Polyhydroxy Fatty Acids and Their Derivatives from Plant Oils

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ABSTRACT: A novel process for the industrial production of hydroxylated fatty acids involves epoxidation of plant oils and their derivatives, followed by catalytic epoxy ring opening in the presence of water or other hydrogen donors, such as alcohols, diols, and amines. Depending on the starting material, epoxidation followed by opening of the oxirane ring leads to fatty acids that contain vicinal diol groups or to other substituted hydroxylated fatty acid derivatives. As an example for the preparation of a substituted hydroxylated fatty acid derivative, the reaction of epoxidized rapeseed oil with monobutylamine as hydrogen donor is described. Apart from the intended formation of hydroxyl groups with vicinal aminoalkyl groups, partial aminolysis of the ester compound was also observed. Another example describes the reaction of epoxidized rapeseed oil with different molar proportions of 1,4-butanediol as hydrogen donor. Depending on the molar proportion of the hydrogen donor, interesterification, or intermolecular ether formation were observed as side reactions. The properties of various technical hydroxylated fatty acids and their derivatives, prepared according to this novel process, are given, and potential applications of these products are suggested.

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KEY WORDS: 9,10-Dihydroxy stearic acid, dihydroxy tetrahydrofuran octadecanoic acid, estolides, hydroxylated fatty acid derivatives, hydroxylated fatty acids, hydroxylated triglycerides, polyhydroxy fatty acids.

Hydroxy fatty acids are of great interest to the industry because of their different behavior compared with ordinary fatty acids. Among these fatty acids, only ricinoleic acid is available in sufficient amounts from castor oil as natural source and is used as raw material in many different industrial applications (1). It is, therefore, challenging to evolve suitable processes for the preparation of hydroxy fatty acids by functionalization of the alkyl chain of unsaturated fatty acids in common glycerides from commercial fats and oils.

Various procedures have been described (2–9) for the preparation of hydroxylated fatty acids (HOFA). However, none of these have gained industrial importance so far. The decreased reactivity of middle-positioned epoxide rings in the alkyl chain of fatty acids (2) compared with end-standing epoxide groups requires quite strong reaction conditions, such as concentrated sulfuric acid (2–5). In other procedures, in the first step the epoxide ring is opened by addition of acetic (5) or formic acid (6,7), and in the second step saponification of the esters leads to the desired vicinal diols. Special oils, such as jojoba oil (10), allow the hydrolysis of the epoxides with aqueous hydrochloric acid, and, under *p*-toluenesulfonic acid catalysis, alcoholysis is possible. But these conditions are not generally applicable to common fats and oils (triglycerides). The present publication describes a novel process (11–14), which is used for the preparation of HOFA as well as their alkoxy and hydroxy-aminoalkyl derivatives by using a direct method in an economical and environmental safe route. For these new oleochemicals, a great number of interesting applications have already been suggested, such as polymer additives and plastics, as well as surfactants and lubricants (15–25). Even their use as corrosion inhibitors in lubricants (26) and auxiliaries for the textile industry (27) have been investigated.

EXPERIMENTAL PROCEDURES

Chemicals. High-performance liquid chromatography (HPLC)-grade solvent [tetrahydrofuran (THF)] and all other reagents were purchased from E. Merck (Darmstadt, Germany). Monobutylamine, diethanolamine, and 1,4-butanediol were provided by BASF AG (Ludwigshafen, Germany). Acidic bleaching earth KSF/0 from Süd Chemie (München, Germany) was used as catalyst. Epoxidized oils were products of Harburger Fettchemie Brinckman & Mergell GmbH (Hamburg, Germany).

Reactions. The reactions were carried out in a thermostated 1.5-L autoclave from Andreas Hofer (Mühlheim, Germany). Without using any solvent, the epoxidized oils (soybean oil: 6.8% oxirane oxygen; rapeseed oil; 5.8% oxirane oxygen) and the hydrogen donor, such as methanol, were reacted in equimolar proportions (related to the oxirane oxygen value) in the presence of 0.1% by weight of the catalyst [sulfuric acid-activated bleaching earth (KSF/0)] by vigorous stirring at temperatures between 160 and 200°C. Table 1 shows the reaction conditions of different conversions.

During the reaction, several samples were drawn at different times, freed by vacuum distillation (15 mbar, 130°C) from unreacted reactants and analyzed as described below. The re-

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TABLE 1
Reaction Conditions of the Hydroxylation of Epoxidized Oils with Various Reactants

Hydrogen donors	Amount (g)	Reaction temperature (°C)	Reaction time (h)
1 kg Epoxidized rapeseed oil reacted with			
Monobutylamine	265	180	*ca.* 6
Diethanolamine	381	200	*ca.* 4
Triethanolamine	540	200	*ca.* 2
Polyethyleneglycol 400	725[a]	200	*ca.* 2
1,4-Butanediol	326	180	*ca.* 3
n-Butanol	268	180	*ca.* 3
Ethanol	167	180	*ca.* 3
Methanol	116	180	*ca.* 3
Water	100	160	*ca.* 4
1 kg Epoxidized soybean oil reacted with			
Diethanolamine	446	200	*ca.* 3
Ethanol	196	180	*ca.* 4
Methanol	136	180	*ca.* 4
Water	100	160	*ca.* 4

[a]With 500 g epoxidized rapeseed oil.

action was stopped when the oxirane oxygen value reached less than 0.1%. The product was cleaned by vacuum distillation (15 mbar, 130°C) from unreacted reactants and analyzed as such. The yield of the isolated product was generally between 90 and 95%.

Analytical methods. Acid value (28) and hydroxyl value (29) were determined by standard procedures. The oxirane oxygen and amine value were determined titrimetrically with perchloric acid (30,31). The infrared (IR) spectra were recorded by a Fourier transform IR 1600 from Perkin-Elmer (Überlingen, Germany) with the substances (as is) spread between NaCl plates. Gel permeation chromatography (GPC) was carried out on 300 × 7.5 mm columns supplied by Latek (Eppelheim, Germany) PL gel (5 µm, 500 Å; Polymer Laboratories, Shopshire, United Kingdom) for molecular weights of 500–20000; and 100 Å, for molecular weights <4000, in combination with a 50-mm guard column. A pump 325 (KONTRA, Eching, Germany) was used with IR detector 131 (Gibson, Villiers le Bel, France). The substances for GPC analysis were dissolved in 100% THF at concentrations of 5% and eluted with 0.75 mL THF/min.

RESULTS AND DISCUSSION

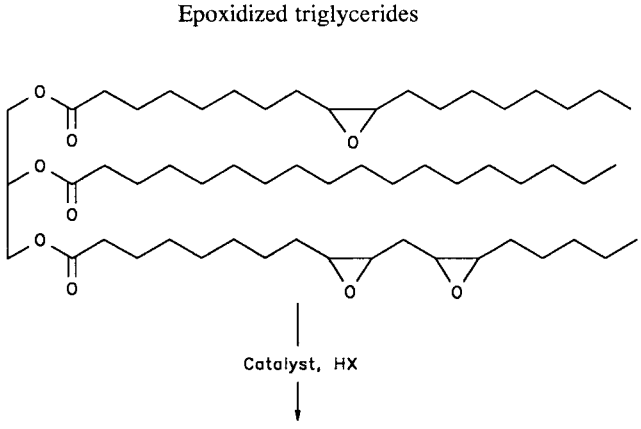
The constituent fatty acids of the triglycerides of rapeseed oil, sunflower oil, and linseed oil, as well as a high-oleic *Euphorbia lathyris* oil consist mainly of oleic and linoleic acids. In the first step of the process reported here (11–13), these unsaturated fatty acids or acyl moieties are epoxidized in a conventional manner with formic acid and hydrogen peroxide (32), leading to the corresponding mono- or diepoxy fatty acids or acyl moieties. Catalytic opening of the oxirane rings in the presence of water or other hydrogen donors, such as alcohols, diols, and amines, leads to introduction of hydroxyl groups into the fatty acid chain according to Scheme 1.

The catalysts used are acid-activated carriers with large surfaces and good adsorption abilities. Typical catalyst materials are acid-activated bleaching earths of the montmorillonite type, silicates, or activated carbons. The epoxidized material is reacted in an autoclave by stirring at temperatures between 80 and 200°C (11–13).

Vicinal diols are obtained when water is used as hydrogen donor, whereas with other hydrogen donors, hydroxylated compounds with other substituents are formed. The substituted compounds are characterized by one hydroxyl group and another vicinally substituted group.

Examples with chemical and physical characteristics of the various technical products obtained by catalytically reacted epoxidized rapeseed and soybean oils with water, alcohols, diols, and amines are given in Table 2.

The reactions described in Table 2 were carried out with stoichiometric proportions of epoxidized oil and various hydrogen donors, except the reaction of epoxidized rapeseed oil



SCHEME 1

TABLE 2
Characteristics of Hydroxylated Fatty Acid Derivatives Formed upon Catalytic Oxirane Ring Opening of Epoxidized Oils with Various Reactants

Epoxidized oil	Hydrogen donor	Amine value	OH value	Viscosity (°C/mPa s)
Rapeseed	Water		220–250	40/13000–19400
Soybean	Water		210–235	25/28000–45000
Rapeseed	Methanol		118–141	25/3100
Soybean	Methanol		120–150	25/2500–4000
Rapeseed	Ethanol		115–144	25/2700–7300
Soybean	Ethanol		125–140	25/3700–5200
Rapeseed	*n*-Butanol		120–150	25/12000–24000
Rapeseed	*n*-Butanol[a]		110–130	25/3500–4500
Rapeseed	PEG[b]		190–230	25/300–500
Rapeseed	1,4-Butanediol		270–298	25/8600–12000
Rapeseed	Methylglycol		119–146	25/3100–4800
Rapeseed	Diethanolamine	100–110	400–430	40/20000–24000
Soybean	Diethanolamine	110–130	450–470	40/18000–25000
Rapeseed	Triethanolamine	132–146	435–463	25/10900–18800
Rapeseed	Monobutylamine	100–110	300–330	25/5000–7000

[a]Epoxidized rapeseed oil/*n*-butanol = 1:2. [b]Polyethyleneglycol 400.

with *n*-butanol, marked by (a). Depending on the hydrogen donor used, different products, characterized by a wide range in hydroxyl values, can be obtained. The influence of the fatty acid composition of the epoxidized oils on the characteristics of the hydroxylated products is rather small.

With epoxidized rapeseed oil as starting material, the ring opening reaction with monobutylamine was examined closely. The reaction was carried out at 180°C with stoichiometric proportions of epoxidized rapeseed oil and monobutylamine. Acid value, amine value and oxirane oxygen content were determined continuously to follow the course of the reaction. The acid value was used as an indicator for hydrolysis, and the reaction progress is shown in Figure 1.

During the course of the reaction, the content of oxirane oxygen decreased continuously, indicating the progress of ring opening. The amine value increased continuously to a stable level of about 110, whereas the acid value remained nearly unchanged during the reaction. The progress of the reaction as followed by IR spectroscopy revealed partial aminolysis of the triglycerides (Fig. 2).

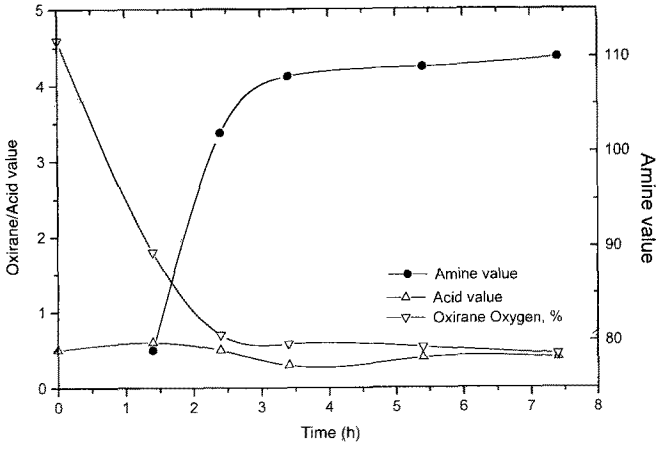


FIG. 1. Changes of acid value, amine value, and oxirane oxygen content during the reaction of epoxidized rapeseed oil with monobutylamine.

The ester band at 1740 cm^{-1} continuously decreased, whereas a concomitant increase of the amide band at 1650 cm^{-1} was observed. During opening of the oxirane ring, a secondary hydroxyl group and a vicinal aminoalkyl group were formed. The formation of the hydroxyl group caused increased IR absorption at 3320 cm^{-1}. IR absorption at 1550 cm^{-1} results from the ν-(CN) and δ-(CNH) oscillation of the secondary amide. It is, therefore, evident that monobutylamine simultaneously reacts with the ester bond and the oxirane ring. However, the aminolysis is incomplete as is evident from Figure 2c, which shows that the ester bond at 1740 cm^{-1} is still present in the IR spectrum.

To study the influence of the quality of the hydrogen donor on the reaction progress and the reaction product, epoxidized rapeseed oil was reacted with different amounts of 1,4-butanediol. The reaction was carried out at 180°C. Acid value, hydroxyl value, and oxirane oxygen content were determined to follow the reaction. The reaction progress of the three experiments is shown in Figures 3 and 4.

With 1,4-butanediol and epoxidized rapeseed oil in stoichiometric proportions, the oxirane ring was opened almost spontaneously when the temperature reached 180°C. The acid value increased at the end of the reaction, thus indicating a partial cleavage of the triglyceride. The decrease of the oxirane oxygen content was paralleled by an increase in hydroxyl value.

Similar reaction progress was observed when 1,4-butanediol and epoxidized rapeseed oil were used in molar propor-

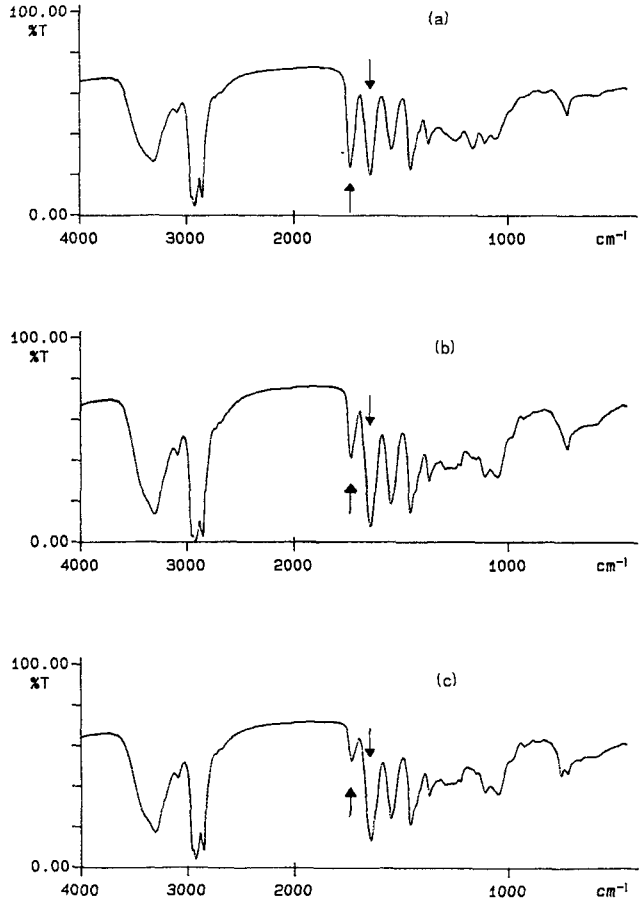


FIG. 2. Infrared spectra of the products formed during the reaction of epoxidized rapeseed oil with monobutylamine at different times: (a) 1.4 h; (b) 3.4 h; (c) 7.4 h (final product). The arrows at 1740 cm^{-1} and 1650 cm^{-1} indicate ester band and amide band, respectively.

tions of 1:2 or 1:3. Upon reaching 180°C, the oxirane oxygen content decreased rapidly. Near the end of the reaction, the acid value increased due to the cleavage of the ester bonds of the triglycerides. In contrast to the reaction with stoichiometric proportions of 1,4-butanediol, at the end of the reaction the hydroxyl value decreased again. GPC analysis of the final samples is presented in Figure 5.

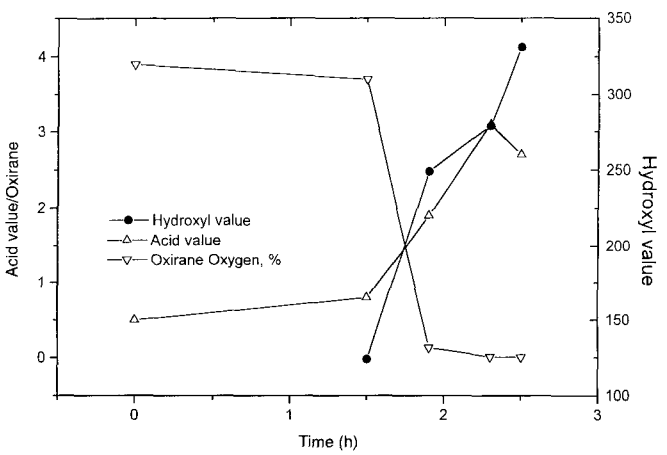


FIG. 3. Changes of acid value, hydroxyl value, and oxirane oxygen content during the reaction of epoxidized rapeseed oil with 1,4-butanediol in stoichiometric proportions.

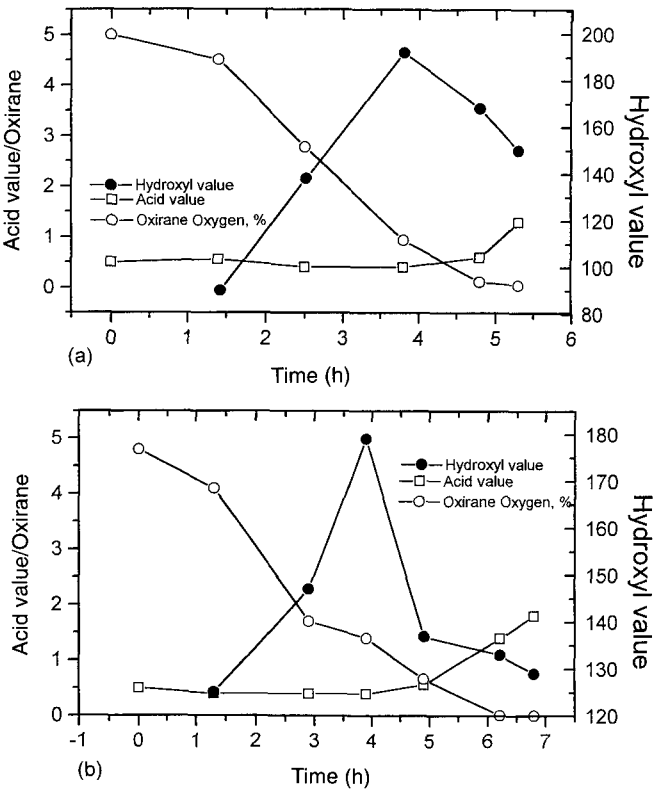


FIG. 4. Changes of acid value, hydroxyl value, and oxirane oxygen content during the reaction of epoxidized rapeseed oil with 1,4-butanediol in different proportions. Epoxidized rapeseed oil/1,4-butanediol: (a) 2:1; (b) 3:1.

The product from the reaction with stoichiometric proportions of starting materials still contains residual 1,4-butanediol (Fig. 5, peak 6) and a relatively high content of monomeric hydroxylated triglycerides (Fig. 5, peak 4). Peak 5 indicated that interesterification with 1,4-butanediol has taken place.

By reducing the quantity of 1,4-butanediol, the molecular composition is shifted to oligomeric hydroxylated triglycerides (Fig. 5, peaks 1, 2, 3), whereas 1,4-butanediol (Fig. 5, peak 6) completely disappears from the reaction mixture. From the absence of peak 5, it can be concluded that no interesterification has taken place. It is assumed that one molecule of 1,4-butanediol has reacted with two epoxy groups of different triglycerides. Therefore, oligomers with higher molecular weights were formed.

Alkaline hydrolysis of HOFA esters of various plant oils also yields the corresponding HOFA (14). Examples and characteristics of HOFA are shown in Table 3.

Weber *et al.* (33) have shown that hydroxylated rapeseed fatty acids contain *threo*-9,10-dihydroxy stearic acid and various dihydroxy THF octadecanoic acids as major components. Both these HOFA and the remaining saturated fatty acids react with each other to build up estolides (34).

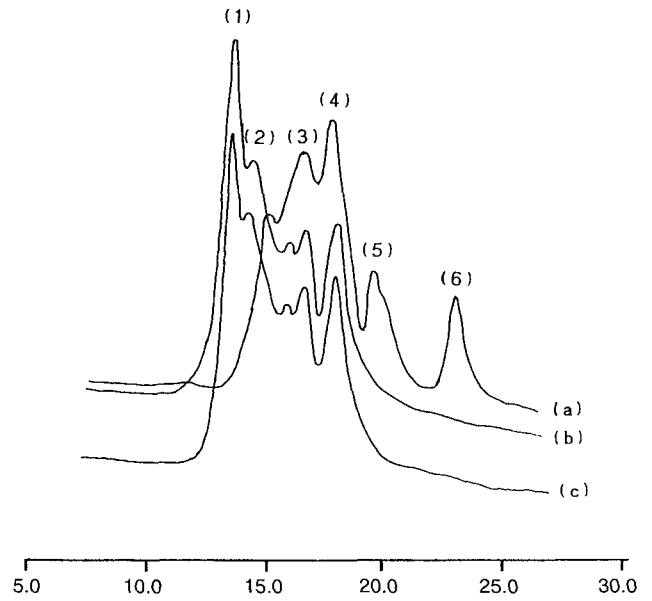


FIG. 5. Gel permeation chromatographics of the final products of the reaction between epoxidized rapeseed oil and 1,4-butanediol in different molar ratios. Epoxidized rapeseed oil/1,4-butanediol: (a) 1:1; (b) 2:1; (c) 3:1. Relative retention time (RRT) 13.4–16.4: (1), (2), (3) oligomeric hydroxylated triglycerides; RRT 17.5: (4) monomeric hydroxylated triglycerides; RRT 19.3: (5) 1,4-butanediol fatty acid esters; RRT 22.6: (6) 1,4-butanediol.

The experiments described here show that the ratio of the reactants determines the characteristics of the products. For example, reduction in the proportion of the hydrogen donor, such as 1,4-butanediol, leads to an increase of intermolecular ether formation as possible side reaction. Further experiments have shown that a distinct surplus of alcohol is able to suppress side reactions. When primary amines are used as hydrogen donors, apart from the intended formation of hydroxyl groups with vicinal aminoalkyl groups, partial aminolysis of the ester compounds was also observed. Under defined conditions, the HOFA and fatty acid derivatives are obtained in reproducible quality.

It is an object of current studies to find out how the characteristics of the hydroxylated products can be influenced by further modifications of the reaction conditions.

TABLE 3
Characteristics of Technical Hydroxylated Fatty Acid Derivatives from Various Epoxidized Oils by Catalytic Oxirane Ring Opening with Water

Epoxidized oil	Acid value	Saponification value	OH value	Viscosity °C/mPa s
Rapeseed	144	210	221	40/2400
Olive	148	214	160	40/900
Euphorbia lathyris	138	222	232	40/1500
Sunflower	140	212	222	40/3100
Soybean	156	210	255	40/23200
Tall	127	206	257	40/52300
Linseed	137	219	237	40/32200
Fish	142	202	204	40/920

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