# Composition and Properties of Birch Syrup (*Betula pubescens*)

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Syrup with optimized flavor was produced from birch (*Betula pubescens* Ehrh.) sap (1° Brix) by reverse osmosis and evaporation under reduced pressure. The soluble solids content (70–75° Brix) gave an adequate consistency to the syrup, which needed a low-heat treatment to obtain the desired color ($IU_{560}$ about 3.5 $cm^{-1}$ °$Brix^{-1}$) and flavor. Excess heating produced a dark brown color and a burned flavor. More than 90% (w/w) of the dry matter consisted of sugars (48% glucose, 41% fructose, 0.6% sucrose, 0.5% galactose), 3.1% malic acid, 2.8% ash, and 0.4% free amino acids. The syrup varied between pH 5.6 and 6.5, showing a decreasing tendency when heated.

Birch syrup is a new, all-natural sap syrup that contains neither additives nor preservatives. The unit processes in the production of the syrup are the removal of water with reverse osmosis and concentration under reduced pressure and an optimized heat treatment. The closest reference product commonly available is maple syrup, although its chemical composition and sensory properties differ clearly from those of birch syrup.

In maple syrup the share of sugars is high, typically 88–99% of the dry-matter content (Willits and Hills, 1976). The sugar in the fancy-grade syrup is almost pure sucrose with minor amounts of invert sugar, 0–12% (Willits and Hills, 1976; Merrow and Clarke, 1977; Storz et al., 1986). The content of the most abundant acid, malic acid, is not high, only about 1% of the dry-matter content of the syrup. Trace amounts of other citric acid cycle intermediates in sap and syrup are also available (Porter et al., 1951; Willits and Hills, 1976; Mollica and Morselli, 1984). The high sugar to acid ratio affects especially the sweetness of maple syrup.

The amino compounds never dominate in maple sap and syrup; according to Morselli (Merrow and Clarke, 1977; Morselli and Whalen, 1986) the amino nitrogen varied in one experiment between 59 and 236 $mg \cdot kg^{-1}$ in different grade syrups. However, together with traces of glucose and fructose it is responsible for the color formation of the product. Of the dry matter of maple syrup 1% is ash with potassium as the main constituent. Some minerals precipitate during the syrup processing as malate in the "sugar sand" (Willits and Hills, 1976). The content of sodium in all-natural maple syrup is always low, typically around 3 $mg \cdot kg^{-1}$ (Whalen and Morselli, 1984). The natural deviations of the contents of the basic sap components may be high, and thus the quality of maple syrup varies especially in terms of color and flavor.

The aim of this study was to describe the properties of a novel maple syrup analogue, Finnish birch syrup, which was produced from the sap of *Betula pubescens* and clearly differs from the maple sap product with regard to flavor and chemical composition.

## MATERIALS AND METHODS

**Birch Sap and Syrup.** The birch sap of *B. pubescens* Ehrh. from Katiskoski, Finland (61° 60′ N, 24° 30′ E), was preconcentrated by reverse osmosis from the dry-matter content of 1 to 10° Brix at 60 °C and 5 MPa with a ZF-99 membrane (Kallio et al., 1985b). The concentrate was stored at −20 °C, thawed at +5 °C, and processed to syrup under reduced pressure with a rotary batch evaporator, the temperature of the continuously boiling product being 40 °C. Syrups with the dry-matter contents of about 66.5, 70, and 75° Brix were prepared in 600-mL batches; the concentrate was evaporated to 63° Brix and divided in three lots, which were heated to boil and refluxed for 0, 12.5, or 16.5 min. Hot products were filtered through a paper filter (Schleicher & Schüll 602 eh) at 2-MPa pressure and evaporated to the final dry-matter content. In addition, syrups with soluble solids (50.0, 60.1, 64.8, 70.4, 75.0, 79.8° Brix) were prepared from the mixed sap of *Betula pendula* Roth and *B. pubescens* with the procedure mentioned above and refluxed to boil. These samples were used to determine the dependence of the viscosity on temperature and dry-matter content.

**Dry Matter and Ash.** Dry matter of the syrup (%, w/w) was determined by using both the dilution method (0.2 g of syrup + 5 mL of ion-exchanged water, 102 °C, 12 h) and the quartz sand method (0.2 g of syrup, 100 °C, 12 h). The refractometric dry weight (degrees Brix, calibrated on sucrose) was followed during the evaporation using an Atago hand refractometer. For the ash determination, 2 g of syrup was dried with quartz sand for 4 h at 100 °C. The sample in four replicates was heated to ash and, after 2 mL of concentrated HCl was added, kept for 12 h at 115 °C and burned for 8 h at 540 °C.

**Sugars and Acids.** The sugars and acids were determined by GLC as their TMS derivatives with sorbitol as an internal standard. A 1-g sample of syrup was diluted to 100 mL with water. The analyses were carried out with an SE-30 fused silica capillary column (26 m × 0.32 mm (i.d.); film thickness 0.15 μm) on a Varian Aerograph 3700 gas chromatograph and Hewlett-Packard 3388A integrator (Kallio et al., 1985a).

**Amino Acids and Total Nitrogen.** The syrup was diluted with water to obtain about the same dry-matter content as in the sap. The proteins were precipitated with cold ethanol, the filtrate was evaporated under reduced pressure, the residue was dissolved in HCl, and the amino acids were purified with ion exchange (Ahtonen and Kallio, 1988).

The amino acids were determined as PFPA (pentafluoropropionic anhydride)–isobutyl alcohol derivatives (Abe et al., 1983) with the same chromatograph and column as used in the analyses of sugars and acids. The temperature of the oven was programmed after a 2-min isothermal run from 90 to 200 °C, at a rate of 4 °C/min. The temperature of the split injector was 190 °C (split ratio

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**Table I. Overall Properties of Birch Syrup**

| dry matter | | heat treatment, | content, g/100 g DW | | | | | | | $IU_{560}$, $cm^{-1}$ °$Brix^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| °Brix | %, w/w | min | ash | total N | sugars | malic acid | free AA | viscosity,[a] cP | pH | filtered | unfiltered |
| 66.4 | 64.7 | to boil | 2.7 | 0.16 | 90.0 | 3.6 | 0.42 | 130 | 6.5 | 1.8 | 2.6 |
| 66.6 | 65.1 | 12.5 | 2.7 | 0.16 | 96.2 | 3.6 | 0.60 | 130 | 6.0 | 2.6 | 4.3 |
| 66.4 | 64.8 | 16.5 | 2.8 | 0.16 | 88.2 | 3.4 | 0.15 | 120 | 5.7 | 5.5 | 5.8 |
| 70.2 | 68.6 | to boil | 2.9 | 0.18 | 96.0 | 3.2 | 0.30 | 270 | 6.4 | 2.0 | 2.7 |
| 70.2 | 68.7 | 12.5 | 2.8 | 0.16 | 93.1 | 3.2 | 0.47 | 280 | 5.9 | 3.6 | 4.6 |
| 70.1 | 68.5 | 16.5 | 3.0 | 0.19 | 83.2 | 3.0 | 0.33 | 190 | 5.7 | 5.9 | 6.5 |
| 75.0 | 72.7 | to boil | 2.7 | 0.18 | 92.0 | 2.8 | 0.35 | 860 | 6.1 | 3.0 | 4.0 |
| 74.9 | 73.2 | 12.5 | 2.7 | 0.16 | 89.0 | 2.7 | 0.34 | 780 | 6.2 | 3.2 | 3.3 |
| 75.0 | 72.8 | 16.5 | 2.9 | 0.17 | 86.1 | 2.4 | 0.40 | 850 | 5.6 | 5.6 | 6.1 |

[a] 23 °C, shear rate 7000 $s^{-1}$.

**Table II. Sugars in Birch Syrup**

| | | content, g/100 g DW | | | | |
|---|---|---|---|---|---|---|
| dry matter, °Brix | heat treatment, min | fructose | glucose | galactose | sucrose | inositol |
| 66.4 | to boil | 40 | 49 | 0.40 | 0.60 | 0.043 |
| 66.6 | 12.5 | 45 | 50 | 0.56 | 0.61 | 0.048 |
| 66.4 | 16.5 | 41 | 46 | 0.53 | 0.69 | |
| 70.2 | to boil | 45 | 50 | 0.44 | 0.55 | 0.046 |
| 70.2 | 12.5 | 42 | 50 | 0.49 | 0.60 | 0.043 |
| 70.1 | 16.5 | 37 | 45 | 0.52 | 0.63 | 0.039 |
| 75.0 | to boil | 42 | 49 | 0.47 | 0.52 | 0.040 |
| 74.9 | 12.5 | 41 | 47 | 0.45 | 0.55 | |
| 75.0 | 16.5 | 40 | 45 | 0.46 | 0.55 | 0.042 |

1:70) and that of the detector 280 °C. The flow rate of the nitrogen carrier was 1.4 mL·$min^{-1}$. Norleucine was used as an internal standard. For quantitative measurements the correction factor for each amino acid was determined by using authentic reference compounds. All the samples were determined in four replicates. The retention indices based identifications were verified with a VG Analytical 7070E EI-mass spectrometer (70 eV) with the reference compounds on the same column and program as in the GC analysis.

Total nitrogen was determined from 2 g of syrup by the Kjeldahl method (Kjeltec 1007/Kjeltec Tecator 1002).

**Viscosity.** The viscosity was measured with a Haage PG 142 rotating viscometer coupled to an Apple computer. A Searle type HS2 measuring head was used. The effect of shear rate on the viscosity was measured (0–1400 $min^{-1}$ in 0.5 min).

**$IU_{560}$ Values.** The optical density of the unfiltered and filtered syrups (Schleicher & Schüll RC 55, 0.45 μm) was measured spectrophotometrically at 560 nm (Perkin-Elmer 550s) as ICUMSA color (Schneider, 1979) at 50° Brix, pH 7.0.

**Sensory Properties.** A panel consisting of six trained judges evaluated the syrups using the scoring method (Amerine et al., 1965). The relative importance of various qualitative properties was taken into account in the scoring scales, which ranged from 0 = very poor to 4 = very good for appearance, color, and consistency and from 0 = very poor to 10 = excellent for taste. Altogether, nine syrup samples were evaluated: 66.5, 70.0, and 75.0° Brix boiled either 0, 12.5, or 16.5 min. Special attention was paid to pleasantness or, possibly, off-flavors and off-tastes.

## RESULTS AND DISCUSSION

It was possible to produce birch syrup with acceptable color, flavor, and dry matter by using the process described. Preconcentration to 75° Brix and filtering guaranteed a visually clear product. The relatively high dry matter of the syrups (66.5–75° Brix) was chosen because the main sugars in birch sap and syrup are glucose and fructose (Beveridge et al., 1978; Kallio et al., 1985a), which give lower viscosity to the products than would sucrose. No risk of crystallization occurred above 66.5° Brix, as is the case in maple syrup. The dry weights of the products (%, w/w) were on average 1.7% units lower than the soluble solid content measured with a refractometer (degrees Brix) (Table I).

The major acid in syrup was malic acid, consisting of about 3% of the dry-matter content. Phosphoric, succinic, and citric acids existed only in trace amounts. Concentrating and heat treatments lowered the pH as is typical of the Maillard reaction (Table I). In a good-quality birch syrup, pH was between 5.5 and 6.5. The heat treatment increased the acidity but the pH of the syrup was about 1 pH unit higher than reported by Kok et al. (1978). We observed that frozen storage slowly increased the pH of the reverse osmosis concentrate. The ash content (on average 2.8%, w/w) was in the same range as defined by Kok et al. (1978).

The values for glucose, fructose, galactose, sucrose, and inositol are listed in Table II. They exist in the sap of the same birch species at about the same ratios as in syrup (Kallio et al., 1985a). The apparent decrease in the content of glucose and fructose with increasing heat treatment of the syrup was not statistically significant because of the high standard deviation. However, the browning of the product when heated, is mainly a sugar-consuming Maillard reaction. Galactose, sucrose, and inositol were only minor components and might not have any special influence on the quality of the product.

The total nitrogen content of the syrup was low (0.17%, w/w), and not statistically significant differences between the varying heat treatments could be observed. The syrups contained free amino acids on average 0.37% (w/w), but the variations were extremely high (Table III). This was due, e.g., to the low analytical repeatability of citrulline and glutamine, which were the main free amino acids. The three most abundant ones, citrulline, glutamine, and glutamic acid, formed about 80% of the amino acid pool of birch syrup. All the other amino acids identified existed at only 10–100 ppm range. The physiological role of the amino acids in the sap is to transport the active amino groups to the developing cells all over the tree for the final synthesis of protein amino acids. This might be an ex-

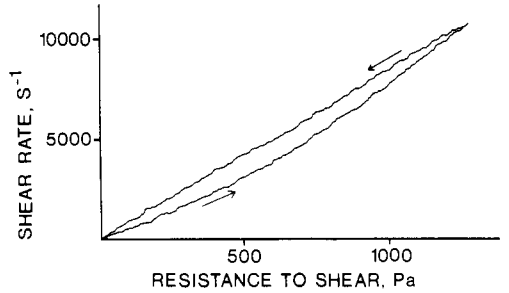


**Figure 1.** Flow diagram of the 66.4° Brix birch syrup, which was heated to boil. Measurement carried out at 22 °C.

**Table III. Free Amino Acids in Birch Syrup (Nine Good-Quality Syrup Samples (64.8–73.2%, w/w), pH 5.7–6.4)**

| amino acid | content,[a] mg/100 g DW ± SD |
|---|---|
| citrulline | 145 ± 95 |
| glutamine | 100 ± 60 |
| glutamic acid | 52 ± 14 |
| asparagine + aspartic acid | 14 ± 2 |
| isoleucine | 13 ± 2 |
| γ-aminobutyric acid | 12 ± 3 |
| phenylalanine | 12 ± 1 |
| valine + threonine | 10 ± 1 |
| tyrosine | 10 ± 3 |
| proline | 4 ± 2 |
| leucine | 2 ± 1 |
| serine | 1 ± 1 |
| | 373 ± 124 |
| | (from 148 to 598) |

[a] 12.5-min boiling lowered the amino acid content by 5.7% (NS); 16.5-min boiling lowered the amino acid content by 6.5% (NS).

planation for the "unusual" composition of the free amino acids in sap and syrup. No specific overall changes could be shown in the free amino acids during heating.

The birch syrups were pseudoplastic liquids at the studied viscometer shear rate range, 0–$10^4$ $s^{-1}$ (Figure 1). The viscosity decreased logarithmically with increasing shear rate and also showed thixotrophic properties. The dependence of the viscosity on temperature and dry matter is shown in Figure 2. The viscosity lowered approximately logarithmically with increasing temperature. The higher the dry matter, the higher was the effect of temperature on the viscosity. The good-quality 70–75° Brix syrup exceeded the viscosity 100 mPa at temperatures of 50–60 °C. Heat treatments did not affect the viscosity of the syrups.

The syrups did not have adsorption maxima on UV or visible area. The $IU_{560}$ values increased with heat treatment (Table I) and decreased on an average ca. 20% by filtering.

The sensory analyses summarized in Table IV indicate which factors affect the acceptability of the products. All

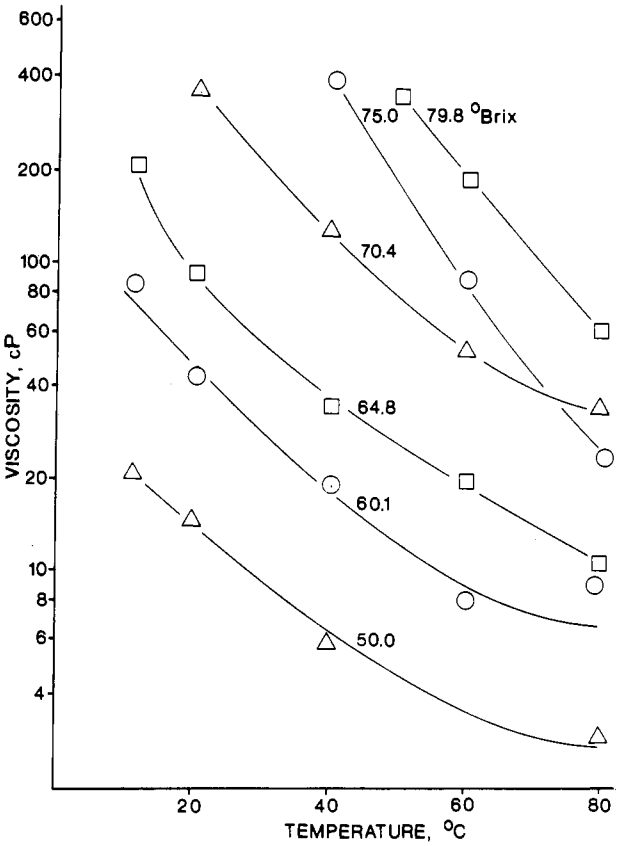


**Figure 2.** Effect of temperature and content of soluble solids on viscosity of birch syrup.

the samples were clear with no visible particles or sediment. No heat treatment after the filtration can be recommended because of the obvious possibility of formation of new sediment. During 6-month storage at −20 °C, no precipitation was observed in the syrups.

The soluble solid content 66.5° Brix (dry matter about 65%, w/w), which is that of a good-quality maple syrup, was evaluated as too thin and watery. The optimal consistency occurred at 70–75° Brix. The syrups were almost colorless after reverse osmosis and vacuum concentrating. The best light golden yellow color was obtained with a mild heat treatment of the concentrated syrup. It is very important to control the heating carefully, because the 66.4° Brix syrup heated to boil gave a too light, slightly greenish color and the 16.5-min boiling gave too dark a product, especially at 70 and 75° Brix levels.

For optimal taste and aroma, the products needed moderate heat treatment but too long a boiling time gave a bitter aftertaste (Kallio et al., 1987). The concentrated

**Table IV. Sensory Quality of Birch Syrup**

| sample | | | | | | | |
|---|---|---|---|---|---|---|---|
| °Brix | heat treatment, min | appearance and color (0–4) | aroma (0–4) | consistency (0–4) | taste (0–10) | score (0–22) | description |
| 66.4 | to boil | 2.3 | 3.0 | 2.5 | 7.1 | 14.9 | color light yellow greenish, aroma mild, too watery, taste some sour and sharp |
| 66.6 | 12.5 | 3.8 | 3.3 | 2.9 | 7.7 | 17.7 | color nice, consistency some thin, taste smooth and pleasant, aftertaste some bitter |
| 66.4 | 16.5 | 3.3 | 3.3 | 3.0 | 7.7 | 17.3 | consistency some thin, aroma and taste good but mild, sharp aftertaste |
| 70.2 | to boil | 3.8 | 3.3 | 3.0 | 8.3 | 18.4 | aroma and taste good and fine, but some mild, consistency some thin |
| 70.2 | 12.5 | 4.0 | 3.5 | 3.4 | 8.4 | 19.3 | color pleasant, aroma and taste smooth and in balance, consistency good |
| 70.1 | 16.5 | 3.5 | 3.6 | 3.5 | 8.4 | 19.0 | color dark, consistency quite thick, aroma and taste strong and good, aftertaste some bitter |
| 75.0 | to boil | 3.3 | 3.4 | 3.5 | 7.9 | 18.1 | color light, aroma good but mild, taste good but aftertaste some bitter |
| 74.9 | 12.5 | 4.0 | 3.6 | 3.8 | 8.6 | 20.0 | color and consistency pleasant, aroma strong toffee-like, taste good, well in balance |
| 75.0 | 16.5 | 3.5 | 3.3 | 3.6 | 8.3 | 18.7 | color dark, consistency quite thick, aroma strong and some burned, taste good and intensive, aftertaste some bitter |

birch sap as such has a very mild, slightly wooden aroma, and the optimal birch syrup aroma was thought to have developed as a result of volatiles formed through Maillard reaction and caramelization. Samples of optimal overall quality had a total soluble solids content of 70–75° Brix.

It is possible to reach the desired quality of the syrup by optimizing the heat flow of the evaporating process without any additional heating of the finished product. In the case of birch syrup we cannot, however, use open atmospheric boiling (Kok et al., 1978) following the reverse osmosis concentrating as done in the maple syrup industry.

**Registry No.** GABA, 56-12-2; Gln, 56-85-9; Glu, 56-86-0; Asn, 70-47-3; Ile, 73-32-5; Phe, 63-91-2; Val, 72-18-4; Tyr, 60-18-4; Thr, 72-19-5; Asp, 56-84-8; Pro, 147-85-3; Leu, 61-90-5; Ser, 56-45-1; $N_2$, 7727-37-9; malic acid, 6915-15-7; phosphoric acid, 7664-38-2; succinic acid, 110-15-6; citric acid, 77-92-9; fructose, 57-48-7; glucose, 50-99-7; galactose, 59-23-4; sucrose, 57-50-1; inositol, 87-89-8; citrulline, 372-75-8.

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# Occurrence of 2-(4-Methoxyphenoxy)propanoic Acid in Roasted Coffee Beans: Analysis by Gas–Liquid Chromatography and by High-Performance Liquid Chromatography

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Aqueous extracts of roasted Colombian Arabica coffee beans were fractionated by solvent extraction and preparative-layer silica gel chromatography and analyzed by gas–liquid chromatography–mass spectrometry (GC–MS) equipped with BP5 or BP20 fused silica capillary columns (25 m × 0.3 mm (i.d.)) and by high-performance liquid chromatography (HPLC) equipped with a Chromspher $C_{18}$ reversed-phase column (250 × 4.6 mm (i.d.)) and a diode array UV detector. The fractionated aqueous extract was shown by HPLC to contain 2-(4-methoxyphenoxy)propanoic acid. Its methyl ester, methyl 2-(4-methoxyphenoxy)propanoate, was found to be more amenable to analysis by GC–MS (greater volatility) and by HPLC (better resolution) than the acid. The purified extract was therefore methylated, and the presence of methyl 2-(4-methoxyphenoxy)propanoate was confirmed by GC–MS and HPLC analysis. The concentration of 2-(4-methoxyphenoxy)propanoic acid in roasted coffee beans was found to be 0.55–1.2 ppm.

2-(4-Methoxyphenoxy)propanoic acid is a new flavoring and a subject of Tate & Lyle PLC's British Patent Application No. 2157148A and corresponding patent applications worldwide (Lindley and Rathbone, 1985). Although it is poorly volatile and has little intrinsic flavor other than an acid taste, it may prove to be an important component for some formulated flavors. Of particular interest is the use of 2-(4-methoxyphenoxy)propanoic acid in formulated sweet products where its ability to modulate high sweetness could be applied to advantage. Structural analogues of 2-(4-methoxyphenoxy)propanoic acid are reported to occur naturally in foods (Van Straten and Maarse, 1983), for example 2-phenylpropanoic acid (wine and beer), 3-phenylpropanoic acid (wine, grape, strawberry, and soya bean), 4-methoxyphenylacetic acid (cocoa), phenylacetic acid (grape, strawberry, beer, cocoa, wine, and honey), 4-methoxybenzoic acid (currants, cocoa, and aniseed), and 3-(2-methoxyphenyl)propanoic acid (cinnamon).

A preliminary investigation by reversed-phase high-performance liquid chromatography (HPLC) led to the conclusion that the acid might be present in green Guatemalan Arabica coffee beans, based on similarity in chromatographic retention time under a number of different elution conditions and similarity in peak height behavior over a limited UV detector wavelength range

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