# Seasonal Variations of the Acids in Birch Sap

## H. Kallio & S. Ahtonen

Department of Chemistry and Biochemistry, Laboratory of Food Chemistry, University of Turku, SF-20500 Turku, Finland

(Received 11 December 1986; accepted 13 January 1987)

#### ABSTRACT

The alterations of acids in birch sap (Betula pendula Roth. and B. pubescens Ehrh.) used for birch syrup production in Finland were observed in the flow seasons of 1983 and 1984. The pH of the sap decreased from over 7.5 to 5.5 during the spring. Malic acid increased from 100 to 600 mg litre<sup>-1</sup> and dropped quickly after bud opening. The level of phosphoric acid was about one-tenth that of malic acid increased progressively from about 10 to  $300 \text{ mg litre}^{-1}$  and that of citric acid from 5 to 20 mg litre<sup>-1</sup>. No differences were observed between the acid contents of the two species. The sugar-acid ratio decreased rapidly during the first flow week and remained nearly constant (between 10 and 25) during the main flow period.

### **INTRODUCTION**

Sugars and acids are the most important factors in birch sap when sap is considered as a foodstuff. The identification of sugars and acids has been reported before (Kallio *et al.*, 1985*a*) as well as the seasonal alterations of sugar contents (Kallio & Ahtonen, 1987).

As early as 1837, Brandes (1837) measured the acidity of birch sap using litmus paper. The results have been verified in subsequent publications. Johnson (1944) measured values between pH 6.8 and 7.6, Nordal (1944) 5.1 and 5.4, Löhr (1953) 5.6 and 6.4, Tomchuk *et al.* (1973) 6.1 and Essiamah (1980) 5.3 and 5.7. Essiamah (1980) found the pH of birch sap to be almost

285

Food Chemistry 0308-8146/87/\$03.50 © Elsevier Applied Science Publishers Ltd, England, 1987. Printed in Great Britain

constant during the spring. However, some trees had a more acidic sap at a height of 0.5 m than 2.5 m higher.

In birch sap the main acid is malic acid (Schroeder, 1871, 1877; Hornberger, 1887; Richter, 1925; Nordal, 1944; Kallio *et al.*, 1985*a*). The other acids verified are phosphoric (Kallio *et al.*, 1985*a*; Hornberger, 1887), succinic (Kallio *et al.*, 1985*a*; Nordal, 1944), citric and fumaric (Kallio *et al.*, 1985*a*).

The aim of this study was to monitor the alterations of the main acids in the spring sap of *Betula pendula* and *B. pubescens* in Finland to obtain the best quality of sap for commercial purposes.

## MATERIAL AND METHODS

#### Sap

The sap of *Betula pendula* and *B. pubescens* was gathered in 1983 and 1984 in the Natural Park of Aulanko in Finland. In 1983 collection of sap was performed at 8 am and 8 pm each day during the flow season and during two 2-day periods at 3-h intervals. In 1984 the sap samples were gathered only once a week. The samples were the same as reported before (Kallio & Ahtonen, 1987).

#### Analytical methods

The analyses of acids were carried out by capillary-GLC as their TMSderivatives (Kallio *et al.*, 1985*a*).

### **RESULTS AND DISCUSSION**

The pH and acid content of the birch sap were monitored during the entire flow seasons in the spring in 1983 and 1984. The pH of the sap was typically slightly acidic. In the beginning of the flow season in 1983, pH was, however, even higher than 7.5, decreasing to around 6.0 within 2 weeks (Fig. 1). The lowest values,  $5 \cdot 3 - 5 \cdot 5$ , were reached at the end of April and in the beginning of May. In 1984, pH was between  $5 \cdot 5$  and  $6 \cdot 0$  during the entire flow season. No differences could be observed between the two birch species studied.

The contents of the most abundant acids, malic, phosphoric, succinic and citric, are presented in Figs 2 and 3. The main acidity of the sap was due to malic acid; all six trees monitored showed an analogous pattern. The concentration of malic acid increased from 0.1-0.2 g litre<sup>-1</sup> to 0.5-0.7 g litre<sup>-1</sup> in about 4 weeks in April and dropped quickly within a few

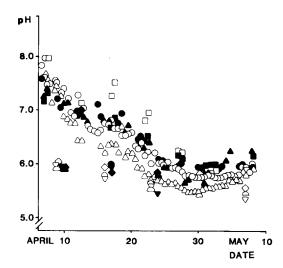


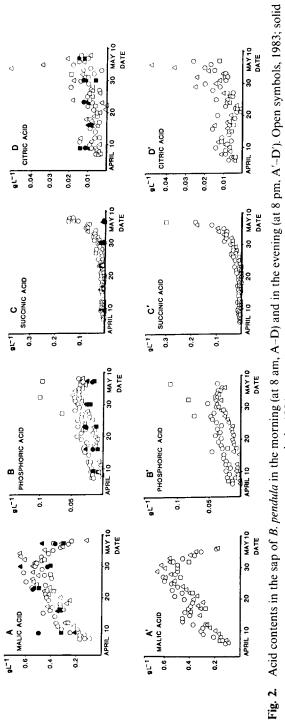
Fig. 1. pH of the sap of *B. pendula* (△ pe-1, ○ pe-2, □ pe-3) and *B. pubescens* (▲ pu-1, ● pu-2, ■ pu-3) in 1983. In 1984 ∨ pe-1, △ pe-2, ◇ pe-3, ♥ pu-1, ▲ pu-2, ◆ pu-3.

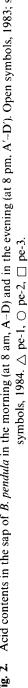
days in the beginning of May. This is in good agreement with the studies of Schroeder (1865, 1871, 1877) and Hornberger (1887). They showed that the content of malic acid increased during the spring and dropped at the end of the season. Schroeder also noticed that warm weather speeds up, and cold weather slows down, the formation of malic acid. The highest values measured were in the order of 0.7 g litre<sup>-1</sup>.

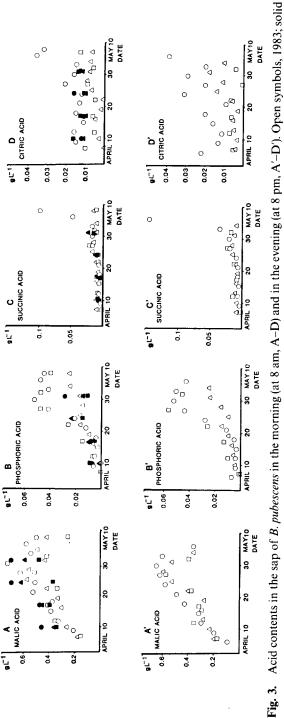
The concentration level of phosphoric acid was only about one-tenth that of malic acid, although it showed an analogous development trend during spring. The decrease in the content at the end of the season was, however, less clear than in the case of malic acid (Fig. 2B, B' and 3B, B'). In some very early samples phosphoric acid was totally absent (less than 2 mg litre<sup>-1</sup>) but later its content even exceeded 100 mg litre<sup>-1</sup>. The range observed by Hornberger (1887) was 20–80 mg litre<sup>-1</sup>. Both Schroeder (1865) and Hornberger (1887) could see a slight increase during the spring. According to Schroeder (1865), the content of phosphoric acid is highest in the root sap and decreases higher in the trunk.

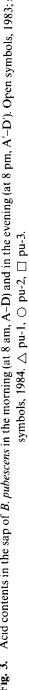
Most of the samples contained a concentration of succinic acid less than 100 mg litre<sup>-1</sup>. Only the last aliquots at the end of the season reached higher values, up to 300 mg litre<sup>-1</sup>. The development of succinic acid was very symmetrical, especially in the trees of *B. pendula* in 1983 (Fig. 2C, C').

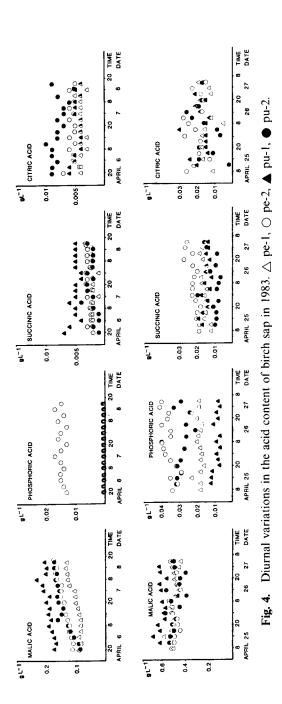
The figure for citric acid was less uniform with wide deviations (Fig. 2D, D' and 3D, D'). Typically, the contents were higher in the beginning of May than one month earlier. In only one sample did the concentration exceed 50 mg litre<sup>-1</sup>.











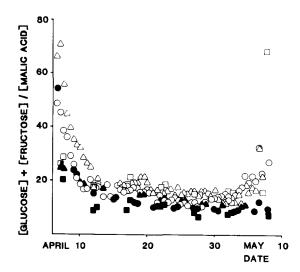


Fig. 5. The sugar-acid ratio of birch sap in 1983.  $\triangle$  pe-1,  $\bigcirc$  pe-2,  $\square$  pe-3,  $\blacktriangle$  pu-1,  $\bigoplus$  pu-2,  $\square$  pu-3.

No diurnal variations were seen in the acid contents of sap during the two 2-day periods, April 6–8 and April 25–27 (Fig. 4). The data in Figs 2 and 3, observed in 12-h intervals, also verified this result. The deviations were random and no equal trend between the individual trees or species could be seen. No differentiation between the acid contents of the two species studied was recognized.

The acids alone do not fix the acidic taste nor the sugars the sweetness of a weak water solution like birch sap. Especially in concentrated sap (Kallio *et al.*, 1985*b*) or syrup the sugar-acid ratio is decisive in the sweetness and overall flavor of the product. In the beginning of the season the syrup is sweeter than syrup made from the sap of the main flow period. Over 90% of the gathered sap volume had a sugar-acid ratio between 25 and 10 (Fig. 5). The sugar contents of the same sap samples have been published earlier (Kallio & Ahtonen, 1987).

The results show that the birch sap has no standard acid composition, but the fluctuation must be taken into account when collecting birch sap for commercial purposes.

#### ACKNOWLEDGEMENTS

Suomen Luonnonvarain Tutkimussäätiö (The Foundation for Research of Natural Reserves in Finland) and The Ministry of Trade and Industry are acknowledged for financial help.

### REFERENCES

- Brandes, R. (1837). Chemische Untersuchung des Birkensaftes. Arch. Pharm. 10, 170-6.
- Essiamah, S. (1980). Spring sap of trees. Ber. Deutsch. Bot. Ges. 93, 257-67.
- Hornberger, R. (1887). Beobachtungen über den Frühjahrssaft der Birke und Hainbuche. Forst. Blätter 128, 321-36.
- Johnson, L. P. V. (1944). Sugar production by white and yellow birches. *Can. J. Res.* **22(C)**, 1–6.
- Kallio, H. & Ahtonen, S. (1987). Seasonal variations of the sugars in birch sap. *Food Chem.*, **25**, 293–304.
- Kallio, H., Ahtonen, S., Raulo, J. & Linko, R. (1985*a*). Identification of the sugars and acids in birch sap. J. Food Sci. 50, 266–7, 269.
- Kallio, H., Karppinen, T. & Holmbom, B. (1985b). Concentration of birch sap by reverse osmosis. J. Food Sci. 50, 1330-2.
- Löhr, E. (1953). Die Zuckerarten im Blutungssaft von Betula und Carpinus. *Physiol. Plant.* **6**, 529–32.
- Nordal, A. (1944). Tilskot til kjennskapet av innhaldstoffa i bjørkesevje. Medd. Norsk Farmac. Selsk. 6(7), 159–68.
- Richter, K. (1925). Beiträge zur Chemie des Blutungs- oder Frühjahrssaftes einiger Gehölze. *Mitteil. Deutsch. Dendrol. Ges.* **35**, 138–46.
- Schroeder, J. (1865). Üeber den Frühjahrssaft der Birke. Jahresber. Agrikulturchem. 8, 157–69.
- Schroeder, J. (1871). Die Frühjahrsperiode der Birke (*Betula alba* L.) und des Ahorn (*Acer platanoides* L.). *Lantw. Vers.-Stat.* 14, 118–46.
- Schroeder, J. (1877). Untersuchung der chemischen Constitution des Frühjahrssaftes der Birke, seiner Bildungsweise und weiteren Umvandlung bis zur Blattbildungsperiode. Arch. Naturkunde Liv-, Ehst- und Kurlands (II) VII, 1–82.
- Tomchuk, R. I., Korolyak, I. S., Fedchuk, N. F. & Kyba, Y. G. (1973). The use of birch sap in the food industry. *Lesn. Khoz.* 5, 16–18.