Investigation of Chemical and Physical Properties of Southwestern Wisconsin Maple Syrup

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Abstract

Maple syrup is produced in the early spring from February through April when maple sap runs from the maple trees. It is traditionally known that the maple syrup produced from the sap in the later season tends to have a darker color. Interestingly, although the maple syrup grading system in the United States gives lower grades and values for darker maple syrup, some consumers prefer dark syrup to light syrup. Therefore, the seasonal variation of important maple syrup parameters was investigated. The other aspect of this study was to determine whether the filtration process in maple syrup production removes some nutritional value from the product. In this research, filtered and unfiltered samples, prepared weekly during the five-week season, were compared with respect to their physical and chemical properties. It was found that the concentrations of calcium, iron, fructose and glucose tended to be higher, while sucrose tended to be lower as the season progressed. The filtration process did not seem to be a significant factor in influencing the concentrations of minerals and sugars.

Introduction

Maple syrup is one of the most common sweeteners in the United States. The maple syrup industry is quite dominant in Canada and eastern North America including Wisconsin. Maple syrup is produced from maple sap, a slightly sweet, transparent liquid, tapped from maple trees. Maple sap is boiled down to 1/35 to 1/40 in volume when it becomes syrup. Maple syrup is then pasteurized, filtered, graded, and packaged before it is marketed. Compared to table sugar, which consists of only sucrose, maple syrup contains a variety of nutrients such as

minerals, organic acids, amino acids, and vitamins as well as sucrose and other sugars such as glucose and fructose.

The United States' legal definition of maple syrup states that maple syrup contains "not more than 35 percent of water, and weighs not less than 11 pounds to the gallons (231 cubic inches)" (Willits & Hills, 1976, p. 93). This definition allows the industry to standardize the properties of maple syrup in order to ensure a certain quality. In fact, a grading system is used to guarantee maple syrup quality. The grade of maple syrup is determined mainly by the color of the product measured by means of accepted grading kits such as the United States Department of Agriculture (USDA) permanent glass color standards. Maple syrup is graded based upon its color. Lighter maple syrup receives higher grades, while darker syrup receives lower grades. The standards give three grade levels: United States Grade A, United States Grade B, and Substandard. United States Grade A is the highest grade in the United States (with the exception of the state of Vermont, where "Fancy" grade is the highest) and it is the lightest color among the three grades. United States Grade A is subdivided into three more grades, United States Grade A Light Amber, United States Grade A Medium Amber, and United States Grade A Dark Amber according to the color of product. United States Grade B is darker than United States Grade A Dark Amber, and considered unsuitable for consumer labeling. The standards also describe the higher grade maple syrup as having better flavor, clearer color and fewer defects.

The color of the maple syrup is mainly a result of the time of season the maple sap is collected from maple trees. It is generally known that the later in the season the sap is collected, the darker the color of the resulting maple syrup. Driscoll (1998) described in her article how the dark color of maple syrup is a function of the size of sugar molecules in maple sap. As the season progresses, the temperature warms and wild yeasts begin to break down the sugar molecules into smaller components which absorb more light than larger molecules. In fact, microorganisms convert sucrose that is in maple sap to glucose and fructose (invert sugar) by enzymatic hydrolysis (King & Morselli, 1983; Morselli & Whalen, 1991).

Driscoll (1998) determined from blind taste tests of maple syrups that consumers tended to prefer dark maple syrup since they wanted syrup that tasted like the "real thing." This result is quite interesting since the maple syrup preference given by consumers does not agree with the level of grade, where the lighter maple syrup is given a higher grade.

Though the color of maple syrup is dark, there is a possibility that its nutritional value is equal to or better than lighter syrup. The other aspect of this study was to investigate if the filtration process in the maple syrup production removes some nutritional values from the maple syrup products. In this research, five different seasonal filtered maple syrup samples and their unfiltered samples were investigated concerning their physical properties (density, absorption spectrum, solid content, and water activity) and their chemical properties (pH, mineral contents and sugar contents).

Methodology

Materials

Ocooch Mountain Acres, LLC, Westby, Wisconsin supplied ten glass bottles of maple syrup, including five unfiltered and five filtered samples. Maple sap used for these samples was collected five times from March 17 through April 4 in 2004 from Westby, Wisconsin, and separately processed by the syrup maker. Since the first four samples were made from the sap collected for a four-day period, and the last sample was made from the sap collected for a three-day period, the samples are designated as follows: 4D-N, 8D-N, 12D-N, 16D-N, and 19D-N for unfiltered samples, and 4D-F, 8D-F, 12D-F, 16D-F, and 19D-F for filtered samples. The earliest seasonal samples, 4D-N and 4D-F, had the lightest color, while the latest seasonal samples, 19D-N and 19D-F, had the darkest color. Filtered samples were produced by going through all processes including boiling, pasteurization, filtration, and packaging. Unfiltered samples were collected in glass bottles right after the boiling process, but no pasteurization or filtration were applied.

Density and pH Analysis

Prior to the measurement of density and pH, each maple syrup sample was kept in a Fisher Isotemp Water Bath (FisherScientific) at 25 degrees Celsius. Density was determined by measuring the weight of the maple syrup sample and the specific volume (1.00 mL). To measure the exact 1.00 mL of sample, a Repeater 4780 (Eppendorf) was used with the 12.5 mL combitip. The weight of the sample was recorded to four decimal places by using an analytical balance (AG balance-AG 135, Mettler-Toledo GmbH). Three measurements were done per sample (triplicate), and the average for each sample was calculated. The pH for each sample was measured once and determined using a model 6050 (Sargent-Welch Scientific Company) pH meter with a glass combination

electrode. Calibration of the meter was accomplished with pH 7.0 and 4.0 buffers.

Visible and UV Light Absorption Spectrum

Prior to the measurement of absorbance, maple syrup samples were diluted appropriately with Milli-Q water (Millipore) according to the color of the products. Samples 4D-N, 8D-N, 12D-N and 4D-F, 8D-F, 12D-F were diluted by the factor of 50, and samples 16D-N, 19D-N and 16D-F, 19D-F were diluted by the factor of 100. Absorbance of each sample was measured by using a Hewlett Packard 8452A Diode Array UV-Vis spectrophotometer with the wavelength range from 250 nm to 750 nm. Due to the measurements in UV range, a 1-cm quartz cell was chosen in this experiment. As a reference, Milli-Q water was used. The relationship between absorbance and wavelength was plotted in the computer as graphics, and the possible compounds were estimated according to the wavelength at which the maximum absorbance was observed.

Solid Content

About 1g of each maple syrup sample was put in a 30-mL beaker by using a Repeater 4780. The weight of the empty beaker and the sample taken in the beaker were separately measured by using an analytical balance. The sample was dried by using a Fisher Isotemp® Model 282A Vacuum Oven (Fisher Scientific) until all water was dried out. The temperature of the vacuum oven was set at 75 degrees Celsius, and the pressure was set at 5.0 to 8.0 in Hg. The total weight of the beaker including the sample was measured, and then solid content was calculated with the following equation. Duplicate measurements were done per sample.

Solid content (%) = Wa/Wb x 100

Where:

Wa (g) = weight of a sample after dried

Wb (g) = weight of a sample before dried

Water Activity

Water activities of maple syrup samples were measured by using an AquaLab Series 3 Model TE (Decagon Devices, Inc.). The instrument was kept with a set temperature at 25 degrees Celsius prior to measurements. The small portion of maple syrup sample, temperature equilibrated with room temperature, was poured in a plastic sample dish until the

bottom of the dish was covered by the sample, and then the dish was loaded in the instrument. Water activity was automatically measured in approximately 5 minutes. The measurement was done once per each sample.

Mineral Analysis

In order to carry out the quantitative analysis, standard solutions of three elements (potassium, calcium, and iron) were prepared. For the potassium and calcium standard solutions, 0.5, 1.0, 2.0, and 4.0 mg/L solutions were prepared, and for the iron standard solution, 0.1, 0.3, 0.5, and 0.8 mg/L solutions were prepared. For the K and Ca analysis, maple syrup samples were diluted by the factor of 1000, and for Fe analysis, the samples were diluted by the factor of 100. Mineral contents were measured by using a Thermo Elemental SOLAAR S4 atomic absorption spectrophotometer with appropriate hollow cathode lamps as light sources. The wavelengths for the measurements of minerals were set at 766.5 nm for K, 422.7 nm for Ca, and 248.3 nm for Fe. Air-acetylene was used as oxidant-fuel combinations. Standard solutions and diluted maple syrup samples were measured three times per each (triplicate). By using standard curves, mineral contents in the maple syrup samples were determined.

Sugar Analysis

Five different concentrations: 0.1, 0.25, 0.5, 1.0, and 2.0% were used for the standard solutions of glucose, fructose, and sucrose. For the glucose and fructose, the maple syrup samples were diluted by the factor of 20, and for the sucrose, the samples were diluted by the factor of 40. All standard solutions and diluted maple syrup samples were passed through a 0.45 Ìm syringe filter (Arbor Technologies, Inc.) in order to remove particulates prior to HPLC analysis. Samples were analyzed on a Waters HPLC (system) equipped with a manual UGK injector, and a Waters R401 differential refractometer detector using a SupelcosilTM LC-NH2 column (250 mm x 4.6 mm, 5 Ìm) (Supelco). Chromatograms were plotted employing Dynamax MacIntegrator II software (Rainin Instrument Co., Inc). As mobile phase, the solution of 85% acetonitrile and 15% Milli-Q water was filtered and degassed in a vacuum filtration system. Flow rate and injection volume were set at 2.0 mL/min and 20 Ìm, respectively. From the chromatograms, standard curves were constructed according to the peak areas and sugar concentrations of the standard solutions.

Result and Discussion

According to the pH measurements (Table 1), all samples were slightly acidic. This indicates that maple syrup is not a pure solution of sugars, but a complex compound containing minerals and organic acids. The unfiltered maple syrup samples showed slightly lower pH than the filtered maple syrup samples. The removal of the sugar sand, which consists of calcium and magnesium salts and malic acid, may have affected the pH and increased it in filtered samples compared to unfiltered samples. Sample 16D-N, 4D-F, and 16D-F showed a slightly higher pH and density than the other samples. This is probably because the compositions of maple syrup, such as minerals and organic acids, and their amounts will change according to the season when the maple sap was taken. By comparing the data obtained by Stuckel and Low (1996), the pH of maple syrup produced in Wisconsin ranged from 6.20 to 7.90. The mean of the pH of filtered sample obtained from this experiment was in this range. Though one of the unfiltered samples was slightly lower than the range, it was still higher than the lowest pH (pH = 5.64) found in the maple syrup produced in Quebec in Canada (Stuckel & Low, 1996).

The mean of moisture content calculated by subtracting the mean of solid content (Table 1) from 100 for unfiltered and filtered samples was 32.08% and 32.37%, respectively. According to the data obtained by Stuckel and Low (1996), the moisture content of maple syrup produced in Wisconsin ranged from 28.1% to 33.0%. From this data, the moisture content and the solid content of the ten maple syrup samples used in this experiment are well within the range observed for Wisconsin maple syrup. Sample 16D-N, 4D-F, and 16D-F gave slightly higher solid content than other samples, which exactly corresponded to the result of density.

From the result of solid content and water activity (Table 1), it was observed that the higher the moisture content the maple syrup sample is, the higher the water activity. In general, the food which has higher moisture content tends to have higher water activity though some exceptions are found (Fennema, 1996). Regarding the microbial spoilage of food product, it is reported that most spoilage bacteria do not grow below aw = 0.91 and most spoilage molds and yeasts do not grow below aw = 0.80 and 0.88, respectively. According to the data obtained, all water activities were below 0.86, which indicates that pathogenic bacteria are not likely to grow in the maple syrup. Although most spoilage molds and yeasts are hardly seen in the condition, there is still possibility that some types of molds and yeasts could be found in syrup if once contaminated.

According to the measurements of maximum absorbance (Table 1), all maximum absorbance were observed in the same wavelength in ultraviolet region (271 nm to 275 nm). This result indicates that the maximum absorbance was obtained by the same or similar type of compounds existed in the maple syrup. One possibility for the source of these compounds is a series of phenolic compounds such as benzoic acid derivatives, cinnaic acid derivatives, and coniferyl alcohol. Kermasha, Goetghebeur, and Dumont (1995) detected these phenolic compounds with the wavelength at 280 nm. It was also found that the later the season when the maple sap was taken, in other words, the darker the color of maple syrup is, the greater the maximum absorbance is. From the above discussion, the darkening of the color of the maple syrup may be caused by the certain group of compounds found in higher concentration in the later season.

Table 1

pH, Density, Solid Content, Water Activity, and Maximum Absorbance of Unfiltered and Filtered Maple Syrup Samples

Sample Number	pH	Density (g/mL)	Solid content (%)	Water activity	Maximum Absorbance (AU)
4D-N	6.28	1.320[a] ± 0.003[b]	67.3	0.842	0.25333
8D-N	5.96	1.322 ± 0.003	67.7	0.844	0.36195
12D-N	5.87	1.324 ± 0.002	67.1	0.843	0.75463
16D-N	6.46	1.329 ± 0.008	69.2	0.841	0.82042
19D-N	6.32	1.323 ± 0.003	68.3	0.847	1.9668
4D-F	6.64	1.333 ± 0.004	68.8	0.854	0.24387
8D-F	6.53	1.322 ± 0.002	67.2	0.851	0.32938
12D-F	6.36	1.325 ± 0.002	67.1	0.848	0.71874
16D-F	6.60	1.333 ± 0.006	69.1	0.854	0.82836
19D-F	6.33	1.318 ± 0.002	65.9	0.855	1.81418

Note. [a]Mean; [b]standard deviation

From the result of mineral analysis (Table 2), the K+ concentration remained static through the whole season. The Ca2+ concentration, on the other hand, showed clear elevation as the season progressed. The Fe2+ concentration did not show any clear tendency in the change of concentration through the season although a slight tendency of elevation was observed. The data of mineral content in maple syrup obtained in this experiment was compared to the data in the literature (Stuckel & Low, 1996; Robinson, Mac Lean, & Mac Connell, 1989). Although the average concentration of each mineral obtained in this experiment was relatively higher than the average values in the literature, most of the concentrations of Ca2+ and Fe2+ were still found in the higher range of concentrations in the literature. Any individual concentration of K+ slightly exceeded the maximum value found in the literature, however, they were similar. By comparing the unfiltered samples to the filtered samples, the concentration of K+ and Ca2+ in unfiltered samples was more or less lower than those in filtered samples. The concentration of Fe2+ in unfiltered samples was, however, slightly higher than those in filtered samples. There is a possibility that some additional minerals could be introduced into maple syrup from the pasteurization, filtration, or packaging process although some type of minerals would be removed with sugar sand by filtration process.

The concentration of fructose, glucose, and sucrose is shown in Table 2. In terms of the seasonal effect, there was a slight tendency for the concentration of fructose and glucose to increase as the season progressed, while concentration of sucrose decreased. This change was especially significant in the latest seasonal samples (19D-N and 19D-F). This tendency corresponds to the fact that when the season progresses and the weather becomes warm, bacterial activity proceeds the decomposition of sucrose in the maple sap in maple trees, and the sucrose is converted into the invert sugars (glucose and fructose) (Driscoll, 1998). Driscoll (1998) also noted that more concentration of invert sugars in maple sap would result in a darker maple syrup product.

There was no important difference observed between filtered and unfiltered samples in each sugar concentration. According to the data obtained by Stuckel and Low (1996), the concentration of fructose, glucose, and sucrose in maple syrup samples produced in Wisconsin was 0.22 ± 0.51%, 0.27 ± 0.22%, and 69.9 ± 1.2%, respectively. By comparing the data obtained from this experiment to the literature data, fructose and glucose concentration was slightly higher but sucrose concentration was slightly lower than the literature data of the Wisconsin maple syrup.

This data indicates the possibility that the more inversion of sucrose may have occurred in the trees before sap was taken.

Table 2

Concentrations of Minerals (Potassium, Calcium,and Iron) and Sugars (Fructose, Glucose, and Sucrose) in Unfiltered and Filtered Maple Syrup Samples

Sample Number	Mineral concentration (mg/L)			Sugar concentration (%)		
	Potassium	Calcium	Iron	Fructose	Glucose	Sucrose
4D-N	2968[a] ± 209[b]	1104 ± 16	11 ± 2	0.31	1.24	65.94
8D-N	2693 ± 154	1310 ± 13	11 ± 0	0.32	1.49	61.98
12D-N	3087 ± 122	1588 ± 4	13 ± 1	0.55	1.99	68.81
16D-N	3375 ± 122	1715 ± 10	9 ± 1	0.44	2.14	68.43
19D-N	3111 ± 122	2278 ± 16	20 ±1	1.47	3.33	61.00
4D-F	3568 ± 22	1211 ± 11	10 ± 2	0.42	1.49	70.29
8D-F	3141 ± 17	1177 ± 25	9 ± 1	0.42	1.48	62.26
12D-F	3501 ± 15	1642 ± 20	11 ± 2	0.87	2.27	64.78
16D-F	3802 ± 2	1787 ± 25	19 ± 2	0.38	1.97	69.27
19D-F	3620 ± 27	2565 ± 34	16 ± 2	1.20	3.21	61.77

Note. [a] Mean, [b] standard deviation

Summary and Conclusion

The values of pH, solid content, mineral contents, and sugar contents of maple syrup samples obtained in this research were compared to the literature values. All of the values were reasonable and found in the literature except K+ concentration, which was quite close to the range. All values of pH and solid content were in the range found in maple syrup produced in Wisconsin, except one pH value, which was still found in the range of Quebec maple syrup.

Seasonal effects

The result of visible and UV light absorption spectrum showed that the later the season the maple syrup sample was produced, the greater

the maximum absorbance observed at a wavelength of 271nm to 275 nm. Although specific chemical compounds were not identified in this research, according to the literature, phenolic compounds were some of the possible compounds which are known as the influential factors of the color and flavor of maple syrup. The result of the mineral analysis showed that calcium concentration in maple syrup increased as the season progressed, and a slight increase in iron concentration was also observed. This result indicates that the warmer weather affects the metabolisms of maple trees, and more calcium and iron exist in the sap later in the season. The result of the sugar analysis showed that fructose and glucose concentrations increased and sucrose concentration tended to decrease as the season progressed. This result corresponded to the fact that the amount of invert sugars affects the darkening of maple syrup. The pH, density, solid content, and water activity did not show any clear tendency in terms of seasonal effect, although 16D-N, 4D-F, and 16D-F showed higher pH, density, and solid content than the other samples.

Filtration effects

It was expected that the concentrations of minerals and sugars in filtered samples were lower than the concentrations in unfiltered samples due to the removal of those components by filtration; however, the numbers of the measurements of filtered samples which showed lower concentration of minerals and sugars than unfiltered samples were only 10 out of 30 measurements (33.3%). This data indicates that the filtration process used for producing the maple syrup samples was not a significant factor in influencing the concentrations of minerals and sugars.

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