



Flavor Origins in Distilled Spirits: From Start To Finish

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www.alcbevtesting.com

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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 tippie

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

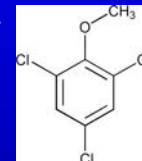
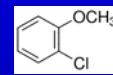
(yeast autolysis)

(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.

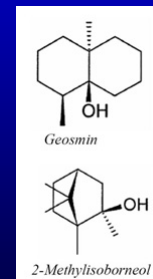
[Also 2 – methylisoborneol earthy-musty]

These compounds

Extremely low flavor threshold

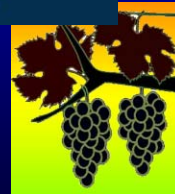
Difficult to remove

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"



PIRAZINES
cooked
roasted
toasted



PYRROLES
cereal-like
nutty



ALKYLPYRIDINES
bitter
burnt
astringent



ACYLPYRIDINES
cracker-like
cereal



FURANONES
sweet
caramel
burnt



FURANS
meaty
burnt
caramel-like



OXAZOLES
green
nutty
sweet



THIOPHENES
meaty
roasted

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

Raw Materials for Distilling - Cereals - Whiskies

	Barley [<i>Hordeum polystichum</i>]	Rye [<i>Secale montanum</i>]	Wheat [<i>Triticum vulgare</i>]	Corn [Maize] [<i>Zea mays</i>] {US-Dent Corn - <i>Zea mays indentata</i> }
Usually malted	Usually malted	Usually cooked to gelatinize starch	Usually cooked to gelatinize starch	Usually cooked to gelatinize starch
Sometimes peat smoked	Sometimes peat smoked			High starch content
Low Nitrogen Well modified	Low Nitrogen Well modified	Lower % starch than corn or wheat	Soft red & white wheat: suitable for alcohol yields	Bourbon- min. 51% corn - up to 75-80%
Two and six row varieties	Two and six row varieties	Distinctive spicy flavor	Lower % alcohol yield comparably and foaming issues	
Characteristic flavor contributions	Degree of kilning/roasting plays role today for craft distillers! Some traditional peated malts	Distillates: spicy, estery, sweet or fruity	Distillates: floral, sweet, soft, creamy not spicy!	Corn distillates: estery, sweet, mealy or grainy Heavier, more oily & fuselly notes

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Grapes & Flavors + Terpenes (Gins)

Key Flavor Components or Flavor Precursors Derived from Grapes

Terpenes

- Geraniol
- Linalool
- Terpineol
- Nerolidol
- β -Damascenone
- β -Ionone

Exocarp

- Terpenes
- Geraniol
- Linalool
- Terpineol
- Nerolidol
- Norisoprenoids
- β -damascenone
- β -ionone
- Thiols
- S-3-(hexan-1-yl)-L-cysteine

Mesocarp

- Organic acids
- Malate
- Tartrate
- Sugars
- Glucose
- Fructose

Acids

- Malic Acid
- Tartaric Acid

Sugars

- Glucose
- Fructose

Norisoprenoids

- β -Damascenone
- β -Ionone

Thiol

- S-3-(hexan-1-yl)-L-cysteine

<http://www.compoundchem.com/category/alcohol-chemistry/>

THE CHEMISTRY OF GIN

COMPOUND GIN
Compound gins are made from a variety of botanical ingredients and are often used in gin and tonics.

POT-DISTILLED GIN
Pot-distilled gins are made from a variety of botanical ingredients and are often used in gin and tonics.

COLUMN-DISTILLED GIN
Column-distilled gins are made from a variety of botanical ingredients and are often used in gin and tonics.

Gin comes in a number of different varieties, with widely varying chemical compositions. This stems from the different botanical ingredients that can be included. All gins must be primarily flavoured by juniper berries, but many other ingredients, including coriander, dry citrus peel, almonds, and nutmeg, can also be incorporated.

JUNIPER BERRY COMPOUNDS

Juniper berry compounds are responsible for the characteristic piney flavor of gin. They are primarily terpenes, with the most prominent being alpha-pinene and sabinene.

CORIANDER COMPOUNDS

Coriander compounds are responsible for the characteristic citrusy flavor of gin. They are primarily terpenes, with the most prominent being linalool and linalyl acetate.

TONIC WATER

Tonic water is a beverage that is often served with gin. It is typically made from a variety of botanical ingredients, including quinine and sweetener.

CASTELGY LONDON DRY GIN

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Chemistry & Formulas – Terpenes: Classes

Construction and Formulas of Terpenes

Structure of isoprene unit: $CH_2=C(CH_3)CH=CH-CH_3$

Classification of Terpenes

Classes	No. of isoprene unit	No. of carbon atoms
Hemiterpenes	1	5
Monoterpenes	2	10
Scapolterpenes	3	15
Diterpenes	4	20
Triterpenes	6	30
Tetraterpenes	8	40
Polyterpenes	n	C _{4n}

Hemiterpenes

Ayclic monoterpenoids

Sesquiterpenoids

Diterpenoids

Chemical structures - representative terpenes

More Terpene Chemistry

Structures of different chemical classes of monoterpenes

Hydrocarbons

limonene menthane pinene terpinene

Ethers (Oxides)

anethole cineole limonene oxide pinene oxide

Ketones

carvone menthone pulegone pipertone

Alcohols

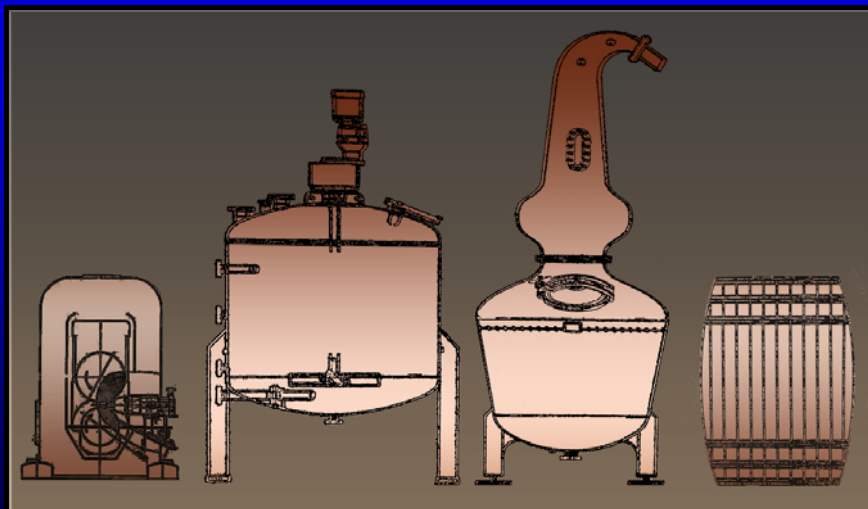
carvacrol linalool menthol terpineol

Monoterpenes C₁₀ = two isoprene units

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
α -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, rose-like
Cumin aldehyde	Sharp, acid, pungent, woody, oily
Cuminyl alcohol	Floral, oily-spicy, dilliced- and caraway-like
Cymen-8-ol	Weak citrus-like
<i>p</i> -Cymene	Fresh, weak citrus-like, lemon and bergamot notes
Geraniol	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
<i>cis</i> - β -Ocimene	Herbal, warm-herbaceous, sweet-floral, neroli-oil-like
<i>trans</i> - 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
<i>cis</i> -Sabinene hydrate	Mild, pleasant, warm, woody-balsamic
<i>trans</i> -Sabinene hydrate	Warm, balsamic-woody, mild
Terpinen-4-ol	Stimulating, spicy, woody-fatty, lilac-like
γ -Terpinene	Refreshing, lemon-citrus-like
δ -Terpinene	Fresh-herbaceous, citrus-like
α -Terpinolol	Floral, lilac-like
Terpinolene	Sweet-piney, 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.]

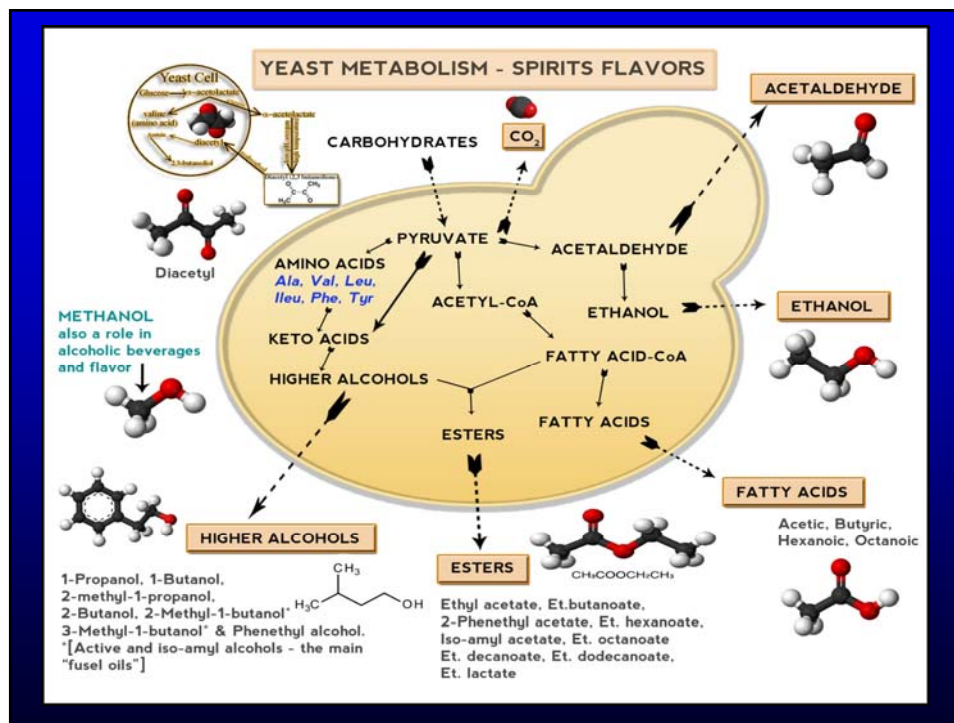
Fermentation

- 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

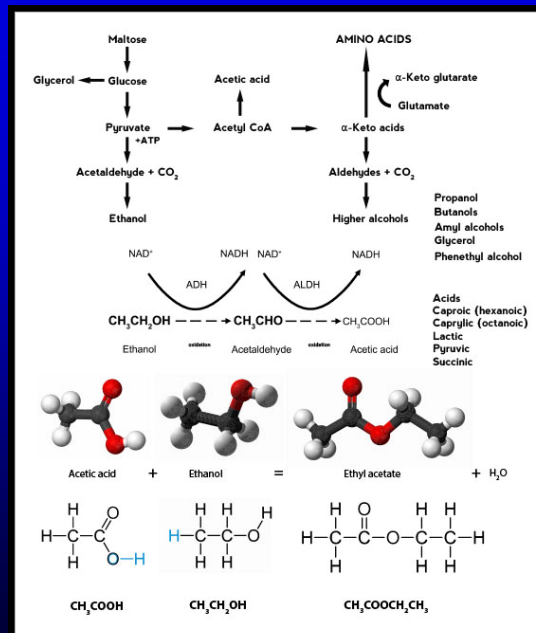
- **Congeners production:**
 - **Yeast & flavor metabolism – volatile congeners:**
 - **Rise with inc. in inoculation size**
 - **Rise with inc. in agitation**
 - **Rise with higher ferment'n temp**
 - **Any inc. in ferment'n rate favors congener production**



Of Acids, Alcohols and Esters

o 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 st. 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)

	methyl 1 carbon	ethyl 2 carbons	propyl 3 carbons	2-methyl propyl 4 carbons	butyl 4 carbons	pentyl 5 carbons	hexyl 6 carbons	benzyl benzene ring 7 carbons	heptyl benzene ring 7 carbons	octyl 8 carbons	nonyl 9 carbons
methanoate 1 carbon	ETHEREAL	ACIDIC	ETHEREAL	FRUITY	FRUITY	FRUITY	"GREEN"	FRUITY	FRUITY	FRUITY	?
ethanoate 2 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	JASMINE	FRUITY	FRUITY	FRUITY	?
propanoate 3 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
2-methyl propanoate 4 carbons, branched	ETHEREAL	ACIDIC	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
butanoate 4 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
pentanoate 5 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
hexanoate 6 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
heptanoate 7 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
octanoate 8 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
phenylacetate benzene ring + 2 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
nonanoate 9 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?
decanoate 10 carbons	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	FRUITY	?

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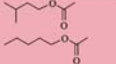
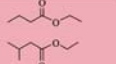
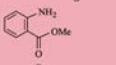
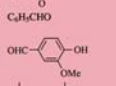
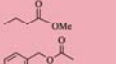
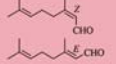
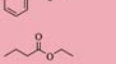
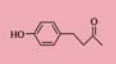
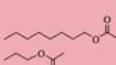


Esters

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- 4 carbons	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	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	"GREEN"	ETHEREAL	ETHEREAL	ETHEREAL	?
ethanoate 2 carbons	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	JASMINE	ETHEREAL	ETHEREAL	?
propanoate 3 carbons	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	?
2-methyl propanoate 4 carbons, branched	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	?
butanoate 4 carbons	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	?
pentanoate 5 carbons	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	?
hexanoate 6 carbons	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	ETHEREAL	?

Fruit and Nut Flavors - Characteristic of notes of suitable descriptors for spirits and liqueurs

Banana (<i>Musa paradisiaca</i> and other species, Fam. Musaceae/Araceae)	Isoamyl acetate Amyl acetate		Strawberry (<i>Fragaria vesca</i> , Fam. Rosaceae)	Ethyl butyrate Ethyl isovalerate	
Grape (<i>Vitis vinifera</i> , Fam. Vitaceae)	Methyl anthranilate and volatile isoprenoids		Almond (<i>Prunus amygdalus</i> , Fam. Rosaceae) Vanilla (bean) (<i>Vanilla planiflora</i> , Fam. Orchidaceae)	Benzaldehyde Vanillin	C_6H_5CHO 
Apple (<i>Malus sylvestris</i> , Fam. Rosaceae)	Methyl butyrate		Lemon (<i>Citrus limon</i> , Fam. Rutaceae)	Z-Citral (Neral) E-Citral (Geranial)	
Peach (<i>Prunus armeniaca</i> , <i>P. persica</i> , Fam. Rosaceae)	Benzyl acetate		Raspberry (<i>Rubus pratincola</i> , Fam. Rosaceae)	4-p-Hydroxyphenylbutan- 2-one (Raspberry ketone)	
Pineapple (<i>Ananas comosus</i> , <i>A. sativus</i> , Fam. Bromeliaceae)	Ethyl butyrate		Mango (Indian)	α- and β-Pinene, cis- Ocimene, Myrcene	
Orange (<i>Citrus reticulata</i> , Fam. Rutaceae)	Octyl acetate				
Pear (<i>Pyrus communis</i> , Fam. Rosaceae)	n-Propyl acetate				

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



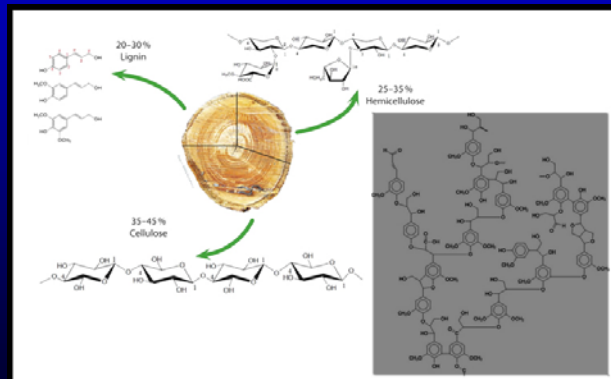
Maturation

- **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.)**



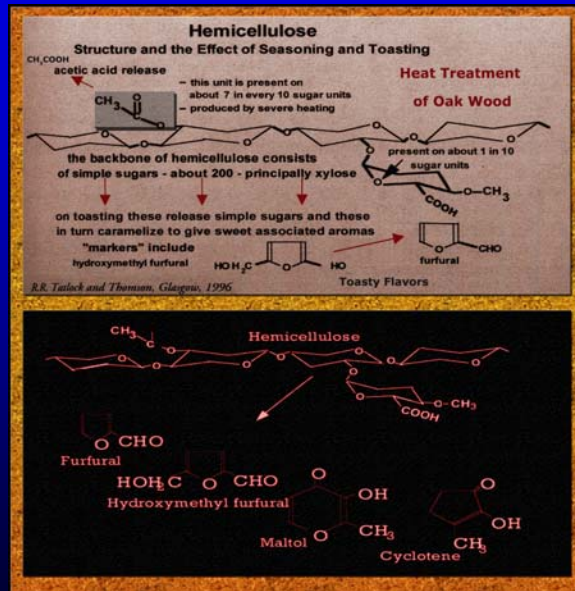
Aging: Oxidative Reactions

- 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!

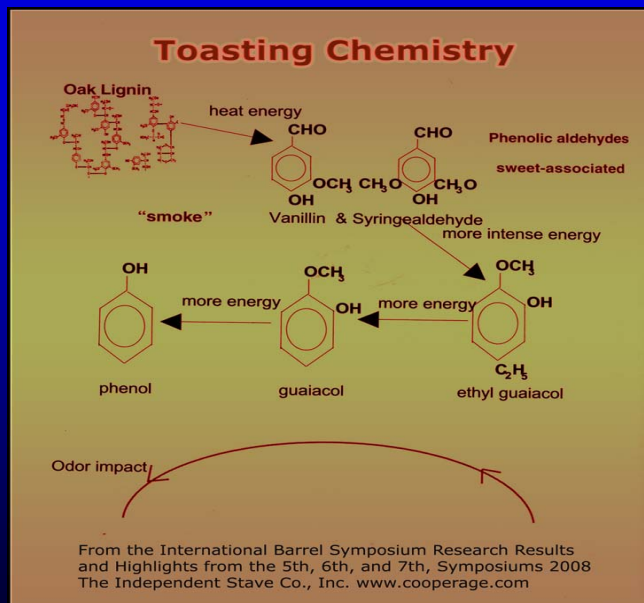
Aging: Evaporation & Chemical Balance

- 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

- > 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"

							
PYRAZINES cooked roasted toasted	PYRROLES cereal-like nutty	ALKYLPYRIDINES bitter burnt astringent	ACETYPYRIDINES cracker-like cereal	FURANONES sweet caramel burnt	FURANS meaty burnt caramel-like	OXAZOLES green nutty sweet	THIOPHENES meaty roasted

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

oxygen from the air (penetrating into the wood)

A transition metal must be present to enable this change.

hydrogen peroxide

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

$$C_2H_5OH + H_2O_2 \rightleftharpoons CH_3CHO + 2H_2O$$

ethyl alcohol acetaldehyde water

Green, unripe, raw aromas. Very reactive.

STEP 3 IN CASK DRIVEN OXIDATION - diethyl acetal is produced

$$C_2H_5OH + CH_3CHO \longrightarrow CH_3CH(OC_2H_5)_2 + H_2O$$

more ethyl alcohol diethyl acetal water

Delicate, light, fragrant. Gives top-note.

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

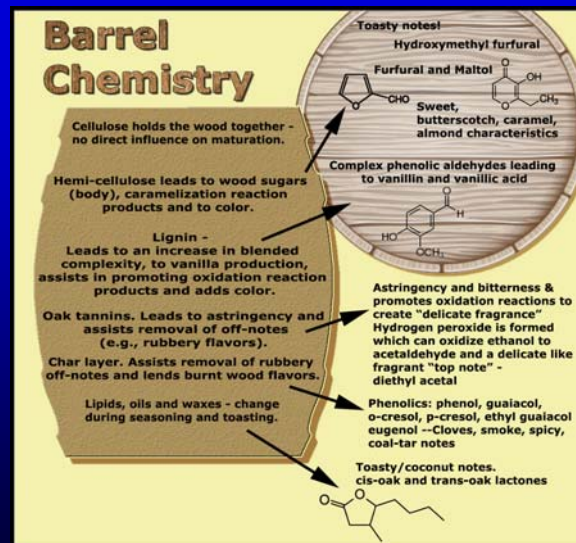
Transesterification

[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?

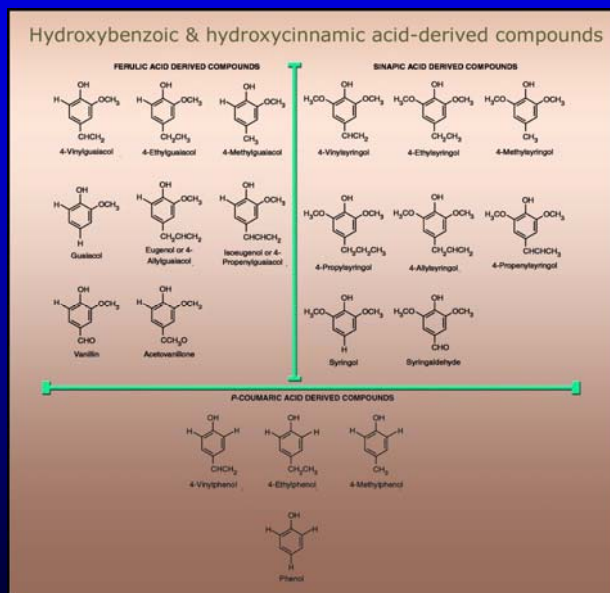
- ✓ Acids – hint of vinegar!
- ✓ Aldehydes – leafy & floral
- ✓ Sulfury – meaty & rubbery
- ✓ Oily – nutty butter anyone?
- ✓ Sweet – honey & vanilla – nice!
- ✓ Woody – resiny & piney
- ✓ Lactones – coconut & more
- ✓ Phenolics – wood smoke, cloves & medicinal
- ✓ Feint of heart – a tail here? – leather & 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

The diagram illustrates the aromatic profile of a wooden barrel, centered around a barrel with various descriptors. Surrounding the barrel are chemical structures for several key compounds:

- Ethyl hexanoate**: CCCCC(=O)OCC
- Phenethyl acetate**: CC(=O)OCCc1ccccc1
- Methyl 2-methyl-3-furyl disulfide**: CC1=CC=C(C1)SSC
- Acetaldehyde**: CC=O
- Furfural**: O=Cc1ccoc1
- Whiskey Lactone**: CC1OC(=O)CC1
- Diacetyl**: CC(=O)C(C)=O
- Vanillin**: O=Cc1ccc(O)c(O)c1
- Guaiacol**: Oc1ccc(Oc2ccccc2)cc1
- Cresols**: Oc1ccccc1 (ortho), Oc1cccc(O)c1 (meta), Oc1ccc(O)cc1 (para)
- alpha-Pinene**: CC1=CCC2C(C1)C=CC2

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_3CH_2OH) 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_3CHO [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_3COOH [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 CH_2CCHO [Acraldehyde, Acrylic aldehyde]	Piercing, disagreeable odor, peppery, hot/acid, 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.

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The Team at BDAS, LLC





END

Flavor Origins in Distilled Spirits: From Start To Finish

More Information from the team at BDAS, LLC

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