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Phenylglycosylamines in melanoidin reaction

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Abstract

By the example of N-carboxy-phenylglycosylamines and N-hydroxy-phenylglycosylamines we have studied the dependence of transformation of N-glucoside – a key product of Maillard reaction on reaction medium pH and temperature [1,2]. We have determined the intensity of the mentioned aryl-N-glucosamines' transformation into melanoidin according to number of formed melanoidin complexes (λ =470), and we have compared this process to melanoidin formation from respective amine component and glucose. We have conducted reaction in phosphate buffer medium, at following pH values: 5,0; 7,0; 9,2; at 1000°C during 2 hours, concentration of aryl-N-glucosamines or respective sugar-amine reacting mixture was 0.1 mole/l. Melanoidin reaction rate has been determined according to extinction of the formed melanoidin pigment (λ=470 nm). According to our experiment, N-glucosides and their respective sugar-amine mixtures participate in melanoidin reaction in a similar fashion: they generate melanoidin with roughly similar intensity at identical pH. At that, some difference has been noted between aminobenzoic acids and aminophenols; in particular, N-hydroxy-phenylglycosylamines and their respective sugar-amine mixtures intensively generate melanoidin pigments at high pH (9,2) and melanoidin reaction intensity reduces with increase of acidity. This fact makes aminophenols similar to

aliphatic amino acids, which exactly in alkaline medium take more active part in melanoidin reaction [3].

Key Words: Aminobenzoic acid, Aminophenol, Toluidine, Phenylglycosylamines, Melanoidin reaction

According to ability to form melanoidin pigment, activity of aminophenols and their respective N-glucosides decreases in the following series: p > o > m. N-carboxy-phenylglycosylamines and their respective sugar-amine mixtures actively generate melanoidin pigment at low pH (5,0) and melanoidin reaction intensity reduces with decrease of acidity. Thus, in the context of participation in melanoidin reaction, aminobenzoic acids differ markedly from aminophenols and aliphatic amino acids. According to ability to form melanoidin pigment, the activity of aminobenzoic acids and their respective N-glycosides decreases in the following series: m > o > p. Experimental results are given in the Table 1.

Table 1: Melanoidin product formation during glucose and amine component interaction (phosphate buffer, 100°C, 2 hours; concentration of reacting components 0,1 mole/l)

Amine component	**pH**	**Melanoidin product extinction λ 470 nm**
o - aminobenzoic acid	5,0	1,38
	7,0	1,32
	9,2	1,23
m - aminobenzoic acid	5,0	*
	7,0	1,39
	9,2	1,32
p - aminobenzoic acid	5,0	0,67
	7,0	0,25
	9,2	0,20
o - aminophenol	5,0	1,53
	7,0	1,78
	9,2	1,88
m - aminophenol	5,0	0,92
	7,0	1,10
	9,2	1,18
p - aminophenol	5,0	1,60
	7,0	1,81
	9,2	2,10

* The reaction proceeds very vigorously and melanoidin pigment is released.

As we mentioned, the first stage of sugar-amine reaction is N-glycosylation of amine components, while this process of N-glycosylation is influenced by alkaline nature of the reacting amine. pKa value of o-, m- and p-aminobenzoic acids equals to 2.11; 3.12; 2.41, respectively.

During o-, m- and p-aminobenzoic acids' interaction with glucose, the carboxyl group, due to its negative inductive and negative mesomeric effect, reduces electron cloud density on nitrogen atom and, respectively, basic nature of nitrogen atom. In this case, N-glucoside, due to its high stability, is produced with higher yield. Relatively lower yield of N-glucoside in the event of o-aminobenzoic acid can be explained by presence of spatial factor. Due to presence of negative mesomeric effect of the carboxyl group, m-aminobenzoic acid is a stronger base, than o- and p-aminobenzoic acids, therefore N-m-carboxyphenyl-D-glucosylamine is a less stable compound and, respectively, its yield is low as well.

Thus, the stronger base the amine is, the easier it participates in N-glycosylation reaction, but also the easier are the following transformations (Amadori rearrangement, Maillard reaction, deamination, decarboxylation, furanose nucleus formation etc.) of the formed N-glycoside [4, 5, 6]. This circumstance is clearly seen from Figures 1-3, where the results of N-o-, -m- and –p-carboxyphenyl-glucosylamine hydrolysis process are given. Number of aminobenzoic acid generated resulting from hydrolysis of these N-glycosides in acid or neutral medium is higher in the case of o- and p- isomers, compared to m-isomer. This difference becomes more evident with rise of hydrolysis process temperature [7].

Figure 1

N-o-carboxyphenyl-glucosylamine (0,017 mole/l) hydrolysis in 0,1 M phosphate buffer, hydrolysis duration is 150 minutes: 1 – pH 5,0; 2 – pH 7.0; 3 – pH 9,2.

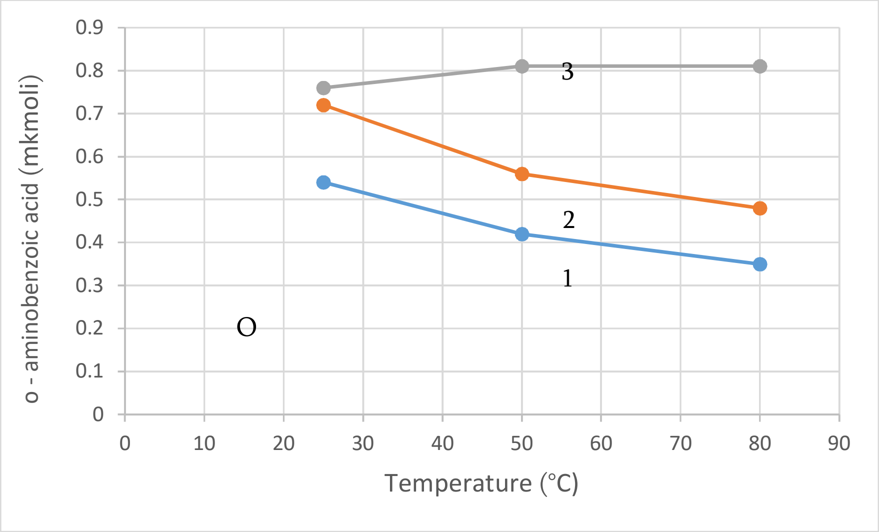


Figure 2

N-m-carboxyphenyl-glucosylamine (0,017 mole/l) hydrolysis in 0,1 M phosphate buffer, hydrolysis duration is 150 minutes: 1 – pH 5,0; 2 – pH 7.0; 3 – pH 9,2

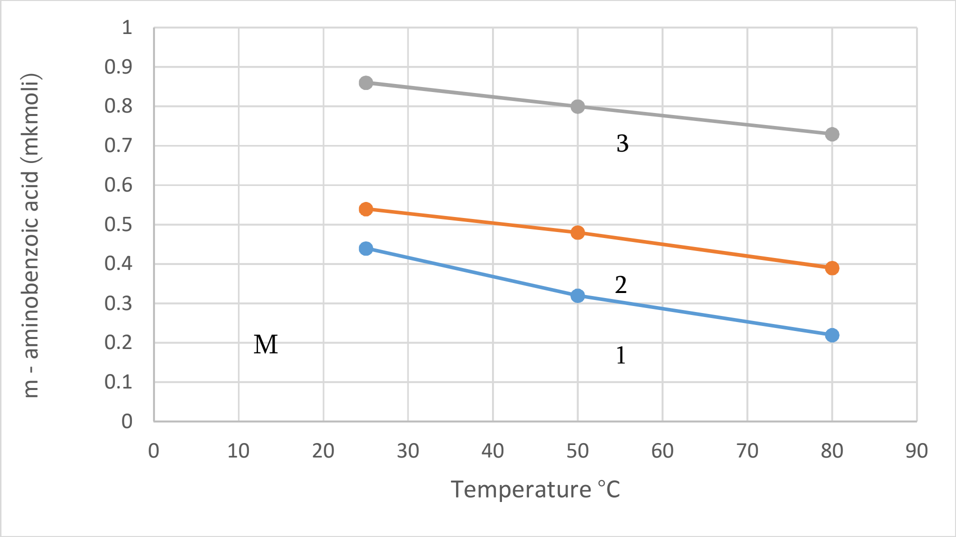
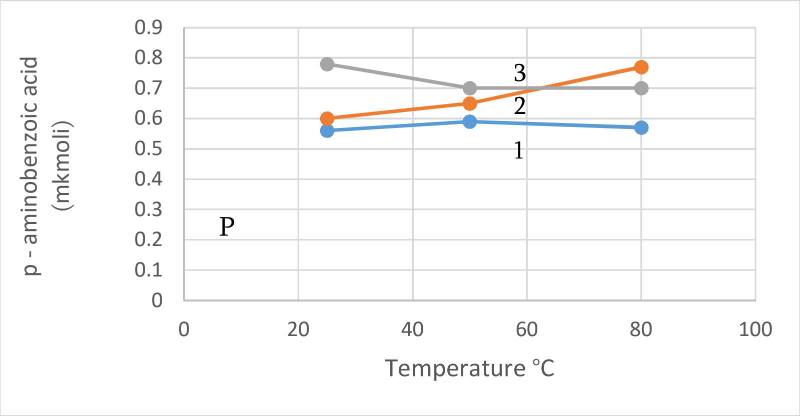


Figure 3

N-p-carboxyphenyl-glucosylamine (0,017 mole/l) hydrolysis in 0,1 M phosphate buffer, hydrolysis duration is 150 minutes: 1 – pH 5,0; 2 – pH 7.0; 3 – pH 9,2

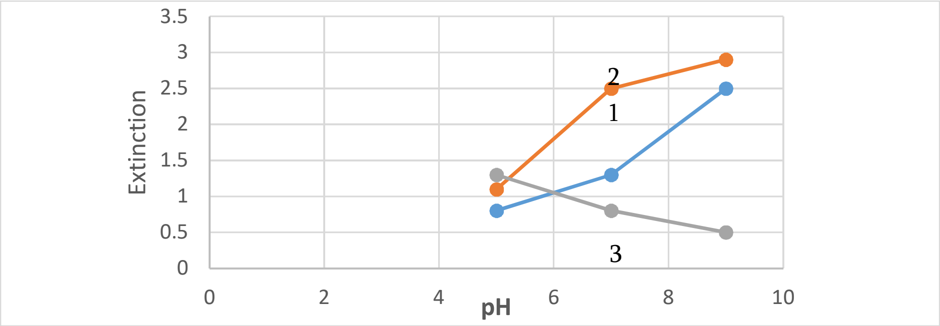


It is obvious, that in parallel with N-carboxyphenyl-glucosylamine hydrolysis process, aminobenzoic acid and glucose formed in the same medium, interacts again according to Maillard reaction scheme. This is evidenced by melanoidin pigment formation in the hydrolysis area, which is especially intense at high temperatures (80°C). Presence of hydroxymethyl-furfural in hydrolysis area also points at Maillard reaction. Identifying of the latter has been managed in area of hydrolysis carried out at 80°C, while in case of N-m-carboxyphenyl-glucosylamine – in the hydrolysis area carried out at 50°C. Thus, the comparative analysis of results of N-carboxyphenyl-glucosylamine hydrolysis shows, that among izomeric aminobenzoic acids, m-isomere or its respective N-glucoside take especially active part in Maillard reaction. It should be noted that when heating in non-aqueous solutions, aminobenzoic acid N-glucosides form melanoidin pigments only under long-time heating conditions and then in negligible quantity, while, as we can see, hydroxymethylfurfural is not produced at all [8].

The obtained results show that in contradistinction from protein amino acids, which take more active part in Maillard reaction being in base medium, isomeric aminobenzoic acids react with more energy being in acid medium. In this regard, comparison of toluidines, aminophenols and aminobenzoic acids provide interesting picture.

Figure 4

Melanoidin reaction in the mixture of: (1) D-glucose + p toluidine; (2) D-glucose + p-aminophenol; (3) D-glucose + p-aminobenzoic acid; melanoidin products' formation is calculated on 353 sec (molar ratio 1:1, 0,1 M phosphate buffer, reaction temperature 100°C, duration 2 hours)



During this comparison a definite regularity has been noted: in particular, activity of toluidines and aminophenols in Maillard reaction increases with rise of pH, while in case of aminobenzoic acids this activity decreases, on the contrary. A case in point is represented in Figure 4, where activity of p-isomers of these compounds in Maillard reaction is compared under the same conditions.

This regularity in a certain way is associated with pKa values of the mentioned compounds, which are represented in Table 2. As is seen, among phenylamines, compounds with high ionization constant take more active part in Maillard reaction in weak acid medium, while compounds with lower ionization constant – in weakly alkaline medium, on the contrary [9].

Table 2

pKa values of substituted phenylamines

Compound	**pKa**
o -Toluidine	4,39
m -Toluidine	4,60
p -Toluidine	5,12
o - aminophenol	4,72
m - aminophenol	4,17
p - aminophenol	5,17
o - aminobenzoic acid	2,11
m - aminobenzoic acid	3,12
p - aminobenzoic acid	2,41

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