**ALCOHOLIC BEVERAGES**

They are aqueous solutions containing a certain amount of ethyl alcohol that has been produced by:

- fermentation of sugar solutions (fermented alcoholic beverages);
- fermentation and distillation (fermented and distilled alcoholic beverages);
- or dissolving aromatic substances in sugar alcoholic solutions (liquors).

<table>
<thead>
<tr>
<th>fermented alcoholic beverages</th>
<th>Wine, beer, cider</th>
</tr>
</thead>
<tbody>
<tr>
<td>fermented and distilled alcoholic beverages</td>
<td>Grappa, Whisky, Brandy, Rum, Vodka</td>
</tr>
<tr>
<td>liquors</td>
<td>After dinner drinks, sweet or dry liquors</td>
</tr>
</tbody>
</table>
• Italy is among the countries consuming the highest amount of alcohol beverages;
• ethyl alcohol affords 7 Kcal/g and has not nutritional value, on the contrary, if its intake is prolonged, it can cause physical and psychic damages and addiction;
• ethyl alcohol is absorbed quickly and 90% is metabolized by liver while a little percentage is eliminated by kidney and lung.
• three diverse systems oxidize ethanol in hepatocytes, producing acetaldehyde:
**Catalase in peroxisomes:**

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_3\text{C} = \text{O} + 2\text{H}_2\text{O}
\]

*in pathological states*

- Acetaldehyde in excess (which is produced with high levels of alcohol intake) and ethanol itself, damage mitochondria and can cause several serious pathologies:

  *hepatitis, liver disease cirrhosis, gastritis, pancreatitis, etc.*

- **Maximum daily intake:**

  - **Adult men**: 60g
  - **Adult women**: 40g
  - **Children under 16-18 year and pregnant women**: 0g

  - alcohol in blood is lower or higher depending if the consumption precedes or follows the meal;

  - is lower if diet contains mainly carbs.

- **Wine glass**, 120 ml, **11.3g of ethanol** (12% vol.)
- **Beer**, 330 ml, **13g of alcohol** (5% vol.)
- **Whisky**, 30 ml, **9.5g of alcohol** (40% vol.)
Cis and trans resveratrol and their glycosides:

These compounds act hampering LDL oxidation which is caused by free radicals and lowering cholesterol accumulation in arteries and thus atherogenesis and cardiovascular diseases.

WINE

It is the product obtained by total or partial alcoholic fermentation of fresh grape or grape juice (must).

Grape is cultivated in all the continents, but the major producers are Italy, France, Spain. Sicily is the region with the larger surface devoted to the cultivation of grapes while Tuscany, with Chianti, is the most famous in the world.

Wine can be produced with only one kind of grape (e.g. Barol) or with mixed cultivars (e.g. Chianti: 75-90% San Giovese, 5-10% Canaiolo nero, 2-5% Trebbiano toscano and Chianti Malvasia).
GRAPES

- The grape is constituted by:

  - stem (4-5%) having a branched ligneous structure;

  - berries (95-96%) having round or oval shape constituted by the skin (10%), pulp and grapeseeds. On the surface there is a protective wax, keeping microorganisms.
Costituents of the skin

- **PHENOLIC SUBSTANCES**: phenolic acids, flavonols, tannins, anthocyanins (only in red grapes), stilbenes (cis and trans resveratrol and their glycosides)

- **AROMATIC SUBSTANCES**: 400 compounds have been identified by gas-chromatography, among which: alcohols, esters, aldehydes, ketones, hydrocarbons, fatty acids.

- **NITROGEN SUBSTANCES**

- **PECTINS**

- **ENZYMES** (Polyphenoloxidases, catalases, peroxydases).
PHENOLIC SUBSTANCES

Phenolic acids

*Benzoic acids*

*Cynamic acids*

<table>
<thead>
<tr>
<th>Benzoic acids</th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>Cynamic acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-hydroxybenzoic</td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td>H</td>
<td>p-Cumaric</td>
</tr>
<tr>
<td>Protocatechuic</td>
<td>H</td>
<td>OH</td>
<td>OH</td>
<td>H</td>
<td>Caffeic</td>
</tr>
<tr>
<td>Vanillic</td>
<td>H</td>
<td>OCH₃</td>
<td>OH</td>
<td>H</td>
<td>Ferulic</td>
</tr>
<tr>
<td>Gallic</td>
<td>H</td>
<td>OH</td>
<td>OH</td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td>Syringic</td>
<td>H</td>
<td>OCH₃</td>
<td>OH</td>
<td>OCH₃</td>
<td>Sinapic</td>
</tr>
<tr>
<td>Salicylic</td>
<td>OH</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Gentisic</td>
<td>OH</td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td></td>
</tr>
</tbody>
</table>

- *They are found as esters or glycosydes;*
- *They can undergo oxidation forming yellow pigments;*
- *They are forrunners of volatile phenols.*
- **Flavonols**: they afford the **yellow color**, they are mono or diglucosydes, the most important is quercetin:

![Flavonol structure](image)

- **Antocyanins** (1 g/l): **they give color to red grapes**, they are mono or diglucosydes and they can be free or linked to tannins.

![Antocyanin structure](image)
- Catechins or flavan-3-ols

TANNINS

- **Condensed or non hydrolyzable tannins**: they are polymers of catechins having *astringent action* (they precipitate the proteins of saliva) and they have spiral structure.

- **Hydrolyzable tannins**: found in traces, they are polymers of gallic, digallic and ellagic acid, esterified by a molecule of sugar.

**Gallic acid**

**Ellagic acid**
Aroma compounds
400 compounds can be separated by gas-chromatography: alcohols, esters, aldehydes, ketons, hydrocarbons, fatty acids.

Enzymes
Polyphenoloxidases, catalases, peroxidases.

• **Pulp constituents**
  • Water 70-85%,
  • sugars 15-30% *(glucose/fructose ~ about 0,9, pentoses in small amount)*,
  • Organic acids 5-10 g/l *(90% tartaric and malic (in ratio about 1,0-1,5:1,0), citric, succinic and lactic in small amount)*,
  • minerals, nitrogen substances and colloids (pectins and proteins).

<table>
<thead>
<tr>
<th>Sugars</th>
<th>acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.0%</td>
<td>0.46%</td>
</tr>
<tr>
<td>18.7%</td>
<td>0.87%</td>
</tr>
<tr>
<td>16.6%</td>
<td>1.35%</td>
</tr>
</tbody>
</table>

*If the pressure is light, the must is sweeter*

• **Grapeseeds constituents**: tannins *(they occur in the outer part and pass into the must)*,
  lipids *(10-20%) they are used to produce a vegetable oil.*

Grapeseeds should not break during vinification, otherwise MeOH content increases.
Transformations taking place in grape during ripening:

- *sugar content increases* (15-22%);
- *acidity decreases* (5-10 g/l);
- *minerals increase*;
- *anthocyanins in skin increase*;
- *tannins decrease*.

• Characteristics of grape depend much on climate. The proper time for the harvest can be determined evaluating the content of sugars and acids.

• Grape is harvested by hand or mechanically and is transported to the canteen and mixed eventually with other cultivars to ameliorate quality;

• The working process must be immediate and anyhow grape cannot be amassed in order to avoid the break of berries, which would start fermentation processes (that's why bisulfite can be applied also to the grape).
MUST
Must is produced by pressing the grapes in machineries allowing the separation of stems, peels, and seeds, too rich in tannins and pectic substances.

Must is then transferred into vats where the fermentation will take place.

- **Water (65-80%)**
- **Dry matter**
- **Electrolyte fraction**
- **Non electrolyte fraction**
- **Ash 3-5 g/l**

**Sugars**
- **glucose/fructose = about 1/1.** In much ripened grapes fructose prevails;
- they are the forunner of some organic acids;
- if grapes are left withering, concentration of sugars increases due to the evaporation (to 40%);
- they are **fermentable** (1g gives 0.6 ml of alcohol) and produce EtOH, CO₂ and secondary products (e.g.glycerol);

**Tartaric, malic (90% of the total acids), citric acids and their anions (0.5-1.5%).**

**Anions (Cl⁻, SO₄²⁻, PO₄³⁻)**

**Cations (K⁺, Na⁺, Ca²⁺, Mg²⁺, Fe, Cu)**

**Sugars 15-30% (glucose, fructose)**

**Nitrogen substances**

**Pectic substances**

**Tannins**
• they are **reducing**;
• they react with **bisulphite and sulphurous anhydride** eventually added;
• **saccarose is present in traces** (it is quickly hydrolized during fermentation);
• also **pentoses** (arabinose, xylose) in traces are present, reducing but non fermentable;
• **complex polysaccharides**;
• **polyalcohols** (sorbitol, inositol).

**Acids**

• the main are: **tartaric, malic, citric**;

![Diagram of acids]

- **Tartaric acid**: Its concentration remains constant during grape ripening. Its salts are weakly soluble in hydroalcoholic solutions and precipitate during fermentation.
- **Malic acid**: Its concentration decreases during ripening because it is used to produce sugars. It is soluble (also its salts).
- **Citric acid**: it is synthetized from sucrose and other sugars. Its concentration doesn’t change. It is soluble as also its salts.

• Acidity in must is in the range 5-14 g/l (as tartaric acid), **pH=3-3.6**;
• Minor acids: lactic, piruvic, fumaric, cis-aconitic, succinic, oxalacetic, salicilic, formic, acetic, propionic, butyric, etc.
Nitrogen substances
• 0.2-1 g/l: derive mainly from the skin, they are amino acids, polypeptides, and very low nitrites, nitrates and ammonia;
  • very important in fermentation: yeasts transform them into superior aromatic alcohols;
  • proteins, if present in high concentration, they can precipitate linking tannins;
  • enzymes.

Pectic substances
• 0.1-1 g/l: they are found in the cell wall material of the pulp;
  • their amount depends on the level of pressure and presence of skin during wine making;
  • their content in wine is lower because they precipitate linking proteins and they hydrolyze producing MeOH.

Vitamins C, B (their content decreases after pasteurization).
MUST ANALYSIS AND CORRECTION

• **Total sugars.** They can be increased with:

  *partially fermented must;*

  *sulphitated partially fermented must;*

  *concentrated must.*

• **Acidity level:** it can be increased by adding **tartaric acid** (partially precipitating as tartrate (fermentation is thus favored and coloring substances are better solubilized); a decrease can be done eventually on wine with K tartrate, KHCO$_3$, K$_2$CO$_3$, CaCO$_3$).

• Nitrogen substances (sparkling wines): they can be increased with ammonium salts; decreased with tannins or centrifugation;

• **Coloring substances:** contact with mash is prolonged or reduced; or very coloured must is added;

• **Tannins:** stems can be left with the must during wine making or enologic tannin can be added.
SO₂ in enology

In must and in wine SO₂ can be found:

- in free state:
  - SO₂ (gas) ⇌ SO₂ (acq)
  - SO₂ (acq) + H₂O ⇌ HSO₃⁻ + H⁺  \( \text{bisulfite} \)
  - HSO₃⁻ + HSO₃⁻ ⇌ S₂O₅²⁻ + H₂O \( \text{metabisulfite} \)
  - HSO₃⁻ ⇌ SO₃²⁻ + H⁺ \( \text{sulfite} \)

- in bound state:
  \( \text{R} - \text{H} + \text{HSO}_3^- \rightleftharpoons \text{R} - \text{OH} - \text{SO}_3^- \) \( \text{Hydroxysulphonic acid} \)

- 5-30 g/hl: selective antiseptical action (saccharomyces are not destroyed);
- 130-180 g/hl: must becomes non fermentable;
- SO₂ action depends on:
  Concentration, type, quantity and conditions of microorganisms, temperature, acidity, must composition.

Side effects:
irritating,
Bad taste,
Causing headhake,
allergizing, etc.
SO₂ has these functions:

• selective *antiseptical*;

• *solubilizing* (acidifying…);

• *acidifying* (direct and indirect: inhibits malo-lactic fermentation);

• *defecant*;

• *antioxidant*: reducing properties, mainly toward peroxides formed from polyphenols; deactivates oxidases that make wine turbid.

- Can be used in several forms (*gas, liquid, solid*); little producers usually use its salts; this additive can be added in different stages, but it is preferred to add it before the fermentation.

- It is used in largest amount for white wine making in order to hamper browning and malo-lactic fermentation.

- SO₂ is still the best additive in enology.
TRANSFORMATIONS DURING WINE MAKING

With the grape pressing yeast pass from skin to must;

✓ ALCOHOLIC FERMENTATION

Several kind of yeasts with different activity carry out the fermentation, e.g.: high fermenting strains are used to produce high alcohol wines;

Yeasts that are resistant to high alcohol and tannins, are used for making red wines.

Glucose $\rightarrow$ 2 CH$_3$CH$_2$OH + 2 CO$_2$ + 18 Kcal

Pyruvate decarboxylase

$\Rightarrow$ Acetic aldehyde + CO$_2$

Attention to:

- quantity of yeasts, temperature, air,...
✓ **TRANSFORMATION OF NITROGEN SUBSTANCES**: formation of alcohols with 3-5 atoms of carbon (known as *superior alcohols*)

✓ **HYDROLYSIS OF PECTIC SUBSTANCES**: formation of MeOH

Young wine continues to change:

1. **slow alcoholic fermentation**;

2. **malolactic fermentation**, due to lactic bacteria (fundamental for wine quality, taste is rounded and color is weakened): lactic acid is formed and thus acidity decreases.

3. **tartrate precipitates** (acidity decreases).

- *Fundamental in red wines*
- *To be avoided in white wines*
CHEMICAL COMPOSITION OF WINE

ALCOHOLS

- **ethyl alcohol**: 10-18% (vol./vol.) it can be transformed into acetic acid by acetic bacteria and to esters (aroma compounds).

- **glycerol**: 4-15 g/l, sweet, round taste;

- **methyl alcohol**: 20-200 mg/l, (max 0.25% of total alcohol in red wine, 0.20% in white);

- **superior alcohols**: 100-500 mg/l, 1-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 2-methyl-1-butanol (iso-amyl alcohols), derive mainly from the degradation of amino-acids and can negatively influence organoleptic characteristics;

- **butylenglycol**: 0.3-0.5 g/l

- **inositol**, it is already present in the grape;

- **sorbitol**, in small amount in the grape (higher amount in apples and pears);

- **mannitol**, it can be formed from fructose.

**CO₂**

- It is partly dissolved giving an acid-sparkling taste. It can be added to table wine.
ACIDS

From the grape
- Tartaric (2-6 g/l)
- Malic (0-5 g/l)
- Citric (0-0.7 g/l)
- Succinic (0.6-1.2 g/l)

From fermentation
- Lactic (1-5 g/l)
- Acetic (0.4-1 g/l)

**Fixed acidity**
- It can be added to acidify

**Volatile acidity**
- It is related to the health state of wine. In g/l, it can be max 1/10 of alcohol content in vol. %
- It can be added to solubilize Fe³⁺

**Volatile acidity**
- aroma
SUGARS

Hexoses (glucose, fructose): 0-2 g/l (dry wines), 2-70 g/l (sweet wines);
arabinose, xylose, ribose, raffinose: 0,3-1 g/l.

VOLATILE SUBSTANCES

ALDEHYDES: acetic aldehyde, propanal, hexanal, eptanal,…

KETONES: mainly acetyl carbinol, diacetyl.

ESTERS (main constituents of wine aroma): ethyl acetate, lactate and ethyl succinate,…

LACTONES: γ-butyrolactone,…

NITROGEN SUBSTANCES: polypeptides, amino acids, proteins, ammonia, ammides, nitrous and nitric acids.

COLOR PIGMENTS

PECTIC SUBSTANCES, GUMS, MUCILAGES

MINERAL SALTS

Inorganic anions (Cl⁻, SO₄²⁻, PO₄³⁻)

Cations (K⁺, Na⁺, Ca²⁺, Mg²⁺, Fe, Cu) Max 5mg/l di Zn, 1 Cu, 0.3 Pb, 1 Br.
Amelioration

- Blending (to rectify defects, refresh old wines, deepen the color, enhancing the bouquet, increase alcohol content);
- decanting (to separate dregs);
- re-fermentation (with fresh marc’s or selected yeasts, to ferment sugar left, ameliorate characteristics, volatile acidity,…);
- acidity adjustment (increasing by using tartaric, citric acid or decreasing by carbonates, tartrates);
- tannins adjustment;
- clarification by filtration, centrifuge, refrigeration.
- stabilization (by pasteurization, to maintain clearness).
MAIN CHEMICAL ANALYSIS

• *Ethyl alcohol content*

• *total acidity*

• *volatile acidity (wine health)*

• *dry extract*

• *quantification of ash*

• *quantification of reducing sugars (sweetness)*

• *quantification of SO$_2$ (toxicity)*

• *quantification of MeOH (toxicity)*

• *phenolic substances content (quality)*

• *volatile compounds content (quality)*