15th International Symposium and Summer School on Bioanalysis, Tîrgu Mureș, Romania, July 13-18, 2015

CHARACTERIZATION OF VOLATILE COMPOUNDS IN MACEDONIAN EDIBLE OILS

Violeta Ivanova-Petropulos

Faculty of Agriculture, University "Goce Delčev", Štip, Republic of Macedonia

Sasa Mitrev, Erich Leitner, Ernst Lankmayr, Barbara Siegmund, Trajce Stafilov

Introduction

- Oils (liquid) and fats (solid) are common and important items in the diet of humans.
- Most of the ones we use come from seeds (or animals).
- The use of seed oils is ancient.
- Concentrated sources of energy providing essential fatty acids
- Different classes of compounds are present in edible oils, such as:
  - ✓ Fatty acids,
  - ✓ Volatile compounds
  - ✓ Tocopherols,
  - ✓ Phenolic compounds,
  - ✓ Phytosterols,
  - ✓ Carotenoids
  - ✓ Thioglycosides

Introduction

The fatty acid composition is different in different edible oils. Depends on:

- ✓ type of seeds,
- ✓ variety,
- ✓ state of ripeness,
- ✓ area in which the plants are grown,
- ✓ climate conditions.

Fatty acids are classified according to their degree of saturation:

- **Saturated**
- **Unsaturated**.

The major unsaturated fatty acids are **oleic acid** (OA), **linoleic acid** (LA) and **α-linolenic acid** (ALA).

An even number of carbon atoms, from 16 to 18, with a single carboxyl group, are the most common fatty acids present in vegetable oils.

Introduction

- Unsaturated fatty acids tend to oxidize in presence of *radicals, oxygen, metal catalysts or lipoxygenase enzymes*, producing **volatile organic compounds (VOCs):**
  - have low molecular weights (usually less than 300 Da)
  - easily vaporized at room temperature producing an odour
  - may have positive or negative (off-flavour) characteristics
  - the presence/absence of VOCs in different proportions can be taken as a marker for identifying adulteration.

- The positive aroma compounds in oils are mainly produced by the endogenous plant enzymes as a result of the lipoxygenase pathway.

- The off-flavour compounds are predominantly formed during the chemical oxidation of lipids (autoxidation) or in the presence of exogenous enzymes, usually during the microbial activity.
  - They are responsible for the sensory defects of oils, referred to the oxidative rancidity.

Analytical techniques

- ✓ **High-performance liquid chromatography (HPLC)** – for identification and quantification of fatty acids, triacylglycerols, sterols, tocopherols and hydrocarbons
- ✓ **Gas chromatography (GC)** - for the analysis of fatty acids, usually coupled with a flame-ionization detector (FID) or for analysis of volatile compounds
- ✓ **GC or HPLC in combination with mass spectrometry** allow structural identification and quantification by single-ion monitoring (SIM) or multiple-ion monitoring (MIM) of different classes of compounds, are used for the analysis of different classes of compounds present in the oils
- ✓ Headspace comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (**Headspace GC×GC–TOF/MS**) – for classification of volatiles from vegetable oils

Materials and Methods

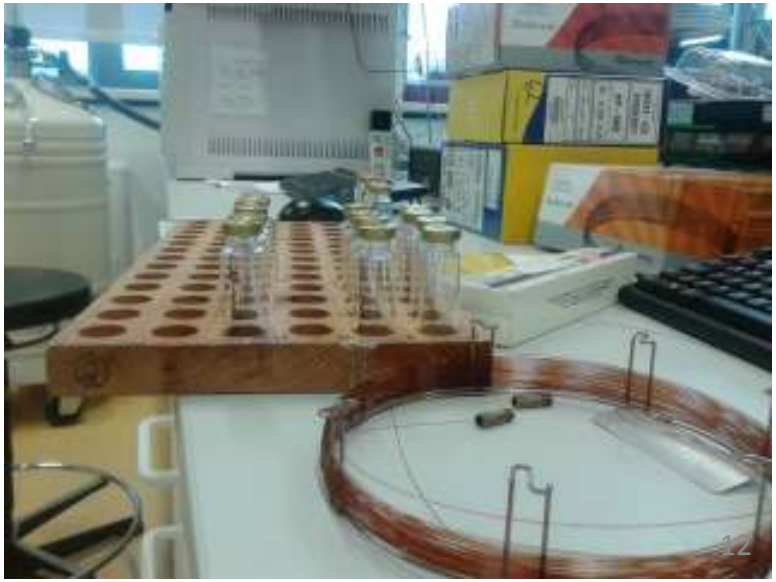
Oil samples

Sunflower, Pumpkin seed, Flax, Rape and Sesame seeds oils (2014)

HS-SPME-GC-MS analysis of flavour compounds

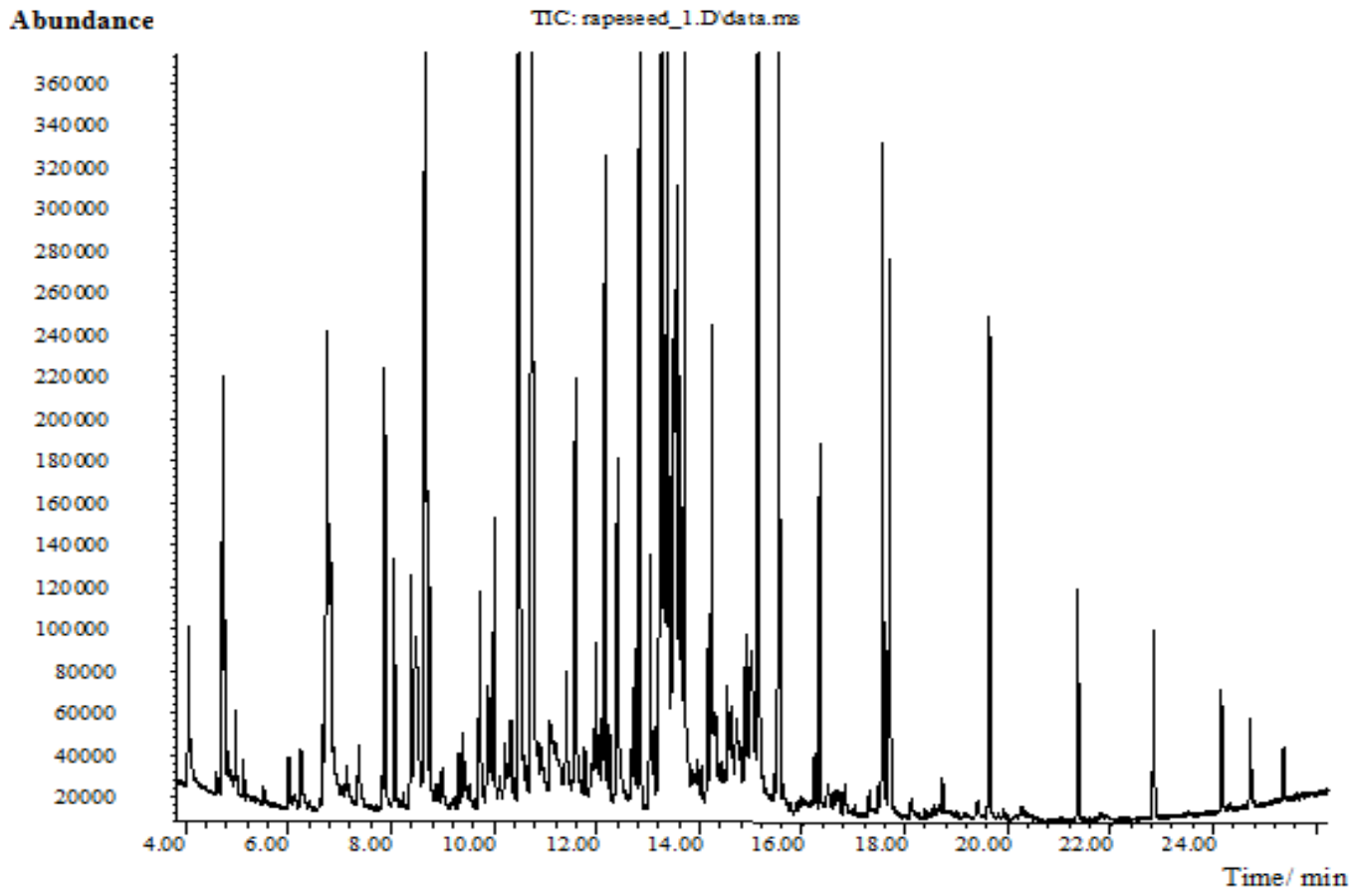
- ✓ Automated HS-SPME system combined with GC-MS
- ✓ 100 mg of oil was transferred into a 20 mL headspace vial.
- ✓ SPME fiber was used: DVB/Carboxen/PDMS 50/30, 2 cm stable flex (Supelco, Bellfonte, USA) exposed into the headspace of the sample for 10 minutes at 60°C.

- ✓ GC-MS analysis: Agilent system (GC 7890, MS 5975c VL MSD)
- ✓ Column: HP5MS, 30m*0.25mm*1µm, Agilent Technologies
- ✓ Temperature program: -10 °C for 1 min with a temperature ramp of 12 °C min^{-1} up to 280 °C (holding time 3 min).

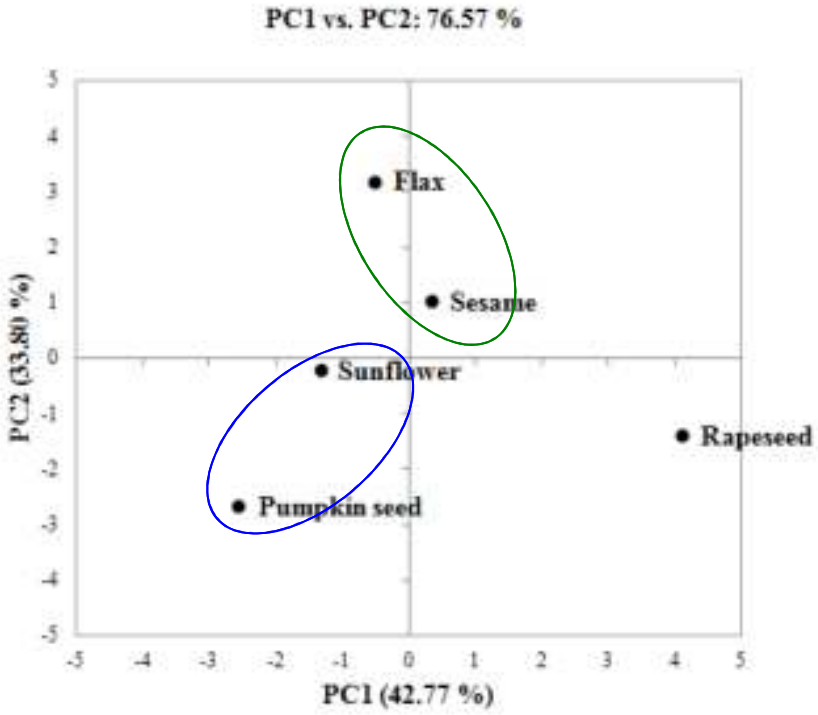


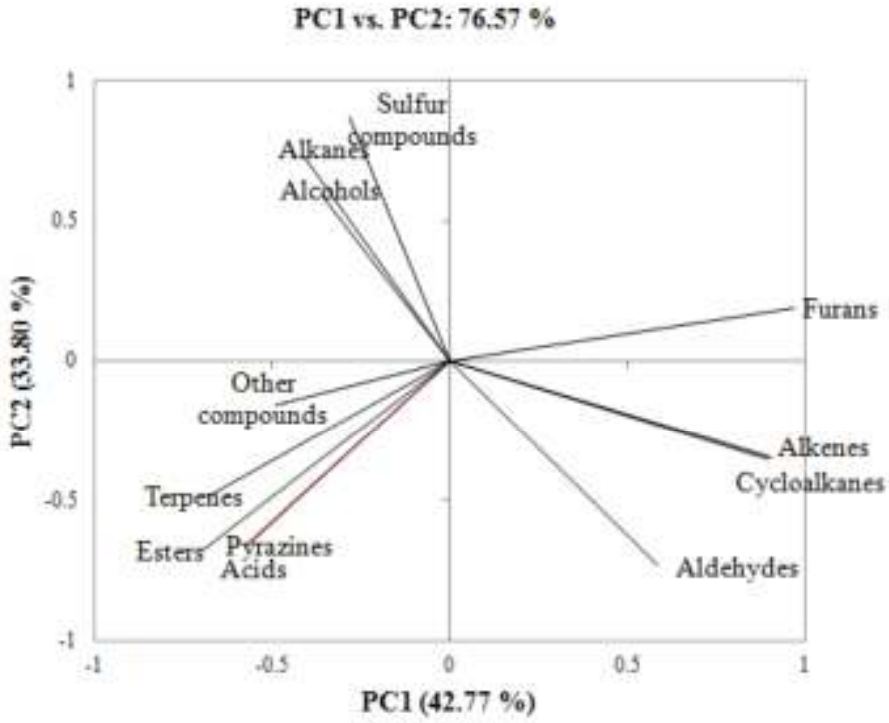
Results and Discussion

- **101 individual volatile compounds** were identified and reported for the first time in Macedonian oil samples.
- Acids, alcohols, aldehydes, alkanes, alkenes, cycloalkanes, esters, furans, pyrazines, sulfur compounds, terpenes and other compounds.



Principal component analysis





- These groupings could be related to **varietal character**, but more probably, could be related to the processing and storage conditions of the samples.

Conclusion

- ✓ In total, 101 volatile compounds were identified an semi-quantified in the Macedonian edible oils.
- ✓ Sunflower and pumpkin seed oils - richest in terpenes and esters, highest average amount of total volatile compounds.

- ✓ Provide important information for the Macedonian oil production which aim to develop brands for edible oils especially regarding seeds - such as pumpkin and sunflower seeds - that have traditionally been used as sources for edible oils.