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Selective epoxidation of sesame oil with peracetic acid

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ABSTRACT

The course of epoxidation of sesame oil (SO) with peracetic acid formed "in situ" by the reaction of 30 wt% hydrogen peroxide and acetic acid in the presence of sulfuric acid(VI) as a catalyst was studied. The iodine number (IN), epoxy number (EN), a relative conversion to oxirane and oxirane oxygen content were determined every hour during the reaction. Under optimal conditions the selectivity of transformation of ethylenic unsaturation to oxirane rings is S = 93.5%, conversion of ethylenic unsaturation C_{SO} = 77.2%, relative conversion to oxirane RCO = 78.1%, oxirane oxygen content EO_e = 5.1%, IN = 0.03 mol/100 g, EN = 0.33 mol/100 g. Decreasing of the selectivity of transformation to oxirane rings is mainly caused by their hydration to glycols.

1. Introduction

Sesame oil is used in limited quantities as food grade oil in halva and other confectionery products [1], however it is not suitable for frying because of a low decomposition temperature. As sesame oil is produced in large amounts, attempts have been made at its transesterification into biodiesel fuel [2]. A high content of sterols, tocopherols and other unsaponifiable matter like phenolic compounds, terpene alcohols in various grades of oil from roasted sesame seeds has stimulated its use in the manufacture of creams and ointments and as a natural antioxidant for biodiesel [3].

The high content of oleic and linoleic acid facilitates its functionalisation. Most often the functionalization proceeds via a direct epoxidation or hydroxylation of ethylenic unsaturation and followed by the reaction of hydroxyl and oxirane. Much effort has been paid to obtain epoxidized vegetable oils with the highest selectivity of transformation of ethylenic unsaturation to oxirane ring at a high conversion of vegetable oil. This applies particularly to the use of epoxidized oils as plasticizers and stabilizers. In industrial applications it is achieved by reaction of peracetic or performic acid with soybean or rapeseed oil in the presence of sulfuric acid as catalyst, at the manufacture on a small scale in the presence of cationic ion-exchange resins (Amberlite IR-120H, IR-122 and KU-2×8). In this case, peracids were prepared in situ in a the reactor for epoxidation by the reaction of hydrogen peroxide and acetic or formic acid [4–8].

On a laboratory scale, much attention has been paid to the methods of epoxidation with hydrogen peroxide in the presence of phosphotungstate heteropolyacids as catalyst and the phase-transfer catalysts ($H^+/WO_4^{-2}/PO_4^{-3}/Q^+X^-$), QX – onium salt [9,10]. The epoxidation processes using hydrogen peroxide or organic hydroperoxide over titanium-silicalite catalysts (Ti-MCM-41, Ti(IV)-SiO_2, Ti/SiO_2 amorphous) [11–14], or in the presence of transition metal complexes as catalysts (CH_3ReO_3 or CH_3ReO_3/Nb) [15,16], and chemoenzymatic epoxidation [17–20] are of similar interest.

The aim of this study was to determine the influence of technological parameters of epoxidation of sesame oil and establish the conditions for reaching the highest selectivity of transformation of ethylenic unsaturation to oxirane rings. The influence of technological parameters on the course of epoxidation and determination of the optimal parameters have not yet been studied. However, the application of epoxidized sesame oil as PVC plasticizer was reported [21]. As follows from the studies of epoxidation of other oils with the use of peracetic acid, the presence of mineral acid (H_2SO_4) is necessary for increasing the rate of peracide production [22]. Unfortunately, the presence of mineral acid also reduces the selectivity of transformation to oxirane rings mainly by increasing the opening rate of oxirane rings and formation of glycols and hydroxyesters. This conventional method allows to achieve a high selectivity of transformation of ethylenic unsaturation to the oxirane rings and conversion of ethylenic unsaturation. It is used most often frequently for the epoxidation of different vegetable oils. The processes are carried out industrially at different volume of production.

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Table 1
Molar mass of sesame oil and content of a given fatty acid.

A[a]:B[b]	Fatty acid		g [wt%]	M_{GT} [g/mol]	M_x [g/mol]
16:0	palmitic	$CH_3(CH_2)_{14}COOH$	10.6	806	85.4
18:0	stearic	$CH_3(CH_2)_{16}COOH$	5.7	890	50.7
18:1	oleic (*9 cis*)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	45.1	884	398.1
18:2	linoleic (*9 cis, 12 cis*)	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOH$	32.9	878	288.6
18:3	linolenic (*9 cis, 12 cis, 15 cis*)	$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$	4.3	872	37.5
20:4	arachidonic (*5-,8-, 11-, 14-cis*)	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	0.6	974	6.1
20:1	gadoleic (*9-cis*)	$CH_3(CH_2)_9(CH{=}CH)(CH_2)_7COOH$	0.4	968	4.3
22:1	erucic (*13-cis*)	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	0.4	1052	4.2

g – the content of a given fatty acid, M_{GT} – the mass fraction of particular carboxylic acid triglyceride. Molar mass of sesame oil $M_{SO} = \Sigma M_x = 874.9$ g/mol.
[a] Number of carbon.
[b] Number of double bonds.

2. Experimental

2.1. Materials and methods

Sesame oil was obtained from Biooil Laboratory, Poland. Glacial acetic acid (99.8 wt %), sulfuric acid(VI) (100 wt %), hydrogen peroxide (30 wt %) were purchased from POCh, Poland.

2.2. Epoxidation procedure

Epoxidation was carried out in a round bottom flask of 250 mL capacity, placed in thermostated oil bath, equipped with a mechanical stirrer, thermometer, reflux condenser, dropping funnel. The flask was charged with a known amount of sesame oil and the necessary amounts of acetic acid and catalyst (H_2SO_4). The mixture was continuously stirred for 15 min. Then, the calculated amount of 30 wt % aqueous hydrogen peroxide was added dropwise to maintain the desired reaction temperature. After the complete addition of hydrogen peroxide, the reaction was continued further for the desired duration of the process. The hydrogen peroxide addition was assumed as time zero. The intensive mixing and dispersion of oil was maintained during the experiments. The course of the reaction was followed by collecting the samples at every hour. The influence of the following technological parameters: temperature, the molar ratios of hydrogen peroxide to ethylenic unsaturation and acetic acid to ethylenic unsaturation, amount of sulfuric acid introduced, effect of stirring speed and reaction time were studied. The samples were cooled to ambient temperature, the separated organic layer was neutralized by a 5 wt % solution of sodium carbonate to obtain pH 7. The organic layer was rinsed with water and dried over anhydrous $MgSO_4$.

2.3. Analytical techniques

For each sample the epoxy number (EN) was determined by the reaction of oxirane groups with hydrobromic acid solution in glacial acetic acid [23] and followed by the determination of the iodine number [24]. The content of fatty acids in sesame oil was evaluated by gas chromatography [25]. The analyses were carried out using Thermo Scientific Focus GC apparatus with a flame ionization detector. A capillary column TR-WAX 30 m × 0.26 mm × 0.5 μm worked at 210 °C, at detector temperature of 250 °C. The carrier gas was helium – 144 mL/min. The sample to be measured was introduced to a feeder with a partition (split ratio 1:90).

On the basis of the analysis of iodine and epoxide numbers the conversion of sesame oil (C_{SO}), the selectivity of transformation to oxirane ring (S), a relative conversion to oxirane (RCO) and oxirane oxygen content (EO_e) were calculated. The conversion was calculated according to the following equation:

$$C_{SO} = (IN_o - IN)/IN_o \times 100\% \quad (1)$$

where IN_o – is the iodine number of sesame oil before epoxidation (110.3 g/100 g), IN – is the iodine number of sesame oil at a given moment of epoxidation.

The selectivity of transformation of ethylenic unsaturation to oxirane rings was calculated from the equation:

$$S = [EO_e/EO_t \times IN_o/(IN_o - IN)] \times 100\% \quad (2)$$

where EO_e (%) – is the experimentally determined oxirane oxygen content in 100 g of oil, $EO_e = EN \times A_o$, where EN – is the epoxy number, $A_o = 16$ g/mol is the atomic weight of oxygen.

EO_t (%) – the theoretical maximal oxirane oxygen in 100 g of oil was calculated as follows [26]:

$$EO_t = \{(IN_o/2A_I)/[100 + (IN_o/2A_I)A_o]\} \times A_o \times 100 \quad (3)$$

where $A_I = 126.9$ g/mol is the atomic weight of iodine. For $IN_o = 110.3$ g/100 g of oil (0.43 mol/100 of oil) EO_t is equal to 6.5%. A relative conversion to oxirane was determined using the following formula: $RCO = EO_e/EO_t \times 100$.

3. Results and discussion

The molar mass of sesame oil was calculated from the assay of fatty acids. The content of a given fatty acid in sesame oil, the mass fraction of triglyceride of particular carboxylic acid and the molar mass of sesame oil are presented in Table 1.

On the basis of preliminary studies [27] and the results of epoxidation of linseed oil [28] the influence of technological parameters on the sesame oil epoxidation using peracetic acid was studied in the temperature range 30–90 °C, at the molar ratio of acetic acid to ethylenic unsaturation $CH_3COOH/{-}C{=}C{-} = 0.2{:}1$ to 1.1:1, hydrogen peroxide to ethylenic unsaturation molar ratio $H_2O_2/{-}C{=}C{-} = 0.8{:}1$ to 3.5:1, at stirring speed 400–1000 rpm and the sulfuric(VI) acid concentration, measured in relation to the epoxidizing agent within the range $H_2SO_4/(H_2O_2 + CH_3COOH) = 0.5$ to 3.0 wt %. For each changed parameter the values of EN and IN were determined every hour in the interval 1–7 h and calculated: C_{SO}, S, EO_e and RCO.

3.1. Effect of temperature

On the basis of the results of linseed oil epoxidation [27] with peracetic acid the following constant parameters were established: the molar ratio $H_2O_2/{-}C{=}C{-} = 1.5{:}1$ and $CH_3COOH/{-}C{=}C{-} = 0.5{:}1$; amount of catalyst in relation to the epoxidizing agent $H_2SO_4/(H_2O_2 + CH_3COOH) = 1.0$ wt %; stirring speed 700 rpm. Each experiment was performed at a different temperature selected from the range of 30–90 °C and for different the reaction time from the range 1–7 h (Fig. 1).

Increase in temperature considerably increases the amount of oxirane groups at temperatures 75 °C and 90 °C and leads to high values of EN after 6 h. The highest EN is reached at 90 °C after 6 and 7 h. (EN = 0.144 mol/100 g). The values of EN are much smaller