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Red wine aging in oak barrels: evolution of the monosaccharides content

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Abstract

A study of the evolution of the monosaccharides arabinose, rhamnose, galactose, glucose, xylose, mannose, fructose and ribose in a red wine aged in oak barrels is presented. The influences of the barrel manufacture, the variety and the origin of the oak wood have also been considered. The monosaccharide variations depend on the type of wood; higher values during aging are observed for galactose, fructose and xylose. The relationships between monosaccharides explain some structural ratios and their sequence of formation can also be deduced. The oak variety and the coopery have an influence on the monosaccharide composition of the aged wine, which indicates a structural difference between the hemicelluloses of French and American oak wood. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

During the aging of wines and spirits in oak barrels, chemical changes occur, related to the phenolic compounds that can come from the wine (Bourzeix & Saquet, 1975; Di Stefano & González-SanJose, 1991) or from the wood (Delgado & Gómez-Cordovés, 1986; Estrella, Allonso & Revilla, 1987; Viriot, Scalbert, Lapierre & Moutounet, 1993; Gómez-Cordovés, Gonzalez-SanJose, Junquera & Estrella, 1995). In most studies, special attention has been paid to the variation undergone by some phenolic compounds during the aging and also their combination with other substances.

One of the first studies of monosaccharides during the aging process is related to the variations of the sugar content and migration from the wood fibres to brandy at temperatures of 45–50°C and 70–75°C. The increase in the galactose, fructose, xylose, arabinose and glucose content are mentioned by Dzhanpoladyan, Mndzhoyan, Saakyan and Akhnazaryan (1969).

When brandies are aged for 40 years, an increase in the sugar content up to 200 mg/hl occurs, whereas, when cognac is aged in oak barrels for 30 years, this increase can reach values of 500 mg/l. This effect is usually attributed to the hydrolysis of the wood hemicellulose with the subsequent release of sugars (Belchior & Carneiro, 1972; Viriot et al.,1993).

Similarly, the presence of arabinose, glucose, xylose, rhamnose and fucose in brandy, aged for a period of 6 months in Limousin oak barrels, has also been confirmed. If oak wood extracts are added during brandy aging, there are increases, not only the polyphenol content, but also the sugar level (Bozhinov, Bakalov & Balaanskii, 1984).

In order to explain the appearance of such sugars, the relationship between phenolic compounds and sugars should also be taken into account, since the increase in the monosaccharide contents can be derived from the degradation of the flavonol glycosides (Harborne, Mabry & Mabry, 1975), as they have *O*-glycosidic bonds with glucose, galactose, xylose, rhamnose or arabinose. In a recent work, in which a new pigment, organic acids and sugars are determined in a red wine, it is concluded that the sugars would be linked to the already present anthocyanin to give complexones

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Table 1
Characteristics of barrels used

Barrel	Variety	Origin	Cooperage
m1	*Q. alba*	American	A
m2[a]	*Q. alba*	American	B
m3[a]	*Q. alba*	American	B
m4	*Q. alba*	American	C
m5	*Q. alba*	American	D
m6	Q. alba	American	D
m7[b]	*Q. robur*	French	D
m8[b]	*Q. sessilis*	French	D
m9[b]	*Q. sessilis*	French	D

[a] Different time used.
[b] Different region of France.

(Cameira-dos-Santos, Brillonet, Cheiniert & Moutounet, 1996).

Variations in monosaccharide contents in brandy aging have been studied (Bozhinov et al., 1984; Dzhanpoladyan et al., 1969). However, they have not been related to red wine aging, which could be of great importance to oenological studies. Residual sugars that remain in wine after alcoholic fermentation are a source of energy for yeast and bacteria; also they are related to the colour and flavour, so they may have a great influence on the quality of aged wine.

Considering this, we decided to study the variation of the monosaccharides during wine aging, examining aspects such as oak wood origin and influence of the barrel manufacturer.

2. Materials and methods

A red wine from grapes of *Vitis vinifera* L., c.v. Tinto del País, made in the Ribera del Duero Appellation of Origin to a basic level of quality suitable for aging was stored in nine Bordeaux barrels with a 225-l capacity, manufactured from different types of oak. The characteristics of the oak are summarised in Table 1. According to the suppliers, the 225-l barrels were made from American and French oak. The woods were seasoned for 24 month (American oak) and 36 month (French oak) with natural drying and given a medium toasting. The wines were aged at the same wine cellar in humidity conditions ranging between 80 and 90% and temperature conditions ranging between 10 and 14°C over the aging period.

A total of nine samples were taken from each barrel over an aging period of one year; 91 samples were analysed. The first sample was taken three months after the wine had been transferred to the barrels, to give the wine time in which to reach an equilibrium state after transfer. Differences in composition caused by the wood during aging first become perceptible after three months (Gómez-Cordovés & González SanJosé, 1995). The total aging time, monitored over the sampling period, was 12 months.

The carbohydrate analysis was carried out using anion exchange HPLC with pulsed amperometric detection (Bernal, Del Nozal, Toribio & Del Alamo, 1996). All analyses were done in triplicate. Statistical treatment was applied using the STATISTICA program Stat Soft. Inc. 1992 (Microsoft Corp.)

3. Results and discussion

In Table 2 the results obtained, mean and standard deviation, for each monosaccharide in the different barrels over 10 months are listed. The S.D. has been calculated in terms of the time; the highest and lowest values obtained are bold-typed. As can be appreciated, the monosaccharides in bold type are not the same for every wood considered, although those of smaller variation are almost always the pentoses, except in the m4 and m9 barrels, where the smallest variation is for the hexose, mannose. Quite unexpectedly the highest average concentrations are for galactose, fructose and xylose but not for glucose. The minimum average values are for rhamnose (methylpentose) and mannose (hexose). Rhamnose is the second less abundant sugar in the wines aged in barrels from the named D coopery.

Table 2
Mean and standard deviation for each monosaccharide (mg/l) in the different barrels

	m1		m2		m3		m4		m5		m6		m7		m8		m9	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Arabinose	13.1	**5.44**	8.90	4.67	12.4	5.36	14.4	6.96	20.7	8.36	20.4	9.15	14.9	7.45	16.0	7.50	16.4	7.84
Rhamnose	13.7	6.46	11.3	6.85	14.0	7.63	14.3	5.67	15.1	6.91	13.1	6.69	14.5	5.79	13.8	10.1	13.8	4.56
Galactose	37.1	9.35	34.5	13.33	41.2	10.18	28.3	**20.44**	39.7	9.07	29.30	**11.15**	33.99	9.88	36.91	11.52	30	15.2
Glucose	23.7	13.36	26.0	**24.88**	19.7	7.89	13.5	7.88	20.8	11.5	23.9	9.69	22.0	**11.7**	35.9	**34.6**	23.5	11.4
Xylose	31.4	27.20	23.2	5.41	23.8	6.23	23.8	3.60	27.8	**3.76**	27.3	**5.71**	24.7	**4.74**	27.9	6.18	33.4	13.6
Mannose	10.5	6.32	11.6	7.63	9.13	5.59	5.77	**2.49**	11.8	6.19	11.3	9.59	7.84	4.91	8.92	5.56	5.60	**1.86**
Fructose	48.8	**48.85**	50.6	22.14	31.8	**28.11**	16.0	11.4	25.0	**19.9**	21.8	9.89	26.2	9.32	34.9	22.6	31.1	**26.8**
Ribose	20.9	20.36	16.1	**2.02**	17.8	**4.21**	16.0	6.58	15.3	5.05	17.1	7.21	18.7	10.6	14.2	**4.19**	16.9	6.03

In Table 3 the correlations of the monosaccharides, with one another and with the sum of all of them, are presented. The statistically significant correlations are bold-typed. These correlations show relationships between sugars according to their structures; thus glucose and mannose (epimer compounds) are correlated with each other. Both of them have, as a structural precursor, the arabinose; however, they do not show a statistically meaningful correlation with arabinose, but there is a correlation between the glucose and the xylose. A possible reason could be that D-glucose and D-xylose have the same conformation. Also, L-rhamnose is a L-xylose methylderivative and is an anologue of L-mannose which is a glucose epimer (Brewster, 1954).

On the other hand, both glucose and mannose have a negative correlation with rhamnose that suggests they can be the precursors of this methylpentose. As rhamnose is a methylderivative of xylose, this may be the reason why there is a positive correlation between glucose and xylose.

The fructose content has a positive correlation with galactose and ribose, which could be explained by the formation of fructose from ribulose.

All the monosaccharides have significant correlation with the total sum, except rhamnose and arabinose.

As a consequence of these observations, the monitoring of the variations in concentration during wine aging must be focused on hexoses other than glucose and fructose and also the pentoses that are related to the oak wood.

The concentrations found during the aging process, considering the coopery and the kind of wood used, are shown in Table 4, where the ANOVA results related to time as a factor are also included. Table 4 shows the results for barrels of different cooperies but always using American oak wood as well as the results obtained from barrels of the same coopery with American oak and French oak. From these data, several conclusions regarding the incidence of the barrel manufacture and the difference due to origins of oak wood can be drawn.

Table 3
Correlation levels between monosaccharides

	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose	Fructose	Ribose	*S. mono*
Arabinose	1.000	–	–	–	–	–	–	–	–
Rhamnose	0.200	1.000	–	–	–	–	–	–	–
Galactose	**0.324**[a]	−0.018	1.000	–	–	–	–	–	–
Glucose	−0.183	**−0.338**	0.042	1.000	–	–	–	–	–
Xylose	0.010	−0.076	−0.124	**0.251**	1.000	–	–	–	–
Mannose	0.009	**−0.243**	−0.032	**0.319**	0.109	1.000	–	–	–
Fructose	−0.079	−0.139	**0.286**	0.075	−0.035	0.056	1.000	–	–
Ribose	−0.061	−0.027	0.064	0.006	−0.040	0.119	**0.352**	1.000	–
S. mono	0.172	−0.093	**0.512**	**0.476**	**0.293**	**0.306**	**0.746**	**0.423**	1.000

[a] Bold significant at $P < 0.05$.

Table 4
ANOVA results[a]

	Component							
	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose	Fructose	Ribose
American oak wood barrels made from different cooperies								
Fcal.	3.24	15.98	4.89	3.39	1.07	1.48	0.94	1.88
Fcrít.	2.27	2.27	2.27	2.27	2.27	2.27	2.27	2.27
Sig.	**	***	***	**	N.S.	N.S.	N.S.	N.S.
American oak wood barrels made by the same coopery								
Fcal.	43.49	1.92	1.45	1.64	2.78	2.02	1.48	1.05
Fcrít.	3.48	3.48	3.48	3.48	3.48	3.48	3.48	3.48
Sig.	***	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
French oak wood barrels made by the same coopery								
Fcal.	0.23	4.38	4.64	0.84	0.77	1.59	0.80	0.69
Fcríti	3.48	3.48	3.48	3.48	3.48	3.48	3.48	3.48
Sig.	N.S.	**	**	N.S.	N.S.	N.S.	N.S.	N.S.

[a] N.S.**,***: Not significant, significance at $P < 0.01$ and $P < 0.001$, respectively.

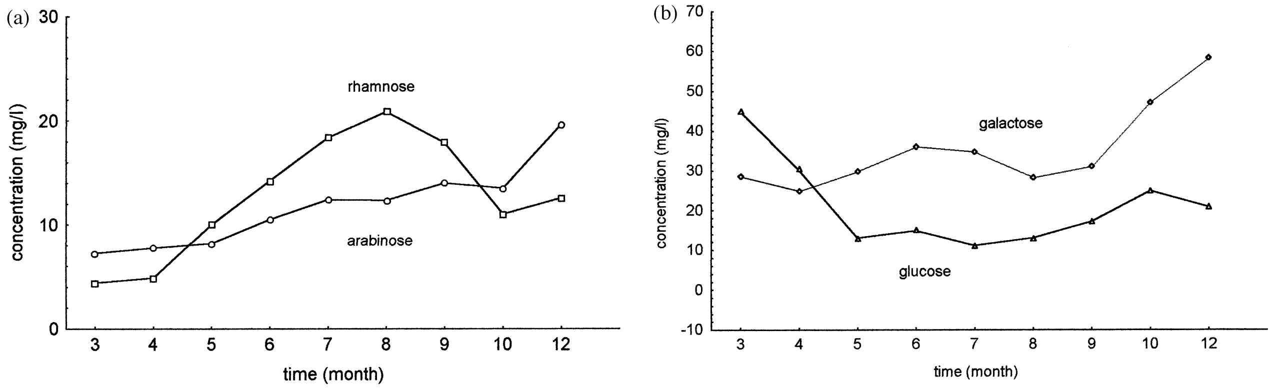

Fig. 1. Changes in the (a) arabinose and rhamnose (b) glucose and galactose contents during the aging of wine in American oak wood barrels from different cooperies.

4. Wine aged in American oak wood barrels made by different cooperies

The concentrations of arabinose, rhamnose, galactose and glucose are statistically significant when the barrel is made of American oak, whoever the barrel maker was, as can be seen in Fig. 1a and b.

4.1. Pentoses

The arabinose content increases slightly with duration in the barrel, which indicates that the wine is enriched in this pentose, as Bozhinov et al., (1984) have observed in brandies, due to the degradation of the hemicellulose. The rhamnose content also increases in the first 6 samples (this period really corresponds to eight months of aging) but decreases afterwards, perhaps due to either its combination as a glycoside with other compounds, such as polyphenols, or by transformation into hexose.

4.2. Hexoses

The glucose content diminishes in the first month and from the 3rd month of sampling shows a slight tendency to increase. Galactose content increases in the wine during aging, though the trend varies according to the time, indicating that its accumulation in the wine can be related to the evolution of the pentoses.

5. Wine aged in barrels from the same manufacturer but made of different wood

5.1. American oak

Arabinose is the only monosaccharide whose variation in concentration with time is statistically significant (Table 4). Arabinose increases but only significantly when the wine is kept in American oak wood, with high values in some cooperies (Table 2). In Fig. 2, the arabinose sequence in American oak wood barrels from the same coopery is presented. Comparing Figs. 1a, 2 and 4 it is deduced that not only the type of oak wood but also the manufacture of the barrel have great influence in the subsequent degradation process of the hemicellulose.

5.2. French oak

The time factor acts in such a way that the concentrations of rhamnose and galactose are the only ones that present statistically significant differences (Table 4). In Fig. 3 it can be observed that the galactose content undergoes few variations between month 4 and 8; from then on it increases. From these results (Table 4) it is deduced that the French oak wood presents greater difficulty for the hemicellulose degradation because the trends are very slight and, consequently, its component contribution to the wine would be slower. Furthermore, as the sugars released are different, it can be said that the geographical origin of the oak wood also modifies the monosaccharide evolution (Figs. 2 and 3).

Related to the arabinose content (Fig. 4), it can also be observed that, only for the American oak wood, the variation is clearly rising, which seems to confirm the

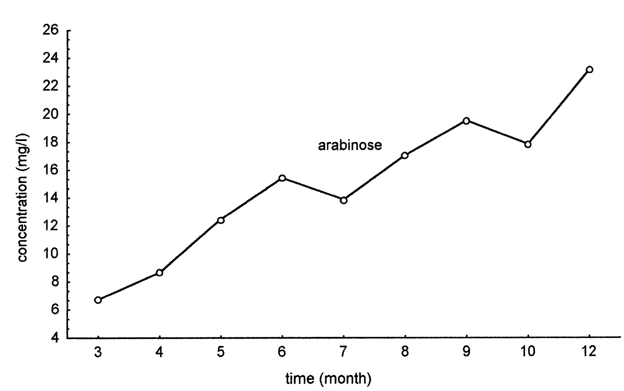

Fig. 2. Changes in the arabinose content during the aging of wine in American oak wood barrels from the same coopery.

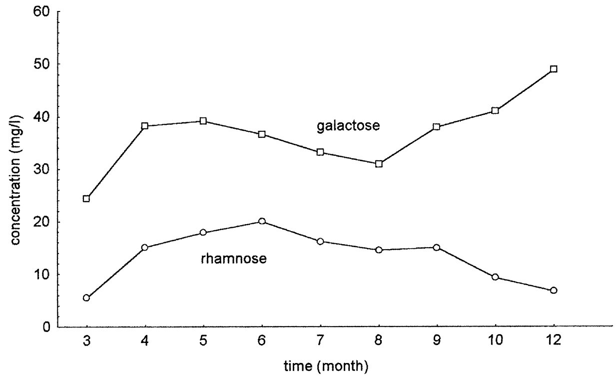

Fig. 3. Changes in the galactose and rhamnose contents during the aging of wine in French oak wood barrels from the same coopery.

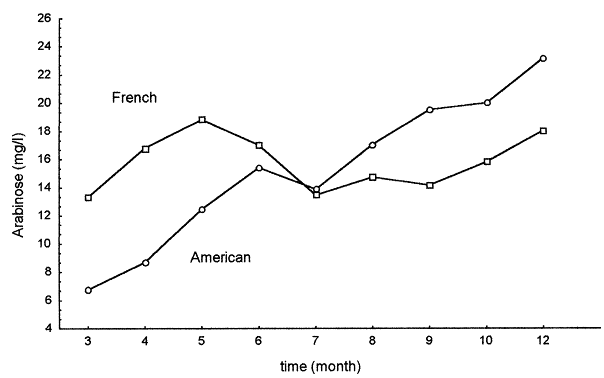

Fig. 4. Change in the arabinose content over time in barrels for both French and American oak wood barrels.

previous commentary on the constitution of the hemicellulose of the French oak that makes it less extractable into the wine and, because of that, the release of its components to the wine is slower.

The galactose increases as much in American oaks as in French ones (Figs. 1b and 3); however, it seems that its evolution is affected by the coopery because, as can be seen in data for the coopery D, statistically significant increases are observed when the wine has been aged in French oak wood (Table 4).

6. Conclusions

The monosaccharide analysis of wine that has been aged for 1 year in oak barrels from different origin and by different manufacturers, shows some interesting aspects: the hexoses are the ones whose variation is the greater; this variation depends on the type of oak wood. Average higher values during the aging are observed for galactose, fructose and xylose.

The relationships between monosaccharides explain some structural ratios and also their sequence of formation can be deduced.

The oak wood variety and the coopery (this latter possibly due to the manufacturing process) have an influence on the monosaccharide composition in the aged wine, which indicates a structural difference between the hemicelluloses of the French and American oak woods.

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