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Analytical Methods

Identification of the origin of commercial enological tannins by the analysis of monosaccharides and polyalcohols

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ABSTRACT

The monosaccharide and polyalcohol composition of 28-samples of different commercial tannins, including oak wood, grape seed and skin, plant gall, chestnut, quebracho and gambier, has been evaluated by gas chromatography–mass spectrometry after derivatization into their trimethylsilyl ethers. Quercitol was found to be characteristic of oak tannins, whereas gall plant tannins could be differentiated by their content of pinitol. *Myo*-inositol and arabitol were detected in tannins from quebracho. These polyalcohols, together with *muco*-inositol and *chiro*-inositol, were found in tannins from chestnut while bornesitol was found to be characteristic of tannins from gambier. Monosaccharide composition also helped to distinguish among tannin origins: arabinose, xylose, fructose and glucose were quantified in oak, quebracho and chestnut tannins, whereas only fructose and glucose were detected in plant gall and grape tannins. These results imply that the qualitative study of monosaccharides and polyalcohols could help to determine and control the authenticity of enological tannins.

1. Introduction

The use of enological tannins in winemaking is a long-used technological practice. These tannins are natural substances, of plant origin, which are from several botanical species. Generally, these products are classified according to their origin into two groups: (i) hydrolysable tannins, derived mainly from oaks or other plant species, and (ii) condensed tannins, mainly from grapes. According to the International Enological Codex of the International Organization of Vine and Wine (O.I.V.), enological tannins should be extracted from the gall nuts of *Quercus* sp. (such as Aleppo galls) or tara (*Caesalpinia spinosa*), oak wood (*Quercus* sp.), grape seeds (*Vitis vinifera*), the trunk of certain trees such as quebracho (*Schinopsis balansae)* or chestnut (*Castanea* sp.) and from the stems and leaves of some plants, such as gambier (*Uncaria gambier*).

Although tannins are commonly used in enology to protect musts from undesirable oxidations, in recent years, different complex preparations of tannins have been formulated in order to contribute to wine structure and to stabilize the colouring material. On the other hand, the employment of tannins in wines is a very useful tool to improve their astringency (Parker et al., 2007). A wide spectrum of enological tannins is available on the market, mostly classified according to their enological properties. Nevertheless, sometimes their nature is not adequately defined, so it is not always possible to know their botanical origin. From an economical and technological viewpoint, it is important to develop analytical methods to study the differences existing among commercial tannins which could help to determine their authenticity. Moreover, wine organizations, such as O.I.V., encourage the development of new procedures that can be used to guarantee the authenticity of commercial tannins in order to respond satisfactorily to winemakers' needs. In these terms, a study based on the characterisation of proanthocyanidin composition of grape and quebracho tannins has recently been undertaken, using MALDI-TO-MS (Vivas et al., 2004).

Polyols, such as arabitol, xylitol, mannitol and *myo*-inositol, have been extensively investigated in wine (Dubernet, Bertrand, & Ribéreau-Gayón, 1974; Olano, 1983; Sponholz, Lacher, & Dittrich, 1986), but to the best of our knowledge, their presence in tannins has not yet been evaluated. *Scyllo*-inositol has also been detected in grapes and wine (De Smedt, Liddle, Cresto, & Bossard, 1981) and has been proposed, along with *myo*-inositol, to control the genuineness of the concentrated rectified grape must (Monetti, Versini, Dalpiaz, & Raniero, 1996; Versini, Dallaserra, & Margheri, 1984). More recently, *chiro*-inositol and quercitol have been detected for the first time in wines (Carlavilla, Villamiel, Martínez-Castro, & Moreno-Arribas, 2006). Quercitol (1,3,4/2,5-cyclohexanepentol) is present in different oak species (Anderson, 1972) and has also been proposed as a marker to differentiate oak honeydew honeys from honeys of different origins (Sanz, González, de Lorenzo, Sanz, & Martínez-Castro, 2005). *Chiro*-inositol has also been found in citrus fruits, such as grapefruit, lemon, lime, mandarine and orange (Sanz,

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Villamiel, & Martínez-Castro, 2004). In relation to the monosaccharides transferred from wood to different matrices, the sugar content has recently been proposed as an important parameter to classify Brandy de Jerez according to its ageing (Martínez-Montero, Rodríguez Rodero, Guillén Sánchez, & García Barroso, 2005).

The current work was undertaken to study the monosaccharide and polyalcohol composition of commercial enological tannins from different origins (plant galls, chestnut, seed and skin grape, oak wood, quebracho and gambier) by GC–MS analysis. These studies represent an easy way to characterise the enological tannins currently found on the market.

2. Materials and methods

2.1. Reagents

Trimethylsilylimidazole (TMSI) and trimethylchlorosilane (TMCS) were from Sigma-Aldrich Chem. Co. (Steinheim, Germany) and dried pyridine was from Merck (Darmstadt, Germany).

2.2. Standards

Phenyl-β-glucoside (internal standard), glucose, fructose, arabinose, xylose, arabitol, pinitol, *myo*-inositol, *scyllo*-inositol, *muco*-inositol and *chiro*-inositol were acquired from Sigma-Aldrich Chem. Co. (Steinheim, Germany). As quercitol and bornesitol were not commercially available, aqueous extracts were prepared from oak acorns of *Quercus* sp. and from *Echium vulgare* leaves, respectively. The extracts were evaporated at low temperature under vacuum, silylated and injected as described below. Carbohydrate composition (in triplicate, RSD $\leqslant$ 5%) of the acorn extract was 68% quercitol, 20% fructose and 18% glucose; for the *Echium* extract, composition was 20% fructose, 33% glucose, 27% bornesitol, 2% *myo*-inositol and 19% sucrose. GC–MS data of quercitol and bornesitol are shown in Fig. 1.

2.3. Samples

Twenty-eight samples of different commercial tannins, namely oak wood (O; $n = 4$), grape seed (S; $n = 6$), grape skin (H; $n = 2$), plant galls (G; $n = 6$), chestnut (Ch; $n = 3$), quebracho (Q; $n = 3$), gambier (GMB; $n = 1$) and mixtures labelled as grape + quebracho (GQ; $n = 1$), quebracho + chestnut + plant gall (QChG; $n = 1$) and chestnut + quebracho (ChQ; $n = 1$) tannins, were directly purchased in the market or supplied by the manufacturers. Moreover, water extracts of oak and chestnut wood, grape skin, grape seed, tara pods, and quebracho leaves were analyzed as references.

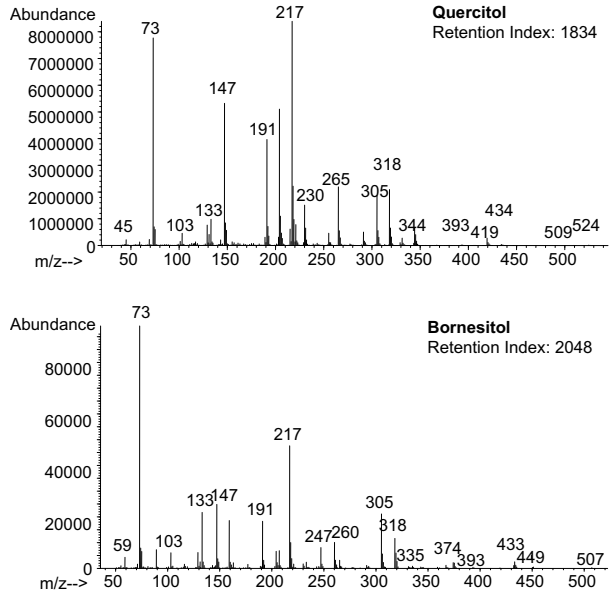

Fig. 1. GG–MS data of quercitol and bornesitol.

2.4. Analysis of carbohydrates and polyalcohols

2.4.1. General

Analysis of carbohydrates and polyalcohols was carried out in duplicate by GC according to the method described by Carlavilla et al. (2006). Samples were previously converted to their trimethylsilyl ethers: 50 mg of tannins were dissolved in 5 ml of deionized water and filtered through Whatman No. 1 filter paper. One millilitre of the sample was mixed with 1 ml of phenyl-β-glucoside (1 mg ml^{-1} prepared in 70% methanol), as internal standard. This mixture was evaporated under vacuum and trimethylsilyl derivates were formed by addition of 100 μl of anhydrous pyridine, 100 μl of trimethylsilylimidazole (TMSI) and 100 μl of trimethylclorosilane (TMCS), shaking after each addition. Extraction of trimethylsilyl (TMS) derivatives was carried out using 100 μl of hexane and 200 μl of water. One microlitre of the hexane upper layer was injected on the GC.

2.4.2. GC–FID analysis

GC analyses were carried out in a gas chromatograph equipped with a flame ionisation detector (FID) (HP 5890, Palo Alto, CA, USA), using nitrogen as carrier gas. A 25 m × 0.25 mm i.d. × 0.25 μm film thickness fused silica column coated with SPB-1 (crosslinked methyl silicone) from Supelco (Bellefonte, PA, USA) was used. Injector and detector temperature were 300 °C. Oven temperature was maintained at 100 °C for 1 min, then programmed at 200 °C at a heating rate of 30 °C min^{-1} and kept for 15 min and finally programmed at 270 °C at 15 °C min^{-1} and maintained for 20 min. Injections were made in splitless mode. Chromatographic peaks were measured using a Chrom-Card 1.20 acquisition system (CE Instruments, Milan, Italy). Quantitative analysis was carried out using the response factor (RF) of each standard relative to phenyl-β-D-glucoside (internal standard) over the expected range. The concentration of compounds for which standards were not available was estimated assuming a response factor equal to 1. Reproducibility of the method was evaluated by analyzing one sample on five different days. The detection (LOD) and quantitation (LOQ) limits were calculated for each compound according to Foley and Dorsey (1984). Mean values of 0.004 mg g^{-1} and 0.013 mg g^{-1} were obtained for LOD and LOQ, respectively.

2.4.3. GC–MS analysis

GC–MS analyses were carried out using a Hewlett–Packard 6890 gas chromatograph coupled to a 5973 quadrupole mass detector operating in electronic impact (EI) mode at 70 eV (both from Hewlett–Packard, Palo Alto, CA, USA). Operating conditions other than carrier gas (He at 1 ml min^{-1}) were similar to those previously described for GC analysis. Acquisition was done using a HPChem Station software (Hewlett-Packard, Palo Alto, CA, USA).

3. Results and discussion

Fig. 2 shows the chromatographic profiles of the seven tannin sources analyzed by GC. Identity of each compound was confirmed by comparing their retention times and mass spectra, using the GC–MS method, with those of standards. The heterogeneity of their carbohydrate composition, including eight polyalcohols (mainly

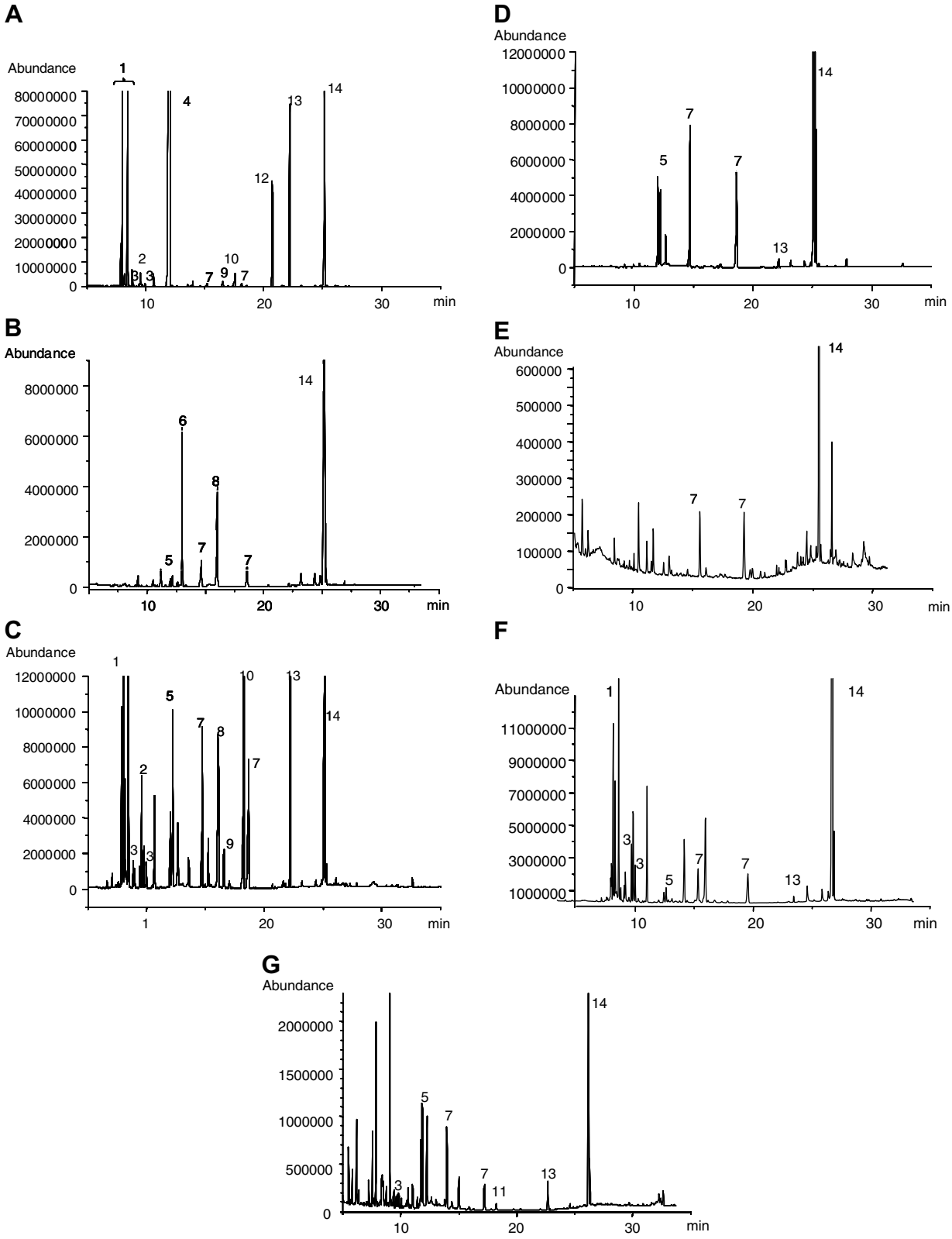

Fig. 2. Gas chromatographic profiles of polyalcohols and carbohydrates in commercial tannins of (A) oak wood, (B) plant gall, (C) chestnut wood, (D) seed grape, (E) skin grape, (F) quebracho wood, (G) Gambier. 1-Arabinose, 2-arabitol, 3-xylose, 4-quercitol, 5-fructose, 6-pinitol, 7-glucose, 8-gallic acid, 9-*muco*-inositol, 10-*chiro*-inositol, 11-bornesitol, 12-*scyllo*-inositol, 13-*myo*-inositol, 14-phenyl-β-D-glucoside (i.s.).

cyclitols) and four monosaccharides, could be related to the plant origin of the samples.

Polyalcohol contents of the 28 commercial tannins from the different origins are shown in Table 1. Quercitol, together with arabitol, *muco*-inositol, *chiro*-inositol, *scyllo*-inositol and *myo*-inositol, appeared in oak wood tannins. Chestnut tannins also presented a complex composition of polyalcohols: arabitol, *muco*-inositol, *chiro*-inositol and *myo*-inositol were detected; however, the

Table 1
Concentration of polyalcohols (mg/100 g) in commercial enological tannins

		Arabitol (mg/100 g)	Quercitol (mg/100 g)	Pinitol (mg/100 g)	Bornesitol (mg/100 g)	*Muco*-inositol (mg/100 g)	*Chiro*-inositol (mg/100 g)	*Scyllo*-inositol (mg/100 g)	*Myo*-inositol (mg/100 g)
Oak wood	O1	0.06	6.92	–	–	0.10	0.10	0.52	0.49
	O2	0.06	4.49	–	–	0.11	0.11	0.57	0.55
	O3	0.05	1.57	–	–	0.04	0.02	0.13	0.12
	O4	0.09	3.14	–	–	0.14	0.17	0.17	0.30
Gall plant	G1	–	–	0.73	–	–	–	–	–
	G2	–	–	0.26	–	–	–	–	tr*
	G3	–	0.03	0.07	–	–	–	0.03	tr
	G4	–	0.06	0.06	–	–	–	0.04	–
	G5	–	–	1.35	–	–	–	–	0.02
	G6	–	–	–	–	–	–	–	–
Seed grape	S1	–	–	–	–	–	–	tr	0.16
	S2	–	–	–	–	–	–	tr	0.01
	S3	–	–	–	–	–	–	0.38	2.34
	S4	–	–	–	–	–	–	tr	0.01
	S5	–	–	–	–	–	–	–	0.01
	S6	0.64	–	–	–	–	–	tr	0.25
Skin grape	H1	–	–	–	–	–	–	–	–
	H2	–	–	–	–	–	–	–	tr
Chestnut	Ch1	0.08	–	–	–	0.14	0.55	–	0.62
	Ch2	0.04	–	0.49	–	0.03	0.33	–	0.05
	Ch3	0.07	–	–	–	0.19	0.52	–	0.49
Quebracho	Q1	tr	–	–	–	–	–	–	0.01
	Q2	0.02	0.05	0.09	–	–	–	–	tr
	Q3	0.03	–	–	–	0.02	–	–	0.05
Gambier	GMB	0.01	–	tr	0.02	–	–	–	0.03
Grape + quebracho	GQ	0.10	–	0.19	–	0.02	0.06	–	0.07
Quebracho + chestnut + gall	QChG	0.03	–	0.19	–	0.03	0.12	–	0.12
Chestnut + quebracho	ChQ	0.05	–	–	–	0.13	0.56	–	0.53

* tr, traces.

presence of *scyllo*-inositol and quercitol was not observed. It is worth noting that these two polyalcohols, together with *myo*-inositol, were the most abundant in oak tannins. Pinitol was only detected in one chestnut sample (Ch2) which could come from the contribution of other tannin sources.

Tannins from plant galls were characterised by the presence of pinitol. Gallic acid was also detected in all plant gall tannins, although the derivatization method used in this work was not the most appropriate for acids, so this was not quantified. Owing to the unusual composition of G6, which only showed high amounts of gallic acid, this sample was excluded from the study. The remaining examined gall tannins probably proceed from tara (*C. spinosa*) or maybe *Acacia* sp. Both trees belong to the *Fabaceae* family which is characterised by the presence of pinitol. Small amounts of quercitol and *scyllo*-inositol were observed in G3 and G4 which could indicate the contribution of oak galls in these samples.

Apart from arabitol in S6, only *scyllo*- and *myo*-inositol could be detected in tannins from seed grapes, whereas no polyalcohols were noted in the skin grape tannins in contrast to that found in young wines (*chiro*-inositol, *scyllo*-inositol and *myo*-inositol) (Carlavilla et al., 2006). The *myo*-inositol/scyllo-inositol ratio was high, as reported previously in musts and wines (Monetti et al., 1996; Versini et al., 1984), in contrast to that found in oak wood and tannins (Table 1). Only small amounts of some polyalcohols, such as arabitol or *myo*-inositol, were detected in tannins from quebracho. The presence of low concentrations of quercitol and pinitol in sample Q2 could indicate the presence of mixtures of oak and tara galls in this sample. Only one sample from gambier could be acquired, which showed the presence of bornesitol and small amounts of *myo*-inositol. Bornesitol is a methyl-inositol which has been found in the *Rubiaceae* family to which *U. gambier* belongs (Plouvier, 1963).

The mixture containing quebracho and chestnut showed relatively high amounts of *muco*-, *chiro*- and *myo*-inositol, as did the chestnut sample. On the other hand, the mixture of quebracho, chestnut and gall plant (QChG) seems to have a lower contribution of chestnut, on the basis of inositol contents and a higher contribution of plant gall tannins, implied by its pinitol contents. A similar GC profile to QChG was found for the mixture of grape and quebracho, indicating the contribution of plant galls and chestnut in this sample.

Regarding the monosaccharide composition (Table 2), arabinose, xylose, glucose and fructose were found in tannins from oak, chestnut and quebracho, whereas tannins from gall and from seed grapes only showed glucose and fructose, with the exception of sample S5 in which xylose was detected. Both skin grape tannins showed the presence of glucose, although H2 was also composed of xylose, arabinose and fructose. Glucose and fructose were the main monosaccharides for the gambier tannin and only small amounts of xylose were detected in this extract.

The value of these compounds for distinguishing the different origins of tannins was tested using some original samples as references (oak wood, grape skin, grape seed, tara gall and quebracho leaves). Quercitol was only found in oak wood, which confirms its usefulness as a marker in oak tannins. Grape skin and seeds mainly showed glucose, fructose, *scyllo*- and *myo*-inositol. This carbohydrate composition confirms that the high amounts of xylose and arabinose found in tannin H2 could come from its mixture with a tannin of different botanical origin, such as quebracho. Fructose, glucose and high amounts of pinitol were observed in tara pods as in plant gall tannins. Quebracho extract showed small amounts of *myo*-inositol and some pentoses and hexoses, as in the corresponding tannins. Chestnut wood extract was mainly composed of sucrose (80%) followed by glucose and fructose (11% and 7%, respectively); *muco*-, *chiro*-, *scyllo*- and *myo*-inositol (0.4, 0.8, 0.1 and 0.6%, respectively) were also found in this extract. Except for *scyllo*-inositol (which was very low), these polyalcohols were found in chestnut tannins which confirms the identity of their botanical source. Pinitol was not detected in chestnut extract,

Table 2
Concentration of monosaccharides (mg/100 g) in commercial enological tannins

		Xylose (mg/100 g)	Arabinose (mg/100 g)	Fructose (mg/100 g)	Glucose (mg/100 g)
Oak wood	O1	0.29	1.18	–	0.22
	O2	0.57	2.53	–	0.07
	O3	0.37	0.85	0.12	0.58
	O4	0.41	1.84	1.82	2.69
Gall plant	G1	–	–	0.26	0.42
	G2	–	–	0.07	0.17
	G3	–	–	0.05	0.05
	G4	–	–	0.11	0.16
	G5	–	–	0.50	0.63
	G6	–	–	–	–
Seed grape	S1	–	–	10.0	9.59
	S2	–	–	0.64	0.50
	S3	–	–	45.2	32.5
	S4	–	–	0.61	0.46
	S5	0.13	–	–	0.03
	S6	–	–	1.22	tr*
Skin grape	H1	–	–	–	0.07
	H2	0.31	0.48	0.30	0.67
Chestnut	Ch1	0.50	1.46	1.15	0.78
	Ch2	0.41	1.04	0.95	0.91
	Ch3	0.65	1.55	0.28	0.69
Quebracho	Q1	0.30	0.44	0.22	0.20
	Q2	0.07	0.10	0.05	0.10
	Q3	0.16	0.42	0.32	0.59
Gambier	GMB	0.02	–	0.42	0.12
Grape + quebracho	GQ	0.07	0.11	0.25	0.28
Quebracho + chestnut + gall	QChG	0.04	0.07	0.17	0.30
Chestnut + quebracho	ChQ	0.29	1.29	1.34	1.46

* tr, traces.

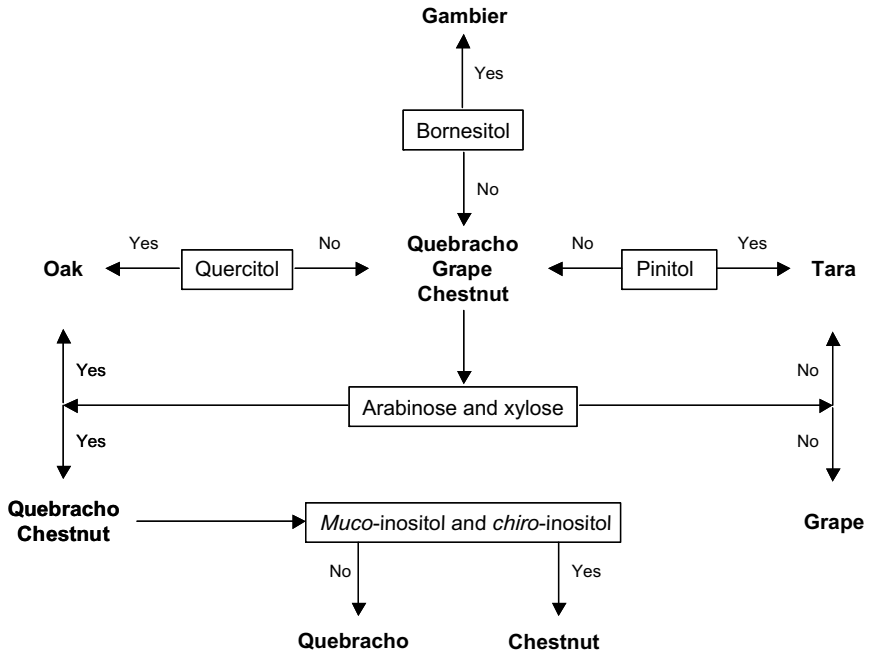

Fig. 3. Scheme of tannins classified according to their monosaccharide and polyalcohol composition.

indicating that its presence in Ch2 tannin was probably due to the contribution of gall tannin in this sample.

From the above results, tannins could be classified according to the scheme suggested in Fig. 3. The presence of quercitol is indicative of tannins from oak wood, whereas pinitol is mainly an indicator of tannins from tara galls and bornesitol from those of gambier. The monosaccharide composition can also be used to distinguish the different botanical origins: absence of arabinose and xylose in samples with pinitol may confirm the gall origin, while these sugars should be present in tannins with quercitol. Therefore, quercitol, pinitol, bornesitol, arabinose and xylose could be used to unequivocally differentiate these products, and, to distinguish these tannins from the other products analyzed.

Tannins from galls and grapes can easily be differentiated from other origins due to the absence of arabinose and xylose in their monosaccharide composition. The presence of *muco*- and *chiro*-inositol could be useful for distinguishing tannins of chestnuts from those of quebracho.

It is also essential to consider that tannins can be composed of mixtures of different origins and both main source and other contributions could easily be revealed by the saccharide and polyalcohol composition. Nevertheless, more samples of these origins are required in order to confirm the results obtained here.

In conclusion, the overall chromatographic profiles, including polyalcohols (arabitol, quercitol, pinitol, bornesitol, *chiro*-inositol, *muco*-inositol, *scyllo*-inositol and *myo*-inositol) and monosaccharides (arabinose, xylose, fructose and glucose) can be a useful tool for distinguishing tannins of different origins. These results suggest that the analysis of certain polyalcohols and carbohydrates could be used in the wine industry to select or control the authenticity of enological tannins.

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