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Identification of compounds that contribute to trigeminal burn in aqueous ethanol solutions

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ABSTRACT

The influence of carbonyl species on the trigeminal burn of distilled spirit model systems was investigated. Quantities of the intrinsic carbonyl compounds were significantly altered in 40% ethanol solutions using two methods; (1) increasing or decreasing the product pH, to induce hemiacetal formation and acetal stabilization or induce and stabilize carbonyl species such as aldehydes, respectively and (2) utilizing a sulfonyl hydrazine polymer treatment. Samples with reduced carbonyl concentrations had significantly lower perceived trigeminal burn intensity. Sensory recombination experiments revealed that addition of carbonyl compounds increased trigeminal burn perception in model systems; confirming the direct relationship between the concentration of carbonyl compounds and trigeminal burn. The strongest potentiators of the trigeminal response were carbonyl compounds octanal, nonanal, benzaldehyde and 2-heptanone suggesting the probability that carbonyl species such as saturated aldehydes and ketones act as agonists to activate nociceptors such as TRPV1 and TRPA1 and elicit trigeminal burn.

1. Introduction

Smoothness and maturity of alcoholic beverages is a general descriptor predominately correlated with higher palatability and consumer preference. From a sensory perspective it is often associated with decreased trigeminal burn sensation, sourness, astringency and overall mouth-feel (Piggott, 2012). Alcoholic beverages, such as vodka, tequila, rum, bourbon, scotch and brandy are generally produced through a distillation process. Once produced, in order to improve the taste and smoothness, many products are aged/matured. For example, bourbons and scotches are typically aged at least three years. Rums, tequilas and brandies are aged anywhere from 2 to 10 years or more. Though effective in improving the palatability of spirits, distillation and aging techniques have changed little over the last several hundred years and the costs associated with multiple distillation, filtration and clean up processes as well as conventional aging are high, often accounting for half to two-thirds of the cost of the spirit.

Traditionally trigeminal burn has been almost exclusively attributed to ethanol content as a correlation has been established (Green, 1987). More recently ethanol was shown to activate polymodal nociceptors on the tongue and palate (Trevisani & et al., 2002). These neurons have vanilloid receptors (TRPV1), which are activated by many noxious stimuli and generate heat or pain sensations. These tactile perceptions belong to the sense of touch and can enhance the overall perception of flavor. Tasters typically describe the sensation of alcohol burn using temperature and tactile descriptors. In alcoholic beverages, such as distilled spirits, trigeminal burn intensity has also been correlated with pungency, the lack smoothness and has been shown to decrease during maturation (Clyne, Conner, Paterson, & Piggot, 1993) or after application of multiple distillations and filtration steps while the ethanol content remains constant. This reduction is associated with improved smoothness perception suggesting that trigeminal burn might be influenced by other molecular species that likely activate or act synergistically (with ethanol) to activate vanilloid receptors or other nociceptors of the transient receptor potential (TRP) family such as TRPA1. Little is known regarding the chemistry changes in distilled spirits during maturation that affect taste and the tactile and trigeminal sensations, which can undoubtedly impart smoothness. However activation of TRP receptors by natural products (especially ones used for medicinal purposes) has been examined. Among the chemicals found to act as agonists of TRPV1 and TRPA1 were α, β-unsaturated dialdehydes and aldehydes respectively. Isovelleral and merulidial were among the α, β-unsaturated dialdehydes found to activate TRPV1 (Jonassohn, Anke, Morales, & Sterner, 1995; Szallasi et al., 1996, 1998) while cinnamaldehyde, 4-hydroxynonenal, acetaldehyde as well as acrolein and crotonaldehyde were found to activate TRPA1

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(Andrè et al., 2008; Bandell et al., 2004; Bang, Kim, Yoo, Kim, & Hwang, 2007; Trevisani et al., 2007). Though aldehydes are major components of alcoholic spirits their impact on trigeminal burn perception and thus in smoothness has not been examined.

The majority of studies thus far have focused on changes on volatile markers during production (fermentation, distillation, clarification, filtration and other clean up steps depending on the final product) as well as during maturation-storage and their effect on aroma character of the spirit at hand (Apostolopoulou, Flouros, Demertzis, & Akrida-Demertzi, 2005; Caldeira, Anjos, Portal, Belchior, & Canas, 2010; MacNamaral, van Wyk, Augustyn, & Rapp, 2001; Nykanen, 1986).

It is known that the equilibrium between aldehydes, ketones, alcohols, hemiacetals and acetals is critical for the overall character and sensory properties in distilled spirits and alcoholic beverages (Russell, 2003) and these compounds have been extensively studied for their contribution to the aroma profile. In fact an important part of the aging of distilled spirits is the evaporation of aldehydes or their reaction to form acetals (Nitz, 1985; Nitz, Kollmannsberger, & Drawert, 1989). Aldehydes have been associated with pungent, sharp aromas as well as astringency while acetals and hemiacetals have been linked to more pleasant and fruity attributes (Perry, 1986, 1989). Ethanol levels as well as pH (Perry, 1986) of an alcoholic beverage are known to influence formation of hemiacetal and acetal species from aldehydes and alcohol. Though the contribution of those species on the aroma of alcoholic beverages, and intrinsic factors that affect their concentration have been extensively studied there is little known regarding their effect on trigeminal sensations and their impact on the smoothness of alcohol containing products.

Thus, the objective of this work was to further explore the molecular drivers of trigeminal burn. More specifically this work aimed to qualitatively and quantitatively determine how the chemical balance of carbonyl species might relate to overall trigeminal alcohol burn sensation of distilled spirits, and thereby impart smoothness. This approach could potentially afford better understanding of the molecular drivers of trigeminal burn, thus facilitating the development of flavor improvement strategies and creating opportunities for wide platform of alcoholic product optimization including spirits, personal hygiene and pharmaceutical products with alcohol content.

2. Materials and methods

2.1. Chemicals

Hexanal, 2-heptanone, heptanal, methyl hexanoate, benzaldehyde, octanal, nonanal, decanal, sodium carbonate, monopotassium phosphate, sodium azide, deuterium oxide and the polymer resin sulfonyl hydrazine were purchased from Sigma-Aldrich Co. (St. Louis, MO.), 3-(trimethylsilyl)-propionateacid-d4 was purchased from Thermo Fischer Scientific Inc. (Waltham, MA).

2.2. Model systems

In order to determine the effect of carbonyl species on trigeminal burn and obtain translatable results for a wide platform of alcoholic products a model system consisting of 40% ethanol (v/v, FCC) and nanopure water was selected. Native carbonyl species were identified and quantified. pH adjustment and carbonyl scavenger polymer resins were used to either alter the balance between carbonyl and ketal species or reduce carbonyls species load in the model system respectively.

The intrinsic pH of 40% aqueous solution of ethanol was 6.3 and two adjustments were performed at pH 3.0 and 8.0 in order to establish the quantitative effect of pH on the levels of carbonyl species and the qualitative effect of the carbonyl concentration on the trigeminal burn and smoothness perception.

2.3. pH modulation treatment

The pH was adjusted using phosphoric acid for the acidic range (pH 3.0) and sodium hydroxide for the basic range pH (8.0). The pH of each sample was measured using a sure-flow pHe electrode (8172BN) specifically designed for pH measurements in high ethanol content solutions (Thermo Fischer Scientific Inc. Beverly, MA) and coupled with an Orion 5-star plus pH meter (Thermo Fischer Scientific Inc. Beverly, MA). The samples were subsequently stored for 24 h, prior to sensory evaluation and quantitation. The effect of the different pH values on the levels of carbonyl species was determined using a dynamic headspace GC/MS method.

In order to examine and confirm that pH modulation of the model ethanol solution did not alter the volatility of the carbonyl species quantified (by headspace analysis), 200 ml of water with pH adjusted to either 3.0 or 8.0 was spiked with l0 mg/L of butanal, hexanal, heptanal, octanal, nonanal, decanal and benzaldehyde, and carbonyls species were quantified via dynamic headspace GC/MS.

2.4. Polymer-bound hydrazine/carbonyl scavenger treatment

Sulfonyl hydrazine (0.5 gr) with a loading capacity of 1.6–3 mmol/g and carbonyl scavenging properties was added to 100 ml of distilled spirit. The sample was stirred for an hour and the polymer resin was subsequently removed via filtration. The concentration of the carbonyl compounds were then analyzed by dynamic headspace GC/MS and sensory evaluation was conducted using a degree-of-difference test to measure trigeminal-ethanol related burn.

2.5. Quantification of carbonyl species – dynamic headspace GC/MS-scan and SIM

A dynamic headspace (DHS) method was utilized for the identification and quantification of aldehydes, ketones, acetals/hemiacetals and fusel oils. Briefly, 1 ml of sample (40% ethanol content) was placed in a 20 ml headspace vial and diluted with nanopure water to final volume of 10 ml. Methyl hexanoate was added as an internal standard (10 μg). Both MS scan and single ion monitoring (SIM) modes were used for identification and quantification of compounds, respectively.

Analysis was performed using a 6890 GC equipped with a 5973 Mass Selective Detector (Agilent Technologies), Thermal Desorption Unit (TDU, Gerstel), PTV inlet (CIS 4, Gerstel) and MPS 2 with headspace and DHS option (Gerstel). A highly inert CP-SIL 5CB GC (0.15 mm × 2.0 μm) column was used for chromatographic separation with 0.5 ml/min constant flow of Helium. The headspace vials were then incubated at 55 °C for 12 min and subsequently purged with nitrogen at a rate of 20 ml/min for a total time of 15 min while agitated at 500 rpm to increase volatility. The trap (Tenax TA) was then dry purged for 5 min at a rate of 10 ml/min and transferred to a thermal desorption unit. The trapped volatiles were then desorbed, cryofocused at −100 °C, and injected in solvent vent mode (30 ml/min) at 0 kPa following splitless starting at 0.5 min. Initial temperature of the TDU was 20 °C for 0.5 min followed by a ramp of 720 °C/min up to 110 °C and after 1 min hold ramp of 720 °C/min was resumed until reaching a final temperature of 300 °C (4 min hold). The column heating profile was at 40 °C for 10 min, then ramped to 280 °C at 10 °C/min and hold for 6 min. The MS was collected in single ion monitoring mode (SIM) and the parameters for quantification of selected chemical