METABOLISM OFF-FLAVOR IN MAPLE SYRUP

Part I: Identification of the compound responsible for metabolism off-flavor

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INTRODUCTION

The characteristic flavor of pure maple syrup is derived from a complex mix of aroma and flavor compounds, including phenolic compounds, carbonyl compounds, alcohols and acids, and pyrazines (Alli et al. 1992). Off-flavors which are not part of this characteristic flavor profile can also occasionally develop in maple syrup. When off-flavors occur they can usually be attributed to some single or combination of factors, including some that are intrinsic to maple sap and some that arise from external sources such as contamination during production or storage (Perkins et al. 2006). 'Metabolism' is a term often used to describe a variety of maple syrup off-flavors. More specifically, however, the term metabolism (also called 'woody') refers to a distinct off-flavor described as 'earthy to bitter' which can develop at any time during the season, and at times can occur simultaneously over a large regional scale (Perkins et al. 2006). In some years it can affect up to 25% of the total annual maple syrup crop (Perkins and van den Berg in press). The presence of metabolism off-flavor significantly reduces the economic value of maple syrup, often causing syrup to be downgraded to commercial grade (Perkins and van den Berg in press).

Research on metabolism off-flavor in maple syrup at the University of Vermont Proctor Maple Research and Extension Center (PMREC) had two main objectives. The first was to identify the primary compound(s) responsible for metabolism off-flavor in maple syrup. Once the responsible compound or compounds were identified, measures to reduce or remove the off-flavor from finished maple syrup could be investigated. Thus, the second main objective was to determine whether a technique could be found that maple producers and packers might employ to effectively remediate the flavor, and thereby increase the economic value, of metabolized maple syrup.

This paper addresses the first objective, to identify the compound or com-

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pounds responsible for metabolism off-flavor in maple syrup. A subsequent paper will focus on efforts to reduce or remove metabolism off-flavor.

MATERIALS AND METHODS

Experts in maple syrup flavor evaluation selected four maple syrup samples. Two of the syrup samples were determined to possess 'pronounced' and 'severe' metabolism off-flavor, respectively, without the presence of other off-flavors. The other two syrup samples were determined to have representative flavor characteristic of pure maple syrup without the presence of off-flavors, and served as controls.

The syrup samples were analyzed with gas chromatography/mass spectroscopy (GC/MS) to determine the identity and quantity of flavor/aroma compounds present in each. The flavor profiles of the metabolized syrup samples were compared to those of the control samples to determine if any clear differences existed. We hypothesized that compounds which were present in both the metabolized syrups, but absent in the control syrups, were likely to be responsible for producing metabolism off-flavor.

RESULTS AND DISCUSSION

Figure 1 shows an example chromatogram generated by GC/MS for a maple syrup sample with metabolism off-flavor. Generally, GC/MS chromatograms show the profiles of flavor/aroma compounds present in each sample. Each peak on the chromatogram represents the presence of an individual compound. The area of each peak corresponds to the relative quantity of that compound present in the sample; larger peaks indicate compounds present in larger quantities. Chromatograms generated by GC/MS are compared to known chemical libraries to determine the identity of the compound indicated by each peak.

An examination of the chromatograms generated for the four maple syrup samples in this study (not shown) revealed the presence of one major peak in both of the metabolized samples that was absent in the flavor profiles of the con-

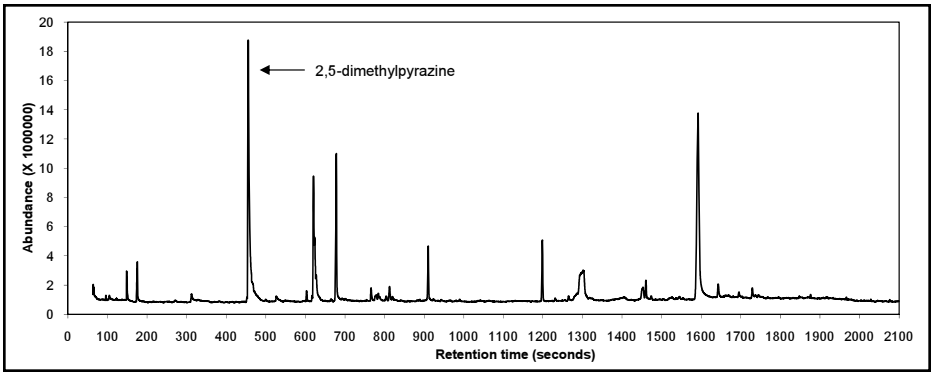

Figure 1. An example chromatogram generated by gas chromatography/mass spectroscopy of a maple syrup sample with metabolism off-flavor. The arrow indicates the location of the peak corresponding to the compound 2,5-dimethylpyrazine.

trol syrup samples. The identity of this compound was determined to be 2,5-dimethylpyrazine by comparison with a known library. To further investigate the potential relationship between this compound and the presence or absence of metabolism off-flavor, the precise amount of 2,5-dimethylpyrazine present in each of the four syrup samples was quantitatively determined.

Table 1 shows the quantity of 2,5-dimethylpyrazine determined to be present in each of the four syrup samples tested. The syrup sample evaluated as having 'severe' metabolism off-flavor contained 462 parts per billion (ppb) 2,5-dimethylpyrazine, while the sample evaluated as having 'pronounced' metabolism off-flavor contained 166 ppb. The compound was not present in either of the two control syrup samples without the off-flavor (Table 1). The apparent correlation between the quantity of 2,5-dimethylpyrazine present and the degree of metabolism off-flavor, as well as the presence of this compound in metabolized syrup and its absence in control syrup strongly suggest that 2,5-dimethylpyrazine is the primary compound responsible for metabolism off-flavor in maple syrup.

2,5-dimethylpyrazine is a naturally-occurring volatile flavor compound found in a variety of heat-processed foods, including roasted beef, cocoa, bacon, and coffee (Maga 1992), as well as maple syrup (Alli et al. 1992, Akochi-K. et al. 1997). However, the quantity of 2,5-dimethylpyrazine typically present in maple syrup ranges between 10 and 17 parts per billion (Akochi-K. et al. 1994, Akochi-K. et al. 1997), approximately 10 to 40 times less than the amount found in the metabolized syrup samples analyzed in this study.

2,5-dimethylpyrazine and other pyrazines are formed during the Maillard reaction (Maga 1992), a complex set of reactions responsible for the development of a diverse array of flavor and color compounds in many heat-processed foods (Belitz et al. 2004, Davidek and Davidek 2003), including maple syrup (Perkins and van den Berg in press). Pyrazines are responsible for a variety of both desirable and undesirable flavors and aromas in foods (Maga 1992). 2,5-dimethylpyrazine in particular has a characteristic aroma described as strong nutty, musty, meaty roast or green (Maga 1992), though the precise nature of the aroma can depend greatly on the concentration of the compound present. 2,5-dimethylpyrazine has an extremely low odor threshold, approximately 38 ppb, and thus at the concentrations present in the metabolized syrup samples analyzed in this study it would be expected to produce an extremely pungent aroma and flavor.

Table 1. Quantity of 2,5-dimethylpyrazine (in parts per billion) determined by gas chromatography/mass spectroscopy present in four pure maple syrup samples with (Metabolized) and without (Control) metabolism off-flavor.

	2,5-dimethylpyrazine (ppb)	Off-flavor
Control-1	0	No off-flavor
Control-2	0	No off-flavor
Metabolized-1	462	Severe metabolism
Metabolized-2	166	Pronounced metabolism

We hypothesize that in metabolized syrup, the specific pathways of the Maillard reaction leading to 2,5-dimethylpyrazine formation predominate during sap processing to syrup, yielding large concentrations of this compound which overwhelm the presence of other flavor constituents. This process could be influenced by the presence or abundance of specific precursors in sap, conditions during sap processing to maple syrup, such as the temperature, pH and length of processing time, or a combination of any of these factors.

In conclusion, the results of this study strongly suggest the compound 2,5-dimethylpyrazine is responsible for what is referred to as 'metabolism' off-flavor in maple syrup. With the responsible compound identified, subsequent research focused on developing techniques to remediate the flavor of metabolized syrup by targeting 2,5-dimethylpyrazine for removal from maple syrup.

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