Dehydrogenation of omega-6 fatty acid esters

(SHORT COMMUNICATION)

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SUMMARY: The reactivity of fatty-acid ethyl esters (FAEE) is studied. Several experiments have been performed to understand and propose a mechanism for the obtaining of fatty-acid esters containing an aromatic group. These experiments gave evidence of the dehydrogenation of ethyl linoleate to yield omega-3 ethyl linolenate at 200ºC using active carbon as catalyst. Gas Chromatography fitted to Mass Spectrometry (GC-MS) and ultraviolet (UV) spectroscopy have been used to identify the products. Further research to avoid the cyclation and re-hydrogenation steps is currently in progress.

INTRODUCTION

Essential fatty acids and their derivatives have acquired a growing interest in the last years. Among these compounds, ω-3 polyunsaturated fatty acids have achieved a special interest, because of their clinical and nutritional benefits [1-3]. Sources of such compounds, despite their scarcity, are found in certain vegetable oils and fish. However, new synthetic routes might be of great commercial interest if conveniently developed [4]. There are several studies related to the desaturation reaction of fatty acids and their derivatives using enzymes as catalysts [5, 6]. However, to our knowledge, a study concerning the catalytic dehydrogenation of fatty acid derivatives has not been carried out, so far.

The model compound for the study of our reaction has been ethyl linoleate. The dehydrogenation reaction of omega-6 ethyl linoleate aims at obtaining an omega-3 tri-unsaturated derivative. The use of an ester instead of a fatty acid improves the thermal stability of the starting material, by protecting the acidic functionality, which helps us to concentrate our interest on the reactivity of the polyunsaturated chain. Besides, fatty acid ethyl esters (FAEE) are also considered to be bioactive compounds with therapeutical applications [7].

The conversion of ethyl linoleate to ethyl linolenate and other pure products with desirable physiological or industrial properties by a chemical procedure may be of great interest. This preliminary work attempts the paths to reach that goal starting from ethyl linoleate.

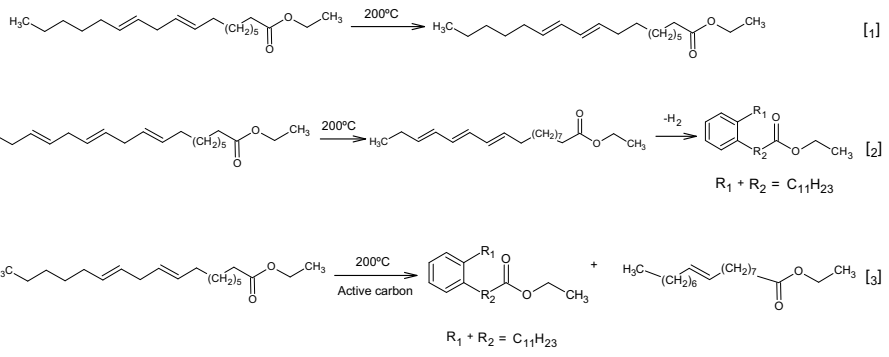
EXPERIMENTAL

The catalytic reaction has been carried out in a continuous tubular quartz reactor specially designed for this work. The reactor displays a double column which allows the preheating and

the evaporation of the starting material before the catalytic bed. This reactor has been placed inside a temperature-programmed oven. Argon has been used as carrier gas (13.5 mL/min). The feeding reactant has been injected into the reactor with a piston pump, at a Weight Hourly Space Velocity (WHSV) of 0.12 h^{-1}. These samples have been analyzed by GC using a Flame Ionization Detector (FID) and a high polar column HP-FFPA. The following experiments have been performed: 1) using only ethyl linoleate (Fluka, Germany), as starting reactant 2) using only ethyl linolenate (Sigma-Aldrich, Germany), as starting reactant 3) using a mixture of ethyl linoleate and ethyl linolenate, and 4) using ethyl linoleate as starting reactant and activated carbon (Fluka, Germany) as catalyst. A reaction temperature of 200ºC has been set in all cases. Several techniques, such as GC-MS and ^{1}H Nuclear Magnetic Resonance (NMR) have been used in order to identify the most relevant products obtained. Ultraviolet spectroscopy (UV) has been also used to identify conjugated and non-conjugated isomers. The active carbon catalyst has been characterized by Fourier-transform infrared spectroscopy (FTIR), elemental analysis and Brunauer-Emmett-Teller (BET) method.

RESULTS AND DISCUSSION

The results of the different studied reactions are summarized as shown below, in [1], [2] and [3]. The product structures in chemical equations represent one of the possible conjugated isomers.



Experiment 1. An isomerization reaction is obtained when the non-conjugated ethyl linoleate at 200ºC under inert conditions partially converts to the corresponding conjugated product as it has been detected by UV spectroscopy. A conjugated diene appeared as a broad band centered at 232 nm. The applied temperature promotes the mobility of double bonds along the hydrocarbon chain (equation [1]).

Experiment 2. An isomerization reaction is obtained from the non-conjugated omega-3 alpha ethyl linolenate at 200ºC under inert conditions. Analogously to experiment 1, the effect of temperature leads initially to the formation of the corresponding conjugated tri-unsaturated compound. Regarding UV-spectroscopy analysis, the band assigned to conjugated trienes was centered at higher wavelengths (approximately, 270 nm).This three double-bond compound cycles very easily with subsequent loss of hydrogen and formation of the aromatic derivative (equation [2]). The cyclation of the tri-unsaturated ethyl fatty acid ester, due to the effect of temperature, is known as a sigmatropic electrocyclic reaction. Depending on the double bond position, different aromatic compounds are obtained. The structure of this compound consists of an aromatic ring with two *ortho* substitutes which accounts for the cyclation of ethyl linolenate with subsequent dehydrogenation of the ring. R_1 and R_2 in equations [2] and [3] illustrate the chain length (number of carbons and hydrogens) of the aromatic substitutes. Cyclic compounds come from conjugated tri-unsaturated fatty-acid ethyl esters ((equation [2] and Scheme 1).The structural determination of aromatic compounds has been done using both ^{1}H-NMR and GC-MS. The mass spectra of several compounds (previously separated by GC) have the same peak profile and differ in their abundance. The spectra are certainly of ethyl esters in that there is a gap of 46 a.m.u. from the molecular ion at m/z = 304 to 258, and the fragment at m/z = 88 is the McLafferty ion. Ions at m/z = 91 and 105 are typical of highly unsaturated structures such as parinarate or benzene rings. The mass spectrum in figure 1 represents the general profile of such aromatic compounds. The ions at m/z = 173 and 145 (in figure 1, breakings 1-3 and 1-2, respectively) may be the key to the structure though there would have to be a loss of protons to give the correct numbers. Ions at m/z = 131 and 117 could be formed by sequential loss of methylene groups from this.

The results of ^{1}H-NMR analysis of the reaction mixture showed the presence of some aromatic compounds (see figure 2), since chemical shifts around 7-7,5 ppm correspond to such aromatic protons. The small peak-size of aromatic compounds can be explained because of the low conversion of ethyl linoleate to aromatic compounds.

Experiment 3. When the mixture of both, ethyl linoleate and ethyl linolenate, is conducted along the reactor, at 200ºC under inert conditions, the same products of experiments 1 and 2 are detected by GC, as expected. The ethyl linolenate partially converts to the aromatic compounds and hydrogen as in experiment 2. Additionally, one or two unsaturated bonds from the other mixture component ethyl linoleate may hydrogenate (with hydrogen from previous dehydrogenation) to give ethyl oleate or stearate, respectively (the hydrogenation reaction appears feasible because of thermodynamic reasons). The dehydrogenation of the cyclohexadienic compound is powered by the concomitant hydrogenation of ethyl linoleate and ethyl linolenate to oleate and stearate. The consumption of hydrogen by the non-converted starting material is supposed to be the driving force to the formation of aromatic compounds (Scheme 1). We should also remark that either ethyl linoleate or alpha ethyl linolenate did not undergo any degradation reaction in a continuous reactor under inert conditions. We have not detected the reported formation of cyclic fatty acids [9], possibly due to the design of the experimental system and the higher thermal stability of fatty acid esters.

Experiment 4 When the reaction of pure ethyl linoleate at 200ºC under inert conditions using active carbon as catalyst is carried out, the presence of both, aromatic fatty acid ethyl esters (dehydrogenation) and ethyl oleate and ethyl stearate (hydrogenation) are detected, as in experiment 3 and unlike the results of experiment 1. Then, active carbon appears to work as a dehydrogenating catalyst. The conjugated tri-unsaturated Compound is not detected as it converts very quickly to the cycled compounds and hydrogenated compounds. ((equation [3] and Scheme 1). The main conclusions to be emphasized are the overall mechanism proposed in Scheme 1 and that ethyl linoleate may be dehydrogenated at 200º C under inert conditions in the presence of active carbon as a catalyst to give ethyl linolenate.

ACKNOWLEDGEMENTS

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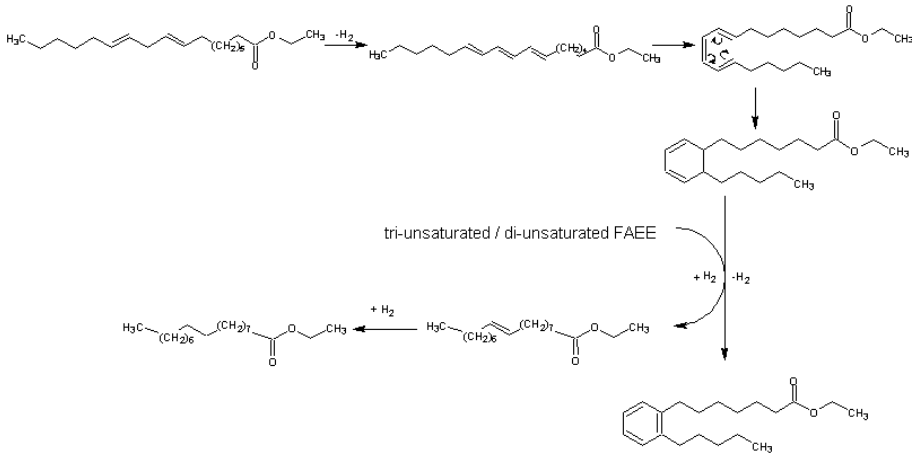
LEGENDS

Scheme 1. Proposed mechanism for the dehydrogenation of ethyl linoleate

Fig. 1. General mass spectrum of aromatic compounds.

Fig. 2. ^{1}H-NMR spectrum of the reaction product



Scheme 1, Cabus et al.

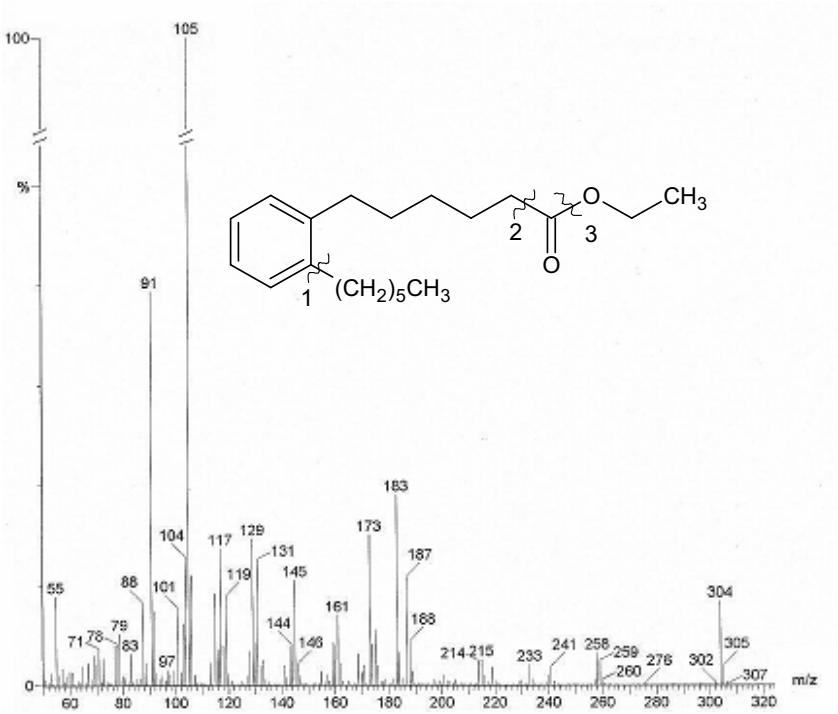


Fig. 1, Cabus et al.

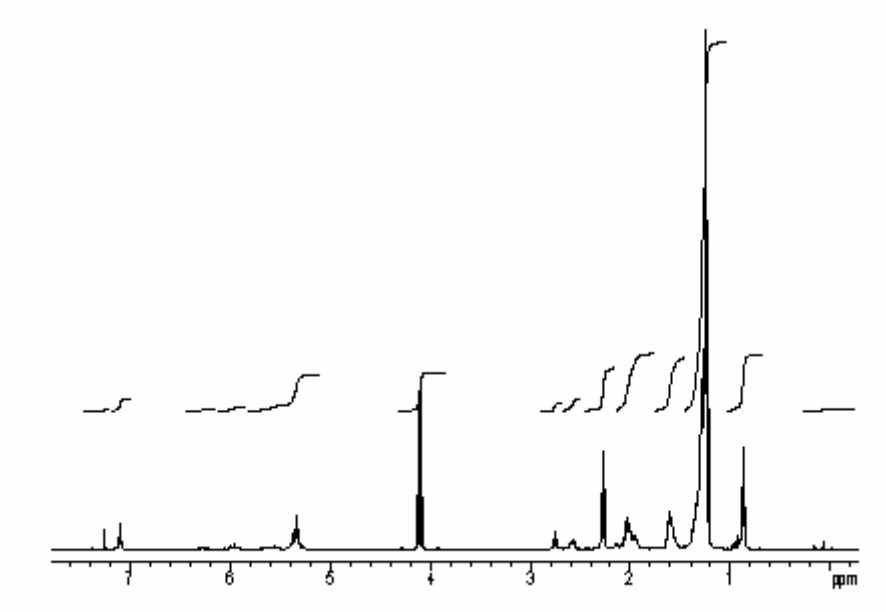


Fig.2, Cabus et al.