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Journal of Chromatography A, 767 (1997) 335–339

JOURNAL OF CHROMATOGRAPHY A

Short communication

Use of capillary gas chromatography for determining the hydrogenation level of edible oils[1]

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Received 16 July 1996; revised 26 November 1996; accepted 29 November 1996

Abstract

Capillary gas chromatography is nowadays a widely used chromatographic method, used in particular for its excellent resolution. A new alternative method for the hydrogenation of edible oils is being developed. For determining the rate of hydrogenation and the level of isomerisation development during the hydrogenation process capillary gas chromatography has been chosen as the most suitable method for analyses. Fatty acids from partially hydrogenated oils/triglycerides have been converted into methyl esters. By using special capillary columns, Supelco SP 2380 and SP 2560, not only the methyl esters of individual fatty acids, but also the geometrical and positional isomers have been separated.

Keywords: Vegetable oils; Olive oil; Soybean oil; Positional isomers; Geometrical isomers; Fatty acids

1. Introduction

Oils used for edible purposes are produced from natural sources. Sometimes oils are used without modification, but sometimes the requirements for edible oils are considerably different from those of natural ones so they have to be modified to reach the appropriate properties. Hydrogenation of vegetable oils is one of the earliest and most common commercial modifying methods [1]. Hydrogenation changes the melting and solidification characteristics of the oils treated, and is usually employed to reduce the degree of unsaturation of the naturally occurring triglycerides. Vegetable oils, which are hydrogenated, contain trienic and dienic fatty acids in a mixture with monoenic and saturated ones. The main purpose of partial hydrogenation is to obtain monounsaturated fatty acids from the polyunsaturated ones, and thus obtain new, attractive organoleptic changes and a greater chemical stability, especially with regard to oxidation.

In the search of an optimal hydrogenation procedure an alternative and new method for the hydrogenation of edible oils and fats, *catalytic transfer hydrogenation* is being developed. Where in the classical technique molecular hydrogen is used, hydrogen donors as a source of hydrogen are used in a catalytic transfer reduction [2]. The generalised equation represents this process:

$$DH + A \xrightarrow{\text{catalyst}} D + AH$$

A represents acceptor and D hydrogen donor.

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[1] Presented at the 10th International Symposium on Advances and Applications of Chromatography in Industry, Bratislava, 30 June–4 July 1996.

PII S0021-9673(96)01061-8

Hydrogenation is an extremely complex series of saturation and isomerisation reactions of the double bonds of unsaturated fatty acids. During the hydrogenation process not only hydrogen is added to the double bond but also migration and geometrical isomerisation of double bonds occurs. The simplified [3] reaction scheme, which does not indicate either positional or geometrical isomers that are always formed during hydrogenation, can be written as:

$$Le \overset{k_{Le}}{\rightarrow} L \overset{k_{L}}{\rightarrow} Ol \overset{k_{Ol}}{\rightarrow} S$$

where *Le*, *L*, *Ol* and *S* are the concentrations of linolenic, linoleic, oleic and stearic fatty acid and k_{Le}, k_L, k_{Ol} and k_S represent rate constants of linolenic, linoleic, oleic and stearic fatty acid.

Saturation selectivities can be calculated from the rate constants as ratios of the relevant rate constants $S_{Le}=k_{Le}/k_L$ and $S_L=k_L/k_{Ol}$.

High linoleic selectivity (S_L) yields oil with the lowest melting point for a given unsaturation. High linolenic (S_{Le}) selectivity increases the oxidative stability of oil without changing its liquidity [1]. These ratios should be as high as possible to reach high saturation selectivity. To obtain the products with desired properties the amount of *trans*-isomers formed during the hydrogenation process is a very important factor. The *trans*-isomer formation leads to high solid content values at a certain temperature but at a relatively high level of unsaturation [1]. The specific isomerisation (*cis–trans* isomerisation) is defined [4] as the ratio of produced *trans* double bonds and all eliminated double bonds.

In the present paper a method for determining the fatty acids using capillary gas chromatography is described. Special columns were used, which allows separation of "iso"-forms of fatty acids. "Iso"-forms of fatty acids are all positional and geometrical (*trans*) isomers except for naturally occurring fatty acids [5]. The data obtained with this method permits the calculation not only of the rate constants (k_{Le}, k_L and k_{Ol}) but also of the isomerisation selectivity (S_i).

2. Experimental

2.1. Materials

Hydrogenation was carried out with different commercial vegetable oils (Table 1): soybean and olive oil (GEA-Slovenska Bistrica), sunflower, peanut and corn oil (Oljarica Kranj).

Aqueous sodium formate (Fluka) solution was used as hydrogen donor and palladium on activated carbon (E 101 NN/D 10%, Degussa) as catalyst. The stabiliser used was Mayodan M-612, supplied by Grindsted Companies.

2.2. Hydrogenation procedures

Oil (50.00 g) with emulsifier (Mayodan M-612, 0.20 g), donor solution (9.44 g HCOONa and 50.00 g water) and catalyst (1.00 g 10% Pd/C) were agitated at 600 rpm in a 250 ml round-bottom flask. The mechanical stirrer with 3-cm round-shaped PTFE blade was used. A water bath was used to thermostat the flask (80°C).

The progress of the hydrogenation reaction was monitored by determining the fatty acid composition of the samples periodically removed during the process. Analyses were carried out by gas chromatography.

2.3. Methods of analyses

Fatty acids (FA) content were determined as fatty acid methyl esters (FAME) prepared by IUPAC [6] method II.D.19. For analysis the fused-silica capillary columns SP-2380 (30 m×0.32 mm I.D., 0.20 μm film thickness) and SP-2560 (100 m×0.25 mm I.D., 0.20 μm film thickness) were used. 0.5 μl of the sample was injected into a Varian 3400 gas chromatograph equipped with an all glass splitter system and flame-ionisation detector. The injector was operated in the splitless mode. Detector and injector were both maintained at 220°C. Helium was used as carrier gas with a flow-rate of 1.2 ml/min. The temperature-programmed mode was used for both capillary columns. The program was started at 150°C for 3 min and then the temperature was increased to 200°C with a heating rate of 3°C/min. Identification of geometrical (*cis–trans*) isomers was realised with standards supplied by Sigma (oleic acid methyl ester *cis–trans* isomers and linoleic acid methyl ester *cis–trans* isomers).

Table 1
Fatty acid composition of untreated and partially hydrogenated oils and values of rate constants, saturation and isomerisation selectivities calculated from experimental data

	Olive oil	Peanut oil	Corn oil	Soybean oil	Sunflower oil
	Untreated oils (fatty acids composition in %, w/w)				
$C_{16:0}$	12.9	11.7	9.3	10.9	7.0
$C_{18:0}$	2.6	1.9	2.8	4.7	4.5
$C_{18:1}$	74.3	40.9	30.6	27.1	22.2
$C_{18:2}$	10.4	40.7	55.4	50.4	65.2
$C_{18:3}$	–	2.0	0.4	7.0	–
	Partially hydrogenated oils (fatty acids composition in %, w/w after 120 min)				
$C_{16:0}$	12.9	11.7	9.3	10.9	7.0
$C_{18:0}$	45.0	21.6	11.0	22.2	8.9
$C_{18:1}$	41.8	62.3	76.8	64.5	79.6
$C_{18:2}$	0.2	0.6	2.8	0.9	3.6
$C_{18:3}$	–	0	0	0.3	–
k_{Le}	–	0.145	0.139	0.170	–
k_L	0.110	0.047	0.038	0.062	0.059
k_{OI}	0.001	0.002	0.002	0.002	0.002
S_{Le}	–	3.1	3.7	2.7	–
S_L	11	18.8	22.4	38.8	32.8
S_i	0.74	0.87	0.84	0.47	0.80

k_{Le}, k_L, k_{OI} are in min^{-1}.

3. Results

As mentioned above both geometrical and positional isomerisation takes place during the hydrogenation process. As a result of these processes the number of chromatographic peaks increases sharply (Fig. 1). In case when the special capillary columns are used better insight into the whole process of hydrogenation is provided because positional and geometrical isomers of a particular fatty acid could be separated (Fig. 2). We used standards to determine geometrical isomers forming during the hydrogenation process but the qualitative determination of all peaks appearing as a consequence of isomerisation is very difficult. To determine the isomerisation level we use the modified Coenen definition [4] and presented isomerisation selectivity as:

$$S_i = \frac{\text{"iso"} - \text{forms}}{\text{all hydrogenated double bonds}}$$

On the basis of the calculated saturation selectivities some conclusions could be made. k_{Le} and k_L are quite similar in comparison to k_{OI} (Table 1). This behaviour may indicate that more reactive conjugated double bonds [7] are formed by migration of double bond in polyunsaturated compounds [8]

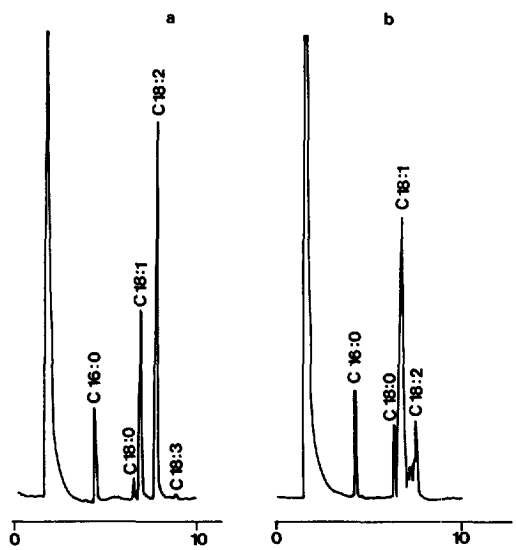

Fig. 1. Chromatograms of untreated (a) and partially hydrogenated (b) corn oil analysed on a SP 2380 capillary column (30 m×0.32 mm I.D., 0.20 μm film thickness).

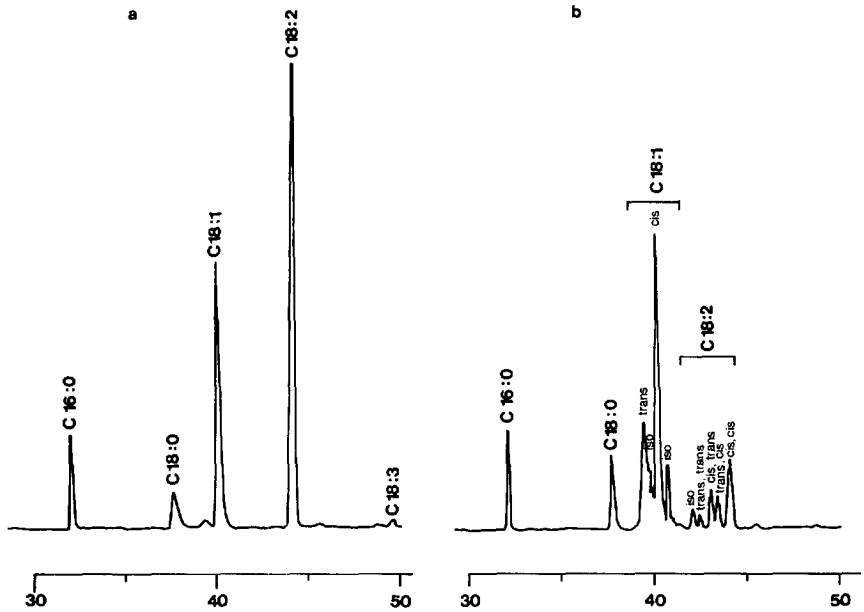

Fig. 2. Chromatograms of untreated (a) and partially hydrogenated (b) corn oil analysed on a SP 2560 capillary column (100 m×0.25 mm I.D., 0.20 μm film thickness).

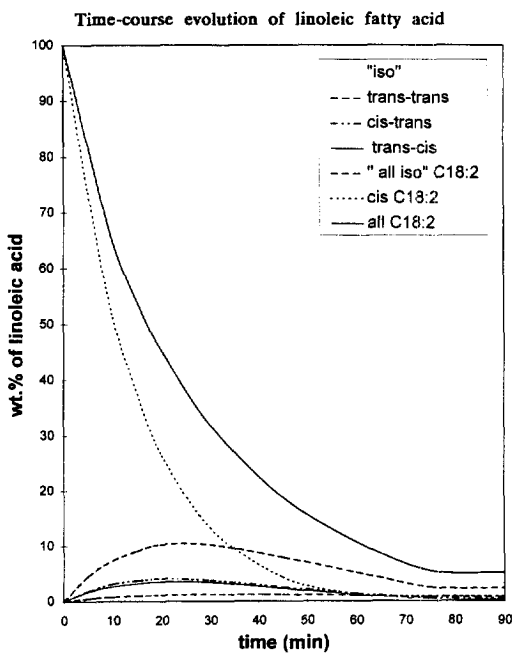

Fig. 3. Time-course evolution of linoleic fatty acid (one of the fatty acids present in corn oil); geometrical and positional isomers detected with special capillary column Supelco SP 2560 are expressed as percentages of linoleic acid.

(triunsaturated and diunsaturated) during hydrogenation. This results in a higher reactivity of diens and especially triens in comparison with monounsaturated compounds. This saturation mechanism produces the positional and geometrical isomers of linoleic acid (Fig. 3) from *cis*-linolenic acid. The hydrogenation of monoenic compounds runs much more slowly. Oleic acid molecules are, because of their lesser affinity for the catalyst, more or less excluded from the competition for adsorption in the initial stage of hydrogenation process.

The extent of iso-acids increases at the beginning of hydrogenation (Fig. 3). It is reasonable to suppose that double bond migration begins at the same time as the hydrogenation. As a result of double bond migration more reactive conjugated dienes are formed. These dienes are quickly hydrogenated, and therefore the concentration of "iso"-acids decreases.

4. Discussion

An alternative and new method for hydrogenation of edible oils and fats, the catalytic transfer hydrogenation, is being developed. In catalytic transfer

Table 2
Reproducibility was tested on soybean oil

Time	% of all double bonds					% of all "iso" fatty acids				
(min)	1	2	3	S.D.	R.S.D. (%)	1	2	3	S.D.	R.S.D. (%)
0	100.00	100.00	100.00	0	0	0.00	0.00	0.00	0	0
2.5	90.73	92.5	90.21	1.20	1.32	15.54	16.11	16.49	0.48	2.98
5	85.69	83.45	86.20	1.46	1.72	24.68	24.04	23.77	0.47	1.93
10	77.35	78.10	78.20	0.46	0.60	33.16	34.11	33.79	0.48	1.43
15	70.21	69.74	71.10	0.69	0.98	38.91	37.50	36.98	1.00	2.64
20	67.23	66.20	67.50	0.69	1.02	43.03	41.89	42.77	0.60	1.40
30	61.23	58.37	60.91	1.56	2.60	47.52	46.95	46.11	0.71	1.51
45	55.95	56.80	54.29	1.27	2.28	53.31	53.21	52.65	0.36	0.67
60	49.92	50.31	51.80	0.99	1.96	54.28	55.01	53.88	0.57	1.05
75	50.30	48.49	50.40	1.07	2.15	56.44	57.36	57.93	0.75	1.31
90	46.82	47.40	47.10	0.29	0.62	58.75	58.67	58.02	0.40	0.68

R.S.D.s of the hydrogenation process were calculated as the sum of all eliminated double bonds. R.S.D.s of "iso" fatty acids were calculated comparing the sum of all "iso" fatty acids generated during the hydrogenation process.

reduction, hydrogen donors are used as a source of hydrogen (whereas in the classical technique molecular hydrogen is used). Besides good selectivity, short reaction times and excellent reproducibility the catalytic transfer hydrogenation methods allows safe and easy handling.

The maximum value of relative standard deviation (R.S.D.) of the hydrogenation process was below 3%. For R.S.D. calculations the sum of all eliminated double bonds was used. R.S.D. values of "iso" fatty acids were also calculated comprising the sum of all "iso" fatty acids generated during hydrogenation process and lying under 3% (Table 2).

To obtain a complete overview of the products developing during hydrogenation process the fatty acid composition of partially hydrogenated oils was analysed by a SP 2560 capillary column. Results obtained with this column enable the calculation of saturation and isomerisation selectivity of the process and give an excellent insight into the whole process of hydrogenation. When only the rate of reaction is tested and no interest of the degree of isomerisation exists, the usage of a SP 2380 column is preferred because of the very short analysis time in comparison with a SP 2560 capillary column.

Acknowledgments

This investigation was supported by the Ministry of Science and Technology of Slovenia (J2-7242-0104-95). We thank Dr. Bogdan Kralj for mass spectra determinations (Mass Spectrometry Center at Jožef Stefan Institute) and Dr. Jože Kobe and Dr. Tine Kolioni for valuable advice.

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