Food Research Institute
UNIVERSITY OF WISCONSIN–MADISON

2/6/2023 Volatile Compounds and Maillard Reaction

Research Questions: (1) Are any of the volatile compounds in the list below associated with the Maillard reaction or other reactions that result in color changes of foods?; (2) Are the compounds only contributors to aroma/ flavor, color or a combination of both?; (3) If the compounds are associated with the Maillard reaction or other color change reactions, where in the reaction pathway are they located?

Compound List

2-methyl-1-butanal
2-methyl-1-propanal
3-methyl-1-butanal
benzaldehyde
benzeneacetaldehyde
decanal
dimethyl disulfide
dimethyl trisulfide
ethyl acetate
furfural
hexanal
hexanoic acid
nonanal
octanal

FRI Response:

Numerous papers report that levels of one or more of these compounds increase (due to the Maillard reaction) in parallel to changes in the color of a food product during heat treatment, fermentation, or storage. These compounds are associated with aroma and flavor. However, these volatiles have not been shown to be **responsible** for the color changes (but the studies don't necessarily rule this out, either):

- A detailed review article states that the presence of aldehydes in beer (not specified, but many of the aldehydes in the list above are found in beer) has been associated with changes of color during storage (Schubert et al., 2022). However, it's not clear that the aldehydes themselves are directly involved in the color change.
- Another review reported that "recent works have reported difficulty in correlating the production of color and the concentration of specific aroma-active volatiles" in malted barley and that "the correlation between color and aroma is of big complexity" (Prado et al., 2021).
- Another paper found correlations between the formation of various volatile compounds (including some of those in the list above) and the color of heat-dried pasta, and suggested that

such volatiles could be used as potential markers for the intensity of the heat treatment (such as online monitoring of the drying process for pasta) (Pasqualone et al., 2014).

- The levels of some of these volatile compounds increase during the fermentation of shrimp paste in parallel to changes in the color of the shirmp paste, but no role for the volatiles in promoting the color change was proposed by the researchers (Deng et al., 2022).
- Storage of cauliflower soup powders for 12 weeks at 40°C increases the levels of 2-methyl- and 3-methyl butanals (Strecker aldehydes that form in Maillard reactions). Dimethyl disulfide in the soup powder headspace also increases, indicating free radical-initiated protein oxidation. During the storage time, the soup powders became more brown, but no causative role for volatiles in the color change was mentioned (Raitio et al., 2011).
- Low molecular-weight aldehydes are involved in degradation of pigments in cranberry juice (Bueno et al., 2018; Dorris and Bolling, 2021).

The following reports some more information, including mechanism of formation, for some of these compounds:

2-methyl-1-butanal

- A search of Web of Science (all databases) with (2-methyl-1-butanal) AND (Maillard or color) AND food found no relevant documents.

2-methyl-1-propanal

- A search of Web of Science (all databases) with (2-methyl-1-propanal or isobutylaldehyde) AND (Maillard or color) AND food found no documents. Several papers were found in which neither the Maillard reaction or color were linked to these terms, however:
- One other paper did find that this compound was produced after baking sourdough bread, and the volatile profiles before and after baking “showed the influence of amino acids”; later in the paper the authors discuss how amino acids (especially lysine, valine and leucine) affect bread flavor through the Maillard reaction (but color was not discussed) (Gobbetti et al., 1995).
- Another paper said that amino acids in beer are a source of aldehydes, including 2- methyl-propanal and 3-methyl-butanal. Their formation is increased when valine or leucine are added and oxygen is present. The reaction is catalyzed by Fe and Cu ions and is thought to occur via Strecker degradation of amino acids (Vanderhaegen et al., 2006).

3-methyl-1-butanal:

- A search of Web of Science (all databases) with (3-methyl-1-butanal) AND (Maillard or color) AND food found no relevant documents.
- One paper said that amino acids in beer are a source of aldehydes, including 2- methyl-propanal and 3-methyl-butanal. Their formation is increased when valine or leucine are added and oxygen is present. The reaction is catalyzed by Fe and Cu ions and is thought to occur via Strecker degradation of amino acids (Vanderhaegen et al., 2006).

benzaldehyde

- The Maillard reaction (MR) promoted the formation of aldehydes, especially heptanal and benzaldehyde, in sweet potato protein isolates (Habinshuti et al., 2021).
- This compound was not found in potato and sweet potato protein hydrosylates of potato and sweet potato, but was found in their Maillard reaction products (supplementary material for (Habinshuti et al., 2022). The authors of that paper stated that "the formation of aldehydes might be mainly due to the oxidation of fatty acids".

benzeneacetaldehyde:

- In sweet potatoes, branched aldehydes such as benzeneacetaldehyde might come from amino acid degradation, potentially a nonenzymatic process. In malt, benzeneacetaldehyde levels increase during roasting and with longer roasting times (Hou et al., 2020).
- In fish floss, the formation of benzeneacetaldehyde was mainly due to the Maillard reaction and was linked to flavor (no discussion of its specific impact on color, although the study does report that Maillard reaction products in general contribute to color in foods) (Chen et al., 2022).

decanal

- Decanal was detected from "Maillard reacton liquid" from soybean meal hydrosylate and had an important effect on meat flavor (color was not mentioned) (Zheng et al., 2017).
- Hexanal, nonanal, and decanal are produced from high-temperature Maillard reactions in baked glutinous rice powder where they are key flavor substances (Rui et al., 2019).
- Decanal levels increased as color changed during oxidative aging of a sweet wine, but it's not clear decanal played any role in the color change (Chaves et al., 2007).

dimethyl disulfide

- Dimethyl disulfide is considered a "secondary product" from the reaction of amino acids and glucose (Chan and Reineccius, 1994).
- Dimethyl disulfide (and many other volatiles, including decanal) levels increased during the 8 years of fermentation of shrimp paste; during this same time period the shrimp paste became progressively darker (Deng et al., 2022).

dimethyl trisulfide (DMTS)

- Formed during beer storage by the reaction between methanesulfenic acid and hydrogen sulfide. Methanesulfenic acid is formed by beta-elimination from S-methylcysteine sulfoxide, introduced to beer from hops. Other DMTS precursors may be 3-methylthiopropionalehyde and its reduced form, 3-methylthiopropanol (Vanderhaegen et al., 2006). No mention was made of the Maillard reaction or color formation, though.

ethyl acetate

- Among various types of beer, color correlated strongly with the final thanol, propanol, and ethanol-sio-amyl alchol content, but NOT with ethyl acetate

furfural

- This volatile doesn't contribute significantly to the aroma of fresh sweet potatoes until sweet potatoes are roasted. It is associated with a roasted nut odor and produced in roasted sweet potatoes when "carbohydrates degrade into dark polymers" (Tsai et al., 2021).
- Furfural is produced in low levels in beer as a result of the Maillard reaction (Vanderhaegen et al., 2006).
- One study (full paper was not retrieved) appears to report that novel Maillard pigments can form from furfural and xylose under weakly acidic conditions (Murata, 2009).
- Furfural is also reactive with polyphenols {Es-Safi, 2000 #16393}.

hexanal

- The Maillard reaction promoted the formation of aldehydes, especially heptanal and benzaldehyde, in sweet potato protein isolates (Habinshuti et al., 2021).
- This compound was not found in potato and sweet potato protein hydrosylates of potato and sweet potato, but was found in their Maillard reaction products (supplementary material for (Habinshuti et al., 2022). The authors of that paper stated that "the formation of aldehydes might be mainly due to the oxidation of fatty acids".

hexanoic acid

- Not found in potato protein isolate, but was detected in Maillard reaction products of potato protein isolate (Habinshuti et al., 2022)

nonanal

- This compound was present but did not change much between potato protein isolate or Maillard reaction products from potato protein isolate (Habinshuti et al., 2022).

octanal

- The level of this compound was higher in the MRP of potato protein isolate than in the starting potato protein isolate (Habinshuti et al., 2022).

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Compiled by Wendy Bedale, Food Research Institute

bedale@wisc.edu