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Profiling fatty acids in vegetable oils by reactive pyrolysis–gas chromatography with dimethyl carbonate and titanium silicate

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Abstract

A novel methodology in on-line pyrolysis–gas chromatography (Py–GC) for the fast analysis of fatty acids in vegetable oils with minimal sample treatment and the use of non-toxic reagents is described. Pyrolysis at 500 °C for 10 s of sub-microgram quantity of vegetable oil dissolved in dimethyl carbonate (DMC) and in the presence of nanopowder titanium silicon oxide resulted in the production of fatty acid methyl esters (FAMEs) as unique products. Pyrolysis performed by means of a resistively heated filament pyrolyser interfaced to a GC–MS apparatus enabled the direct analysis of evolved FAMEs. The DMC/Py–GC–MS analysis was tested on soybean, coconut, linseed, walnut and olive oil and the results compared to the classical BF_3–methanol as reference methodology. The DMC method exhibited a lower precision and was biased towards lower levels of polyunsaturated fatty acids (PUFA) in comparison to the BF_3–methanol method, but was more advantageous in terms of reduced sample treatment, waste generation and risk factors of employed chemicals.

Keywords: Pyrolysis methylation; Thermochemolysis; Py–GC–MS; Linoleic; Linolenic; Nanomaterials; Titanosilicate; Green chemistry

1. Introduction

Gas chromatography is often the technique of choice for analysing the composition of fatty acids in lipids [1]. Fatty acids mostly occur as involatile triglycerides in vegetable oils, therefore their conversion into the corresponding methyl ester derivatives (FAMEs) is commonly accomplished prior to GC analysis. The production of FAMEs from triglycerides requires procedural steps which may include extraction, hydrolysis, methylation, *trans*-esterification, and so forth. Methanolysis with boron trifluoride (BF_3) followed by solvent extraction is a well-established procedure for profiling fatty acids in oils and fats [2]. However, it needs a relatively large amount of solvents and laborious sample manipulation, such as heating under reflux conditions, that hamper automated determinations [3]. More in general, sample preparation is often time consuming and requires toxic or corrosive substances which may pose environmental and health hazard. Reducing the use of dangerous or waste-generating chemicals is of interest also in the field of analytical methodology, and to this purpose the term green analytical chemistry has been quoted in the literature [4–7]. Although the amount of chemicals employed for lipid analysis is generally low, the overall quantity can be significant for laboratories dealing with elevated sample throughput (e.g. quality control in food industry). In this context, reducing tedious manual work-up and preventing the use of dangerous solvents or reagents is of interest in method development. Pyrolysis-methylation or thermochemolysis with an in situ *trans*-methylating reagent is a solvent-less one-step procedure, as the production of FAMEs takes place directly inside a thermal unit directly interfaced to a GC or MS apparatus for on-line detection [8–15]. In recent years, researchers have adopted novel approaches to on-line GC/MS coupling for in situ *trans*-methylation of fatty acids in complex matrices [10–15]. However, pyrolysis methylation is generally accomplished with corrosive *trans*-methylating reagents, such as tetramethylammonium hydroxide (TMAH) and trimethylsulphonium hydroxide (TMSH). Dimethyl carbonate (DMC) can be used as an alternative *trans*-methylating reagent for the production of FAMEs under pyrolytic conditions [16]. DMC is reputed a green reagent in organic synthesis with several advantages, as it is neutral,

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odourless, cheap, non-corrosive, non-toxic, and exhibits good solvent properties [17–19]. In order to act as a methylating reagent, DMC requires the use of a catalyst. In our previous work, we found that zeolite 13X promoted the formation of FAMEs as predominant products, but solely under off-line pyrolysis conditions [16].

In this study, we show that when vegetable oil and excess DMC are pyrolysed in the presence of a commercially available titanium silicate, FAMEs are formed as unique products under on-line Py–GC conditions. The performance of the procedure for profiling fatty acids is discussed by comparison with the popular BF_3–MeOH method.

2. Experimental

2.1. Materials

Soybean and coconut oils were purchased from Larodan Chemicals, linseed and walnut oil from Kremer, olive oil from Remilia. Dimethyl carbonate (DMC), BF_3 (50% in methanol), fatty acids methyl ester standard mixture (palmitic, stearic, oleic, linoleic and linolenic) and titanium silicon oxide (99.8%, nanopowder) were from Sigma–Aldrich. The following abbreviations were used for FAMEs: 8:0, octanoic; 10:0, decanoic; 12:0, dodecanoic; 14:0, tetradecanoic; 16:0, hexadecanoic (palmitic); 18:0, octadecanoic (stearic); 18:1, (*Z*)-9-octadecenoic (oleic); 18:2, (*Z*,*Z*)-9,12-octadecadienoic (linoleic); 18:3, (*Z*,*Z*,*Z*)-9,12,15-octadecatrienoic (linolenic); acid methyl esters.

2.2. DMC procedure

Oils were dissolved in DMC to a 1% (w/w) final concentration. An aliquot (10 μL) of the oil/DMC solution was spread into 5 mg of nanopowder titanium silicate held at the central part of a quartz tube sample holder by quartz wool. The mixture was pyrolysed at 500 °C for 10 s at the maximum heating rate using a CDS 1000 pyroprobe heated platinum 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).

Preliminary experiments performed at different pyrolysis temperatures in the 400–800 °C range resulted in similar GC–MS profiles. The effect of pyrolysis time was not investigated, but presumably the *trans*-esterification reaction took place rapidly prior to the fast volatilisation of DMC. Pyrolysis temperature and time were set at 500 °C and 10 s, respectively, to conform with published works on TMAH-thermochemolysis with the same pyrolytic apparatus [14].

2.3. BF_3–methanol procedure

Oils were analysed following the AOAC-IUPAC official method with slight modifications [2]. About 150 mg of oil were refluxed for 10 min with 4 mL methanolic NaOH 0.5 M. Then, 5 mL of methanolic BF_3 were added and the mixture refluxed for 2 min followed by the addition of 10 mL of *n*-hexane. After cooling a saturated NaCl aqueous solution was added under stirring, then the hexane layer containing FAMEs was separated, dried over anhydrous sodium sulphate and diluted prior to GC–MS analysis.

2.4. GC–MS analysis

A Supelco Omegawax capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, non-bonded poly(ethylene glycol) as stationary phase) was used with a temperature programme from 120 to 220 °C (held for 10 min) at 10 °C min^{-1} with helium as carrier gas. For the analysis of coconut oil, the thermal programme was from 50 to 220 °C (held for 10 min) at 10 °C min^{-1}. 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 ionisation 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 GC–MS injection of pure compounds.

FAME distribution was expressed as percentage peak area determined in the total ion chromatograms and reported as mean ± standard deviation (SD) from at least three replicate analyses.

3. Results and discussion

3.1. Qualitative aspects

On-line pyrolysis of soybean oil in the presence of dimethylcarbonate (DMC) and nanopowder titanium silicate produces the GC–MS profile exemplified in Fig. 1A. It is evident from the GC–MS results that the only reaction products are fatty acid methyl esters (FAMEs). Underivatised fatty acids and hydrocarbons, which are typically formed upon pyrolysis without any added reagent [16,20], are not detected. In our previous study, we observed that FAMEs could be obtained only as minor products when pyrolysis of soybean oil with DMC was performed in the presence of zeolite 13X [16]. In that case, the low yield of FAMEs was attributed to the fast volatilisation of DMC from the hot Py–GC interface which prevented the methylation of pyrolytically formed fatty acids. Here, the stronger efficiency of nanopowder titanium silicate in trapping DMC and promoting its methylating activity are probably responsible for the rapid formation of FAMEs.

The chromatogram obtained from DMC/Py–GC–MS is rather similar to that deriving from the BF_3–MeOH procedure (Fig. 1B). However, besides the main peaks associated to the typical fatty acids of soybean oil (i.e. palmitic, stearic, linoleic and linolenic acids), the DMC-derived pyrogram contains smaller peaks which are absent or negligible in the chromatogram from the BF_3–MeOH procedure. According to the GC–MS characteristics, these additional peaks are assigned to structural isomers of methylated linoleic acids. The catalytic properties of titanium silicon oxides are possibly responsible for the thermal isomerisation of double bonds [21].