Aromatic FAEE: a real product of a dehydrogenation reaction

The identification of aromatic FAEE (see *Chapter 3.2*) as a reaction product involved further research to know where they did come from. Several experiments were performed to understand and, if possible, to propose a mechanism for the obtaining of aromatic-containing FAEE. In Chapter 3.1, thermal behaviour of fatty acids in a batch reactor has been studied. The results showed that such compounds are extremely sensitive to oxidative conditions. To our knowledge, no thermal studies of FAEE under inert conditions in a continuous vapour phase system had been performed before. These experiments evidenced the dehydrogenation of ethyl linoleate to yield aromatic FAEE at 200 °C using active carbon as a catalyst. Currently, there is a submitted article to European Journal of Lipid Technology concerning the results obtained in this study (see Annex V).

3.3.1   Introduction

The thermal behaviour under inert conditions of mono- and poly-unsaturated fatty acids, MUFA and PUFA, respectively, has attracted several research studies. Wheeler et al. [1] reported the formation of dimeric acid structures by thermal reaction of methyl linoleate at 290 °C. Monocyclic, bicyclic and tricyclic structures were detected by mass spectrometry. The mechanism for the thermal dimerization of the ethyl linoleate was a Diels-Alder mechanism [2], where previously the conjugated linoleate works as a diene adding to a double bond of a normal or conjugated linoleate, which works as a dienophile. This mechanism gives place to the monocyclic structure. The bicyclic dimer might be explained by the free radical coupling theory, with the subsequent rapid intramolecular cyclization. Finally, the tricyclic dimer might arise by an intramolecular alkylation reaction of an exocyclic double bond of the bicyclic dimer. Nevertheless, more recent studies have shown that heat treatment of vegetable oils, containing fatty acids, leads to the obtaining of cyclic fatty acid monomers at temperatures, between 200 °C and 275 °C [3-9]. This fact has been observed both under oxidative [3, 4] and inert conditions [8, 9]. Even though mechanisms remain speculative and require further work, it has been proposed that free radicals are almost certainly involved [9-13], even under inert

conditions, when free radical formation is apparently not possible. It seems that oils probably contain trace amounts of endogenous peroxides, when they are not previously deoxygenated or no endogenous radical scavenger level is present [9]. Recently, a concerted cycloaddition mechanism undergoing [1,6]- or [1,7]-prototropic migration has been suggested as being consistent with the formation of primary cyclic fatty acid monomer products [14].

Floyd et al. reported the aromatization of linoleic acid in a batch reactor at 270 °C for 6 hours using Pd/AC as a catalyst. The aromatization may proceed via cyclization and ulterior hydrogen transfer [15].

Even though the number of studies concerning the heat treatment of fatty acids and their derivatives appear to be abundant, to our knowledge no heat treatment of FAEE in vapour phase in a continuous system has been studied. Therefore, the heat treatment of the unsaturated FAEE with and without catalyst was carried out in order to elucidate, if possible, the cause of the aromatic FAEE formation.

3.3.2   Experimental

The catalytic reaction was carried out in a continuous tubular quartz reactor specially designed for this work. This reactor was placed inside a temperature-programmed oven at 200 °C. Argon was used as carrier gas (13.5 mL/min). The feeding reactant was injected into the reactor with a piston pump, at a Weight Hourly Space Velocity (WHSV) of 0.12 h^{-1}. The following experiments were performed: Experiment 1) using only ethyl linoleate (99%, Fluka, Germany), as starting reactant, Experiment 2) using only ethyl linolenate (99%, Sigma-Aldrich, Germany), as starting reactant, Experiment 3) using a mixture of ethyl linoleate and ethyl linolenate, and finally, Experiment 4) using ethyl linoleate as starting reactant and activated carbon (Fluka, Germany) as a catalyst. GC, GC-MS and UV spectroscopy were performed to the product samples in order to determine their composition.

3.3.3   Results and Discussion

The results of the different studied reactions are summarized in Scheme 3.3.1, where the general structures represent the families of compounds, in order to draw a qualitative picture of the products obtained.

Experiment 1

An isomerization reaction was obtained when the non-conjugated ethyl linoleate at 200 °C under inert conditions partially converted to the corresponding conjugated product as it was detected by UV spectroscopy. A conjugated diene appeared as a broad band centred at 232 nm [16]. The applied temperature promoted the mobility of double bonds along the hydrocarbon chain. A representative MS spectrum of the main product obtained is shown in Fig. 3.3.1.
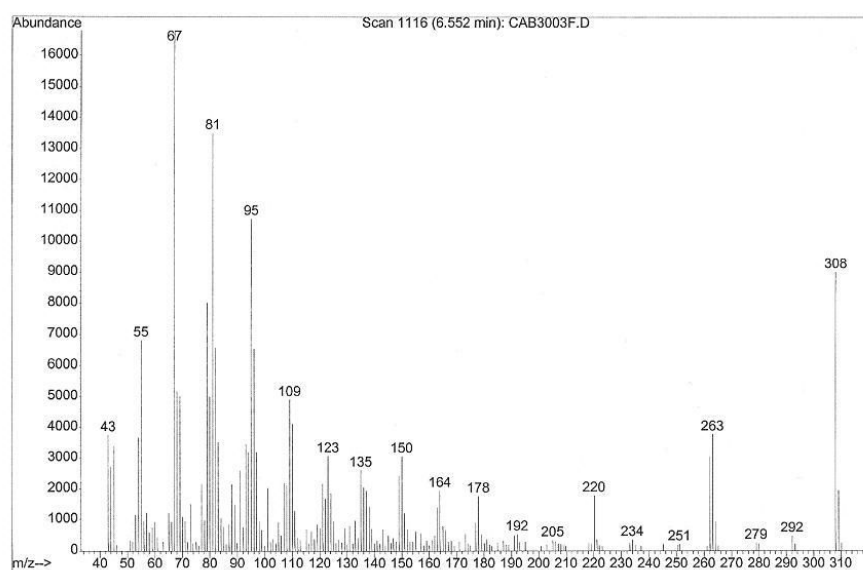

Figure 3.3.1 Representative mass spectrum of di-unsaturated FAEE obtained in Experiment 1.

Experiment 2

An isomerization reaction was obtained from the non-conjugated omega-3 alpha ethyl linolenate at 200 °C under inert conditions. Analogously to the experiment 1, the effect of temperature lead initially to the formation of the corresponding conjugated tri-unsaturated compound. Regarding the UV-spectroscopy analysis, the band assigned to conjugated trienes was centred at higher wavelengths (approximately, 270 nm) [17]. GC peaks were eluted at retention time associated

to the standard ethyl linolenate. Aromatic FAEE and hydrogenation products were also detected in low concentrations.

Experiment 3

When the mixture of both, ethyl linoleate and ethyl linolenate, was conducted along the reactor, at 200 °C under inert conditions, the same products of experiments 1 and 2 were detected by GC, as expected. Additionally, hydrogenated FAEE, such as ethyl oleate was detected in a higher concentration than in Experiment 2.

Experiment 4

When the reaction of pure ethyl linoleate at 200 °C under inert conditions using active carbon as catalyst was carried out, the presence of both, aromatic FAEE and hydrogenated FAEE (oleate) were detected, as in experiment 3 and unlike the results of experiment 1.

In Experiment 1, GC, GC-MS and UV spectroscopy results showed that neither the cycloaddition reaction such as Diels-Alder nor the formation of cyclic FAEE
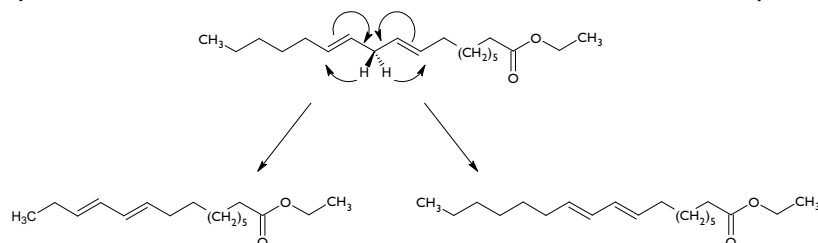

Figure 3.3.2 Formation of isomers by intramolecular [1,3]-sigmatropic rearrangement.

occurred, as it had been reported [1-9] for temperatures above 200 °C. The isomerization reaction under inert conditions was expected to occur at 200 °C [18-20]. The responsible of obtaining conjugated isomers of di-unsaturated FAEE may be an intramolecular mechanism. The migration of double bonds is promoted by thermal effects [18] and a sigmatropic migration of an allylic hydrogen atom may be accountable for such a structural rearrangement [18, 19] (Fig. 3.3.2). Thus, temperature seems to play an important role for the formation of cyclic FAEE and isomers. Temperatures around 200 °C appeared to be a critical point for the nature of the components [4].
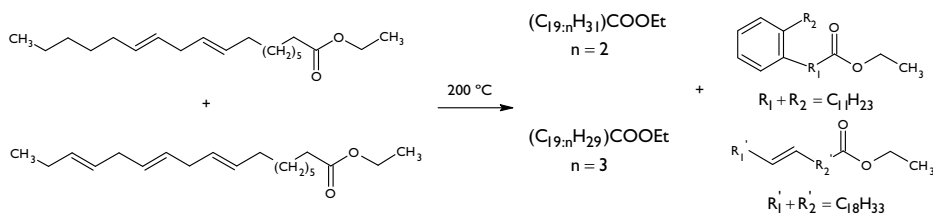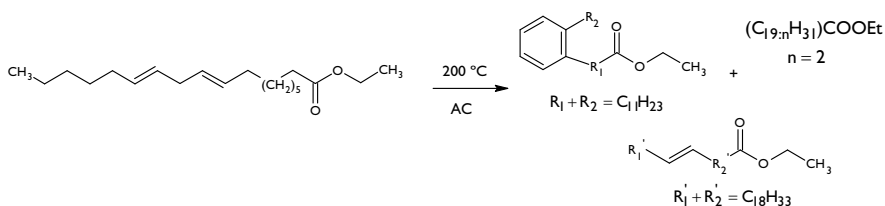
Experiment 1
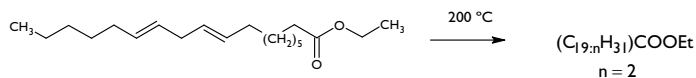
Experiment 2
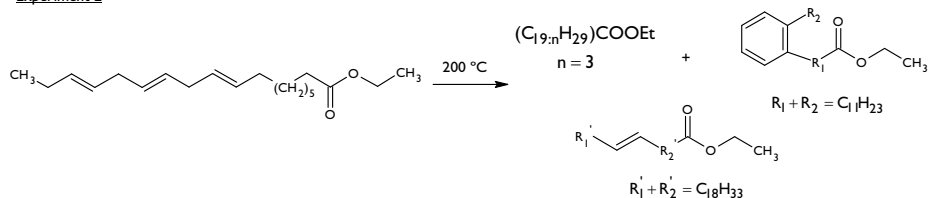
Experiment 3

Experiment 4

Scheme 3.3.1 Scheme of the product reaction obtained in the different experiments.

Concerning the results of Experiment 2, an analogous mechanism for isomerization of di-unsaturated FAEE may be attributed to the obtaining of isomers of tri-unsaturated FAEE. The heat treatment of linolenic acid and derivatives may form cyclic fatty acid monomers. Each basic structure illustrated in Fig. 3.3.3 has a ring structure with an unsaturated bond in the ring and another in the aliphatic chain. The rings are formed by five or six carbons giving place to cyclopentyl or cyclohexenyl fatty acids, respectively [8]. Mossoba and colleagues reported the

formation of some cyclic fatty acids with conjugated double bond systems [21-24]. This mechanism may be the explanation to the obtaining of the compounds, whose
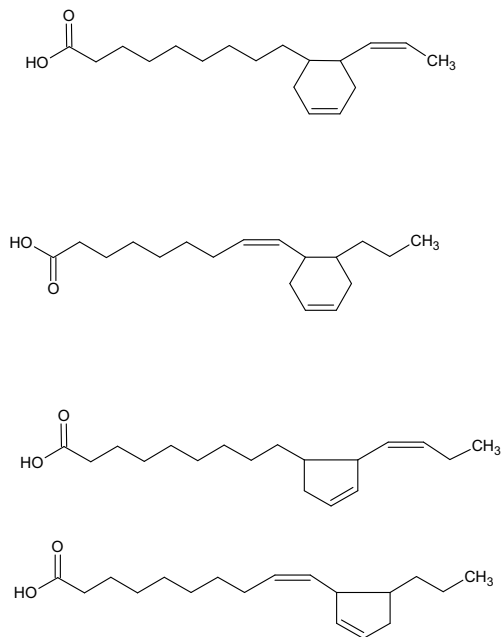

Figure 3.3.3 Structural formulae of cyclic dienoic acids.

m/z was equal to 302. Mono- and di-unsaturated FAEE are the products of the hydrogenation reaction of the starting material. If a hydrogenation reaction is to be assumed, then a hydrogen source has to be suggested under the starting inert conditions. In comparison with the tri-unsaturated FAEE (ethyl linolenate), whose molecular peak, and extensively its molecular weight, is 306, the aromatic FAEE showed a m/z of 304. It means that the formation of aromatic FAEE supposed a loss of 2 a.m.u., which may be put down to the hydrogen loss from a dehydrogenation reaction. If aromatic FAEE had come from the cyclohexenyl structures in Fig. 3.3.3, then four hydrogen atoms would be formed until aromatization was achieved. This hydrogen loss would suppose a decrease of 4 a.m.u. at the MS molecular peak; that is from 306 to 302 which was not detected in Experiment 2.

The conjugated octadecatrienoic systems are susceptible of suffering an electrocyclic reaction that drives to the formation of di-unsaturated cyclic compounds. This reaction may advantageously proceed under heating conditions.

Definitely, using water as a solvent, the rearrangement may proceed at temperatures from 160 °C to 180 °C for reaction periods between 0.5 hour and 4 hours. The cycle-opening reaction may occur by $h\upsilon$ radiation (Fig. 3.3.4) [25-29]. A thermodynamically favourable dehydrogenation reaction of the cyclohexadienyl compounds may give the aromatic FAEE. The released hydrogen may partially hydrogenate the starting material to give less unsaturated compounds, such as the di-unsaturated FAEE (linoleate) or the mono-unsaturated FAEE (oleate). Moreover, this mechanism also explains the difference of 2 a.m.u. between the tri-unsaturated FAEE and the aromatic FAEE.
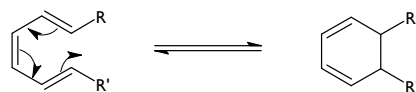

Figure 3.3.4 Sigmatropic electrocyclic reaction.

In Experiment 3, the obtaining of the products illustrated in Scheme 3.3.1 may be accounted for the previous Experiment 1 and 2 discussions. The fact that more mono-unsaturated FAEE was detected is presumably due to higher rate kinetics of the di-unsaturated FAEE vs. the tri-unsaturated FAEE hydrogenation. In addition, the
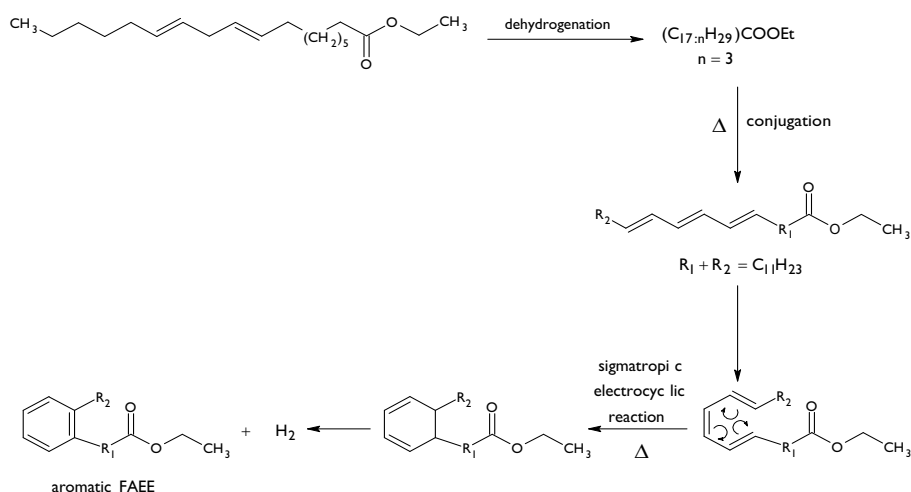
Scheme 3.3.2 Mechanism proposal for the obtaining of aromatic FAEE in Experiment 4.

addition of two moles of hydrogen to tri-unsaturated FAEE to give the mono-unsaturated FAEE directly has not been reported to our knowledge.

In Experiment 4, aromatic FAEE and mono-unsaturated FAEE were mainly detected. On one hand, the formation of cyclic FAEE had not been detected in Experiment 2; on the other hand, aromatic FAEE had before only been identified in Experiment 3. Additionally, the catalyst used in Experiment 4, active carbon, has been reported to show dehydrogenating properties [30-38] . Thus, the inclusion of a dehydrogenation step in the mechanism proposal is justified. Considering all observations and statements presented up to now, a mechanism for the synthesis of aromatic FAEE using ethyl linoleate as starting material and AC as a catalyst is proposed in Scheme 3.3.2. The mechanism shows essentially the formation of aromatic FAEE in several steps: dehydrogenation of di-unsaturated FAEE to obtain tri-unsaturated FAEE, conjugation of tri-unsaturated FAEE, electrocyclic sigmatropic reaction to give cyclohexadienyl FAEE and last, dehydrogenation of the cycle to give aromatic FAEE. The research concerning the control of the electrocyclic reaction had been carried out and is put forward in the following chapters of this work.

3.3.4 Conclusions

The heat treatment of di-unsaturated FAEE under argon at 200 °C in vapour phase in a continuous vapour-phase system did not give place to cyclic FAEE. Basically, isomerization of the di- occurred at this temperature. Neither degradation nor Diels-Alder reaction were detected.

The tri-unsaturated FAEE underwent an isomerization reaction at 200 °C to give conjugated systems, which were sensible to suffer an electrocyclic sigmatropic reaction. Thus, cyclohexadienyl compounds were obtained; their ulterior dehydrogenation with concomitant hydrogenation of the starting material gave place to the aromatic FAEE. As in the case of di-unsaturated FAEE no cyclic FAEE was identified. In a continuous vapour-phase system under argon the observed reactivity is different to that reported in liquid-phase batch reactors.

In comparison to fatty acids (oleic acid), FAEE in vapour phase were more stable to the thermal treatment, since no degradation, such as polymerization, was detected. The higher stability may be assigned to the ester group, which plays a protecting role on a reactive functionality such as, the carboxylic acid. Moreover, possible endogenous FAEE peroxides, which are very reactive species, seemed not

to be an important threat for the degradation of FAEE under the conditions chosen in this work.

Active carbon appears to work as a dehydrogenating catalyst according to the mechanism suggested in Scheme 3.3.2. The conjugated tri-unsaturated compound is barely detected as it converts very quickly to the aromatic FAEE compounds.

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