LASER DIODE THERMAL DESORPTION ATMOSPHERIC PRESSURE CHEMICAL IONIZATION TANDEM MASS SPECTROMETRY AS A TOOL TO ANALYZE TRIACYLGLYCEROLS

MP 561

Réal E. Paquin[1], Serge Kaliaguine[2]

[1]Département de physique, génie physique et optique, Université Laval, Québec, Canada

[2]Département de génie chimique, Université Laval, Québec, Canada

UNIVERSITÉ LAVAL

INTRODUCTION

Trialcylglycerols (TAGs) are relatively simple lipid substances in that they are made of free fatty acids esterified to the 3-carbinol oxygen atoms of glycerol. TAGs play an important role in nutrition and other biological processes They are the primary means of energy storage in animal and humans. A major source of TAGs is seed oils which are a widely available agricultural raw materials. Because of its high market price compared to other edible oils, olive oil is a target for adulteration. Characterization of vegetable oils from different origins and assessment of their identity is a real challenge.

Biodiesel fuels based on plant oils have gained increasing attention due to their relative compatibility with existing motors. But this approach has a direct impact on food production. Therefore there is a growing interest in algae-based TAG production.

In all these domains, rapid and high sensitivity methods to characterize the fatty acid distribution is required. The laser diode thermal desorption is a fast and simple technology that allows direct detection of TAGs with minimal sample volumes and preparation steps

LDTD ion source technology

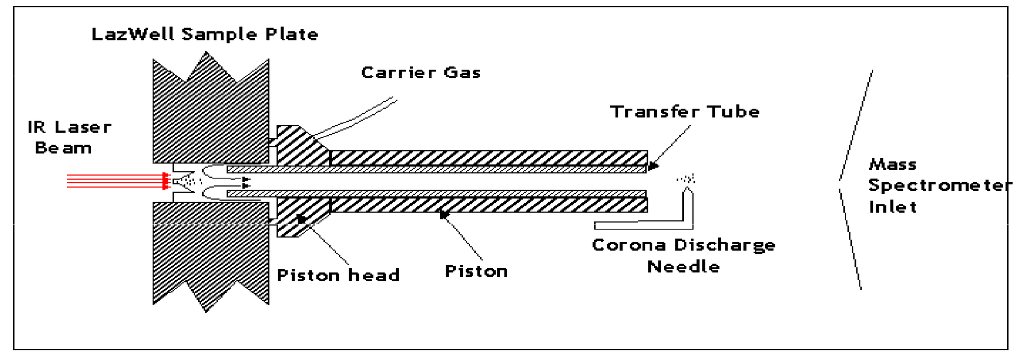

Figure 1 Schematic of the LDTD ionization source.

LDTD (Figure 1)

The LDTD ionization source is used in mass spectrometry as an alternative way to introduce samples in a mass spectrometer equipped with an atmospheric inlet. The LDTD uses a Laser Diode to produce and control heat on the sample support . The energy is then transferred through the sample holder to the sample which vaporizes prior to be carried in an APCI region for ionization.

The composition of the gas in the APCI region of a LDTD source differs from the one currently used in LC-APCI-MS. Since there is no solvent involved, traces of water remains the main reactant. Hydronium ions (H_3O^+) and their clusters ions ($H_3O^+(H_2O)_n$) are the main reactants in the proton transfer reaction (PTR)

METHOD

Instrumentation:(figure 2)

–LDTD model T-960, Phytronix Technologies
–TSQ® Vantage™ Triple-quadrupole Mass spectrometer, Thermo Fisher Scientific

Figure 2 LDTD-MS/MS analytical system

Sample preparation:

Triolein, corn oil and olive oil were diluted with ethyl acetate until a concentration of 10µg/ml was obtained. 2µL of this solution was used to tune the LTDT-MS/MS system operated in positive mode, which represents 20 ng of TAGs. Additional steps with ethyl acetate were used to determine the detection limits of the instrument and established a calibration curve.

MS Parameters

- APCI (+)
- Scan time : 0.02 s
- Q1 and Q3 width : 0.50 amu
- Q2 CID : 1.5 mTorr (Ar)

LDTD Parameters

- Laser power pattern :
  - Increase laser power to 45 % in 1.0 s
  - Hold at 45 % for 2.0 s
  - Decrease laser power to 0 %
- Carrier gas flow : 3 L/min (Air)
- Corona voltage value : 5 kV

DISCUSSION

APCI gives rise to some fragmentation which facilitates structural characterization. Data from triolein are presented in comparison with corn and olive oils. The most abundant ion in the spectrum of triolein fig. 3 corresponds to diacylglycerol fragment ion (m/z) = 603,4), the protonated molecule (M+H) (m/z)=885,6) being also present at 10% intensity. Ion products spectra of mass 885,6 (fig. 4) confirms the presence of oleic fatty acid. The thermalization process in the LDTD ion source seems efficient, producing very few chain-shortened TAGs.

For corn oil, the seven most important TAGs have been detected (fig.5) and fig. 6 shows diacylglycerol fragment ions present in the full scan mass spectra.

In the olive oil mass spectra (fig. 7), the nine most abundant TAGs have also been detected. In fig 8, a MS/MS spectra of an appropriate precursor ion m/z= 857 confirms the presence of the POL triacylglycerol.

RESULTS

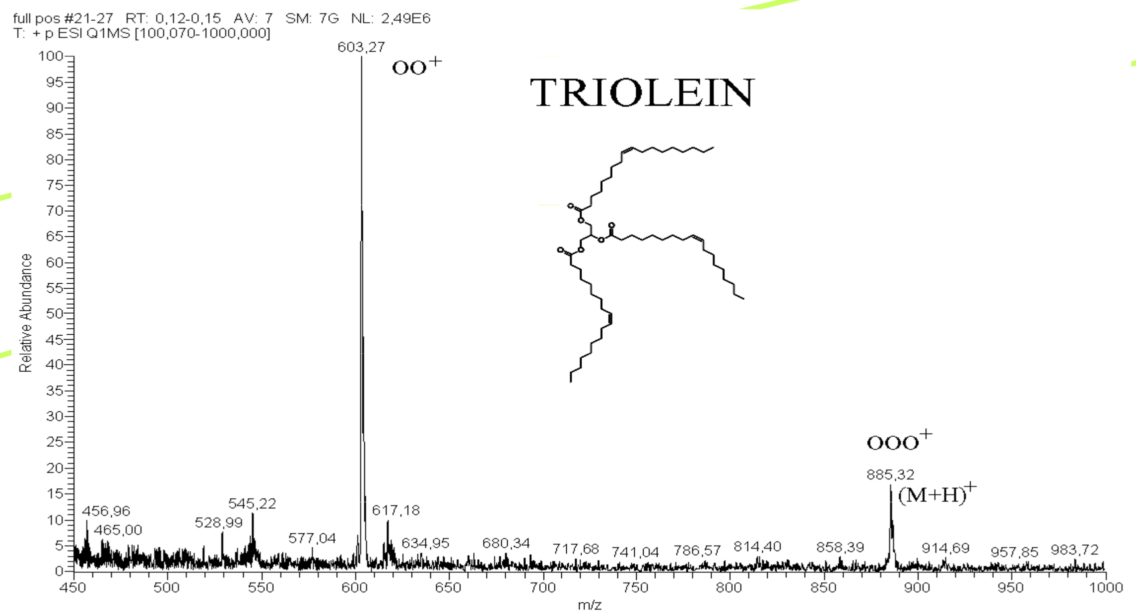

Fig. 3 LDTD-MS full scan mass spectra of triolein

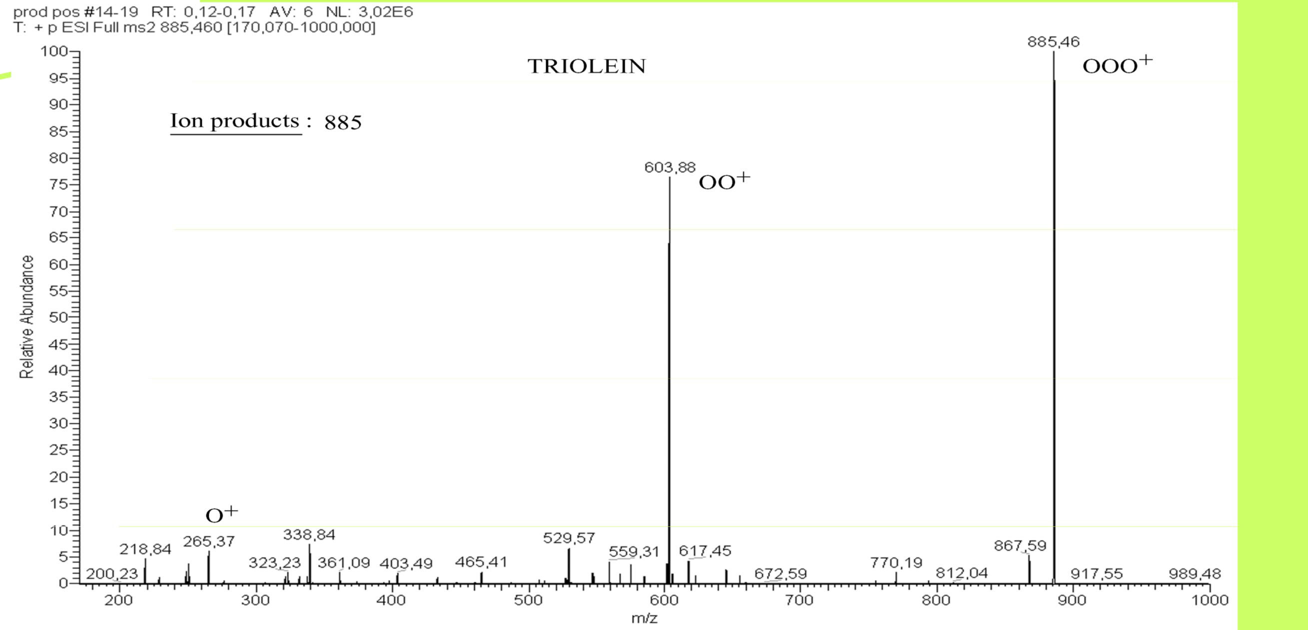

Fig. 4 LDTD-MS/MS mass spectra of ion products of mass 885

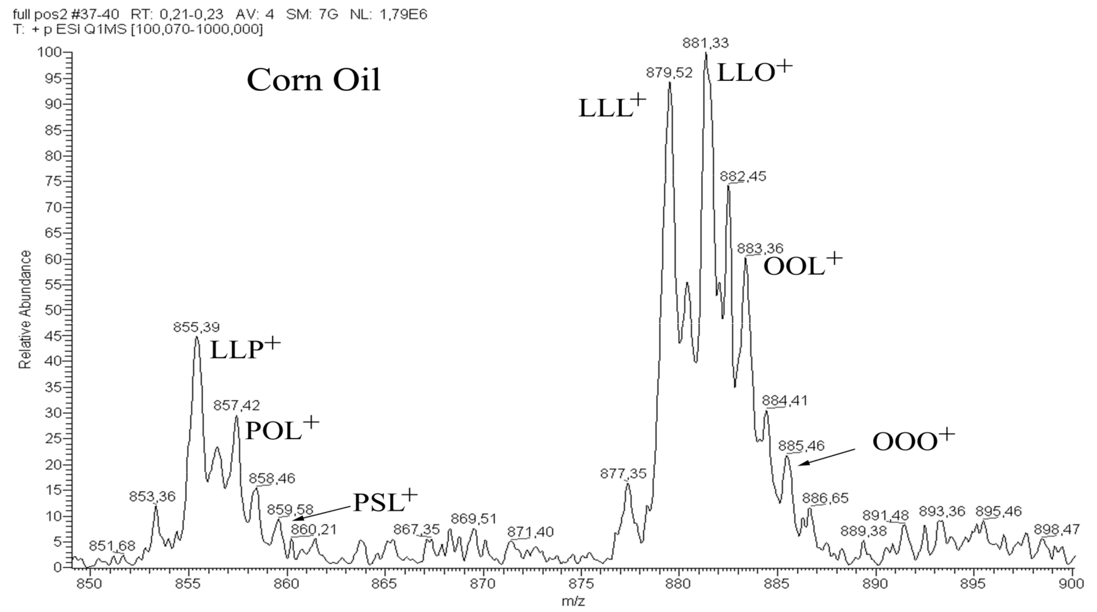

Fig. 5 LDTD-MS mass spectra of corn oil (high mass side)

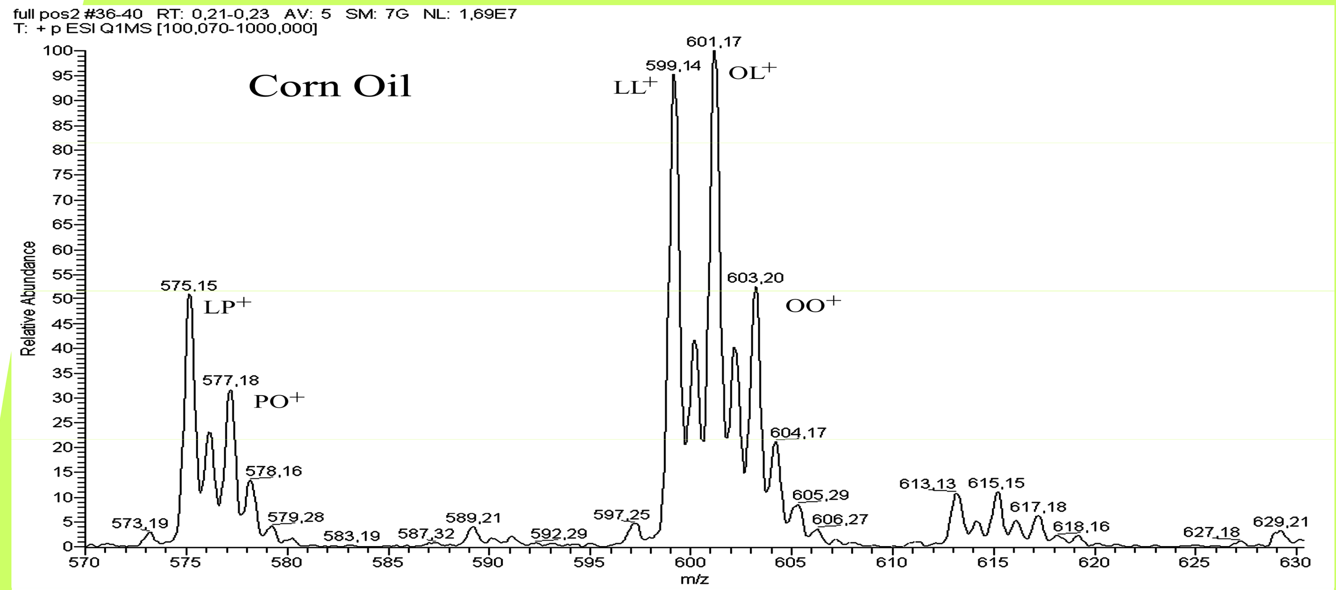

Fig. 6 LDTD-MS mass pectra of corn oil (medium mass side)

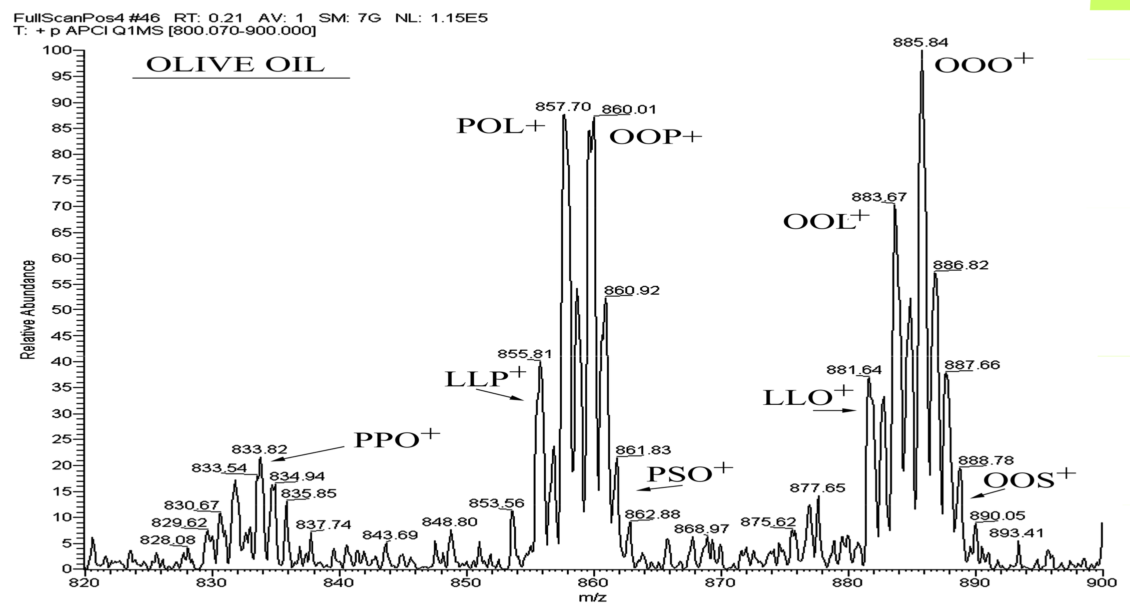

Fig. 7 LDTD-MS mass spectra of olive oil (high mass side)

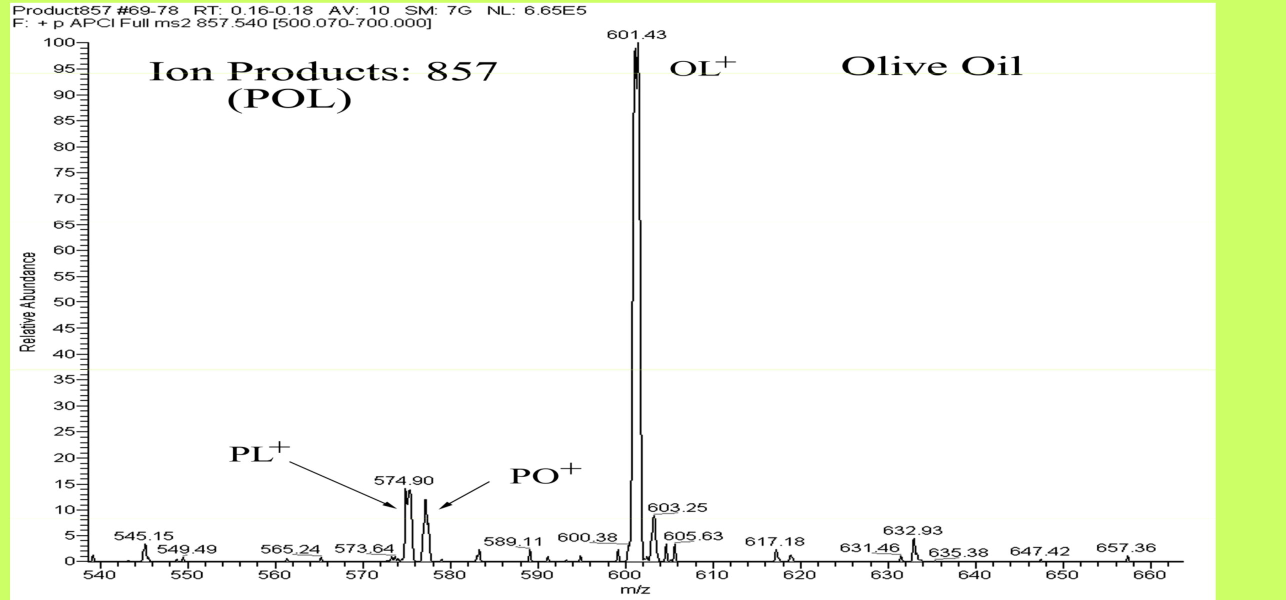

Fig. 8 LDTD-MS/MS mass spectra of ion products mass 857 (POL)