Original paper

Influence of cider-making technology on low-boiling-point volatile compounds

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Einfluß der Methode der Apfelweinherstellung auf niedrigsiedende, flüchtige Verbindungen

Zusammenfassung. Die hauptsächlich niedrigsiedenden Aromakomponenten aus zwölf Apfelweinen, die mit verschiedenen technischen Methoden (verschiedene Preßgeschwindigkeiten und Klärungssysteme) erhalten wurden, wurden durch Gaschromatographie analysiert. Die chromatographischen Daten zeigten, daß der Anteil an Ethylacetat, Methanol, Propanol, *Isobutanol*, 2-Methylbutanol und 3-Methylbutanol von der Preßgeschwindigkeit abhängt, ebenso wie der Anteil an Methanol, *Isobutanol*, 2-Methylbutanol und 3-Methylbutanol vom Klärungssystem. Ein Einfluß beider Faktoren wurde nur für *Isobutanol* und 3-Methylbutanol beobachtet, während der Butanolanteil von der angewandten Technologie unabhängig ist.

Abstract. Major low-boiling-point aroma components present in twelve ciders obtained by different technological methods involving different pressing speeds and clarification systems were evaluated by gas chromatography. Variance analysis of chromatographic data show that ethyl acetate, methanol, propanol, isobutanol, 2-methylbutanol and 3-methylbutanol contents depend on the pressing speed. In the same way, the methanol, isobutanol, 2-methylbutanol and 3-methylbutanol contents depend on the clarification system employed. The interactive effect of both factors was observed only for *isobutanol* and 3-methylbutanol whereas the butanol content was independent of the technology used.

Introduction

Cider is a very popular beverage in West European regions where, because of their peculiar climatic characteristics, grape-vine cultivation is not recommendable. In

these countries, the traditional methods of manufacturing cider are simple: hammer mills are used to crush the fruit on batch mechanical presses to express the juice. Fermentations are allowed to take place naturally using wild microflora of the fruit or, more likely, that residing on the press and fermentation casks. These traditional methods as well as being very expensive can cause uncontrolled fermentations that determine strong variations in the cider quality and may even spoil it. However, if the process goes ahead correctly a cider with good character and a great wealth of aromas is obtained, particularly if suitable cider-apple cultivars are used.

The introduction of new methods required for increased productivity and reducing the costs of production can seriously affect the quality of the cider obtained because it is well known that the taste and flavour quality of cider are, on the one hand, a matter of its composition conditioned by the apple varietal characteristics [1] and by the industrial process [2, 3] employed for juice extraction and fermentation, and on the other, a matter of human perception and hedonics. The taste of cider depends more on the apple composition than on the odour, whereas cider odour depends more on technological parameters, in addition to types of yeasts [4] and growth factors, than on apple variety because volatile compounds of cider are formed during fermentation from precursors in the apples [5]. Since volatiles dependent on raw materials are found only in minor amounts, they provide the difference between cider and other fermented beverages and even between ciders made from different apple cultivars, these differences being very pronounced if table-apples are used instead of cider-apples. The aim of this paper was to evaluate the effect of the main cider aroma components of new technological methods employed in its fabrication.

Material and methods

Cider. The cider used during this work was prepared from the juice of a mixture of cider apples with different sensory properties – Col-laos (mildly sharp) 30%, Raxao (sharp) 40%, Durón Arroes (sweet)

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Fig. 1. Experimental design of the pilot plant

10%, Coloradona (bittersweet) 15%, and Meana (bittersharp) 5% – endowing the resulting juice with an overall acidic nature. Such a mixture was processed in a pilot plant using two technological procedures: traditional and alternative systems (Fig. 1). Traditional cider-making technology employs unwashed apples and involves milling with a hammer mill and slow pressing with a batch mechanical press (4 day pressing time). The alternative system employs washed apples and involves milling with a grating mill and a fast press cycle with a rack and frame press (30-min pressing time plus 15 h of maceration). – From the must obtained from both systems we investigated the effects of spontaneous and enzymatic clarification. The enzymatic clarification method developed in the Station de Recherches Cidricoles et de Biotechnologie Végétale (Rennes, France), was carried out by adding 1,200 units/Hl of pectin methyl esterase (rapidase CPE-Gist-Brocades) and 10 mmol of Ca^{2+} as dihydrate calcium chloride to the apple juice. Fermentation was allowed to take place by natural microflora, mainly *Saccharomyces cerevisiae* and *Kloeckera apiculata*.

Gas chromatography (GC): For analytical GC, the following instrument and column was used: a Perkin-Elmer 8500 gas chromatograph fitted with flame ionization detector and 5 m $\times$ 0.85 mm stainless steel column packed with 4% (w/w) carbowax 300+ bis 2-ethyl-hexylsebacate (92:8 w/w) on desilanzed volaspher A-2 (120:140 mesh) [6] using a flow of 27 ml/min of He and isothermal elution at 70° C. The injection port and detector were maintained at 170° C.

Analysis of volatiles. Qualitative and quantitative analysis of major low-boiling-point components present in cider were carried out directly on cider by injection of 1 μ l cider previously filtered through a 0.22- μ m Millex membrane. Compounds were identified by comparing the retention time of the GC peak with authentic compounds. Quantification of volatile compounds was carried out by the internal standard method on the basis of the peak areas.

Results and discussion

We monitored the changes in each of the major volatile compounds (ethyl acetate, methanol, propanol, isobutanol, butanol, 2-methyl butanol and 3-methyl butanol; ethyl formate, ethyl propionate and acetaldehyde was not

detected in the cider studied) by GC in twelve ciders obtained according to the methods shown in Fig. 1. GC examination of low-boiling-point components of the aroma gave the separation illustrated in Fig. 2. Quantification was carried out for each cider in triplicate before and after adding known amounts of different volatile compounds. Three concentration levels of spiked volatiles were analysed. The average recoveries obtained ranged between 92% and 103%, demonstrating the accuracy of the method used to analyse these compounds. The coefficients of variation for the three replicates of each sample

Fig. 2. Chromatogram of a synthetic solution of low-boiling-point components: (1) acetaldehyde; (2) ethyl formate; (3) ethyl acetate; (4) ethyl propionate; (5) methanol; (6) ethanol; (7) propanol; (8) isobutanol; (9) butanol; (10) 4-methyl 2-pentanol (internal standard); (11) 2-methyl butanol; (12) 3-methyl butanol. The chromatographic conditions are described in the text

Table 1. Low-boiling-point volatile contents (mg/L) in ciders obtained from different technologies

Barrel	Pressing	Clarification	Acet	Met	Prop	Isobut	But	Amyl	Isoamyl
1	Traditional	Spontaneous	116.1	116.3	7.1	9.3	7.3	15.3	41.4
2	Traditional	Spontaneous	122.9	127.7	8.7	9.6	7.9	14.1	44.6
3	Traditional	Spontaneous	98.6	106.2	5.6	7.7	6.1	10.0	31.0
4	Traditional	Enzymatic	84.9	74.9	4.8	5.3	5.5	8.1	16.4
5	Traditional	Enzymatic	161.4	106.9	7.9	8.9	7.3	13.4	28.1
6	Traditional	Enzymatic	111.0	74.4	5.3	6.3	5.2	9.7	23.2
7	Fast press	Spontaneous	19.1	83.5	5.6	27.1	6.4	20.5	140.5
8	Fast press	Spontaneous	14.6	88.4	5.2	23.6	6.7	22.4	128.5
9	Fast press	Spontaneous	21.6	91.3	4.1	21.8	6.8	25.1	127.4
10	Fast press	Enzymatic	42.1	77.3	4.0	10.3	6.3	16.4	64.3
11	Fast press	Enzymatic	33.8	72.0	3.3	13.1	6.3	15.4	70.5
12	Fast press	Enzymatic	49.5	86.4	5.7	13.2	7.4	17.9	80.8

Acet, ethyl acetate; Met, methanol;
Prop, propanol; Isobut, isobutanol;
But, butanol; Amyl, amyl alcohol;
Isoamyl, isoamyl alcohol

were usually less than 4%. The results obtained for volatile contents in the twelve ciders studied at 3 months after bottling are summarized in Table 1. Analysis of variance [7] was performed on data obtained with speed of pressing and the clarification system as the main factors.

There was a significant effect of speed of pressing for ethyl acetate ($P=0.0001$), methanol ($P=0.03$), propanol ($P=0.04$), isobutanol ($P=0.0001$), 2-methyl butanol ($P=0.0004$) and 3-methyl butanol ($P=0.0001$) contents; and the clarification system for methanol ($P=0.02$), isobutanol ($P=0.0002$), 2-methyl butanol ($P=0.01$) and 3-methyl butanol ($P=0.0001$).

The higher contents of ethyl acetate and methanol present in cider made using traditional pressing system should be explained as a consequence of the longer pressing and maceration periods under aerobic conditions. In this situation, the acetification process and the greater incorporation in the apple juice of high methoxylate pectins from the middle lamella of the apple cells are favoured.

The higher alcohols, isobutanol, and 2- and 3-methyl butanol are synthesised from oxo-acids originating during amino acid and sugar metabolism. It is logical to think that a major conversion of sugars during alcoholic fermentation provides a superior content of these compounds and vice versa. In fact, we have verified that employing a fast press cycle and a spontaneous clarification system (barrels 7, 8, and 9), the sugar conversion was practically complete as the consequence of great microbiological activity and, as can be seen in Table 1, the higher alcohol contents are greater. In contrast, the ciders made using a traditional pressing cycle with enzymatic clarification (barrels 4, 5, and 6) gave rise to ciders with more sugars and lower higher alcohol contents.

Only in the case of isobutanol ($P=0.002$) and 3-methyl butanol ($P=0.0008$) were interactive effects between both factors (pressing and clarification) observed.

A major concentration of both higher alcohols was obtained with traditional press technology and spontaneous clarification, probably because of the much higher level of solids. On the other hand, the butanol contents in the cider studied were independent of the technology employed because this alcohol is included in the primary aroma of the fruit. In other words, the butanol content is a varietal characteristic.

We conclude that the analytical method presented has good reproducibility, accuracy and sensitivity. The cider-making technology significantly influences the major volatile compounds content. In particular, a greater higher alcohols level is obtained using the alternative system and spontaneous clarification. Ciders prepared by traditional technology were higher in ethyl acetate, more microbiological disorders, and methanol, which determined the sensorial and toxicological properties of the products.

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