hz, H-3), 5.27(dd, 1H, $J_{4,5a}$ = 10.0 Hz, $J_{5a,5b}$ = 1.0 Hz, H-5a), 5.4(dd,1H, $J_{4,5b}$ = 17.0 Hz, $J_{5a,5b}$ = 1.0 Hz, H-5b), 5.78-5.98, (m, 1H, H-4)

Anal. Calcd for $C_8H_{14}O_3$ (158.19): C, 60.74; H, 8.9 Found : C, 60.62; H, 8.90.

4,5-Dideoxy-2,3-*O* -isopropylidene-L-*erythro* -pent-4-enoic acid (3a). To a solution of compound **2** (1.00 g, 6.32 mmol) in dry dichloromethane (10 mL), a mixture of PCC (2.05 g, 9.5 mmol), sodium acetate (1.04 g, 12.68 mmol) and powdered molecular sieves 4A° (1.00g) were added at 0 °C under N_2 atmosphere and stirred at room temperature for five h. The reaction mixture was concentrated at an ambient temperature and the residue passed through a small bed of silica gel eluting with ether. Ether was removed in *vacuo* to get the crude aldehyde.

To a solution of the aldehyde in *t*-BuOH and H_2O (16 mL, 1:1), 2-methyl but-2-ene (6.74 mL, 63.65 mmol) was added at 0 °C. Then NaH_2PO_4. H_2O (4.32 g, 31.43 mmol) and Na_2HPO_4 (0.027 g, 0.194 mmol) were added at 0 °C, followed by $NaClO_2$ (1.43 g, 15.81 mmol). The stirring was continued for 1.5 h at 25 ° to 30 °C. The reaction mixture was cooled back to 0 °C and saturated aqueous Na_2SO_3 (4 mL) was added followed by water. The mixture was extracted with ethyl acetate (2x25 mL) and the organic extracts were dried (Na_2SO_4) and concentrated to get the acid, which was purified by base-acid treatment to get pure **3a** (0.76 g, 70%) as an oil: $[\alpha]_D$ + 21.76 (*c* 2.6, $CHCl_3$) [lit.[18] $[\alpha]_D$ +22.8 (*c* 2.6,$CHCl_3$)]; IR (neat) 3600-2880 (b,s), 1715 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ 1.36, 1.56 (2S, 6H, Me_2C), 4.69 (d, 1H, $J_{2,3}$ = 7.0 Hz, H-2), 4.8 (dd, 1H, $J_{2,3}$ = 7.0 Hz, $J_{3,4}$ = 7.0 Hz, H-3), 5.25 (d, $J_{4,5a}$ = 10.0 Hz, H-5a), 5.4 (d, $J_{4,5b}$ = 17.0 Hz, H-5b), 5.65-5.85 (m, 1H, H-4).

4,5-Dideoxy-2,3-*O* -isopropylidene-L-*erythro* -pent-4-enoic acid methyl ester (3b). To a solution of compound **3a** (0.5 g, 2.89 mmol) in ether (5 mL), a cooled ethereal solution of diazomethane (generated from nitrosomethyl urea and 20% potassium hydroxide solution in ether) was added at 0 °C and stirred for 30 min. The reaction mixture was concentrated and the residue chromatographed (EtOAc:Pet.ether, 5:95) to get the ester **3b** (0.51 g, 94%) as an oil: $[\alpha]_D$ +45.4 (*c* 0.975, $CHCl_3$) [lit.[17] $[\alpha]_D$ -48.3 (*c* 5.07, $CHCl_3$) for its enantiomer]; IR (Neat) 1758, 1370 cm^{-1}; ^{1}H NMR ($CDCL_3$) δ 1.42, 1.65 (2S,6H, Me_2C), 3.72 (S, 3H, CO_2Me), 4.66 (d,1H, $J_{2,3}$=7.5 Hz, H-2), 4.8 (dd, 1H, $J_{2,3}$=7.5 Hz, $J_{3,4}$ =7.5 Hz, H-3) 5.25 (d,1H, $J_{4,5a}$ = 10.0 Hz, H-5a), 5.45 (d, 1H, $J_{4,5b}$ = 17.0 Hz, H-5b), 5.65-5.84 (m, 1H, H-4).

2,3-*O*-Isopropylidene-L-ribono 1,4-lactone (6).

Via epoxidation. To a solution of compound **3a** (0.3 g, 1.74 mmol) in dry dichloromethane (5 mL), MCPBA (0.450 g, 2.61 mmol) was added and stirred for 12 h at room temperature. Then the reaction mixture was cooled to 0 °C and a saturated aqueous solution of Na_2SO_3 (4 mL) was added, concentrated and extracted with ethyl acetate (2 x 10 mL). The organic extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed (EtOAc:Pet. ether, 20:80) to give **6** (0.129 g, 40%): mp 137 °C, $[\alpha]_D$ + 60 (*c* 0.7, pyridine) [lit.[6c] $[\alpha]_D$ +54 (*c* 2.13, pyridine) and for isomer lit[10] $[\alpha]_D$ -57.5 (*c* 2.13, Pyridine), mp 135-138 °C] ; IR ($CHCl_3$) 1790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38, 1.46 (2S, 6H, Me_2C), 3.78 (dd, 1H, $J_{5a,5b}$ = 12.2 Hz, $J_{4,5a}$ = 1.4 Hz, H-5a), 3.99 (dd, 1H, $J_{5a,5b}$ = 12.2 Hz, $J_{4,5b}$ = 2.2 Hz, H-5b), 4.60 (t, 1H, $J_{4,5b}$ = 2.0 Hz, $J_{4,5a}$ = 1.0 Hz, H-4), 4.73 (d, 1H, $J_{2,3}$ = 5.4 Hz, H-3), 4.79 (d, 1H, $J_{2,3}$ = 5.4 Hz, H-2) and 2,3-*O*-isopropylidene-D-lyxono lactone (**7**) (9 mg, 2.7%): mp 87 °C, $[\alpha]_D$ + 104 (*c* .15, acetone) [lit.[7c] $[\alpha]_D$+ 108 (*c* 1, acetone) mp 88-93 °C]; IR ($CHCl_3$) 1790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38, 1.45 (2S, 6H, Me_2C), 3.97 (m, 2H, H-5a,5-b), 4.58 (m, 1H, H-4), 4.88 (m 2H, H-2, H-3).

Via dihydroxylation. To a solution of **3b** (0.2 g, 1.07 mmol) in acetone: water (9:1, 10 mL), osmium tetroxide [0.13 mL (10% solution in toluene) 0.05 mmol] and NMO [0.16 mL (60% solution in water) 1.6 mmol] were added and stirred for 6 h at room temperature. The reaction mixture was cooled and aqueous $NaHSO_3$ solution (2 mL) was added. Solvents were removed and the residue was dissolved in ethyl acetate (15 mL), washed with water, dried (Na_2SO_4), concentrated and chromatographed (EtOAc:Pet. ether, 20:80) to give compound **6** (0.120 g, 55%).

Benzyl 4,5-anhydro-2,3-*O*-isopropylidene-D-ribonate (9a). To a suspension of potassium hydride (0.584 g, 2.92 mmol, 20%) in dry THF (10 mL), under N_2 atmosphere benzyl alcohol (0.3 mL, 2.92 mmol) was added and stirred for 0.5 h at room temperature. The reaction mixture was cooled to -20 °C, compound **8** (1.00 g, 2.92 mmol) in THF (5 mL) was added over 10 min and stirring continued for 0.5 h at the same temperature. The reaction mixture was concentrated, diluted with hexane and filtered. The filtrate was concentrated and the residue chromatographed (EtOAc:Pet.ether, 2:98) to give compound **9a** (0.642 g, 79%) as an oil: $[\alpha]_D$ +8.53 (*c* 0.75, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.44, 1.49 (2S, 6H, Me_2C), 2.77 (dd, 1H, $J_{5a,5b}$ = 5.0 Hz, $J_{4,5a}$ = 2.5 Hz, H-5a), 2.8 (dd, 1H, $J_{5a,5b}$ = 5.0 Hz, $J_{4,5b}$ = 4.0 Hz, H-5b), 3.19 (m, 1H, H-4), 4.18 (dd, 1H, $J_{2,3}$ = 7.0 Hz, $J_{3,4}$ = 4.0 Hz, H-3), 4.36 (d, 1H, $J_{2,3}$ = 7.0 Hz, H-2), 5.2(S, 2H, OCH_2Ph), 7.34 (m, 5H, Ph-H) HRMS Calcd for $C_{14}H_{15}O_5$: 263.0919 $(M-CH_3)^+$. Found:263.0925.

2,3-*O*-Isopropylidene-L-lyxono-1,4-lactone (10):

An ethereal solution of compound **9a** (0.60 g, 2.15 mmol, in 10 mL) was subjected to hydrogenolysis using 5% Pd/C (60 mg) under an atmosphere of hydrogen (balloon). After two h, the reaction mixture was filtered and concentrated. The residue was passed through a column of silica gel (EtOAc:Pet.ether, 20:80) to give compound **10** (0.18 g, 44%): mp 95-97 °C, $[\alpha]_D$ -95° (*c* 0.595, acetone) [lit.[7c] $[\alpha]_D$ + 108 (*c* 1, acetone) and mp 88-93 °C for its enantiomer]; IR ($CHCl_3$) 1790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38, 1.45 (2S,6H,Me_2C), 3.97 (m, 2H, H-5a,5b), 4.58 (m, 1H, H-4), 4.88 (m,2H,H-2,H-3). HRMS Calcd for $C_8H_{12}O_5$; 188.0684. Found : 188.0677.

5-Deoxy-5-iodo-2,3-*O*-isopropylidene-L-ribono-1,4-lactone (11) and 5-deoxy-5-iodo-2,3,-*O*-isopropylidene-D-lyxono-1,4-lactone (12).

Method A. To a solution of compound **3a** (0.20 g, 1.16 mmol) in dry acetonitrile, (10 mL) a solution of I_2 (0.885 g, 3.48 mmol) in dry THF (3 mL) was added at 0 °C under N_2 atmosphere and stirred at 0 °C for 2 h. The reaction mixture was concentrated and the residue dissolved in ethyl acetate (10 mL) and washed successively with 5% $NaHCO_3$ (5 mL), 5% $Na_2S_2O_3$ (5 mL) and water (5 mL). The organic layer was dried (Na_2SO_4) and concentrated. The residue was dissolved in 2,2-dimethoxypropane (5 mL), PTSA (5 mg) was added and the mixture was stirred at room temperature for one h. The reaction mixture was neutralised with triethylamine and concentrated. The residue was chromatographed (EtOAc:Pet. ether, 7:93) to give compound **12**[19] (0.188 g, 55%): mp 89 °C, $[\alpha]_D$ +23.1 (*c* 0.83, acetone); IR ($CHCl_3$) 1792 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43, 1.47 (2S, 6H, Me_2C), 3.38 - 3.40 (m, 2H, H-5a,H-5b), 4.57 - 4.70 (m, 1H, H-4) 4.81 (d, 1H, $J_{2,3}$ = 5.2 Hz, H-2), 4.85 - 4.95 (dd, 1H, $J_{2,3}$ = 5.2 Hz, $J_{3,4}$ = 3.26 Hz, H -3). HRMS Calcd for $C_7H_8O_4I$; 282.9467 $(M-CH_3)^+$. Found : 282.9466.

Method B. To a solution of compound **3a** (0.20 g, 1.16 mmol) in dry acetonitrile, (10 mL) solid $NaHCO_3$ (2.92 g, 34.8 mmol) was added followed by iodine (0.88 g, 3.48 mmol) at 0 °C and stirred for two h at this temperature. The reaction mixture was concentrated and the residue was dissolved in ethyl acetate (15 mL). Then the organic portion was washed successively with 5% $NaHCO_3$ (5 mL), 5% $Na_2S_2O_3$ (5 mL) and water (5 mL), dried (Na_2SO_4) and concentrated. The residue was chromatographed (EtOAc: Pet. ether, 7:93) to give compound **12** (0.198 g, 58%).

Method C. To a mixture of compound **3a** (0.30 g, 1.74 mmol), $NaHCO_3$ (0.144 g, 1.74 mmol) and KI (0.432 g, 2.61 mmol) in deionised water (5 mL), a solution of sodium persulfate (1.242 g, 5.22 mmol) in deionised water (5 mL) was added dropwise at 0 °C and the reaction mixture stirred for two h. It was then extracted with dichloromethane (15 mL) and the organic portion was washed with 5% $NaHCO_3$ (5 mL), 5% $Na_2S_2O_3$ (5 mL) and water (5 mL), dried (Na_2SO_4) and concentrated. The residue was chromatographed (EtOAc:Pet. ether, 7:93) to give **11** (0.06 g, 11.6%) and **12** (0.147 g, 28%) in a 3:7 ratio. Compound **11**[19] - mp 88 °C, $[\alpha]_D$ + 34° (*c* 0.25, acetone) [lit.[20] $[\alpha]_D$ -31.8 (*c* 1.33, acetone) and mp 92 °C for D isomer]; IR ($CHCl_3$) 1793 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 , 1.44 (2S,6H, Me_2C), 3.3-3.48 (dd,dd,2H, $J_{4,5a}$ = 5.0 Hz, $J_{4,5b}$ =3.5 Hz, $J_{5a,5b}$ = 12.0 Hz, H-5a,5b), 4.52 - 4.6 (m, 2H, H-3, H-4), 4.89 (d, 1H, $J_{2,3}$ = 6.0 Hz, H-2)

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REFERENCES AND NOTES

1. IICT Communication No. 3535
2. R. M. D. Lederkremer and O. Varela, *Adv. Carbohydr. Chem. Biochem.* **50**, 125 (1994).
3. a) K. L. Bhat, S. Y. Chen and M. M. Joullie, *Heterocycles,* **23,** 691 (1985); b) J. Mann and A. Thomas, *Tetrahedron Lett.*, **27**, 3533 (1986); c) S. M. Ali, K. Ramesh and R. T. Borchardt, *Tetrahedron Lett.*, **31,** 1509 (1990).
4. T. S. Lin, M. Z. Luo, M. C. Liu, S. B. Pai, G. E. Dutschmann and Y. C. Cheng, *J. Med. Chem.* **37,** 798 (1994).
5. N. Cohen, B. L. Banner, A. J. Laurenzano and L. Carozza, *Organic Synthesis,* **63,** 127 (1985).
6. a) T. E. Walker and H. P. C. Hogenkamp, *Carbohydr. Res.*, **32,** 413 (1974); b) S. Takano, K. Inomata and K. Ogasawara, *Heterocycles,* **27,** 2413 (1988); c) T. Hudlicky and J. D. Price, *Synlett,* 159 (1990); d) J. F. Witte, R. Frith and R. W. McClard, *Carbohydr. Lett.* **1,** 123 (1994).
7. a) R. J. Schaffer, *Res. Natl. Bur. Stand. Sect. D.* **65A,** 507 (1961); b) W. J. Humphlett, *Carbohydr. Res.*, **4,** 157 (1967); c) S. Morgenlie, *Acta Chem. Scand.* **B29,** 367 (1975); d) G. W. J. Fleet, S. Petursson, A. L. Campbell, R. A. Mueller, J. R. Behling, K. A. Babiak, J. S. Ng and M. G. Scaros, *J. Chem. Soc. Perkin Trans. 1*, 665 (1989); e) Y. Wang, G. W. J. Fleet, R. Storer, P. L. Myers, C. J. Wallis, O. Doherty, D. J. Watkin, K. Vogt, D. R. Witty, F. X. Wilson and J. M. Peach, *Tetrahedron Asymmetry,* **1,** 527 (1990); f) O. Varela and P. A. Zunszain, *J. Org. Chem.*, **58,** 7860 (1993).
8. H. C. Kolb, S. V. Ley, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc. Perkin Trans. 1*, 2735 (1992).
9. a) A. H. Hoveyda, D. A. Evans and G. C. Fu, *Chem. Rev.*, **93,** 1307 (1993); b) R. W. Friesen and S. Bissada, *Tetrahedron Lett.*, **35,** 5615 (1994).
10. L. Hough, J. K. N. Jones and D. L. Mitchell, *Can. J. Chem.*, **36,** 1720 (1958).
11. D. B. Collum, J. H. McDonald III and W. C. Still, *J. Am. Chem. Soc.*, **102,** 2118 (1980).

12. a) A. R. Chamberlin, R. L. Mulholland, Jr., S. D. Kahn and W. J. Hehre, *J. Am. Chem. Soc.,* **109,** 672 (1987). b) F. Freeman and K. D. Robarge, *J. Org. Chem.,* **54,** 346 (1989). c) G. Cardillo and M. Orena, *Tetrahedron,* **46,** 3321 (1990).
13. A. C. Royer, R. C. Mebane and A. M. Swafford, *Synlett,* **12,** 899 (1993).
14. P. A. Bartlett and J. Myerson, *J. Am. Chem. Soc.,* **100,** 3950 (1978).
15. J. K. Cha, W. J. Christ and Y. Kishi, *Tetrahedron,* **40,** 2247 (1984).
16. A. Fürstner and H. Weidmann, *J. Org. Chem.,* **54,** 2307 (1989).
17. V. Jäger and B. Häfele, *Synthesis,* 801 (1987)
18. T. Hudlicky, H. Luna, J.D. Price and F. Rulin, J. Or Chem., **55,** 4683 (1990)
19. The spectral data of **11** & **12** were identical with the nentic samples prepared from the corresponding 2,3-*O*-isopropylidene 1,4-aldonolactones using triphenyl phosphine, iodine and imidazole.(ref.20)
20. C. Papageorgiou and C. Benezra, *Tetrahedron Lett.,* **25,** 6041 (1984).