Identification of Compounds that Influence Alcohol Smoothness

Devin Peterson

Kokkinidou and Peterson, 2014. Provisional Patent

Outline

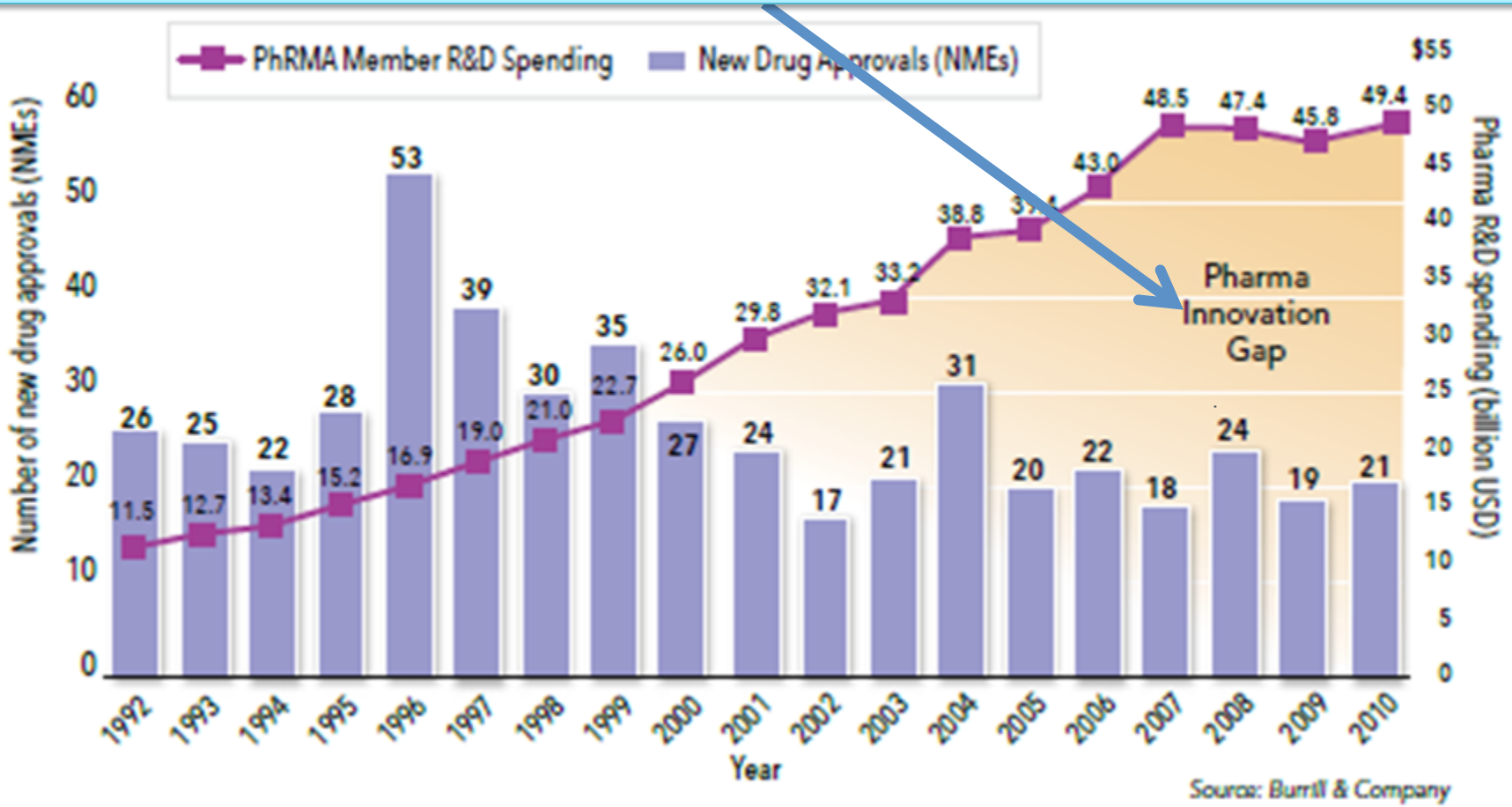
1. Introduction (15min)
   - Flavor Research & Education Center
2. Understanding Alcohol Flavor (30min)

Why Develop a Academic-Industrial Flavor Center?

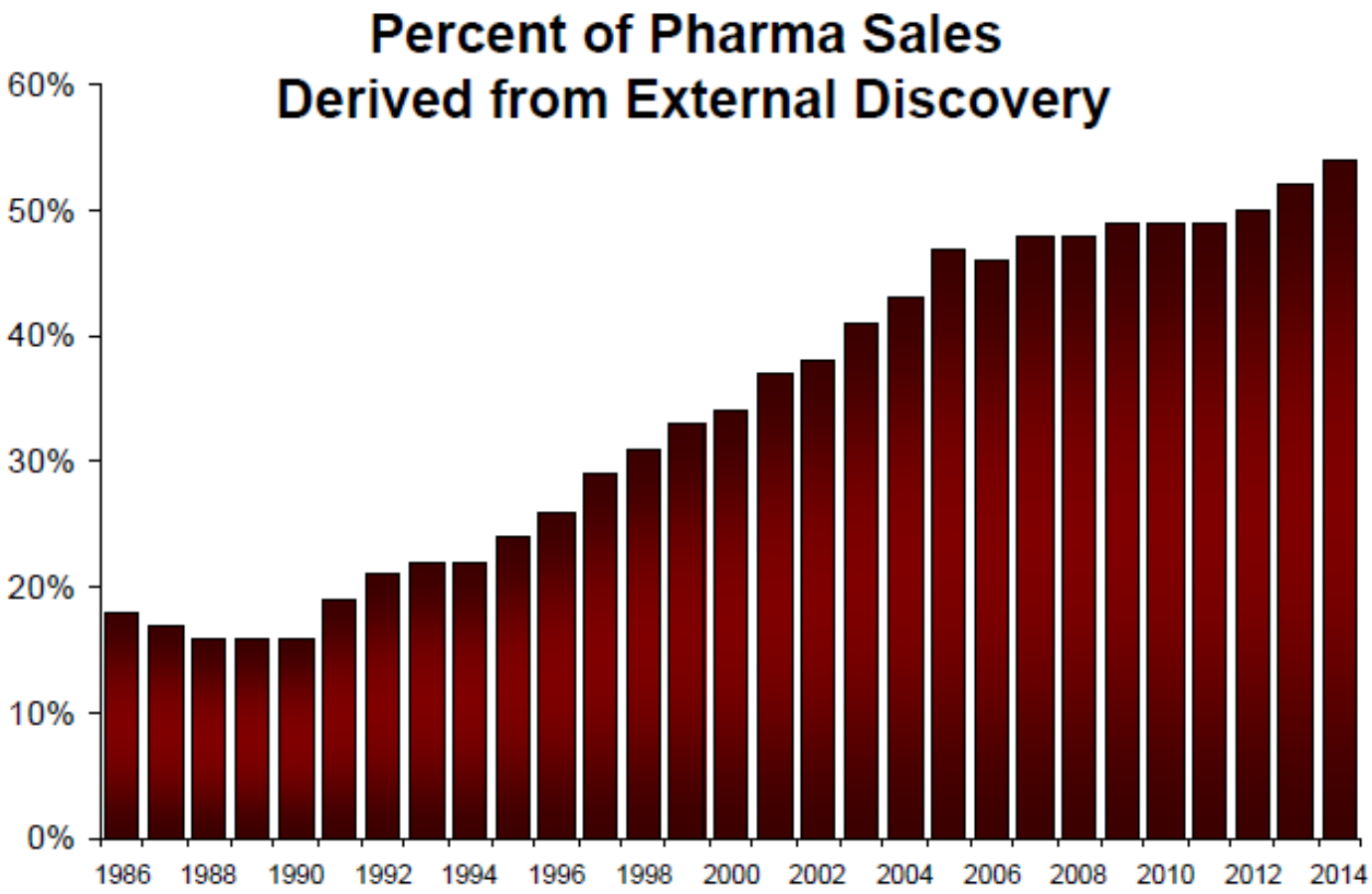
1. Universities can have a more pivotal role in food innovation,
2. Universities are *uniquely* positioned to provide knowledge that currently limits food innovation, and
3. Open innovation model is needed

Challenges in Industrial Research

Innovation Gap = More money spent with declining drug approvals



Externally-Sourced Programs Drive Increasing Share of Pharma Revenue



EvaluatePharma

DefinedHealth
unconventional insight

Consortium: Academic-Industry Partnerships

Innovation in Food Limited by Federal Funding

- In 2014 approximately 9M in competitive grants given by USDA-AFRI
  - Food Safety, Nutrition, and Health
    - Priority Areas include
      - Safety; Microbial
      - Improving Food Quality
      - Function and Efficacy of Foods
  - U.S. consumers spend nearly 10 percent of the Gross Domestic Product (GDP)
    - Over 1 trillion dollars

Open Innovation: Flavor Technology

- *Flavor Research and Education Center* – August 2011
  - Academic-Industry Partnership
- The cost of innovation is spread across many different companies, while each member has the opportunity to work with us one-on-one for proprietary solutions to unique business needs.
- Offers the opportunity to explore long range, high-risk projects at a lower cost by providing a vehicle for proof-of-concept prior to considerable investment.

Knowledge Drives Innovation

Membership Companies

Societal Value: Flavor Discovery

- People eat what they like, not what is good for them
  - Top 3 factors underlying food choice
    - Flavor, cost and convenience
      - Carrillo et al., J. Sensory Studies, 2011, 26:85-95
      - Glanz et al., J. Amer. Diet. Assoc., 1998, 98:1118-26
  - Health Implications

- Commercial value
  - people buy foods that taste good
  - number one complaint from customers is flavor (off-flavors)

Health & Diet

- Dietary factors are thought to account for about 30% of cancers in western countries
  - The human cost of chronic diseases in the United States, such as cancer, heart disease and diabetes are responsible for 70% of deaths
  - The financial costs are also staggering
    - Chronic diseases account for $3 out of $4 spent on healthcare

Chronic Disease Overview: Costs of Chronic Disease; Centers for Disease Control and Prevention

Health & Diet

- WHO - World Cancer Report (2014)
  - "More commitment to prevention and early detection is desperately needed in order to complement improved treatments and address the alarming rise in cancer burden globally"
    - Christopher Wild - Director of International Agency for Research on Cancer
  - "A fundamental goal of research on diet and cancer is to identify constituents of food including both classic nutrients and other aspects of diet that increase or decrease the risk of cancer."
    - Walter C Willet- Professor of Epidemiology and Nutrition at Harvard School of Public Health and Professor of Medicine at Harvard Medical School
- Departments of Food Science and Nutrition can play a pivotal role in advancing our food supply
  - More nutritious foods with higher acceptability
    - Need to understand food chemistry

THE
WELLBEING LECTURE SERIES

UNIVERSITY OF MINNESOTA
Center for Spirituality & Healing
Driven to Discover℠
FAIRVIEW

84%

of all medical costs in the U.S. are caused by physical inactivity, food choices and portion size, tobacco, and unmanaged stress.

September 11, 2014
3:30 Lecture followed by Q&A

Register at z.umn.edu/roizen

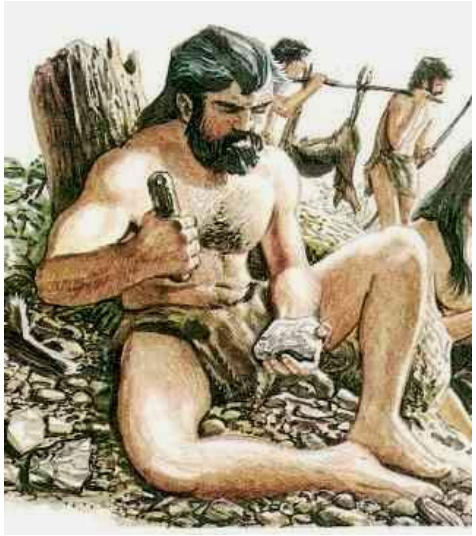
Application of Flavor Science: Topics

- Whole Grain
  - Taste and Aroma
- Clean Labels
  - i.e. Reduced sugar, preservatives
- Salt Reduction
  - Delivery
- Alcohol Flavor Quality
  - Smoothness

Health and Wellness

Whole Grain and Health Impact

- Hard Evidence
  - Coronary heart disease
  - Cancer
- Strong Evidence
  - Stroke
  - Diabetes

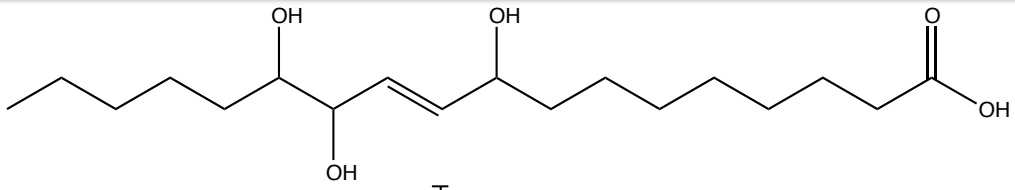


Only 5% of Americans consume recommended amount (USDA guidelines)

Agronomic Practices

- Focus has been on yield and resistance
  - Not on flavor acceptability

Crumb Bitterness: Processing



9,12,13-Trihydroxy-trans-10-octadecenoic acid

% MRM Response 329 -> 211

100
80
60
40
20
0

Generation during processing

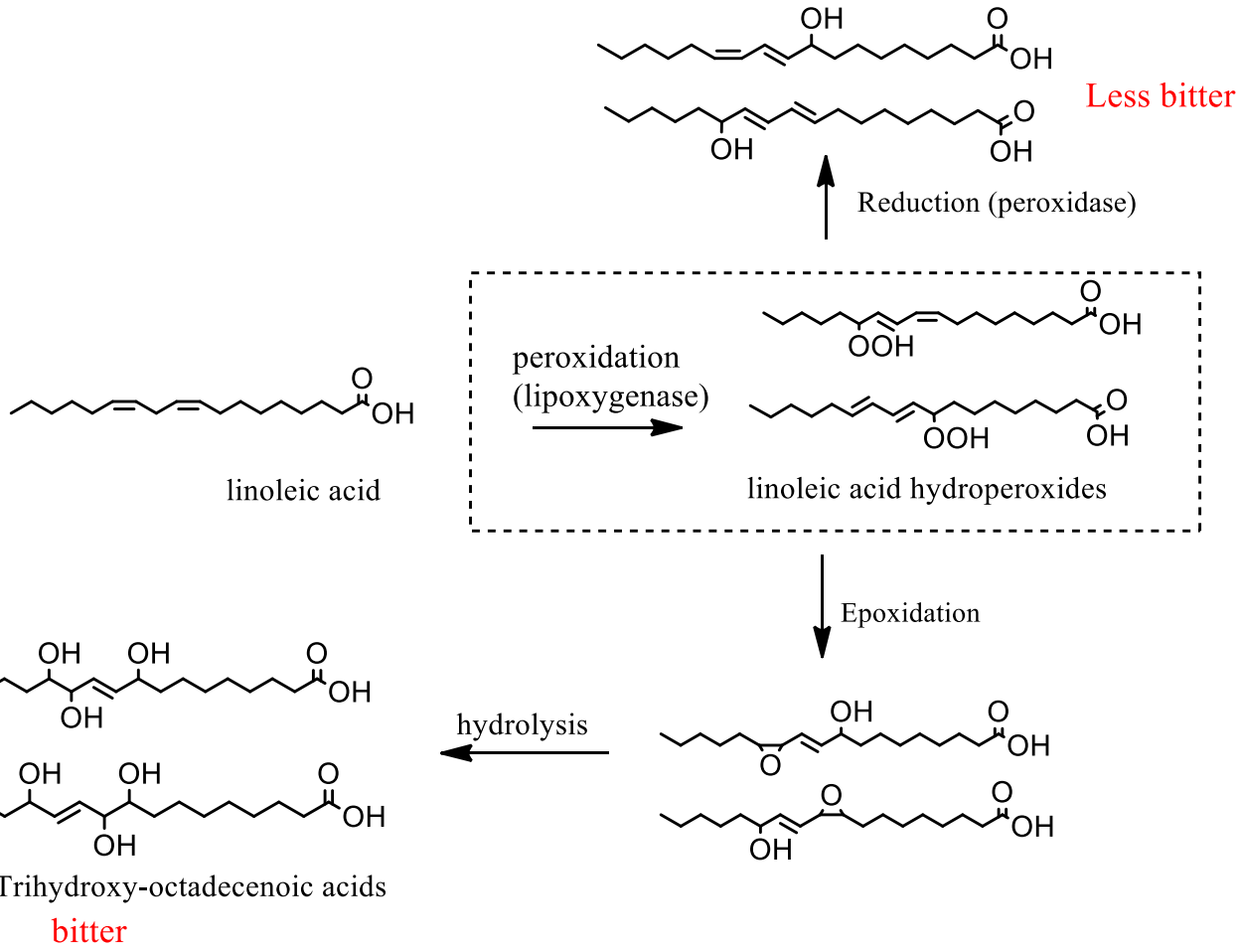
HRS flour
HWW flour
HRS crumb
HWW crumb
HRS crust
HWW crust

Figure shows the relative concentrations of THOA across different WW samples

(Bin and Peterson, In Preparation)

Pathways of Origin: Isotope Labeling

- Generated from oxidative changes of the linoleic acid



Flavor Quality: Alcoholic Beverages

- Understanding art and nature

Flavor Quality: Alcoholic Beverages

- Smoothness and maturity are desirable sensory traits

- Not accurately defined - changes with the alcoholic product at hand

Kokkinidou and Peterson, 2014. Provisional Patent
(Kokkinidou and Peterson, Manuscript in Preparation)

Smoothness and Maturity

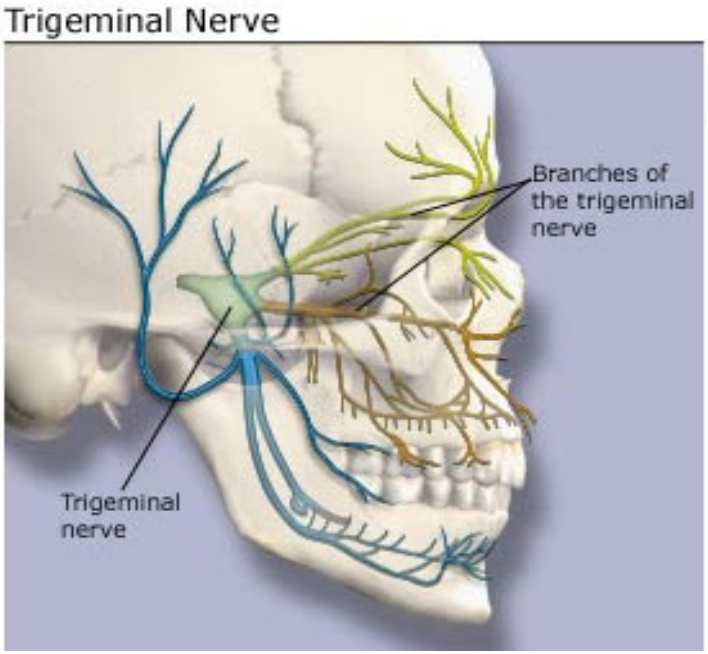
- Smoothness and maturity of alcoholic beverages are general descriptors predominately correlated with higher palatability and consumer preference
  - Sourness
  - Astringency
  - Overall mouth-feel and
  - **Trigeminal burning sensation**

- Understanding the chemical drivers of those sensations can give rise to ingredient or processing technologies for improved palatability
  - Flavor quality optimization
  - Cost and time efficiency

Smoothness and Maturity

- Smoothness of distilled spirits increases over time and trigeminal burn decreases
- **Ethanol levels do not change**

What are the chemical species responsible for trigeminal burn?



Ethanol content ≠ Trigeminal burn

Smoothness and Maturity

Most studies thus far have focused on changes on volatile markers

- Aldehydes, ketones, esters, lactones and other congeners during production and maturation-storage and their *effect on aroma*
    - Aldehydes have been associated with pungent, sharp aromas and acetals are more pleasant and fruity

- Equilibrium between volatile species such as aldehydes, ketones, alcohols with hemiacetals and acetals thought to be important for aroma development

Can these changes be related to trigeminal sensation and thus smoothness and maturation?

Russell I., Stewart G., Whisky: Technology, Production and Marketing 2003, Elsevier Ltd.
Perry, DR 1989: Odour intensities of whisky compounds. In Distilled Beverage flavor: Recent developments. Piggot, JR and Paterson, A. Ellis Horwood, Chichester, UK,pp200-207.
Perry, DR 1986: Whisky maturation mechanisms. In Proc. 2nd Aviemore Conf. Malt. Brew. Distilling, (eds) Campell, I and Priest, FG. Institute of Brewing, London, pp409-412.

Initial Steps: Drivers of Burn

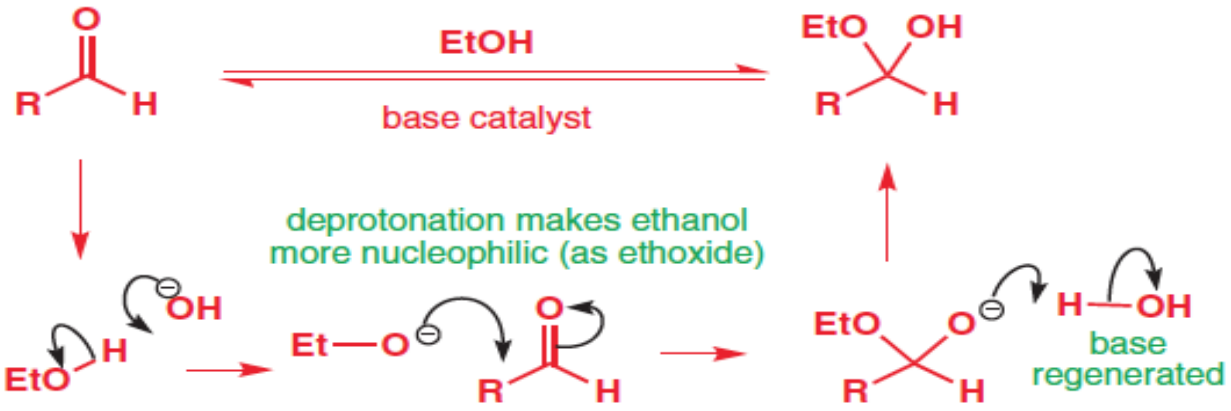
- Vacuum distillation of alcohol product (40%)
  - Distillate made up at 40% had a lower perceived burn

Hypothesis-pH Effect

Balance between hemiacetals and acetals, aldehydes, ketones as well as fusel oils affects not only aroma but trigeminal burn and smoothness

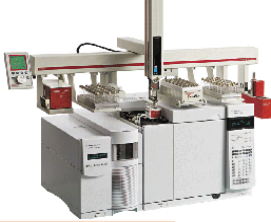
- equilibrium is known to be affected by pH and ethanol levels

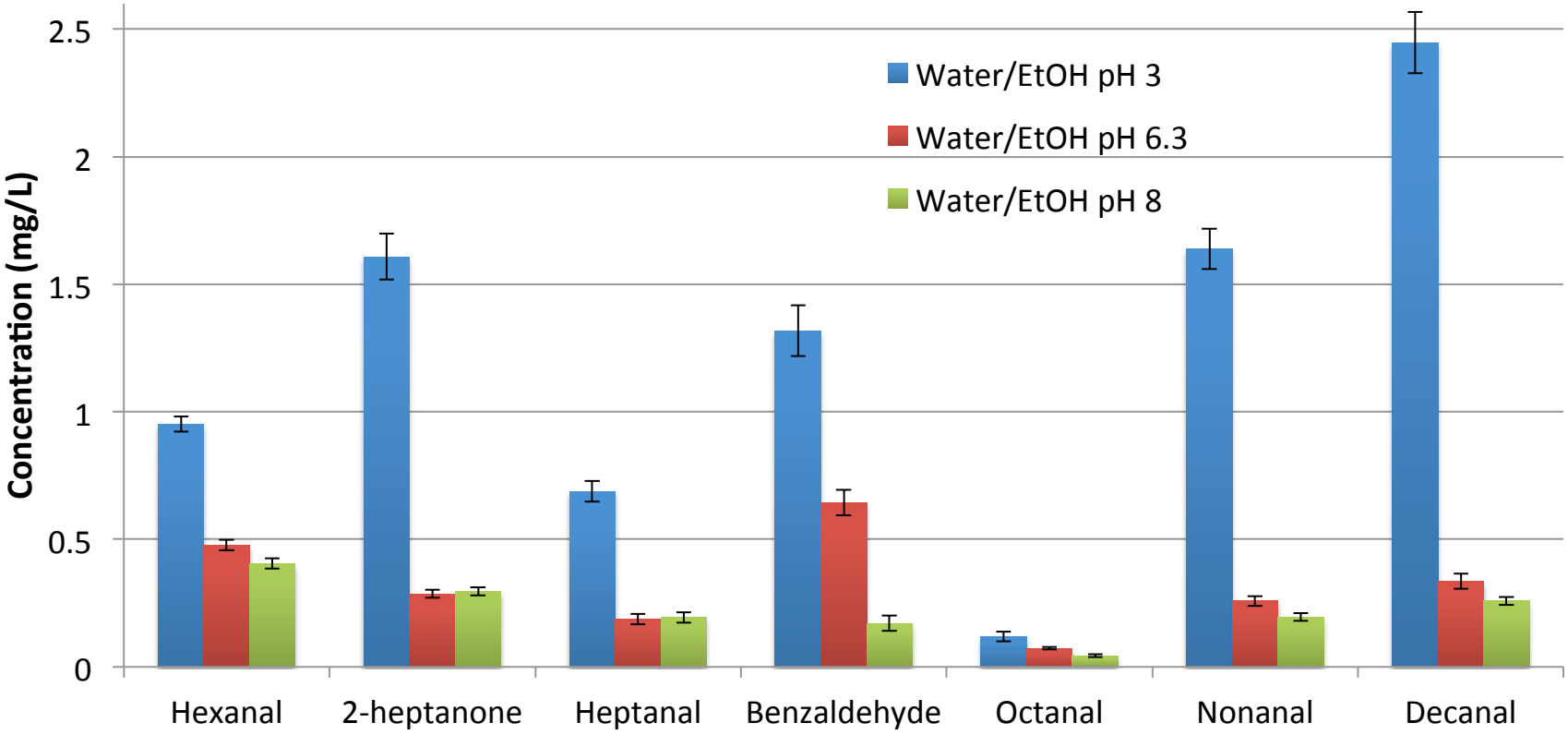
Perry, DR 1986: Whisky maturation mechanisms. In Proc. 2nd Aviemore Conf. Malt. Brew. Distilling, (eds) Campell, I and Priest, FG. Institute of Brewing, London, pp409-412.



(Kokkinidou and Peterson, Manuscript in Preparation)

40% Aqueous ETOH: pH Effect





(Kokkinidou and Peterson, Manuscript in Preparation)

Sensory Evaluation: Smoothness

Sample	Rating (Nose Clips)
Water/ethanol (pH 6.30) - (blind control)	0.75
Water/ethanol (pH 3.00)	-8.40*
Water/ethanol (pH 8.00)	4.10*

*significantly different from control, determined by one-way ANOVA analysis

- More positive number = less trigeminal burn

(Kokkinidou and Peterson, Manuscript in Preparation)

Causality: Carbonyl Conc. on Burn Intensity

Sample	Rating (nose clips)
Water/ethanol (pH 6.3)	6.00[a]
Water/ethanol (pH 6.3) - Carbonyls at levels of pH 3	8.62[b]

- Recombination models to confirm causality of carbonyl species on trigeminal burn sensation

(Kokkinidou and Peterson, Manuscript in Preparation)

Causality

Sample	Rating
Water/ethanol + 2-heptanone	7.56
Water/ethanol + nonanal	7.31
Water/ethanol + octanal	7.13
Water/ethanol + benzaldehyde	7.13
Water/ethanol + hexanal	6.75
Water/ethanol + decanal	6.56
Water/ethanol + heptanal	6.25
Water/ethanol	6.00

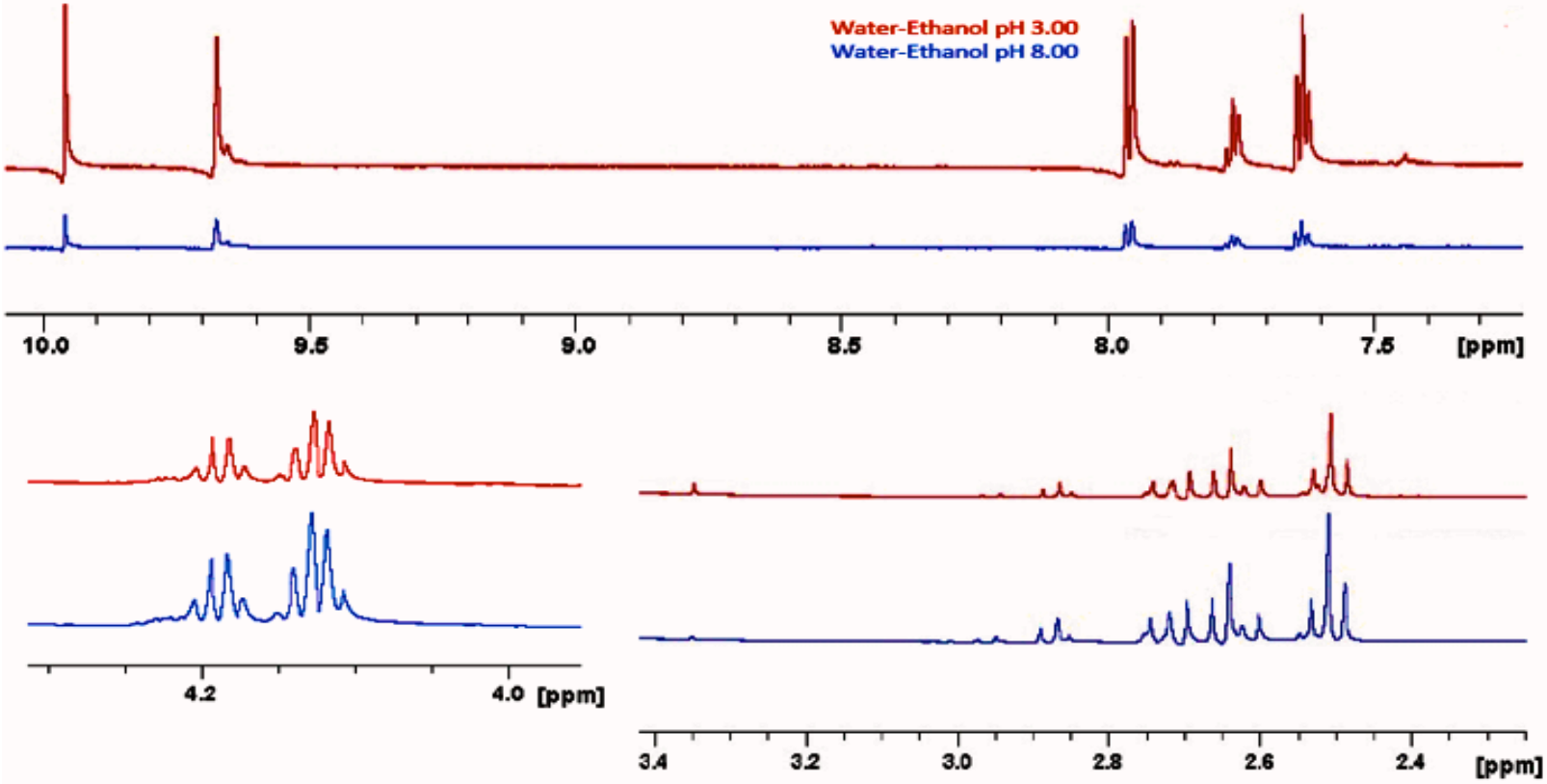
Compound	Concentration (ppm)
Hexanal	0.48
Heptanal	0.50
Octanal	0.05
Nonanal	1.38
Decanal	2.11
Benzaldehyde	0.67
2-heptanone	1.32

- Differences can help identify the more causative carbonyls

(Kokkinidou and Peterson, Manuscript in Preparation)

Carbonyl Species Shift-NMR Analysis

Shaped pulse sequence was used during the relaxation delay to suppress the eight 1H-NMR frequencies of water and ethanol namely, OH of H_2O and OH of ethanol, the CH2 quartet and the CH3 triplet of ethanol.



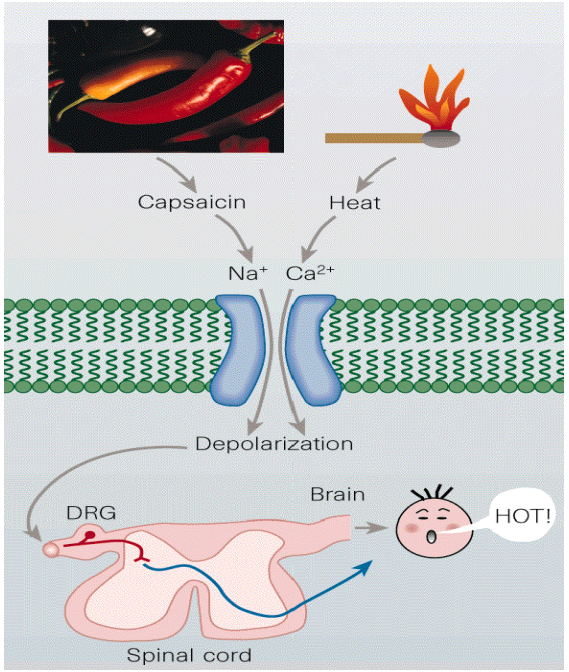
- 2-5ppm characteristic region of acetals, hemiacetals, ethers and esters

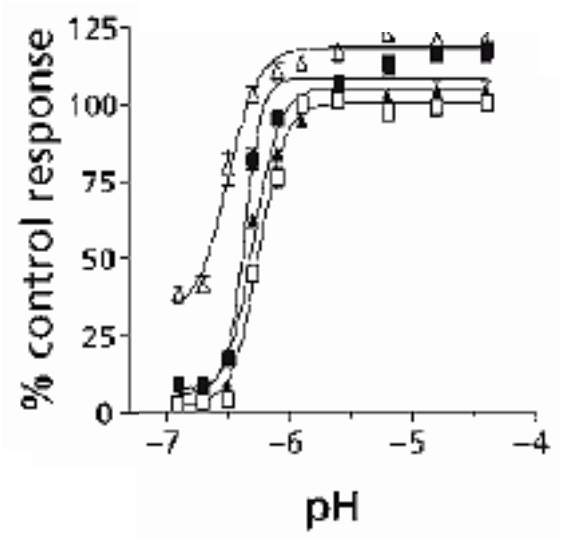
(Kokkinidou and Peterson, Manuscript in Preparation)

Burn and pH

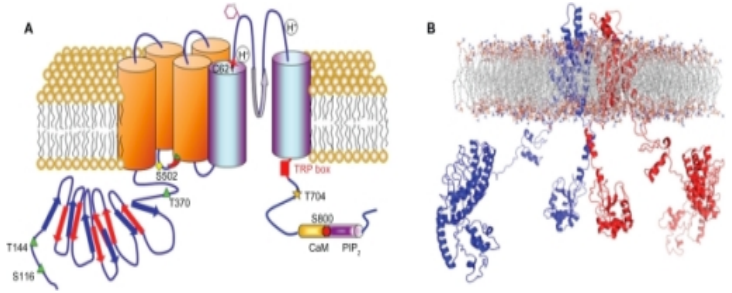
Vanilloid receptor-1 (VR1) is a heat-gated ion channel that is responsible for the burning sensation elicited by capsaicin

Ethanol potentiates the same receptors and pH has an affect on the response





absence (□) or presence of 0.1% (▲), 0.3% (■) or 1% (△) ethanol.



M Trevisani, D Smart, M J. Gunthorpe, M Tognetto, M Barbieri1, B Campi, S Amadesi, J Gray, J C. Jerman, S J. Brough, D Owen, G D. Smith, A D. Randall, S Harrison, A Bianchi, J B. Davis & P Geppetti. **Ethanol elicits and potentiates nociceptor responses via the vanilloid receptor-1. Nature *neurosci.* 5 (6) (546-551) 2002.**

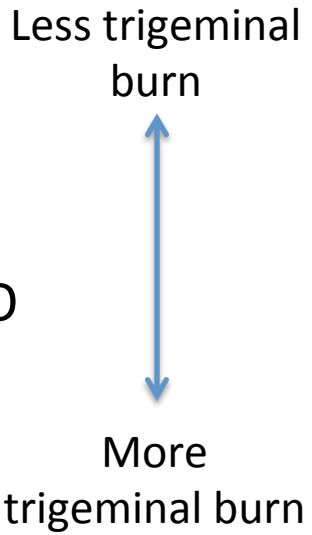
Vodka Samples and Quality index

Products

Zyr (Russian) – Wheat and rye 5x (90)
UV (Minnesota, USA) - Grain 4x (78)
Skyy 90 (USA) – Wheat 5x (83)
Ketel One (Holland) - Wheat 3x (78)
Jean-Marc XO (France) – Wheat 9x (73)
Grey Goose (France) – Wheat 5x (70)
Crystal Head (Canada) – Grain 3x (Not rated)
Chopin (Poland) – Potato 4x (81)
Prairie Organic (Minnesota, USA) – Grain ?x (82)
Gordon's (London, England) (Not rated)
Luksusowa (CT) – Potato ?x (75)
Karkov (MN) – Grain ?x (39)

Sensory rating

Zyr
UV
Grey Goose
Jean-Marc XO
Luksusowa
Karkov



What makes these products so different?

(Kokkinidou and Peterson, Manuscript in Preparation)

Intrinsic Properties: Alcohol

- Ethanol percent, presence of glycerin and pH

Zyr (8.00)
UV (6.55)
Grey Goose (6.10)
Jean-Marc XO (5.70)
Luksusowa (5.65)
Karkov (3.00)

Zyr
UV
Grey Goose
Jean-Marc XO
Luksusowa
Karkov

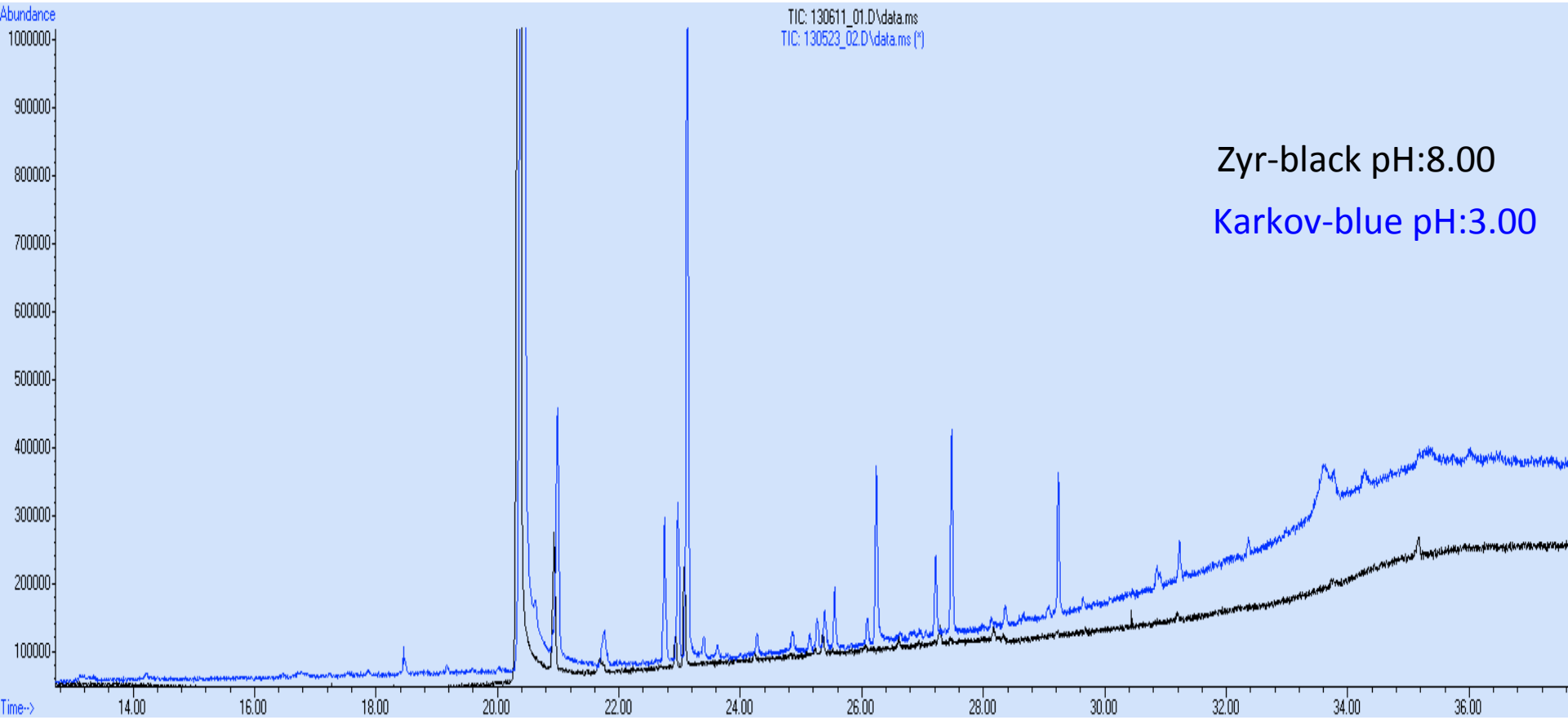
Less Burn/chemical, harsh taste

More Burn/chemical, harsh taste

Increasing pH values correlated with initially sensory liking and acceptability

(Kokkinidou and Peterson, Manuscript in Preparation)

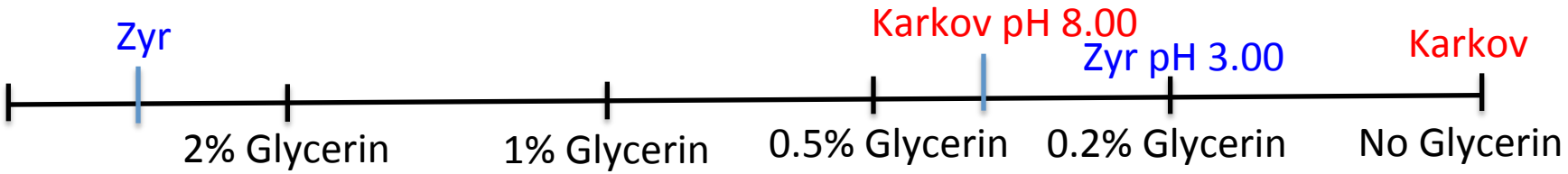
GC-MS: Carbonyl Species



- Sensory results and pH correlated with levels of carbonyl species present in those spirits (Kokkinidou and Peterson, Manuscript in Preparation)

Sensory Evaluation: Burn

- Original samples: Karkov (pH 3) and Zyr (pH 8)
- pH modified samples: Karkov (pH 8) and Zyr (pH 3)

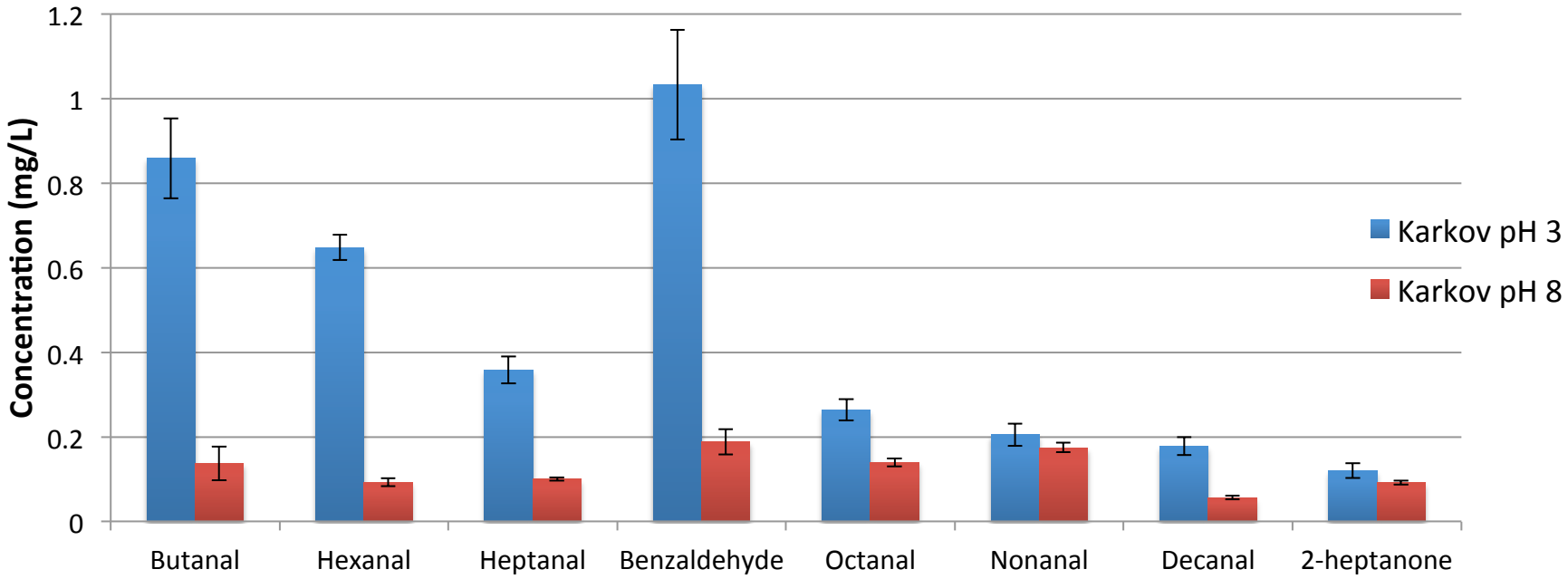


pH increase improved smoothness and burning sensation, Karkov with increased pH was described as having more warming and less chemical/alcohol burn.

Astingency and bitterness of Karkov was also **decreased** when pH increased compared to original sample

(Kokkinidou and Peterson, Manuscript in Preparation)

pH Effect on Carbonyl Species



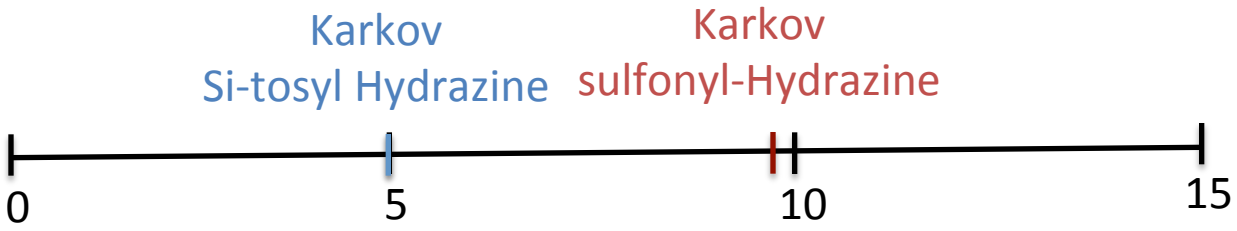
At higher pH acetal (acetaldehyde diethyl acetal) and heptanal diethyl acetal also increased by 60 and 45% respectively.

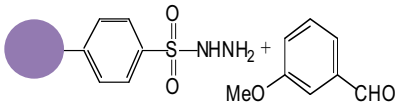
(Kokkinidou and Peterson, Manuscript in Preparation)

Trigeminal Burn and Carbonyl Contribution

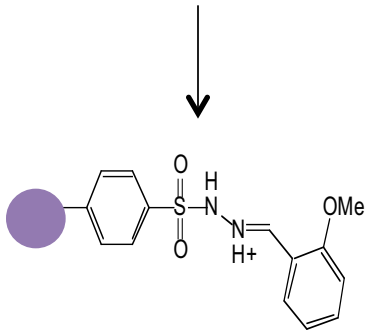
Degree of difference test

Taste : nose clips

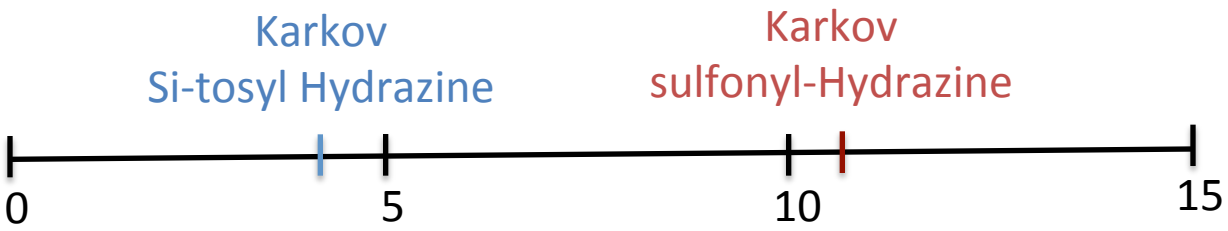




Both hydrazine treated samples were found to have improved smoothness as compared to Karkov



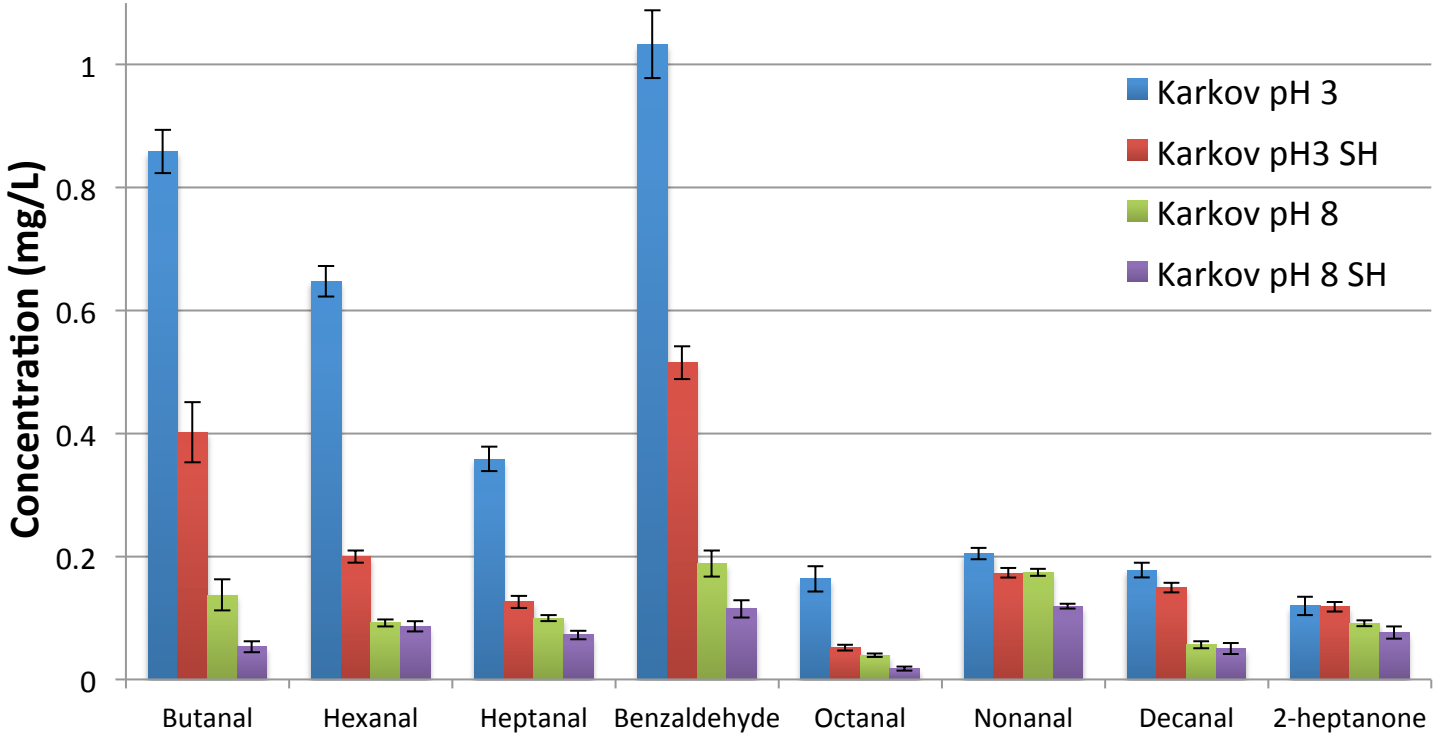
Aroma: no nose clips

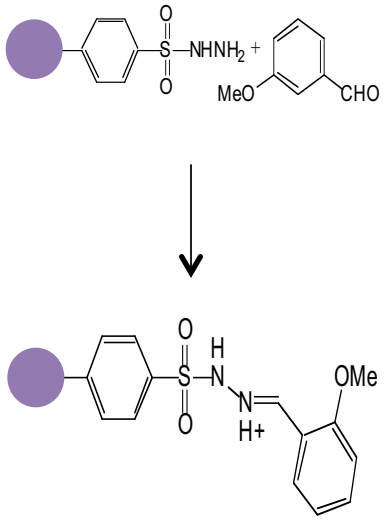


Both hydrazine treated samples were found to have improved aroma and smoothness as compared to Karkov

(Kokkinidou and Peterson, Manuscript in Preparation)

Carbonyl Species and Smoothness





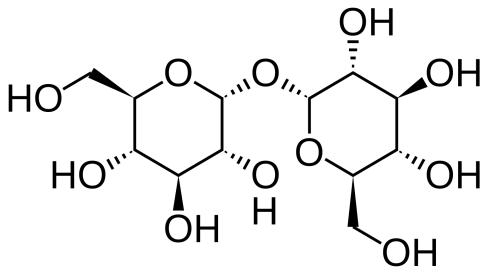
Panelists were asked to ranked the samples based on increasing smoothness

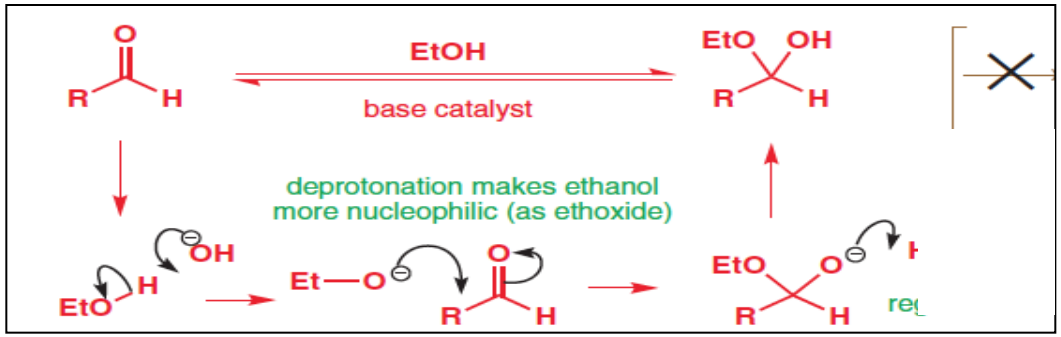
Karkov pH 3 <Karkov pH 3 SH < Karkov pH 8 < Karkov pH 8 SH

(Kokkinidou and Peterson, Manuscript in Preparation)

Alternative Ingredients: Alcohols

- Trehalose was examined as a potential carbonyl scavenger when in combination with pH modifiers.
  - Nucleophilic under alkaline conditions-more reactive towards electrophilic carbonyls such as aldehydes.
  - GRAS status, naturally occurring sweetener
- The disaccharide was added at 0.2%
  - Degree of difference test





(Kokkinidou and Peterson, Manuscript in Preparation)

Sensory Evaluation: pH, Trehalose

Average smoothness rating of commercial Karkov vodka and treatments

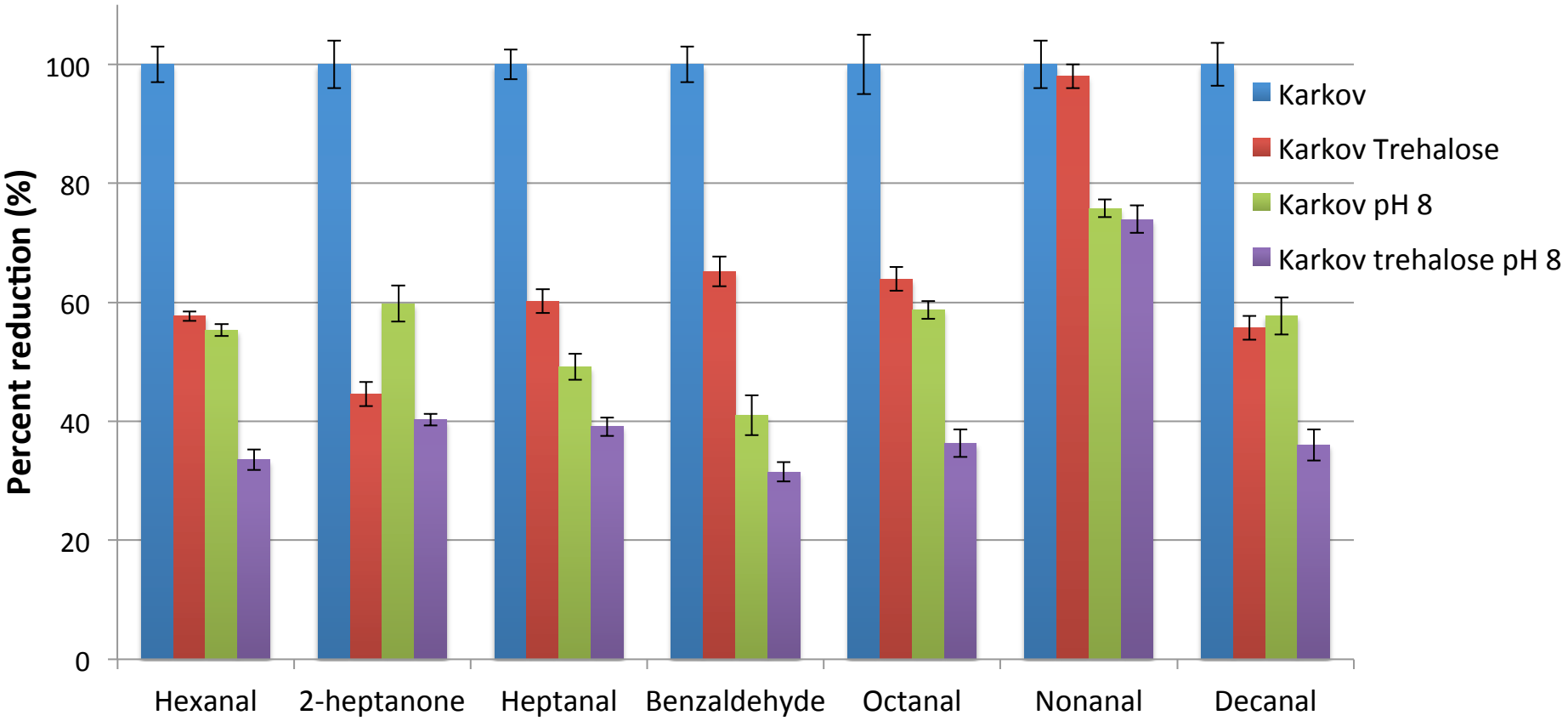
Sample	Rating
Karkov	1.40[a]
Karkov trehalose	3.40[b]
Karkov pH 8.00	8.00[c]
Karkov pH 8.00 trehalose	9.40[d]

Different letters indicate statistically significant difference determined by one-way ANOVA analysis

- addition of trehalose significantly ($p<0.05$) increased smoothness perception and reduced trigeminal burn

(Kokkinidou and Peterson, Manuscript in Preparation)

Effect of Trehalose: Carbonyl Species



Reduction of carbonyl species correlates with sensory data

Karkov trehalose pH 8 >Karkov pH 8> Karkov trehalose > Karkov

(Kokkinidou and Peterson, Manuscript in Preparation)

Brandy: Modifying Smoothness

Sample	Rating
E&J VS brandy (pH 4.35) (blind control)	0.90[a*]
E&J VS brandy pH 7.00	5.50[b]
E&J VS brandy pH 7.00-trehalose	7.00[b]

Different letters indicate statistically significant difference determined by one-way ANOVA analysis. * Sample was not significantly different than control

Sample	Rating
E&J VS (pH 4.35) (blind control)	0.90[a*]
E&J VS (pH 4.35)-CNA-VNL	-1.70[a]
E&J VS pH 7.00-CNA-VNL	8.20[b]
E&J VS pH 7.00-CNA-VNL-trehalose	9.40[b]

Different letters indicate statistically significant difference determined by one-way ANOVA analysis. * Sample was not significantly different than control. CNA: cinnamic aldehyde. VNL: vanillin.

(Kokkinidou and Peterson, Manuscript in Preparation)

Applications: Alcohol Burn/Smoothness

- Beverages
  - spirits, wine, beer, etc.,
    - *Design smoothness*
- Oral care and hygiene products
  - mouth wash
- Pharmaceuticals
  - cough medicine

Thank you