# Volatile Monoterpenes in Black Currant (*Ribes nigrum* L.) Juice: Effects of Heating and Enzymatic Treatment by *β*-Glucosidase

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Changes of terpenes in black currant juice induced by the action of heat were investigated in the present study. Limonene, α-terpinene, linalool, α-terpineol, 4-terpineol, and menthol added to either black currant juice or a model system were thermally treated at 90 °C for 30 min. Similar heat-induced decreases in the concentration of the terpenes were observed in the two systems. The concentration of a range of terpene hydrocarbons and oxygenated terpenes increased, α-terpineol being a main conversion product of most of the examined compounds. In the main, the measured loss of compounds exceeded the detected concentrations of products formed. In addition, determination of glycosidically bound terpenes in the juice was carried out by two methods of enzymatic hydrolysis, namely, addition of *β*-glucosidase to an Amberlite XAD-2 isolate or directly to black currant juice. The two methods gave the same patterns of seven released volatile aglyconic terpenes. However, none of the released terpenes are important for the odor of black currant juice.

## INTRODUCTION

The industrial production of black currant berries to juice involves crushing, enzyme treatment, pressing, clarification, filtration, and several heating steps. Heat-facilitated concentration of fruit juices is in addition often applied in order to reduce the volume and stabilize the juice for storage and transport. Each processing step alters to some extent the aroma compound profile of the berry, and especially operations involving the application of heat can lead to major changes in sensory characteristics (*1−7*).

Terpenes together with esters and alcohols are the major groups of aroma compounds in black currant juice. Some of the volatile terpenes have been identified by gas chromatography−olfactometry (GC-O) as being important for black currant juice odor (*1, 8, 9*). During processing, terpenes are converted to other terpenes via the hydration of double bonds, dehydration, rearrangements, and cyclization under acidic conditions similar to those found in black currant juice (*10*). Early work by von Sydow and co-workers showed that large changes in the monoterpene complex occur when black currant juice or mash is subjected to heat treatment (*11*), and the sensory changes that take place during heating can be correlated with the decrease of terpene hydrocarbons and an increase of dimethyl sulfide and aliphatic aldehydes (*12*). More recently, thermal treatment of black currant juice has been shown to cause an increase in

the concentration of several terpenes, such as limonene, α-terpinene, and α-terpineol, and a decrease in the concentration of a few terpenes, namely, linalool and 4-terpineol (*7*). A loss of most terpenes occurs during the concentration of black currant juice, whereas the concentration of some oxygenated terpenes increase, suggesting that these compounds are released from a pool of glycosides or otherwise bound species (*5, 6, 13*). In fruits, potentially volatile aroma compounds can be released from their glycosidic precursors by the action of heat-facilitated acid and/or enzymatic hydrolysis. Hence, the changes in terpene concentrations during thermal processing might be a combination of acid-catalyzed terpene reactions and release from a pool of glycosidically bound terpenes. The presence of monoterpene glycosides in black currants has previously only been indicated (*14*), but recently, a range of aliphatic and aromatic alcohols were identified as glycosidically bound in black currant juice (*15*).

The aim of the present study was to evaluate the importance of acid-catalyzed reactions and release of aroma compounds from glycosides as the causes of the changes observed in the terpene complex during thermal treatment of black currant juice. Thermal treatments of terpene aroma compounds were performed in juice, as well as in model solutions, in order to detect possible concomitant terpene formations and degradations. The role of glycosidically bound terpenes was studied by examining the effect of enzymatic hydrolysis by application of *β*-glucosidase in juice and on isolated glycosides.

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## MATERIALS AND METHODS

**Materials.** A commercial black currant juice (14 °Brix) of the variety Ben Lemond was obtained from an industrial plant. Details of the juice preparation are described in ref 7. The juice was stored at −18 °C and thawed immediately before use.

A model solution resembling the black currant juice (glucose concentration, 48 g/L; fructose concentration, 61 g/L; and citric acid monohydrate concentration, 39 g/L in water) was adjusted to pH 3.1 (same as black currant juice). Single terpenes (limonene, α-terpinene, linalool, α-terpineol, 4-terpineol, or menthol) were added in the model solutions (0.5 mg/L). A 0.1 M concentration of citrate-phosphate buffer (pH 5) was used. Almond β-glucosidase enzyme solution (10 mg/mL, Sigma-Aldrich, Denmark) in 0.1 M citrate-phosphate buffer (pH 5) was used. Amberlite XAD-2 (20−60 mesh) adsorbent resin (Sigma-Aldrich, Copenhagen, Denmark) was used. The aroma standards used were α−terpinene, linalool oxide, rose oxide, cumin aldehyde, and *p*-cymene (Fluka, Buchs, Switzerland); menthol, menthone, citronellol, bornyl acetate, terpinolene, and 4-terpineol (Roth, Karlsruhe, Germany); and β-damascenone (Firmenich, La Plaine, Switzerland), and the remaining compounds were from Sigma-Aldrich (Copenhagen, Denmark).

**Heating of Samples.** One hundred milliliters of black currant juice or single terpene model solution (0.5 mg/L) was transferred into a 250 mL blue cap flask equipped with a screw cap. Heating was performed in a closed system in order to avoid evaporation. To obtain the desired temperature of 90 °C, samples were heated in a microwave oven (Samsung Classic Collection microwave oven-b30) and then transferred to a preheated 90 °C water bath, where they were kept under magnetic stirring for 30 min. Immediately after heating, the samples were cooled in an ice−water bath and stored at 5 °C until solvent extraction was carried out. Control samples of juice and model solution were not subject to any heating. The heat treatments were performed in triplicate.

**Solvent Extraction of Aroma Compounds.** Fifty milliliters of black currant juice or single terpene model solution was transferred into a 250 mL blue cap flask and 50 mL of diethyl ether/pentane 1:1 and 1.00 mL of internal standard (50 μL/L 4-methyl-1-pentanol, Aldrich, Steinheim, Germany) were added. Volatiles were extracted for 30 min under magnetic stirring (100 rpm). The sample was then left for separation of phases for 15 min and placed in a freezer allowing the water phase to freeze and the solvent phase to be decanted. The solvent phase was then dried with Na$_2$SO$_4$ and concentrated to 0.080 g under a gentle stream of nitrogen. The extract was stored at −18 °C until GC analysis. Quantifications for the solvent extraction method were carried out on commercially availably terpenes. The aroma compounds to be quantified were divided into three series because the purity of the compounds was less than 100% for some of the compounds. For each series, 100 mg/L of aroma standard stock solutions in ethanol was diluted with the model solution (see Materials) to 0.5 mg/L. During data processing, linear calibration curves of each aroma standard were based on entries of 0 and 0.5 mg/L. Solvent extractions were performed in duplicate under the same conditions as applied to the samples.

**Glycoside Isolation.** Isolation of glycosidically bound volatiles was performed according to the method described by Boulanger (*16*). One hundred milliliters of black currant juice was poured (1.5 mL/min) onto a solvent washed XAD-2 column (9 × 1.6 cm), and water soluble components were eluted with 50 mL of distilled water. The free volatile fraction was extracted with 50 mL of pentane/diethyl ether (1:1) (1.5 mL/min) and discarded. The glycosidically bound aroma fraction was extracted with 50 mL of methanol (1.5 mL/min), concentrated under reduced pressure to approximately 1 mL, and redissolved in 2.0 mL of 0.1 M citrate-phosphate buffer (pH 5). The glycosidic methanol extract was washed twice with 2 mL of pentane/diethyl ether (1:1).

**Enzymatic Hydrolysis.** *Enzymatic Hydrolysis of Glycosidic Extract.* Half of the glycosidic extract was mixed with 2.0 mL of β-glucosidase in 0.1 M citrate-phosphate buffer (pH 5), and the other half was mixed with 2.0 mL of 0.1 M citrate-phosphate buffer (pH 5), constituting the control sample.

*Direct Enzymatic Hydrolysis.* Black currant juice and 0.1 M citrate-phosphate buffer (pH 5) (1:1) were adjusted to pH 5. Fifty milliliters of the mixture was transferred to a 250 mL glass flask equipped with

a lid, and 2.0 mL of β-glucosidase in 0.1 M citrate-phosphate buffer (pH 5) was added. The juice control sample constituted 50 mL of the juice and buffer (1:1) and 2.0 mL of 0.1 M citrate-phosphate buffer (pH 5). All samples were incubated for 19 h in a 37 °C water bath.

**Dynamic Headspace Collection.** Immediately after the enzyme treatments, dynamic headspace collection was carried out. The glycosidic extract sample was transferred to a 250 mL glass flask equipped with a purge head and dissolved with water to 50 mL. The glass flask containing direct enzymatic hydrolyzed juice was equipped with a purge head. One milliliter of internal standard (50 μL/L 4-methyl-1-pentanol) was added. The sample temperature was equilibrated in a 30 °C water bath for 10 min. Under magnetic stirring (200 rpm), the sample was then purged with nitrogen (100 mL/min) for 60 min. The volatiles were collected into traps containing 250 mg of Tenax TA (mesh size = 60/80, Buchem bv, Apeldoorn, The Netherlands). Quantification for the dynamic headspace collection was carried out on commercially available terpenes. A 100 mg/L amount of aroma standard stock solution in ethanol was diluted with the model solution (see Materials) to 0.2 mg/L. During data processing, linear calibration curves of each aroma standard were based on entries of 0 and 0.2 mg/L. For dynamic headspace collection, 50 mL of model solution and 0.1 M citrate-phosphate buffer (pH 5) (1:1) adjusted to pH 5 was used. Dynamic headspace collection was performed in triplicate, under the same conditions as applied to the juice samples.

**Gas Chromatography−Mass Spectrometry (GC-MS).** From the enzymatic experiments, the collected volatiles were thermally desorbed using an Automated Thermal Desorber (ATD 400, Perkin-Elmer, United States), and separation and identification of aroma compounds were carried out on a Hewlett-Packard (Palo Alto, CA) G1800A S GC-MS system equipped with a J & W Scientific DB-Wax column (30 m × 0.25 mm × 0.25 μm). Settings were the same as described by ref *8*. From the heating experiments, 2 μL of the extracted volatiles was injected with a split ratio of 1:10, and separation and identification of aroma compounds were carried out on a Hewlett-Packard G1530A S GC-MS System with the same parameters as described above. Identifications were carried out by probability-based matching with mass spectra in the G1035A Wiley library (Hewlett-Packard) and comparisons with mass spectra and retention indices (RI) of authentic reference standards. Linear retention indices were calculated after analysis under the same conditions of an *n*-alkane series (C9−C24). Peak area calculations were based on single ions, and peak areas of aroma compounds were divided by peak area of the internal standard.

## RESULTS AND DISCUSSION

**Analysis of Terpenes in Black Currant Juice.** Terpenes in black currant juice were determined by GC-MS after isolation by either solvent extraction or dynamic headspace collection (**Table 1**). Other compounds such as alcohols, esters, phenols, and furans were also identified in the black currant juice (not shown). More terpene compounds were recovered by dynamic headspace collection than by solvent extraction as previously reported (*8*) (**Table 1**). However, in this study, solvent extraction was used for isolation of aroma compounds in the thermally treated samples since some of the terpenes of interest have been shown to decompose and rearrange on the adsorbent material during headspace sampling (*17*).

**Reactivity of Terpenes during Thermal Treatment of Black Currant Juice and Model Solution.** The stability and reactivity of selected terpenes (limonene, α-terpinene, linalool, α-terpineol, 4-terpineol, and menthol) were studied by adding the pure compounds to either black currant juice or a model system and heating the samples for 30 min at 90 °C. The model system was designed to have the same acidity (pH 3.1), °Brix-value, and concentration of citric acid, glucose, and fructose as black currant juice. Thermal treatment of black currant juice has been shown to cause changes in the concentration of all of the selected terpenes except menthol (*7*). Linalool, α-terpineol,

**Table 1.** Terpenes Identified in Black Currant Juice

| | | isolation method, occurrence[a] | |
| --- | --- | --- | --- |
| compound[b] | RI[c] | dynamic headspace collection | solvent extraction |
| α-pinene[d] | 1008 | − | + |
| α-terpinene[d] | 1167 | + | + |
| 1,4-cineole[d] | 1169 | + | + |
| limonene[d] | 1184 | + | + |
| 1,8-cineole[d] | 1194 | + | + |
| γ-terpinene[d] | 1223 | + | + |
| p-cymene[d] | 1253 | + | + |
| terpinolene[d] | 1266 | + | + |
| rose oxide[d] | 1337 | + | − |
| menthone[d] | 1438 | + | − |
| cis-linalool oxide[d] | 1451 | + | + |
| isomenthone[d] | 1465 | + | − |
| linalool[d] | 1524 | + | + |
| bornyl acetate[d] | 1554 | + | − |
| neomenthol[e] | 1574 | + | − |
| 4-terpineol[d] | 1577 | + | + |
| p-menthene-9-al[e] | 1584 | +[f] | − |
| β-cyclocitral[d] | 1590 | + | − |
| menthol[d] | 1618 | + | + |
| 1,8-menthadien-4-ol[e] | 1662 | + | + |
| α-terpineol[d] | 1674 | + | + |
| phellandral[e] | 1696 | + | − |
| 3-caren-10-al[e] | 1711 | +[f] | − |
| cumin aldehyde[d] | 1716 | + | − |
| citronellol[d] | 1750 | + | − |
| β-damascenone[d] | 1800 | + | − |
| p-cymen-8-ol[e] | 1824 | + | − |
| geraniol[d] | 1830 | + | − |
| exo-2-hydroxycineol[e] | 1845 | − | + |

[a] +, Compounds identified; −, not detected. [b] Other compounds identified in black currant juice; see, e.g., ref 7. [c] RI on a DB-WAX column. [d] Mass spectra and RI agreed with authentic standards. [e] Tentatively identified; mass spectrum agreed with the Wiley library. [f] Only identified in the glycosidic fraction.

and 4-terpineol have been shown to be of importance to the odor of black currant juice by GC-O (1, 8, 9).

The thermal treatment led to decreased concentrations of the terpenes added to the model solutions (**Table 2**). Menthol was the most stable of the studied terpenes with a loss of only 5%. 4-Terpineol and α-terpineol were degraded by 29 and 21%, respectively. 1,4-Cineole was formed from the latter two compounds, and γ-terpinene was also formed from 4-terpineol. Limonene and linalool were degraded to similar extents, 69 and 62%, respectively. α-Terpineol was formed from both, and nerol and geraniol were formed in addition from linalool. α-Terpinene was subject to the most extensive degradation (92%), but no conversion products were detected. In the case of linalool, most of the loss could be accounted for, but generally, the measured loss of compounds exceeded the detected increases in concentrations of products formed.

The thermal treatment of terpenes added to black currant juice resulted in losses similar to what were observed with the model system. Compounds formed in the model system were also formed in the juice system, and in addition, small amounts of some other products were formed, α-terpineol being a main conversion product of most of the compounds (**Table 2**). The loss of 4-terpineol and most of the linalool loss could be accounted for by increased concentrations of other teprenes. However, even though more of the loss could generally be accounted for in the juice system than in the model system, an overall loss of compounds occurred. An exception from this was menthol, where somewhat more products were formed than lost.

The heat-induced losses of added terpenes in the model solution and in black currant juice were in the same range for the majority of the compounds (**Table 2**). Also, similar patterns of products formed were observed in the two systems. The ability of the model system to simulate the behavior of the terpenes in black currant juice during heating suggests that no other major components of the juice than the model system parameters selected, i.e., sugars, acid content, pH, and °Brix, influence the degradation of the terpenes.

The main conversion product of linalool and limonene in stored model solutions of orange juice was also α-terpineol, and in addition, cis-1,8-p-menthanediol was formed. Linalool also rearranged to nerol and geraniol (18). Under acidic conditions, nerol and geraniol in terms cyclize to form α-terpineol and terpene diols (19). In a model citrus juice, α-terpineol was converted to unidentified products faster than it was formed from both linalool and limonene and its formation was strongly pH- and temperature-dependent. The formation of α-terpineol from linalool was faster than its formation from limonene (20). The primary product of the acid-catalyzed hydration of limonene

**Table 2.** Terpene Degradation during Thermal Treatment (90 °C for 30 min)

| | model solution | | black currant juice | |
| --- | --- | --- | --- | --- |
| terpene standard | loss (%) | conversion products[a,b] (%) | loss (%) | conversion products[a,c] (%) |
| α-terpinene | 92 ± 1 | | 86 ± 3 | α-terpineol (5 ± 1), linalool oxide (4 ± 0), 4-terpineol (4 ± 0), 1,4-cineole (1 ± 0), terpinolene (1 ± 0) |
| limonene | 69 ± 14 | α-terpineol (1 ± 0) | 75 ± 3 | α-terpineol (3 ± 1), p-cymene (1 ± 0) |
| linalool | 62 ± 2 | α-terpineol (31 ± 1), geraniol (18 ± 1), nerol (6 ± 0) | 78 ± 1 | α-terpineol (39 ± 1), geraniol (12 ± 0), nerol (4 ± 0) |
| 4-terpineol | 29 ± 5 | 1,4-cineole (3 ± 0), γ-terpinene (1 ± 0) | 28 ± 3 | α-terpinene (6 ± 2), α-terpineol (6 ± 1), 1,4-cineole (6 ± 0), linalool oxide (4 ± 0), γ-terpinene (3 ± 1), p-cymene (2 ± 1), terpinolene (1 ± 1) |
| α-terpineol | 21 ± 6 | 1,4-cineole (1 ± 0) | 21 ± 6 | terpinolene (2 ± 4), 1,4-cineole (1 ± 0) |
| menthol | 5 ± 2 | | 0.4 ± 2 | α-terpineol (3 ± 1), α-terpinene (2 ± 0), linalool oxide (2 ± 0), p-cymene (2 ± 0), terpinolene (1 ± 0), 1,4-cineole (1 ± 0) |

[a] Compounds constituting ≥1% of the initial terpene standard concentration. Values are given as averages ± standard deviations (n = 3). [b] Concentration of the conversion product in the heated model system/concentration of the terpene standard in the nonheated model system × 100. [c] (Concentration of the conversion product in the heated juice added terpene − concentration of conversion product in heated juice)/concentration of the terpene in the nonheated model system × 100.

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**Table 3.** Glycosidically Bound Monoterpenes in Black Currant Juice

| compound | enzymatic hydrolysis of glycosidic extract ($\mu$g/L)[b] | direct enzymatic hydrolysis of black currant juice | | |
|---|---|---|---|---|
| | | free[a] ($\mu$g/L)[c] | bound ($\mu$g/L)[d] | bound (%) |
| linalool oxide | 25 | 24 ± 2 | 5 ± 2 | 19 |
| neomenthol[e] | 11 | 1 ± 0 | 14 ± 2 | 95 |
| *p*-menthene-9-al[f] | 23 | 0 ± 0 | 9 ± 1 | 100 |
| menthol | 5 | 7 ± 0 | 11 ± 1 | 60 |
| 3-caren-10-al[g] | 3 | 0 ± 0 | 3 ± 0 | 100 |
| cumin aldehyde | 441 | 80 ± 8 | 313 ± 12 | 80 |
| geraniol | 30 | 11 ± 2 | 52 ± 9 | 83 |

[a] Refer to **Table 1** for other free terpene compounds identified in the juice. [b] Values are not directly comparable with those of direct enzymatic hydrolysis (*n* = 1). [c] Concentrations are given as averages ± standard deviations (*n* = 3). [d] Concentration of enzymatically hydrolyzed juice − concentration of untreated juice ± standard deviation (*n* = 3). [e] Quantified on the basis of menthol standard. [f] Quantified on the basis of $\beta$-cyclocitral standard. [g] Quantified on the basis of camphene standard.

was also in other studies reported to be $\alpha$-terpineol, but at elevated temperatures, $\beta$-terpineol and terpinolene (*21*) as well as 1,8-*p*-menthanediol (*10*) were formed in addition. 1,8-*p*-Menthanediol and other terpene diols are reported to form from $\alpha$-terpineol and 4-terpineol by acid-catalyzed hydration and further transformation to 1,8-cineole or 1,4-cineole (*10, 20, 22, 23*). According to a review by Clark and Chamblee (*10*), little work has been done on the reactions of $\alpha$-terpinene, since it is relatively stable due to slower rates of hydration for conjugated double bonds in aqueous acids. In a study of thermal treatment of $\alpha$-terpinene with aqueous acid (*21*), no evidence of hydration was observed, but it in part oxidized to *p*-cymene.

In the present study, a possible formation of terpene diol intermediates similar to the reported 1,8-*p*-menthanediol might explain the overall loss of products observed during heating of some of the terpenes. Terpene diols might not be extracted into the ether/pentane phase as suggested by ref *10*, and because of their low volatility, these components might not be recovered by headspace collection either. The use of more polar solvents might lead to improved recovery of this type of product (*24*).

**Release of Bound Terpenes in Black Currant Juice.** Heat treatment could potentially lead to a release of terpenes bound as glycosides thus increasing the amount of volatile terpenes. The amount and identity of glycosidically bound terpenes in black currant juice were examined by the enzymatic release of terpenes from glycoside isolates obtained by Amberlite XAD-2 fractionation of black currant juice and from direct enzymatic treatment of the juice.

Several terpenes in black currant juice were found to be bound to glycosides. Seven terpene alcohols and aldehydes were identified after enzymatic treatment of the glycosidic extract with $\beta$-glucosidase (**Table 3**). No volatile compounds were released from a control sample of the glycosidic extract. Hence, the other terpenes identified in black currant juice (see **Table 1**) are not present as glycosidically bound. Direct enzymatic treatment of black currant juice with $\beta$-glucosidase gave the same pattern of released volatile aglyconic compounds (**Table 3**). However, the concentration levels are not directly comparable due to the different methods used. *p*-Menthene-9-al and 3-caren-10-al were identified in the glycosidic fraction only. The glycosidically bound fraction was larger than the free fraction for all compounds except linalool oxide. Cumin aldehyde was the compound found in the highest concentration as glycosidically bound. Also, some glycosidically bound

alcohols were found in the black currant juice as described elsewhere (*15*). Some of the identified glycosidically bound terpenes have been reported as aglycones in other fruits (*25*).

**Relationship to Terpene Changes Observed during Heating and Concentration of Juice.** Several terpenes have previously been found to increase in concentration in black currant juice during heat application (*5−7, 11, 13*), but only linalool oxide and cumin aldehyde were found to be glycosidically bound in the present study. Evidence of aromatic glycosides in black currant berry has previously been indicated by Marriott (*14*) who found monoterpene alcohols and their corresponding alkenes in a ratio of 5:1. In that study, the predominant aglyconic terpene alcohols were 4-terpineol and $\alpha$-terpineol, and evidence of *p*-cymene-8-ol was found. In the present study, none of these compounds were found to be glycosidically bound. The terpene alcohols linalool, 4-terpineol, and $\alpha$-terpineol identified in black currant juice are glycosidically bound in many other fruits (*25*); hence, these and other bound compounds might have been released during earlier steps of the juice processing. However, none of the identified glycosidically bound terpenes have been reported to be of importance to the odor of black currant juice (*1, 8, 9*), and the release of free terpenes from a pool of glycosides is therefore not expected to be of major importance for the heat-induced changes of the odor of black currant juice.

The increase of linalool oxide observed by thermal treatment of black currant juice in the present study and refs *5, 7,* and *11* can in addition to a possible glycosidic release originate from heat-induced conversion of 4-terpineol or $\alpha$-terpinene. Likewise, the increase in concentration of $\alpha$-terpineol as also observed in refs *7* and *11* could be caused by acid-catalyzed conversion of various terpenes. On the other hand, the decrease of linalool (*7, 13*) may be explained by the rearrangement and cyclization into other terpineols. The increase of *p*-cymene, $\gamma$-terpinene, $\alpha$-terpinene, and terpinolene observed in refs *7, 11,* and *13,* too, arise from degradation of other terpenes. The observed changes in terpene alcohols can possibly affect the odor of the juice as these compounds are important aroma constituents of black currant juice (*1, 8, 9*).

In conclusion, the terpene changes observed during thermal treatment of an aqueous acidic system like black currant juice can be explained mainly by acid-catalyzed terpene reactions and to a minor degree glycosidic release. The reactions are part of a complex system where compounds are formed and degraded simultaneously.

## ABBREVIATIONS USED

GC-O, gas chromatography−olfactometry; GC-MS, gas chromatography−mass spectrometry; RI, retention index; min, minutes.

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