SOME ASPECTS OF THE CHARACTERIZATION OF VEGETABLE GUMS: *PRUNUS PERSICA* (PLUM) and *PRUNUS DOMESTICA* (CHERRY)

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The paper deals with the characterization of some vegetable gum exudates (plum tree, cherry tree) by FTIR spectroscopy, C^{13} NMR spectroscopy, thermo-gravimetric and rheological analyses of the dilute aqueous solutions. The functional groups and main components of the studied gums have been identified: galactan, xylan, arabinan. It is emphasized that there are differences in thermal stability between the two gums. For the dilute aqueous solutions of the analyzed gums, with a concentration ranging between 0.005-2.0 g/dL, Huggins constant values [K] and intrinsic viscosity [η], which are dependent on the structure, molecular weight and interactions between existing functional groups, were established.

Keywords:vegetable gums, termogravimetric analysis, intrinsic viscosity, C^{13} NMR, FTIR

INTRODUCTION

Vegetable gums are exudates secreted as a result of pathogenic action, caused either by the attack of microorganisms, or by injuries to trees. Vegetable gums may be also extracted by water boiling of wood samples. The first details of the polysaccharide from plum tree gum analysis were given by a British researcher in 1950, who separated a plum gum component, GlcpA-(1-6)-Gal,[1] after acid hydrolysis. The chemical composition of gums is not uniform, varying by season and wood species. The macromolecular chains of vegetable gums have a complex structure, being formed by a primary chain composed from elementary units of D-galactopyranose connected by C_1-C_3 and C1-C6 glycosidic links. Other types may also contain basic units of D-mannopyranose and side chains, which generally consist of D-glucuronic acid elementary units and units of L-ramnopyranose, L-arabinopyranose and D-xylopyranose.[2] For a better understanding of plum and cherry gum properties and structure, the following analytical techniques were used: FTIR spectroscopy, C^{13} NMR, TG-DSC and rheological characterization of aqueous solutions.

EXPERIMENTAL

Materials

The vegetable gums from *Prunus domestica* (plum) and *Prunus avium* (cherry) species were collected as tree exudates from the north-east of Romania, Husi region. After the collection, gums were dried at room temperature and powdered.

FTIR spectroscopy

FTIR spectra of the plum and cherry gums were obtained by KBr pellet technique on a Digilab FTS 2000 spectrometer. Scans (32) were performed in the range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}.

C^{13} NMR spectroscopy

The C^{13} NMR spectra of the plum and cherry gums were obtained by using a BRUKER AVANCE 400 WB spectrometer. The powdered samples were packed uniformly in 4 mm-zirconia rotors, which were spun at 9.5 kHz under air flow. High-resolution solid state C^{13} NMR spectra were recorded with cross polarization/magic angle spinning (CP/MAS). The external standard for the calibration of the chemical shift scale was tetramethylsilane ($Si(CH_3)_4$). The integration of the spectral region was performed by using Knowitall® Academic Edition (Bio-Rad Laboratories, Inc) software.

Thermogravimetric analysis

In order to determine the changes occurring during the heating process, the TG-EGA-FTIR analysis line consisted of a Diamond TG/DTA (PerkinElmer), a TG-FTIR (PerkinElmer) gas transfer accessory (1.6 m stainless steel 1.5 mm tube heated at 220 °C), a heated gas cell of 100 mm length with KBr windows (heated at 150 °C) and a FTIR spectrometer Spectrum 100 (PerkinElmer). The Spectrum TimeBase (PerkinElmer) software records every 15 s a single spectrum within the 700-4000 cm^{-1} range, at the resolution of 4 cm^{-1}. The analyses were run on 20 mg sample for plum gum and 6 mg sample for cherry, both placed into a platinum crucible, under dynamic dry atmosphere (100 mL/min), at a heating rate of 10 °C/minute within the 30-400 °C temperature range.

Rheological and viscosimetric characterization

Viscometric measurements were carried out using an Ubbelohde viscometer V_2, K = 0.003 at 25 ± 0.01 °C. Several dilutions were made *in situ*. [η] was determined using a Huggins plot of η_{sp}/c versus c, where c is concentration and η_{sp} is specific viscosity. The concentration range used in the determination was 0.1-2 g/dL, in the case of the plum gum, and 0.03-0.25 g/dL, in the case of the cherry gum.

RESULTS AND DISCUSSION

FTIR spectroscopy

Figures 1 and 2 display the FTIR spectra of the studied plum and cherry gums. Their characteristic spectral bands point out to some functional groups. Absorbance values, functional groups and vibration mode are presented in Table 1.

C^{13} NMR spectroscopy

C^{13} NMR spectra of the plum and cherry gums are shown in Figures 3 and 4. The major reported peaks are: (60-70 ppm) range corresponding to C6, (70-81 ppm) corresponding to C2, C3 and C5 with overlapped signals, (81-93 ppm) corresponding to C4, (102-108 ppm) corresponding to C1 anomeric carbon and (172-175 ppm)[10] corresponding to carboxyl groups. The main polysaccharide components of the plum and cherry gums are presented in Table 2. In the 70 ppm region, there are chemical shifts of a single carbon linked by one oxygen atom. The chemical shift of the carbon atoms bound to oxygen atoms is also present in the 105 ppm region.[14,9] In this case, the C3 carbon from the structure of arabinan is linked to a single oxygen atom; the C1 from the structure of galactan would be linked to two oxygen atoms. The chemical shift at 175 ppm can be attributed to C6 from the glucuronic acid structure. In Figures 5 and 6 displays the structures of arabinan and galactan, the components identified using C^{13} NMR analysis.

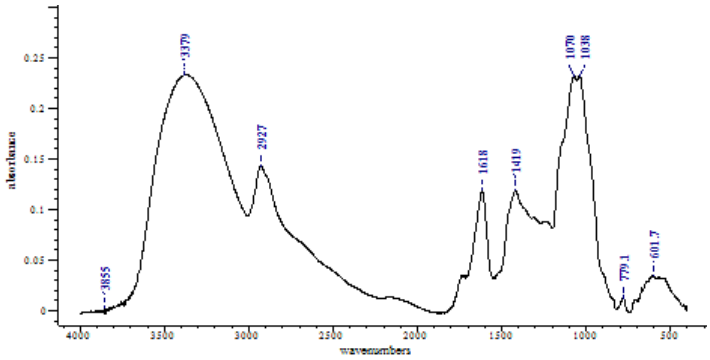

Figure 1: FTIR spectrum of plum gum

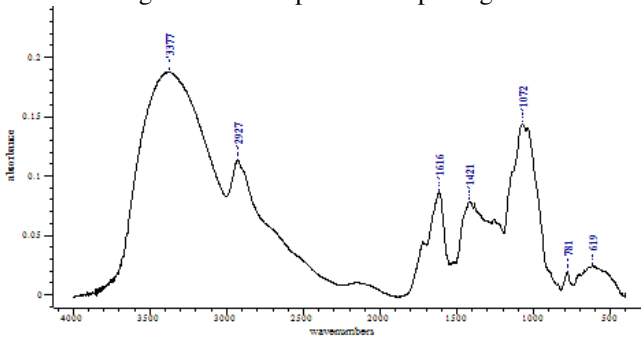

Figure 2: FTIR spectrum of cherry gum

Table 1
Value absorbances, functional groups and types of vibration of plum and cherry gum

Wave number, cm-1 Plum gum sample	Wave number, cm-1 Cherry gum sample	Functional groups/vibration mode	References
3379	3377	O-H groups, stretching vibration	[3]
2927	2927	C-H stretching, symmetric, asymmetric	[4]
1618	1616	COO groups, valence vibration	[5]
1419	1421	COO groups, symmetric stretching	[6]
1070 (1038)	1072 (1038)	C-O, valence vibration of uronic acids	[7]
779, 601	781, 619	C-C-O, C-O-C groups, symmetric, asymmetric	[8]

Table 2
Characteristics of solid state C^{13} NMR spectra of plum and cherry gums

Assignment	Chemical shift, ppm	References
Carboxyl group	175	[11]
Galactan C1	104	[11, 16]
Arabinan C2	82	[12]
Xilan C2	74	[13]
Arabinan C3	71	[12]
Xilan C5	64	[11]

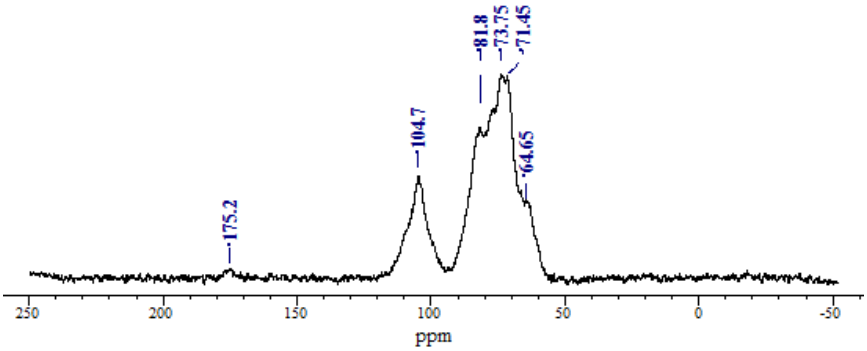

Figure 3: C^{13}NMR spectrum of plum gum

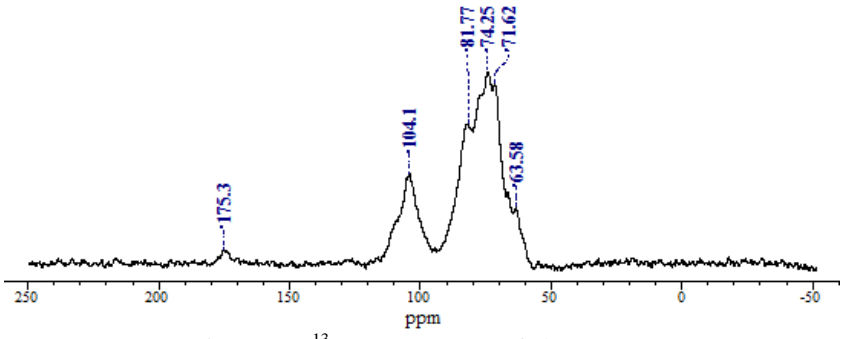

Figure 4: C^{13}NMR spectrum of cherry gum

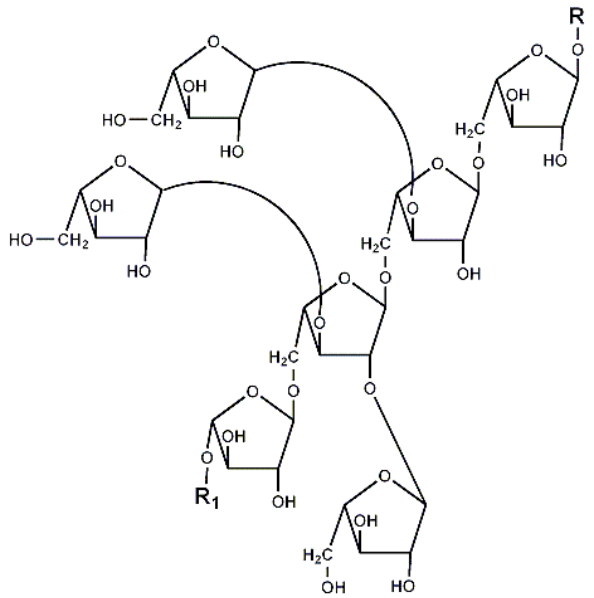

Figure 5: Structure of arabinan isolated from plum seeds proposed by Dourado *et al.*[15]

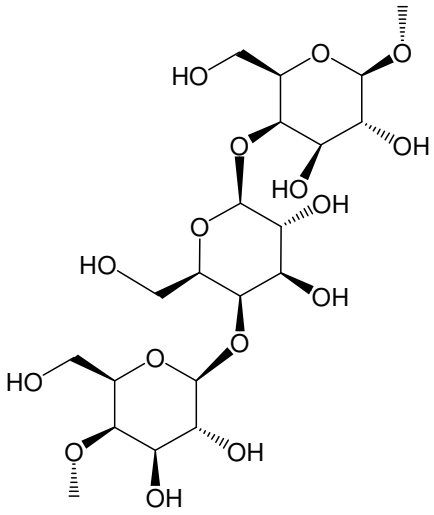

Figure 6: Structure of galactan

Thermal analysis

In Figure 7, the thermal decomposition process for cherry gum can be observed: the first phase decomposition takes place in the 30-200 °C temperature range with a maximum degradation rate at 80 °C, the mass loss being of 10.6%; the second phase (the total mass loss is of 60.8%) holds multiple decomposition processes, as follows:

- in the range of 200-266 °C, the maximum rate occurs at 252 °C, with a mass loss of 24.3%;
- between 266-307 °C, the maximum rate is reached at 268°C, with a mass loss of 19%;
- in the interval 307-400 °C, the maximum rate is achieved at 323 °C, with a mass loss of 17.6%.

Analyzing the thermal decomposition process of plum gum (Figure 8), two distinct phases can be highlighted. The first phase corresponds to water removal (gas phase analysis indicates only the presence of water), the process taking place between temperatures of 30-86 °C with a maximum degradation rate at 86 °C and weight loss of 12.1%. In the second phase, there are several stages of plum gum degradation: the first stage shows the maximum mass loss at the temperature of 250 °C, the other stages of degradation are not clearly separated, the total mass loss up to 400 °C being of 64%.

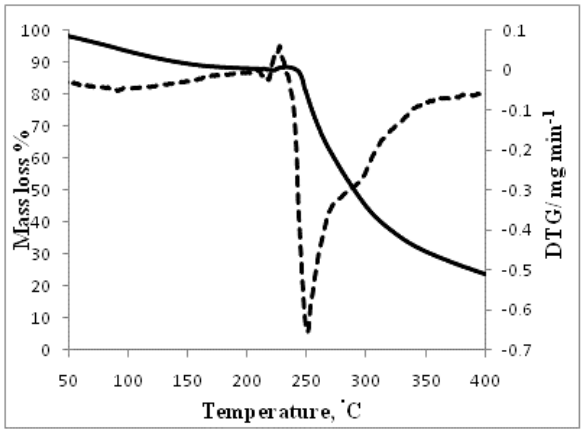

Figure 7: Thermogravimetric TG (-) and DTG (- -) curves of cherry gum measured by the thermal balance of TG-FTIR system in air at flow rate of 100 mL/min (heating rate 10 °C/min)

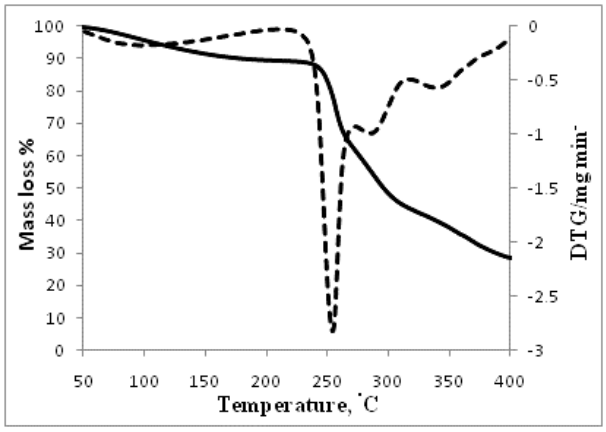

Figure 8: Thermogravimetric TG (-) and DTG (- -) curves of plum gum measured by the thermal balance of TG-FTIR system in air at flow rate of 100 mL/min (heating rate 10 °C/min)

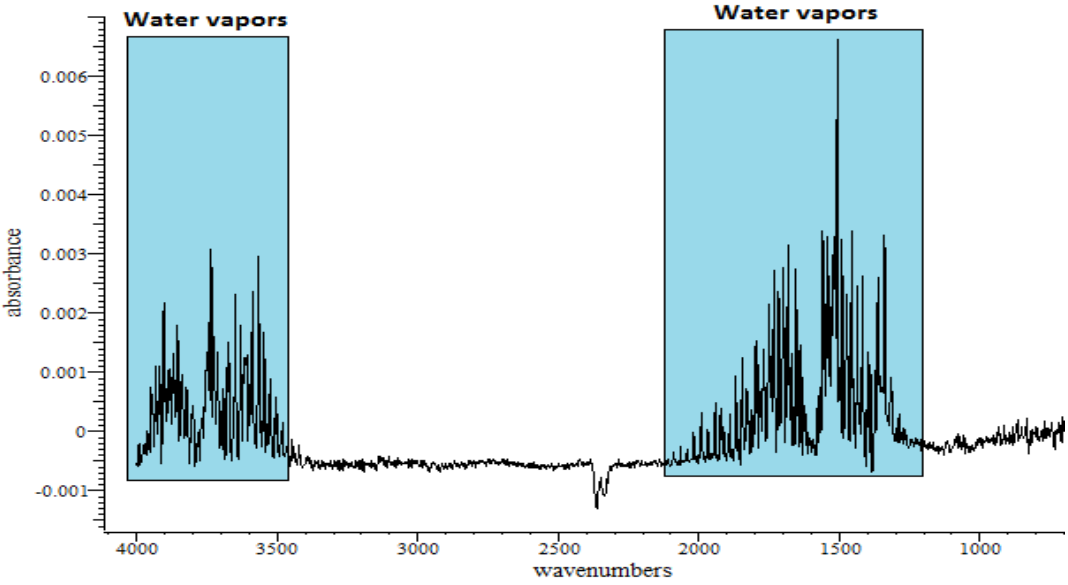

Figure 9: FTIR spectra of gaseous mixtures evolved from plum and cherry gums in air at 80 °C, measured by the online TG-FTIR system (heating rate 10 °C/min, initial mass 6 mg cherry, 20 mg plum)

Dehydration and depolymerization can be considered the main processes associated with the degradation.[17] FTIR gas phase analysis indicates a mixture of volatile compounds,[18] the identifiable ones being H_2O, CO and CO_2. The absorption bands 3550-3800 cm^{-1} and 1300-1900 cm^{-1} correspond to the H_2O vapors resulted from degradation. The absorbance of compounds such as CO_2 with very high peak intensity can be observed between 2100-2450 cm^{-1}; CO absorption corresponds to the region 2050-2230 cm^{-1}. A significant mass loss is preceded by a small increase in weight (observed in the DTG curve), due to oxidation of the polymer active sites, being immediately followed by the rapid elimination of oxidation products: CO, CO_2, H_2O. The DTG curve of the first decomposition area shows that the eliminated water comes from physically bounded water existing in the sample. The maximum decomposition rate occurs under 100 °C and the slow elimination of water is caused by water diffusion in sample mass. The FTIR spectra of the gas phase at 80 °C and at 250 °C are shown in Figure 9, and respectively, Figure 10.

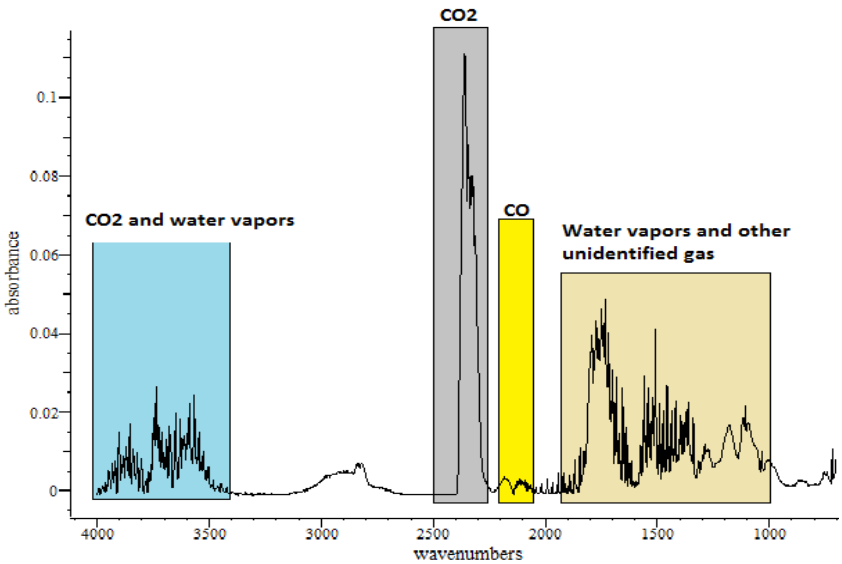

Figure 10: FTIR spectra of gaseous mixtures evolved from plum and cherry gums in air at 250 °C, measured by the online TG-FTIR system (heating rate 10 °C/min, initial mass 6 mg cherry, 20 mg plum)

Table 3
Viscosimetric measured parameters

Exudate gum	Huggins constant, k_H	Intrinsic viscosity, $[\eta]_H$ (dL/g)
Cherry	0.954	7.088
Plum	0.309	3.841

Rheological characterization and intrinsic viscosity

The values of the rheological parameters are presented in Table 3 and the evolution of intrinsic viscosity with concentration is shown in Figure 11. The interpretation of intrinsic viscosity parameter for polymer coils is difficult because they can interpenetrate and shrink as concentration increases; k_H is related to the expansion coefficient.[19] Concentration-dependent aggregation leads to increases of k_H. Especially in the case of polysaccharides, a value of $k_H \geq 0.8$ indicates that the polysaccharides are associated. Conformation changes with concentration could be related to intra-molecular interactions.[20,21]

The exudate gums (plum, cherry) have been analyzed with the GPC/SEC method for molecular weight determination according to Amarioarei *et al.*[22] It was found that the molecular weights of the studied gum samples were the following: *Prunus persica* (plum) M_w = $5{,}681\times10^6$ Da, with a polydispersity index of 1.479; and *Prunus domestica* (cherry) M_w = 5.0892×10^5 Da. The gum solutions have a high proportion of neutral-sugar side chains and therefore a highly branched structure similar to that of arabic gum and related plant exudate gums, as other authors have previously noted.[23,24] The intrinsic viscosity values (Table 3) of cherry tree exudate gum solutions (in H_2O, 25 °C) are much higher than those of arabic gum (0.6, g/dL) and cashew gum (0.1 g/dL), which is related to the difference in the molecular weight and polydispersity, and – probably – to the chains' association.[25]

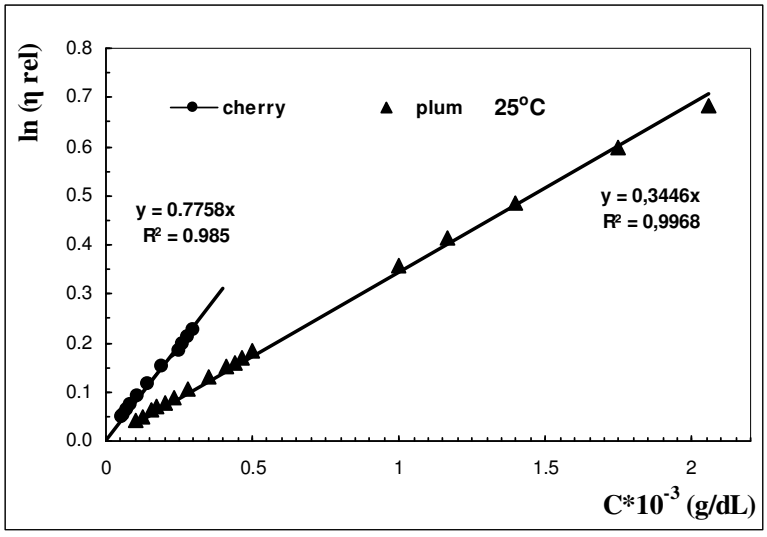

Figure11: Logarithmic plot of intrinsic viscosity of cherry and plum gums

CONCLUSION

By using different techniques of investigation (FTIR and C^{13} NMR spectroscopy and rheological study), the main components of plum and cherry gums, such as galactan, arabinan, xylan, uronic acids, were identified. The analysis also included the identification of their characteristic functional groups. Thermogravimetric analysis highlighted the mass loss and degradation stages. Also, the results emphasized some differences in the thermal stability of the two gums.

Huggins constant [k_H] and intrinsic viscosity [η] values for dilute aqueous solutions (C = 0.05-2.0 g/dL) of the studied gums were established and found to be dependent on the structure, molecular weight and interactions between existing functional groups.

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