

Dimethyl carbonate as a novel methylating reagent for fatty acids in analytical pyrolysis

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Abstract

Dimethyl carbonate (DMC) was investigated as a mild, harmless and odorless reagent for pyrolytic methylation of fatty acids. Soybean oil was selected as test material for its high content of (poly)unsaturated fatty acids. Pyrolyses were performed at 500, 700 and 900 °C by means of a heated platinum filament pyrolyser *on-line* and *off-line* to the GC–MS apparatus. Methyl esters of palmitic, linoleic, oleic and stearic acid were formed as prominent products from *off-line* pyrolysis of soybean oil in the presence of DMC and zeolite 13X. Fatty acid methyl esters (FAMES) were not observed at important levels in the absence of zeolite, while *on-line* Py–GC–MS experiments resulted principally in the formation of free fatty acids and hydrocarbons. The FAME profiles obtained from the DMC/zeolite *off-line* pyrolysis were compared to those resulting from tetramethylammonium hydroxide (TMAH) thermochemolysis and BF₃–methanol procedure. The observed differences between pyrolysis and methanolysis methods were principally attributed to the thermal degradation of unsaturated fatty acids. The effectiveness of the DMC/zeolite pyrolytic methylation was further demonstrated by the analysis of tripalmitine and soybean seeds.

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1. Introduction

Pyrolysis (Py) in the presence of the methylating reagent tetramethylammonium hydroxide (TMAH), in combination with gas chromatography (GC) and/or mass spectrometry (MS), is a well established technique for studying the composition of fatty acids in oils [1], waxes [2], biopolyesters [3,4], and complex matrices, such as bacteria [5,6] and sediments [7]. Pyrolysis with TMAH, also termed as thermally assisted hydrolysis and methylation or thermochemolysis, has the advantage to convert ester bound fatty acids directly into the corresponding fatty acid methyl esters (FAMES), performing saponification and methylation in a single step so that sample manipulation is minimal.

Two principal techniques have been adopted: (1) *on-line*, thermochemolysis products are directly swept into the GC injector port through a hot Py–GC interface [1,2,5], (2)

off-line, thermochemolysis products are collected prior to GC–MS analysis [3,7]. The former procedure is less time-consuming, but the injection of TMAH excess into the Py–GC–MS apparatus may cause overloading, column deterioration, and memory effects. Moreover, the strong basicity of TMAH promotes double bond isomerisation of (poly)unsaturated fatty acids, making their determination difficult [1,8–10]. Isomers of the methyl ester of linoleic (i.e. (Z,Z)-9,12-octadecadienoic) acid have been reported as TMAH thermochemolytic products of soybean oil and linoleic acid itself, attributed to base-catalysed Z to E conversion and double bond migration [1,9]. These side-reactions could be prevented with other methylating reagents, such as tetramethylammonium acetate [9], trifluoromethylphenyl-trimethylammonium hydroxide [1], and trimethylsulfonium hydroxide (TMSH) [10]. However, the former two reagents are less effective as transmethylating reagents for bound fatty acids, due to their reduced basic character. A recent quantitative study comparing different injection techniques and several methylating salts has shown that transmethylation is

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never complete for triglycerides of unsaturated fatty acids [11]. So far, the most common transmethylation reagents for fatty acids employed in analytical pyrolysis (i.e. TMAH and TMSH) share a common chemical nature: a hydrolysing alkaline anion and a methylating cation. However, unless special precautions are taken, the anion might promote base-catalysed side reactions, while the cation may produce a disturbing smell for its thermal degradation compounds (trimethylamine, organic sulfides). In searching for a methylating reagent structurally different from organic alkali, our attention was driven to dimethyl carbonate (DMC).

DMC has emerged as a safe, eco-friendly methylating reagent in organic synthesis [12–18], but to our knowledge its potentiality for analytical pyrolysis has not been investigated yet. Nonetheless, DMC has several advantages, as it is neutral, odorless, cheap, non-corrosive, non toxic, and exhibits good solvent properties [12,18]. If we add its thermal stability (at least up to 350 °C [19]), it is reasonable to consider DMC as a good candidate reagent for pyrolytic methylation. Moreover, methylation of carboxylic acids for the synthesis of the corresponding methyl esters using DMC in the presence of a catalyst has been described in the literature [16,17].

The aim of this study was to develop a transmethylation procedure in analytical pyrolysis for profiling fatty acids using DMC as a methylating reagent. Since (poly)unsaturated fatty acids are particularly difficult to analyse under pyrolytic conditions, the experiments were focused to soybean oil for its high content of linoleic acid. Both *on-line* and *off-line* pyrolysis techniques in combination with GC–MS detection of evolved products were investigated [20].

2. Experimental

2.1. Materials

Soybean oil, dimethyl carbonate (DMC) and zeolite 13X (reported characteristics: 1 Na₂O:1 Al₂O₃:2.8 SiO₂) were kindly provided by Dr. Marcello Notari, Polimeri Europa. Tripalmitine (1,2,3-propanetriol-*tris*-hexadecanoate), potassium carbonate, tetramethylammonium hydroxide (TMAH, 25% aqueous solution), BF₃ (50% in methanol), anhydrous methanol, and charcoal cartridges for air monitoring (Orbo 32 solvent desorption tubes) were from Sigma–Aldrich. Quartz wool was purchased from Alltech and dichloromethane (pesticide grade) from Baker.

DMC is classified as a flammable liquid (melting point 4.8 °C, boiling point 90.3 °C, flash point 21.7 °C), which does not have irritating or mutagenic effects either by contact or inhalation, and its oral acute toxicity is 13.8 g kg⁻¹ as LD₅₀ for rat [18].

Soybean oil or tripalmitine were dissolved in DMC to a 10% (w/w) final concentration. Soybean seeds were milled by a IKA A11 analytical mill and mixed with zeolite 13X in the 1:2 ratio.

2.2. On-line Py–GC–MS

An aliquot (2 µl) of the soybean oil/DMC solution was evenly spread into about 3 mg of solid material (quartz wool, K₂CO₃ or zeolite 13X) fitted into the central part of a quartz tube sample holder. A rather high solid to liquid ratio has been adopted to improve the retention of DMC onto the catalyst for reducing its volatilisation from the hot Py–GC interface. The soybean/DMC/catalyst mixture was pyrolysed at the set temperature (500, 700 or 900 °C) for 10 s at the maximum heating rate using a CDS 1000 pyroprobe heated filament pyrolyser (Chemical Data System, Oxford, USA) directly connected to the injection port of a Varian 3400 gas chromatograph coupled to a Saturn 2000 ion trap mass spectrometer (Varian, Walnut Creek, CA, USA). A Supelco Equity-5 capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness, poly(5% diphenyl-95% dimethyl)siloxane stationary phase) was used with a temperature programme from 50 °C (held for 5 min) to 310 °C (held for 5 min) at 5 °C min⁻¹ with helium as carrier gas. The Varian 1078 programmable split/splitless injector (split mode) was maintained at 250 °C and the Py–GC interface at 250 °C. Mass spectra were recorded at 1 scan s⁻¹ under electron impact at 70 eV, scan range 45–650 *m/z*. Structural assignment of the products was based on match with the NIST 1992 mass spectra library and comparison with literature data [21–24].

2.3. Off-line pyrolysis

About 10 mg of solid material (quartz wool or zeolite 13X) were inserted into the central part of a quartz capillary tube and 20 µl of the soybean oil (or tripalmitine)/DMC solution were evenly spread into the solid. For the analysis of the vegetal matrix, about 10 mg of soybean-seed/zeolite mixture were inserted into the quartz tube sample holder and 20 µl DMC added prior to pyrolysis. For TMAH thermochemolysis experiments, 2 µl of soybean oil were injected into quartz wool (10 mg) and pyrolysed in the presence of 20 µl TMAH solution.

The pyrolyser was the same as for on-line Py–GC–MS, but the pyroprobe was inserted into a glass chamber fluxed with nitrogen (200 ml min⁻¹), connected to a charcoal cartridge for air monitoring. The off-line apparatus has been described in detail in a previous publication [20]. Pyrolyses were carried out at the set temperature (500, 700 or 900 °C) for 10 s at the maximum heating rate, and the evolved products trapped onto the charcoal were eluted with 5 ml dichloromethane.

The dichloromethane solution was concentrated by gas blow-down and analysed by GC–MS using a Varian 3400 gas chromatograph coupled to a Saturn II ion trap mass spectrometer. Temperature of the Varian 1077 split/splitless (splitless mode) was kept at 250 °C. The capillary column and mass spectra conditions were the same as for on-line Py–GC–MS. The GC temperature programme for qualitative analysis was from 50 °C (held for 5 min) to 310 °C (held for 5 min) at 5 °C min⁻¹. For quantitative analysis the programme was

from 150 °C (held for 5 min) to 250 °C (held for 5 min) at 5 °C min⁻¹.

The proportions of the various fatty acids were expressed as percent peak areas determined in the total ion chromatograms. The following fatty acids were quantified: palmitic (hexadecanoic), linoleic ((*Z,Z*)-9,12-octadecadienoic), oleic ((*Z*)-9-octadecenoic) and stearic (octadecanoic).

2.4. BF₃-methanol procedure

About 30 mg of soybean oil were refluxed for 1 h with 1.5 ml anhydrous methanol containing 0.5 ml BF₃ methanolic solution. Methylated fatty acids were extracted

with *n*-hexane and analysed by GC–MS using the conditions described above in the previous section.

3. Results and discussion

3.1. On-line Py–GC–MS

Soybean oil is pyrolysed in the presence of excess dimethyl carbonate (DMC) using quartz wool as solid support to retain the sample mixture. The evolved products are directly analysed by GC–MS and a representative MS-pyrogram is depicted in Fig. 1a. The principal products identified in the pyrolysates are included in Table 1. Fatty acids with

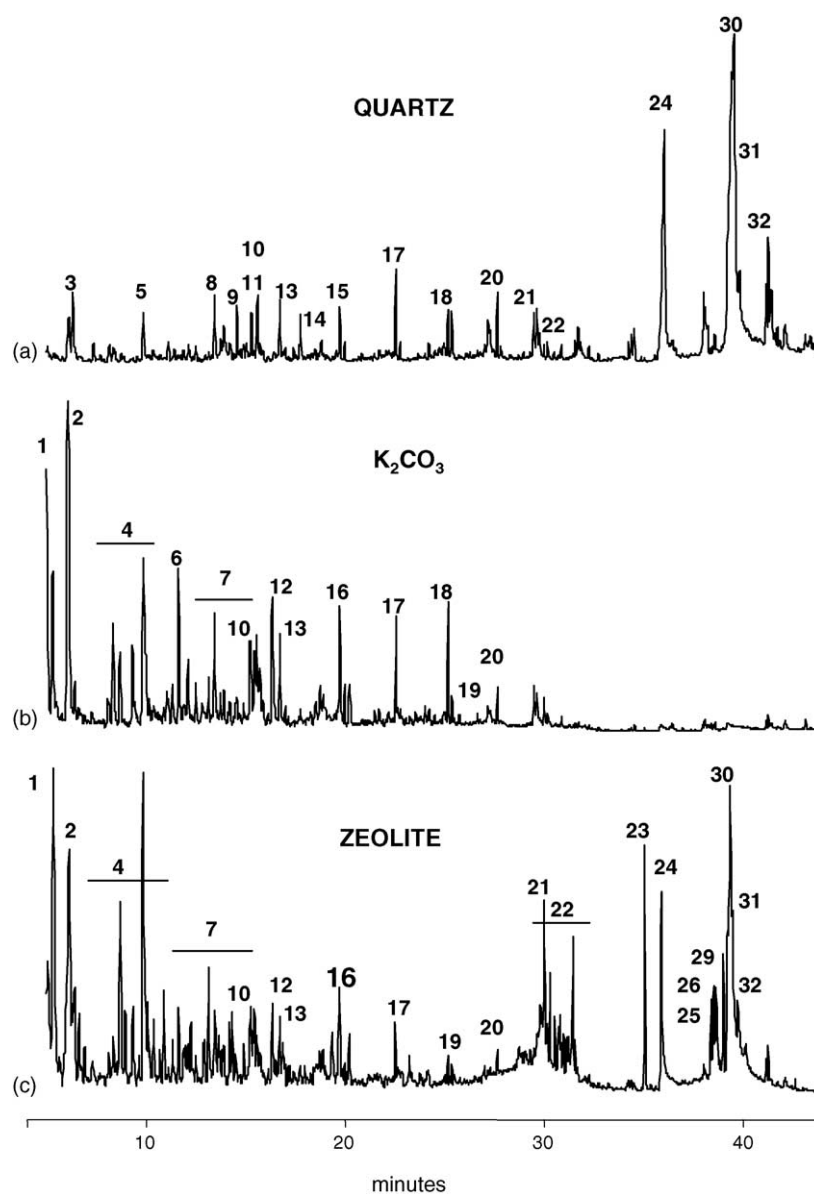


Fig. 1. Total ion chromatograms obtained from on-line pyrolysis (at 900 °C) of soybean oil with dimethyl carbonate in the presence of (a) quartz wool, (b) potassium carbonate and (c) zeolite 13X. Peak numbers refer to compounds listed in Table 1. FAMES correspond to peaks 23, 25, 26 and 29.

Table 1

List of compounds detected by GC–MS evolved from pyrolysis of soybean oil with dimethyl carbonate under various conditions

No.	Name
1	Ethylbenzene + <i>m/p</i> -xylene
2	Styrene + <i>o</i> -xylene
3	<i>n</i> -Non-1-ene
4	C3-Benzenes
5	<i>n</i> -Dec-1-ene
6	Indene
7	C4-Benzenes
8	<i>n</i> -Undec-1-ene
9	<i>n</i> -Undecadiene
10	<i>n</i> -Pentylbenzene
11	<i>n</i> -Undecatriene
12	Naphthalene
13	<i>n</i> -Dodec-1-ene
14	<i>n</i> -(<i>E</i>)-1,3-Dodecadiene
15	<i>n</i> -Tridec-1-ene
16	Methylnaphthalenes
17	<i>n</i> -Tetradec-1-ene
18	<i>n</i> -Pentadec-1-ene
19	C2-Naphthalenes
20	<i>n</i> -Hexadec-1-ene
21	<i>n</i> -Heptadec-1-ene
22	C ₁₇ H ₃₂ isomers (<i>n</i> -heptadecadienes)
23	Palmitic acid, methyl ester
24	Palmitic acid
25	Linoleic acid, methyl ester
26	Oleic acid, methyl ester
27	<i>E</i> -Octadecenoic acid, methyl ester
28	Linolenic acid, methyl ester
29	Stearic acid, methyl ester
30	Linoleic acid
31	Oleic acid
32	Stearic acid
33	Octadecadienoic acid, methyl esters

16 (palmitic acid) and 18 (linoleic, oleic and stearic acids) carbon atoms are the principal pyrolysis products. These fatty acids are typical pyrolysis products of neat soybean oil [21]. The pyrogram is also characterised by a homologue series of *n*-alk-1-enes up to 17 carbon atoms and other hydrocarbons derived from the radical scission of the alkyl chain of the fatty acid moiety [22–24]. Fatty acid methyl esters (FAMEs) are not detected. Thus, solid base catalysts among those employed for methylation reactions with DMC, namely potassium carbonate and zeolite 13X [13,15], have been tested in place of quartz wool to promote methylation of fatty acids.

With potassium carbonate, hydrocarbons are the main pyrolysis products and neither fatty acids nor their corresponding methyl esters are detected in the pyrolysates (Fig. 1b). In addition to the series of linear aliphatic hydrocarbons observed in the absence of catalyst, the pyrogram exhibits intense peaks associated to aromatic hydrocarbons, principally styrene and alkylated benzenes. Indene and naphthalenes are also abundant products.

The chemical nature of evolved hydrocarbons is consistent with the pyrolytic behaviour of metallic salts of fatty acids described in the literature [22–24]. Pyrolysis of zinc stearate yields a series of linear hydrocarbons up to C₁₇ [24], while

a homologue series of *n*-alk-1-enes and *n*-alkanes up to C₁₅ are produced from pyrolysis of the sodium salt of palmitic acid [23]. In the case of unsaturated fatty acids, the pattern of pyrolysis products is more complex, and several hydrocarbons are generated in addition to *n*-alk-1-enes and alkanes depending on the position and number of double bonds. Pyrolysis of sodium oleate generates linear alkenes up to C₁₁, and linear alkadienes ranging from C₁₁ to C₁₇, including both *E* and *Z* isomers indicative of isomerisation reactions [23]. Alkadienes and alkatrienes, principally with 11 and 17 carbon atoms, and *n*-alkylbenzenes are typical pyrolysis products of sodium linoleate [22,23]. Polyaromatics are supposed to be mainly formed from pyrolysis of unsaturated fatty acids, as it has been shown that their emission increases with increasing degree of unsaturation of the alkyl chain [25].

FAMEs are formed at significant levels when pyrolysis of soybean oil with DMC is performed in the presence of zeolite. As Fig. 1c shows, peaks corresponding to the methyl esters of palmitic, linoleic, oleic and stearic acids are clearly evident in the pyrogram, along with underivatized free fatty acids. Aromatic hydrocarbons (benzenes and naphthalenes) represent a consistent fraction of pyrolysis products and are dominant over aliphatic hydrocarbons. Fatty acids and aromatic hydrocarbons are predominant products evolved from pyrolysis of soybean oil in the presence of zeolite only (data not shown). The pyrogram with DMC/zeolite is also characterised by a cluster of peaks displaying similar mass spectra with a base peak at *m/z* 67 and a molecular ion at *m/z* 236, tentatively assigned to isomers with formula C₁₇H₃₂ (e.g. heptadecadienes).

Attempts to increase the yield of FAMEs by changing experimental conditions, such as pyrolysis temperatures (500–900 °C range), Py–GC interface temperature (250–150 °C range) and DMC/soybean/zeolite ratios, resulted unsuccessful. As the low degree of methylation can be partly ascribed to the fast volatilisation of DMC in the hot Py–GC interface, the off-line procedure has been considered.

3.2. Off-line pyrolysis

In the off-line pyrolysis procedure, the pyroprobe is inserted into a pyrolysis chamber and products evolved from pyrolysis are transferred by a nitrogen stream onto a charcoal adsorbent from which they are solvent-desorbed for GC–MS analysis [20]. As the pyrolysis chamber is not heated, evaporation of DMC from the sample mixture prior to pyrolysis is suppressed (the boiling point of DMC is 90 °C). In fact, off-line pyrolysis of soybean oil with excess DMC produces FAMEs as minor components, but fatty acids and hydrocarbons are still the main products (data not shown).

However, FAMEs become the predominant products when pyrolysis is conducted in the presence of zeolite, as shown in Fig. 2. Free fatty acids and alkylated benzenes/naphthalenes, featuring chromatograms obtained from on-line Py–GC–MS, occur at almost undetectable levels. However, the C₁₇H₃₂ isomers still represent important

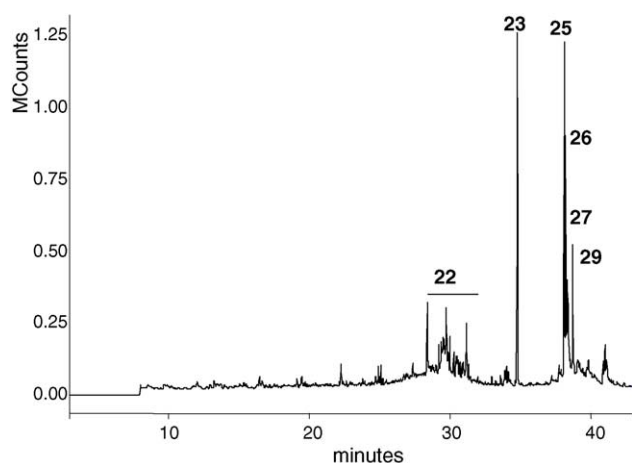


Fig. 2. Total ion chromatogram obtained from off-line pyrolysis (at 900 °C) of soybean oil with dimethyl carbonate in the presence of zeolite. Peak numbers refer to compounds listed in Table 1. FAMES correspond to peaks 23, 25, 26, 27 and 29.

pyrolysis products, indicating a significant degradation of unsaturated C18 fatty acids. The formation of FAMES as principal products is observed at all the three pyrolysis temperatures examined in this study (500, 700 and 900 °C), even though with a different distribution (see below).

Peak distribution of FAMES is better evidenced in Fig. 3a showing a partial chromatogram in the time region of interest. The presence of palmitic, linoleic, oleic and stearic acid methyl esters is in accordance to their occurrence in soybean oil triglycerides. However, the methyl ester of linolenic acid ((*Z,Z,Z*)-9,12,15-octadecatrienoic) is not detected and other FAMES are observed in the GC–MS trace which are not typical of soybean oil. A peak (no. 27) eluting close to the peak of oleic acid methyl ester and displaying the same mass spectrum is assigned to its *E* isomer. A cluster of smaller peaks (no. 33) eluting after stearic acid methyl ester are tentatively identified as *E*, *Z* and conjugated isomers of linoleic acid methyl ester from their mass spectra [8]. The formation of these atypical FAMES is also observed in TMAH thermochemolysis (see below) and is attributed to the base catalysed isomerisation of double bonds. Since DMC is a neutral compound, the formation of FAME isomers is imputed to zeolite.

Saturated fatty acids are not subjected to thermal side reactions as evidenced from the analysis of tripalmitine. Fig. 4 shows that DMC/zeolite pyrolysis of tripalmitine produces essentially the methyl ester of palmitic acid (peak 23), and minor amounts of other FAMES, whereas hydrocarbons and free fatty acids are not revealed.

3.3. Comparison with TMAH thermochemolysis and BF₃–methanol procedure

The FAME profile obtained from off-line pyrolysis of soybean with DMC/zeolite is compared with those resulting from the classical BF₃–methanol procedure (Fig. 3b) and with TMAH thermochemolysis (Fig. 3c). Important differ-

ences can be noticed in the FAME distribution obtained from these different thermal and chemical degradation procedures. In particular, both pyrolytic methods are flawed by the formation of thermal isomerisation products of unsaturated fatty acids (oleic and linoleic acids). The isomerisation of linoleic acid is less pronounced with DMC/zeolite than with TMAH. However, in the presence of zeolite unsaturated fatty acids are subjected to decarboxylation with formation of C₁₇H₃₂ hydrocarbons which may explain the lower levels of linoleic acid with respect to the BF₃–methanol procedure.

3.4. Quantitation

The percentage distribution of fatty acids obtained from triplicate pyrolyses of soybean oil with the DMC method is reported in Fig. 5 for three different pyrolysis temperatures (500, 700 and 900 °C). The relative standard deviations generally fall between 1% and 10%, indicating a fairly good precision (repeatability).

The distribution seems to be dependent on pyrolysis temperature, with increasing levels of saturated palmitic and stearic acids over the unsaturated linoleic and oleic acids as the temperature increases. For instance, the percentage abundance of linoleic acid decreases in the order (mean ± standard deviation) 41 ± 4%, 33 ± 1% and 29 ± 2% as the pyrolysis temperature increases in the order 500, 700 and 900 °C, respectively. These values are lower than those obtained from the BF₃–methanol procedure for linoleic acid (53 ± 1%), but more consistent with respect to TMAH thermochemolysis for which the obtained percentage abundance of linoleic acid is less than 2% (at 500 °C).

3.5. Off-line pyrolysis of soybean seeds

The DMC procedure is applied to soybean seeds to the end of evaluating its performance for the analysis of complex matrices. The obtained results are exemplified in Fig. 6, showing the GC–MS trace of the volatile products evolved from off-line pyrolysis of milled seeds in the presence of DMC and zeolite. The multitude of peaks featuring the chromatogram reflects the complex composition of the sample. Phenol, methylated phenols, benzenepropanenitrile and indole are pyrolysis products arising from proteins, a major component of seeds. Remarkably, FAMES are prominent products and no peaks associated to free fatty acids are detected. Hence, DMC is effective as a transmethylating reagent of fatty acids even in the presence of other important constituents (proteins, carbohydrates). However, as observed for the analysis of soybean oil, the chromatogram exhibits the cluster of peaks attributed to the thermal degradation of unsaturated fatty acids (C₁₇H₃₂ isomers).

3.6. Reaction mechanism

The experimental evidences gathered with this preliminary study are certainly not sufficient to draw a detailed

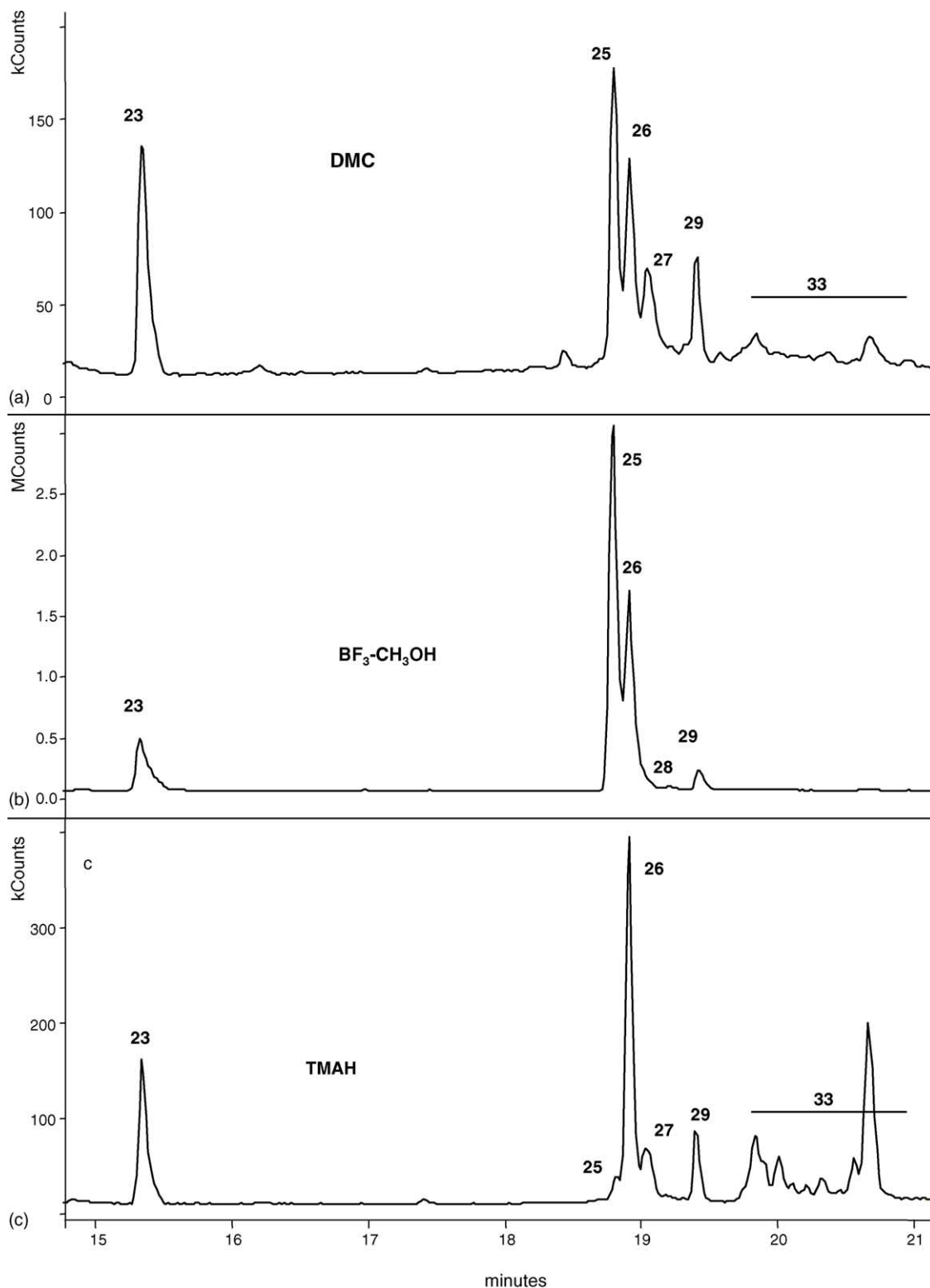


Fig. 3. Partial GC-MS chromatogram in the region of FAMEs obtained from the analysis of soybean oil by (a) off-line pyrolysis with dimethyl carbonate/zeolite (at 500 °C), (b) BF_3 methanolysis, (c) TMAH thermochemolysis (at 500 °C). Peak numbers refer to FAMEs reported in Table 1.

mechanistic scheme, nonetheless plausible pathways leading to fatty acid methyl esters (FAMEs) and by-products can be formulated for discussion. The overall process, exemplified for linoleic acid, is depicted in Fig. 7. Upon pyrolysis,

the triglyceride yields the free acid (Fig. 7; reaction 1), which is mostly thermally released as such from the sample and in part thermally degraded to aliphatic hydrocarbons (Fig. 1a). This view is in agreement with literature data on

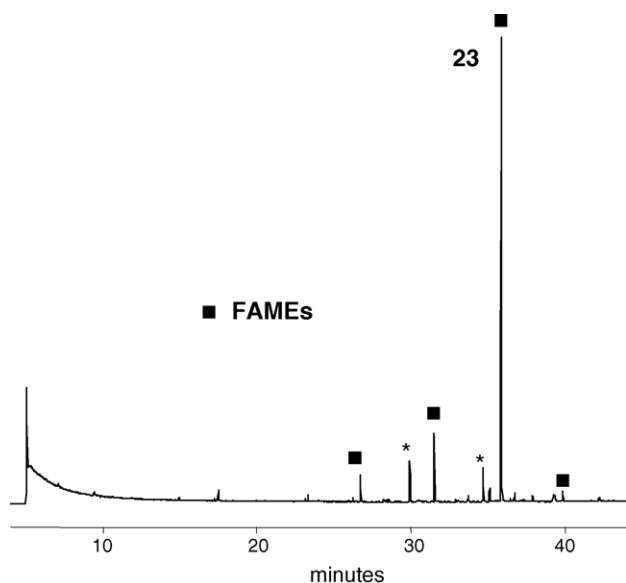


Fig. 4. Total ion chromatogram obtained from off-line pyrolysis (at 500 °C) of tripalmitine with dimethyl carbonate in the presence of zeolite. Peak 23 is the methyl ester of palmitic acid (Table 1). (*) Plastic additive contaminants.

the pyrolytic behaviour of free fatty acids and soybean oil [21,22,24].

In the presence of a base catalyst, the carboxylic group of the fatty acid interacts with the basic sites onto the surface of the solid and is converted into the carboxylate anion (Fig. 7; reaction 2). In its ionic form, the fatty acid is unvolatile and cannot be detected by GC–MS, while hydrocarbons derived from the thermal fragmentation of the alkyl chain are enhanced in the chromatogram (Fig. 1b).

In the case of zeolite, acid–base interactions hold both the fatty acid and DMC onto the catalyst which promotes the attack of the carboxylate ion to the methyl group of DMC forming the FAME (reactions 3 and 4). In fact, at high temperatures (>160 °C), DMC acts towards nucleophilic compounds as a methylating agent with a bimolecular, base-catalysed, alkyl

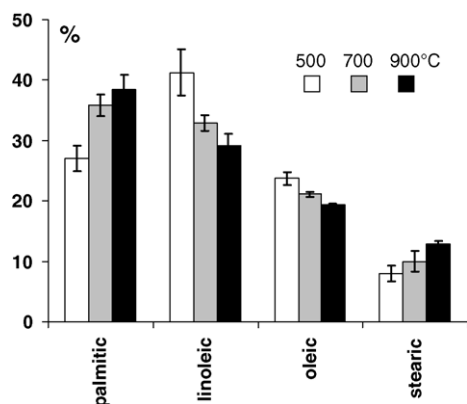


Fig. 5. Percentage abundance of fatty acids in soybean oil obtained from off-line pyrolysis in the presence of dimethyl carbonate/zeolite at different pyrolysis temperatures. Mean values and standard deviation from three replicate measurements.

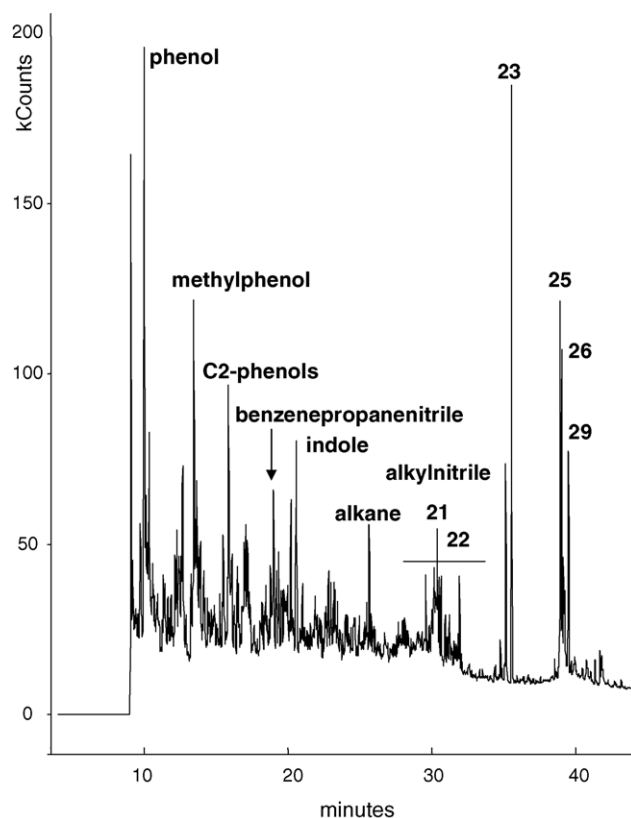


Fig. 6. Total ion chromatogram obtained from off-line pyrolysis (at 900 °C) of soybean seeds in the presence of dimethyl carbonate and zeolite. Peak numbers refer to compounds listed in Table 1. FAMEs correspond to peaks 23, 25, 26 and 29.

cleavage mechanism (Fig. 7) [18]. Once formed, FAMEs are rapidly vaporised and can be detected by GC–MS along with unreacted fatty acids and thermal fragmentation products of the alkyl chain (Fig. 1c). The formation of these latter compounds can be tentatively explained by radical reactions

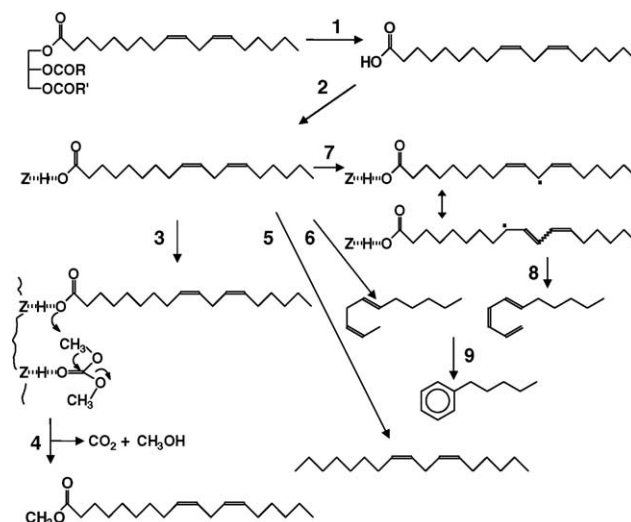


Fig. 7. Proposed mechanism of formation of relevant products discussed in this study, exemplified for linoleic acid.

initiated by the homolytic scission of the weakest C–C bonds [23]. Fig. 7 shows the possible formation of characteristic pyrolysis products found in the pyrolysate (e.g. heptadecadienes, undecadienes, undecatrienes, *n*-pentylbenzene; Table 1). For the sake of simplicity, only the all *Z* isomer is depicted in Fig. 7 for each group of isomeric compounds.

Heptadecadienes are supposed to result from the homolytic cleavage of the C–C bond adjacent the carboxylic group (reaction 5). The formation of a cluster of several C₁₇H₃₂ products also suggests that zeolite promotes isomerisation and migration of double bonds along the alkyl chain. Similarly, undecadienes can be formed from the homolytic cleavage of the allylic C(7)–C(8) bond (reaction 6). The production of secondary radicals (e.g. by H abstraction) and subsequent homolytic β-scission (e.g. reactions 7 and 8 leading to C_{11:3}) yields several linear alkenes, alkadienes and alkatrienes with different chain lengths depending upon which C–C bond undergoes cleavage. According to this mechanism, 1,8-heptadecadiene isomers can be formed from oleic acid by the homolytic β-scission of a secondary radical at the β carbon atom [23]. Finally, the occurrence of at least two double bonds in the alkyl chain favours cyclisation and aromatisation reactions responsible for the production of alkylbenzenes (e.g. reaction 9).

The above mentioned reactions explain the complexity of the chromatogram observed in on-line pyrolysis of soybean oil with DMC and zeolite. Under off-line pyrolysis conditions, excess DMC favours the 1–4 route of Fig. 7, that is esterification over thermal fragmentation (Fig. 2). Notably, the principal hydrocarbons generated under these conditions are C₁₇H₃₂ isomers, probably *E* and *Z* heptadecadienes, while neither shorter chain aliphatic hydrocarbons nor aromatic hydrocarbons have been detected at significant levels. This finding suggests that the cleavage of the C–C bond adjacent to the carboxylic group is the principal thermal fragmentation promoted by zeolite with excess DMC.

4. Conclusions

The results presented in this study indicate that DMC is a promising in situ (trans)methylating reagent in analytical pyrolysis. Using a simple off-line apparatus, FAMES for GC–MS analysis are produced by simply pyrolysing the sample in presence of excess DMC and zeolite. Methylation is effective for bound (triglycerides) fatty acids in lipid

materials soluble in DMC as well as for solid insoluble vegetal matrices. Isomerisation of linoleic acid is less important with DMC than with the caustic TMAH, but the employed zeolite has the inconvenience to promote the formation of thermal degradation products. Future studies will consider other zeolite types to improve the proposed methodology by limiting side reactions for unsaturated fatty acids.

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