Aroma Composition and Polyphenol Content of Ciders Available in Latvian Market

Rita Riekstina-Dolge, Zanda Kruma, Daina Karklina

Abstract—Aroma forming volatiles are important components of fermented beverages. The aim of current research is to evaluate the volatile compounds and phenolic contents of commercial ciders. Volatile aroma compounds and TPC of seven commercial ciders were determined. Extraction of aroma compounds was performed using solid phase microextraction (DVB/Car/PDMS fibre). Analysis of volatile aroma compounds was made using a Perkin Elmer Clarus 500 GC/MS. Total phenol content (TPC) was determined according to the Folin-Ciocalteau spectrophotometric method and results were expressed as gallic acid equivalents. The highest volatile compounds were in apple ciders with pear flavor. The highest TPC and lower content of volatile compounds were detected in French ciders.

Keywords—cider, TPC, volatile compounds

I. INTRODUCTION

CIDER is fermented drink obtained from apple juice. Apple production is one of the largest fruit-growing sectors of Latvia. Most apples are sold fresh, but part of the apple, which does not meet the requirements of the market, has to be processed and fermented beverage production from apples could be good perspective.

Usually cider is produced using two different methods:
1) sparkling cider made from concentrated apple juice and/or fresh apple must, the addition of sugars and carbon dioxide being permitted, as well as the use of different stabilization processes;
2) “natural cider”, is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider”, is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider”, is made according to traditional methods, which imply, among other practices (such as the prohibition of "natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of "natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of "natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of "natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of "natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider”, is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider”, is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider”, is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider”, is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider”, is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural cider", is made according to traditional methods, which imply, among other practices (such as the prohibition of “natural

Different technology of the production affects the final quality of the drink. The quality of fermented drinks like cider is characterized with presence of aroma compounds in product [2], that are influenced by several factors, namely apple variety, yeast strains, fermentation conditions, the production process and fining treatments [3, 4, 5]. Cider flavour is composed by a wide range of compounds with different aromatic properties.

Moreover, the main cider aroma holds a close relationship with the type and concentration of aromatic compounds derived from apples (varietal flavour), other compounds are produced by yeasts and bacteria during alcoholic and malolactic fermentation (fermentative flavour) and compounds that appear during the ageing process (post-fermentative flavour) [6, 7] and it consists mainly of esters, higher alcohols, fatty acids, aldehydes, ketones, terpenes, lactones

II. MATERIALS AND METHODS

A. Ciders

Seven commercially available ciders originating from different countries and from five companies were used. Four apple ciders and three apple ciders with pear aroma were used. A list of all ciders analyzed in this study is presented in Table 1.

B. Determination of total polyphenolic contents by the Folin-Ciocalteau method

The total polyphenolic concentration was determined spectrophotometrically according to the Folin-Ciocalteau colometric method [19]. Cider was diluted with ethanol/acetic acid solution (1:20 v/v). Ethanol/acetic acid solution was prepared using acetic acid water solution (2.5%) and ethanol (98% vol.) in ratio 10:90(v/v). 0.5 ml of aliquot was mixed...
with 0.25 ml Folin-Ciocalteu reagent, after 3 minutes 1 ml 20% Na₂CO₃ and 3.25 ml distilled water were added. Samples were heated for 10 min. at 70 °C and kept for 30 minutes at 18 ±2 °C temperature. The absorbance was measured at 765 nm using a spectrophotometer JENWAY 6300. Total phenols were expressed as gallic acid equivalents (mg L⁻¹). Each determination was performed in triplicate and results are expressed as mean ± SD.

C. Determination of volatile aroma compounds

Volatiles from ciders were extracted using solid phase microextraction (SPME). 5 g of sample were weighed in a 20 mL headspace vial and capped with a septum. A divinylbenzene/carboxen/polydimethylsiloxane (DVB/Car/PDMS) fiber (Supelco Inc., Bellefonte, PA, USA) was used for headspace SPME sampling. SPME parameters were: incubation time 30 min, extraction temperature 22±2 °C, extraction duration 30 min, desorption 15 min, 250 °C. For the analysis of the SPME extracts, a Perkin Elmer Clarus 500 GC/MS and an Elite-Wax ETR (60 m × 0.25 mm i.d.; DF 0.25 μm) was used. Working conditions were as follows: injector 250 °C; transfer line to MSD 260 °C; oven temperature start 50 °C, hold 2 min, programmed from 50 to 100 °C at 5 °C 1 min⁻¹ hold 5 min, and from 100 to 210 °C at 5 °C min⁻¹ hold 15 min; carrier gas (He) 1 mL min⁻¹; split ratio 2:1; ionization EI+; acquisition parameters in full scan mode: scanned m/z 40-300. Compounds were identified by comparison of their mass spectra with mass spectral libraries (Nist98), and by calculation of linear retention indexes and comparison with literature data. All analyses were performed in triplicate. As a quantitative measure, the share in the total GC peak area for each compound is given.

D. Statistical analysis

Each determination was performed in triplicate and results are expressed as mean ± SD. Analysis of variance was performed by ANOVA procedure and p<0.05 was considered as statistically significant.

III. RESULTS AND DISCUSSION

A. Volatiles compounds of ciders

Aroma is very important characteristic of ciders and the highest total peak area of identified volatile compounds in samples 5, 6 and 3 were identified (Fig.1.).

In typical French ciders (samples 1 and 2) significantly lower amount of volatiles were detected. Possibly it could be explained that in some commercial ciders additionally flavouring substances were added, that are very volatile and easy absorb to the SPME fiber. Esters, alcohols, acids and terpenes were the most abundant classes in cider (Fig.2.).

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name of cider</th>
<th>Producer</th>
<th>Country</th>
<th>Alcohol vol</th>
<th>Charactization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cidre Bouche Brut De Normandie</td>
<td>SAS Calvados Christian Drouin</td>
<td>France</td>
<td>4.5</td>
<td>Brut</td>
</tr>
<tr>
<td>2</td>
<td>Cidre Bouche Doux Lieblich</td>
<td>Jean de Loret</td>
<td>France</td>
<td>2</td>
<td>Sweet</td>
</tr>
<tr>
<td>3</td>
<td>Lucky Dog Apple</td>
<td>AS Latvijas balzams</td>
<td>Latvia</td>
<td>5</td>
<td>Sweet</td>
</tr>
<tr>
<td>4</td>
<td>Upcider apple cider natural</td>
<td>Harvall Ltd</td>
<td>Finland</td>
<td>4.7</td>
<td>Sweet</td>
</tr>
<tr>
<td>5</td>
<td>Lucky Dog Pear</td>
<td>AS Latvijas balzams</td>
<td>Latvia</td>
<td>5</td>
<td>Sweet</td>
</tr>
<tr>
<td>6</td>
<td>Upcider pear cider natural</td>
<td>Harvall Ltd</td>
<td>Finland</td>
<td>4.7</td>
<td>Sweet</td>
</tr>
<tr>
<td>7</td>
<td>Sun cider pear</td>
<td>ISK Kalnapiļa Tauro grupa</td>
<td>EU</td>
<td>4.5</td>
<td>Sweet</td>
</tr>
</tbody>
</table>
Mainly samples were dominated by ester compounds, except sample 1 that dominate by alcohol compounds. Terpenes were identified only in samples 3, 5 and 6. Totally twenty volatile compounds were indentified in analysed commercial cider samples (Table 2 and Table 3). The major volatile compounds quantified in analysed samples were acetic acid hexyl ester, 1-butanol, 3-methyl acetate and limonene. Peng, Yue, and Yuan [20] reported that key aroma components in cider are ethyl acetate, acetic acid isobutylester, isopentylalcohol acetate, ethyl caprylate, ethyl 4-hydroxubutanolate, isopentylalcohol, 3,4,5-trimethyl-4-pentanol, nonyl alcohol, 3-methylthio-1-propanol.

The compound 1-butanol is a primary volatile compound of apples. Its concentration does not depend on processing technology and is cultivar and maturity dependent [21], [22]. The biosynthesis of higher alcohols is considered to be linked to amino acid metabolism. Higher alcohols are formed as by-products of anabolic and catabolic metabolism [23]. 3-methyl-butanol is fusel alcohol is derived from isoleucine and leucine [24] and fusel alcohols 3-methyl-1-butanol and is important flavor compound in yeast-derived beverages [25]. Esters give fruitlike flavors and aromas to beverages. The alcohol 3-methylbutanol (12,148.51–36,238.69 μg/L) is considered the most quantitatively important alcohol in Chinese ciders, while

<table>
<thead>
<tr>
<th>Compounds</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Terpenes</strong></td>
<td>n.d.</td>
<td>n.d.</td>
<td>18.79 ± 0.67</td>
<td>0 ± 0</td>
<td>15.08 ± 0.54</td>
<td>n.d.</td>
<td>8.22 ± 0.29</td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>1-butanol, 3-methyl acetate</td>
<td>21.85 ± 0.78</td>
<td>5.61 ± 0.2</td>
<td>5.3 ± 0.19</td>
<td>3.82 ± 0.14</td>
<td>5.13 ± 0.18</td>
<td>4.3 ± 0.15</td>
<td>8.65 ± 0.31</td>
</tr>
<tr>
<td>1-hexanol</td>
<td>5.72 ± 0.2</td>
<td>7.61 ± 0.27</td>
<td>n.d.</td>
<td>11.07 ± 0.4</td>
<td>n.d.</td>
<td>3.35 ± 0.12</td>
<td>1.23 ± 0.04</td>
</tr>
<tr>
<td>8-heptadecanol</td>
<td>15.49 ± 0.55</td>
<td>7.55 ± 0.27</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Phenylethyl alcohol</td>
<td>10.04 ± 0.36</td>
<td>2.05 ± 0.07</td>
<td>1.13 ± 0.04</td>
<td>1.65 ± 0.06</td>
<td>1.32 ± 0.05</td>
<td>1.37 ± 0.05</td>
<td>3.96 ± 0.14</td>
</tr>
<tr>
<td><strong>Acids</strong></td>
<td></td>
<td></td>
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<tr>
<td>Octanoic acid</td>
<td>2.32 ± 0.08</td>
<td>3.9 ± 0.14</td>
<td>1.38 ± 0.05</td>
<td>2.04 ± 0.07</td>
<td>1.26 ± 0.05</td>
<td>1.2 ± 0.04</td>
<td>2.65 ± 0.09</td>
</tr>
<tr>
<td>Sorbic acid</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.08 ± 0.04</td>
<td>7.09 ± 0.25</td>
<td>1.19 ± 0.04</td>
<td>5.07 ± 0.18</td>
<td>4.95 ± 0.18</td>
</tr>
<tr>
<td>Decanoic acid</td>
<td>5.46 ± 0.19</td>
<td>23.04 ± 0.82</td>
<td>1.95 ± 0.07</td>
<td>1.3 ± 0.05</td>
<td>1.09 ± 0.04</td>
<td>0.73 ± 0.03</td>
<td>2.92 ± 0.1</td>
</tr>
</tbody>
</table>

n.d. – not detected
1-hexanol (5.39–472.12 μg/L) is considered a characteristic volatile compound of fruits other than apples and is produced during the enzymatic oxidation process of linoic acid [26]. Limonene were identified in samples 3 and 5 and its aroma in literature is described as lemon and mint [27].

B. Total phenols of ciders

The content of total phenols in ciders varied between 6.54 mg L⁻¹ to 79.13 mg L⁻¹ (Fig. 1.). These results are in accordance to Berrueta, Gallo and Vicente [28] who reported varieties, yeast strains, added addition) and by preparation could be explained by the different raw materials (apple – new products and technologies (Nat Res)”

Corresponding apple juice. Higher content of TPC were in commercial French ciders and ranged between 53.29 mg L⁻¹ to 79.13 mg L⁻¹. Variation of cider TPC could be explained by the different raw materials (apple varieties, yeast strains, added addition) and by preparation technologies and conditions.

IV. CONCLUSION

Cider quality is related with taste and aroma, and it is influenced by the volatile compounds and phenols. Amount of volatile and phenols compounds are dependent on production technology. The highest TPC and lower volatile compounds were detected in French ciders.

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REFERENCES


Fig. 3 Total phenol content in cider samples

Our previous study showed the content of total phenols in cider from Latvian apples varied between 27.78 mg L⁻¹ to 92.32 mg L⁻¹ and it was 1.1 to 2.3 times lower than in corresponding apple juice. Higher content of TPC were in ciders from cider apples between 69.90 mg L⁻¹ to 92.32 mg L⁻¹ [30]. Results of current research showed the highest content of total phenols was in commercial French ciders and ranged between 53.29 mg L⁻¹ to 79.13 mg L⁻¹. Variation of cider TPC could be explained by the different raw materials (apple varieties, yeast strains, added addition) and by preparation technologies and conditions.


