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A NOVEL SYNTHESIS OF SUGAR DERIVATIVES FROM THE TELOMERS OF VINYLENE CARBONATE

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Synthesis in carbohydrate field has been concerned mainly with the chemical modifications of either naturally occurring or readily obtainable monosaccharides[1]. Most syntheses of monosaccharides from simple non-carbohydrate substances reported so far involve non-specific processes in the lengthening of carbon chain, functionalization or separation steps.

As described in the previous paper[2], telomerization of vinylene carbonate (I) with polyhalomethanes (II) afforded the telomers of type III, whose formation was stereoselective owing to the strong tendency of trans radical addition.

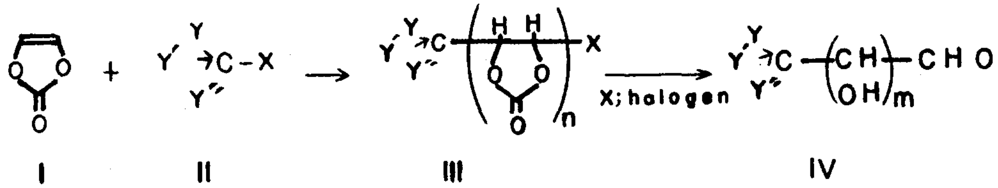


Table 1 Isomeric n=2 Telomers of Type III

$Y'Y''YC-$	X-		m.p (°C)	
CH_2Br	Br	$C_7H_6O_6Br_2$	170-1 (Va),	126-8 (Vb)
$CHBr_2$	Br	$C_7H_5O_6Br_3$	133-4 (Vc),	162-3 (Vd)
CCl_3	Cl	$C_7H_4O_6Cl_4$	185-6 (Ve),	159-60 (Vf)
CCl_3	H	$C_7H_5O_6Cl_3$	185-6 (Vg),	152 (Vh)

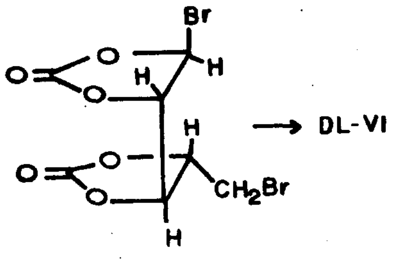
Hydrolysis of the telomers (III) would give, in one step, natural or unnatural carbohydrates (IV). And therefor, careful control of the telomerization would provide a novel and facile route to various carbohydrate derivatives. This communication describes a new stereoselective synthesis of 5-bromo-5-deoxy-DL-pentoses by hydrolysis of the telomers III (n=2).

Among eight possible n=2 telomers which could be syn and anti forms of trans-trans, trans-cis, cis-trans and cis-cis configurations at carbonate rings, only two isomeric telomers, Va,b, Vc,d, Ve,f and Vg,h were preferentially obtained in all cases where CH_2Br_2, $CHBr_3$, CCl_4 and $CHCl_3$ were used as the telogens, respectively. (Table I)

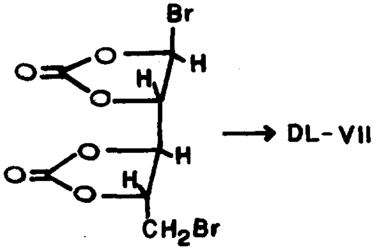
In view of mechanistic aspects on the formation of the telomers, it can be assumed that the n=2 telomers thus obtained are syn and anti forms of trans-trans configurations, which on hydrolysis of the carbonate groups, lead to 5-bromo-5-deoxy-DL-lyxose (DL-VI) and 5-bromo-5-deoxy-DL-xylose (DL-VII), respectively. This was confirmed as described below by the ppc and glpc analyses of the hydrolysis products, DL-VI and DL-VII comparing with authentic samples of 5-bromo-5-deoxy-D-lyxose (VI) and 5-bromo-5-deoxy-D-xylose (VII).

Benzyl 2,3-O-isopropylidene-5-O-methanesulfonyl-α-D-lyxofuranoside (VIII) prepared form D-mannose through six steps according to the Brimacombe's method[3] was treated with LiBr and hexamethylphosphoramide (HMPA)[4] in toluene to give benzyl 5-bromo-5-deoxy-2,3-O-isopropylidene-α-D-lyxofuranoside (IX) in 98% yield, b.p. 130° (0.03mmHg), $[\alpha]_D^{20}$ 91.6° (c=1.31, MeOH), ir (neat) 1610, 1590, 1385, 740 and 700 cm^{-1}, nmr ($CDCl_3$) δ7.32 (aromatic), 5.15 (C_1-H, s), 4.49 (Ph-CH_2-, q), 3.52 (CH_2Br, m), 1.52 (CH_3, s) and 1.36 (CH_3, s).

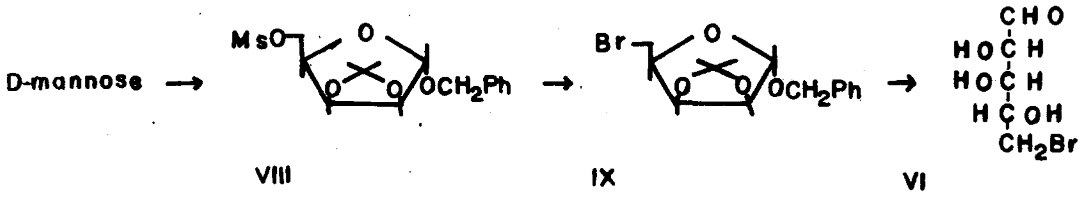
The preparation of 1,2-O-isopropylidene-5-O-p-toluenesulfonyl-D-xylofuranose (X) was carried out by the method of P.A. Leven[5] starting with D-xylose through three steps. The displacement of tosyl group with LiBr in the presence of HMPA similarly produced 5-bromo-5-deoxy-1,2-O-isopropylidene-D-xylofuranose (XI) in 93% yield, m.p. 93-4°, $[\alpha]_D^{20}$-22.2° (c=1.58, MeOH), ir (nujol), 3420 and 1385 cm^{-1}: nmr ($CDCl_3$) δ5.95 (C_1-H, d, J=4 Hz), 3.55 (CH_2Br, m), 1.56 (CH_3, s) and 1.36 (CH_3, s).

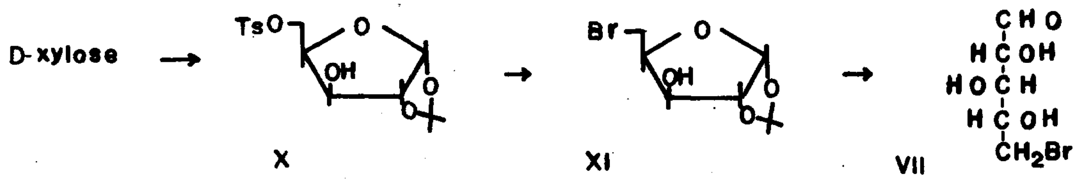


Va



Vb





Simultaneous cleavage of protecting groups of IX and XI with dil.H_2SO_4 gave quantitatively 5-bromo-5-deoxy-D-lyxose (VI) and -xylose (VII) as a syrup, respectively. The carbonate groups of Va and Vb could be readily cleaved with dil.H_2SO_4 to give the quantitative yields of sirupy products, DL-VI and DL-VII, respectively.

Paper chromatography of EtOH solutions of VI, VII, DL-VI and DL-VII was performed using n-BuOH-pyridine-H_2O (6:4:3), and the materials were detected with diphenylamine aniline reagent[6]. Each of VI and DL-VI showed a single pink spot with the same Rf value 0.69. VII and DL-VII also gave the identical single spot (Rf 0.65). Each of these bromodeoxy sugars was converted to the trimethylsilyl (TMS) ethers by the usual procedure[7] for gas chromatographic analysis. The retention times for TMS-derivatives of DL-VI and DL-VII (15% EGS column at 140°) were 6.0 and 7.0 minutes, respectively, which agreed with those of the authentic TMS-derivatives of VI and VII.

Dibromomethyl groups of the telomers Vc and Vd stereoselectively formed on telomerization with CH_2Br_2 as unusual ones[2] were selectively reduced with $Ni(CO)_4$ in THF[8] to the monobromomethyl compounds, which were identical on their ir spectra and melting points with Va and Vb, respectively.

These chemical correlations indicate the stereochemistry of the telomers Vc and Vd to be trans-syn-trans, and trans-anti-trans configurations, respectively. Thus, it has been shown that 5-deoxy-5-substituted-DL-lyxose and -xylose could be derived from the n=2 telomers (III) stereoselectively obtained in the telomerization of vinylene cerbonate with polyhalomethanes.

Transformation of other telomers of type III to carbohydrates is in progress.

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