

The Reaction of Aniline with Isopropylidene-D-glyceraldehyde

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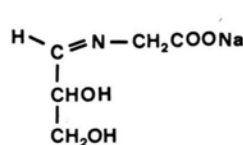
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Maillard Reaction

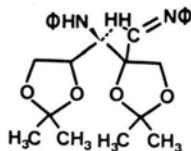
The reaction of aniline with 2,3-O-isopropylidene-D-glyceraldehyde supplies the dimeric form of the expected Schiff's base which may serve as a model for the initial step of the Maillard reaction.

The non-enzymic browning reaction between reducing sugars and amino acids or proteins (often called the Maillard reaction [1]) may involve Schiff's base formation as an early step in the process [2]. We, therefore, tried to find some model reactions between simple sugars and amino acids in order to be able to isolate the corresponding Schiff's bases. The reactions between glyceraldehyde or dihydroxyacetone, respectively, and the sodium salts of glycine or alanine [3] always lead to amorphous brown products which cannot be purified by common chromatographic processes. The IR-Spectra of these compounds show the band of C=N-stretch vibration superposed from the COO⁻-vibration. The IR-Spectra coincide with other observations [4]. These compounds can be treated with Ni/H₂. The hydrogenation not always passes quantitatively. The formation of oligomeric compounds already on this early step in the reaction sequence, cannot be excluded.

Thus we tried to prevent the possible oligomerisation by blocking the OH-groups of the glyceraldehyde. In order to stabilise the Schiff's base, an aromatic amine (aniline) was used. The resulting colourless substance, however, is the dimeric product of the expected Schiff's base **2**. The monomeric form cannot be isolated. Dimeric products of Schiff's bases have been observed several years ago [5].



1



2 (dimer)

The analogous reaction between aniline and dihydroxyacetone in contrast leads to a brown

polymer product. The reaction between dihydroxyacetone with blocked OH-groups and aniline is still observed.

The spontaneous dimerisation of the Schiff's base to **2** leads us to the reception that the first reaction of a condensation between glyceraldehyde and an amino acid may be the formation of the dimeric Schiff's base which can polymerize by spontaneously forming coloured products.

Experimental

Melting points: uncorrected, Büchi 510. – ¹H-NMR: Bruker WH 270, TMS as internal standard. – IR: Perkin-Elmer IR 580 B.

Condensation of glyceraldehyde with sodium glycinate (**1**): 0.9 g (0.01 mole) DL-glyceraldehyde and 0.96 g (0.01 mole) sodium glycinate are shaken four days in 50 ml dry MeOH at 25 °C. While adding ether to the solution a brown solid precipitates. It is centrifuged and dried over P₄O₁₀ *in vacuo*, m.p. 250 °C (decomp.), yield 1.5 g (91%). IR (KBr): 3390 (OH), 1600 (CO₂⁻, C=N), 1400 cm⁻¹ (CO₂⁻).

C₅H₈NNaO₄ (169.1)

Calcd	C 35.51	H 4.77	N 8.28,
Found	C 35.54	H 4.71	N 7.92.

1,2:4,5-Di-O-isopropylidene-2-(N-phenylimino)-(R,S)-3-phenylamino-1-(R)-2,4,5-tetrahydroxypentane (**2**): To a solution of 0.65 g (5 mmole) 2,3-O-isopropylidene-D-glyceraldehyde in 10 ml carbon tetrachloride an equimolar amount of fresh distilled aniline in carbon tetrachloride is dropped at room temperature. After several hours a colourless substance precipitates. m.p.: 285 °C (decomp.), yield: 1.66 g (81%). ¹H-NMR ([D₆] acetone): δ = 1.31, 1.41, 1.47 and 1.48 (3H each, s, CH₃), 3.93 (1H, mc, A-part of an ABM-spectrum, J_{AB} = 8.5 Hz, J_{AM} = 6 Hz), 4.03 (1H, d, J_{AA'} = 9 Hz, CH₂OR), 4.08 (1H, mc, B-part of an ABM-spectrum, J_{BM} = 7 Hz), 4.24 (1H, d, J_{A'A} = 9 Hz, CH₂OR), 4.63 (2H, mc, M-part of an ABM-spectrum and CHNHAr), 4.76 (1H, d, J = 9 Hz, NH), 4.87 (1H, s, HC=NAr), 6.53–7.2 (10H, m, ArH). – EI-MS: *m/e* = 410 (M⁺, 14%), 395 (M⁺–CH₃), 196 (100%).

C₂₄H₃₀N₂O₄ (410.5)

Calcd	C 70.22	H 7.37	N 6.82,
Found	C 70.24	H 7.54	N 6.86.

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