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THE CONVERSION OF D-XYLOSE AND D-GLUCURONIC ACID TO 2-FURALDEHYDE[a]

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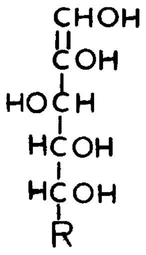
3-Deoxyglycosuloses (III) which are thought to arise from sugar 1, 2-enediols (I) via the enolic form (II) have been suggested as intermediates in a number of carbohydrate conversion reactions. Although recent findings, based on deuterium exchange experiments, do not substantiate the presence of such intermediates in the acid-catalyzed dehydration of hexoses ($R=-CH_2OH$) to 5-(hydroxymethyl)-2-furaldehyde (HMF)[2] the findings are consistant with the presence of such compounds during the alkaline degradation of D-glucose to the metasaccharinic acids (3-deoxy-D-ribo-and 3-deoxy-D-arabino-hexonic acids), and, in some cases, during the acid-catalyzed conversion of Amadori products (1-amino-1-deoxy-ketoses) to HMF[4].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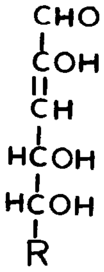
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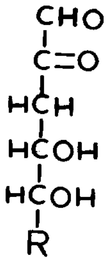
III

The conversion of pentoses and hexuronic acids to 2-furaldehyde in acid solution provide an interesting parallel to the above reactions since, in both cases, analogs of III (R=H for pentoses; R=-COOH for hexuronic acids)

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have also been suggested as intermediates[5,6]. Although the mechanism of conversion of pentoses to 2-furaldehyde might be expected to be analogous to that of the hexoses to HMF, the conversion involving hexuronic acid is more complex, since the reaction involves a decarboxylation step wherein carbon atom 6 is lost as CO_2. A number of mechanisms have been proposed for the uronic acid conversion, and, aside from the analogue of III[6] as a suggested intermediate, which predicts solvent proton exchange at C-3 (corresponding to position 3 of the furan ring) during the reaction, other mechanism proposals predict that no exchange would occur at any position during the reaction[7], and, that exchange would occur at C-5[8] (corresponding to position 5 of the furan ring) after the decarboxylation step.

This work describes a determination of the importance of III and other suggested intermediates in such reactions by converting D-xylose and D-glucuronic acid to 2-furaldehyde in acidified deuterium oxide solution. A determination of the amount of deuterium incorporated at the three furan ring positions after such a conversion would be expected to reflect the relative importance of the proposed reaction pathways.

For the conversions, 3.0 g of carbohydrate was dissolved in 500 ml of deuterium oxide (containing 86 atom per cent deuterium) which was 3.0 N in DCl and distilled for 2.0 hr. The 2-furaldehyde, in 200 ml of distillate was converted to 2-furoic acid by air oxidation[9], and then converted to the methyl ester with diazomethane. Deuterium incorporation measurements were made by n.m.r. spectroscopy at 60 MH_z in chloroform-d solution at a concentration of 150 mg per ml. Using an authentic sample of methyl 2-furoate, the ring protons signals appeared at δ 7.20 (multiplet, position 3); δ6.51 (multiplet position 4) and δ 7.58 (multiplet, position 5) relative to tetramethyl silane. In the case of the furoic acid obtained in the above experiments the signal intensites of the ring protons were compared with one another and with the methyl ester proton singlet at δ 3.88 and no deuterium incorporation could be detected in either sample to the extent of ± 0.1 atom per molecular position. Total isotope exchange was further and more accurately (± 0.01 atom per position) verified by repeating the conversions in acidified, tritrated water (0.49 μc per millimole). The furoic acid obtained from D-xylose was purified by 3 sublimations at 80° and 0.2 mm and had a specific activity of 9.0×10^{-3} μc per millimole and that from D-glucuronic acid contained 4.2×10^{-2} μc per millimole representing, respectively, 2% and 8.4% the activity of the solvent.

The findings thus indicate that the conversions proceed without substantial reversible enolization of intermediates and, in this respect, are analogous to the acid-catalyzed conversion of hexoses to HMF. It is noteworthy in this respect that Isbell[7] has suggested mechanisms for the conversions of both pentoses and uronic acids to 2-furaldehyde which are consistant with the findings presented here.

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