Role of Strecker aldehydes on beer flavour stability

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1. ABSTRACT

In this work, attempts were made in order to measure the importance of "Strecker aldehydes" on flavour stability of beer correlating chemical and sensory data. It has been observed that methional and phenylacetaldehyde accumulates during storage and that these molecules were well correlated with "Aroma Quality". A "fresh beer" was spiked with methional, phenylacetaldehyde and also with *trans*-2-nonenal, singly and in combination, the "Similarity Value" was then determined, between samples and an "aged beer". The highest value was 72 % when the three compounds were added simultaneously and the combination of the two Strecker aldehydes increases by 54 % the degree of similarity.

2. INTRODUCTION

A large number of studies devoted to flavor stability of beer are available in the literature [1-6] Several mechanisms are recognized as contributors to the undesirable "stale character" typical of flavor deterioration [6]. Two are widely accepted as the most relevant: Lipid Oxidation, and Maillard reaction [3]. The first pathway is responsible for the presence of *trans*-2-nonenal, one of the most undesirable aromas in beer described as "cardboard" with an extremely low odor threshold of 0.035 μg/L [1].
The Strecker degradation is a minor pathway of the second mechanism and is responsible for the formation of many volatile organic compounds, the "Strecker aldehydes". In beer, the 3-methylbutanal, 2-methylbutanal and 2-methylpropanal, are considered to be responsible for the "malty" character [2,3]. However, methional was related to the flavour of "aged" beer [4]. Yeast activity plays an important role on the levels of free carbonyl compounds, in fact they are reduced to alcohols during fermentation, [7] and on other hand the SO2 formed during the process can bind these

molecules, thus contributing to a reduction in the perceived "aged character". Nevertheless the possible release of aldehydes from the sulphite adducts during bottle storage may also contribute to the accumulation of these molecules in beer.
The aim of this work was to select suitable chemical substances, responsible for aroma deterioration, to be monitored during beer production, in order to provide information concerning the key steps along the process, which most affect the flavour stability and thus the lager type beer shelf-life.

3. MATERIAL AND METHODS

Lager Beers - Group 1: In order to promote aroma degradation of beer, a "forced aging" experiment was implemented. 34 lager beer samples were divided into two groups: *(i)* one was stored at a temperature of 37 ºC, for 7 days; *(ii)* The other, was kept at 4 ºC for 180 days. **Group 2**: Eight beer samples were analyzed after the six-months corresponding to the shelf-life period of the product. Two were kept at + 4ºC at the brewery and the other six, kept under commercial storage conditions, had been returned to the point of production after the shelf-life period had expired.
Sensory studies: Sensorial panel was composed of 17 trained assessors, Brewery workers, university students and laboratory personnel. They were trained weekly for two months, using tulip glasses containing 30 mL of beer in a room at T= 20 ºC.
Descriptor selection and Similarity tests: The AFNOR NFV-09-021 [8] procedure was used to select the most important descriptors related to the typical aroma of aged beer. Methional, phenylacetaldehyde, and *trans*-2-nonenal, were added singly and in combination to a fresh beer in the following concentrations 3 μg/L; 4 μg/L and 0.25 μg/L. The "Similarity Value" (SV), of each sample with the aged beer was determined by a comparison test using a discontinuous scale from 0 to 10. The **"**Quality Scoring" was evaluated using a continuous "quality scale" from +1 (no defect) to –3 (major defect), as normally used at the Brewery.
Chemical Studies *Gas Chromatography*: GC-O analysis was employed using dichloromethane extracts in order to identify the substances responsible for the aromatic notes associated with descriptors of the aged beer. Methional, phenylacetaldehyde quantify by GC-MSMS as described [7].

4. RESULTS

Four descriptors "malty", "honey like", "cooked potato" and "metallic", were selected using AFNOR NFV-09-021 [8] procedure as the most relevant on the characterization of the typical aroma of "aged" beer. By GC-Olfactometry analysis it was possible to highlight six odor-active zones showing aromas close to the descriptors selected they were described as "aged beer like", "bread", "cooked potato" for a retention index (RI = 1463), "honey" (RI = 1690), "melted sugar" (RI = 2038) and "aged Port" (RI = 2189). It was possible to identify, using GC/MS and chemical standards, the corresponding molecules for the retention indices: methional (RI=1463), phenylacetaldehyde (RI=1690), *β*-damascenone (RI= 1838) and Sotolon (RI=2189).

Strecker aldehydes levels in samples. Aroma deterioration was promoted by "forced aging" experiment group 1 samples, in order to correlate the quantities of methional and phenylacetaldehyde with the "flavour quality". The quantities of aldehydes founded are significantly higher in samples stored at the higher temperature and it was observed a high correlation value (r = 0.7567) between them indicating a concomitant formation during Strecker degradation. These results are in agreement with previous works [6]. Due to the extreme conditions applied to "forced aged" samples, which may promote reactions different from those produced during regular aging, methional and phenylacetaldehyde were also analyzed in beers submitted to normal aging during six-month the shelf-life period both for samples exposed to commercial storage temperature, and on a control group kept at 4 ºC ("group 2" samples). The first group presented higher levels of both aldehydes, indicating that these molecules are formed in "normal aging" conditions, with an average value of 0.5 μg/L (SD= 0.2) and 2.4 μg/L (SD= 0.5) for methional and phenylacetaldehyde respectively, while the levels observed in samples kept at 4 ºC were, for the same molecules, 0.3 μg/L and 1.4 μg/L.
Strecker aldehydes formation is greatly affected by (*i*) temperature and *(ii)* levels of dissolved oxygen, mainly when close to saturation [6]. Since the values of oxygen in these samples were inferior to 0.2 mg/L, the observed variations within the commercial storage samples most likely related to temperature. All these results point toward a progressive accumulation of methional and phenylacetaldehyde during storage. The "flavour quality" the samples were evaluated using "group 1" beers. Average scores for each beer were calculated and it was observed a good correlation with methional and phenylacetaldehyde concentrations with r = 0.6103 and r = 0.6009 respectively.
Sensorial impact validation. Methional and phenylacetaldehyde were added separately or in combination to a "fresh" beer, in the concentrations close to those found in the "aged" beers respectively 3.0 μg/L and 4.0 μg/L. Considering the high impact of *trans*-2-nonenal on the beer aroma degradation, this compound was also included in the test, at 0.25 μg/L level. A simple comparison pair test was carried out in order to rate the degree of similarity between each of the supplemented samples and the "aged beer". Tukey test was used to determine statistical different for each pair. Mean Rating Scores (MRS) were arranged according to magnitude, and the LSD at 95% was determined [9]. The average of the similarity values and the standard error (SE) calculated for each pair, as well as the Tukey test, is given in figure 1.

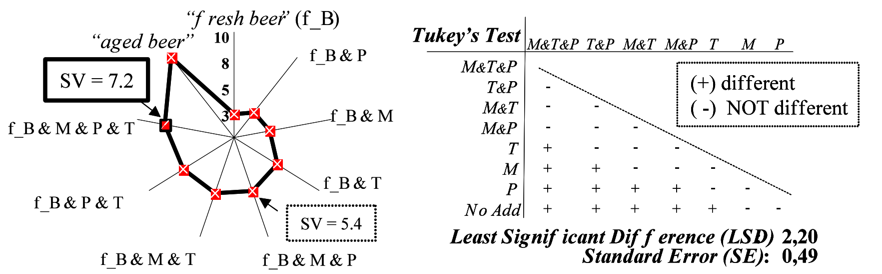

Figure 1: Similarity Values and Tukey results, for each pair: supplemeted sample-"aged beer"

The ANOVA calculations for the data showed differences between samples (*p-value* = 8.19 e-9) at 95% level and no significant differences between assessors. All pair additions contributed in a high degree to "aroma spoilage" perception, SV ranged from 5.44 to 6.0. It is interesting to note that the SV for both "Strecker aldehydes" additions (5.4) were close to the *trans*-2-nonenal SV=5.0. The combined effect of the two Strecker aldehydes, formed continuously by Maillard mechanisms during aging, has a higher impact on the perceived aroma associated with the "aged" beer.

5. DISCUSSION AND CONCLUSION

Methional and phenylacetaldehyde are key odorants on the perceived aroma of "aged" beer. Due to the cumulative behavior observed during aging, measuring their concentration can be useful to establish the best storage conditions as well as indicators of self-life period. These findings look promising in view of the possible applications in shelf-life control by minimizing the Strecker aldehydes formation.

References

1. Liegeois, C.; Meurens, N.; Badot, C.; Collin, S.; Release of Deuterated (E)-2-N during Beer Aging Labeled Syn. before Boiling. J. Agric. Food Chem.; 2002; 50(26); 7634-8.
2. Schieberle, P., Fritsch, H., Changes in key aroma compounds during boiling of unhopped and hopped wort. 29th Inter. Congr. Europ. Brewing Convention Dublin, Ireland, 2003.
3. Perpète, P., Collin, S., Contribution du 3-méthylthiopropionaldéhyde à la flaveur de moût des bières sans alcool, European Brewery Convention, Cannes, 1999, 14, 95-102.
4. Visser, M.K. and Lindsay, R.C.; 1971. Role of methional in the development of off-flavors in beer. . J American Society Brewing Chemists (ASBC Proceedings) pp 230-237.
5. Moll M. Et Moll N.; 1990. Voies principales de formation des composés carbonylés par condensation aldolique, Revue de la Brasserie et des boissons, 6, 99-122.
6. Silva Ferreira, A.C., Guedes de Pinho, P., Hogg, T., Identification of Key Odorants Related to the Typical Aroma of spoiled Wines J. Agric. Food Chem. 2003, 51 (5), 1377-1381.
7. Peppard TL, Halsey SA; Malt Flavor - Transformation of carbonyl-compounds by yeast during fermentation. J. Inst. Brew. 1981, 87 (6): 386-390.
8. AFNOR NFV09-021. Recueil de normes françaises, IBSN2-12-190843-9, 1991, (4ª ed.).
9. Sensory Evaluation Techniques. M. Meilgaard, G. V. Civille, B. T. Carr. 3rd eds. 1999, CRC Press LLC.