Review: Steam distilled spirits from fermented grape pomace

Revisión: Bebidas destiladas obtenidas de la fermentación del orujo de uva

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Grape pomace is the solid residue left after juice extraction from grapes, and represents in Mediterranean countries the most important by-product of the winemaking industry. Steam distillation of fermented grape pomace will eventually produce a spirit, designated as *bagaceira* in Portugal, *orujo* in Spain and *grappa* in Italy. This paper comprehensively reviews fundamental and applied aspects of the manufacture of these spirits, encompassing their composition as well as metabolic reactions and microbial ecology that determine such composition during fermentation. These spirits adhere to maximum levels of methanol (potential toxic compound) and 2-butanol (potential flavor defect) fixed by EC regulations. Available studies pertaining to *bagaceira, orujo* and *grappa* have indicated that the final quality of these spirits depends strongly on the quality of the fresh grapes, the storage conditions, and the distillation equipment and procedure employed.

Keywords: bagaceira, orujo, grappa, alcoholic fermentation, distillation, volatiles

El orujo de uva es un residuo sólido que queda después del extrujado de la uva, y que representa en los países mediteráneos el producto residual más importante de la industria vinícola. De la destilación del orujo fermentado se obtiene una bebida, denominada *bagaceira* en Portugal, orujo en España y *grappa* en Italia. En este trabajo se revisan los fundamentos de la elaboración de estas bebidas, en los que se incluyen tanto su composición asi como las reacciones metabólicas y la flora microbiológica que determina tal composición durante la fermentación. Estas bebidas destiladas rozan los máximos contenidos de metanol (compuesto potencialmente tóxico) y de 2-butanol (defecto potencial de sabor) fijados por las normas de la Comunidad Europea. Los trabajos que hacen referencia al *bagaceira, orujo* o *grappa* coinciden en que la calidad final de estas bebidas depende esencialmente de la calidad de la uva, de las condiciones de almacenamiento, del equipo empleado en la destilación y del procedimiento empleado.

Palabras clave: bagaceira, orujo, grappa, fermentación, destilación, aroma

INTRODUCTION

Portuguese *bagaceira*, Spanish *orujo* and Italian *grappa* are spirits similar to one another with respect to organoleptic properties (characterized by unique flavors quite different from those of wine brandies), chemical composition and manufacturing techniques. These spirits are obtained via steam distillation of anaerobically fermented grape pomace, which results from crushing the grapes during winemaking; they contain *c.* 50%(v/v) alcohol and are highly appreciated in Mediterranean countries, especially after gourmet meals. However, their *per capita* annual consumption in these countries is relatively low, e.g. 1.8 L of *bagaceira* in Portugal (Cascão, 1989).

In the aforementioned countries, distillation of fermented grape pomace is an ancient technique for manufacture of spirits, which has been passed from generation to generation without major improvements or seminal modifications. Owing to a lack of detailed knowledge on the volatiles of commercial *bagaceira, orujo* and *grappa*, prejudiced arguments rather than rational queries have been raised concerning such traditional

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spirits. Additionally, exports of these specialty drinks have in recent years been increasingly hampered by progressively stricter food quality standards set forth in most European countries (e.g. EC Regulation no. 1567/89), in particular with regard to their methanol content. According to the aforementioned regulation, these spirits are supposed to be obtained from fermented grape pomace (with or without addition of lees in volumetric proportions not above 25%) and distilled, either directly by steam or after addition of water; the volatile content of these spirits should not be below 1400 mg/L of ethanol, whereas the methanol content should not be above 10 000 mg/L of ethanol.

Bagaceiras are produced all over Portugal, although those originating from *Região dos Vinhos Verdes* are particularly appreciated due to their specific bouquet and they have possessed an *Appélation d'Origine Protegée* status since 1986; for eventual certification, *bagaceiras* should satisfy the Portuguese standards NP no. I3261–I3263. Such strongly flavored *bagaceiras* have been in great demand, so *Commissão de Viticultura da Região dos Vinhos Verdes*, by appointment to the Portuguese government, has enrolled in major programs of technical support in attempts to make winemakers aware of the importance of proper anaerobic preservation of pomace coupled with attempts to help them improve distillation techniques, so that the resulting spirits will possess a consistently high quality and will be suited for widespread sale and export.

Orujo is mainly produced in Galicia, the northern region of Spain; the local government (through their various official services) has recently started the process that will eventually lead to establishment of the *Denominacion d'Origine Orujo de Galicia*. The standard requirements were already approved in 1993 (Xunta de Galicia, 1993), and, among other parameters, included minimum and maximum thresholds for various compounds.

Standards in the various countries pertaining to these spirits share several values, namely:

1. Compositional characteristics: (*i*) alcohol content between 37.5 and 50.0% (v/v); (*ii*) methanol content between 1500 and 10 000 mg/$L_{ethanol}$; (*iii*) 2-butanol content below 300 mg/$L_{ethanol}$; (*iv*) total acidity below 1500 mg/$L_{ethanol}$; (*v*) acetaldehyde content below 1000 mg/$L_{ethanol}$; (*vi*) ethyl acetate content below 2500 mg/$L_{ethanol}$; (*vii*) sum of contents of higher alcohols between 3000 and 6000 mg/$L_{ethanol}$; (*viii*) sum of contents of volatiles above 3000 mg/$L_{ethanol}$; and (*ix*) copper content below 100 mg/$L_{ethanol}$.
2. Organoleptic characteristics: (*i*) transparent and clear appearance, (*ii*) colorless and (*iii*) intense, fine and delicate flavor.

The major goals of this review are to describe the protocols of the manufacture of *bagaceira*, *orujo* and *grappa* (i.e. from after crushing of fresh grapes down to distillation of the fermented grape pomace), as well as the microbiological composition of the pomace and the chemical composition of the distillates, followed by critical discussion of existing fundamental knowledge pertaining to the influence of the technology used on the quality of the final spirits.

MANUFACTURE OF STEAM DISTILLED SPIRITS

The major operations associated with the manufacture of *bagaceira*, *orujo* or *grappa* are: (*i*) production of grape pomace, (*ii*) storage of grape pomace (under anaerobic conditions, also known as ensiling); and (*iii*) distillation of the fermented grape pomace.

Production of grape pomace

Following harvest, the red grapes are stripped off their stems, placed in a wooden tank where they are (even today) smashed by men's feet, and the must is left in the tank for no more than 3 days. During this time, a spontaneous fermentation process occurs. Thereafter, the liquid is separated from the solid portion, which is then further pressed. The solid waste obtained after extraction of the grape juice (and known as grape pomace) accounts for *c*. 15% (w/w) of the total grape mass, and is comprised mainly of skins and seeds and, to a varying extent, of stalks. The fermented grape pomace is directly subject to distillation because it is already quite rich in alcohols and poor in sugars.

Following harvest, white grapes are stripped off their stems, smashed and placed in a concrete tank which allows continuous removal of grape juice from the bottom of the tank; the remaining solid portion is then pressed once or twice. The sugar content of this grape pomace is still high, and the alcohol content is concomitantly low, so a further step of fermentation is required prior to distillation.

Ensiling

Before storage, the grape pomace is inspected in order to assess organoleptically its current quality and to anticipate, to some extent, the final quality of the spirit to be obtained. Such assessment is usually done in terms of color (which is an indication of grape origin and variety, as well as of vinification system used) and brightness (a bright pomace indicates that it is sound and dry, whereas an oily pomace indicates that it has already undergone fermentation to some extent).

Immediately before storage, the grape pomace is sometimes sprayed with 5–10% (w/w) aqueous tartaric acid (or, alternatively, sulfuric or phosphoric acid) at ratios of *c*. 1 L of acid solution per 400 kg of grape pomace (Versini and Inama, 1981; Rankine, 1989a; Varajão, 1992; Orriols, 1994; Silva *et al*., 1995b; Silva and Malcata, 1998).

Grape pomace is traditionally stored under anaerobic conditions in different types of containers (Orriols, 1990;

Varajão, 1990; Castiñeira, 1991; Versini, 1992b), from horizontal tunnels to large tanks, made of plastic, wood or concrete, and with a mobile lid on their top, or covered with plastic bags and sand. The grape pomace is poured into such a container, often in a manual fashion, after which the container is tightly closed. Grape pomace is stored for *c.* 12 weeks (Varajão, 1990; Orriols, 1994; Silva *et al.*, 1995a), without controls of temperature or relative humidity. Therefore, the prevailing outer weather conditions determine directly the inner fermentation environment. The extent of the natural anaerobic fermentation brought about by indigenous microorganisms on grape pomace is monitored via an essentially empirical process, based on the degree of maturity of the grapes upon harvest, and the outer temperature and relative humidity, and is also determined by availability of tank space. Processing of grape pomace during storage takes advantage of spontaneous alcoholic fermentation, in which yeasts catabolize sugars mainly to ethanol, coupled with spontaneous malolactic fermentation, in which lactic acid bacteria convert sugars to lactic and acetic acids, which are in turn converted to alcohols, esters, carboxylic acids and aldehydes by yeasts.

Distillation of fermented grape pomace

Three major purposes can be ascribed to distillation: (*i*) extraction of volatiles present in the fermented grape pomace, namely 0.3–1% (v/v) of the total alcohol inventory; (*ii*) selective concentration of desirable volatile compounds and selective dilution of less volatile compounds that may also pose health and/or organoleptic hazards; and (*iii*) promotion of specific chemical reactions that originate compounds with an effect on aroma. Therefore, distillation plays an active role in determination of the final quality of the spirit.

After previous assessment of aroma and consequent approval, the fermented grape pomace is loaded into a still made of copper or a copper-based alloy (e.g. bronze); the liquid on the bottom of the tank is then drained out, although alternatively it can be strongly acidified and later sprayed onto other grape pomaces during ensiling. The fermented grape pomace is then heated using a burner (fueled by firewood or, in more recent times, by natural gas) or supersaturated steam, to bring about partial vaporization. The vapor is then condensed outside the heating vessel using a cooling coil (usually set at *c.* 18 °C) and the distillate is collected as three sequential fractions; the deliberate cuts between distillate fractions should be carefully made.

The first cut is aimed at separating the head fraction, whereas the second cut separates the heart fraction from the tail one. The head fraction is whitish or greenish; the heart fraction is colorless, and is the only one that possesses a commercial value; the tail fraction is highly turbid. To determine the best cutting time between the three fractions of distillate, a compromise ought to be reached between the qualitative and quantitative profile of alcohols, esters, fatty acids and aldehydes, with special attention paid to the contents of methanol (which is toxic) and 2-butanol (which produces unpleasant flavors); however, cutting is still done in a completely empirical fashion, based on the winemaker's experience and on the bulk concentrations of alcohols as assessed by densitometry. The cut between head and heart fractions is typically made between 70 and 80% (v/v) ethanol, whereas the cut between the heart and tail fractions is typically made between 35 and 50% (v/v) ethanol. Often times the heart fraction is too rich in methanol, so a second distillation (known as rectification or demethanolation) is required to lower the methanol content to within legal specifications.

With respect to distillation techniques, two different processing patterns can be followed: (*i*) direct distillation of the fermented pomace (possibly added with lees and water immediately before distillation), which is probably the most popular; and (*ii*) distillation of the liquid resulting from previous wash of the fermented pomace with water. Distillation may, in turn, be carried out batchwise or continuously; in both cases, it is usually good practice to carry it out slowly so as to avoid the development of hot spots, and consequent accelerated thermal degradation of the final spirit.

The distillation equipment and associated practices that are most frequently used in Portugal, Spain and Italy are: (*i*) *alquitara* (Figure 1) and *alambic* (Figure 2), where the still is heated directly by fire, a water bath or steam, and the distillates are obtained by a Charentais-type system; (*ii*) steam distillation unit (Figure 3), where the distillate is obtained after a single distillation pass; and (*iii*) vacuum system distillation unit (Figure 4), the most recent apparatus, which allows distillation temperatures to be as low as 35 °C, and is aimed at obtaining distillates with delicate and fragrant aromas (Versini and Odello, 1990; Sensidoni *et al.*, 1991, 1992).

Since only the heart products have commercial interest, the head products are eventually added to the tail products, and these are possibly mixed with grape pomace, or mixed together and redistillated for non-food purposes. The grape pomace, after distillation, remains a waste product that may be used as soil fertilizer or for cattle feed; such spent grape is sometimes stored in tanks where sodium chloride is added up to 1–2% (w/w), pressed in the absence of air and covered on top with a layer of sand for later use. Grape seeds may also be considered as an added-value by-product owing to their oil content, as sometimes happens in Italy (Fantozzi and Betschart, 1979).

MICROBIOLOGICAL STUDIES

Grape pomace is a rather restrictive medium for microbiological growth, and during fermentation it becomes more and more restrictive chiefly because of its increasing alcohol content. The population of microorganisms

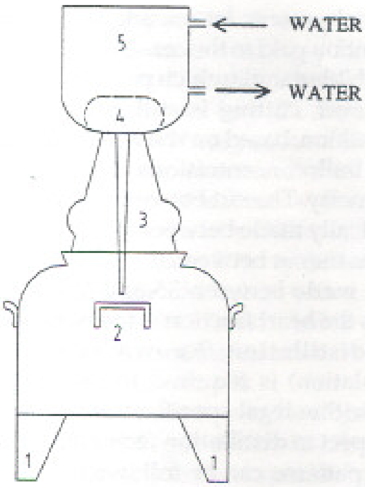

Figure 1. Traditional *alquitara* (adapted from Orriols, 1994): (1) iron structure, (2) boiler, (3) helmet, (4) condenser's serpentine and (5) condenser's chamber.

Figura 1. Alquitara tradicional (adaptación de Orriols, 1994): (1) estructura metálica, (2) caldera, (3) camisa (4) condensador del serpentín y (5) condensador.

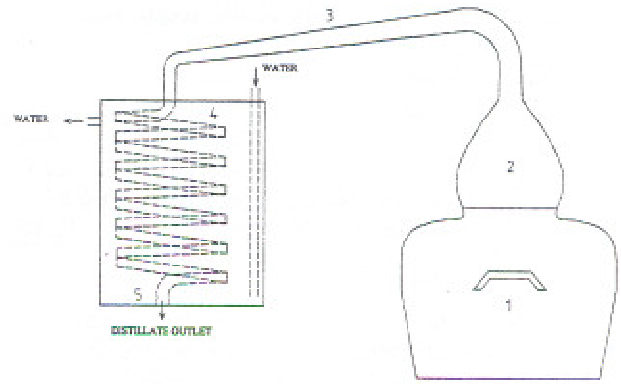

Figure 2 . Traditional alambic (adapted from Orriols, 1994): (1) boiler, (2) coil pipe (also called *col de cigne*), (3) condenser's chamber and (4) condenser's serpentine.

Figura 2. Alambique tradicional (adaptación de Orriols, 1994): (1) caldera , (2) adaptador, (3) condensador y (4) condensador del serpentín.

that can tolerate such harsh environmental conditions comprises several strains of yeasts and bacteria, which are essentially limited to two groups: lactic acid bacteria and acetic acid bacteria (Rankine, 1989a; Silva *et al.*, 1995b; Pina, 1998). Molds grow only at the beginning of fermentation, as they are quickly inhibited by alcohols produced during it (Rankine, 1989a). The changes caused by yeasts and bacteria are important in that they play a major role in development of organoleptic properties in the final spirits. Hence, microbiological sampling of grape pomace along fermentation would be an obvious aid in monitoring the fermentation process. However, it is technically unfeasible, not only because of the intrinsic heterogeneity of the feedstock, but also because suitable *in situ* sampling would disturb the anaerobic nature of the process.

Yeasts

There are *c.* 10^{11} cfu/g viable microorganisms on the surface of grape berries by the time of harvest, of which at least between 10^3 and 10^6 cfu/g are yeasts, depending on the recent weather conditions, harvesting practices, processing hygiene and geographical location (Barnett *et al.*, 1972). *Hansenula anomala* is a spoilage film yeast that is commonly found, and which produces high levels of ethyl acetate, acetaldehyde and acetic acid (Ribéreau-Gayon *et al.*, 1975). *Saccharomyces ludwigii* appears at much lower levels, and is very resistant to sulfur dioxide (a common preservative employed in winemaking) and ethanol (Lafon-Lafourcade *et al.*, 1984).

High viable numbers of yeasts (*c.* 10^8 cfu/g) are found in Portuguese white grape pomaces just before anaerobic storage, but they show a monotonically decreasing trend (Silva *et al.*, 1995b; Pina, 1998; Silva and Malcata, 2000). This behavior is explained by the increasing ethanol content, as yeasts are inhibited by ethanol above the threshold of 40 g/L (Ribéreau-Gayon *et al.*, 1975), coupled with decreasing oxygen concentration, caused by the preferential aerobic activity of yeasts when actively growing during the first week of ensiling. However, ecological selection towards yeasts tolerant to higher levels of ethanol occurs throughout storage; ethanol inhibits growth via denaturation of a few glycolytic enzymes and disruption of specific membrane structures (Miller *et al.*, 1982; Rose *et al.*, 1982).

Fleet *et al.* (1984) reported that yeasts of the genera *Rhodotorula*, *Pichia* and *Candida* are found in freshly extracted French grape pomace but die off soon after the start-up of fermentation; on the other hand, *Hanseniaspora uvarum*, *Torulopsis stellata* and *Saccharomyces cerevisiae* proliferate and will eventually drive alcoholic fermentation. The species *Torulaspora delbrueckii* (which dominates initially), *Debaryomyces hansenii* and *Rhodotorula mucilaginosa* were identified in fermented white Portuguese grape pomace (Pina, 1998); as time elapses, *S. cerevisiae* becomes the dominant yeast (Silva *et al.*, 1995a; Pina, 1998) until the twelfth week. Ecological selection during fermentation also derives from distinct tolerances to various toxins gradually released by yeasts; these include free fatty acids (e.g. *Brettanomyces* spp. produce high levels of acetic, isobutyric and isovaleric acids), which inhibit growth and consequently affect the overall fermentation process (Lafon-Lafourcade *et al.*, 1984).

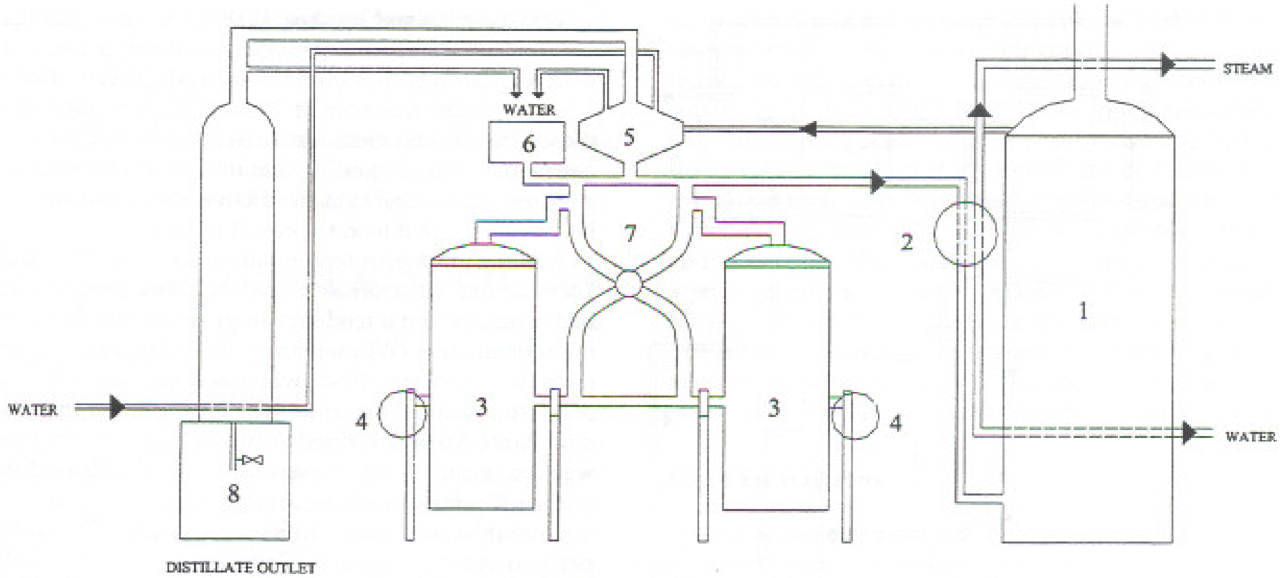

Figure 3. Steam distillation unit (adapted from Orriols, 1994): (1) boiler, (2) water level regulator, (3) distillation vessel, (4) discharge steering wheel, (5) fractional distillation column, (6) water collector, (7) steam circuits and (8) hydrometer.

Figura 3. Unidad de destilación a vapor (adaptación de Orriols, 1994): (1) caldera, (2) regulador del nivel de agua, (3) destilador, (4) llave de descarga, (5) columna de fraccionamiento, (6) colector de agua, (7) circuito de vapor y (8) hidrómetro.

Spoilage yeasts, namely *Saccharomyces oviformis, Saccharomyces ludwigii, Pichia membranefaciens, Hansenula anomala* and *Kloeckera apiculata*, produce high levels of ethyl acetate and acetaldehyde, particularly when they grow aerobically, and these compounds can also act as toxins (Zyl *et al.*, 1963; Lafon-Lafourcade *et al.*, 1984). These yeasts may also present a great spoilage problem because they tolerate sulfur dioxide (up to 500 mg/L) and ethanol (up to 110 g/L) (Scheffer and Mark, 1951; Zyl *et al.*, 1963).

Survival of yeasts on grape pomace also depends on fermentation temperature, pH and presence (e.g. via deliberate addition) of glycolytic enzymes. The death rate of yeasts increases with temperature, with maximum values at 20–25 °C; above 35 °C extensive death is actually observed (Amerine and Ough, 1980; Fleet and Heard, 1993; Pina, 1998; Silva and Malcata, 2000). This can be explained by the synergistic effect of temperature and ethanol concentration in their immediate vicinity. Considering the effect of pH, yeasts generally grow better at pH 4 than 3; in particular, Peynaud (1982) and Fleet and Heard (1993) reported that *S. cerevisiae* grows better at pH 3.5 than 3.0. The pH of Portuguese white grape pomace during ensiling decreases typically from 4.6 to 3.5 (Silva and Malcata, 1995a, b; Pina, 1998). The positive effect of pectinases up to 2% (w/w) on the viable numbers of yeasts (Silva *et al.*, 1995b) can be explained by the increasing availability of fermentable monosaccharides brought about by the hydrolytic action of the aforementioned enzymes on pomace pectins; this metabolic enhancer balances, to a considerable extent, the death rate of these microorganisms.

Rankine (1989b) claimed that differences in composition of spirits manufactured with distinct yeasts are apparently much more quantitative than qualitative in nature, i.e. the products of fermentation are essentially identical but differ only in their relative amounts.

Lactic acid bacteria

Fleet (1993) has claimed that lactic acid bacteria (LAB) detected in grape pomace originate in both the original grapes and the winery. Such microorganisms can generally vegetate on the grape skins and vine leaves, usually at low viable numbers (*c.* 10^2 cfu/g), although such values depend on the degree of ripening of the grapes (Wibowo *et al.*, 1985). Rankine (1989b) reported that, immediately upon pressing, the must contains *c.* 10^3–10^4 cfu/mL, and that the dominant species are *Lactobacillus plantarum, Lactobacillus casei, Leuconostoc mesenteroides, Leuconostoc oenos* and *Pediococcus cerevisiae*; all these species die off as alcoholic fermentation evolves (Lonvaud-Funel *et al.*, 1983; Fleet *et al.*, 1984; Wibowo *et al.*, 1985).

The ensiling conditions promote a significant proliferation of anaerobes (or facultative anaerobes), so a significant increase in the viable numbers of LAB occurs

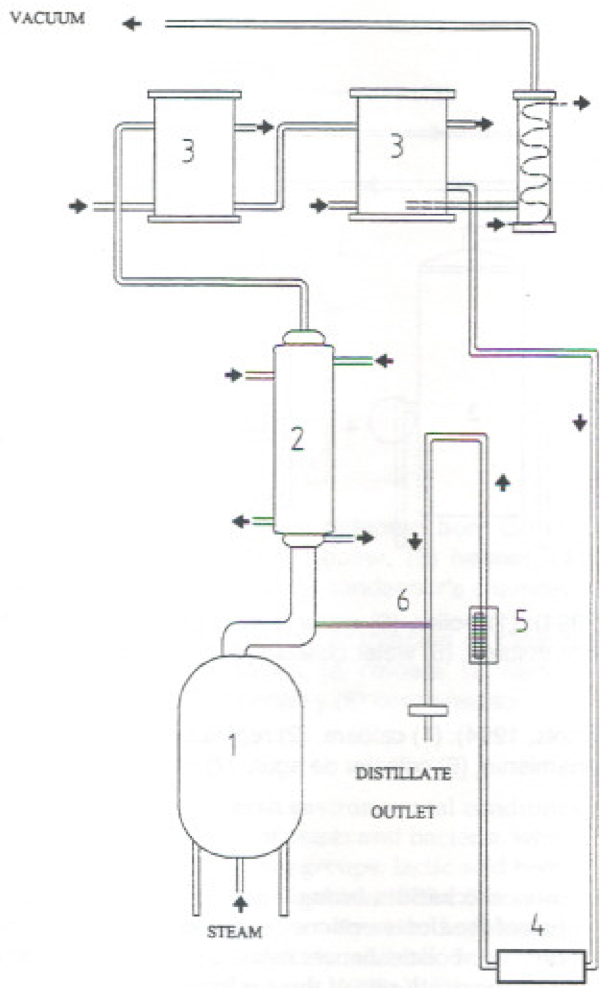

Figure 4. Vacuum system distillation unit (adapted from Cantagrel *et al.*, 1990): (1) boiler, (2) column, (3) condensers, (4) centrifuge pump, (5) monitoring device and (6) valve.

Figura 4. Unidad de destilación a vacío (adaptación de Cantagrel *et al.*, 1990): (1) caldera, (2) columna, (3) condensadores, (4) bomba centrífuga, (5) sistema de control y (6) válvula.

until they will eventually dominate the microbial population (Seale, 1986). Such realization is mainly due to the ability of LAB to bring about malolactic fermentation, with production of mainly lactic acid (which decreases pH), as well as to their resistance to acidic environments (Woolford, 1984). High numbers of LAB were detected in Portuguese white grape pomace (*c.* 10^7 cfu/g) just prior to anaerobic storage, and they showed a tendency to increase during the first three weeks of storage up to *c.* 10^9 cfu/g followed by a decrease (Silva *et al.*, 1995b; Pina, 1998; Silva and Malcata, 2000). This behavior has been rationalized in terms of ethanol tolerance (Costello *et al.*, 1983) and antagonistic effects by yeasts (Amerine and Kunkee, 1968; Pardo and Zuniga, 1992), which compete for available nutrients and produce compounds that inhibit bacterial growth. However, the viable numbers of LAB become higher than those of yeasts and remain as such throughout the storage period, thus suggesting that this group of microorganisms resists better to the restrictive acidic and anaerobic conditions that tend to prevail *in situ*.

Additionally, heterofermentative lactobacilli (such as *Lactobacillus hilgardii* and *Lactobacillus brevis*) and pediococci exhibit a tendency to grow in number during fermentation (Whittenburry, 1968; Lonvaud-Funel *et al.*, 1983; Woolford, 1984), whereas homofermentative ones tend to die. Silva *et al.* (1995b) reported that the dominant LAB in fermented Portuguese grapes, by four weeks of ensiling, is *Lactobacillus hilgardii* followed by *Lactobacillus brevis* and *Leuconostoc oenos*.

Growth of lactic acid bacteria is strongly affected by pH and ethanol content (Davis *et al.*, 1986). While *Pediococcus* and *Lactobacillus* spp. do not usually grow at pH below 3.5, *Leuconostoc oenos* tends to dominate (Pina, 1998). For alcohol contents above 10% (v/v), survival and growth of LAB decrease linearly as the alcohol content increases; however, several species of *Leuconostoc* and *Pediococcus* can tolerate alcohol up to a maximum of 12–14% (v/v), and *Lactobacillus* spp. can even survive up to 15% (v/v) alcohol (Wibowo *et al.*, 1985). Fermentation temperature, nutrient content and oxygen level, combined with interaction with yeasts, also affect the viable numbers of LAB. Pina (1998) and Silva and Malcata (2000) reported that, above 20 °C, the numbers of LAB correlate negatively with the temperature of fermentation; this behavior is similar to that of yeasts, as seen before. Considering that LAB are anaerobic or microaerophilic microorganisms, absence of molecular oxygen stimulates their growth, although Wibowo *et al.* (1985) reported that a minimum level of dissolved oxygen is necessary for growth.

Acetic acid bacteria

Members of the family Acetobacteriaceae, commonly called vinegar or acetic acid bacteria (AAB), have been claimed to be responsible for deterioration of wines by oxidation of ethanol to acetic acid via acetaldehyde (Drysdale and Fleet, 1988; Rankine, 1989b). Sound, unspoiled grapes can harbor AAB at low concentrations, generally not exceeding 10^2 cfu/g; *Gluconobacter oxydans* is usually the predominant species (Drysdale and Fleet, 1988). However, damaged grapes can support a much larger population (up to 10^6 cfu/g), which is characterized by dominance of *Acetobacter acetii* and *Acetobacter pasteurianus* (Lafon-Lafourcade *et al.*, 1983; Joyeux *et al.*, 1984a, b; Silva *et al.*, 1995b). *Acetobacter acetii* was the only AAB found in Portuguese fermented white grape pomace by two weeks of ensiling, but even so at a very low level (*c.* 10^2 cfu/g) (Silva *et al.*, 1995a).

It is now accepted that metabolic interactions between AAB and fungi occur on grapes and may eventually influence the composition of must; such interactions may be especially significant in the case of contamination by the fungus *Botrytis cinerea*, which can disrupt grape skins and consequently make grape pulp available for growth of AAB (Sponholz and Dietrich, 1984).

CHEMICAL AND FLAVOR STUDIES

Grape pomace

The bulk composition of grape pomace depends on the winemaking practices; nominal values are 60–70%(w/w) water and 30–40% (w/w) solids before pressing, or *c.* 45–55% (w/w) solids after pressing (Sastre *et al.*, 1994). The solids are composed of *c.* 25% (w/w) stem, *c.* 50% (w/w) skins and *c.* 25% (w/w) stalks (Castiñeira, 1991). The compositions of grape pomaces differ greatly from one another owing to evaporation of water and other volatiles, as well as production of carbon dioxide; weight losses can be as high as 10% (w/w) (Castiñeira, 1991). The presence of stems (as cellulose-rich material) together with pulp is considered detrimental because it contributes to high levels of methanol (Castiñeira, 1991).

Pina (1998) assessed the composition of Portuguese white grape pomaces in terms of organic acids, ethanol and glycerol (Table 1); she concluded that the metabolic reactions of importance take place during the initial stage of ensiling, and that alcoholic fermentation occurs during the whole ensiling period. Glucose and fructose are the sugars degraded first, whereas pentoses are likely used later on; this observation is consistent with reports by Fleet and Heard (1993) according to which some yeasts present in wine are able to ferment pentoses to ethanol under anaerobic conditions. The activity of yeasts is apparent via detection of glycerol and succinic acid under such conditions, which are known to be final products of sugar metabolism by yeasts (Radler, 1973; Boulton *et al.*, 1996). The malolactic fermentation by LAB occurs preferentially during the initial stage of ensiling, as derived from the profile of malic and lactic acids (Peynaud, 1982); the later presence of acetic acid indicates earlier contamination of grape pomace by AAB, whereas a decrease in tartaric acid content (the solubility of which decreases with increasing ethanol concentration) can be explained by formation of potassium bitartaric salts and neutral calcium tartarate.

Table 1. Changes in chemical composition of white Portuguese grape pomace during ensiling in terms of selected sugars, alcohols and organic acids (adapted from Pina, 1998).

Tabla 1. Cambios de la composición química del orujo blanco portugués durante el ensilado (adaptación de Pina, 1998).

Content	Ensiling time (weeks)		
(%, $w/w_{grape\ pomace}$)	0	3	12
Glucose and fructose	11	1	0
Ethanol	1	3	5
Glycerol	0.2	0.6	0.7
Malic acid	0.3	0.2	0.1
Lactic acid	0.0	0.7	0.8
Acetic acid	0.0	0.2	0.4
Tartaric acid	1.7	1.0	1.0
Citric acid	0.2	0.2	0.3
Succinic acid	0.0	0.1	0.2

Distillate fractions

Several studies have been made in attempts to determine whether (and which) significant differences exist between the chemical compositions of the three fractions of distillate, produced after fermentation of grape pomace from different grape varieties using distinct distillation systems (Ribéreau-Gayon, 1971; Bertrand, 1975; Williams and Knuttel, 1983; Orriols, 1990, 1991, 1992; Orriols and Bertrand, 1990; Orriols *et al.*, 1990; Versini, 1992b; Benítez *et al.*, 1994; Silva and Malcata, 1998).

The order of distillation of the various components present in the grape pomace depends on their own vapor pressure and on the extent of solubility in ethanol and in water (i.e. the dominant components, which vary considerably in concentration throughout distillation time); this simple rationale may explain early distillation of compounds with boiling points below those of ethanol (78.3 °C) and water (100 °C). Hence, the head fraction is composed mainly of alcohol-soluble components that are more volatile than ethanol (e.g. methanol, 2-methyl-propanol, 2-methyl-butanol, 3-methylbutanol, ethyl acetate, acetal and acrolein) and which are responsible for strong and pungent smells (Orriols and Bertrand, 1990; Soufleros and Bertrand, 1990; Orriols, 1994; Silva and Malcata, 1998); additionally, ethyl hexanoate, ethyl octanoate, ethyl decanoate and acetaldehyde are typically found in this fraction (Benítez *et al.*, 1994; Orriols, 1994; Silva and Malcata, 1998). The heart fraction is mainly composed of ethanol, as well as higher alcohols (e.g. propanol, butanol and hexanol) and carboxylic acids (e.g. butyric acid) to lower extents (Versini, 1992a; Silva *et al.*, 1995a). The tail fraction is characterized by larger contents of long chain alcohols (e.g. 2-phenyl-ethanol), as well as less volatile acids (e.g. octanoic, decanoic and isobutyric acids) and esters (e.g. ethyl lactate); owing to their insolubility, these compounds cause the turbidity referred to above (Mourão and Marrana, 1990; Soufleros and Bertrand, 1990; Varajão, 1990; Versini and Odello, 1990; Versini *et al.*, 1990; Orriols, 1991; Silva and Malcata, 1998, 1999). In practice, this splitting of fractions can not be taken as absolute and final because, owing to formation of azeotropes, typical head products may, in view of their high volatility, appear in the tail fraction, as sometimes happens with methanol (Orriols, 1994). Usually, the ethanol content is above 60% (v/v) for the first portion of the head fraction, and tends to zero for the last portion of the tail fraction (Orriols, 1994).

Distillation is further used to promote specific chemical reactions in the still because of the relatively high temperatures attained therein (*c.* 90 °C). Such reactions, which encompass hydrolysis, esterification, acetilization and complexation with copper, take place at rates that depend on the grape pomace properties and characteristics (e.g. presence of lees, pH value and titratable acidity), and, to a lesser extent, on the size and shape of the still, the rate of heating, the temperature range of distillation and the time of distillation (Leauté, 1990).

Spirits

Bagaceira, *orujo* and *grappa* are mainly composed of water and ethanol, each at an average individual concentration of *c.* 50% (v/v) (Orriols and Bertrand, 1990; Varajão, 1992; Versini, 1992a; Silva *et al.*, 1995a). However, it is the 300 or more different compounds present, which encompass mainly alcohols, esters, carboxylic acids, aldehydes and acetals (Cantagrel *et al.*, 1990; Carnacini and Antonelli, 1990; Orriols and Bertrand, 1990; Orriols *et al.*, 1990; Paunovic, 1990; Versini and Odello, 1990; Versini *et al.*, 1990; Sensidoni *et al.*, 1991, 1992; Silva *et al.*, 1995a; Silva and Malcata, 1998, 1999) that produce key notes which characterize (as a whole) the unique flavor and aroma of these beverages (Orriols, 1992, 1994). Typical compositions in terms of the most important volatiles for these three spirits are shown in Table 2. The overall quality of these spirits is clearly reduced when such compounds as methanol (the second most abundant alcohol) are present, as well as, to a lesser extent, acrolein, allylic alcohol, diacetyl, ethyl acetate, ethyl lactate, diethyl succinate, 1-propanol, 1-butanol and 2-butanol (Postel and Adam, 1980; Postel, 1982; Silva *et al.*, 1995a; Silva and Malcata, 1998, 1999). Most such compounds arise when low quality raw materials are used, as a consequence of adventitious contamination of grape (Orriols, 1994). The profile of volatile compounds is strongly dependent on the quality of grapes used as feedstock for fermentation (Carnacini and Antonelli, 1990; Guigon and Cogat, 1990; Lurton *et al.*, 1990; Castiñeira, 1991; Varajão, 1992; Versini, 1992a; Benítez *et al.*, 1994; Orriols, 1994).

One classical measure of flavor quality is the so called *natural flavor component index* (NFCI), which is defined as the sum of concentrations of all alcohols (except ethanol and methanol), all esters and all free fatty acids. NFCI values of 1400–3800 mg/L for *bagaceira*, 900–2008 mg/L for *orujo* and 870–1664 for *grappa* have been reported (Orriols, 1990, 1991, 1992, 1994; Orriols and Bertrand, 1990; Orriols *et al.*, 1990; Versini *et al.*, 1990; Versini, 1992a; Silva *et al.*, 1995a), which provide evidence for a wide diversity in terms of physico-chemical (and hence quality) characteristics.

The pathways of formation of major flavor components and the impact thereof on the subsequent final spirits are discussed below in detail.

Alcohols

Ethanol is the major product of yeast-mediated fermentation of carbohydrates naturally present in grapes (i.e. glucose and fructose). The content of ethanol is crucial for taste and body, but has little contribution to aroma (Amerine and Ough, 1980). The amount of ethanol formed during fermentation depends on a number of factors, namely (*i*) amount of fermentable sugars, (*ii*) initial number of yeasts; and (*iii*) type of handling conditions.

Besides ethanol, a number of other mono- and polyalcohols are present in spirits. The alcohols possessing chains longer than ethanol appear in *bagaceira*, *orujo* and *grappa* at relatively high concentrations when compared with commercial spirits (e.g. brandies), and are responsible for some of the most complex and unique sensory attributes of these beverages. These higher alcohols are 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol and 2-phenyl-ethanol (Orriols and Bertrand, 1990; Orriols, 1991; Versini, 1992a; Silva *et al.*, 1995a; Silva and Malcata, 1998, 1999); 1-propanol, 1-butanol, 2-butanol, 1-hexanol, *cis*-3-hexenol and *trans*-2-hexenol are present at much lower concentrations (Bidan, 1975; Silva *et al.*, 1995a; Silva and Malcata, 1998, 1999). The level of amyl alcohols (i.e. 2-methyl-1-butanol and 3-metyl-1-butanol) is of great interest as a predictor of sensory quality (Guymon, 1971); lower levels of amyl alcohols are associated with light-bodied grape marcs. In *bagaceiras* they range from 600 to 1800 mg/L (Silva *et al.*, 1995a), in *orujo* from 150 to 1198 mg/L (Orriols, 1994), and in *grappa* from 229 to 554 mg/L (Versini *et al.*, 1990). Alcohols which have been claimed to contribute favorable key notes to spirits are isobutanol, 2-methyl-1-butanol, 3-methyl-butanol and hexanol (Bertrand, 1975; Orriols, 1992), all of which are organoleptically detected at concentrations lower than 15 $mg/L_{ethanol}$ (Tourliere, 1977); when present above 10 000 mg/L, they will likely generate strong, somewhat unpleasant herbaceous aromas (Orriols, 1992, 1994). Furthermore, 1-propanol has a pleasant sweetish odor, 1-butanol has a penetrating and heavy odor, amyl alcohols are rather flavorful and penetrating, and 2-phenyl-ethanol gives off a very clinging roselike aroma (Nykänen and Suomalainen, 1983; Orriols, 1992).

Higher alcohols do not come directly from grape juice (where they are present only at trace levels), but are instead generated during alcoholic fermentation (Guymon, 1970); they may arise from a number of distinct origins (Bidan, 1975; Harvalia, 1976), namely free amino acids, sugars and ketoacids.

Table 2. Chemical composition (in terms of alcohols, aldehydes, carboxylic acids and esters) of Portuguese *bagaceira*, Spanish *orujo* and Italian *grappa* (mg/L, unless otherwise indicated).

Tabla 2. Composición química (alcoholes, aldehídos, ácidos y ésteres) del *bagaceira* portugués, *orujo* español y *grappa* italiano (en mg/L, a menos que se especifique lo contrario).

Component	*Bagaceira*[1]	*Orujo*[2]	*Grappa*[3]
Ethanol % (v/v)	45.0 ± 4.5	58.1	72.9 ± 7.7
Methanol	3389.2 ± 1279.9	5169	8869.2 ± 4338.3
Ethanal	615.7 ± 317.6	933	254.5 ± 27.6
Acetal	283.2 ± 212.8	58	n.a.
2-Butanol	53.0 ± 36.8	4.7	206.5 ± 33.2
1-Propanol	253.5 ± 75.8	304	1160.0 ± 113.1
2-Methyl-propanol	356.1 ± 159.6	423	99.5 ± 9.2
1-Butanol	22.7 ± 7.1	9.3	17.0 ± 14.1
2-Methyl-1-butanol	275.6 ± 94.4	356	72.5 ± 6.4
3-Methyl-1-butanol	915.5 ± 292.0	842	243.5 ± 17.7
TOTAL	1876.4	1939	1799.0
Allylic alcohol	16.8 ± 18.6	1.2	n.a.
Hexanol	60.6 ± 18.6	161.2	17.9 ± 3.0
trans-3-Hexenol	1.4 ± 3.7	1.3	0.2 ± 0.0
cis-3-Hexenol	2.0 ± 2.1	3.9	1.3 ± 0.1
trans-2-Hexenol	0.3 ± 0.3	3.1	0.7 ± 0.5
2-Phenyl-ethanol	10.0 ± 3.5	11.9	4.8 ± 2.8
Isobutyric acid	2.5 ± 2.7	n.a.	1.7
Isoamylic acid	2.7 ± 1.7	n.a.	0.8
Hexanoic acid	1.8 ± 1.0	5.7	0.7
Octanoic acid	4.0 ± 2.5	5.5	3.1
Decanoic acid	3.7 ± 2.3	3.0	15.8
Dodecanoic acid	1.1 ± 0.7	4.1	3.3
TOTAL	10.6	18.3	22.9
Ethyl acetate	209.2 ± 157.3	849.0	784.5 ± 149.2
Isoamyl acetate	5.6 ± 4.4	3.3	7.2 ± 0.4
Hexyl acetate	0.3 ± 0.2	1.5	0.6 ± 0.1
2-Phenyl-ethyl-acetate	0.3 ± 0.2	0.3	1.5 ± 1.5
TOTAL	6.2	5.1	9.3
Ethyl butyrate	1.2 ± 0.4	1.6	n.a.
Ethyl hexanoate	4.3 ±2.9	9.1	5.1 ± 2.8
Ethyl octanoate	11.0 ± 9.5	22.8	12.6 ± 8.3
Ethyl decanoate	10.7 ± 6.2	19.1	39.6 ± 13.6
Ethyl dodecanoate	2.3 ± 1.3	8.6	16.2 ± 13.2
TOTAL	29.4	61.2	73.5
Diethyl succinate	4.9 ± 3.5	1.1	7.8 ± 2.5
Ethyl lactate	189.9 ± 139.3	9.7	152.0 ± 31.1

[1]Adapted from Silva et al. (1995a).
[2]Adapted from Orriols et al. (1990).
[3]Adapted from Versini (1992a).
n.a., not available

Several factors can affect formation of higher chain alcohols: (*i*) intensity of maceration of grapes during winemaking, because it affects the degree of degradation of pectins by adventitious pectinases (Orriols, 1992, 1994); (*ii*) concentration of fermentable substrates, because the source of nitrogen used by yeasts influences that formation (Bidan, 1975); (*iii*) type of yeasts present during alcoholic fermentation, because they may be differently affected by aeration (Rankine, 1967); and (iv) temperature and pH prevailing during fermentation (Ough *et al*., 1966), because they affect the numbers and kinds of yeasts, as mentioned before.

High contents of methanol and 2-butanol in commercially available *bagaceira*, *orujo* and *grappa* can make these beverages hazardous for public health. In particular methanol possesses a high toxicity potential because, once ingested, it is oxidized to ethanal (or formaldehyde) and formic acid, compounds that are slowly eliminated by the human body; hence, they may eventually accumulate up to dangerous levels (Raposo, 1986), and damage the optical nerve and even cause blindness. The levels of methanol and 2-butanol in *bagaceira*, *orujo* and *grappa* (Table 2) are below the accepted legal threshold set forth by EC Regulation no. 1576/89. Methanol is not a direct fermentation product (Ribereau-Gayon *et al.*, 1975), although this claim has been subject to strong argumentation in the past; in fact, at least one half of it results from enzymatic activity during crushing of the grapes (Orriols, 1992, 1994). After pressing the grapes, two types of enzymes can act upon pectins (i.e. upon the polygalacturonic acid chain partially esterified with methanol): (*i*) polygalacturonases, which bring about cleavage of chains at the glycosidic bonds; and (*ii*) pectinmethylesterases, which catalyze hydrolysis of the chemical function esterified, and thus release methanol. The intensities of action of these enzymes depend upon the grape cultivars (Lee *et al.*, 1975; Gnekow and Ough, 1976). Furthermore, the concentration of methanol in the final *bagaceira* increases as splitting between the head and heart fractions is made earlier (Silva and Malcata, 1998, 1999). High levels of 2-butanol in spirits are usually associated with low quality raw materials, even though spirits rich in 2-butanol may have been produced from good quality starting raw materials (Orriols and Bertrand, 1990). In low quality spirits, 2-butanol accounts for unpleasant aromas and flavors (Guymon, 1971; Bertrand, 1975; Bertrand and Sukuta, 1976). It is well accepted that the formation of 2-butanol proceeds via enzyme-mediated reduction of 2,3-butanediol by lactic acid bacteria (Matarese and Navarra, 1971; Bertrand and Sukuta, 1976; Gargano, 1985; Villalon *et al.*, 1988), or spontaneously via oxidative degradation of 2,3-butanediol (Bertrand and Sukuta, 1976).

Aldehydes

Oxidation of alcohols is a known pathway for increasing the contents of aldehydes during ageing of spirits (Reazin *et al.*, 1976). Although oxidation can occur spontaneously, it is certainly accelerated by several adventitious microorganisms (Suomalainen, 1967; Amerine and Ough, 1980); the highest aldehyde levels are apparently attained when yeasts are well within their exponential growth phase (Radler, 1973). Formation of aldehydes depends on: (*i*) the species of yeasts; (*ii*) nutrient composition; (*iii*) conditions prevailing during fermentation (temperature and pH); and (*iv*) presence (or absence) of sulfur dioxide (Nykänen and Suomalainen, 1983). The amount of aldehydes produced by yeasts varies widely in spirits (typically from 6 to 190 $mg/L_{ethanol}$), and a large number of aldehydes have been detected in fermented beverages (Amerine and Ough, 1980; Nykänen and Suomalainen, 1983; Nykänen, 1986; Maarse and Visscher, 1989). However, only a few are of actual importance in quantitative terms, e.g. ethanal and diacetyl.

Ethanal (acetaldehyde) is usually the major carbonyl compound in *bagaceira*, *orujo* and *grappa*, where it accounts for *c.* 90% (v/v) of the total aldehyde content (Versini *et al.*, 1990; Orriols, 1991; Silva *et al.*, 1995a); so, the ethanal content determined in these spirits is virtually equivalent to the total aldehyde content (Table 2). The amount of ethanal produced, which should not exceed 1200 $mg/L_{ethanol}$ (Cantagrel *et al.*, 1993), is evidence for oxidation of ethanol during alcoholic fermentation via enzymatic decarboxylation of pyruvic acid (Baro and Quiros-Carrasco, 1977); its enological importance derives from the pungent smell it brings along, as well as its chemical reactivity.

Two other carbonyl compounds are also produced to relatively significant extents: 2,3-butanedione (diacetyl) and 3-hydroxy-2-butanone (acetoin). Diacetyl is, like ethanal, an indicator of bacterial-mediated oxidation, and a measure of the extent of unwanted bacterial contamination (Versini *et al.*, 1990). Such other aldehydes as 2-butanal, propanal, 2-methyl-propanal, hydroxyethylfurfural and hexenal are also referred to in the literature as regular constituents of spirits (Boidron and Ribéreau-Gayon, 1967), but they normally appear only at trace levels in *bagaceira*, *orujo* and *grappa*.

Acetals

Saturated and unsaturated aldehydes are relatively unstable compounds, so they react promptly with alcohol to yield acetals (Nykänen and Suomalainen, 1983). Formation of acetals obviously reduces the content of free aldehydes in distillates, so the pungent odor caused by the latter may be efficiently smoothed down. The 1,1-diethoxyethane (or acetaldehyde-diethylacetal, commonly termed acetal) is undoubtedly the dominant compound within this chemical family (Nykänen and Suomalainen, 1983) in *bagaceira*, *orujo* and *grappa*. The acetal content in *bagaceira* is significantly higher than that in orujo (Table 2).

Carboxylic acids

These compounds are, in general, subgrouped into volatile carboxylic acids and fatty acids (Silva *et al.*, 1995a). Acetic acid accounts for more than 90% (v/v) of the total acidity. Caprylic, capric and lauric acids are, second to acetic acid, the most abundant free fatty acids; they are produced by yeast-mediated metabolism of carbohydrates (Webb, 1970). Acids present in much lower quantities are formic, propionic, butyric, isobutyric, caproic, undecanoic, myristic, valeric, isovaleric, 2-methylbutyric and pelargonic acids (Schreier *et al.*, 1979). Short chain free fatty acids have unpleasant odors similar to rancid butter and putrid cheese, and their presence at high levels is an indicator of poor quality grape pomace (Orriols, 1992, 1994).

Esters

Fatty acid esters are probably the group of aroma components that have the highest impact and are qualitatively the largest in *bagaceira*, *orujo* and *grappa*. Both their absolute levels and relative proportions are of great importance with regard to aroma, as will eventually be perceived by the consumer. However, a particular key aroma can rarely be associated with only one specific ester, and collectively they account for an overall pleasant smell; e.g. the fruity and floral character of *orujo* has actually been attributed (at least in part) to volatile esters (Orriols, 1994). Acetates of isoamyl, hexyl and phenyl-ethyl alcohols, as well as ethyl lactate, contribute to intense and persistent aromas, and may affect the global flavor quality of distillates (Tourliere, 1977); e.g. longer chain ethyl esters (e.g. propyl, butyl and isoamyl) contribute negatively to their organoleptic quality (Soufleros, 1978, 1987).

Most esters are exclusively produced via microbial endocellular reactions, which are naturally affected by temperature, microbial strain, medium composition (especially profile of nitrogen-containing nutrients) and presence (or absence) of sulfur dioxide (Ough *et al.*, 1966; Daugh and Ough, 1973; Soles *et al.*, 1982); formation of certain esters (especially those possessing longer chain acid moieties) actually correlates with yeast growth (Onishi *et al.*, 1978). Ethyl caprylate, ethyl caprate and ethyl laurate are recovered in the distillate to significantly greater extents if yeasts cells were present in the grape pomace, whereas the concentrations of isoamyl acetate, ethyl caproate and 2-phenyl-acetate do not depend appreciably upon the viable numbers of yeasts.

Acetate esters can be recognized in sensory tests by smell, even when they are present at minute levels. Ethyl acetate is the most common ester in *bagaceira*, *orujo* and *grappa*, followed by isoamyl acetate (Versini *et al.*, 1990; Orriols, 1991; Silva *et al.*, 1995a); however, *bagaceira* shows usually lower levels of ethyl acetate than *orujo* or *grappa*, which are similar to one another (Table 2). The amount of ethyl acetate formed by bacteria depends directly on the presence of acetic acid (as expected), but it can also depend on growth of such aerobic yeasts as those belonging to the *Hansenula*, *Pichia* and *Acetobacter* genera; on the other hand, esterification brought about by bacteria has a reversible character, so if ethyl acetate were present in sufficiently high proportions its hydrolysis would take place in turn (Peynaud, 1982).

Another group of esters that may give rise to odor notes in spirits is long chain ethyl esters, starting from ethyl hexanoate up to ethyl dodecanoate. The most abundant ethyl esters are usually those of caprylic, capric and lauric acids, and they have a great influence on the final bouquet of the spirits (Orriols, 1994).

The esters present in spirits may ultimately be seen as a portion of a global set made up by all possible chemical combinations of alcohols and carboxylic acids (Ribéreau-Gayon *et al.*, 1975); however, the concentration of acetic acid apparently has little influence on the amounts of acetates formed, and propionic, isobutyric and isovaleric acids do not form ethyl esters at all (Amerine and Ough, 1980).

Post-distillation waste

Typically, 100 kg of grape pomace contain *c.* 0.80 kg of nitrogen, *c.* 0.35 kg of phosphoric acid and *c.* 0.63 kg of potassium. Comparing these values with the *c.* 0.47 kg of nitrogen, *c.* 0.30 kg of phosphoric acid and *c.* 0.85 kg of potassium in 100 kg of a normal fertilizer, one concludes that the former is richer in nutrients, so it is expected to perform better as an agricultural aid (Pato, 1980b).

TECHNOLOGICAL STUDIES

Raw materials

Better spirits are obtained when better quality fresh grape pomace is used, because this pomace has not yet undergone decay via the secondary fermentation routes responsible for formation of methanol and other undesirable compounds (Orriols and Bertrand, 1990), as discussed before. Additionally, the contact time between must and solid grape pomace during winemaking correlates positively with methanol content; this realization is consistent with claims that the methanol content in *bagaceiras* produced from red wines is higher than that of *bagaceiras* produced from white wines (Varajão, 1992). Ethyl acetate concentration is also statistically different between *bagaceiras* produced from white and red grape pomaces; such a difference probably arises from the larger increases in the activities of *Acetobacter* spp. and wild yeasts in the former than in the latter (Castiñeira, 1991; Varajão, 1992).

Castiñeira (1991) reported that a second pressing of the grape pomace following initial juice extraction may lead to release of astringent compounds from the stems, even though it promotes a more complete extraction of fermented sugars; this will in principle lead to more extensive production of alcohols, and thus increase the yield of distillation.

Ensiling

Ensiling encompasses various physico-chemical changes that are not yet completely understood (Woolford, 1984).

Considering that yeasts seldom possess noticeable esterase activity, that might eventually cause pectin demethylation, indigenous pectin esterases from grapes (which are released during their maceration) are solely responsible for pectin degradation, which is the first step in the production of methanol. Therefore, addition of pectinases to freshly crushed and pressed grapes will significantly increase the amount of methanol formed in the final spirits (Rankine, 1989a; Silva and Malcata, 1998). Possible ways to prevent such high levels are via thermal or acid inactivation of enzymes immediately after pressing; however, both these techniques apparently generate more problems than they are able to solve

(Orriols, 1992). Addition of aqueous tartaric acid to grape pomace, e.g. at 0.08% (w/w), had a significant negative influence on the contents of methanol and allylic alcohols, and a positive effect on the 2-phenyl-alcohol content (Silva and Malcata, 1998).

Orriols (1992, 1994) claimed that aeration of grape pomace during storage allows proliferation of some strains of yeasts and acetic acid bacteria, which can negatively affect the fermentation pattern because they increase the levels of acetic acid, short chain fatty acids and 2-butanol; this fact will lead to production of distillates with high levels of methanol, 2-butanol, hexanol, acetic acid, ethanal and acetal, as well as low levels of ethyl esters, thus leading to final poor quality in terms of flavor and aroma. The lower content of 2-butanol in *bagaceiras* produced with plastic instead of wooden containers (Silva and Malcata, 1998) can apparently be attributed to the higher degree of aeration within the latter.

Improper ensiling conditions may cause a 10–20% (v/v) decrease in ethanol content and *c.* 15% (v/v) increase in methanol content (Usseglio-Tomasset, 1971). On the other hand, addition of the remaining liquid on the bottom of the ensiling tanks to non-fermented grape pomace facilitates proper glucidic fermentation, so it considerably improves the organoleptic quality of the final *bagaceira* (Versini and Odello, 1990).

Due to increasing downstream market demands, the average duration of the fermentation period has been deliberately decreased; hence, the fraction of unfermented grape pomace by the time of distillation has been gradually increasing. As a consequence, the amounts of secondary products of fermentation will depend directly on the duration of ensiling (Lopes, 1983). However, Silva and Malcata (1998) showed that the fermentation time has a negative effect on the amounts of the most volatile alcohols, namely propanol, 2-methyl-propanol, 2-methyl-butanol and 3-methyl-butanol. Additionally, Varajão (1992) has specifically reported that *c.* 50% of the total methanol will typically be produced by 5 h of fermentation, and the remaining 50% will be produced between 5 and 24 h, thus suggesting that it is better to start distillation as soon as possible. Ough *et al.* (1996) recommended that the temperature of fermentation should be lower than 24 °C in order to maximize yeast growth and activity, and therefore enhance the quality of the final spirits.

Distillation

Theoretical prediction of the outcome of the distillation of grape pomace is a paramount task because the distillates often contain hundreds of volatile compounds, and it is very difficult to calculate the volatility coefficient for each one in the presence of all the others (except for water and alcohol) (Williams and Knuttel, 1983). In fact, the volatility of each component is a function not only of its characteristic vapor pressure (Williams, 1962; Arce *et al.*, 1988), which is in turn a function of temperature, but also of intermolecular interactions in the liquid phase (measured by activity coefficients), which are complex functions of composition and temperature; remember that composition and temperature evolve continuously throughout distillation. For these reasons, distillation still remains an essentially empirical technique, where a unique mix of experience and art is the only reliable asset of winemakers.

In order for distillation to be taken the maximum advantage of, it must be remembered that: (*i*) white grapes should be preferred to red varieties; (*ii*) grapes should be of high quality; (*iii*) grapes should be at proper maturity stages (i.e. possess a relatively high acid content and a relatively low pH); (*iv*) juice should be separated from skins in the pomace prior to fermentation; (*v*) sulfur dioxide should have been added at very low levels (or preferably not have been added at all); (*vi*) distillation should proceed immediately after fermentation (Orriols and Bertrand, 1990); (*vii*) temperature of the cooling coil for the distillate should be set at *c.* 18 °C (not below 15 °C to avoid hardness of the spirit and not above 25 °C to avoid extensive loss of relevant volatiles) (Varajão, 1990; Orriols, 1992, 1994); and (*viii*) stills should be made of copper. Additionally, since time of distillation will strongly influence putative breakdown reactions and chemical combinations between volatile components, special care should be exercised in order to prevent thermal degradation from taking place (Cantagrel *et al.*, 1990; Orriols, 1991, 1992). The final distillate should be filtered through a clean cloth in order to retain copper soaps; in fact, the copper of the still adsorbs fatty acids that will end up in copper soaps, thus preventing unpleasant odors that form from degradation of fatty acids in the bulk of the still (Benítez *et al.*, 1994).

Studies by Benítez *et al.* (1994) showed that distillation in batch stills generally leads to higher variability, which is inherent to the batch mode of operation (relying, for example, on a manual control of the heating rate), than distillation in columns operated continuously; they also showed that spirits obtained via batch distillation are more flavorful, although continuous distillation, used for larger scale production, allows considerable reduction of labor costs.

Yield

A batch of 100 kg of grapes usually produces 55–65 kg of must, 12–17 kg of wine after pressing, 20–25 kg of grape pomace and 8–10 kg of volatile products that will eventually be lost during fermentation (Pato, 1980a, b). Distillation of 100 kg of grape pomace will produce 10–13 L of spirit, with an average alcoholic degree of 52° (Pato, 1980a). Therefore, the final yield is 10–13% (v/w).

The final yield of spirit depends directly on the moisture content of the initial grape pomace (Orriols, 1994). This content depends on the proportion of wine produced from the fresh harvested grapes, which in turn depends on grape cultivar, geographical origin, degree of maturity and extent of pressing. Orriols (1994) also reported that the proportion between grape pomace and water deliberately added before start-up of distillation, as well as the amount of wine which remains imbedded in the pomace after pressing, both have a major effect on the final quantity of the distillate produced.

The (steam) distillation continuous system is faster but produces a high level of head products, whereas its batch counterpart produces a larger heart fraction (although at the expense of a lower total volume of distillate).

FINAL REMARKS

Although practical experience has it that the chemical composition, and thus the typical flavor of spirits is tightly associated with conditions prevailing during winemaking, ensiling and distillation, the similarities of *bagaceira*, *orujo* and *grappa* (in terms of raw materials and production techniques) allow the conclusions below to be somehow generalized to each of these three beverages, even though some were not experimentally tested for them all.

In general, commercial *bagaceira*, *orujo* and *grappa* are good quality beverages, and safe for human consumption in terms of methanol and 2-butanol contents; nevertheless, they exhibit a large diversity in terms of the main groups of flavor-related compounds (namely alcohols, carboxylic acids, esters and aldehydes).

The wide variation of the final composition of these spirits (and consequently their final flavor) can be rationalized by (*i*) intrinsic variability of raw materials (in terms of chemical and microbial compositions), (*ii*) unpredictable development of the fermentation process (arising from lack of control of temperature, humidity, pH, nutrient concentration and oxygen levels, which affect the growth rate of desirable microorganisms), and (*iii*) diversity of distillation techniques (most of which are employed empirically based on ancient experience).

Although the theoretical prediction of the composition of the heart fraction of distillate is very complex, more fundamental and *in loco* applied studies are necessary to help in making this a more scientifically sound process rather than one's skill that has been passed on through generations. Therefore, it seems necessary to: (*i*) develop a mixed starter (e.g. *S. cerevisiae* and heterofermentative lactobacilli, namely *L. hilgardii*) which should be added to the grape pomace prior to ensiling; (*ii*) standardize technological factors during ensiling (e.g. temperature, humidity, acidification rate and oxygen level) as well as those factors that have been proven to affect significantly the final quality of the spirit (e.g. addition of pectinases and tartaric acid); and (*iii*) optimize distillation apparatus and techniques, on both technical and economic grounds.

It is hoped that, after presentation of the available scientific and technical information on *bagaceira*, *orujo* and *grappa* in a consistent fashion suitable for the international scientific community, these spirits will be able to generate sufficient scientific interest to merit the further research efforts required for their comprehensive and fundamental characterization, which will undoubtedly help toward their eventual preservation as food delicacies.

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