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Formation of Aminoreductones from Maltose

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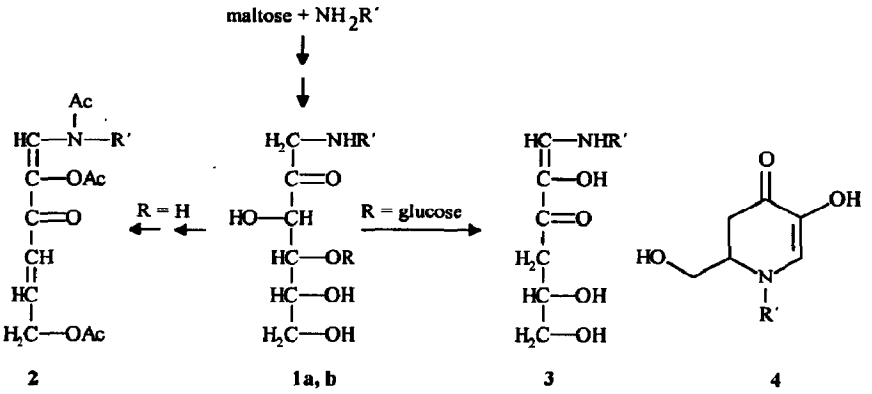
Abstract: Aminoreductones of general structure **3** are obtained by degradation of maltose-derived Amadori compounds (**1**). 3-Hydroxy-5,6-dihydropyridones (**4**) are formed as minor compounds.

Reaction of glucose or maltose with primary or secondary amines leads to the formation of glycosylamines which easily isomerize to give the Amadori compounds **1**, under appropriate conditions in high yields. Amino sugars of type **1** are unstable when heated or stored. Degradation gives rise to a great variety of products with different structures.

Aminoreductones with a cyclopentenone ring system are produced besides several other products, when glucose is brought to reaction with secondary aliphatic amines[1], but a detailed investigation revealed that compounds of this type are not obtained with primary amines[2]. The open chain aminoreductone **2** has been isolated in low yield from a glucose/propylamine reaction mixture after acetylation and chromatographic separation[3]. It is not clear however, whether the acylation conditions had an influence on the formation of **2**.



2 **1a, b** **3** **4**

a: R = H
b: R = glucose

R' = e.g. propyl, butyl

Here we report the isolation and structural identification of an open chain C_6-aminoreductone which is formed as one of the main degradation products of maltose or maltose-derived Amadori compounds.

When the amino sugar **1b** or maltose and butylamine are heated in a phosphate buffered neutral aqueous solution for about 10 min at 100 °C a reaction product with an UV absorption maximum at 325 nm can be detected and purified by HPLC[4]. The structure is derived from spectral data[5]: Mass spectrometry and NMR data revealed the compound to have a molecular formula of $C_{10}H_{19}NO_4$. The aminoreductone structure and the presence of the two ABX systems as shown in the scheme is deduced from ^1H NMR-, ^{13}C NMR-, $^1H^1H$ COSY-, $^1H^{13}C$ COSY- and DEPT spectra. In addition the formula was established by spectral data of the triacetyl derivative[6].

The new compound **3** is unstable under the reaction conditions, so that prolonged heating results in a deminished yield. On the other hand **3** can be obtained in comparatively high amount by alkali catalysed isomerisation of **1b** at room temperature or even below (isolated yield 3.3 %).

Careful separation of the products obtained by degradation of the amino sugar **1b** led to the isolation of a minor component of structure **4**. This compound shows an absorption maximum at 360 nm which is characteristic for 3-hydroxy-5,6-dihydropyridones of this type[7]. Its structure is established by spectral data[8].

Isolation of aminoreductones formed by reaction of glucose with primary amines proved to be more difficult. Our results in this area will be detailed in due time.

References and Notes

1. Weygand, F.; Simon, H.; Bitterlich, W.; Hodge, I.; Fischer, B. *Tetrahedron*, **1959**, *6*, 123 - 128.
2. Ledl, F.; Severin, T. *Z. Lebensm. Unters. Forsch.*, **1979**, *169*, 173 - 175.
3. Estendorfer, S.; Ledl, F.; Severin, T. *Angew. Chem.*, **1990**, *102*, 547 - 548.
4. Seperation was performed on a chrompack, Zorbax ODS RP 18 column (250 mm x 9.8 mm i. d.) with an eluent of water-methanol (9:1).
5. ^1H-NMR ($CDCl_3$): δ 0.95 (t, 3H, CH_3-CH_2), 1.35 (m, 2H, CH_3-CH_2), 1.55 (m, 2H, CH_3-CH_2-CH_2), 2.5-2.6 (dd, 2H, CH_2C=O), 3.2 (t, 2H, CH_2N), 3.5 (dd, 2H, CH_2OH), 3.9 (m, 1H, CHOH). ^{13}C-NMR ($CDCl_3$): δ 14.1 (CH_3-CH_2), 20.7 (CH_3-CH_2), 34.4 (CH_3-CH_2-CH_2), 38.9 (CH_2C=O), 48.5 (CH_2N), 66.7 (CH_2OH), 71.3 (CHOH), 132.2 (C=CH), 138.8 (C=CH), 187.6 (C=O). MS (*m/z*, CI): 218 (M+1), 182, 103. UV (CH_3OH) λ_{max} 322.
6. ^1H-NMR (CD_3OD): δ 0.93-0.97 (t, 3H, CH_3-CH_2), 1.32-1.40 (m, 2H, CH_3-CH_2), 1.55 (q, 2H, CH_3-CH_2-CH_2), 2.00, 2,04, 2,20 (3s, 9H, CH_3CO), 2.65-2.96 (2dd, 2H, $COCH_2$), 3.3 (t, 2H, CH_2N), 4.1 and 4.3 (2dd, 2H, $CHCH_2O$), 5.4 (m, 1H, $CHCH_2O$), 7.7 (2, 1H, CH=C). ^{13}C-NMR (CD_3OD): δ 14.05 (CH_3-CH_2), 20.52, 20.58, 20.63 and 20.92 (CH_3-CH_2 and 3x CH_3CO), 34.24 (CH_3-CH_2-CH_2), 37.29 (CH_2C=O), 48.79 (CH_2N), 65.82 (CH_2O), 70.87 (CH_2-CH-CH_2O), 126.46 (C=CH), 146.96 (C=CH), 170.9, 172.02 and 172.37 (3x CH_3CO), 185.86 (CH_2CO). MS (*m/z*, CI): 344 (M+1), 284. UV (CH_3OH) λ_{max} 300. CHN Anal calcd. for $C_{16}H_{25}NO_7$ C, 55.96; H, 7.34; N, 4.079. Found: C, 55.78; H, 7.49; N, 4.105.
7. Kettner, B.; Ledl, F.; Lerche, H.; Severin, T. *Tetrahedron*, **1991**, *45*, 9351 - 9356.
8. ^1H-NMR (CD_3OD): δ 0.97 (t, 3H, CH_3-CH_2), 1.33-1.45 (m, 2H, CH_3-CH_2), 1.58-1.65 (m, 2H, CH_3-CH_2-CH_2), 2.4 (dd, 1H, J = 17.24 and 3.6 Hz, CH_aH_b-C=O), 2.7 (dd, 1H, J = 17.24 and 6.97 Hz, CH_aH_b-C=O), 3.2 (m, 1H, N-CH_aH_b), 3.3 (m, 1H, N-CH_aH_b), 3.5-3.6 (m, 2H, CH-N and CH_aCH_bOH), 3.7 (dd, 1H, CH_aCH_bOH), 7.1 (s, 1H, CH=C). ^{13}C-NMR (CD_3OD): δ 14.1 (CH_3-CH_2), 20.8 (CH_3-CH_2), 32.9 (CH_3-CH_2-CH_2), 36.8 (CH_2C=O), 55.3 (CH_2N), 59.0 (CHN), 59.9 (CH_2OH), 128.3 (C=CH), 145.4 (C=CH), 184.1 (C=O).

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