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ON SPIRIT (SOUL) FROM WINE

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The article describes the history and basics of production of wine and pomace spirits. It brings information about content, aging (maturation), and nomenclature of various types of wine and pomace distillates.

Keywords: alcohol, cognac, brandy, pomace spirits, Weinbrand, alembic

The sophisticated cultivation of grapes and wine production is already known in Egypt in the third millennium BC. However, it has been shown that three thousand years earlier they had grown wine in Southwest Asia. As for the distillation of this liquid, it seems that the Babylonians began in the second millennium BC and then handed over their art to the Arab alchemists[1] who further advanced to Europeans[2]. Alchemists such as Ibn Badis, not in vain called initially alcohol distilled wine (خمر مصعّد, khamr mseed, or نبيذ مقطر , nabidh muqatar), later they called it arak (عرق, eirq) and much later alcohol (الكحول, alkuhul). However, distillation processes were used by the Chinese in the third millennium BC too.

As can be expected, at the beginning the main product was a wine distillate, whose preparation allegedly was improved by the returned crusader Arnaud de Villeneuve in the mid-13th century in France[3]. In his work "The book on selected drugs to maintain the health of the whole body from human diseases"[4] from 1310 (print 1521) Franciscan theologian, alchemist and cardinal Vital du Four (Vitalis de Furno)[5] persuaded about the beneficial properties of wine distillate.

In the Cognac area, the Chevalier de la Croix Marron, the Lord of the Segonzac, introduced the double distillation[6]. A very pious and somewhat poetic man who dreamed of the Satan who was trying to steal his soul by cooking, and saw himself in a dream in his boiler. His faith was so deep that the knight's soul resisted the first "cooking". The devil to achieve his goals was forced to submit it to the second "cooking". When the knight woke up, he thought of drawing the soul out of Eau-de-vie by second distillation.

Not surprisingly, the winemaker then took this distillate and thought that if he left it in an oak barrel, its taste would improve as in wine. He did not know that transesterification would take place and from the wood would be extracted out vanillin and related compound, known as taste modifiers[7], and also naturally astringent compounds (tannins)[8] of golden yellow-brown to brown colour. This is how a praiseworthy drink, which around the town of Cognac (Grande Champagne, Petite Champagne, Borderies, Fins Bois, Bons Bois and Bois Ordinaires), if it is made of grape varieties of Saint-Emilion des Chants (used in the vast majority), Folle Blanche or Colombard, and if it matured in oak barrels for at least two years, can be called Cognac. Other similar distillates are brandy. Adding any substances to both the must and the distillate, except for the caramel, which can add the colour and a plethora of heterocyclic compounds, is forbidden by law.

In terms of brandy (or Weinbrand, i.e. burnt wine), according to modern EU regulations[9], the spirits, made of wine, mixed or not with a wine distillate distilled to less than 94.8 % of volume, provided that the distillate does not form more than 50 % of the final product, maturing at least one year in oak containers or at least six months in oak barrels with a capacity of less than 1,000 liters containing volatile substances in quantity equal or higher than 125 grams per hectolitre of 100 % ethanol with the origin in distillation or redstillation of raw materials, containing a maximum of 200 grams of methanol per hectolitre of 100 % alcohol, while the resulting alcohol content must be greater than 36 %.

Distillation takes place in almost alchemical copper still facilities such as Charente Alembic (Charentais Alembic; Charente (/ʃa.ʁɑ̃t/) is a department involving the "Cognac" area) as it is known that distillation in a larger volume or device of other type does not yield expected quality product.

The most influential, for the classic taste of distillate, is the concentration of alcohol 40 volume % in the product that is sold to the consumer[11]. The "drinkable" concentration of alcohol 40 % was allegedly determined by D. I. Mendeleev in his dissertation, what is not entirely true, because he dealt with densities of differently diluted alcohol, but not for drinking, but for the sake of taxation[12].

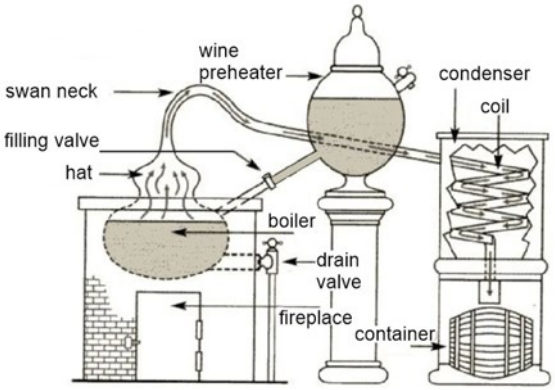


Fig. 1. **Alembic Charenais** (according to ref.[10])

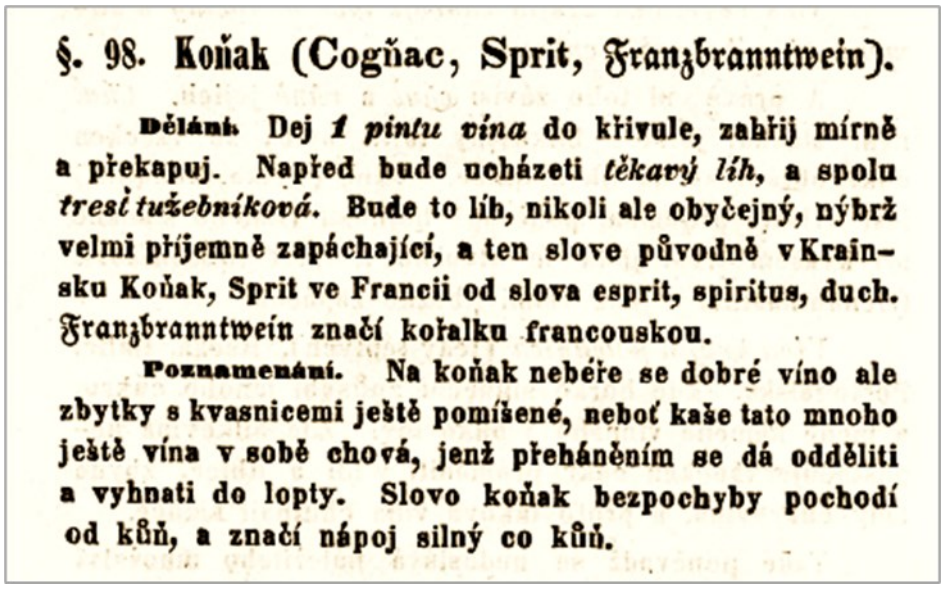
The organoleptic profile of the distillate is formed especially during the first distillation and during this distillation the number of aromatic compounds is increasing, as they are released by heat, for example, terpenes from glycosylated form, esterifications, transesterifications, Maillard reaction and so on. Thus generally, two esters, three aldehydes, 3 terpenes and 12 other isoprenoids are formed during distillation. Other substances come from grapes (primary) wine cider (fermentation), or are formed in aging in wooden barrels, or extracted from wood[13], or also emerging from reactions on the surface of copper[1].

Amerling has already written about the meritorious distillate of wine in 1854 in his Czech textbook (Fig. 2).

Under the term tresť (essence) Amerling means sometimes ether, sometimes ethyl- (trestil), otherwise distillable (aromatic) fraction. "Tresť tužební-ková" (meadowsweet essence) is then smell representing aroma of wine and the flower of vine (ref.[14]).

So let's see what the "tresť tužebníková" can be. Both cognac and brandy first have a hot taste of alcohol in the mouth, which develops into a pleasant aromatic tone, more or less sweetish to sweet. Hundreds of compounds present in the distillate were identified. The most abundant include[15] acetaldehyde, ethyl acetate, methanol, 1-propanol, isobutanol (2-methylpropan-1-ol), and isoamyl alcohol (3-methylbutan-1-ol) found in the amount between 50 and 2000 mg L^{-1}. Fermentation alcohols higher than ethanol are called fusel oils (Czech: přiboudlina, German: Fusel, Fusl) and contribute to aromatic complexity, but are undesirable at higher concentrations. The herb fragrance of the distillate is mainly on hexan-1-ol and hexan-2-ol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol and *cis*-2-hexen-1-ol. If 1-octen-3-ol is present, it adds a fungal aroma, it comes from grapes infected with necrotrophic grey mould *Botrytis cinerea* Pers.

In terms of acids, acetic acid may result from alcohol oxidation or may come from hemicelluloses. Other carboxylic acids such as propionic and butyric, which are associated with bacterial activity, may also be present. Butyric acid is characterized by unpleasant (rancid) butter and cheese scents and its concentration increases during aging. Hexanoic, octanoic, decanoic, dodecanoic, myristic, palmitic and stearic acids are made of yeast. Organic acids are found in the form of esters, logically, ethyl esters prevail, of which were isolated over 160. Examples should be esters of capronic, caprylic and caprinic that are believed to represent typical wine scent. The concentration of ethyl butyrate, similarly as butyric acid grows with aging. Regarding the esters of higher alcohols, it is mainly acetic acid esters, as "fruity"



§. 98. Koňak (Cogňac, Sprit, Franzbranntwein).

Dělání. Dej *1 pintu vína* do křivule, zahřij mírně a překapuj. Napřed bude uháželi *těkavý líh*, a spolu *tresť tužebníková*. Bude to líh, nikoli ale obyčejný, nýbrž velmi příjemně zapáchající, a ten slove původně v Krainsku Koňak, Sprit ve Francii od slova esprit, spiritus, duch. Franzbranntwein značí kořalku francouskou.

Poznamenání. Na koňak nebéře se dobré víno ale zbytky s kvasnicemi ještě pomíšené, neboť kaše tato mnoho ještě vína v sobě chová, jenž přeháněním se dá odděliti a vyhnati do lopty. Slovo koňak bezpochyby pochodí od kůň, a značí nápoj silný co kůň.

Fig. 2. **Excerpt from the textbook by Amerling**, ref.[14]

isoamyl, isobutyl and hexyl esters. The presence of organic acids and the eventual presence of sulfuric acid in synthesis and transesterification of esters are helping here. Higher concentrations of ethyl acetate and isoamyl acetate are considered undesirable.

Acetaldehyde of wine is present at concentrations between 0.20 and 0.25 g L^{-1} and is associated with vomiting and nausea in massive consumption of alcoholic beverages. This is understandable because the LD_{50} (rat) is 4.57 g kg^{-1} (ref.[16]), or even (rat p.o.) 1.9 g kg^{-1} (ref.[17]). Other aldehydes include formaldehyde, 5-hydroxymethylfurfural, acrolein, propionaldehyde, butyraldehyde, benzaldehyde, isovaleraldehyde and valeraldehyde, can easily be identified by HPLC[18]. The β-damasccene and diacetyl (butane-2,3-dion) contribute to pleasant fruity and sweetish smell. Furfural, originated during distillation from pentoses, is present in the amount of 0.2–30 mg L^{-1} and gives the impression of the smell of pastry. Furfural, along with a 5-hydroxymethylfurfural, often come from an added caramel.

The substances that contribute to the organoleptic properties of the distillate can be listed: are mainly furfuryl ethyl ether, furfural, furan-2(5*H*)-one, 2-acetylfuran, 5-methylfurfural, 5-(hydroxymethyl)furan-2-carbaldehyde, (4*S*,5*S*)-5-butyl-4-methyloxolan-2-one (whisky lactone), capronic (hexanoic) acid, guaiacol, syringol, 4-allyl-syringol (4-allyl-2,6-dimethoxyphenol), coumarine, eugenol and vanillin[19]. The fact that the barrel was made not from oak, but from the wood of the chestnut, can be recognized by the increased presence of whisky lactone.

A number of substances that can get into the distillate from agrochemicals are under very strict control, and can therefore occur but in tiny traces.

The miracle, which differs genuine cognac from other brandies, lies in the process of maturing in oak barrels, where substances such as eugenol (clove fragrance) and whisky lactone ("sweet", wooden to coconut scent) are leached. Other substances are decomposed, and thus hydrolysis and subsequent oxidation of lignin and esters of fatty acids (especially the even number of carbons) gave the formation of ketones contributing to something called "rancio" (rancio chatentais)[20]. Enzymes from mushrooms growing on the surface of wooden barrels also contribute here. Rancio can be defined as a set of aromas and flavors that develop only after extensive maturation in oak barrels (more than 10 years, but more often after 15–20 years). Since people can distinguish much more scents than tastes, rancio is easier to distinguish in the nose than on the palate. Typical fragrances that describe well-developed rancio include mushroom, earthy, walnut and cheese, scents of dried fruit, raisins, soap, and rancid butter in various stages. In the last, fourth phase, rancio moves to the scents of tropical fruit, wooden boxes from cigars, cedar wood, old leather, books and parchment. Rancio also affects how cognac feels in the mouth. Some describe the taste as buttery, others as nutty[1]. Although the fragrance of rancid butter (beurre rance) is generally perceived negatively, in the case of an old cognac, it is in some intensity, on the contrary, a sign of the highest quality.

A good homemaker "jumps over the fence" for something to drink, as the legendary Grandmother said. In virtually all cultural areas where they cultivated vines and made wine, the farmers felt sorry for what was left after the grapes were pressed, i.e. pomace (sometimes also marc or mash), as above-mentioned Amerling writes. Whether the fermented red wine or unfermented white wine pomace, it gives some 6 million tons of material in the EU annually[21]. Yes, it can be turned into "piquette (vinous beverage) for Praguers" by adding sugar and water, which can be once again fermented and can go to the market as a "naturally sweet select harvest". However, it seemed better to let the white pomace fermented, dilute the red with water and distil both. Unfortunately, due to the amount of pomace it is often necessary to store it, even for several months (at cold and without air access), which may also result in different quality of distillate.

Pure distillate of the pomace (pomace brandy[9]) is produced either industrially, or at home, around the world. Let's see what it is called by different nations: Bulgaria: dzhibrovitsa (type of rakie); Czechia: matolinovice, vínovice; France: marc; Georgia: chacha; Chile: aguardiente de chillán; Italy, Corsica: grappa; Crete: tsikoudia (also raki); Cyprus: zivania; Hungary: törkölypálinka; Germany: Tresterbrand, Weinbrand; Portugal: bagaceira; Romania: tescovină; Greece: tsipouro; Northern Macedonia: komova rakija; Slovakia: vínovica, terkelica; Slovenia: tropinovec; Serbia and Balkans: rakie, komovica; Spain: orujo. It should be noted, that the valued distillate is produced exclusively by a discontinuous method, and the lower-quality brandy by continuous method. The concentration of methanol in the EU must not exceed 1.5 % of the pure 100 % ethanol[9].

Pomace brandy has a composition essentially similar to the above-described brandy and cognac, but because it is distilled from the pomace mash, the composition contained in more substances, for example, acetic acid extracted from wood hemicellulos even in a mixture with methanol and acetone from "dry distillation" of woody content of pomace, but also with furfural, 2-phenyl-ethanol, acetaldehyde, 2-butanol, and other higher alcohols, which makes pomace brandy different from pure wine spirits. Often pomace brandy is also richer in terpenic alcohols such as citronellol, geraniol, linalool, nerol and α-terpineol[22]. However, it also depends on the technology and care of the distillation process, but also on the length and method of storage of the pomace.

Generally speaking, volatile compounds that at most contribute to the sensory quality of the spirits of pomace brandy are (as with other spirits) esters of fatty acids. These arise during fermentation and are found in the resulting distillate, with their concentration generally different according to the variety of grapes, the method of distillation and storage, and in general, it can be said that the aging of their concentration increases, for example, ethyl hexanoate and octanoate. These two esters contribute to the spirits of oily or wax tones. Acetic esters, such as

hexyl acetate, isoamyl acetate and 2-phenyl acetate, are then responsible for floral-fruity tones. 3-Methyl-1-butanol (isoamyl alcohol) and 2-methyl-1-butanol also contribute. Again, higher concentrations of ethyl acetate and isoamyl acetate are considered undesirable[1] as well as acetic acid.

We bring this paper as another contribution to a series of textbooks describing various interesting aspects of the chemistry of natural substances[23–25], also because we want to respond to the number of fictions, half-truths and nonsense that are spread around the natural compounds today. It is clear that the exploration of natural substances as renewable substances is one of the ways to contribute to general benefit[26,27].

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