Effect of vacuum drying on blackcurrant’s antioxidant components
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ABSTRACT
Fresh consumption of black currant is not typical, it is mainly distributed as processed food (concentrate, jam, frozen, dried powder etc.) For these reasons effect of preservation technologies on changes of valuable components has primarily importance.
Aim of present study was to investigate changes of antioxidant compounds and antioxidant activity of black currant during vacuum drying at different temperature levels (40-50-60°C). As for control atmospheric drying at 60°C was also performed.
Black currant (Ribes nigrum L.) var. Titania grown in Hungary in 2010 was used for the experiments. Samples were dried at three temperature levels (40-50-60°C at 10 mbar) as long as they reached a wet content lesser than 10%. Vacuum drying was performed by an industrial Memmert V 200 vacuum dryer. As a control, atmospheric drying was performed at 60°C using an atmospheric dryer.
During drying process the dry material content, total polyphenol, total anthocyanin, ascorbic acid content and antioxidant activity were determined. Statistical evaluation was performed using Statistica 9. Software.
Antioxidant compounds and antioxidant activity of black currant were affected by drying temperature (40-50-60°C) and pressure (60°C 10 mbar and 1000 mbar). 50°C vacuum drying proved to be the optimal for preserve antioxidant compounds among the dehydration methods investigated.
Based on our results it was concluded that drying temperature affects drying duration, rate of wet decrease and amount of antioxidant compounds. Drying temperature at 50°C proved to be the optimum. Black currant products made by moderate drying technology are suited for production of functional food products (for example: mueslies, teamixes, sauces with fruit pieces, jams etc.) due to their high antioxidant content.

Keywords: black currant; vacuum drying; antioxidant compounds; ascorbic acid; anthocyanin

INTRODUCTION
Food components (vitamins, colouring agents, antioxidants, mineral components etc.) essential for healthy function of human organism, for prevention or medication of certain diseases are more and more known due to development of nutrition science. Valuable components of berries made them prevalent raw materials of processing industry. Due to their high vitamin, mineral, organic acid, pectin and colorant content currants especially black currant (Ribes nigrum L.) are prominent among berries in the field of scientific research.
Main black currant grower countries are Russia, Poland and Ukraine. Hungary produces the tenth greatest amount of black currant on the world by 6-7 thousand tons per year [1].
Black currant fruit contains high amount of biologically active components beneficial for human health. Its high ascorbic acid content (160-240mg 100g\(^{-1}\)) helps strengthen immune system, prevent flu, and overcome fatigue [2,3]. Ascorbic acid content of berries is influenced by many factors such as variety, growing and climate conditions. Black currant has to be harvested with “maturity at processing level” when its sugar-acid ratio, colorants and vitamin C content are harmonized [4]. Other important group of health protective components of black currant are flavonoids especially polyphenols and anthocyanins. It has high polyphenol content [5], which proved to have antioxidant effect. [6,7,8].
Among polyphenols contains primarily anthocyanin components which are popular natural food colorants due to their intensive colouring effect. Four main anthocyanins of black currant are cyanidin-3-glucoside, cyanidin-3-rutinoside, delphinidin-3-glucoside and delphinidin-3- rutinoside [9,10,11]. Presence of vitamin C together with anthocyanins proved to be beneficial as ascorbic acid has protective effect on anthocyanins. [12,13]. Black currant contains almost all of the most important vitamins (B\(_1\), B\(_2\), B\(_6\), biotin) and minerals too (potassium, magnesium, phosphorous and iron [2,3].
Valuable components are changed, usually decreased due to processing technologies. Heat treatment (e.g. pasteurization) resulted in decrease of amount of vitamin C and anthocyanins. Black currant contains many compounds with strong potential for use in natural health products and functional foods [11,14,15]. Fresh consumption of black currant is rare, so selection of an appropriate preservation technology is fundamental in retaining its valuable components. For these reasons effect of preservation technologies on changes of valuable components has primarily importance.
Aim of present study was to investigate changes of antioxidant compounds (vitamin C, total polyphenol, total anthocyanin) and antioxidant activity of black currant during vacuum drying at different temperature levels (40-50-60°C). As for control atmospheric drying at 60°C was also performed.

MATERIALS & METHODS

Materials and drying methods

Black currant (Ribes nigrum L.) var. Titania grown in Hungary in 2010 was used for the experiments. All of the reagents were analytical grade purchased from Sigma Aldrich Hungary Ltd.

Vacuum drying was performed by an industrial Memmert V 200 vacuum dryer (Memmert Gmbh, Schwabach, Germany) at three temperature levels: 40°C, 50°C, and 60°C at 10 mbars. As a control, atmospheric drying was performed at 60°C using an atmospheric dryer (LMIM, Esztergom, Hungary).

In each case 2 kg of black currant was dried in single layer on perforated trays. Samples were taken in every 2 hours until moisture content became lesser than 10 %. For determination of antioxidant activity and amount of phenolic compounds samples were prepared by grinding and extracting by distilled water and then passed a filter paper. That will be mentioned as black currant extract. All of the analytical measurements were performed using 3 replicates.

Examination methods

Dry material content was determined by drying until constant weight at 121°C using a MAC-50 moisture analyzer (Radwag Waagen GMBH, Hilden, Germany).

Total phenolic content (TPC) was determined using a Hitachi U-2900 spectrophotometer (Hitachi High-Technologies Europe GmbH, Krefeld, Germany) by the method of [16]. Samples were prepared with Folin-Ciocalteu’s reagent and sodium-sulphate solution, absorbance was read at 765 nm. TPC in the black currant extract was calculated from the gallic acid standard calibration curve and was expressed as mg TPC g⁻¹ dry material.

Total anthocyanin content (TAC) was determined after extraction by ethanol and hydrochloric acid based on the absorbance at 530 nm as described by [17]. TAC was expressed as mg TAC g⁻¹ dry material.

Ascorbic acid content (AA) was determined by reverse phase HPLC method on a RP-18 column, at 22°C with flow speed of 1 ml/min. A buffer pH 4.75 made of EDTA and phosphoric acid was used for isocratic elution. Absorbance was measured by UV detector at 254 nm. An extraction solution of 5% phosphoric acid and 0.01% sodium-EDTA and a cellulose membrane filter with 0.45 μm pore size were used for sample preparation prior to separation. All measurements were made in duplicate.

Concentration of samples were calculated from a calibration curve developed using 5, 10, 20, 40, and 80 mg/ml standard solutions. Ascorbic acid content was expressed in mg g⁻¹ dry material.

Antioxidant capacity (FRAP) was determined by Ferric Reducing Ability of Plasma (FRAP) assay according to the method of [18]. FRAP reagent was produced by mixing acetate buffer (pH 3.6), 2,4,6-tripryidyl-s-triazine (TPTZ) solution and FeCl₃·6H₂O solution. 5.0 min after addition the black currant extract to the FRAP reagent absorbance at 593 nm was read against the reagent. Results were expressed in ascorbic acid equivalent (mg ascorbic acid g⁻¹ dry material) based on the ascorbic acid standard calibration curve.

Statistical evaluation was performed using Statistica 9, (StatSoft Inc.,Tulsa, USA) Software. One-way ANOVA was used for testing for decide whether drying process caused significant changes in each antioxidant compound. Correlation analysis between antioxidant components and antioxidant capacity was performed using Microsoft Office Excel 2003 software.

RESULTS & DISCUSSION

Dry material content

Decrease loss rate and drying duration needed for reach target value (7-10%) were affected by drying mode (atmospheric, vacuum) and drying temperature (40-50-60°C). (Figure 1.) Initial wet content was 79.62 %. In case of atmospheric drying at 60°C took 16 hours to reach final value, while using vacuum drying at same temperature level it was only 8 hours. When vacuum drying was performed decreasing drying temperature (60-50-40°C) resulted in longer drying time (8-10-12 hours).
During vacuum drying at all temperature levels rapid decrease of wet content was observed during the first two hours when initial wet content decreased until 50-60%. That was followed by a slower drying period until 4 hours and beyond that a rapid decrease was occurred again. On the contrary in case of 60°C atmospheric drying wet content remained almost constant during the first 4 hours (70.78%) and then a more rapid, constant rate wet decrease occurred.

**Total polyphenol**
Total polyphenol content of black currant expressed in mg g⁻¹ dry material decreased compared to initial value (20.26 mg g⁻¹ dry material) during each drying method.(Figure 2.a)
During vacuum drying at 40°C and 60°C a rapid decrease was observed at initial stage of drying process. At 40°C polyphenol content dropped to half (10.43 mg g⁻¹ dry material), then did not show significant change. During vacuum drying at 50°C decrease of polyphenol content was continuous. During atmospheric drying at 60°C polyphenol content showed significant decrease during the first two hours then remained relatively constant. Polyphenol content of the samples with final wet content of 7-10% was higher at higher temperature levels (5.39 mg g⁻¹ dry material, 11.79 mg g⁻¹ dry material, 15.58-17.79 mg g⁻¹ dry material at 40, 50, 60°C, respectively).

**Total anthocyanin**
Total anthocyanin content of black currant (Figure 2.b) did not change significantly during vacuum drying at 50°C and 60°C. During vacuum drying at 40°C total anthocyanin content decreased to half (1.64 mg g⁻¹ dry material), compared to initial value (3.62 mg g⁻¹ dry material) and it is also decreased (to 1.95 mg g⁻¹ dry material) during atmospheric drying.

**Ascorbic acid**
Ascorbic acid content of fresh black currant was 7.6 mg g⁻¹ dry material which is consonant with earlier published values (8.4 mg g⁻¹ dry material) [3]. During all of drying methods tested ascorbic acid content dropped to half during the first 2 hours then remained relatively constant until the end of the drying process. (Figure 2.c) Highest final value (3.5 mg g⁻¹ dry material) in case of vacuum drying at 40°C was observed, while lowest values after drying at 50°C and 60°C in vacuum were measured (2.6 mg g⁻¹ dry material and 2.7 mg g⁻¹ dry material, respectively).
Antioxidant activity

Antioxidant activity did not show significant changes when black currant was vacuum dried at 50°C. (Figure 2.d) In case of other drying methods initial FRAP value (0.13 mg g⁻¹ dry material) decreased most intensively during the first 2 hours then gradually until the end of drying period. Lowest FRAP values of end product were measured in case of 40°C and 60°C vacuum dried samples (0.04 mg g⁻¹ dry material and 0.08 mg g⁻¹ dry material, respectively), while at 50°C vacuum and atmospheric drying there was no significant difference between initial and final FRAP values.

**Figure 2.** Changing of antioxidant capacity and compounds during drying technology

**Table 1.** Correlation coefficients between antioxidant capacity and antioxidant compounds of black currant

<table>
<thead>
<tr>
<th></th>
<th>TAC</th>
<th>TPC</th>
<th>AA</th>
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<tbody>
<tr>
<td>FRAP</td>
<td>0.51</td>
<td>0.81</td>
<td>0.22</td>
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<tr>
<td>TAC</td>
<td>0.63</td>
<td></td>
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<td>TPC</td>
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</table>

FRAP: antioxidant capacity in ascorbic acid equivalent (mg g⁻¹ dry material)
TAC: total anthocyanin content (mg g⁻¹ dry material), TPC: total polyphenol content (mg g⁻¹ dry material)
AA: ascorbic acid content (mg g⁻¹ dry material)

Good correlation (R² >0.8) was observed between FRAP and total polyphenol content indicating that polyphenols are the main components contribute to antioxidant effect of black currant. Surprisingly, poor correlation (R² = 0.2) between FRAP and AA was observed, which can be explained by different decomposition kinetics of AA compared to flavonoids.
Table 2. Effect of drying modes on antioxidant and phenolic compounds of black currant

<table>
<thead>
<tr>
<th></th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>60°C atm</th>
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<tbody>
<tr>
<td>FRAP</td>
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</tr>
<tr>
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<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>AA</td>
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</tbody>
</table>

Results of one-way ANOVA test, p values at 95% confidence

FRAP: antioxidant capacity in ascorbic acid equivalent (mg g\(^{-1}\) dry material)
TAC: total anthocyanin content (mg g\(^{-1}\) dry material)
TPC: total polyphenol content (mg g\(^{-1}\) dry material)
AA: ascorbic acid content (mg g\(^{-1}\) dry material)

Effect of duration on each phenolic compound and FRAP was evaluated by one-way analysis of variance (ANOVA). (Table 2.) Effect of drying pressure and temperature had both significant effect on antioxidant activity and each phenolic compound as indicated by the p values of statistical evaluation.

CONCLUSION
Based on our results it was concluded that drying temperature affects drying duration, rate of wet decrease and amount of antioxidant compounds.
Comparing the final products total polyphenol content of products dried at 60°C proved to be the highest. In case of anthocyanins products vacuum dried at 50°C and 60°C showed the highest value while these samples had the lowest ascorbic acid content. Vacuum drying at 40°C was merely appropriate to preserve ascorbic acid. Evaluating antioxidant capacity products vacuum dried at 50°C and atmospheric dried at 60°C proved to have the highest quality. These two drying methods seem to be optimal for preserve antioxidant compounds. However, advantage of vacuum technology is the shorter drying period needed.
Black currant products made by moderate drying technology are suited for production of functional food products (for example: mueslies, teamixes, sauces with fruit pieces, jams etc.) due to their high antioxidant content.

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REFERENCES


