SOLUBILITY RELATIONSHIPS OF LIMONIN AND THE PHENOMENON OF DELAYED BITTERNESS IN CITRUS JUICES

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GORDON LINDSAY ROBERTSON

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ABSTRACT

Unsuccessful attempts were made to produce cloud-stable, non-bitter citrus juices by enzymic degradation of juice-soluble pectin. The failure of these attempts demonstrated the necessity for a greater understanding of the solubility relationships of limonin and the phenomenon of delayed bitterness.

The solubility of limonin in model solutions was investigated. It proved impossible to prepare aqueous solutions containing high concentrations of limonin without the use of heat. Even though the addition to such solutions of sugar, pectin and polygalacturonic acid at concentrations commonly found in citrus juices had a statistically significant (95% level) effect on the equilibrium limonin concentrations, the magnitude of the effect was quite small. Moreover, the solubility of limonin shaken at 30 C for five days in model solutions containing citrus proteins and lipids was no greater than its solubility in water, leading to the conclusion that neither lipids nor proteins are responsible for high concentrations of limonin in citrus juices. Direct solubilization of limonin cannot therefore account for high limonin concentrations in citrus juices to which no heat has been applied.

High concentrations of limonin in model solutions could be achieved by the application of heat. In refluxed aqueous solutions, the presence of pectin, sucrose and sucrose, glucose and fructose in combination increased the solubility of limonin, the greatest increase occurring with sucrose alone. Even more important was the effect of solutes on slowing down the rate at which limonin came out of solution on cooling. Again the effect of solutes was different, sucrose being more effective than pectin in holding limonin in solution, but high concentrations were maintained longer in solutions containing the sugar mixture or sucrose and pectin. Saturated solutions of limonin in acidic model solutions prepared under reflux deposited limonin with approximately equal rapidity, irrespective of other solutes.

On the other hand, solutions of similar limonin concentration, prepared by adding components of the model solutions (citric acid, pectin and sucrose at concentrations found in citrus juices) to a hot saturated solution of limonin, retained moderately high concentrations of limonin provided pectin was present.

Limonin analysis by extraction at two pH levels demonstrated that the equilibrium operating in the establishment of high concentrations of limonin in model solutions involved neutral hydrolysis of limonin to one or other of its hydroxyacid forms. On cooling such solutions, limonin crystallized out, affecting the hydroxyacid-lactone equilibrium. The effect of solutes is related to their influence on this equilibrium.

When similar extraction procedures were applied to studying the phenomenon of delayed bitterness in citrus juices, evidence was obtained for the presence in freshly extracted citrus juices of two limonin precursors which each showed differing stabilities, both to the presence of natural citrus enzymes and to the application of heat.

All previous work relating the effects of various treatments to limonoid bitterness in citrus juices and model solutions must be reconsidered in the light of the possible involvement of the two limonin precursors, the associated enzymes, and the hydroxyacid forms of limonin.

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Gordon L. Robertson
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