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ANALYTICAL CHALLENGE

Solution to Maillard and grilled steak challenge

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Today's solution to the ABC Analytical Challenge is unusual, because there is no answer yet.

Let us recall the facts. Maillard processes are famous in science and technology, particularly food and medicine. In fact, Maillard processes are said to be responsible for both good and bad [1]: they contribute to the flavour of some cooked food (particularly meat) but also generate glycation products, which can be bad for our health, as is clearly apparent in the proceedings of the Maillard association (IMARS [2]).

It is also true that Maillard processes are "fashionable": in July 2015, a Google Scholar search for "Maillard reaction" led to more than 45,000 answers (250,000 for "Diels-Alder"), including more than 2 000 results for 2015 only. The same growing trend is also apparent from the Pubmed database (Fig. 1). A variety of aspects and models have been studied but, as said in the Maillard Challenge [3], the chemists are not clear what is and what is not a Maillard reaction. Frequently, articles include such statements as "The Maillard reaction is a very complex series of reactions", which is a way of admitting the general perspective is far from clear.

As said in the Maillard Challenge [3], the term "Maillard reaction" should be used to refer to interactions between an amino group and an α-hydroxy carbonyl moiety of a reducing sugar, which produces Amadori or Heyn's products, depending on the particular sugar (aldose, ketose) [4–6]. A cascade of reactions follows, including many that have been studied outside the food context of Maillard reactions (thermolysis, oxidation, hydrolysis, reduction, aldol condensation, etc.), and the issue is whether such reactions should be included in the "Maillard reaction".

Of course, we could consider whether Maillard reactions include all these reactions, but it would result in a very complex system. It has been proposed that the Maillard reaction should be classified into its early, advanced, and final stages [7], but this proposal was recognized as simplistic. Later [8], it was proposed that the propagation of the Maillard reaction could be described by the formation and interaction of so-called "chemical pools" generated from specific precursors. Intermediates produced during the initial stage of the Maillard reaction arise from three well defined principal precursors: sugars (S), amino acids (A), and Amadori or Heyn's products (D). The nature and relative ratio of the principal precursors, which constitute the parent mixture (A + S + D) determines the pathway of the Maillard reaction for particular conditions. The proposal to use the term "fragmentation pools" is not convenient, because what was called "advanced Maillard reactions" involved not only fragmentations but also condensations.

However, such a proposal has the disadvantage that "Maillard reactions" would include chemical reactions for which there is no Schiff base, for example caramelization [9, 10], hence the proposal is to restrict the Maillard reaction solely to the first step of Schiff base formation.

Indeed, the situation is the same as for the discovery of chlorophylls, when the French chemist Joseph-Bienaimé Caventou (1795–1877) proposed the name "chlorophylle" for what cooks had, for centuries, called "spinach green" [11, 12]. Caventou only wanted to conduct a new

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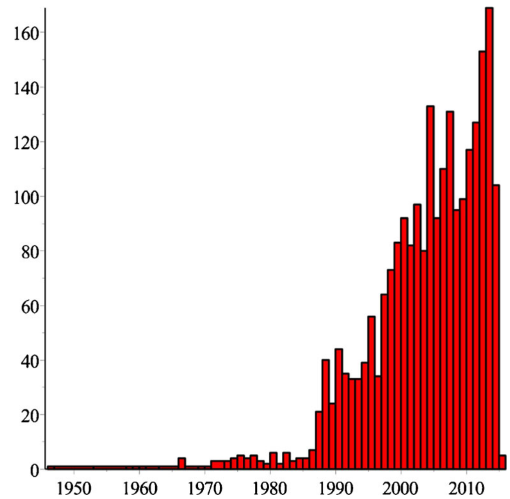

Fig. 1 The number of PubMed references on "Maillard reaction" by year

investigation of such material, and wrote "we have no right to give a new name to a substance well known since a long time ago, and to the knowledge of which we only added some facts; however we propose, without pretending that it has any importance, the name of 'chlorophylle'." [13] Later it was shown that the colouring substance of green plants is a mixture of different compounds, which were separated by Georges Gabriel Stokes [14], then H.C. Sorby and Mikhail Tswett by use of different solvents or chromatography. Such pigments include chlorophylls, carotenoids, and derivatives of these compounds, for example pheophyllins and pheophorbides [15].

The story of chlorophyll is recounted here to emphasise that, in the history of science, new concepts are introduced with new words, and it is probably not a good practice to hide under a general name (Maillard) what should be better distinguished. As proposed in the Maillard Challenge [3], the proposal to enlarge the meaning of "Maillard reactions" does not make the description simpler; on the contrary: any new experimental result in this regard will only increase the complexity, instead of leading to clarity. Hence, the proposal of the Challenge is to restrict the meaning of "Maillard reactions" to the minimum, i.e. to the formation of Amadori and Heyn's products. And because there is no reason to look for an impossible comprehensive description, the proposal was to consider particular cases (meat, vegetables) and particular aspects of the whole transformation.

Because some compounds can arise from sugars or from carbon–nitrogen bond-cleavage reactions of Amadori or Heyn's products, the proposal was to study the different reactions that can occur when grilling steak. Indeed in the previous discussion, we omitted the possibility of speaking of non-enzymatic browning, which is also slightly misleading, because some Amadori and Heyn's product can lead to colourless products; moreover, almost any compound turns brown when heated. Thermolysis and pyrolysis also can be important [16].

In conclusion, it could be helpful for the discussion of "browning" to invite readers to think about the experiment with invisible ink, a substance (e.g. lemon juice) used for writing, which is invisible on application but can later be made visible by use of heat, for example. Indeed, if you perform such an experiment, you will see obviously that paper becomes yellow when lemon juice is added; moreover, from the perspective of heat-induced browning, lemon juice has no particular property, and most organic compounds, even those as simple as acetic acid, can turn brown. Indeed organic chemists know very well that the appearance of a yellow or brown colour is frequent in their heated systems where no Maillard reaction occurs.

Hence the Maillard Challenge is still open!

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