The Chemical Composition of Maple Syrup

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No one is quite sure how it was discovered that the sap of most maple trees can be concentrated into a sweet, delectable syrup. However, by the time European settlers arrived in North America, native Americans had already learned to slash the bark of maple trees in late winter or early spring, collect the near-clear sap that came out, and boil the sap into a thick, sweet product. Indeed, maple syrup production is one of the few agricultural processes native to North America and not introduced by outside settlers (1).

Maple syrup and its drier cousin, maple sugar, were the dominant food sweeteners in the United States until after the U.S. Civil War when improvements in production and transportation made cane sugar the preferred sweetener for nonfarmers (2). Today, about 7.5 million gallons of pure maple syrup are produced, mostly in eastern Canada and, albeit to a much lesser extent, the northeastern United States. At $30 per gallon (which is a conservative estimate), the industry has a $225 million economic impact. Many consumers, however, only consume a corn syrup-based imitation syrup (many of which do not even claim “maple” on their labels!), which is part of an $11 billion industry (3).

This article is not meant to be a primer on how to tap trees and boil sap to make syrup; many such primers are available (see, for example, ref). Instead, this article is meant to be an introduction to the chemistry of maple sap and syrup: in particular, what makes this sweet liquid maple syrup instead of just a concentrated sugar solution? The types of sugars, the trace ingredients, and the mineral content make maple syrup more than just plain sugar water.

Maple syrup is one of only three syrups derived from tree sap. Another is birch syrup, which comes from the boiled sap of paper birch (*Betula papyrifera*) or Alaska birch (*B. neoalaskana*) trees. Produced in Alaska, Canada, Russia, and Scandinavia, birch syrup is distinctive in flavor but differs from maple syrup in that its sugar content is due to fructose and glucose, rather than sucrose. Birch sap is only half as concentrated as maple sap, so a greater concentration of sap is needed to produce birch syrup. A syrup can also be made from black walnut tree (*Juglans nigra*) sap (4); however, we will not consider the latter syrups further here (3).

Sap

Most maple trees can be tapped and the collected sap can be concentrated (either by boiling or by reverse osmosis followed by boiling) to make maple syrup. However, of the thirteen species of the genus *Acer* in North America, the sugar maple (*A. saccharum*), the black maple (*A. nigrum*), and the red maple (*A. rubrum*) provide most of the sap for syrup production. There are two reasons for this. First, the sugar content of their sap is typically higher than other species, at 2.0–2.5%. Second, the annual growth spurt of these species occurs later in the spring than other maple species, increasing the length of the sap-collecting season. Both of these characteristics tend to produce a superior syrup, although syrup made from the sap of other species of maple tree still has the characteristic maple taste and smell (1).

The organic components of maple sap, not including water, are listed in Table 1 (1). To estimate the actual concentrations in raw sap, the numbers in the second column of the table should be divided by 40–50, which has been done in the last column of the table. Note that almost all of the organic content is sucrose. If present at all, glucose has a concentration of well less than 1% of the organic content and only about 0.004% of raw sap. The commanding presence of sucrose is interesting because the two saccharides in sucrose (glucose and fructose) are joined by an alpha glycosidic bond; cellulose, a major structural component of plants, is formed by joining monosaccharides using a beta glycosidic bond, as shown in Figure 1. At some point in the tree’s cells, the sucrose in sap must be broken into its two constituent saccharides before being reassembled into cellulose.

Table 1. Typical Organic Components of Maple Sap

Component	Fraction of Total Organic Content[a,b]	Actual Concentration in Sap
Sucrose	98.0–100%	2–2.5%
Glucose	0–0.17%	0–0.004%
Phenolic compounds	0–4.55 ppm	0–0.1 ppm
Primary amines	0.5–36.1 ppm	0.01–0.9 ppm
Peptides	0.4–18.6 ppm	0.01–0.41 ppm
Amino acids	0–11.3 ppm	0–0.25 ppm
Protein	0–50.9 ppm	0–1.2 ppm
Other organic acids	0–45 ppm	0–1 ppm

[a] The total solids in the sap are 1.0–5.4% and the pH of the sap is 3.9 – 7.9. [b] The data are from ref 1, Appendix 2 and are used with permission.

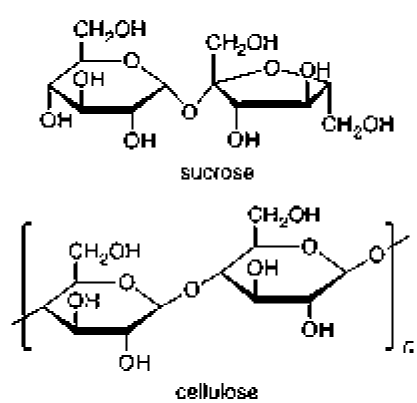

Figure 1. General structures of sucrose and cellulose. The bonds joining the monomers in sucrose have a different orientation from the bonds joining the monomers in cellulose.

Table 2. Average Compositions of Maple Syrup

Component	Quantity
Sucrose	68.0%
Glucose	0.43%
Fructose	0.30%
Water	31.7%
Malic acid	0.47%
Fumaric acid	0.004
Calcium	775 mg/L
Magnesium	167 mg/L
Potassium	2026 mg/L

NOTE: The data are from ref 10 and used with permission. The pH of the maple syrup is 6.7.

Table 3. Mineral Content of Finished Syrup

Mineral	Concentration (ppm)
Potassium	1300–3900
Calcium	400–2800
Magnesium	12–360
Manganese	2–220
Sodium	0–6
Phosphorus	79–183
Iron	0–36
Zinc	0–90
Copper	0–2
Tin	0–33

NOTE: The data are from ref 10 and used with permission.

Maple sap is slightly acidic owing to the presence of several organic acids: oxalic, succinic, fumaric, malic, tartaric, citric, and aconitic (1-propene-1,2,3-tricarboxylic acid) acids. The total quantity of acid in sap starts low, around 8 ppm, then rises to over 45 ppm as the season progresses. Although oxalic acid has the lowest pK_a (1.27) (5), there is about 500 times as much malic acid in sap as there is oxalic acid (45 ppm of malic acid vs 0.1 ppm for oxalic acid). Most sap has a pH ranging from 3.9–7.9 (1).

Sap has detectable quantities of amino acids, some in trace quantities. Amino acids found in sap include glycine, alanine, asparagine, threonine, leucine, isoleucine, valine, and methionine. The quantities and types of amino acids vary over time, with the largest variety of amino acids present near the end of the annual sap running season (1).

Sap also contains minerals but at low concentrations. The two most common minerals in sap are potassium and calcium, found at concentrations of 26–75 and 8–56 ppm, respectively. Sap also contains trace (< 10 ppm) of magnesium, manganese, sodium, phosphorus, zinc, and copper (1). Because these minerals are nonvolatile, they concentrate as sap is processed into maple syrup. This can sometimes cause problems, as the mineral salts of the organic acids present in sap may not be soluble in finished syrup, causing precipitation.

Sap into Syrup

Honey is harvested as a concentrated solution (6), but human intervention is necessary to generate maple syrup. About 98% of the water in sap must be removed to make syrup; it takes 40–50 gallons of sap to make one gallon of maple syrup. This is done by either heat-induced evaporation or by reverse osmosis followed by evaporation (7). It is estimated that it takes about 2600 kJ to evaporate 1 L of sap into syrup. Knowing the enthalpy of methane combustion (890.8 kJ/mol; ref 5), we can also estimate that it takes the combustion of 65 L of natural gas to generate about 20 mL of syrup—about 1.5 tablespoons. Clearly, the production of significant volumes of syrup is an energy-intensive process. Even if reverse osmosis is used, it is only used to remove about 75% of the water; the remaining water is removed using evaporation.

Two important processes occur as sap is transformed into syrup: first, the concentrations of solutes rise, and second, chemical reactions occur between the chemicals dissolved in the sap. While increasing the complexity of the final product, these reactions also give maple syrup its characteristic color, odor, and flavor. Indeed, from the author's own personal observation, if a small quantity of sap were to evaporate to dryness naturally, the remaining solid residue would be white.

Maple Syrup

Sap becomes syrup when the liquid reaches 66–67 degrees Brix (abbreviated °Bx; the Brix scale is used to express the concentrations of sugar solutions, such as honey, maple syrup, and frozen concentrated orange juice. It is defined as the number of grams of sucrose per 100 grams of solution; ref 8). At this point, the syrup is 66–67% sucrose and 33–34% water. With these concentration, the syrup boils about 4.3 °C (7.1 °F) higher than pure water. At higher concentrations sugar will begin to precipitate from the syrup, while at lower concentrations microbes can grow in the syrup, spoiling it. There are also other trace compounds present in the syrup; Table 2 lists the approximate composition of maple syrups from the United States and Canada (9). The dominant component is sucrose, with only small quantities of glucose and fructose present.

The finished syrup has a wide range of minerals, concentrated from the sap. The average mineral content of maple syrup is given in Table 3. Note that, like honey (6), maple syrup can be considered a low- or zero-sodium food. The tin content may be due to the use of tin-plated buckets to collect the sap.

Despite the fact that most maple syrups are graded based on their color, the components that determine the color and flavor of maple syrup are still not completely understood (10). There are three possible sources for the color of maple syrup: Maillard reactions between amino acids and reducing sugars, caramelization of sugars, and formation of polycarbonyl compounds (11, 12). In any case, it is clear that chemical reactions are occurring in the sap to develop the syrup's color and flavor, as normally evaporated sap dries to a white solid.

Table 4. Compounds Identified in Maple Syrup Thought to Contribute to Its Flavor

Phenolic compounds
Vanillin
Syringaldehyde
Dehydroconiferyl alcohol
Syringoyl methyl ketone
2,6-Dimethoxyphenol
Pyrazine compounds
Methylpyrazine
2,3-Dimethylpyrazine
2,5-Dimethylpyrazine
2,6-Dimethylpyrazine
Ethylpyrazine
2-Ethyl-6-methylpyrazine
2,5-Dimethyl-3,6-diisobutylpyrazine
Butylpyrazine
5-Isopropyl-2,3-dimethypyrazine
Other compounds
2-Ethyl-1-hexanol
2-Hydroxymethylcyclopenten-2-enol
2-Furanmethanol
2-Ethyl-1-hexanoic acid
n-Hexanoic acid
n-Nonanoic acid
Carbonyl compounds
2-Hydroxymethylcyclopent-2-en-1-one
2-Hydroxy-3-methyl-2-cyclopenten-1-one
2-Methyl-2-cyclopenten-1-one
2-Methyl-2,5-cyclohexadien-1,4-dione
2,3-Dihydro-3,5-dihydroxy-6-methyl-(4H)-pyran-4-one
2,5-Dimethyl-4-hydroxy-3(2H)-furanone
3-Methyl-3-buten-2-one
3-Methyl-2,5-furandione
3-Methyl-2-cyclopenten-2-ol-1-one
3-Hydroxybutanone
3-Hydroxy-2-pyranone
3-Hydroxy-4-methyl-5-ethyl-2(5H)-furanone
Propionaldehyde

NOTE: Data are from ref 12 and used with permission.

As for flavor, more seems to be known about what causes maple syrup to taste bad than taste good. Excess sodium leads to a salty flavor, and relatively high quantities of amino acids are responsible for an off flavor known as "buddy" (i.e., bud-like) (10). This is typical of late-season sap; as the tree begins the budding process, the relative concentrations of the various amino acids in sap increase dramatically.

Alli and coworkers (12) list several classes of known volatile chemicals in maple syrup (Table 4); however, they admit that the compounds that contribute to the characteristic flavor of maple syrup are not yet established. They suggest that it is likely that these compounds are formed during the evaporation process, as many of these compounds are not present in maple sap. The phenolic compounds are likely due to degradation of lignin components in sap, while the other compounds are formed by reactions between other chemicals found in the sap.

As hot sap is evaporated into syrup, solubility of various salts remains high, but when the finished product is cooled to room temperature, the solubility of certain salts drops below the saturation limit, and crystals precipitate from the syrup. These crystals are called sugar sand (13). Sugar sand can amount to as much as 1.5% of the finished syrup. Sugar sand has a variable composition, but is mostly a combination of small sugar crystals (34–86%) and calcium malate ($CaC_4H_4O_5$; 1–50%). The calcium malate results from the relatively high calcium and malic acid concentrations in the syrup and is one of the least soluble salts in the concentrated syrup. Other components of sugar sand include potassium, magnesium, manganese, phosphorus, and iron. A small percentage (< 3%) of other organic acids may also be present. Most federal and state guidelines involving the sale of pure maple syrup require that the product be clarified (13), so the sugar sand is filtered off from the final product before sale.

Most people actually use imitation maple syrup. Imitation maple syrup is based on corn syrup with added artificial colorings and flavorings. The flavorings include extracts of fenugreek (a spice) or lovage (an herb) and cyclotene (3-methyl-2-cyclopenten-2-ol-1-one, $C_6H_8O_2$), methylcyclopentenol ($C_6H_{10}O$), or a variety of alkyl hydroxyfuranones. Labeling laws usually prohibit the use of the word "maple" unless the product actually contains real maple syrup (14). Most tasters agree that the real product is much tastier than the imitation product, but note that it is also much more expensive!

Conclusion

Maple syrup, native to North America, is much more than a concentrated sugar solution. It contains organic acids, amino acids, minerals, and a wide variety of unidentified chemicals formed during the evaporation process that contribute to its color, odor, and characteristic taste. Derived from the sap collected from trees of the genus *Acer*, it is one of only three syrups derived from tree sap, the others being the less common birch and black walnut syrups. Although the use of corn syrup-based artificial products dwarfs that of real maple syrup in the United States, most people would consider the flavor of real maple syrup superior to any substitute.

Acknowledgment

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