Flavor Origins in Distilled Spirits: From Start To Finish

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Outline

Flavor Notes/YOU/ & A Little Chemistry
Sensory Classes - Aromas/Flavors
Water [Taints & Off-flavors]
Raw Materials
>> Types/Classes of Spirits
Process
  Including Aging/Maturation
Origin of flavor species/flavor terminology
Manipulation & survival of the key notes.

Your Current Perspective

Imagine your favorite tipple

What one flavor term or word comes to mind as you contemplate it?

What is your first aroma (smell) or flavor impression?

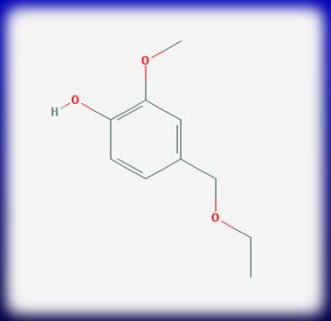
Hold that thought - we begin!

Proposed General Flavor Categories

1 Pungent	12 Soapy (Fatty, cheesy)
2 Solvent	13 Sour
3 Spicy	14 Buttery
4 Grainy	15 Grassy
5 Malty	16 Oily
6 Fruity (estery)	17 Sweet
7 Fruity (other)	18 Pine-like
8 Orange-like	19 Minty
9 Lemon-like	20 Bitter
10 Floral	21 Dry
11 Vanilla	22 Burnt/Maillard/Complex

The Flavors/Classes

Acids & Fatty Acids
Alcohols : Ethanol and Fusel Alcohols
Aldehydes : Acetaldehyde
Esters – Aliphatic
Esters – Aliphatic-Aromatic
Ethers: [Wood related]
Ketones
Lactones
Phenols
Sulfurs-sulfides
Terpenes
and more…….



Origins of Flavors

- Water
- Raw Materials
- Yeast & Fermentation
  - Microbial Flavors: –
    - desirable use other organisms
    - contaminant organisms
- Stills, shape-structure, materials
- Maturation/Aging

Water

- pH
- Minerals

[Ca^{++}, Mg^{++}, Zn^{++}, Fe^{++}/Fe^{+++}]

- Taints

Taints & Off-flavors: Taints Defined

TAINT (“off-flavor”)

- Chemical >> imparts a flavor - unacceptable (atypical)
- Alien to all foods
- May include components (flavors or aromas) from air, water, packaging materials, processing lines.
- May also be a microbial metabolic product - derived from disinfectants and sanitizers.

From water/tainted grains/contaminated raw materials (moldy grains, fruits or sweeteners, etc.)

Taints & Off-flavors: Off-flavors Defined

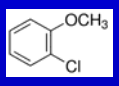
OFF-FLAVOR ("true off-flavor")

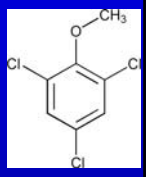
- Arises from a chemical reaction of a naturally occurring component in a beverage
- (or through internal deteriorative changes)
- Gives rise to an atypical compound →
  - Undesirable or unexpected taste.
- May be a microbially-derived flavor note →
  - A metabolic by-product or via autolysis of the organisms
  - (yeast autolysis)
  - (oxidative production of rancid fatty notes)

Taints from water

Chloroanisoles (moldy – musty) from methylation of chlorophenols in water supplies.

[2 or 3 or 4 or 2,4,6-chloroanisoles)



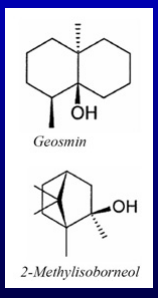


Geosmin – (trans-1, 10-dimethyl-trans-9 decalol) (earthy, musty, beetroot-like) - **cyanobacteria** (**blue-green** algae). Algal blooms – seasonal.

[Also 2 – methylisoborneol earthy-musty]

These compounds

- Extremely low flavor threshold
- Difficult to remove
- Persist to final product if present upfront



Raw Materials

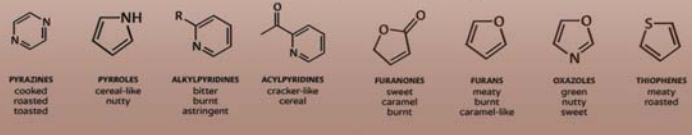
- Barley
- Corn
- Rye
- Wheat
- Grapes
- Stone Fruits
- Potatoes
- Agave
- Molasses/Sugar Cane
- Botanicals

Grains & Beyond: The Maillard Reaction

The Maillard Reaction

> Reactions between sugars and amino acids
> Occurs during roasting/kilning of malts
> Occurs during the process and heat of distillation
> Occurs in toasting/charring of barrels
> Non-enzymatic "Browning Reactions"
> Optimal at 140-165 °C

"cooked, roasted, toasted, bready, cereal-like, nutty, bitter, burnt, astringent, cracker-like, sweet, caramel, meaty, biscuit, even coffee-like, pretzel and chocolate-like, green and woody"



Malt Derived Flavors Brewing/Distilling?

Green malt: Green, grassy, green pea.

Lager malt: Green, malty, nutty, sweet.
[Vienna: malty, biscuit notes.]
[Munich: sweet, malty, biscuit, toast and graham cracker]

Pale ale malt: Malty, nutty, biscuity, sweet, toasted.
[Mild malt: toasty and biscuit character]

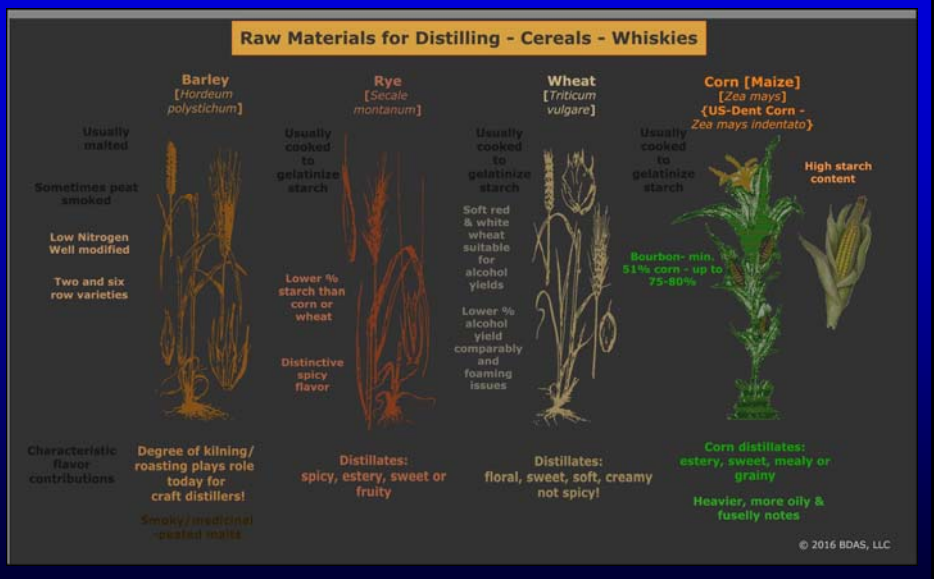
Caramelised:
Caramalt: Sweet, caramel [Carabrown: toastiness with biscuit, nut and graham cracker notes.]
Crystal (Caramel in the US): Sweet, caramel, stewed fruit, toffee, black treacle, burnt. {Different types at different degrees color from kilning – different flavor spectrum. High Lovibond color leads to pronounced caramel flavors of burnt sugar, raisins and prunes}.

Roasted (dry):
Amber malt: Biscuity, baked, malty, bitter
Chocolate malt: Dark, chocolate, cocoa, bitter, burnt, sharp
Black malt: Burnt, black coffee, roasted coffee, sharp, acrid
Roasted barley (unmalted): Burnt, sharp, acrid, dry, black coffee, dark chocolate

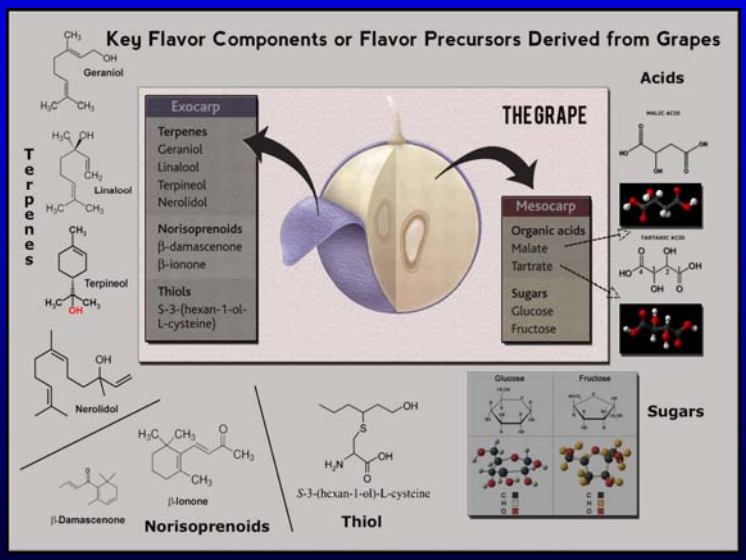
Smoked malts: Strong wood smoke aroma – flavor- sweet, ashy, smoky and earthy. [Cherry wood, Apple wood etc., conveying different nuances.]
Peat Smoked malt: Strong phenolic, whisky-like smoke aroma

Acidulated malts: [Note historically used to alter pH of brewing water in German brewing] Sour, tangy, tart and lactic –e.g., for sour beer styles

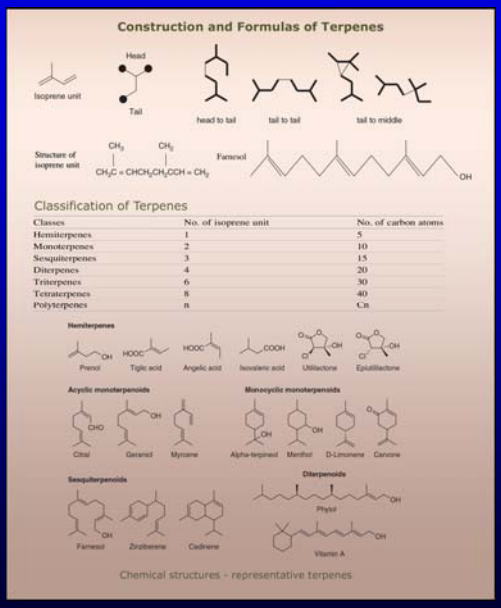
Cereals and Derived Flavors



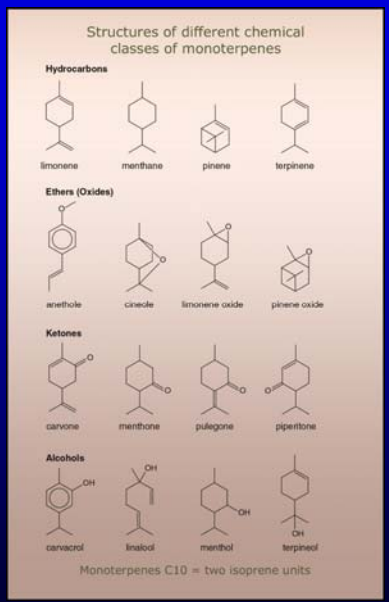
Grapes & Flavors + Terpenes (Gins)



Chemistry & Formulas – Terpenes: Classes



More Terpene Chemistry

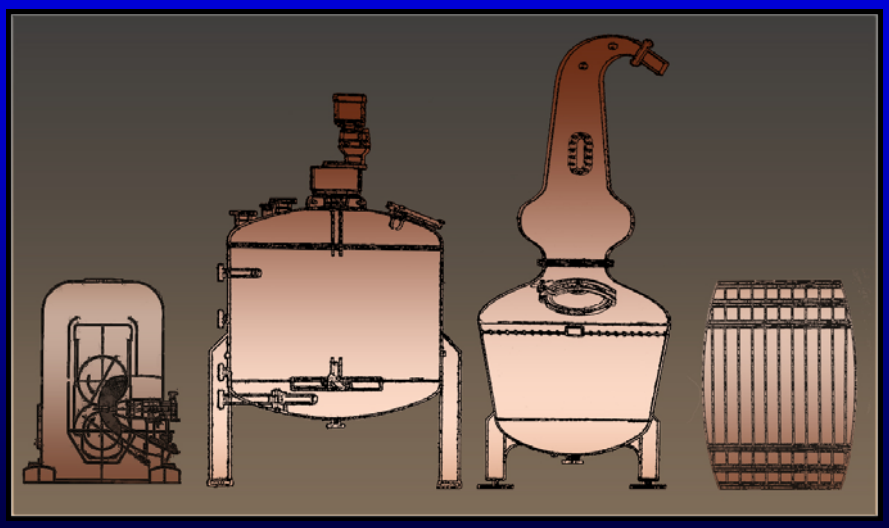


Terpenes and Aromatics

Monoterpenes and their aromatic properties

Compound	Odor
Borneol	Woody-camphoraceous, dry-minty
Isoborneol	Camphoraceous, weak peppery and woody
Camphene	Camphoraceous, mild-oily
Camphor	Camphoraceous, fresh, warm-minty, ethereal
δ-3-Carene	Resinous, sweet, refined-limonene-like, spicy
Carveol	Fresh, caraway- and spearmint-like
S-(+)-Carvone	Spicy, caraway-like
R-(−)-Carvone	Spearmint-like
Citronellal	Minty, citrus-like
Citronellol	Floral, roselike
Cumin aldehyde	Sharp, acid, pungent, woody, oily
Cuminyl alcohol	Floral, oily-spicy, dillseed- and caraway-like
Cymen-8-ol	Weak citrus-like
p-Cymene	Fresh, weak citrus-like, lemon and bergamot notes
Geranial	Lemon, sweet
Geraniol	Floral, lemonlike, minty
Limonene	Fresh, citrus-like, mild lemon and orange notes
Linalool	Fresh, floral, clean, sweet, lemon notes
Myrcene	Mild, sweet, balsamic, plastic note
Neral	Sweet, lemon
Nerol	Rose, sweet
cis-β-Ocimene	Herbal, warm-herbaceous, sweet-floral, neroli-oil-like
trans-β-Ocimene	Herbal, weak floral
α-Phellandrene	Spicy, herbaceous, minty, peppery-woody, fresh, citrus
β-Phellandrene	Peppery, minty, refreshing, citrus-like
α-Pinene	Pine-like, sharp, woody, turpentine-like
β-Pinene	Dry-woody, pine-like, resinous-terpene-like, spicy
Piperitone	Fresh, minty, camphoraceous
Sabinene	Warm, oily-peppery, woody-herbaceous, spicy
cis-Sabinene hydrate	Mild, pleasant, warm, woody-balsamic
trans-Sabinene hydrate	Warm, balsamic-woody, mild
Terpinen-4-ol	Nutmeg-like, spicy, woody-earthy, liliac-like
α-Terpinene	Refreshing, lemon-citrus-like
γ-Terpinene	Fresh-herbaceous, citrus-like
α-Terpineol	Floral, liliac-like
Terpinolene	Sweet-pincy, oily, petroleum-like
α-Thujene	Green, herbal, woody

Spirits Production: Process



Spirits Production: Process

- OVERVIEW
- Milling/Mashing
- Fermentation
- Distillation/Stills
- Botanicals
- Wood Aging or Maturation
- Blending/Bottling and Stability
  [Visual problems hazes etc.]

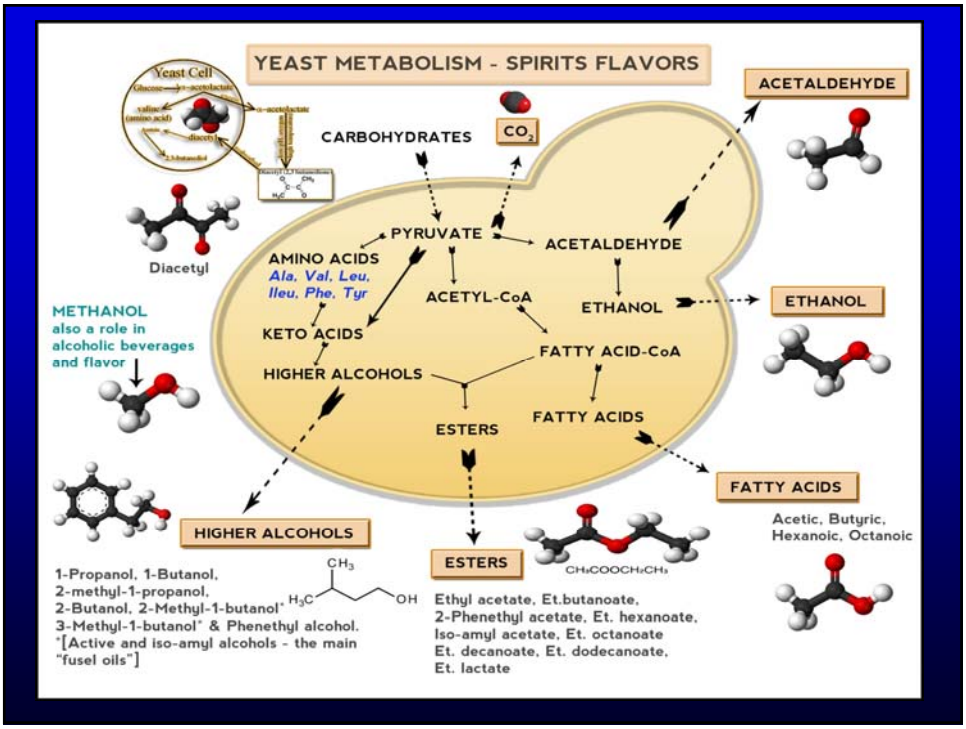
Fermentation

- Yeast and Fermentation
  - > Most important source congeners or
  - congener precursors
  - > Conditions important/yeast strain
- Microbial contaminants

BOURBON: Yeast strains selected for producing congeners (flavor) not alc. yield. Enough need to produce 6%+

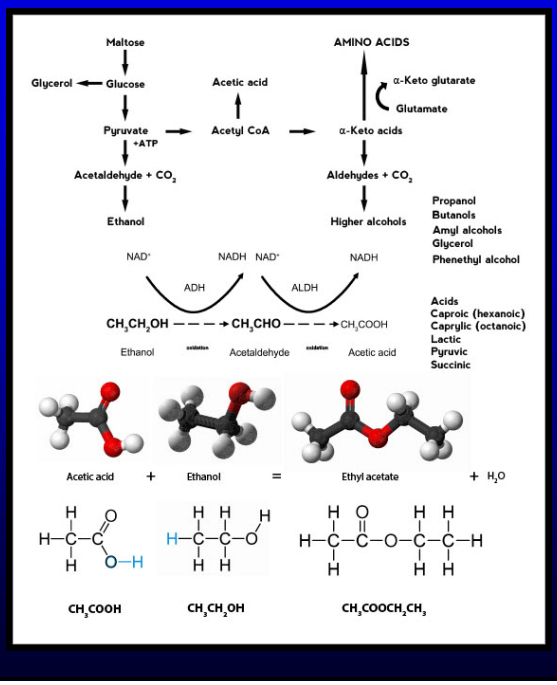
Fermentation - Congeners

- **Congeners production:**
  - **Yeast & flavor metabolism – volatile congeners:**
  - **Rise with inc. in inoculation size**
  - **Rise with inc. in agitation**
  - **Rise with higher ferment'n temp**
  - **Any inc. in ferment'n rate favors congener production**



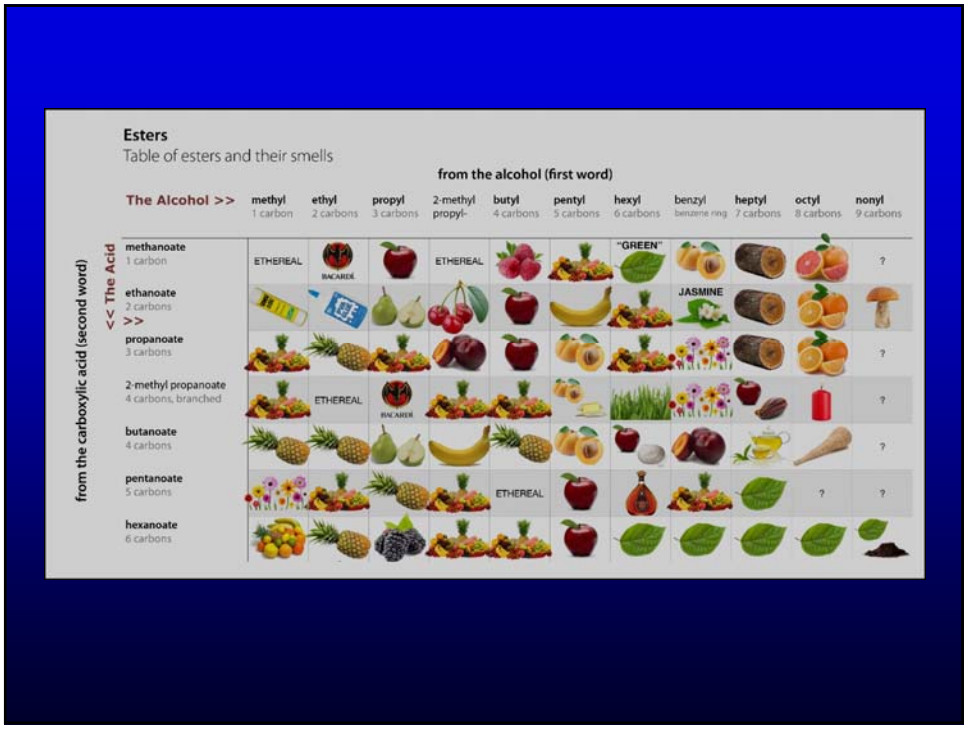
Of Acids, Alcohols and Esters

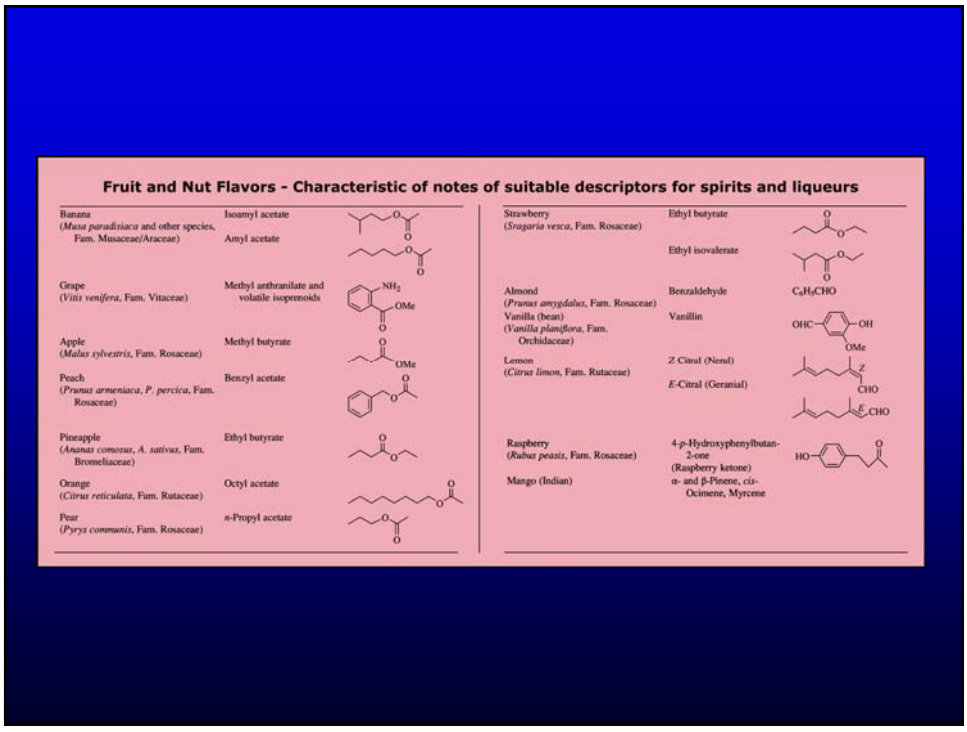
- **Esterification:**
  - Condensation of an acid & an alcohol
  - Important flavor contributions
  - Produced during fermentation
  - Manipulated during distillation
  - Changed during maturation



Esters: From acidic, rancid & harsh solvent "bad" notes to desired & pleasing sweet, fruity & floral notes

Acid	Flavor	Alcohol	Flavor	Ester	Flavor
-COOH		-OH			
Acetic	Vinegar, Sour	Ethanol	Warm, Solvent	Et. acetate	Nail Polish Remover
Acetic	Vinegar, Sour	Isoamyl Alcohol [3me-BuOH]	Alcohol, fusel oil, nail polish, pungent.	Isoamyl acetate	Banana, pear
Butyric acid	Rancid, sharp cheese, buttery, baby vomit, sour, spent grains	Ethanol	Warm, Solvent	Ethyl butyrate	Fruit, juicy fruit, pineapple-like, cognac
Hexanoic (Caproic acid)	Rancid, fatty, sweaty, cheese	Ethanol	Warm, Solvent	Ethyl caproate (hexanoate)	Red Apple, aniseed
Octanoate (Caprylic acid)	Oily, fatty soapy, waxy, goaty	Ethanol	Warm, Solvent	Ethyl caprylate	Apple-like
Decanoic acid	Soapy, waxy, fatty, fruity, rancid, sour, citrus	Ethanol	Warm, Solvent	Ethyl decanoate	Sweet, waxy, fruity, apple, soap
Dodecanoic (Lauric) acid	Fatty, coconut, bay oil	Ethanol	Warm, Solvent	Ethyl dodecanoate	Oily, fatty, floral and fatty-fruity
Lactic acid	Sour, sour milk, yogurt	Ethanol	Warm, Solvent	Ethyl lactate	Fruity, strawberry, mild buttery, creamy hint coconut
n-Propanol	Alcohol, ripe fruit	Ethanol	Warm, Solvent	Ethyl propanoate	Sweet fruity rum-like, juicy fruit, pineapple
3-Phenyl propionic acid	Rose, sweet sl. vanilla -like	Ethanol	Warm, Solvent	Ethyl-3-phenylpropanoate (ethyl hydrocinnamate)	Floral, hyacinth, rose, honey, fruity, rum
Acetic	Vinegar Sour	2-Phenylethanol	Rose, sweetish, floral, perfumed	2-Phenethyl acetate	Roses, honey, sweet
Octanoate (Caprylic acid)	Oily, fatty soapy, waxy, goaty	Isobutanol (2-me-propanol, isobutyl alcohol	Alcohol, whiskey, nail polish, wine-like, fruity	Isobutyl octanoate (2-me-propyl octanoate)	Fruity, green oily, floral


Esters
Table of esters and their smells
from the alcohol (first word)
The Alcohol >>
methyl 1 carbon
ethyl 2 carbons
propyl 3 carbons
2-methyl propyl-
butyl 4 carbons
pentyl 5 carbons
hexyl 6 carbons
benzyl benzene ring
heptyl 7 carbons
octyl 8 carbons
nonyl 9 carbons
from the carboxylic acid (second word)
<< The Acid >>
methanoate 1 carbon
ethanoate 2 carbons
propanoate 3 carbons
2-methyl propanoate 4 carbons, branched
butanoate 4 carbons
pentanoate 5 carbons
hexanoate 6 carbons
ETHEREAL
BACARDI
"GREEN"
JASMINE
?


Fruit and Nut Flavors - Characteristic of notes of suitable descriptors for spirits and liqueurs
Banana (Musa paradisiaca and other species, Fam. Musaceae/Araceae)
Isoamyl acetate
Amyl acetate
Grape (Vitis venifera, Fam. Vitaceae)
Methyl anthranilate and volatile isoprenoids
Apple (Malus sylvestris, Fam. Rosaceae)
Methyl butyrate
Peach (Prunus armeniaca, P. percica, Fam. Rosaceae)
Benzyl acetate
Pineapple (Ananas comosus, A. sativus, Fam. Bromeliaceae)
Ethyl butyrate
Orange (Citrus reticulata, Fam. Rutaceae)
Octyl acetate
Pear (Pyrus communis, Fam. Rosaceae)
n-Propyl acetate
Strawberry (Srugaria vesca, Fam. Rosaceae)
Ethyl butyrate
Ethyl isovalerate
Almond (Prunus amygdalus, Fam. Rosaceae)
Benzaldehyde
Vanilla (bean) (Vanilla planiflora, Fam. Orchidaceae)
Vanillin
Lemon (Citrus limon, Fam. Rutaceae)
Z Citral (Neral)
E-Citral (Geranial)
Raspberry (Rubus peazis, Fam. Rosaceae)
4-p-Hydroxyphenylbutan-2-one (Raspberry ketone)
Mango (Indian)
α- and β-Pinene, cis-Ocimene, Myrcene

Distillation

Distillation: What happens?

- 1) Concentrates aromas
- 2) Selects certain fractions
  - Extent of heads and tails removed during first cut/ # of distillations, recycling of cuts
- 3) Forms new compounds
  - Favorable
  - Unfavorable VOLATILES!
    - Formed
    - Eliminated

Conditions and Reactions

- 1) Heat – cooking
  - Temperature
  - Acidity
  - Duration
  - Role of Copper
- 2) Hydrolysis reactions
  - Esters
  - Terpenes
- 3) Maillard reactions
  - Aldehydes and acetals – Strecker degradation rxns
  - Furfural and derivatives from sugars
- 4) New compounds formed
  - Furans – Pyridines – Pyrazines (cocoa, grilled nuts notes)

Distillation - Stills

- (Pot or Column): shape-structure, materials (copper)
- Operation of (The art & skill of each distiller):
  - Extent of heads and tails removed during first cut/ # of distillations, recycling of cuts
- Different flavors/different concentrations from Continuous distillation?

Stills & Copper

- DISTILLATION & Copper:
  - Aerated wash – more reactive with copper surfaces of the stills -- reduces the amount of sulfury off-notes
  - Soluble copper compounds and complexes form with oxygenated mash that react with and remove sulfur compounds
  - Location of copper as most sulfur removal occurs at phase change

Heads or Tails?

- Heads (Fore-shots):
  - SO2, Acetaldehyde, Ethyl acetate
- Tails (Feints or After-shots):

Cutting out the fats

Ethyl esters of caprylic and caproic acids

Caproic (C6), Caprylic C8) and Capric (C10) acids

Fatty acids: Soapy, goaty, fatty aromas

Ethyl esters: Sweet, fruit, oily

Maturation – Complexity Simply Defined!

"The specific combination of one type of distillate with any one type of cask leading to the development of a flavor profile relative to time"

The Cask or Barrel

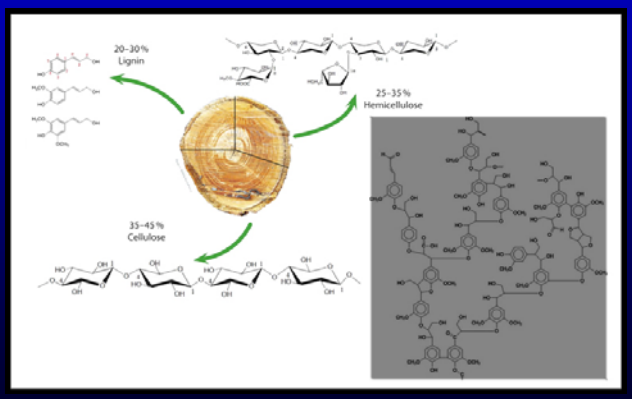
Maturation

- Maturation Time, rxns, temperature
- Fill strength-extraction
- Wood composition & preparation (toast/char)
  - Casks: #Times used/Previous contents!
- New compounds – flavor congeners in maturing spirit

  Storage wooden casks gives rise to whisky lactone, vanillin, guaiacol, eugenol, cresols >> migrate from the wood to the spirit
- Loss of Compounds (e.g., sulfurs lost)

Aging: Wood Extractives

- Lignin derivatives (vanillin)
- Lactones (methyl octalactones)
- Furanic derivatives (furfural etc.)



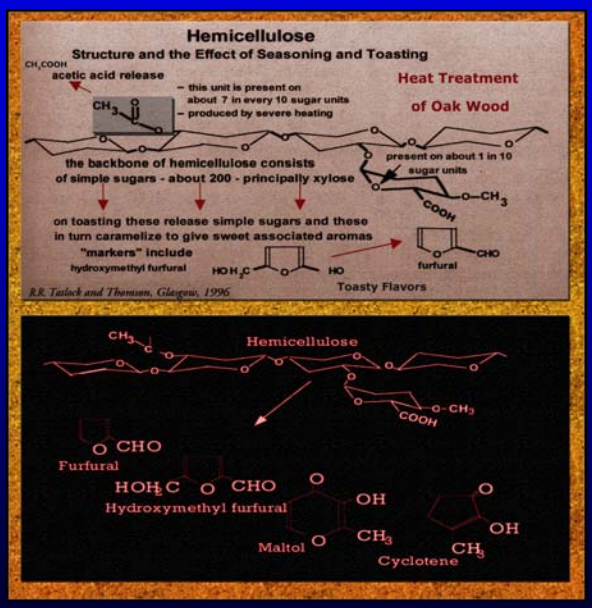
Aging: Oxidative Reactions

- Increase in methyl ketones – β-oxidation fatty acids from new-make spirit
- Formation of Acetaldehyde & Ethyl Acetate through oxidation of Ethanol
- Formation of acetals – top notes!

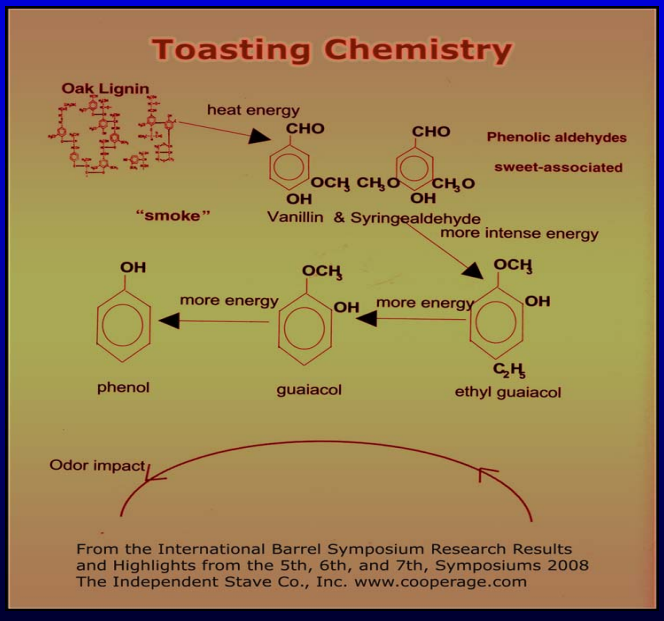
Aging: Evaporation & Chemical Balance

- Due to evaporation the equilibrium balance changes
- Ethanol ⇩ due to the evaporation
- Higher alcohols (less volatile) ⇧
- Higher alcohol esters ⇧ Due to Transesterification
- Interactions between spirit and wood compounds:
  - Esters formed (ethyl vanillate, ethyl syringate)
  - Ethers formed (vanillin ethyl ether, etc.)

Heat Treated Oak Wood = Toasty Notes!



Role of Toasting of Oak in Spirits Flavor Extraction



Remember The Maillard Reaction?

The Maillard Reaction

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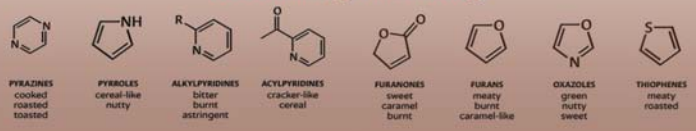
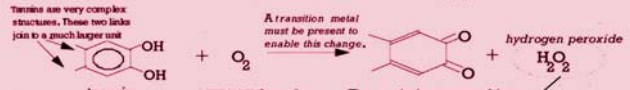


Role of Oak Tannins in Maturation of Spirits

The role of oak tannins in oxidation of wines and spirits

STEP 1 IN CASK DRIVEN OXIDATION - tannins activate oxygen

Tannins are very complex structures. These two links join to a much larger unit



tannin

oxygen from the air (penetrating into the wood)

The tannin is converted into a quinone, most of these are brownish in color.

STEP 2 IN CASK DRIVEN OXIDATION - some alcohol is converted to acetaldehyde

C_2H_5OH + H_2O_2 → CH_3CHO + $2H_2O$

ethyl alcohol

acetaldehyde — Green, unripe, raw aroma. Very reactive.

water

STEP 3 IN CASK DRIVEN OXIDATION - diethyl acetal is produced

C_2H_5OH + CH_3CHO → $CH_3CH(OC_2H_5)_2$ + H_2O

more ethyl alcohol

diethyl acetal — Delicate, light, fragrant. Gives top-note.

water

Do Casks provide enzyme type active sites bringing molecules close to react more rapidly than in solution?

From the International Barrel Symposium May 1997
The Independent Stave Co., Inc. www.cooperage.com

Transesterification

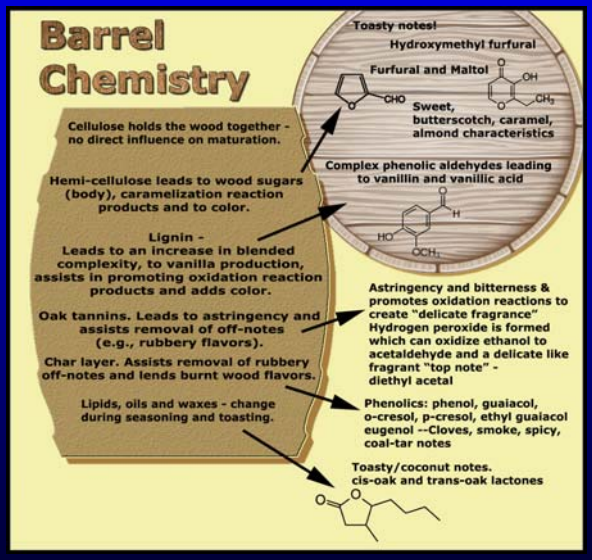
Transesterification

[Occurs during wood maturation of spirits]

One ester converted to another!

"A reaction between an ester of one alcohol and a second alcohol
Forms an ester of the second alcohol and an alcohol from the original ester
E.G., Methyl acetate and EtOH --> ethyl acetate and methyl alcohol"

Barrel Chemistry - Summarized

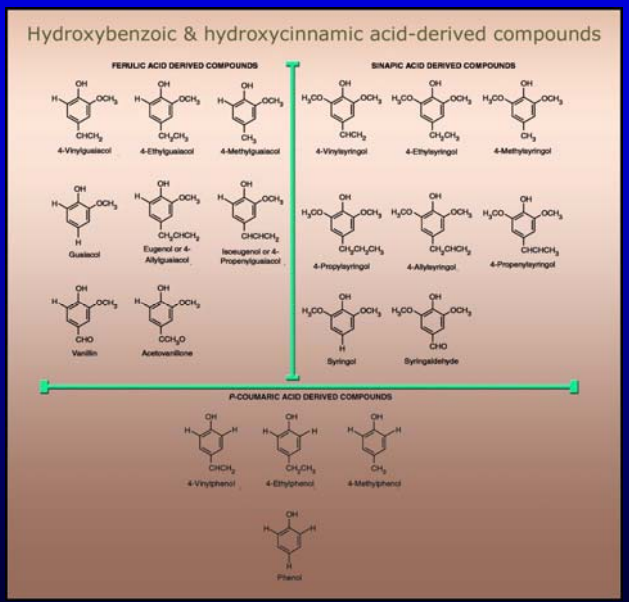


So Who is in the Wood?

- Acids – hint of vinegar!
- Aldehydes – leafy & floral
- Sulfury – meaty & rubbery
- Oily – nutty butter anyone?
- Sweet – honey & vanilla – nice!
- Woody – resiny & piney
- Lactones – coconut & more
- Phenolics – wood smoke, cloves & medicinal
- Feint of heart – a tail here? – leather & tobacco & goats?
- Don't lose your heads. Estery – fruity & fragrant

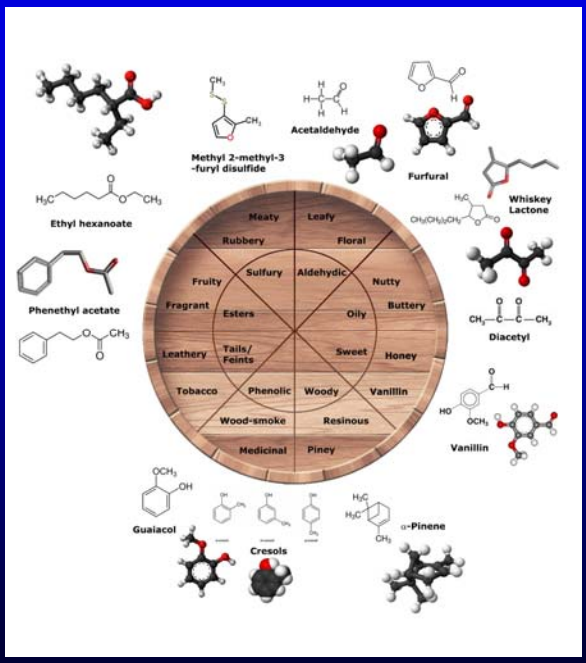
A lot goes into the barrel
A lot of action goes on in the barrel – who goes where – who goes there?
Who stays to play with your taste buds & delight your aroma sensors?

Hydroxy- acids and Phenols from Oak



Toasted Oak Wood-Derived Aromatic Impact Compounds

Compound	Odor/Flavor Descriptor
Furfural	Smoky, almond
Guaiacol	Smoky
cis-Methyl-γ-octalactone/ trans-Methyl-γ-octalactone	Oak, wood
Vinylguaiacol	Phenolic, clove
4-Methylguaiacol	Smoky, burnt wood
4-Ethylguaiacol	Smoky phenolic
4-Ethylphenol	Stable-like, horse
Eugenol	Spicy Clove
Vanillin	Vanilla spicy
o-Cresol	Medicinal. tar
m-Cresol	Medicinal. smoky



Your Present Perspective

You Imagined Your Favorite Tipple

You Defined a Flavor Term or General Descriptor That Came to Mind

Did you Find An Answer to What it Might Be [Chemically] Today?

If So or If Not Continue to Discover More About Flavor Chemistry of Spirits, Liqueurs and Your Other Favorite Foods & Beverages!

DISTILLED SPIRITS AND KEY FLAVORS:

SMELLING ROSES, FRUIT, STINKY FEET AND MUCH MORE IN MY GLASS

WRITTEN BY GARY SPEDDING, PH.D. & JOHNNY JEFFERY, M.S.

Artisan Spirit Fall 2015 PP 53-58

The understanding of the flavor of distilled spirits forms an (CH$_3$CH$_2$OH) itself is a solvent and confers tactile sensations of

TABLE 1:

FLAVORS ASSOCIATED WITH THE PRODUCTION OF DISTILLED SPIRITS
THE GOOD, THE BAD AND SOMETIMES THE UGLY

FLAVOR NOTE	TYPICAL DESCRIPTORS	FLAVOR THRESHOLDS*	COMMENTS AND NOTES
Acetaldehyde CH$_3$CHO (Ethanal)	Green apples, bruised apples, grassy, latex paint, Florists shop (green stems, cut grass), melon, pumpkin, ethereal.	10-25 ppm. (Range in spirits 8-240 ppm. Whiskies (incl. Bourbon): 16-100, Brandies: 52-240, Rum: 8-60 ppm.)	Originates from poor/stressed fermentations and from oxidation aging reactions in the wood. May also arise from bacterial contamination (incl. Acetobacter). Oxidative formation of acetaldehyde from ethanol or from reduction of acetic acid may occur during maturation. However, most aldehydes are formed during fermentation.
Acetic acid CH$_3$COOH (Ethanoic acid, Acetate in the anion form)	Vinegar-like, pungent, sour, acidic	100-200 ppm?	Acetic acid is the major component of the total acids in matured spirits. It may be produced from ethanol via acetaldehyde during maturation. It can also be a bacterial contamination issue. Acetic acid also has a key role in fatty acid metabolism and in ester formation (See Esters).
Acrolein CH2CCHO (Acraldehyde, Acrylic aldehyde)	Piercing, disagreeable odor, peppery, hot/acrid, horseradish. Lachrymator (irritant causes tearing). Known by the term "pepper" by grain alcohol distillers.	Threshold in water – 0.04 ppm. (10 ppm in low proof distillates?)	A low boiling point compound – readily detectable as a pungency in spirits. Often noted in poorer quality GNS (grain neutral spirit). Some lactobacilli convert glycerol excreted by yeast into 3 or β-hydroxypropionaldehyde (peppery note) which is then converted to acrolein by the heat of distillation. Some acrolein is always produced from glycerol in pot still distillation. Acrolein has been reported to disappear over two-three years of aging to yield a less flavorful compound.

Wish to learn more about AROMA/FLAVOR?

The Team at BDAS, LLC

END

Flavor Origins in Distilled Spirits: From Start To Finish

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