Malt Maniacs E-pistle #2010-09

By Kasper Valentin, Denmark

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The Chemistry of Whisky

Inspired by Nabil Mailloux's E-Pistle from March of '09, about whisky and water, and a question on a local whisky forum, I decided to write a little about the underlying chemistry that defines this Aqua Vitae that we all consume with the greatest of pleasure.
Often, whisky is talked about, as an almost mythical liquid, one that we cannot control or predict, despite having distilled what can be recognized as whisky for more than a thousand years.

In reality though, this is hardly the case. We can quickly dissect whisky in all its glorious elements, and anyone with a HPLC-MS (chemist lingo for a machine that can tell what you whisky is made of), like one that's present in most organic chemistry labs, will be able to tell you exactly what makes your favorite dram tick. But of course, it's not quite that simple. Your average whisky contains more than a hundred different organic chemical compounds, all of which add to the character of the whisky.
Most of us know the general compounds, phenols, esters and aldehydes. But that's far from all of them, there's going to be sulphur compounds, and different carbonyl compounds, like ketones and carboxylic acids. But enough with all that, let's move on to something more interesting.

Obviously no two Single Malts are identical, how can this be? I've just concluded that whisky, after all, is just a series of organic compounds, and anyone with high school chemistry knows that there are strict rules as to how two molecules form bonds, so shouldn't the same raw materials field the same end result?
Not by a long shot.

Let's take phenols for instance; we know it as the "smoky flavour" – and while that's true, there are hundreds and hundreds of different phenols, most of them, have no "smoky flavour" – The compound Norpholedrine is a phenol compound, but stimulates the nervous system, and does not smell – at all. So just because a certain compound is present does not guarantee a certain smell or flavour.
A phenolic compound worth noticing however is 4-Ethylphenol, a phenolic compound created during fermentation – also present in beer and wine. This phenol has a medicinal smell, and is present in most whisky – but not all whiskies smell medicinal – explain.

Obviously, some compounds are going to be more pungent, and noticeable than others, but another thing to consider is the weight, solubility and boiling point, which vary greatly from compound to compound. How is this relevant? Remember how whisky is made, the pot stills might have a very low, thick swan neck, a high narrow one, they might even have a reflux installed – this will alter the spirits chemical composition. A low, slanted swan neck, will allow almost all compounds that can be distilled to pass on with the new make – where as a long, tall and gentle sloping swan neck, with a reflux installed, will only allow the purest, alcohol through (perfect for vodka making, but not much fun for whisky making).

To further the confusion, all these compounds which stems from the fermentation and raw materials, called congeners, react with the still and each other during distillation.
The stills are made from copper, a beautiful material – Looks good, nice and heavy, conducts heat and electricity very well – the part with the heat makes it an obvious material to construct stills from – unless you want to use gold or silver. Maybe this is why Highland Park, Mortlach and others, release these ultra-super-premium drams, fetching over £10.000 for a bottle, but I digress.

Copper has another quality it's chemically active – it loves to react with sulphur. And sulphur is an off-note, and downright repulsive for most people. The most well known sulphur-compound is hydrogen sulphide, which we all know as the smell of rotten eggs. Hydrogen sulphide is toxic – very toxic as a matter fact, so, quite cleverly, we can identify even the minutest concentrations – down to 0.00047 PPM (Compared with the 100 PPM phenols present in some the more extremely peated whiskies today). Some aren't quite as bad though, but most people wouldn't drink a whisky which had strong sulphur notes – this is where the copper comes in. It reacts with the sulphur, trapping it, and making sure it doesn't leave the still – to form various, nasty smelling and tasting compounds later. Although – granted, there won't be a lot of sulphur in the whisky at this stage, but we'll redeem that later. Obviously it's not only sulphur, but copper will react to almost anything, and that helps to purify the spirit leaving the still.

Coming out of the still, most new make will actually taste mostly the same – the difference will be in the how oily it is perceived as, due to the amount of large-chain carboxyl acids (Fatty acids) that have made it out of the still, the various esters (Fruity smells) and the concentration of furfural, and obviously the concentration of phenols. Furfural has a quite pleasant smell of almonds and stems from fermentation, new make spirit also have quite a high concentration diacetyl, which is formed during distillation and has a distinct buttery smell.

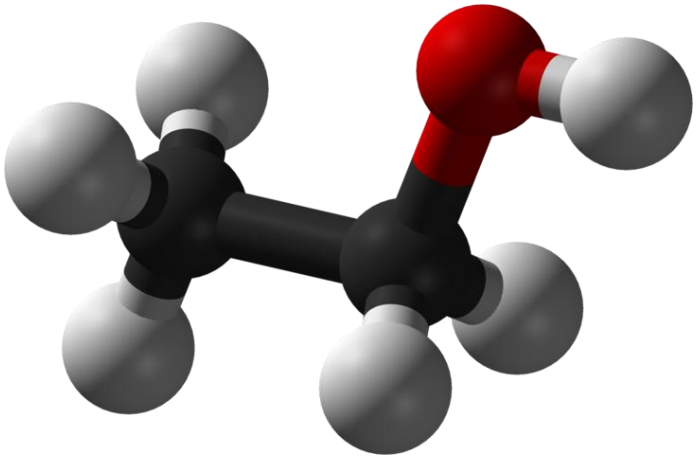

Fig. 1 It's not a dog, it's ethanol

Anyone who has tried new make spirit, will properly agree, it's more, or less, a matter of, is it smoky or not. The differences in new make are not nearly as great as it is in the finished product. Obviously not whisky at this point – but what happens when we let it marinade in oak for a few years?

First, we'll have a look at the oak cask, like we did with the stills. Oak casks used for whisky maturation has usually been filled with something before – either bourbon or sherry. This makes a difference in what compounds it can transfer to the whisky (Well, obviously dummy) – but just as interesting is the fact that the casks have been charred, before transport, to protect the wood. This once again introduces the dreaded sulphur to the mix – just as we had removed it during distillation. This also introduces even more phenols to the wood, and later to the whisky.

So when we pour whisky into oak casks, two things can happen – depending on what has been in the cask before. Stored in bourbon wood, the whisky will draw out more woody

aromas, various ketones, one of which is actually known as "Whisky Ketone", or more correctly, 3-methyl-4-octanolide, which supposedly smells of coconut. Other ketones compounds will impart smells of hay and grass, also, due to the charring, the wood will impart phenols like vanillin, which is the aromatic in vanilla. However the dreaded sulphur notes are rarely found here, as the wood was charred before the cask was filled, meaning any off-notes have been removed by the bourbon. (Which is filtered through activated carbon).

Sherry wood, will also part with the many of the same phenols as the bourbon wood, the vanillin but also an increased amount of acetal compounds, which account for all of the fruity smells we know from a whisky aged in sherry wood. What can happen here, is that the sulphur reacts with the whisky to create everything from quite lovely gunpowder notes, to nasty off-putting hydrogen sulphide. This is the gamble you take when aging in an old sherry cask – one cannot "smell" the sulphur content of the naked cask, which is why some whisky aged in sherry casks are wonderful and some are nauseating. "That's all?" I hear you say – why not store the barrels in vacuum, or store them in a vat of industrial strength detergent during transport, if all charring a ask is good for is off notes?

Well, the burn wood, have other properties – some of it is "just" charred wood, but some of it has been reduced to very fine carbon molecules, called active carbon – which has an amazing ability to absorb organic molecules, including many who could potentially ruin the whisky – including hydrogen sulphide. This makes it a built-in filter in the cask. It'll remove some of the poor aromas and make the whisky seem richer and purer in taste.

However, if you store a whisky for a large number of years in a cask, eventually, the whisky and cask will have reacted all that these congeners can – and there's nothing else to do than to exact every single of these woody aromas – which is typically attributed to a combination of the "whisky ketone" and a combination of eugenol and isoeugenol. These are present in large amounts in oak, and is why a very old whisky will taste "oaky". These aromas need to be exacted from the wood, and will only show with age.

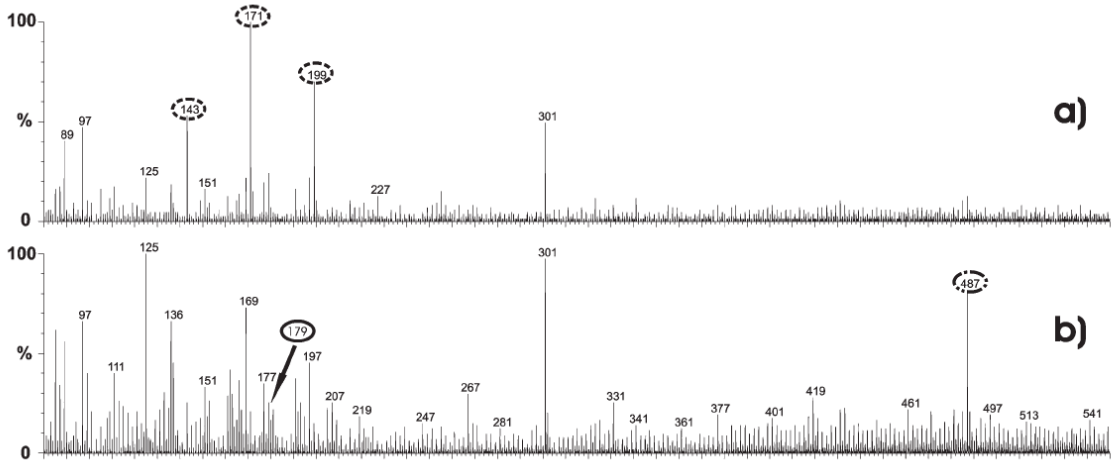

Fig. 2 Comparing Scotch whisky to American bourbon[1]

Now, don't get dishearten – above is an EIS-MS spectra showing a both a single malt Scotch whisky and an American bourbon whisky. The lines represent different compounds, and the length of them is an indication of the concentration of them. A) is a single malt Scotch whisky, b) is an American bourbon.

[1] Figure borrowed from "Electrospray ionization mass spectrometry fingerprinting of whisky: immediate proof of origin and authenticity" by Jens K. S. Møller, Rodrigo R. Catharino and Marcos N. Eberlin

So what does this tell us? Without further investigation, not much, but it's clear to see that, the bourbon stored in American virgin oak, is more chemically "complex", than its scotch cousin. This stems from different materials, different aging and production methods, but still, they share some characteristics. And one might be tempted to say that the single malt, will be more – unique, if you will – as in food, too many different tastes and aromas tend to blend into each other, and become slightly more bland, than if they're separate. Obviously, the single malt could be aged in re-used bourbon barrels. It's though, very likely that the single malt, will seem more brash and rugged in its expression, due to more dominating single flavours, even if it's been stored in bourbon casks.

Still with me so far? Good, almost home. We've now aged our spirit, we've now got whisky, just one more thing to do – drink it. But not straight from the cask, we need to bottle it first.

One thing that can make connoisseur and casual whisky drinkers alike, throw fits and discuss wildly, is bottle aging. Because how can an inactive substance like glass age a whisky? Well – it can't, not technically anyway. Glass is, for all intents and purposes un-reactive. However, the liquid inside, isn't. It's affected by oxidation, reduction and redox reactions, caused by sunlight, temperature, even movement – the liquid is volatile and will keep on developing even after it's been bottled.

There's still one factor we haven't discussed, namely, us. How we perceive things are unique and can vary widely from person to person, and the different compounds, have been shown to smell of different things at different ABVs. Even if we could create whisky with the exact same chemical composition, we could alter the taste and smell by just a little water.

The guys over at Cooking Issues infused vodka with Thai Basil leaves, and distilled it in a Rotovap, then collected fractions for every 20 ml that came out of the Rotovap. Then they let 6 different people taste them[2].

This shows, very clearly – how different ABVs will change our perception of exactly the same compounds. It's just vodka and basil, but at 25% it becomes Worcestershire Sauce and Creamsicle.

sample	mls	total	abv*	notes
1	24	23.5	63%	nail polish, banana
2	20	43.5	62%	more herbal, hospital, harsh, orange peel
3	20	63.5	68%	no hospital, peppermint, Thai basil, smooth
4	22	85.5	70%	acetone, not harsh, minty, chocolate
5	21	106.5	72%	alcohol, herbal, sweet, slight acetone, lavender, spice
6	21	127.5	74%	sweet, fruity, citrus, potpourri, good n plenty
7	21	148.5	68%	alcohol, Thai basil, citrus zest, star anise
8	20	168.5	70%	hospital, after-shave, pine, rough, licorice
9	21	189.5	68%	heavy pine, flowers, sweet, stone fruit, less licorice
10	20	209.5	66%	sweet, berry, lemon, orange, stone fruit
11	20	229.5	64%	starts like orange blossom, finishes like a band-aid
12	20	249.5	62%	hospital, band-aid, apple jolly rancher, apricot
13	21	270	60%	pure Thai basil, sweet, no licorice, not rough
14	20	289.5	57%	super sweet, stone fruit eau de vie, some licorice
15	20	309.5	51%	floral, Thai basil, rose, even flavor, American cheese
16	20	329.5	50%	rough, sweet tea, watery
17	20	349.5	47%	flowers, acid, bbq sauce, wood, vanilla, watery
18	20	369.5	41%	piney basil, juniper, honeysuckle
19	20	389.5	31%	acidic, orange, rough finish, not clean
20	20	409.5	31%	Thai basil, weak, Listerine
21	20	429.5	29%	bbq sauce, a-1 sauce, licorice, orange, weak
22	20	449.5	25%	a-1 sauce, Worcestershire, caramelized, creamsicle
23	20	469.5	21%	citrus, weak, plastic, phenolic finish
24	20	489.5	15%	plastic, weak
25	20	509.5	13%	plastic, weak, sun dried tomatoes
26	20	529.5	12%	menthol, bbq sauce, iced tea, plastic, weak
27	12	541.5	9%	plastic, weak

* abv as measured by a refractometer, low readings at outset might indicate impurities.

[2] Cooking Issues: Head to Tail Drinking: Breaking up Distillations in the Rotovap
May 19th, 2010

But now, we can finally drink our whisky, and marvel how something so similar, in the end, manages to be so very different. And thank god for that.

Kasper Valentin, Denmark

Born in 1988, Kasper Valentin has been exploring whisky ever since he was legal to do so. When not sampling a decent dram, attending fairs and shows or trying to make outrageous claims in E-Pistles, Kasper attends university, and tries to finish a degree in Molecular Biology, and trying to make rid the world of cheap cider and make whisky "hip" again.