

XIX EDICIÓN DE LOS PREMIOS JOSÉ ANTONIO GARCÍA DOMÍNGUEZ

Durante la ceremonia de clausura de la XXIII Reunión Científica de la SECyTA (52.ª Reunión Científica del GCTA) celebrada en Pamplona del 23 al 25 de octubre de 2024 se concedieron los Premios José Antonio García Domínguez en su XIX edición. Como en anteriores ediciones, estos premios están patrocinados por Bruker y se otorgan a las dos comunicaciones orales y los dos mejores pósteres presentados por investigadores jóvenes miembros de la Sociedad. Después de la deliberación por parte del jurado de las respectivas modalidades, se fallaron los premios que se detallan a continuación:

1er Premio a la mejor comunicación oral (800 €)

UNTARGETED LIPIDOMICS BY UHPLC-IMS-QTOF MS FOR DIET INTAKE BIOMARKERS DISCOVERY IN SPARUS AURATA FISH

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Lipids play crucial roles in biology as essential components of cell membranes, signaling molecules and energy-storage substrates. The biological functions of lipids are determined by their structural diversity. Dietary changes can alter the lipidomic profile, resulting in either harmful or beneficial health effects (1). To understand the relationship between diet and health, biomarkers that accurately reflect the consumption of health-relevant foods are needed. Untargeted metabolomics can provide a more comprehensive image of dietary intake by measuring the lipidomic profile in biological samples. For biomarker detection is required a high selectivity and sensitivity, hence high resolution-mass spectrometry techniques (HRMS) are the most suitable option (2). The aim of this work was to study the lipidomic profiling of Sparus Aurata, one of the most consumed fish in the Mediterranean Sea, based on different diets, including fish, plants, byproducts or alternative ingredients. The sample extracts were analyzed by liquid chromatography (LC) coupled to ion mobility separation high-resolution mass spectrometry (IMS-HRMS), in both ionisation modes (ESI+/ESI-). After data processing and multivariate statistical analysis, a total of 35 markers, including phosphatidylcholines (PCs), phosphatidylethanolamines (PEs), and triacylglycerides (TAGs), among others, were annotated as distinctive features. The benefits of IMS in the identification of dietary biomarkers have been demonstrated by the use of collision cross section (CCS) values as an additional structural parameter. Preliminary results have shown a higher presence of triacylglycerides and diacylglycerides in the diet based on alternative ingredients. Health effects based on the presence or absence of these biomarkers are currently being studied.

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2º Premio a la mejor comunicación oral (600 €)

CHEMICAL CHARACTERIZATION OF THE VALORIZED WINERY BY PRODUCT VITIS VINIFERA L. CV. TANNAT POMACE BY COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY (LC X LC)

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Numerous natural products have demonstrated therapeutic properties against various diseases due to the presence of various natural bioactive compounds like phenolic compounds. In this regard, the pomace of *Vitis vinifera* L. cv Tannat, the primary by-product of wine production, is particularly noteworthy. This is due to the Tannat variety is highly rich in phenolic compounds with potential bioactivity, mainly anthocyanidins (AN) and condensed tannins (CT), and the fact that a significant fraction of them remains in the pomace after vinification. However, analyzing some of these bioactive compounds by HPLC, and, in particular tannins, is especially challenging because of their immense chemical complexity, diversity and polymerization degree that results in coelution of different analytes in large unresolved peaks [1]. Therefore, the analysis of such compounds generally requires different preparation methods and/or the application of techniques that provide better separation capabilities, such as comprehensive two-dimensional liquid chromatography (LC x LC) [1].

This work aimed to develop an LC x LC-MS/MS method to analyze CT and AN in samples obtained from the valorization of grape (*Vitis vinifera* L. cv. Tannat) pomace by-product by green processes using pressurized liquid extraction. For the LC x LC method, C18, HILIC and PFP columns were assessed for the first dimension separation (1D), while for the second dimension (2D), different C18 columns were evaluated. The rest of the separation parameters (mobile phases for both dimensions, acids, sample solvent, gradients, modulation times and strategies for reducing the 1D solvent strength [2]) were also deeply evaluated to maximize the resolution and separation capacity of the 2D method. Moreover, different methods of sample preparation were studied, including solid phase extraction, liquid-liquid extraction, and ultra-centrifuge filtration.

The optimized method resulted in a huge peak capacity and therefore it provided a maximized separation and identification power for a wide range of CT and AN from complex Tannat extracts, which is essential as a starting point for subsequent studies on biotransformation during digestion and potential beneficial health effects.

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1er Premio al mejor póster (400 €)

L-ARGININE BASED CHIRAL IONIC LIQUIDS FOR THE ENANTIOMERIC ANALYSIS OF AMINO ACIDS BY ELECTROKINETIC CHROMATOGRAPHY AND LIGAND EXCHANGE CAPILLARY ELECTROPHORESIS. A COMPARATIVE STUDY

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Amino acid-based ionic liquids (AAILs) have demonstrated in the last years a high potential to achieve the enantiomeric separation of different chiral compounds [1]. They can be divided into i) AAILs in which protein amino acids are the anionic counterpart and ii) AAILs in which amino acids are the cationic counterpart. In the field of chiral separations, the use of these AAILs has been described in electrokinetic chromatography (EKC) systems combined with cyclodextrins or in the mode of ligand exchange capillary electrophoresis (LECE). These chiral systems have mainly been employed for the enantioseparation of model drugs and to a lesser extent for amino acids analysis. However, since protein amino acids are the elemental piece for peptide and protein conformation and play an important role in the metabolic pathways, their enantiomeric determination is a challenge in the field of chiral separations.

In this context, this work aimed to perform a comparative study of the potential of different L-arginine-based ionic liquids, some of them synthesized for the first time in this work; for the chiral separation of five model amino acids (tryptophan, phenylalanine, valine, norvaline, and alloseleucine) under two different CE modes: EKC and LECE. In the first case, AAILs containing bis(trifluoromethane)sulfonimide (NTf₂) as anionic counterpart were combined with different cyclodextrins, whereas in the LECE systems AAILs constituted by tetraalkylammonium (TMA) as cationic counterpart participated in the ligand exchange mechanism, forming ternary complexes with the chiral analyte and metallic cations. Under the most favorable conditions, the results demonstrated that the LECE mode based on the use of L-Arg-TMA with Cu (II) enabled the chiral separation of three out of the five amino acids studied (norvaline, citrulline, and phenylalanine). Finally, to demonstrate the potential of the developed LECE methodology, its analytical characteristics were evaluated, and it was applied to the enantiomeric determination of norvaline in dietary supplements.

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2º Premio al mejor póster (300 €)

EXTRACTION AND CHARACTERIZATION OF BIOACTIVE CARBOHYDRATES AND PHENOLICS FROM PHYTOPLANKTON HOLOBIONTS

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In recent years, interest in microalgal research and investment have increased as they represent a novel source of high value bioactive compounds (carbohydrates, phenolics, lipids, etc.) with antioxidant, anti-ageing, or antibacterial properties, and with applications in different industries (e.g. cosmetics) [1]. Moreover, the use of microalgal consortia (also known as phytoplankton holobionts), constituted by different species of microalgae or by microalgae and bacteria, are gaining more importance, as they can produce different bioactive molecules due to cooperative interactions between the co-cultured microorganisms [2]. However, these consortia are still scarcely applied in the cosmetic and nutraceutical fields, being necessary at first instance the characterization of their bioactive composition. Towards a zero-waste approach, in the present work, the simultaneous extraction of phenolic compounds and carbohydrates from two different microalgae consortia was optimized. These consortia were based on *Kamptomonas* sp., *Nannochloropsis oculata*, *Tetraselmis* sp. and *Chlorella* sp. (holobiont 1) and on *Spirulina* sp. and *Chlorella vulgaris* (holobiont 2). Moreover, a multianalytical approach was followed for the characterization of extracts. First, the efficiency of different solvents for the extraction of target bioactives was evaluated; water was selected as the most effective solvent for both consortia. Then, a Box-Behnken experimental design was performed considering extraction time, temperature and ratio between biomass and solvent as independent factors. Extracts obtained under optimal extraction conditions (30°C, 60 min and 0.01 g of biomass mL⁻¹ for holobiont 1 and 51°C, 60 min and 0.02 g of biomass mL⁻¹ for holobiont 2) were treated with citric acid to precipitate proteins. GC-MS analyses of carbohydrates, before and after trifluoroacetic acid hydrolysis, and subsequent derivatization, allowed the identification of their monomeric composition, while size exclusion chromatography (SEC) with light scattering detection (ELSD) provided information about their molecular weight distribution. Other complementary techniques such as infrared spectroscopy, nuclear magnetic resonance and UV spectroscopy were used to get more information about polysaccharide structures. Reverse phase liquid chromatography coupled to mass spectrometry (RPLC-MS) analyses were also used for the determination of phenolic compounds. These studies constitute an advance in the knowledge

of these holobionts which is essential for the development of new applications in the cosmetic and nutraceutical fields, among others.

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