The useful lifespan of new barrels and risk related to the use of old barrels

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Abstract

Wood contributes a great number of compounds to wine: ellagitannins which play a crucial role in the oxidation reduction process, aromas of raw oak and aromas generated by toasting the wood. The structure and chemical composition of old barrels undergo radical and irreversible changes. Wood exhaustion proves to be far slower when the wood has been dried naturally rather than by more recent leaching methods. As wood retains most of its extractable content when dried naturally, wood contributions to wine can multiply by two the lifespan of a barrel. Of all existing barrel refurbishing methods, none is as entirely satisfactory and as good as keeping an old barrel full and suitably looking after it from the start.

Introduction

Wine maturation in barrels is an important step in the production of quality wines and has many relatively well known advantages: wine clarification and decarbonation, softening of tannins, stabilising and darkening the colour, providing complementary aromas to those of grapes and stabilising the colloid structure of wines (Moutounet et al. 1989; Vivas et al. 1991; Vivas et al. 1993; Chatonnet et al. 1992; Vivas and Glories 1993 and 1996; Vivas 1997). Although the need for barrels is widely recognised, it remains nevertheless true that ageing wines in this fashion is a costly operation and only a certain, variable proportion of wine, rarely 100%, can benefit from new wood.

Tasting sessions at different stages of the ageing process have shown that barrels of different ages yield different—positive and sometimes negative—characteristics. Usually, the contributions from wood decline gradually as well as the oxidation reactions. Over the years, the share of the wood in the characteristics of the wine becomes less significant. This is a decisive factor when deciding what proportion of barrels must be replaced. Besides the decrease in positive contributions from the wood, negative ones can appear and get worse with time if one's not careful. It is then crucial to be familiar with and control oenological techniques that make it possible to reduce to a minimum the risks related to using old barrels. Moreover, it is important to know how to prepare old barrels that have been standing empty for any period of time.

Ultrastructure and composition of old barrels

Preliminary trials on new wood have shown how its ultrastructure can be changed by soaking it in alkaline and acid solutions (Vivas 1997). But in the case of wine, an acid hydro-alcoholic medium, can such changes actually take place?

Electron microscope examinations have shown that the wine-saturated layers (2 to 5 mm) often display areas with visible polysaccharide microfibrils and intercellular gaps. This phenomenon is exactly like the effect of a diluted solution of HCl. But in addition, even greater changes can be observed in the structure of the wall of the wood's constituents. We know that the extraction of lignin by dioxane induces the digestion of the middle lamella which comes unstuck.; the secondary walls no longer form a continuous layer between two adjacent cells. When part of the lignin is eliminated, the polysaccharidic structure of the surface of the cell wall becomes visible. By comparing these findings obtained through specific elimination of lignin with the effects of a prolonged utilisation of barrels, we found indications of the same nature. Our observations suggest that wine acts as a solvent in the extraction of polymers (lignins, polysaccharides) during ageing. It is generally considered that, unlike spirits (Puech 1984), wine does not damage the cellular structures of wood tissues (Puech 1992). Ellagitannins, for instance, are extracted by the impregnation of wood tissues by wine, like a perfusion. These are very polar molecules located on the surface of the cell walls or found in a free state inside the cells; their release does not necessitate any alteration of the structure of the wood tissues.

Wine maturation causes major irreversible changes to the composition of the wood. Frequently, the mean composition of that part of the stave in direct contact with the wine is modified (Table 1). When a barrel has been in service for more than five years, few compounds are still measurable and the wood no longer contributes very much to the wine. But in the deeper, non wine-impregnated layers, significant changes take place (Figure 1):

Table 1. Influence of age of barrel on its average chemical composition. Average composition of wine-impregnated zones.

	Age (in years)			
	New	1	5	50
Ellagitannins (mg/g)	130	80	25	0
Polysaccharides[1] (mg/g)	780	650	350	120
Lignins[2] (mg/L)	16	12	8	3
Methyl-octalactone (µg/g)	85	64	5	0
Eugenol (µg/g)	14	6	2	0
Vanillin (µg/g)	18	11	4	2

[1]total polysaccharides (neutrals + acids)
[2]Lignins easily extractable in hydroalcoholic medium

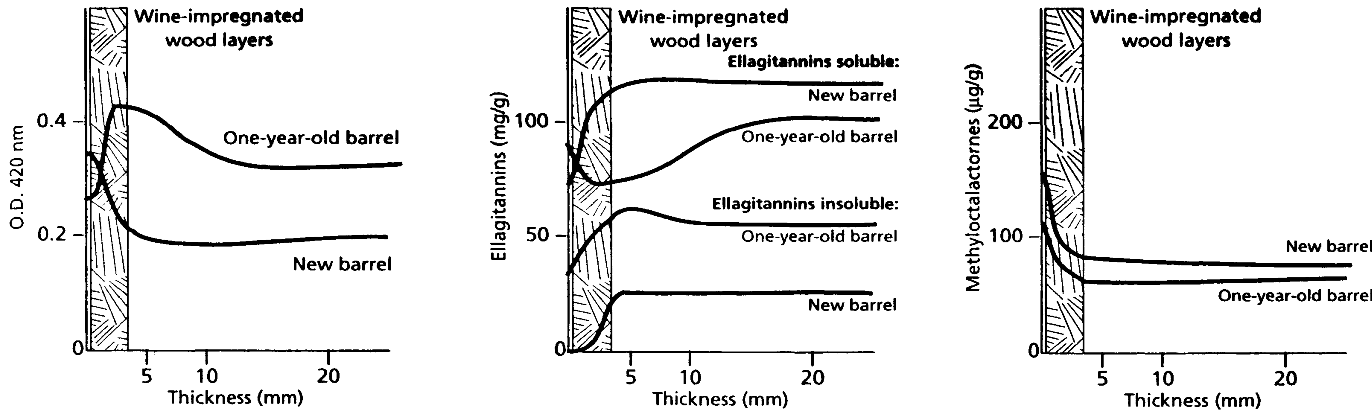

Figure 1. O.D. 420 nm, ellagitannins and methyl-octalactones evolution from new or old staves (one-year-old barrel).

- The yellow hue of the wood measured at 420 nm increases after one year's service of an old versus a new barrel. The yellower hue in the 0–3 mm zone is the result of toasting and the corresponding synthesis of chromophor, the nature of which is still unknown.
- At the same time as the yellowing of the deeper layers of the wood, greater amounts of insoluble ellagitannins can be found, produced by the oxidation of the soluble fraction of ellagitannins. The presence of humidity (30%) partly explains this oxidation which is catalysed by transition metals naturally existing in traces in wood.
- The aromatic composition is also changed. The concentration of wood compounds such as methyloctalactones slightly but measurably decrease throughout the stave profile (Figure 1). Oxidation reactions might explain this event.
- Acetic acid and tannin-harshening sulfates accumulate in the wine-impregnated wood mass, increasing total acidity. These products then accumulate in wines that are kept in old barrels (Figure 2). Soaking barrels before reuse is an adequate and proven remedy in most cases (Vivas et al. 1995).

There is however another problem. During the ageing process, some of the thiols undergo hydrolysis, producing dimethyl sulphide which increases constantly during ageing. Generally, the dimethyl sulphide content is systematically lower in new barrels than in old barrels or in vats (Figure 2).

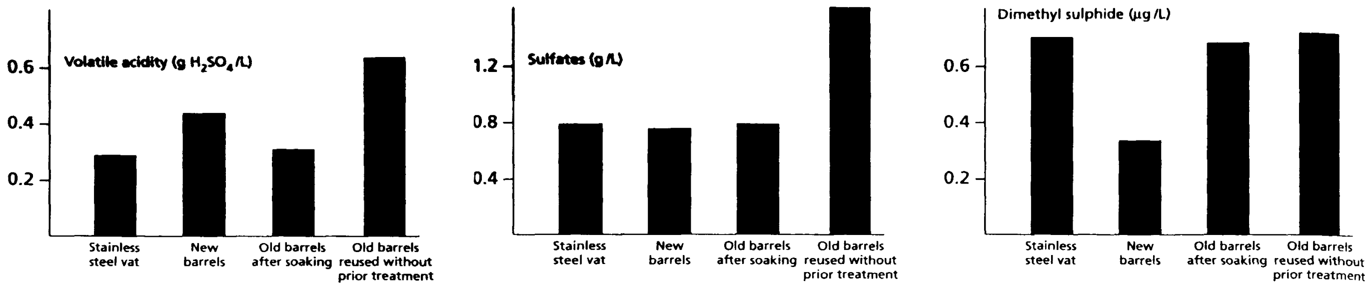

Figure 2. Influence of type of container and preparation method used on volatile acidity, sulfate and dimethyl sulphide contents in a red wine (analysis after 12 months ageing in the same place).

Table 2. Influence of ageing red wines in vats, new versus old barrels (5 years) on colour matter and colour stability after bottling.

	Stainless steel vat		New barrels		Old barrels	
	Ageing 12 months	Storage 2 years in bottles	Ageing 12 months	Storage 2 years in bottles	Ageing 12 months	Storage 2 years in bottles
Anthocyanins (g/L)	0.65	0.38	0.53	0.4	0.6	0.35
Tannins (g/L)	3.7	3.4	3.9	3.5	3.5	3.2
Color intensity	0.9	0.7	1.4	1.2	1.2	0.9
Hue	0.7	0.85	0.6	0.7	0.6	0.7
Origin of red colour (in % of O.D. 520 nm)						
1-Free anthocyanins (dAI)	35	25	15	5	20	10
2-TA combination (dTA) discoloured with SO_2	40	45	55	50	50	50
3-TA combination (dTAT) undiscoloured with SO_2	25	30	30	45	30	40
% of red colour attributed to stable combined form (dTA + dTAT)	60	75	85	95	70	90

Influence of the age of barrels on the degree of normal oxidation reduction reactions. Role of ellagitannins.

Repeated experiments have all shown, more or less clearly, that the ageing of wine in barrels has a favourable effect on wine stabilisation processes (Vivas et al. 1991) (Table 2). Ageing red wines in new barrels usually enhances the red hue, the colour substances being stabilised by forming combinations with grape tannins. In fact, after one-year maturation, most of the colour substances are found in these stable forms that ensure colour-durability once the wine is bottled. On the other hand, when wines are aged in vats, there is only a slight increase in colour intensity and fewer AT combinations occur (60% against 85% in new barrels); when aged in bottles, the hue intensifies indicating the premature development of a brick-red colour. In five-year-old barrels, the results are something midway between the two previous types of containers. The redox reactions have gradually dwindled, but persist nevertheless. But other dangers loom ahead. Tannins also undergo major changes. Controlled oxidation produces ethanol which acts as a focal point for the condensation of tannins; in most cases, the degree of condensation of tannins increases and their astringency drops. Here again, prolonged use of old barrels leads to a gradual decline of oxidation reduction reactions, resulting in a decreased redox potential often followed by a sharp drop in the dissolved oxygen content (Figure 3). These results are at present fully acknowledged (Vivas et Glories 1993).

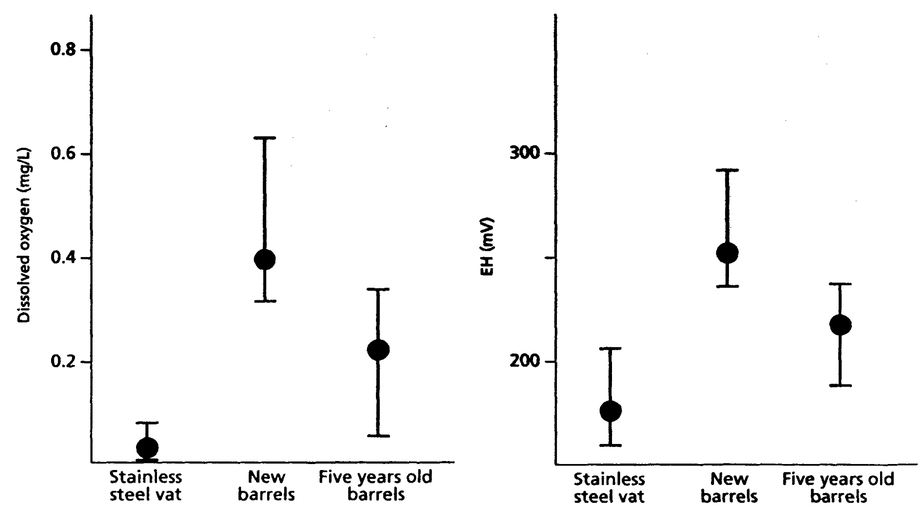

Figure 3. Influence of container on dissolved oxygen content and average redox potential in red wines over a period of five years.

But besides a different oxidation status, the differences are also related to the presence of ellagitannins in solution. These wood-generated molecules are far more oxidisable and constitute far more effective antiradicals than grape tannins

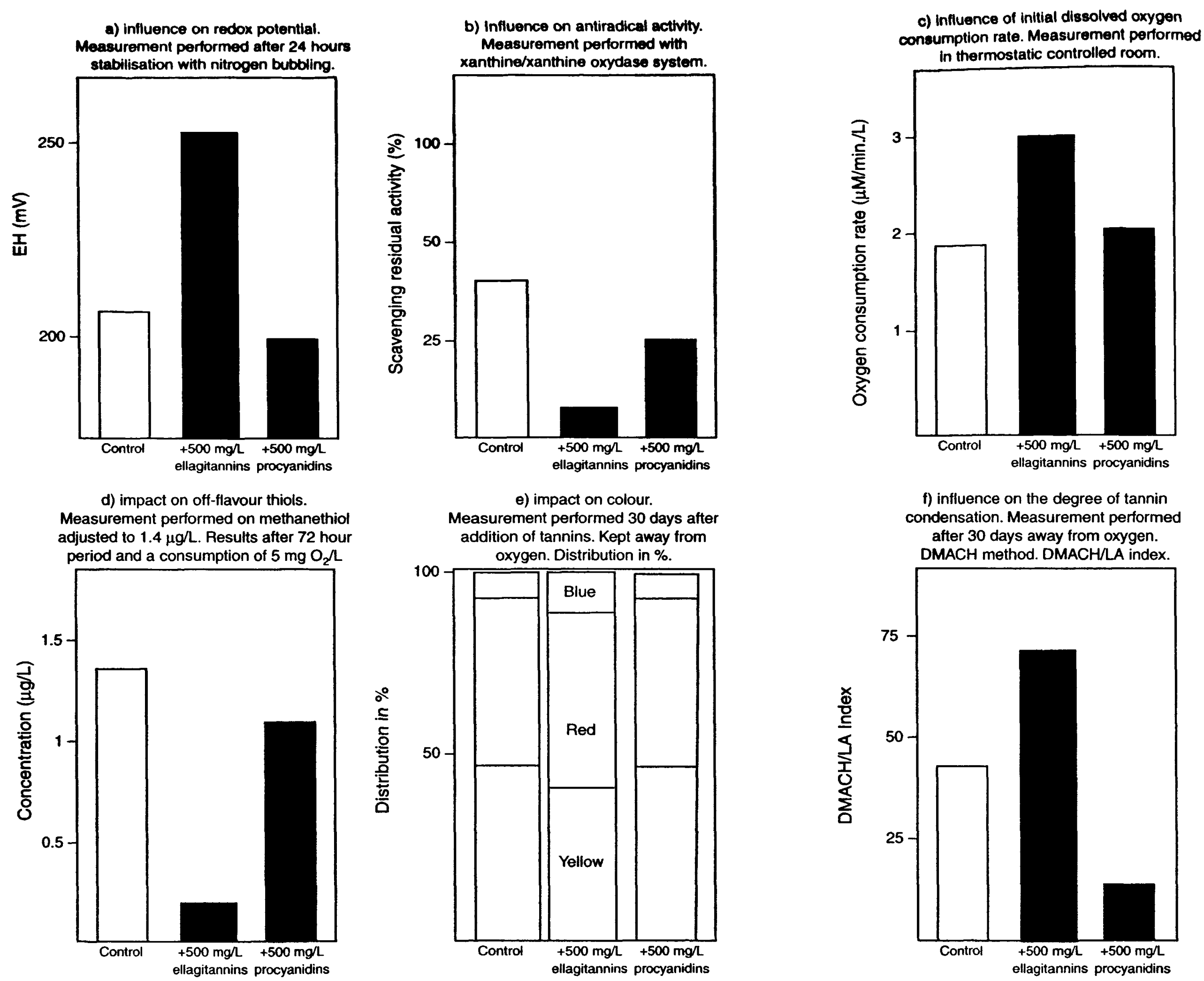

Figure 4. A few properties of ellagitannins. Comparisons with grape proanthocyanidins. Experiments performed in a Merlot Noir wine.

(Saint-Cricq de Gaulejac et al. 1998). These properties give them very special qualities (Figure 4).

- Ellagitannins intensify the redox potential alone without the help of dissolved oxygen (Figure 4a). Resultingly, they make the medium more oxidisable, promoting the whole array of oxidation reactions.
- By massively capturing free radicals, ellagitannins protect wine constituents from the ruthless effects of radicular oxidation (Figure 4b).
- Ellagitannins are able to capture oxygen and make use of it in a number of reactions. Their oxygen consumption rate is extremely high, higher than grape tannins (Figure 4c).
- These basic characteristics result in the degradation of foul-smelling thiols and partially limit the 'reduced' character of wine (Figure 4d). Furthermore, they guarantee a favourable evolution of the colour, deep red and blue-mauve hues predominating, giving wine a brighter, darker and deeper colour (Figure 4e). Lastly, because of the formation of ethanol resulting from oxygen consumption, ellagitannins increase the degree of condensation of grape tannins, reducing their astringency (Figure 4f).

Evolution of contributions from wood to wine during prolonged utilisation of barrels

An important feature to consider when reusing barrels is the perpetuation of the supply of wood substances to the wine. By measuring specific wood components, various well-grounded observations can be made in favour of natural drying processes (Figures 5 and 6). The supply of ellagitannins, whose fundamental role in ageing has already been mentioned, loses practically all effectiveness after a period of three years, mainly because there are not enough of them. It should be noted that toasting can modify the supply curve. With a heavy toast, even if the ellagitannin content in the scorched layers is low, a number of micro fissures develop on the surface of the staves; over time these microfissures enable more tannins to be released. The main explanation for this is that the wine gains better access to the wood mass, an event we have frequently observed. The scented compounds behave differently according to where they originated: the wood or the toast. Wood aromas are released regularly and can contribute significantly to wine aromas for 3 to 4 years. On the other hand, toast aromas are only found in the first 3 mm of the stave exposed to the burner. Accordingly, after a two-year period, only very few toasting aromas remain in the nose of a wine.

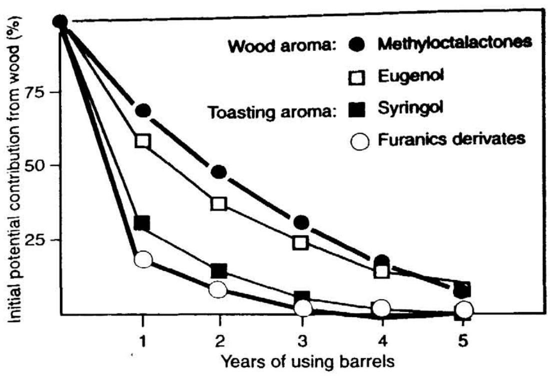

Figure 5. Evolution of wood tannin in wine during barrel use.

But another factor should be considered: the way the wood is matured (Figure 7). One can readily understand that wood that has been speedily dried by leaching produces staves whose positive or negative extractable substances are exhausted, whereas a well-managed natural drying process enables the wood to continue supplying compounds to wine even after the first year. This is confirmed by repeated tastings conducted in the world's major vineyards. Obviously, the wood is rather harsh in the first year, but this lessens with time. Blending wines is a frequent practice though, and to use a complete set of new barrels is rare, this being reserved for the richest wines with a good balance and an exceptional ageing (and return on investment) potential. Finally, one should never judge the quality of the wood before at least six months' maturation.

Optimising the useful lifespan of barrels and a review of different refurbishing methods

There are many methods to give a new lease of life to old barrels. Old barrels have undergone profound and irreversible changes. In these conditions, any form of refurbishing might appear to be illusory. The best technique is said to consist of replacing part of the old wood with new wood: replacing the headings and a few staves; but the cost of the operation rapidly makes it unprofitable.

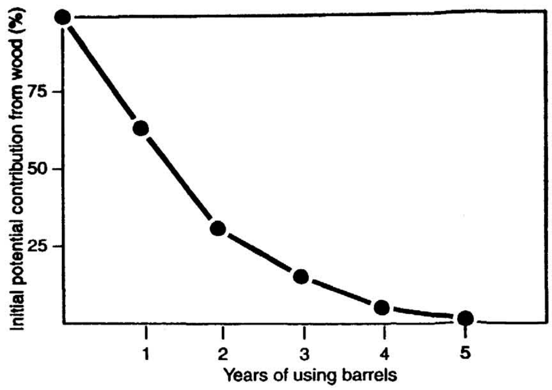

Figure 6. Evolution of aromatic compounds from wood to wine during barrel use.

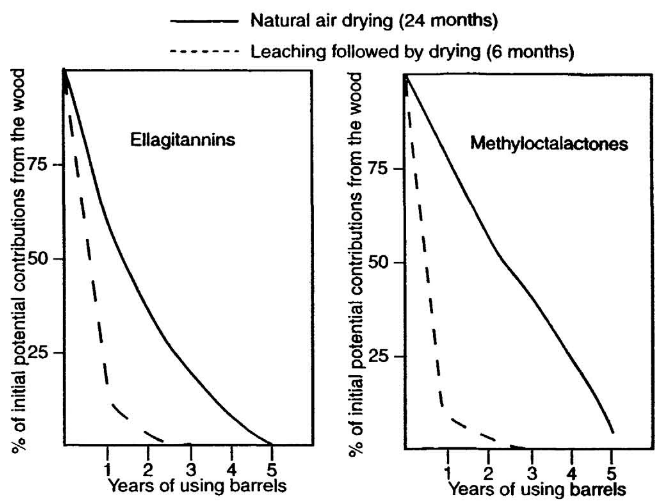

Figure 7. Influence of wood maturation methods on the evolution of wood contribution to wine during barrel use.

Commonly used refurbishing methods include scraping the barrel to eliminate the wine-stained layer, sometimes followed by a second toast. Scraping helps to boost the supply of certain wood substances to wine; however the oxidation reactions within the staves do not yield the same results as a new barrel (Table 3). On the other hand, a second toast is not satisfactory. The substances contained in the 5 litres of wine a 225 litre barrel can absorb undergo pyrolysis during this operation; the result is an accumulation of methylphenols and dimethoxyphenols which give the wine that will be put into the barrel the characteristics of burnt rubber and bitumen. The French term *cramè* (burnt) is used to describe this smell.

The best refurbishing technique for old barrels can probably be summarised in three points:

- To have one's own stock of old barrels to avoid having to import any additional potential risk;
- If possible, have a rotation system for wines to ensure that barrels remain empty for the shortest possible time;
- Systematically soak old barrels for several days, using water with sulfur, before filling them again, in the event they have been standing empty for several months. Then subject the barrel to gaseous sulphiting, after thoroughly draining it (with sulfur wick or SO_2 gas).

Table 3. Influence of scraping and possible re-toasting of barrels on wood contributions to wine.

	BARRELS			
	New	Old (5 years)	Refurbished	
			Scraped	Scraped +re-toasted
Ellagitannins (mg/L)	97	0	43	24
Furanes derivates (mg/L)	8.5	t	t	3.6
Methyloctalactones (µg/L)	184	15	124	142
Eugenol (µg/L)	26	4	3	6
Vanillin (µg/L)	315	42	39	170
Methylphenols (µg/L)	3	t	t	47
Dimethoxyphenols (µg/L)	28	13	6	486

t = trace

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