ON THE PECTIC POLYSACCHARIDES IN WINE

POLIZAHARIDELE PECTICE DIN VIN

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Abstract. *The pectic polysaccharides in wine, wich belong in the ramnogalacturonan class, are characterized by a low degree of polymeriyation (~30) and a molecular mass of 5.3 KDa. They form chelatic bonds with the metal cations in wine and yield stable insoluble chemical compounds. They are little known in our literature and their technological implications for wine are commonly ignored.*
Key words: polyssacharides, ramnogalacturonans, pectine chaine, chelats.

Rezumat. *Polizaharidele pectice din vin, fac parte din clasa Ramnogalacturanilor şi se caracterizează printr-un grad mic de polimerizare (~30) şi masa molecular de 5,3 KDa. Sunt macromolecule puternic ramificate. Formează cu metalele grele din vin compuşi chelatici stabili. Sunt mai puțin cunoscute în literature noastră de specialitate şi implicațiile lor tehnologice în vin, adesea ignorate.*
Cuvinte cheie: polizaharide, ramnogalacturani, lanț pectinic, chelați.

INTRODUCTION

The pectic polyssacharides – neutral or acid – appear during the maturation period of grapes and do not disintegrate during the alcoholic fermentation of the must, consequently they will all make their way into the wine (Țârdea, 2007).

They are macromolecular compounds (mixed polyuronides), which following hydrolysis yield uronic acids of various types: D – galacturonic, D – glucuronic, D – octulosonic, D – deoxy – heptulosaric, L – aceric, as well as monosaccharides – ramnopyranose, mabinofuranose, galactopyranose, xylopyranose, apiofuranose a.o.

The pectic polysaccharides in wine are not sweet. They are part of the structure of the pectins and vegetable gums and mucilages (Brillonet et al., 1990).

Although they exist in small amounts, their presence has important technological implications: the proteic stability of wines; the formation of chelatic compounds with the metals in wines and the filtration of wines (Pellerin and O'Neill, 1998).

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RESULTS AND DISCUSSIONS

We have isolated the pectic polysaccharides neutral and acid, of the ramnogalacturonic type and an aply branched out molecule, which makes for their great chemical stability.

Structure: one main chaine made up of L-D-galacturonic acid and monosaccharides (α - L- ramnose) through 1 → 4 glycosidic bonds, on which are grafted the lateral monosaccharine, mainly rhamnose, chains. The overall structure is aply branched out and this confers ramnogalacturonans a complex chemical stability. According to their respective complexity, ramnogalacturonans fall into two main types: RGI and RGII.

Type I ramnogalacturonans (RGI) are neutral pectic polysaccharides, which result from the insertion of α - 1- ramnopyranose remains between the molecules of D – galacturonic acid in the pectin chain:

[→2) – h – L – Rna p – (1→4) – L – D – Gal Ap – (1 →]

Substitution in the position 1 – 4 of hall of the molecules of – L ramnopyranose by other monosaccharides (arabinose, galactose, xilose) or by means of lateral chains of arabanes, galactans and arabinogalactans (neutral polysaccharides) yields amply branched out RGIs. RGI have been found only in red wines, in amount of < 20 mg/l; they have not been found in white ones (Gerband, 1996).

Type II Ramnogalacturonans (RGII) prevail in wines. These are acid pectic polysaccharides of much greater complexity, being anionic macromolecules. Their main chain is made up of 8 D - galacturonic acid molecules linked by α bonds (1→4) on which are grafted 4 other lateral oligosaccharides chains (branches), well defined, 2 disaccharides and 2 octosaccharides. Their molecules contanins a series of rare saccharides (α - L – fucose, α - D –xylose , α - D – galactose, ß - D – apiose) and rare acids (ß - D – glucuronic, ß - D – heptulosaric, ß - L – aceric), plus ramified chains with α and ß galacturonic acids. The structural pattern is shown in Fig. 1.

Type II ramnogalacturonans (RGII) yield reticulated dimmers with the boric acid esters and are consequently abbreviated as dRGII (d = dimer). They exist in wines in larger amounts which vary within wide limits: 20-50 mg/L in white wines to 100-150 mg/l in red wines. Homogalacturonans made up of identical monomers are found in direct producer hybrid wines and in the wines produced with enzyme mixtures.

Technological implications

Pectic polysaccharides influence the technological filtration of wine (the clearing up of wine through filtration). The most important result in their interaction with the metals in wine and the formation of stable chelatic compounds.

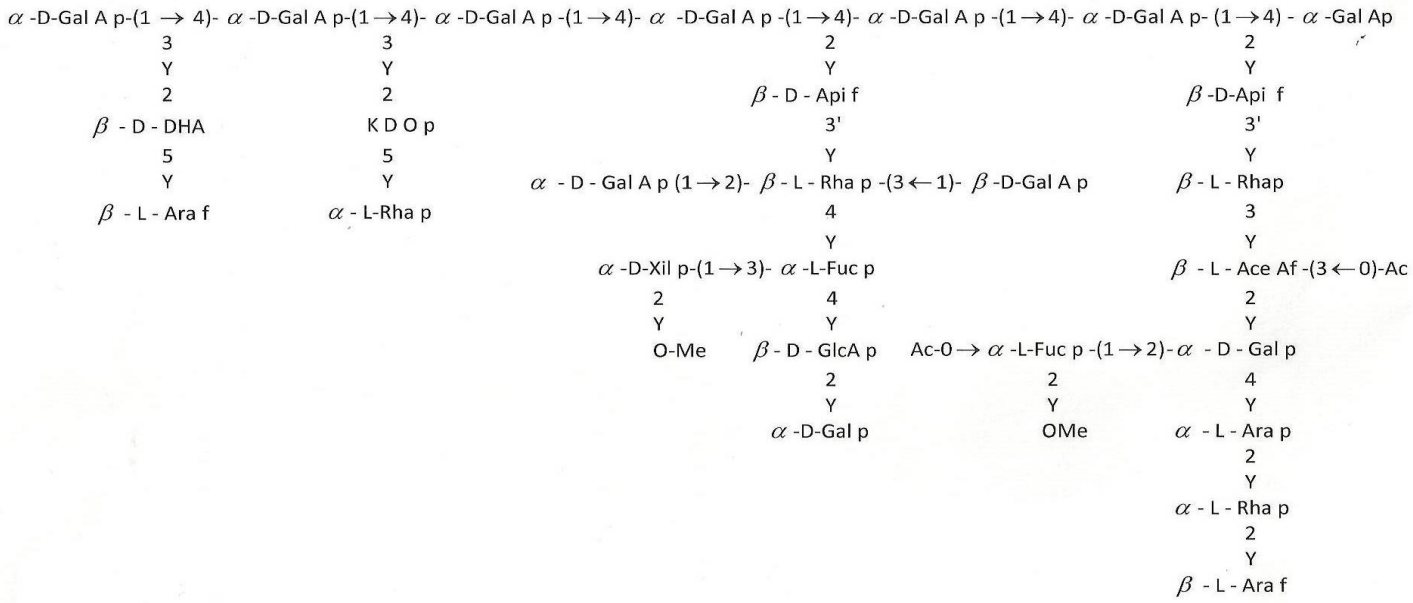

Fig. 1. Structural pattern of the Type II Ramnogalacturuonan (RG II)

Abbreviations:

β - D - DHA = deoxy-heptuloronic acid;
β - L - Ara f = β - L-arabinofuranoza,
β - D - Api f = β -D-apiofuranoza;
K D O p = deoxy-D-octuloronic acid,
β - D - Glic A p = β -D-glicuronic acid,
2-O-Me = 2- O-methyl.

α -D-Gal p = α -D-galacturopyranoza;
α - L - Rha p = α -L-ramnopiranoza;
α - D - Gal p = α -D-galactopiranoză;
β - L - Ace A = β -L-aceric acid,
α -L-Fuc p = α -L-fucopyranoza;

The chelation of the metal cations in wine by the dRGII is highly specific and depends on the physio-chemical proprieties of the cations: +2 or + 3 valence; ion radius > 0.95 A< weak ionization energy and an affinity for oxygen yielding ligands (Pellerin,O'Neil, 1998). The cations with which they yield stable chelatic compounds are those of heavy metals (Pb^{2+}, Ba^{2+}, Sr^{2+}) as well of those of lanthanides/rare metals (La^{3+}, En^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}). There are exclusive essential cations, e.g. Fe^{2+}, Cu^{2+}, Yn^{2+} and Mg^{2+}.

Because Pb2+ is toxic as a result of fixing by means of dRGII, its bioavailability in wines is reduced in the interest in human health (Pellerin et al., 1997).

CONCLUSIONS

To date there is no research on the pectic polysaccharides in the wines produced in the Romanian vineyards. Also, there is no research on the lead content in wines, its bioavailability and its intrinsic toxicity for the human organism.

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