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To: Whom it may concern

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Detection of formaldehyde in non-treated carrageenan, part 2

After my first presentation of a reaction route to formaldehyde in carrageenan, I was challenged by the fact that formaldehyde can also be detected in non-treated carrageenan that does not contain sucrose.

This fact may be explained by a very similar pathway, starting by acid hydrolysis of the carrageenan macromolecule, leading to galactose-4-sulfate which may also enter the same set of reactions, as will be demonstrated in the following.

Carrageenan is a high molecular weight linear polysaccaride comprising repeating galactose units and 3,6-anhydrogalactose, both sulfated and non-sulfated, joined by alternating α-(1,3) and β-(1,4) glycosidic links[1]. In solution, the molecule will be hydrolysed at a rate which is largely increased by addition of acid and/or by increase of temperature, demonstrated In Figure 1 for the building block of κ-carrageenan:

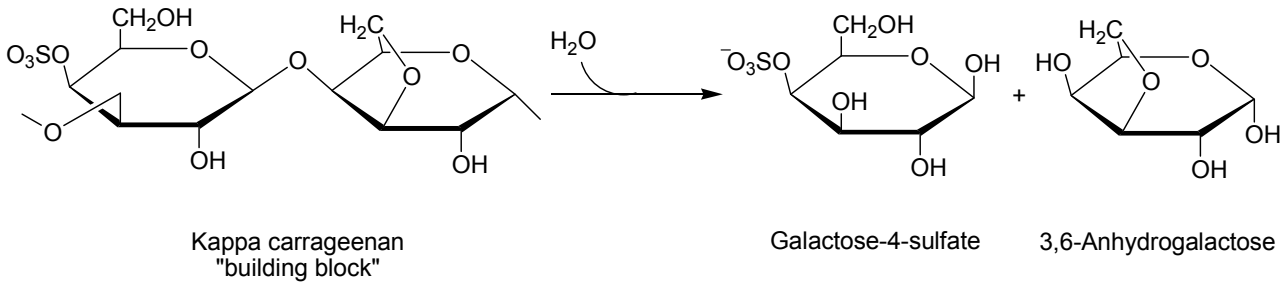

Figure 1: Hydrolysis of a κ-carrageenan building block

Notably, this produces galactose-4-sulfate, which will also be produced from hydrolysis of ι-carrageenan and λ-carrageenan. In contrast to 3,6-anhydrogalactose (or its sulfated forms), galactose-4-sulfate is expected to be reactive in Maillard reactions, i.e. formation of N-glycosides plus consecutive reactions.

[1] Imeson, A.P. "Carrageenan", In Phillips, G.O. and Williams, P.A. "*Handbook of hydrocolloids*", p.87-102.Woodhead Publishing, Cambridge, 2000.

Reaction of galactose-4-sulfate with amines or amino acids (R-NH_2) e.g. resulting from protein hydrolysis leads to formation of a so-called Amadori compound, a 1-amino-1-deoxyketose, which is sulfated in position 4:

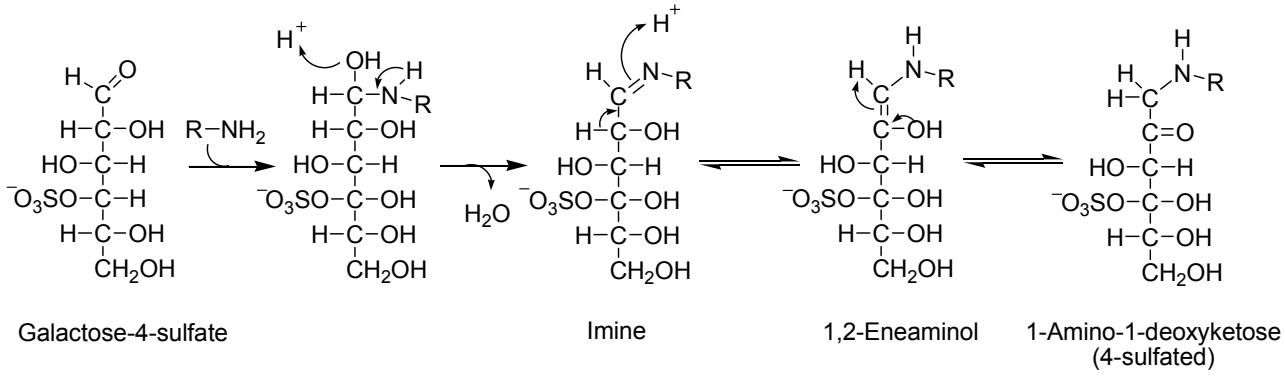

Figure 2: Formation of a 1-amino-1-deoxy-ketose from galactose-4-sulfate

In the reaction scheme of Figure 2, it is notable that it is the unprotonated amine that reacts. Consequently, in basic solution the rate of imine formation is largely increased compared to neutral solution.

Amadori compounds are only intermediates and readily degraded to 1-, 3-, and 4-deoxydicarbonyl compounds (deoxyosones). The formation of the 3-deoxyosone (sulfated in position 4) is shown below:

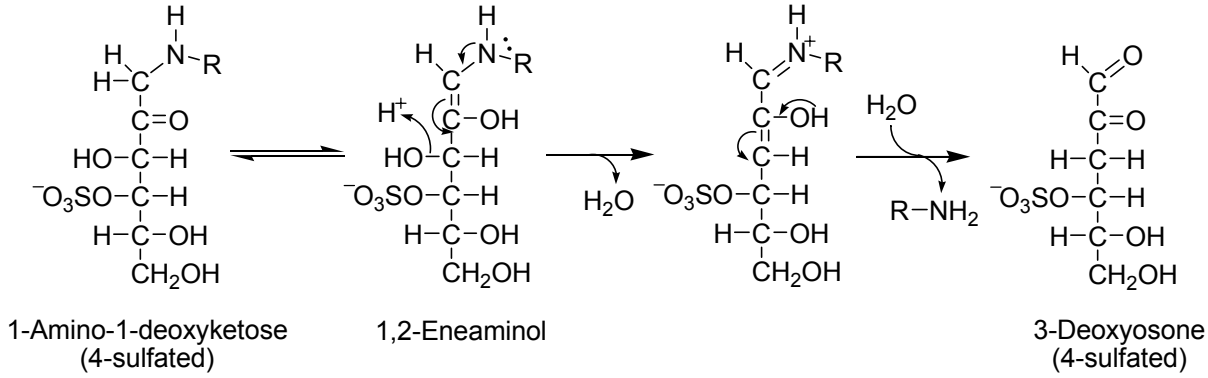

Figure 3: Deoxyosone formation

Deoxyosones react with amino acids, in the so-called Strecker reaction to produce aldehydes, and formaldehyde is thus formed in the reaction with the amino acid glycine (Figure 4):

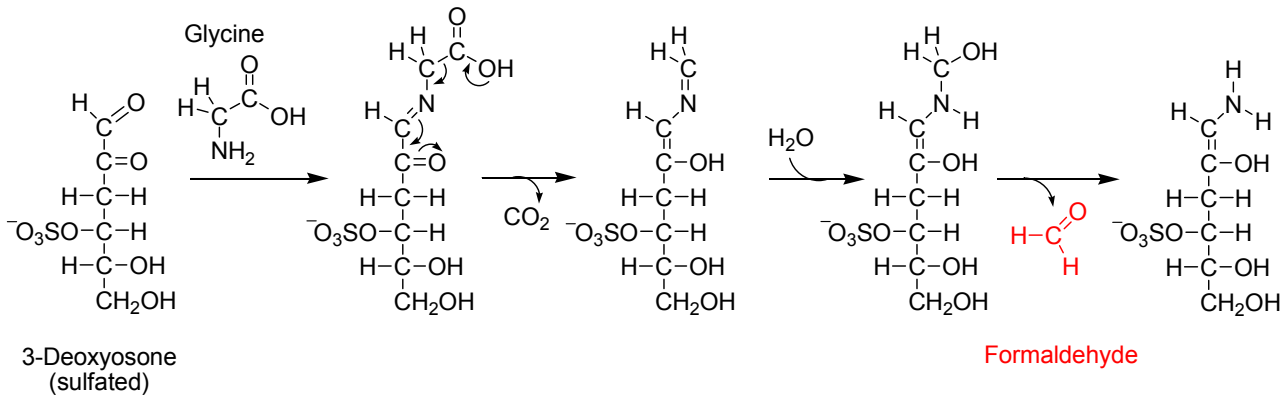

Figure 4: Formation of formaldehyde in the reaction between deoxosones and glycine.

Conclusion

Formaldehyde may, as demonstrated in the reaction schemes[2], be produced in reactions involving heating of non-sucrose added carrageenan. Since the pathway to formaldehyde depends of several steps of which some are promoted in acidic solution and others in basic solution, it is difficult to predict the actual amount formed during the preparative step of the analysis. However, the amount of formaldehyde formed increases with prolonged holding time under all conditions The formation of formaldehyde is expected to be limited by the amount of glycine available for the reaction in Figure 4, since the end product can be oxidized and hydrolyzed, releasing ammonia and re-generate the deoxyosone. Hence, the highest amounts are expected to be found in those products, which have the highest content of protein.

[2] These reactions can be found in advanced Food Chemistry textbooks like Belitz, Grosch & Schieberle "*Food Chemistry*", 3rd revised Edition (Springer, Berlin 2004).