Food Chemistry **24** (1987) 287–299

Effect of Heating on the Headspace Volatiles of Finnish Birch Syrup

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(Received 29 August 1986; accepted 3 October 1986)

ABSTRACT

The volatiles of birch syrup, heated from 0 to 10 min at 100°C, were analyzed by GC, GC-MS, and by an experienced panel of judges. Some aliphatic carbonyl compounds, especially 3-methylbutanal, 2-methylbutanal, and 2,3-pentanedione, as well as dimethyldisulfide increased markedly in the samples upon heating. Heating birch syrup reduced the aroma intensity of vanillin, had little effect on furaneol, and increased development of burnt aromas. The burnt aroma of the heated syrups paralleled the amounts of dimethyldisulfide. Heating samples in open vials generally resulted in less burnt aroma and greater caramel and furaneol aromas. In comparison with maple syrup, birch syrup was distinctly stronger in furaneol, caramel and burnt aromas, and lower in vanillin aroma.

INTRODUCTION

Birch syrup is a product recently developed in Finland for which, unlike honey or maple syrup, neither quality standards nor consumption patterns exist. Because of the unique composition of both raw birch sap and the finished syrup, the qualities of birch syrup are difficult to compare with more common products. Birch sap is a dilute solution of mainly invert sugar (Hornberger, 1887; Beveridge *et al.*, 1978; Kallio *et al.*, 1985) with varying, but moderately low pH (Johnson, 1944; Essiamah, 1980). It contains a

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Food Chemistry 0308-8146/87/$03·50

number of Krebs Cycle 'fruit acids', dominated by malic acid; some phosphoric acid is also present (Hornberger, 1887; Nordal, 1944; Kallio *et al.*, 1985). The content of high molecular weight proteins and free amino acids, while low (Kallio *et al.*, 1986), is sufficient to support Maillard browning reactions.

The major sugars in birch syrup are glucose and fructose, whereas the principal sugar in maple is sucrose. The ratio of minerals and free amino groups to sugars, particularly reducing sugars, is higher in birch syrup (Beveridge *et al.*, 1978), which indirectly affects the sensory qualities of the final product. Because sucrose accounts for only a fraction of the total sugars in birch syrup, finished birch syrup can be concentrated to more than 66–66·5° Brix, which is the fixed level in maple syrup.

Evaporation of birch sap in an open maple syrup pan at atmospheric pressure results in browning reactions and causes burned, unpleasant flavors and extreme darkening (Ganns *et al.*, 1982; Kok, 1977). Maillard and caramelization products then dominate as flavor constituents, completely masking the very mild and unique birch sap flavor. A light colored syrup is obtained when sap is processed with reverse osmosis and vacuum evaporation, followed by a mild heat treatment (Kallio *et al.*, 1986). Storage of the syrup at 5–10°C clearly prolongs the shelf life of the product.

The present study was designed to compare the changes evidenced by sensory and gas chromatographic analysis of low boiling volatiles when samples of birch syrup were carefully overheated at 100°C, while closed, open, and vented.

MATERIALS AND METHODS

Birch syrup and treatments

The syrup was prepared in 1985 by vacuum evaporation of preconcentrated, frozen birch sap (*Betula pubescens* (Ehrh.) collected in Finland (Kallio *et al.*, 1986). The soluble solids content of the syrup was 75·1° Brix, pH *ca* 6, and the ICUMSA color was 3·5/cm Brix measured immediately after production. Six separate lots of syrup that had been stored at −25°C were combined and then divided into seven identical 70 g aliquots. The various heat treatments of the different aliquots were carried out in a boiling water bath in 250 ml Erlenmeyer flasks that were either open (o), vented (v) or closed (c), for 5 or 10 min periods, hereafter referred to as 5-o, 5-v, 5-c, 10-o, 10-v, and 10-c. In the vented samples the Teflon valves were kept open during heating. The bottles were quickly cooled to room temperature (21°C) in a water bath and transferred to 250 ml Erlenmeyer bottles with Teflon valves for GC analysis;

the control syrup was not heated. 30 g of each sample that the headspace had been taken from for GC analysis was later used for aroma evaluation. This yielded three sets of eight samples. Samples of 10 g were placed in 60 ml covered brown bottles.

Gas chromatographic analysis

In 250 ml Erlenmeyer flasks with closed valves, 70 g of syrup was tempered at 21°C and stirred with a magnetic stirrer for 2 h at 90 rev/min. A headspace sample was collected with a 10 ml gastight Hamilton syringe fitted with a 230 mm deactivated fused silica needle (OD 0·25 mm) at a sampling speed of 0·5 ml/min, with the tip of the needle 30 mm above the surface of the syrup. Analyses were carried out with a Hewlett Packard 5890 gas chromatograph equipped with FID (240°C) and interfaced to a 5880A integrator. The 60 m DB-1701 fused silica column (J. & W. Scientific, 0·315 mm ID, 0·25 μm liquid phase) was connected to the on-column injector (J. & W. Scientific). An exceptionally long capillary column was used because the quantitative considerations permitted only cryofocused on-column injections under standardized conditions, without prefractionations. Prior to injection the column head pressure was decreased to 25 kPa and a 20 cm loop of the column inserted into liquid nitrogen. During injection, the tip of the syringe needle within the column was 80 mm above the surface of the coolant. The injection speed was 0·5 ml/min. When the injection was completed the syringe was removed, the injection valve closed, and the column head pressure raised to 100 kPa, resulting in a linear hydrogen velocity of 58 cm/s at 30°C. After 3 min the cold trap was removed and the oven temperature was held for 10 min at 30°C, and increased to 220°C at a speed of 5 degC/min, and held for 10 min. The attenuation was 6 and threshold 5. In a preliminary attempt to describe the aromas of some of the individual GC peaks, these same conditions were employed, but the effluent of the capillary was split to the FID and a sniffing port in a 1:1 ratio.

When measuring the relative contents of the more abundant low boiling volatiles, 2·0 ml headspace samples were injected with attenuation 9 and threshold 6.

Uncorrected integrated relative peak areas of the compounds, the contents of which increased at least twofold when heated, were used for the calculations. Blank injections were made to verify the purity of the analytical system. Kovats' indices were determined with hydrocarbon (n-C_5–n-Cl_8) co-injections.

To determine the content of 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol) and vanillin, the syrup was extracted four times with a mixture of pentane and diethylether (1:2), and the extracts concentrated and analyzed with the same GC conditions used in the headspace analysis. Internal standards (*n*-nonane, *n*-undecane and *n*-dodecane) were used for quantitative determinations.

Mass spectral analysis

A Finnigan MAT 4500 GC/MS/data system was used. The ionization energy was 70 eV, temperature of the ion source was 190°C and the scan speed was 1 sec from m/e 33 to 350. Helium was used as the carrier gas. The capillary column was connected directly to the ion source, which was at 200°C. The analytical conditions were the same as those used for the gas chromatographic analysis.

Descriptive aroma analysis

Preliminary aroma analyses were conducted by two experienced laboratory personnel. Aroma quality of syrups heated in vials at 100°C from 5 to 30 min, with and without lids, differed markedly. Volatiles described as burnt and sulfurous were noticeably lower in the open-heated samples after 5 min of heating.

Selection of aroma descriptors was complicated because of the judges' unfamiliarity with birch syrup and because aromas, particularly the sulfurous burnt component, escaped quickly from the containers when the lids were removed. Maple syrup (MacDonald's, dark amber, Grade A), which is familiar to these judges was selected as an additional sample. Four descriptors; vanillin, furaneol, caramel, and burnt, were selected as the most important aroma notes. Furaneol, a flavoring agent in confectionery products, and vanillin are volatiles in birch syrup. Physical references, developed to represent the quality and intensity of the aroma attributes in the birch syrup, were: 1% vanillin, 100 ppm furaneol, caramel (8 g, light brown, Vernell's brand) dissolved in 100 g distilled water, and a 50/50 mixture of sugar and whole milk cooked until black. The references were placed in 60 ml brown bottles, capped and stored at 5°C (except furaneol which was frozen at −20°C).

Six female and two male students, 18–30 years of age, all with some previous experience in sensory analysis, were selected on the basis of interest and availability. At an initial open session, judges were asked to familiarize themselves with the birch syrup samples that had been used for bench-topping and the aroma references. At the judges' suggestion, minor modifications were made in the concentration of the references, after which two practice sessions were conducted under red illumination to mask visual differences, in individually partitioned booths maintained at 21 ± 23°C.

Eight judges participated in two data-collection sessions on two consecutive weeks. The eight samples were served in a randomized order in two sets of four at 21°C. All samples were rated for aroma intensity of the four attributes in the following order: vanillin, furaneol, caramel, and burnt, the order in which the aromas seemed to appear. The reference standards were available for consultation at all sessions. Intensity was recorded on a 12 cm unstructured line which extended 0·5 cm beyond the end points, which were anchored with the term 'none' and 'very strong'. Beakers of distilled water were provided for the judges to sniff between samples to refresh the nasal passages.

Statistical analysis

The marks on the lines, which represented aroma intensity, were converted to centimetres and the data submitted to analysis of variance (SAS ANOVA). Fisher's least significant difference (LSD) was calculated to determine differences among means at $p < 0{\cdot}05$ and principal component analysis (SAS FACTOR) was performed to show the relationship between the samples and the descriptive terms.

RESULTS AND DISCUSSION

The concentrations of some of the birch syrup volatiles were unaffected by the heat treatment. These constituents were regarded as the 'background aroma' of birch syrup and were excluded from detailed consideration in the present work. Attention was directed to those compounds whose concentrations in the headspace of the syrup were affected by the heat treatments and appear as numbered peaks in Fig. 1. These compounds are listed in Table 1.

The partitioning of the volatiles between the liquid and gas phases is affected by both equilibration time and temperature. It is of great importance that the heated syrups are transferred into clean bottles after cooling because the condensed water on the walls and valve retains part of the volatile compounds. Precise control of variables such as the timing of the heat treatment, the magnetic stirrer speed and the distance between the fused silica needle and the syrup surface during sampling, were also found to be critical.

Generally, the aroma of birch syrup is weak and the concentration of volatiles is low. Therefore, to provide detectable amounts of some volatiles, exceptionally large, 10·0 ml on-column injections were required. Another characteristic of the syrup is the wide range of concentrations of different

TABLE 1
Effect of Heating on the Relative Abundance of Volatiles in Birch Syrup Headspace

Compound	*No.*[a]	*Heated 5 min*			*Heated 10 min*			*Heated, mean*	*Heated, mean*	*Proportion*[b]
		Open	*Vented*	*Closed*	*Open*	*Vented*	*Closed*	*5 min*	*10 min*	
Furan	1	10	8	8	23	5	28	9	17	1·1
2-methylpropanal	2	4	4	4	8	4	11	4	7	28·7
2-methylfuran	3	3	3	3	8	4	8	3	7	1·9
3-methylbutanal	4	8	6	7	17	6	3	7	11	6·3
2-methylbutanal	5	4	4	4	9	4	12	4	9	59·5
2,5-dimethylfuran	6[c]	+	+		+ +	4	+	+	+	0·1
2,3-pentanedione	7[c]	>2	+	+	>5	8	>3	+	+ +	0·0
Dimethyldisulphide	8	2	2	3	4	8	9	2	7	0·3
Octanal	9	1	2	1	1	2	6	2	3	2·1
Benzeneacetaldehyde	10[c]	+	+		+ +	2	+	+	+ +	0·1
3-phenylfuran	11[c]	+	+	+	+ +	5	>4	+	+ +	0·0
2,5-dimethyl-4-hydroxy-3(2H)-furanone	12[d]	2		2	2		2	2	2	
Vanillin	13[d]	2		2	1		2	2	2	

[a] Numbering identical with Fig. 1.

[b] Sum of the relative contents of the compounds (listed) in the headspace of the untreated syrup = 100.

[c] Compounds could not be quantified as they were too low to measure in unheated control.

[d] Analyzed by solvent extraction.

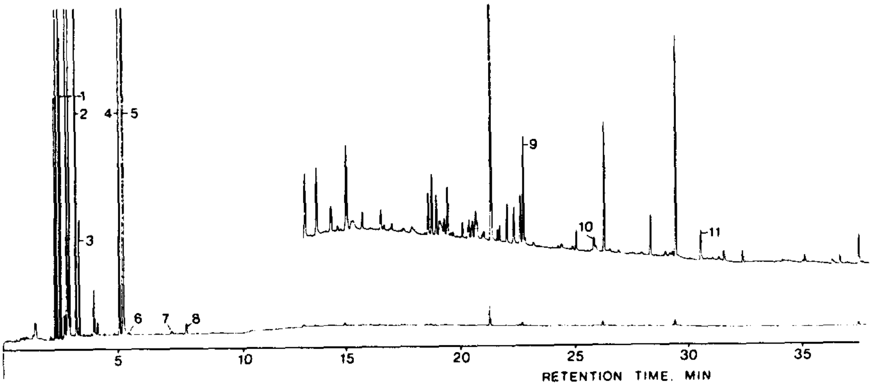

Fig. 1. Headspace chromatogram of birch syrup (10-v). The lower chromatogram: 2 µl injection with attenuation 9 and threshold 6. The upper chromatogram: 10 µl injection with attenuation 6 and threshold 5.

compounds in the headspace: quantitative determinations of volatiles having content ratios even lower than 1:1000 were made. With the 10·0 ml injections, the column was overloaded by the most abundant low boiling volatiles and the capacity of the column was exceeded. Therefore the first part of the chromatogram was quantified using 2·0 ml injections.

Characteristic of the changes in the volatiles was the increase of some aliphatic carbonyl compounds and dimethyldisulphide: 3-methylbutanal, 2-methylbutanal and 2,3-pentanedione increased 10–20 fold in syrups heated for 10 min at 100°C (Table 1). Of the heterocyclics only furan exhibited the same magnitude of increase; lower rates of increase were exhibited by 2-methylfuran, 2,5-dimethylfuran, 2-furancarboxaldehyde and 3-phenylfuran.

One of the character impact compounds of birch syrup is 2,5-dimethyl-4-hydroxy-3(2H) furanone (furaneol). Its vapor pressure is extremely low, but its odor threshold value in water is 0·04 ppb (Pyysalo *et al.*, 1977). Furaneol was verified in the headspace by SIM mass spectrometry technique, but the FID signal was too low to permit quantitative determination. The contents of furaneol and vanillin in the syrup were determined by solvent extraction. To avoid possible degradation of furaneol in the heated injection port (Williams and Mottram, 1981), on-column injection at 30°C was used. Both compounds increased about twofold when the syrup was heated for 10 min at 100°C.

Many of the volatiles listed in Table 1 would be expected to appear in any heated mixture containing carbohydrates and amino acids. Even the pyrolysis of amylose (van der Kaaden & Haverkamp, 1983), glucose (Heyns *et al.*, 1966; Sugisawa, 1966) or cellulose (Sakuma *et al.*, 1981) as well as the heating of furaneol (Shu *et al.*, 1985) or roasting of coffee (Liardon & Ott, 1984) produce most of the compounds mentioned above. A list of volatiles

TABLE 2

Mean Aroma Intensity Scores for Birch Syrup and One Maple Syrup Sample
($n = 8$ judges × 2 reps)

Aroma attribute	*LSD* ($p = 0{\cdot}05$)	*Mean aroma score*							
Vanillin	1·12	10-c 2·06 a	10-v 2·13 a	5-u 2·64 ab	5-c 2·74 ab	10-u 3·01 ab	5-v 3·04 ab	Control 3·48 b	Maple 5·13 c
Furaneol	1·74	Maple 2·31 a	10-c 5·39 b	5-c 5·46 b	10-v 5·56 b	5-u 5·77 b	10-u 5·93 b	Control 6·04 b	5-v 6·26 b
Caramel	1·54	Maple 2·16 a	10-v 3·49 ab	5-c 4·01 bc	5-v 4·03 bc	10-u 4·09 bc	10-c 4·16 bc	Control 4·52 bc	5-u 5·35 c
Burnt	1·15	Maple 1·44 a	5-u 2·53 ab	5-v 3·00 b	10-u 3·26 bc	Control 3·46 bc	5-c 3·59 bc	10-v 4·44 cd	10-c 4·85 d

Means with the same subscript do not differ significantly, $p < 0{\cdot}05$.

should be completed with quantitative and sensory data whenever possible. Even if such data were available for the individual compounds, synergistic and antagonistic effects would not allow the prediction of the final qualities of the product.

The exit port sniffing technique was useful. The aromas of furaneol and vanillin were detected by this method, reinforcing their importance in the overall aroma even at low concentrations.

Sensory analysis

Mean aroma intensity scores for the syrup samples are listed in increasing order in Table 2. Application of least significant differences (LSD) at $p < 0{\cdot}05$ showed that maple syrup was higher in vanillin aroma than any of the birch samples. The unheated birch syrup sample was rated significantly higher in vanillin aroma than were the 10-v and the 10-c samples. All birch samples were rated similarly in intensity of furaneol aroma with lower values for the maple syrup. The latter also was lowest in caramel aroma, while the control and 5-o were highest. Burnt aroma intensity was lowest in maple, intermediate for the unheated control and highest for birch samples 10-v and 10-c.

Table 3 is a summary of the F values from analysis of variance of the aroma intensity data for each of the four attributes. The eight samples contributed significantly to the variation. As expected, judges were a significant source of variation throughout ($p < 0{\cdot}001$), as they used different parts of the intensity scale. The significant interaction of judge X sample for vanillin and burnt ($p < 0{\cdot}001$ and 0·01, respectively) indicated less judge agreement with these terms. For vanillin, furaneol, and caramel, no significant differences were obtained between replications or for the

TABLE 3
F Values and Degrees of Freedom from Analysis of Variance of Aroma Intensity

Source of variation	*df*	*Aroma attribute*			
		Vanillin	*Furaneol*	*Caramel*	*Burnt*
Sample	7	5·97^a	4·12^a	2·69^b	6·92^a
Judge	7	16·15^a	14·87^a	13·92^a	20·65^a
Rep	1	0·11 ns	0·23 ns	0·61 ns	17·26^a
J*S	49	2·80^a	—	—	2·19^c
R*S	7	2·89^b	—	—	—
J*R	7	—	—	—	4·71^a

^{a,b,c} Significant at $p < 0{\cdot}001$, $p < 0{\cdot}05$, and $p < 0{\cdot}01$, respectively.

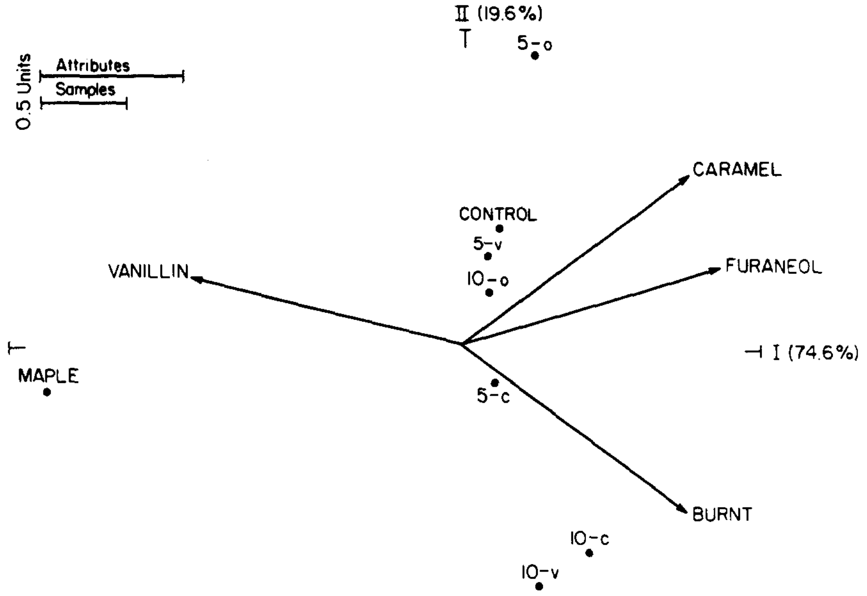

Fig. 2. Projection of aroma attributes of birch syrups on principal components I and II.

interaction of judges X replications, verifying that neither the samples nor the judges' perception of the samples changed significantly across replications. Burnt aromas, however, were significantly greater in the first than in the second replication ($p < 0{\cdot}001$) due to the dual nature of the burnt aroma. The first note was a volatile, sulfurous aroma while the second was a more stable, lingering component. By the second replication, conducted with the same bottles of samples, the sulfurous component had diminished.

Results from principal component analysis of the data are plotted on Cartesian coordinates in Fig. 2. Factor one explained 74·6% of the variation and primarily separated the maple from the birch samples. Factor two represented 19·6% of the variance and separated the birch samples. The closed and more highly heated samples were closely associated with the burnt aroma. Maple syrup was associated principally with vanillin aroma. The unheated control, 5-o, 5-v, and 10-o samples were associated primarily with caramel and furaneol. The attribute associations indicated that vanillin was negatively correlated with furaneol and burnt, and that furaneol and caramel were positively correlated ($p < 0{\cdot}05$).

Comparison of GC and sensory analysis

All the compounds for which relative quantitative data were obtained from the headspace analysis were entered into stepwise regression analysis (BMDP2R) with the burnt and caramel scores. Since the replications for burnt were significant, this was done for each replication separately. Dimethyldisulfide and 3-methyl butanal were the first two peaks entered into the equation to predict the burnt scores for replication 1 (R-sq = 0·65). Qvist *et al.* (1976), using stepwise discriminant analysis for predicting intensity classes of odor qualities for canned beef/soy protein samples, found that dimethyldisulfide was related to a sulfurous odor quality and that 3-methyl butanal was related to the smell of cooked vegetables. Dimethyldisulfide and octanal were the first two variables entered into the equation for replication 2 (R-sq = 0·96). Replication 2 was better explained by the regression equation, indicating that replication 1 was perhaps more variable, and reinforced the hypothesis that the samples were changing in quality over time.

The smell of sulfur-containing volatiles is generally unpleasant in higher concentrations (Ohloff *et al.*, 1985). Dimethyldisulfide increased measurably in the heated samples, but its concentration in the total volatiles remained low. Its threshold in water is low, 12 ppb, but the threshold of dimethyltrisulfide is even lower, 0·01 ppb (Buttery *et al.*, 1976). Dimethyltrisulfide always existed in the heated syrup, but at extremely low concentrations (less than 0·05% of the compounds listed in Table 1). This compound may have affected the aroma of the heated birch syrups. An unpleasant aroma is caused by higher concentrations of 3-methylbutanal, a Strecker degradation product of leucin. This compound increases at the very early stages of Maillard reactions (Eichner & Ciner-Doruck, 1981).

Some of the changes in the volatile content of the syrup were considered positive, e.g. compounds such as furaneol, vanillin and up to a certain level furfural (Furia & Bellanca, 1975). No attempts were made to generate regression equations for furaneol or vanillin. Both these compounds increased about twofold upon heating, but this same trend was not found by the sensory panel. More heated samples tended to be rated as lower in these aromas by descriptive analysis, most likely due to a masking effect of the burnt aroma.

Octanal and furan were the first two variables entered into the regression equation with the caramel scores and explained 84% of the variance in the caramel scores (R-sq = 0·84). While this study has not established definitively that these particular peaks cause the aroma changes observed, they are offered as a possible explanation.

ACKNOWLEDGEMENTS

The authors express thanks to Ms Tuija Teerineen, for the preparation of the birch syrup, to Ms Mary Bills, for her assistance with the analyses and to Mr Robert Flath, for the MS analyses. The Foundation for Research of Natural

Reserves in Finland and The Finnish Food Research Foundation are acknowledged for their financial assistance.

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