Valuation of olive pomace oil: Preparation of gamma (γ) and delta (δ) stearo–lactones using perchloric acid as catalyst

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Abstract
Acidity, iodine index, saponification index, and unsaponifiables rate of commercial oleic acid (COA) and mixture of fatty acids from olive pomace oil (MFAOOP) were determined by chemical titration. Acidic composition of COA (reference fatty acid), and MFAOOP were also determined by gas chromatography (GCP). Lactonization reaction of COA and MFAOOP were achieved using perchloric acid as catalyst. The products obtained were analyzed by IR, GC-MS, and NMR. The results obtained showed that gamma- and, delta-stearo-lactone were formed successfully with a good yield of 89.72 and 92.38% from COA, and MFAOOP, respectively. Thus, olive pomace can be valued because it can lead to the formation of lactones, products with a great industrial interest.

Key words: Commercial oleic acid, olive pomace oil, Lactonization reaction, gamma- and delta-stearo-lactone

1. Introduction
Lactones are cyclic esters generally resulting from the intermolecular cyclization of hydroxy acids. The most important are γ- and δ- lactones:

We can also meet α- and β- lactones:

These compounds are of great industrial interest. Indeed, the lactone rings are in the particular structures of several compounds in flavors and fragrances.

The objective of this work is a contribution to the recovery of severely degraded vegetable oils. It involves the preparation of stearo-lactones from the olive pomace oil, strong acid and high oleic oil.

For this, we initially realized lactonization of commercial oleic acid, reference fatty acid in various acid catalysis conditions (perchloric acid, sulfuric acid). We then identified by chromatographic and spectroscopic methods (IR, GC-MS, and NMR), the obtained stearo-lactones.

Secondly, we realized under the conditions of commercial oleic acid, lactonization of the mixture of fatty acids derived from the oil of olive pomace. Stearo-lactones the thus obtained were also identified by the same chromatographic and spectroscopic methods.
2. Experimental

2.1. Reagents:

The reagents used are:
- Commercial oleic acid (90%)
- Olive pomace oil

The olive pomace oil samples were provided by the company AGRO-ZITEX Sfax (Tunisia). The oils are in the form of a viscous black liquid. The physicochemical analyzes in our laboratory (Laboratory fats) show that these oils are highly degraded and have more than 50% acidity. These oils have been totally transformed into fatty acids.

2.2. Preparation of the mixture of fatty acids derived from the olive pomace oil [1, 2]

300 grams of sodium hydroxide and one liter of distilled water are successively added in 2 liters of olive pomace oil, and heated to 80 °C the mixture while stirring for 6 hours until a consistent paste. The mixture thus obtained, cooled for 24 hours, exhibits two phases, one is solid (soaps), the other containing the excess of aqueous sodium hydroxide and glycerol. The solid consisting of fatty acid salts is separated from the reaction mixture then treated with an excess of hot phosphoric acid, until an acid medium. This forms two liquid phases: an organic phase containing fatty acids and the other containing the excess of aqueous phosphoric acid and soluble impurities in water. Separating the organic phase containing fatty acids is done by decanting hot, since the existence of saturated fatty acids (palmitic, stearic) causes gelling of the fatty acid mixture at room temperature [3]. To remove traces of residual phosphoric acid in the organic phase, it is is washed several times with a saturated solution of sodium chloride. The mixture of fatty acids obtained in the washing result is dried for 24 hours in an oven at a temperature of 80 °C and then assayed according to the NF-T60-204 and NF-T60-221 standards to determine its acidity.

2.3. Characterization of acidic mixtures

2.3.1. Preparation of methyl esters

Esterification was carried out in a homogeneous medium. Weighed a fatty acid test sample of about 10 grams and placed in a ground-necked 250 ml flask. 10 ml of absolute methanol and a few drops of sulfuric acid were added as catalyst, the refrigerant is adapted to the flask. Is heated to boiling for 2 hours, and then cooled under a stream of water. Was added to the flask, 30 ml of hexane, stirred vigorously and allowed to settle until complete separation of the two phases.

The hexane phase was collected. The aqueous phase is depleted again with 30 ml of hexane. The combined hexane extracts two and washed with 5 ml of an anhydrous sodium carbonate solution (5%) and then several times with distilled water until the acidity controlled by the pH meter. Finally, the extract was dried over anhydrous sodium sulfate and filtered over cotton.

2.3.2. Determination of acidic composition by GC [4]

We dissolved 50 mg of shopping oleic acid esters or mixture of fatty acids of olive pomace oil in 0.5 ml of pure hexane for analysis. Then, corresponding chromatograms were recorded.

- Chromatographic conditions

The esters obtained were analyzed using a gas chromatography apparatus of the kind ATI-UNICAM (610 series) equipped with a capillary column Carbowax (stationary phase: polyethylene glycol) 15 m long and 0.5 µm inside diameter; an integrator-recorder: UNICAM 4815 and FID detector.

2.3.3. Acid value [5]

We weighted into an Erlenmeyer flask, 5 g of fatty substance, and 30 ml of neutralized ethanol. After dissolution, the determination of free acidity is a sodium hydroxide solution (7.1 g / l) in the presence of a few drops of phenolphthalein. The end of the assay is marked by the appearance of pink which persists for 15 seconds after agitation. The acidity is given by the following equation:

\[ \text{Acidity} \% = \frac{5V}{m} \]  

\[ m: \text{mass in gram of test sample; V: volume in ml of sodium hydroxide solution} \]

2.3.4. Iodine value [6]:

- Wijs reagent preparation

We dissolved 13 g of iodine in one liter of acetic acid. Dry chlorine is then bubbled into the solution until the color changes from brown to yellow. Chlorine is produced by reacting concentrated hydrochloric acid on potassium permanganate.

\[ 2\text{KMnO}_4 + 16 \text{HCl} \rightarrow 6\text{Cl}_2 + 2\text{MnCl}_2 + 2\text{KCl} + 8\text{H}_2\text{O} \]

The chlore gas thus formed is wet, must be dried in a second flask by passage through a concentrated sulfuric acid solution. It then goes into a third vial containing the diiodine in acetic acid solution where there will be the formation of ICl (Figure 1).
The iodine value is given by the following expression:

$$I_{I_2} = (V_0 - V_1) \times \frac{1.269}{P}$$  \hspace{1cm} (2)

$V_0$: volume of sodium thiosulfate solution necessary to determine iodine in the test without fat (blank) (ml)

$V_1$: volume of sodium thiosulfate solution necessary to determine iodine in the test with fat (ml).

$P$: mass of the test sample (g)

2.3.5. Rate of unsaponifiables [2, 7]

We weighed, to the nearest 0.01 g, in a 250 ml flask, about 5 g of the test sample; we added 50 ml potassium hydroxide 1M and a few boiling regulators solution. The refrigerant is adapted to the flask under reflux and the contents were heated for 1 hour at gentle boiling. Heating was stopped and 50 ml of distilled water was added via the top of the condenser and stirred.

After cooling, the solution is transferred into a separatory funnel of 250 ml; we added 50 ml of hexane.

The ampoule is sealed, shaken vigorously by balancing the pressure by periodic reversal of the funnel and opening the valve.

We allowed the bulb to stand until complete separation of the two phases, and then the lower phase is drawn off as completely as possible by collecting it in a second separating funnel.

We conducted two further extractions of the soap phase, using each time, in the same way 50 ml of hexane; 3 pooled hexane extracts in a separatory funnel, washed several times with distilled water (if an emulsion is formed, we destroyed it by adding small amounts of ethanol).

The hexane solution was transferred to a 250 ml flask previously dried and weighed to 0.1 mg. The solvent was evaporated and the residue was dried for 15 minutes in an oven and then allowed to cool and weighed to the nearest 0.1 mg.

The unsaponifiables rate is given by the following expression:

$$T_I = \frac{m_1}{m_0} \times 100$$  \hspace{1cm} (3)

$m_0$ is the mass, in grams, of the test sample

$m_1$ is the mass, in grams, of the residue

2.3.6. Saponification index [8]

We weighted about 2 g of test sample and we added thereto, using a pipette, 25 ml of the ethanolic solution of sodium hydroxide and a few boiling aids, we heated gently under reflux by stirring occasionally, for 60 minutes. After this reaction time, we added to the hot solution, 0.5 to 1 ml of phenolphthalein solution and we titrated with a standard solution of hydrochloric acid until the pink color of the indicator disappears.

We carried out, in parallel, a blank test following the same procedure.

The saponification index, Is, is given by the following expression:

$$I_s = \frac{C \times \frac{56.1}{V_0} \times (V_0 - V_1)}{m}$$  \hspace{1cm} (4)

$V_0$ is the volume in milliliters, of the titrated solution of hydrochloric acid used to dose the sodium hydroxide in the blank test.

$V_1$ the volume in milliliters, of the titrated solution of hydrochloric acid used to dose the sodium hydroxide in the sample test.

$C$ is the exact concentration in moles per liter, of the standard solution of hydrochloric acid used.

$m$ is the mass of the test portion of the fat in grams.
2.4. Lactonization reaction

It is a reaction transforming unsaturated fatty acid lactones (cyclic esters) catalyzed by mineral acids, resins,... It is of great industrial interest because it allows obtaining cyclic compounds from reactants to side, acyclic chains. The size of the cycle depends on the length of the side chain of the reagent.

2.4.1. In the presence of perchloric acid [9,10]

10 g of fat (commercial oleic acid or mixture of fatty acids from olive pomace oil) were introduced in a three-necked flask. 1 molar equivalent of perchloric acid was added. The refrigerant was adapted and heated to 85 °C for 8.5 hours.

After similar treatment, as in the case with sulfuric acid, we obtained the rough product consisting of lactones, estolides and fatty acids which have not reacted.

- treating of the rough product

The crude product is constituted by the formed lactones, fatty acids which have not reacted and the estolides which may be formed by any polymerization side reactions.

20 ml of hexane were introduced in a test portion of 2 g of crude product placed in a 100 ml Erlenmeyer flask. Sample was stirred until complete dissolution. The mixture was cooled for half an hour in an ice bath. A white solid appears at the bottom of the flask. The latter is recovered by filtration and then recrystallized in hexane.

2.5. Chromatographic and spectroscopic analysis

The lactones prepared are identified by the following techniques: GC-MS, IR and NMR

2.5.1. GC-MS

We dissolved 5 mg of solid product separated in 1 ml of chloroform.

The spectrum recording is performed using an apparatus GC-MS type FI 8000. The column used is of type DBS, of 30 m long and 0.32 mm internal diameter. The film thickness is 0.25 µm. The carrier gas is helium and the injector temperature was 230 °C. The separation temperature was 60 °C for one minute and then it increased to 10 °C per minute to reach 300 °C. This temperature is maintained for 10 minutes.

2.5.2. Infra Red (IR)

IR spectrum was recorded using a spectrometer type JASCO FT-IR 420.

2.5.3. Carbon 13 and proton NMR

5 mg of sample was dissolved in 1 ml of deuterated chloroform. The solution obtained was then introduced in an NMR tube and the spectrum was recorded by a NMR apparatus type Bruker Ultrashield 300 MHz.

3. RESULTS

3.1. Determination of current indices studied fats

The results of analyzes carried out on samples of oleic acid sales (COA), the mixture of fatty acids derived from the oil of olive pomace (MFAOOP), oil of olive pomace (OOP) and virgin olive oil (VOO) as a reference are reported in Table 1.

<table>
<thead>
<tr>
<th>Chemical characteristics</th>
<th>COA</th>
<th>MFAOOP</th>
<th>OOP</th>
<th>VOO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity (%)</td>
<td>91</td>
<td>95</td>
<td>60.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Index of Iodine (g (I₂)/100 g of fats)</td>
<td>97</td>
<td>90</td>
<td>95.80</td>
<td>92.32</td>
</tr>
<tr>
<td>Rate of unsaponifiables (%)</td>
<td>1.21</td>
<td>1.32</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td>Index of saponification (mg of KOH/g of fats)</td>
<td>224.24</td>
<td>196.35</td>
<td>196.35</td>
<td>202.14</td>
</tr>
</tbody>
</table>

Reading the results of table 1, we noted that:

- All the chemical characteristics of olive pomace oil are comparable to those of virgin olive oil with the exception of the acidity that is higher in the case of oil olive pomace. This is due to the degraded state of the oil.
The treatment of olive pomace oil with sodium hydroxide and then by conduit phosphoric acid to a mixture of fatty acids having an acidity of 95%. This mixture is characterized by a saponification and an unsaponifiable rate identical to those of the olive pomace oil.

The index of iodine value of the fatty acid mixture from olive pomace oil is 90. This high value shows that this acidic mixture is mostly made up of unsaturated fatty acids. Knowing that the iodine value of oleic acid is 89 \( \pm 3 \), it is expected that this fatty acid is most abundant in the acidic composition of the mixture of fatty acids derived from olive pomace oil.

The commercial oleic acid has an iodine value of 97, higher than that of the mixture of fatty acids derived from the oil of olive pomace (90). This can be explained by the importance of the proportion of saturated fatty acids present in the mixture of fatty acids derived from the oil of olive pomace. To validate these interpretations, we determined the acidic composition of two mixtures of fatty acids.

### 3.2. Determination of acidic composition

GPC analysis of 2 samples of methyl esters of oleic acid and shopping mixture of fatty acids from olive pomace oil can calculate the weight percentage of each fatty acid. Table 2 shows the acidic compositions of commercial oleic acid and mixture of fatty acids derived from the oil of olive pomace.

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>COA (%)</th>
<th>MFAOOP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{16}:0)</td>
<td>1.953</td>
<td>16.134</td>
</tr>
<tr>
<td>C(_{16}:1)</td>
<td>1.791</td>
<td>2.66</td>
</tr>
<tr>
<td>C(_{18}:0)</td>
<td>3.123</td>
<td>2.84</td>
</tr>
<tr>
<td>C(_{18}:1)</td>
<td>89.45</td>
<td>62.79</td>
</tr>
<tr>
<td>C(_{18}:2)</td>
<td>3.561</td>
<td>15.53</td>
</tr>
</tbody>
</table>

These results showed that:

Oleic acid prevails both in commercial oleic acid in the mixture of fatty acids extracted from the olive pomace oil.

The proportion of linoleic acid is greater in the acidic mixture obtained from the oil of olive pomace.

The ratio of saturated fatty acids unsaturated fatty acids is given by the following expression:

\[
\frac{\% (C_{16}:0 + C_{18}:0)}{\% (C_{16}:1 + C_{18}:1 + C_{18}:2)} \quad (5)
\]

This ratio is 0.05 in the case of commercial oleic acid. It was 0.23 in the case of fatty acid mixture derived from the olive pomace oil. These values confirm that the mixture of fatty acids from olive pomace oil is richer in saturated fatty acids than commercial oleic acid. Oleic acid is a large majority in the 2 acidic mixtures. The palmitoleic acid (C\(_{16}:1\)) present to 2.6% in the olive pomace oil, can lead to the formation of gamma and delta lactones to 16 carbon atoms. Linoleic acid (C\(_{18}:2\)) having 2 unsaturated bonds, can also be lactonized to give gamma and delta lactones with an unsaturated side chain.

### 3.3. Lactonization reaction

#### 3.3.1. Preparation of gamma stearo–lactones

#### 3.3.1.1. Terms and reaction yields

This reaction took place under optimum conditions for obtaining stearo selective gamma-lactones described in the literature [11]. Under these conditions, perchloric acid and fatty acid are in stoichiometric quantities and the reaction is carried out at high temperature (85 °C) in the absence of solvent for 8.5 hours.

Starting from 10 g of fatty acid, we obtained after treatment of the reaction, 9.5 g of crude product from oleic acid sales (90%) and 9.7 g from the mixture of acids fat from olive pomace oil containing 63% oleic acid.

The gross yield of the reaction is given by the following expression:

\[
\text{Gross Yield} = \frac{\text{Reagent mass}}{\text{Product mass}} \times 100 \quad (6)
\]

A gross yield is 95% with commercial oleic acid and 97% with the mixture of fatty acids in olive pomace oil.

The crude products of the lactonization reaction were purified by successive recrystallizations in hexane.

Starting from a test sample of 2 g of crude final product, we obtained a mass of 1.7 g lactones with oleic acid and 1.2 g trading with the fatty acid mixture of pomace olive oil.

Performance is, regardless of the percentage of oleic acid in the fatty acid mixtures used, given by the following expression:
Yield = (mass of lactone/mass of test sample) × gross yield

We obtained (Yield 2) 80.75% with commercial oleic acid and 58.20% with the fatty acid mixture of pomace olive oil (Table 3).

Taking into account the percentage of oleic acid in the fatty acid mixture engaged, the following yields (Yield 3) are obtained: 89.72% from the commercial oleic acid and 92.38% from the mixture of fatty acids derived from the oil of olive pomace (Table 3).

Table 3 Yields in rough products and lactones of acidic mixtures

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Gross yield</th>
<th>Yield 2</th>
<th>Yield 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>COA (%)</td>
<td>95</td>
<td>80.75</td>
<td>89.72</td>
</tr>
<tr>
<td>MFAOOP (%)</td>
<td>97</td>
<td>58.20</td>
<td>92.38</td>
</tr>
</tbody>
</table>

Table 3 showed that almost all of oleic acid is converted into lactones.

3.3.1.2. Spectral characteristics of the gamma stearo-lactone outcome of commercial oleic acid

3.3.1.2.1. IR analysis

IR spectrum shows:
- An absorption band at 1765 cm⁻¹ on the C = O bond
- Two absorption bands at 2920 and 2850 cm⁻¹ for the CH bond

Moreover, the absorption band at 1710 cm⁻¹ on the C = O acid does not appear; even of the absorption band at 3300 cm⁻¹ for the acid OH bond that appears in the form of broadband in oleic acid.

These results confirm the possible formation of a lactone.

3.3.1.2.2. Analysis by GC-MS

Examination of the chromatogram of the lactone obtained from the commercial oleic acid to 90% indicates the presence of a main peak at t_R = 47.70 min (89.46%) and two minor peaks at t_R = 48.83 min (6.43%) and t_R = 41.10 min (4.06%).

Analyses of the different spectra of mass corresponding to these peaks are summarized in Table 4.
Table 4 Retention time (t_R), Percentages (%), fragments, and m/z of main products

<table>
<thead>
<tr>
<th>Peaks</th>
<th>t_R (min)</th>
<th>%</th>
<th>fragments</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_1</td>
<td>47.70</td>
<td>89.46</td>
<td>[C_4H_7]^+</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_5H_9]^+</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_4H_5O_2]^+</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_7H_13]^+</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_8H_15]^+</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[M^- - 62]^+</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[M^- - 18]^+</td>
<td>264</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_18H_34O_2]^+</td>
<td>282</td>
</tr>
<tr>
<td>P_2</td>
<td>48.33</td>
<td>6.43</td>
<td>[C_4H_7]^+</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_5H_11]^+</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_6H_11]^+</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_5H_9O_2]^+</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_8H_18]^+</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[M^- - 36]^+</td>
<td>246</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[M^- - 18]^+</td>
<td>264</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[C_18H_34O_2]^+</td>
<td>282</td>
</tr>
<tr>
<td>P_3</td>
<td></td>
<td></td>
<td>[C_16H_30O_2]^+</td>
<td>254</td>
</tr>
</tbody>
</table>

The main peak at t_R 47.70 min shows a molecular ion (m/z: 282) corresponding to a stearo-lactone. Analysis of the main fragments compared to the mass spectrum described in the literature [10, 11] and the comparison with a reference spectrum database (Wiley275.L) clearly confirm the large majority obtaining of the gamma stearo lactone.

The same analysis on the peak at t_R = 48.33 min confirms that this peak corresponds to the delta stearo-lactone. Peak at t_R = 41.10 min (m/z 254) being identified as the gamma-lactone from palmitoleic acid in the starting fatty acid (Scheme 1)
The ratio of the relative percentages of the gamma- and delta-stearo-lactone is \( R = \frac{89.46}{6.43} = 13.91 \). The ratio indicates that under these reaction conditions gammas stearo-lactone is obtained mainly in a very selective way.

### 3.3.1.2.3. NMR analysis

The analysis by GC-MS and IR of the product obtained shows that the gamma stearo-lactone is predominantly obtained with excellent selectivity. To confirm the structure of this product, we performed the NMR spectrum of the proton and carbon 13. These spectra were performed in deuterated chloroform (CDCl3) and reference tetramethylsilane (TMS).

#### Table 5. Signals and chemical shift of protons characteristics of gamma stearo-lactone from commercial oleic acid

<table>
<thead>
<tr>
<th>Proton</th>
<th>( H_a )</th>
<th>( H_a + H_b )</th>
<th>( H_c )</th>
<th>( H_s )</th>
<th>( H_t )</th>
<th>( (CH_2)_{12} )</th>
<th>( CH_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signals</td>
<td>1m (1H)</td>
<td>1m (2H)</td>
<td>1m (1H)</td>
<td>1m (2H)</td>
<td>1m (2H)</td>
<td>1m (24H)</td>
<td>1t (3H)</td>
</tr>
<tr>
<td>Chemical shift (ppm)</td>
<td>4.43-4.38</td>
<td>2.48-2.19</td>
<td>2.28-2.27</td>
<td>1.83-1.21</td>
<td>1.69-1.47</td>
<td>1.43-1.23</td>
<td>0.79</td>
</tr>
</tbody>
</table>

The proton NMR spectrum of the product obtained (Figure 4) shows the presence of characteristic peaks of proton of the carbon of the carbinol (-O-CH\(_2\)CH\(_2\)C=O) as a multiple at 4.43 to 4.38 ppm. The signal that can be attributed to the same type of proton of delta-stearo-lactone, is absent from the spectrum. The absence of this signal could be explained by the low percentage of this lactone (6.43%).
Table 6 Chemical shifts of carbons of gamma stearo-lactone from commercial oleic acid

<table>
<thead>
<tr>
<th>Carbons</th>
<th>( C_1 )</th>
<th>( C_4 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>( C_{5-17} )</th>
<th>( C_{18} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical shift (ppm)</td>
<td>177.2</td>
<td>80.6</td>
<td>35.4</td>
<td>31.8</td>
<td>29.5-22.5</td>
<td>13.9</td>
</tr>
</tbody>
</table>

Carbon 13 NMR spectrum (Figure 5) shows the presence of 177.2 ppm carbonyl carbon \( C = O \) group and the presence of carbon -CH-OC = O 80.9 ppm. These peaks are characteristic of the gamma-stearolactone.

Gamma-stearolactone from of the olive pomace oil

We have obtained a yield of 92.38% in lactones. The IR and NMR spectra are identical to those obtained from the gamma-stearo-lactone obtained from commercial oleic acid.

The GC-MS examination of the lactone obtained from the mixture of fatty acids derived from the oil of olive pomace with 63% revealed the presence of a main peak at \( t_R = 45.63 \) min (93.07 %) and a secondary peak at \( t_R = 46.01 \) min (6.93%).
The main peak at t_{R} = 45.63 min shows a molecular ion (m / z: 282) corresponding to a stearo-lactone. The analysis of the main fragments compared to the mass spectrum described in the literature [10, 11] as well as comparison to a reference spectrum of the database (Wiley.275.L) clearly confirms the obtaining of gamma stearo-lactone in major proportion.

The same analysis performed on the peak at t = 46.01 min confirms that this peak corresponds to the delta-stearo-lactone.

The ratio of the relative percentages of the gamma- and delta-stearo-lactone is R = 13.43; value comparable to that found in the case of commercial oleic acid.

We can notice the absence of the gamma-lactone from palmitoleic acid, in this case, probably removed during recrystallization.

Nevertheless, we can expect the formation of an unsaturated lactone from linoleic acid present in significant amounts (15.53%) in the acidic mixture resulting from the pomace olive oil. The absence of the formation of this lactone could probably explain the persistence of the conjugation of double bonds in the same reaction conditions preventing thus the formation of this lactone.

4. Conclusion

This study is a contribution to the promotion of olive pomace oil, as main product of the oil industry.

We, in this context, made the synthesis of gamma and delta-lactone stearo from the mixture of fatty acids extracted from the olive pomace oil.

This study was performed, at first, on the 90% commercial oleic acid have been characterized including its acidic composition by GC-MS to optimize reaction conditions.

In an acid medium (perchloric acid), we obtained mainly gamma-stearo-lactone, thermodynamic product and stearo-delta-lactone in minor proportion, kinetic product.

Products reactions isolated were characterized and identified by IR, GC-MS and proton NMR and carbon-13.

Second time, we realized under the conditions of commercial oleic acid, lactonization of the mixture of fatty acids from olive pomace oil which its acidic composition is also characterized by GC-MS.

We found that the lactonization reaction proceeds also, as well as with commercial oleic acid, with good yield and good chemio-selectivity.

REFERENCE