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ACID-CATALYZED ISOMERIZATION OF 1-C-CARBOMETHOXY-1-DEOXY-2,3,4-TRI-O-ACETYL-L-THREO-PENT-1-ENOPYRANOSE

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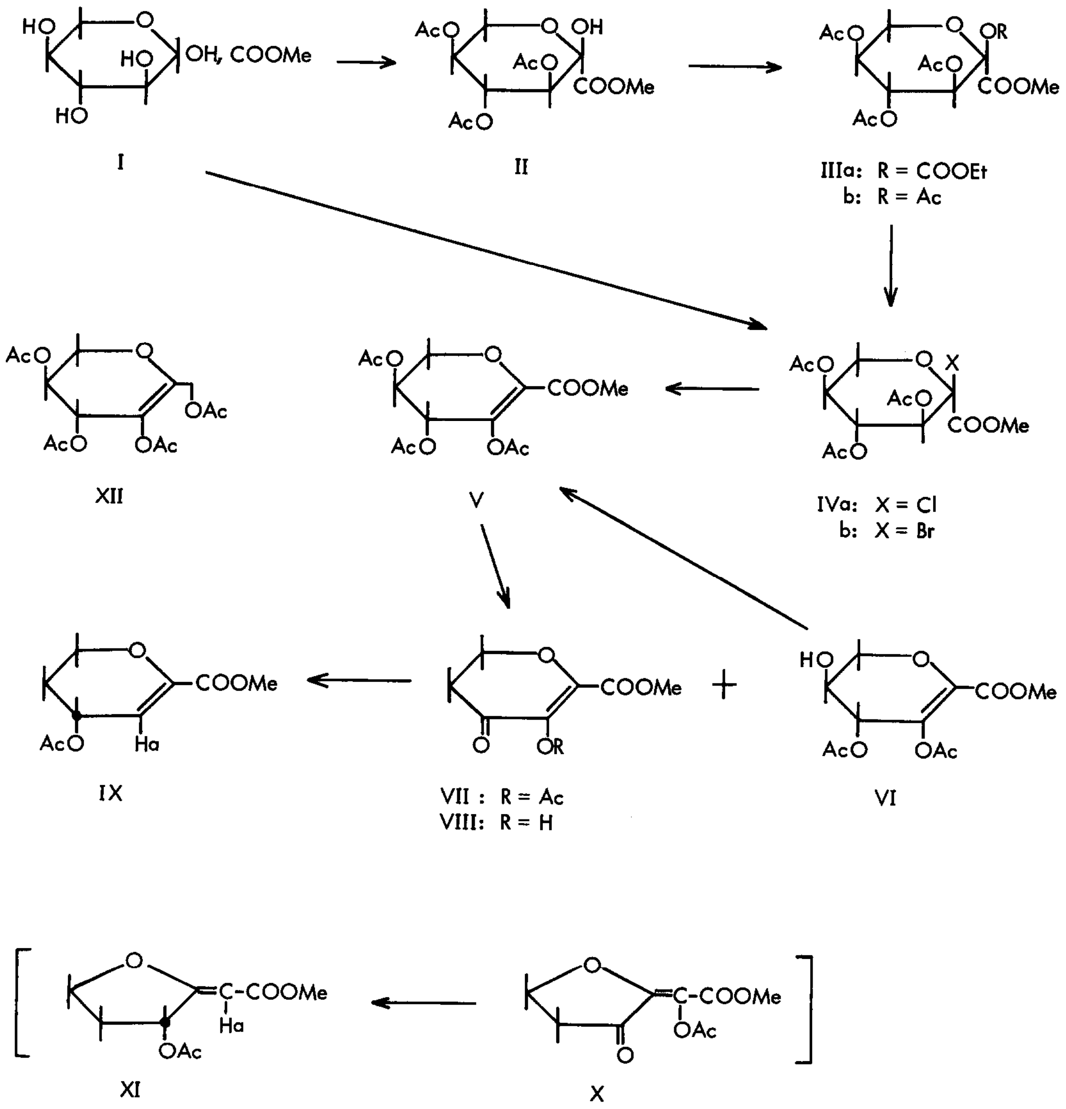
In view of the behavior of unsaturated sugars in acidic media (1,2), the acid-catalyzed isomerization of 1-C-carbomethoxy-1-deoxy-2,3,4-tri-O-acetyl-L-threo-pent-1-enopyranose (V) seemed to be of interest. The synthesis of V was attempted by the scheme outlined in Chart (I → II → III → IVa → V). This procedure was similar to that for 1,3,4,5-tetra-O-acetyl-2-deoxy-L-threo-hex-2-enopyranose (XII) (2), but not feasible because of a poor yield of IVa in the chlorination of III. We prepared IVb directly from I (3) by Lemieux's method using red phosphorus and bromine (4). The dehydrobromination of IVb with mercuric cyanide in toluene afforded V, whose structure was supported by spectral data.

The treatment of V in acetic acid-water (1 : 9 v/v) on a boiling water bath for 9 hours resulted in the formation of a mixture of at least three products (A, B and C) in the thin-layer chromatograms. These products could be resolved by preparative thin-layer chromatography using several solvent systems (5).

The monoacetylation of compound A gave V. The PMR spectrum shows that a multiplet due to H_4 appears at a higher field as compared with that of V. Therefore, the structure was identified as VI.

The IR spectrum of compound B, $C_9H_{10}O_6$, shows the characteristic bands due to a double bond and three kinds of C=O groups. The PMR spectrum also shows two 3-proton singlets due to one carbomethoxyl and one acetoxyl and two 2-proton triplets, which constitute an A_2X_2 system. These data and the UV spectrum suggested the structure to be VII or X. The reduction of compound B with sodium borohydride in pyridine followed by acetylation yielded an acetate, $C_9H_{12}O_5$, as major product. The combined data of spectral and elemental analyses showing the presence of one acetoxyl, one carbomethoxyl and a double bond suggested that the acetate should be IX or XI. However, a signal due to Ha (see Chart) appears as a doublet (J = 5 Hz). As the Ha signal of XI should appear as a singlet or a narrow doublet, the structure



of the acetate was determined to be IX and, consequently, that of the compound B should be VII.

The structure of compound C was identified as VIII, because its acetylation gave VII.

The data of the above-described compounds are reported below (PMR spectra were measured in $CDCl_3$ and chemical shifts were expressed in τ unit. Optical rotations were observed in $CHCl_3$). II: mp 110-112°, $[\alpha]_D^{25}$ -27.0 (c, 0.995). IIIa: mp 103-104°, $[\alpha]_D^{23}$ -80.2 (c, 1.003). IIIb: mp 118-119°,

$[\alpha]_D^{25}$ -73.9 (*c*, 0.973), PMR 4.45^d (H_2, $J_{2,3}$ 9.8 Hz), 4.14^q (H_3, $J_{3,4}$ 9.0 Hz), 4.86^m (H_4, $J_{4,5}$ 6.0 Hz), 6.09^m (H_5, $J_{5,5'}$ 11.5 Hz), 6.56^m ($H_{5'}$, $J_{4,5'}$ 10.5 Hz) (6). IVa: syrup, $[\alpha]_D^{24}$ -88.3 (*c*, 0.891). IVb: mp 110-111°, $[\alpha]_D^{21}$ -137.5 (*c*, 1.067), PMR 4.80^d (H_2, $J_{2,3}$ 9.0 Hz), 4.47^t (H_3, $J_{3,4}$ 9.0 Hz), 4.91^m (H_4, $J_{4,5}$ 5.8 Hz), 5.75^m (H_5, $J_{5,5'}$ 11.3 Hz), 6.10^m ($H_{5'}$, $J_{4,5'}$ 10.7 Hz) (6). V: mp 71-72.5°, $[\alpha]_D^{21}$ 236.9 (*c*, 0.966), UV $\frac{\text{EtOH}}{\text{m}\mu}$ 243 (ϵ 7600), PMR 4.58^m (H_3), 5.02^m (H_4), 5.60^m (H_5), 5.97^m ($H_{5'}$) (The pattern is quite similar to that of XII (2)). VI: syrup, $[\alpha]_D^{22}$ 222.1 (*c*, 0.592), UV $\frac{\text{EtOH}}{\text{m}\mu}$ 246 (ϵ 14700), PMR 4.65^m (H_3), $5.9\text{-}6.2^m$ (H_4). VII: mp 149-150°, UV $\frac{\text{EtOH}}{\text{m}\mu}$ 285 (ϵ 8100), IR $\frac{\text{KBr}}{\text{cm}^{-1}}$ 1765, 1737, 1690 (C=O), 1620 (C=C), PMR 7.23^t (2H) (H_4), 5.38^t (2H) (H_5). VIII: mp 78-79°, UV $\frac{\text{EtOH}}{\text{m}\mu}$ 325 (ϵ 8300). IX: syrup, UV $\frac{\text{EtOH}}{\text{m}\mu}$ 240 (ϵ 7400). IR $\frac{\text{KBr}}{\text{cm}^{-1}}$ 1740 (C=O), 1644 (C=C), PMR 3.89^d (H_2), 4.71^m (H_3), $7.8\text{-}8.2^m$ (2H) (H_4), $5.4\text{-}6.1^m$ (2H) (H_5).

It is of interest to note that the acid-catalyzed isomerization of V yields dihydro-4-pyrone (VII and VIII) mainly (7) as compared with that of XII yielding furan derivatives (2).

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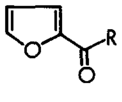
5. Solvent systems used were as follows: chloroform-acetone (9 : 1 v/v), ether-pet. ether (4 : 1 v/v and 1 : 2 v/v) and benzene-ether (3 : 1 v/v).
6. *J* values supported the pyranose structure. See, T. Maeda, *Bull. Chem. Soc. Japan* **40**, 2122 (1967).
7. We have isolated some furan derivatives as minor products. The structure of the one of them was tentatively proposed to be XIII because its PMR spectrum is quite similar to that of XIV (2). However, furans were not derived from the further acidic treatment of VII or VIII.



XIII: R = COOMe
XIV: R = CH_2OAc