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Comparison of carbonyl profiles from Czech and Spanish lagers: Traditional and modern technology

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ABSTRACT

Beer is one from the most popular alcoholic beverages worldwide. For consumer acceptance, a significant factor is its flavour and taste; carbonyl compounds play an important role as indicators of the deterioration of flavour and aroma in beers. The aim of this study was to characterize differences in the carbonyl profile from Czech and Spanish beers, based on tradition and modern technology, respectively.

Headspace solid-phase microextraction and gas-chromatography mass spectrometry were used to compare lager beers. The technique of on-fibre derivatization with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBOA) was used to achieve satisfactory recovery and sensitivity.

Statistical factor analysis showed three principal components, two of them explaining more than 79% of the variability and these results were related to ANOVA-significant difference analysis based on the country of origin. These two factors were related to Strecker aldehydes and Maillard products. PCA analysis scatterplot confirmed a significant difference between the Spanish and Czech beers, particularly with regard to the content of diacetyl and *(E)*-non-2-enal.

1. Introduction

The term beer refers to very wide range of beverages produced from different malts and brewing water, hopped by dozens of different varieties of hops and fermented using two species of yeast – top-fermenting (*Saccharomyces cerevisiae* – wheat beers, ale, stout) and bottom-fermenting (*Saccharomyces pastorianus* – lager beers) (Priest & Stewart, 2006). Part of Europe, to which the Czech Republic geographically belongs, is characterized by the production of Czech-type lager beers, which is a tradition established in Pilsen (from which the name of this beer – Pilsner - is derived) in 1842 by brewer Josef Groll (Basařová, Hlaváček, Basař, & Hlaváček, 2011). Although it is difficult to distinguish beer according to its place of origin only on the basis of clearly defined analytical characteristics, strong conservatism of Czech brewers in choosing technologies, and the diversity of raw materials used, led to the emergence of the specific type of beer (Olsovska, Cejka, Sigler, & Honigova, 2014), so different from other lagers that it is legislatively protected by the European Union Protected Geographical Indication, "Czech beer". This designation clearly defines the origin of the raw materials and technology used, and greatly emphasizes the unique analytical and sensory characteristics of the product (Anonymous, 2006).

The most appreciated sensory characteristics of beer is fresh flavour (Bravo et al., 2008), and flavour stability is thus an important quality criterion, and a concern for the brewing industry (Guido et al., 2004; Moreira, Meireles, Brandao, & de Pinho, 2013; Saison et al., 2010). Despite carbonyl compound concentrations being generally very low in fresh beer, these compounds make an important and mostly unwanted contribution to the flavour profile because of their particular sensory descriptors (Table 1) and low flavour thresholds (Blanco, Andrés-Iglesias, & Montero, 2014; Saison, De Schutter, Delvaux, & Delvaux, 2009a). The off-flavours that typically develop in aged beer include cardboard, sweet and toffee, but also butter notes (Guido et al., 2004), and some

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Table 1
Carbonyl compounds studied, flavour threshold, formation in beer and flavour descriptors.

Name	Groups	Threshold (μg/l)	Formation/description	Flavour descriptors
2-Methylpropanal	Strecker aldehyde	86–1000	Produced through Strecker degradation of the amino acid valine; may be released by the oxidative degradation of isohumulones; component of aged beer and inappropriate storage of the finished beer in addition to oxygen exposure; created by insufficient boiling of wort (too little evaporation).	Grainy, Varnish, Fruity (1, 4)
2-Methylbutanal	Strecker aldehyde	45–1250	Produced through Strecker degradation of the amino acid isoleucine; increased formation at high oxygen concentrations, inappropriate storage of the finished beer (oxygen).	Almond, Apple-like, Malty (1, 4)
3-Methylbutanal	Strecker aldehyde	56–600	Produced through Strecker degradation of the amino acid leucine; component of aged beer and inappropriate storage of the finished beer, as well as oxygen exposure, indicator of thermal load.	Malty, Chocolate, Cherry, Almond (1, 4)
Benzaldehyde	Strecker aldehyde	515–2000	Increased formation with high oxygen concentrations during brewing and packaging as well as inappropriate storage of the finished beer, component in aged beer.	Almond, Cherry, Stone (1, 4)
Heptanal	Linear aldehyde	75–80	Created by the degradation (enzymatic, auto- or photooxidative) of the fatty acid oleic acid during ageing.	Aldehyde, Vinous, Bitter (2)
Octanal	Linear aldehyde	40	Created by the degradation (enzymatic, auto- or photooxidative) of the fatty acid oleic acid during ageing.	Aldehydic, Orange peel, Bitter (2, 4)
Furfural	Heterocyclic compound	15,000–150,000	Product of the Maillard reaction, formed during boiling, indicator for flavour instability in beer, component of aged beer.	Caramel, Bready, Cooked meat (1, 4)
(E)-Non-2-enal	Linear aldehyde	0.03–0.11	Can be created by auto-oxidation or an enzymatic oxidation of linoleic acid and linolenic acid with lipoxygenases during mashing and malting, also created by the reaction between heptanal and acetaldehyde, (E)-non-2-enal can be enzymatically reduced by yeast using an enzyme that acts like an aldehyde reductase; decreases significantly after 36 h of fermentation; inappropriate storage of the finished beer increases its level.	Cardboard, Papery, Cucumber (1, 2, 3, 4)
2,3-Butanedione (Diacetyl)	Ketone	100–200	From α-acetohydroxy acids that are excreted during fermentation by yeast cells to the wort where they undergo spontaneous oxidative decarboxylation to diacetyl; occurs at the end of the conventional main period of fermentation and during the maturation of beer; formation correlates to the amino acid content in wort; may be formed in packaged beer as a result of Maillard reactions or oxidation of acetoin and 2,3-butanediol; too short maturation, poor yeast vitality, too many repitches, old yeast, yeast stored too long also increases diacetyl content; can be formed by contamination with some microorganisms.	Butterscotch, Buttery, Buttermilk, Rancid (2, 3, 4, 5)
2,3-Pentanedione	Ketone	900–1000	Intermediate product during the synthesis of valine and isoleucine; can be formed by bacterial infection.	Moldy, Wood-like (5)

(1) (Baert et al., 2012); (2) (Meilgaard, 1975); (3) (Guido, Rajendram, & Barros, 2009); (4) (Saison, De Schutter, Uyttenhove, Delvaux, & Delvaux, 2009b); (5) (Krogerus & Gibson, 2013).

aldehydes and ketones have been considered to be the most important factors in the deterioration of beer flavour and the formation of off-flavours (Bueno, Zapata, & Ferreira, 2014; Gonçalves et al., 2014; Rossi, Sileoni, Perretti, & Marconi, 2014).

There are many ways in which carbonyls get into beer. These compounds can originate from a raw material, which is typical for furfural derivatives arising from Maillard reactions during kilning of the malt (Yahya, Linforth, & Cook, 2014). Malting technology and the quality of raw materials is also significant with regard to the formation of precursors of carbonyl compounds and activation of enzymatic systems, allowing their conversion at later stages of brewing. An important reaction is the activation of lipoxygenases, enabling enzymatic oxidation of unsaturated fatty acids during mashing, which, together with corresponding non-enzymatic oxidation during beer storage, is the main cause of the formation of carbonyl compounds such as hexanal, and *(E)*-non-2-enal (Noel et al., 1999; Yu et al., 2014). Moreover, malt and hop polyphenols inhibit the activity of reactive oxygen species (hydroxyl and hydroperoxide radicals, singlet oxygen, hydrogen peroxide, superoxide anion), which is a crucial factor in the formation of carbonyl compounds during storage of the finished beer (Mikyska, Krofta, Haskova, Culik, & Cejka, 2011; Vanderhaegen, Neven, Verachtert, & Derdelinckx, 2006) Saaz hop is known for its high content of polyphenolic compounds (Jelinek et al., 2012; Lermusieau, Liegeois, & Collin, 2001) and its use can become an important factor affecting the sensorial quality of the product.

Decisive steps in brewing technology for changes in carbonyl content are mashing, fermentation and maturation (Briggs, Boulton, Brookes, & Stevens, 2004). In addition to fatty acid oxidation, the formation of the Strecker aldehydes 2-methylpropanal, 2-methyl butanal, 3-methylbutanal and phenylacetaldehyde by degradation of amino acids valine, isoleucine, leucine and phenylalanine respectively, occurs during mashing (da Costa et al., 2004). Therefore amounts of these amino acids in wort, resulting from proteolytic modification of malt (Stephan, Kusche, & Stettner, 2007), or the use of malt adjuncts, usually in the form of rice or maize (Taylor, Dlamini, & Kruger, 2013) plays an important role. Apart from economic reasons, these adjuncts became popular in recent years with respect to the production of gluten-free beer, which can be consumed by customers suffering celiac disease (Yeo & Liu, 2014). Metabolism of amino acids also plays an important role during fermentation, particularly when using modern high-volume cylindro-conical fermenters. Their gradual filling with fresh wort from multiple batches leads to intensive synthesis of the branched chain amino acids valine and isoleucine by yeast cells, and thus to the formation of vicinal diketones (diacetyl and 2,3-pentadione) that at very low concentrations gives beer an unwanted buttery off-flavour (Krogerus & Gibson, 2013). Modern