Comprehensive characterization of eight different olive tree derived matrices using LC-ESI/APCI-QTOF and GC-APCI-QTOF and a non-targeted software workflow

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Introduction

Over the last decades, virgin olive oil consumption has been associated to a lower incidence of some chronic diseases such as cancer, diabetes or coronary diseases, largely due to the non-glyceridic minor compounds found in it.

Some of these phytochemicals with healthy properties are secondary metabolites of plants, which may also be found in other vegetal tissues derived from the olive tree. Currently, the transformation of the olive fruit and the valorization of by-products are considered as parts of the same integral cycle of use, so the deep characterization of the main parts of the olive fruit and tree is a key step when trying to find natural sources of bioactive compounds.

Herewith, we present the results of the study of eight different samples (oils and tissues) coming from Picudo cv. olive trees, which can help to understand the biosynthesis and distribution of these compounds in the studied matrices.

Methods

Picudo cv. samples were prepared using an unselective liquid/solid-liquid extraction protocol. The extracts were analyzed by LC and GC coupled to a Bruker compact QTOF mass spectrometer by means of ESI and APCI interfaces in the case of LC and a GC-APCI source in GC. In LC, the analytes were eluted with a 15 min gradient on a C18 column (2.1 x 100 mm, 1.8 µm), with acidified water and acetonitrile at 40 ºC. The silylated extracts were also analyzed with a 50 min GC gradient (BR-5 column, 30 m x 0.25 mm i. d., 0.25 µm) with a T gradient from 150 to 320 ºC (ramped at 4 ºC/min). MS and AutoMS/MS data were acquired.

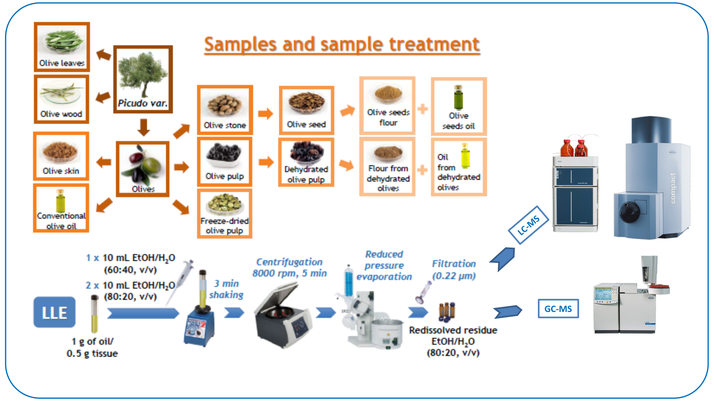

Fig. 1: Eight different matrices (oils and tissues) derived from the olive tree were prepared with a simple LLE procedure. After extraction they were analyzed with LC-ESI-MS and LC/GC-APCI-MS on a Bruker compact QTOF MS in pos and neg mode.

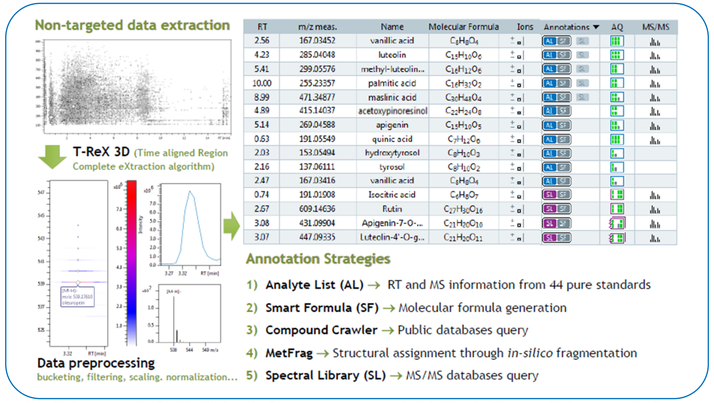

Fig. 2: Data acquired with all the platforms was processed with MetaboScape, which automatically extracts and combines isotopes, adducts and fragments belonging to the same compound into one feature. The following scheme shows how non-targeted data extraction is done, alignment, data preprocessing and the possibilities regarding annotation strategies.

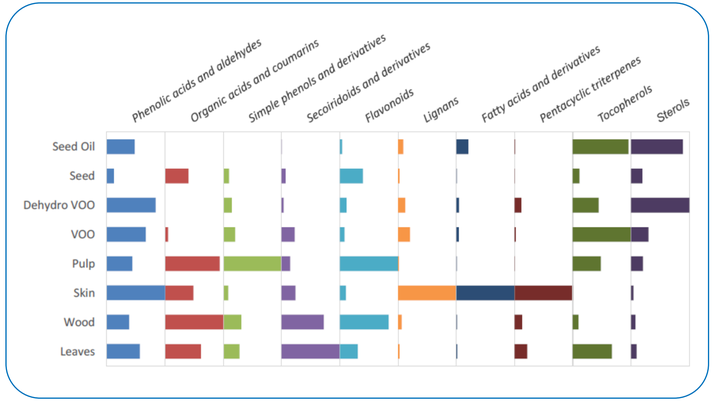

Fig. 3: Bars graph representing relative distributions of each evaluated chemical class in the eight studied olive tree derived samples from Picudo cv.

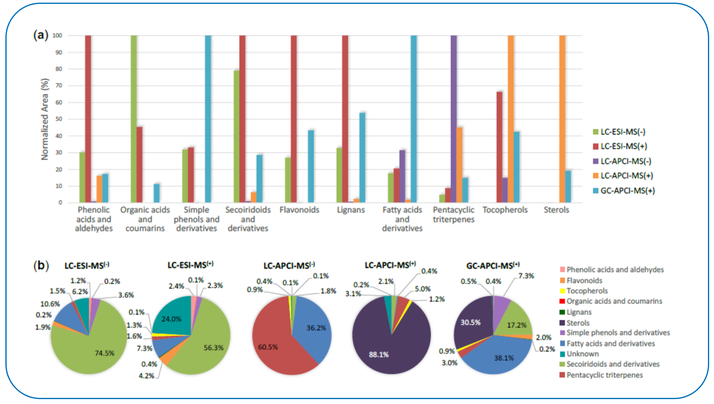

Fig. 4: (a) Bars graph representing the sum of areas (in a normalized axis) of the compounds found in the oil obtained from stoned and dehydrated olives (grouped by chemical class), by means of each tested platform and polarity; (b) Pie charts showing the share of every chemical class (in terms of area (% of the total area)) in the chromatograms obtained with each employed methodology for the same sample as in part (a).

Results

The extracts (from lyophilized olive pulp, olive seed, fruit skin, leaves and wood from the branches, as well as virgin olive oil, olive oil obtained from pitted and dehydrated fruits and oil obtained from the seed contained inside the pit) were prepared and analyzed. The acquired data were processed with MetaboScape 3.0 (Bruker), which automatically extracts and combines isotopes, adducts and fragments belonging to the same compound into one feature. The software automatically generates molecular formula of all unknown compounds, followed by getting structures from public databases, structural assignment through in-silico fragmentation and spectral library search. Information obtained from MetaboScape was studied to point out the applicability of each methodology for the determination of each family of compounds, as well as to describe the distribution of the identified plant metabolites within the selected olive oils and tissues (their presence, absence, relative area in each matrix and relative response in each platform were checked). The coupling to a high-resolution MS through different ionization sources (ESI and APCI in LC and APCI in GC) allowed the detection of compounds from different chemical classes. GC-APCI-Q TOF preserves the pseudo-molecular ion information, which is a great advantage over the "classical" GC-EI-MS systems and facilitates the identification of unknown compounds. The identification of about 150 compounds from the extracts (phenolic compounds, triterpenic acids and dialcohols, tocopherols, sterols and free fatty acids) was achieved.

Conclusions

- Two methodologies (LC-MS and GC-MS) have been applied to the study of minor bioactive compounds in 8 matrices derived from the olive tree.
- Sample treatment and chromatographic conditions were optimized so as to monitor as many compounds as possible with a wide range of polarity/volatility.
- The coupling to a high resolution MS through different ionization sources (ESI and APCI in LC and APCI in GC) has allowed the detection of compounds belonging to different chemical classes.
- The use of more than 40 standards, several isolated fractions of secoiridoids, and the annotation strategies within MetaboScape® 3.0 lead to the identification of around 150 compounds in the extracts.

QTOF / Foodomics