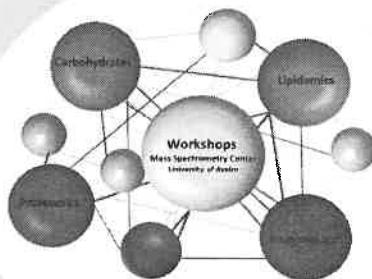




Mass spectrometry and carbohydrates 6th Workshop

24.05.2017

Anfiteatro do
Departamento de
Ambiente e Ordenamento
Universidade de Aveiro



BOOK OF ABSTRACTS



**6th Workshop
Mass Spectrometry and Carbohydrates**

PROGRAM

14h00| Registration

14h15| Opening session

14h30| Rosário Domingues, UA

Analysis of carbohydrates and derivatives by mass spectrometry (MS): an overview

15h00| Vítor Martins, IPB

Using MS techniques for the elucidation of structural features of immunostimulatory polysaccharides from medicinal plants aqueous extracts

15h30| Joana Simões, UA

Hydroxyl radical-induced oxidation of amylose and amylopectin: a MS structural characterization

15h45| Sofia Reis, UP

Migration of high molecular weight polyphenols and polysaccharides from natural cork stoppers to wine model solutions

16h00 | Coffee break

16h30| Fernando Nunes, UTAD

Formation of resistant starch by dry heating of starch: a MS approach

17h00| Ana Moreira, UA

Understanding coffee melanoidins formation using model systems and MS-based approaches

17h15| Soraia Silva, UA

Honey oligosaccharides – What is the bees role?

17h30| Concluding remarks

17h45| Closing

ORGANIZING COMMITTEE

Prof. Rosário Domingues

Prof. Manuel A. Coimbra

Prof. Pedro Domingues

Ana Moreira

Cláudia Nunes

Cláudia Passos

Elisabete Coelho

Joana Simões

Mass Spectrometry Center

QOPNA, Department of Chemistry, UA

Núcleo de Estudantes de Química



USING MASS SPECTROMETRY TECHNIQUES FOR THE ELUCIDATION OF STRUCTURAL FEATURES OF IMMUNOSTIMULATORY POLYSACCHARIDES FROM MEDICINAL PLANTS AQUEOUS EXTRACTS

MARTINS V. M. R.^{1,2}, SIMÕES J.², FERREIRA I.^{3,4}, CRUZ, M.T.^{3,4}, DOMINGUES M. R. M.², COIMBRAM.A.²

¹ CIMO, Escola Superior Agrária de Bragança, Bragança, Portugal.

² QOPNA, Departamento de Química, Universidade de Aveiro, Aveiro, Portugal.

³ CNC, Universidade de Coimbra, Coimbra, Portugal.

⁴ Faculdade de Farmácia, Universidade de Coimbra, Coimbra, Portugal.

E-mail: vmartins@ipb.pt

Abstract

Polysaccharides are well known for their immunostimulatory properties, which are closely related to structural features, such as molecular weight, branching, acetylation degree and acetylation pattern, and presence of specific structures [1, 2]. The electrospray ionization-mass spectrometry (ESI-MS) and electrospray ionization tandem mass spectrometry (ESI-MS/MS) have shown to be powerful techniques that can provide detailed information regarding the structural features of polysaccharides and help to clarify its relation to some of the observed immunostimulatory properties [3-6]. The present work describes the use of ESI-MS and ESI-MS/MS in the confirmation and elucidation of structural features of immunostimulatory polysaccharides present in the aqueous extracts of *Fraxinus angustifolia* dried leaves and *Pterospartum tridentatum* dried inflorescences.

The polysaccharides present in the aqueous extracts of *F. angustifolia* dried leaves and *P. tridentatum* dried inflorescences were isolated and fractionated using dialysis, ethanol precipitation, and anion-exchange chromatography. Sugar and linkage analysis suggested that the aqueous extracts of *F. angustifolia* were mostly composed of pectic polysaccharides, while those from *P. tridentatum* contained a mixture of pectic polysaccharides, galactomannans, and also xyloglucans. Selected fractions isolated from the aqueous extracts of *F. angustifolia* and *P. tridentatum* evidenced an *in vitro* macrophage immunostimulatory activity, expressed through the production of nitric oxide (NO).

Enzymatic hydrolysis of the isolated polysaccharides, followed by size exclusion chromatography of the resulting oligosaccharides (OS), and ESI-MS and ESI-MS/MS characterization allowed to confirm the presence of pectic polysaccharides, possibly with xylogalaturonan domains, in the aqueous extracts of *F. angustifolia*. For the aqueous extracts of *P. tridentatum* it was possible to detect the presence of galactomannans acetylated at O-2. Moreover, it was possible to identify acetylated OS that presented an acetylation pattern with much more acetyl groups than those observed for galactomannans from coffee infusions [3]. The saponification of the fraction isolated from the aqueous extracts of *P. tridentatum* dried inflorescences, which contained the acetylated galactomannans, caused a decrease in the NO macrophage production, confirming the galactomannans acetylation as an important structural feature for the expression of the *in vitro* macrophage immunostimulatory activity previously registered.

References

- [1] Paulsen, B.S. Biologically active polysaccharides as possible lead compounds. *Phytochem Rev.* **2002**, *1*, 379.
- [2] Ferreira, S. *et al.* Structure-function relationships of immunostimulatory polysaccharides: A review. *Carbohydr. Polym.* **2015**, *32*, 378.
- [3] Simões, J. *et al.* Structural features of partially acetylated coffee galactomannans presenting immunostimulatory activity. *Carbohydr. Polym.* **2010**, *79*, 397.
- [4] Simões, J. *et al.* Demonstration of the presence of acetylation and arabinose branching as structural features of locust bean gum galactomannans. *Carbohydr. Polym.* **2011**, *86*, 1476.
- [5] Simões, J. *et al.* Mass spectrometry characterization of an *Aloe vera* mannan presenting immunostimulatory activity. *Carbohydr. Polym.* **2012**, *90*, 229.
- [6] Martins, V.M.R. *et al.* *In vitro* macrophage nitric oxide production by *Pterospartum tridentatum* (L.) Willk. inflorescence polysaccharides. *Carbohydr. Polym.* **2017**, *157*, 176.