Solution to blue garlic challenge

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Solution

The explanation of the “greening” or “blueing” of garlic (*Allium sativum* L.) and “pinkening” of onion (*Allium cepa* L.) given here will conclude with a new challenge of its own.

Color changes of *Allium* tissues have been studied by several investigators since Joslyn, in 1958 [1]. In the 1960s, the reactions involved in the formation of pink pigment in onion purée were investigated [2] and a three-step reaction scheme was proposed: (1) the formation of a colorless, ether-soluble substance [the color developer (CD)] by the catalytic action of alliinase (enzyme EC 4.4.1.4) upon then-unknown precursors in the fraction of neutral and basic amino acids; (2) the formation of a colorless, ether-insoluble pigment precursor (PP) from the color developer and an amino acid such as glycine; (3) the formation of a pink pigment from the pigment precursor PP and a naturally occurring carbonyl (NOC) substance such as formaldehyde. It was then assumed [3] that a blue pigment-forming “carbonyl” was present in garlic, and when reacted with the pigment precursor PP in place of NOC from onion, a blue color would form.

Subsequently, it was found [4] that the blue pigment-forming “carbonyl” was derived from isoalliin (a substrate for alliinase, a minor precursor in garlic flavor, but the major precursor of onion flavor), and the same reactions were responsible for “greening” of garlic and of the mixture of garlic and onion.

But our understanding of the *Allium* chemistry advanced significantly when Eric Block and his colleagues [5–8] introduced methods for the study of *Allium* chemistry and produced a wealth of results based on such methods. Based on their work, it was established (see Fig. 1) that the pigment precursor was a 3,4-dimethylpyrrole derivative. It is thought to be formed by condensation of the amine group of *Allium* amino acids with the thial/thial S-oxide formed by [3]-sigmatropic rearrangement of bis-1-propenyl thiosulfinate, in turn formed by the action of alliinase on 1-PeCSO (isoalliin). The thial/thial S-oxide is an intermediate in the formation of zwiebelanes, and is closely related in structure to (Z,Z)-d,l-2,3-dimethyl-1,4-butanedithial S,S'-dioxide, a compound isolated from onion preparations, which could play a role in forming the pigment precursor. A second key aspect to the formation of colors in *Allium* preparation requires the intermediacy of thioacrolein.

Using such information, a positive correlation between thiosulfinate concentration and pink pigment formation was first observed [9], and 1-propenyl-containing thiosulfonates were confirmed to be the major color-developing compounds [10]. Then in 2005, Bai et al. [11] studied the mechanisms of the green color formation in “Laba” garlic, a preserve of garlic including vinegar and sometimes sugar: both alliinase and acetic acid are required for the color formation, and the decrease in the total thiosulfonates in garlic cloves is associated with the pigment formation.

The plant chemistry, however, is always wonderfully complex, so that other studies are not useless. Imai et al. [12] established a model reaction system that comprised only well-defined constituents and reported identifications of new

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