Alkali-Catalyzed Alcoholysis of Crambe Oil and Camelina Oil for the Preparation of Long-Chain Esters[1]

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ABSTRACT: The alcoholysis of crambe and camelina oils was carried out with oleyl alcohol, alcohols derived from crambe and camelina oils, and *n*-octanol using potassium hydroxide as catalyst to prepare alkyl esters. Conversions to alkyl esters were about 70% with oleyl alcohol, 20–45% with crambe and camelina alcohols, and 60% with *n*-octanol. The conversion to esters for crambe and camelina oil with oleyl alcohol and *n*-octanol increased with increasing molar excess of alcohol. Composition of the alkyl esters formed was as expected from the composition of the reaction partners.

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KEY WORDS: Camelina oil, crambe oil, long-chain esters, potassium hydroxide-catalyzed alcoholysis, transesterification.

Crambe (*Crambe abyssinica*) and camelina (*Camelina sativa*) are less investigated oil plants, whose cultivation on poor nutrient soils is expected to be successful. These oil plants are regarded as industrial resources for different oleochemical applications because crambe oil is a rich source (1,2) of erucic acid (*cis*-13-docosenoic acid; *ca*. 56%), and camelina oil is a source (3) of α-linolenic acid (all-*cis*-9,12,15-octadecatrienoic acid; *ca*. 38%).

The objective of the present work was to prepare alkyl esters of crambe and camelina oils that may have useful applications in lubricants and cosmetics. Transesterification (alcoholysis) of triacylglycerols with alcohols catalyzed by alkali (4–7) or acid catalysts (8,9) is well known and often used for the preparation of alkyl esters. We report here the potassium hydroxide-catalyzed alcoholysis of crambe and camelina oils with long-chain alcohols, such as oleyl alcohol and alcohols derived from crambe and camelina oils, for the preparation of mixtures of long-chain and very long chain wax esters resembling those of jojoba oil. Although the main chain lengths of the expected wax esters are C40 and C44, these esters may be useful as surrogates for jojoba (*Simmondsia chinensis*) wax esters, which have a main chain length of 42 carbon atoms (*ca*. 50% of the wax esters) (10,11). Jojoba wax is used in cosmetics, pharmaceuticals, and in the food industry because of its practically unchanged viscosity over a wide range of temperatures (12). Owing to the high price of the final product (inability to economically cultivate the plants) it is desirable to find a low-cost jojoba oil substitute (13). We also report the alkali-catalyzed alcoholysis of crambe and camelina oils with *n*-octanol and isopropanol. The goal was to obtain products similar to enzymatically prepared medium-chain and short-chain esters (14) with properties suitable for applications in cosmetics.

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EXPERIMENTAL PROCEDURES

Materials. Crambe and camelina were grown in experimental fields. The seeds and refined oils were supplied by the Institut für Pflanzenbau der Landesforschungsanstalt für Landwirtschaft und Fischerei Mecklenburg-Vorpommern (Gülzow, Germany). Fatty acid composition of the oils (designated by number of carbon atoms:number of *cis*-double bonds) was as follows. Crambe oil: 16:0 = 2%, 18:0 = 1%, 18:1 = 17%, 18:2 = 9%, 18:3 = 6%, 20:0 = 1%, 20:1 = 4%, 22:0 = 2%, 22:1 = 56%, 24:1 = 1%; camelina oil: 16:0 = 5%, 18:0 = 3%, 18:1 = 14%, 18:2 = 16%, 18:3 = 36%, 20:0 = 1%, 20:1 = 15%, 22:0 = <1%, 22:1 = 3%, 24:1 = <1%. The alcohols from crambe and camelina oils were prepared from their distilled methyl esters by hydrogenolysis at Deutsche Hydrierwerke (DHW) (Rodleben, Germany). Composition of the alcohols (designated by number of carbon atoms:number of *cis*-double bonds) was as follows. Crambe alcohols: 16:0 = 3%, 18:0 = 2%, 18:1 = 21%, 18:2 = 1%, 18:3 = 2%, 20:0 = 2%, 20:1 = 4%, 22:0 = 5%, 22:1 = 56%, 24:0 = 2%, 24:1 = 2%; camelina alcohols: 16:0 = 10%, 18:0 = 5%, 18:1 = 30%, 18:2 = 10%, 18:3 = 3%, 20:0 = 6%, 20:1 = 27%, 22:1 = 9%. Oleyl alcohol (technical grade: 18:0 = 4%, 18:1 = 90%, 18:2 = 5%, 20:1 = 1%) was purchased from Sigma-Aldrich-Fluka (Deisenhofen, Germany), and percolated prior to use over alumina under argon. *n*-Octanol and isopropanol were supplied by E. Merck (Darmstadt, Germany). All distilled solvents and reagents were of analytical grade, obtained from E. Merck. Reference lipid standards were from Sigma-Aldrich-Fluka and Nu-Chek-Prep (Elysian, MN).

Alcoholysis. Reactions were carried out in glass tubes equipped with Teflon-lined screw-caps using 0.3 mmol oil (crambe oil or camelina oil) with the stoichiometric amount

or a molar excess of alcohol (oleyl alcohol, crambe alcohols, camelina alcohols, *n*-octanol or isopropanol). The concentration of potassium hydroxide used was 0.2 wt% of reactants. All reactions were carried out with magnetic stirring at a temperature of 60°C under nitrogen. Samples were withdrawn at reaction times of 0.5, 1, and 2 h.

Product isolation and analysis. Products from the alcoholysis of crambe and camelina oil with long-chain alcohols (oleyl alcohol, crambe alcohols, and camelina alcohols) were isolated as follows. Samples of 50 µL were added to 1 mL isohexane/diethyl ether (1:1, vol/vol) and the resulting solution washed with water until pH-neutral. To remove soaps formed the sample was washed repeatedly with an aqueous sodium chloride solution (10% wt/vol). The organic phase was dried over sodium sulfate. The solvent was removed and the sample dissolved in isohexane.

Products from the alcoholysis of crambe oil and camelina oil with *n*-octanol or isopropanol were isolated as follows. Samples of 50 µL were added to 15 mL of a mixture of dichloromethane/methanol/water (1:2:0.8, vol/vol/vol) containing a few drops of 6 M hydrochloric acid and homogenized. Thereafter 5 mL dichloromethane and 5 mL water were added and mixed vigorously. The resulting mixture was centrifuged and the lower organic phase was removed. The organic phase was washed with water until it was pH-neutral. The sample was dried over anhydrous sodium sulfate, the solvent removed, and the sample dissolved in isohexane.

For quantitative analysis of the amount of esters formed a known amount of methyl heptadecanoate was added as internal standard to an aliquot of the reaction products and the mixture separated by thin-layer chromatography on Silica Gel H using isohexane/diethyl ether/acetic acid (80:20:1, vol/vol/vol) as developing solvent. The lipid fractions were made visible by exposing the edges of the chromatoplates to iodine vapor. The fraction containing alkyl esters of fatty acids together with the internal standard was scraped off, eluted with water-saturated diethyl ether, dried, and dissolved in isohexane. The mixture of alkyl esters was analyzed by gas chromatography using a Hewlett-Packard 5890 instrument (Hewlett-Packard GmbH, Waldbronn, Germany) equipped with flame-ionization detectors. A Quadrex 400-5HT column (25 m × 0.25 mm i.d. × 0.1 µm film) (Quadrex Corporation, New Haven, CT) was used with hydrogen as carrier gas (column pressure 50 kPa). Temperature program was from 160 (2 min isothermal) to 310°C, 10°C/min, then to 420°C, 5°C/min, 5 min isothermal. Peaks were identified by comparison with reference standards and wax esters of jojoba oil, and quantitated using HP GC Chem Station Rev. A.06.3 [509] software (Hewlett-Packard) using correction factors that were obtained from mixtures of known composition.

Composition of alcohols was determined by gas chromatography in a Hewlett-Packard 5890 instrument on a HP-1 column (25 m × 0.32 mm i.d. × 0.52 µm film) with nitrogen as carrier gas (column pressure 85 kPa). Temperature program was from 180 (2 min isothermal) to 260°C, 6°C/min (5 min isothermal). Quantitation was made using HP ChemStation B.01.02 software (Hewlett-Packard). Peaks were identified by comparison with reference standards.

RESULTS AND DISCUSSION

Alcoholysis of crambe oil and camelina oil with oleyl alcohol. Figure 1 shows the time course of potassium hydroxide-catalyzed alcoholysis of crambe oil and camelina oil with oleyl alcohol. The alcoholysis of crambe oil with oleyl alcohol leads to conversions of about 50–60%, whereas with camelina oil the conversion of *ca*. 70% is attained. The reactions level off after about 2 h and decrease thereafter (Fig. 1), possibly owing to the reverse reaction, i.e., hydrolysis.

The compositions of the wax esters formed by potassium hydroxide-catalyzed alcoholysis of crambe oil and camelina oil with oleyl alcohol are given in Figure 2. The product from the alcoholysis of crambe oil with oleyl alcohol contains wax esters of chain lengths of mainly C36 (*ca*. 30%) and C40 (*ca*. 60%), whereas the wax esters formed by alcoholysis of camelina oil with oleyl alcohol are predominated by chain lengths of nearly 70% C36 and 20% C38 (Fig. 2).

Figure 3 shows the effect of the molar ratios of reactants on the conversion to wax esters in the potassium hydroxide-catalyzed alcoholysis of crambe oil and camelina oil with oleyl alcohol. If the molar ratio of crambe oil (Fig. 3A) and camelina oil (Fig. 3B) to oleyl alcohol is increased from 1:3 to 1:6 and then to 1:10, the conversions to wax esters rise from 5–10% to 20–40% and to 70–95%, respectively. The conversions of crambe oil (Fig. 3A) are somewhat higher than those of camelina oil (Fig. 3B) at all molar ratios.

Alcoholysis of crambe oil and camelina oil with crambe alcohols and camelina alcohols. The results of the potassium hydroxide-catalyzed alcoholysis of crambe oil with crambe alcohols and camelina alcohols (Fig. 4A) and of camelina oil with crambe alcohols and camelina alcohols (Fig. 4B) show that the conversions of crambe oil as well as camelina oil with

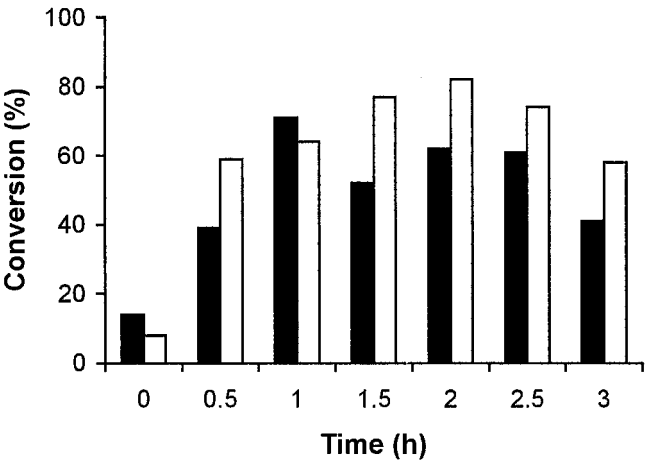

FIG. 1. Time course of potassium hydroxide-catalyzed alcoholysis of crambe oil (solid bar) and camelina oil (open bar) with oleyl alcohol (molar ratio of triacylglycerols/alcohol = 1:3).

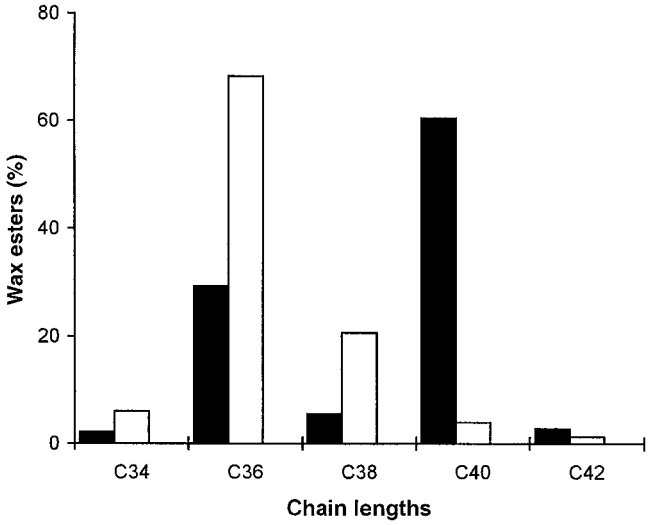

FIG. 2. Composition of the wax esters formed by potassium hydroxide-catalyzed alcoholysis of crambe oil (solid bar) and camelina oil (open bar) with oleyl alcohol (molar ratio of triacylglycerols/alcohol = 1:3, time of reaction = 3 h).

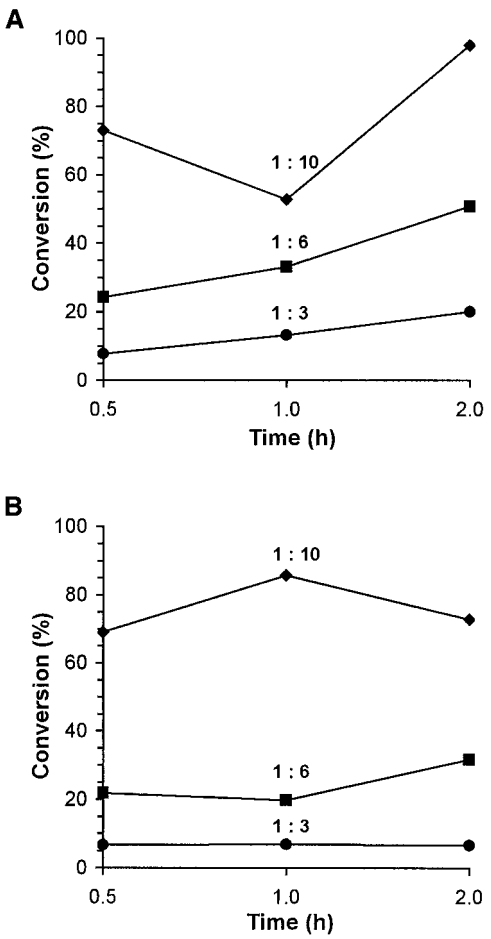

FIG. 3. Time course of potassium hydroxide-catalyzed alcoholysis of (A) crambe oil and (B) camelina oil with oleyl alcohol at different molar ratios of triacylglycerols/alcohol.

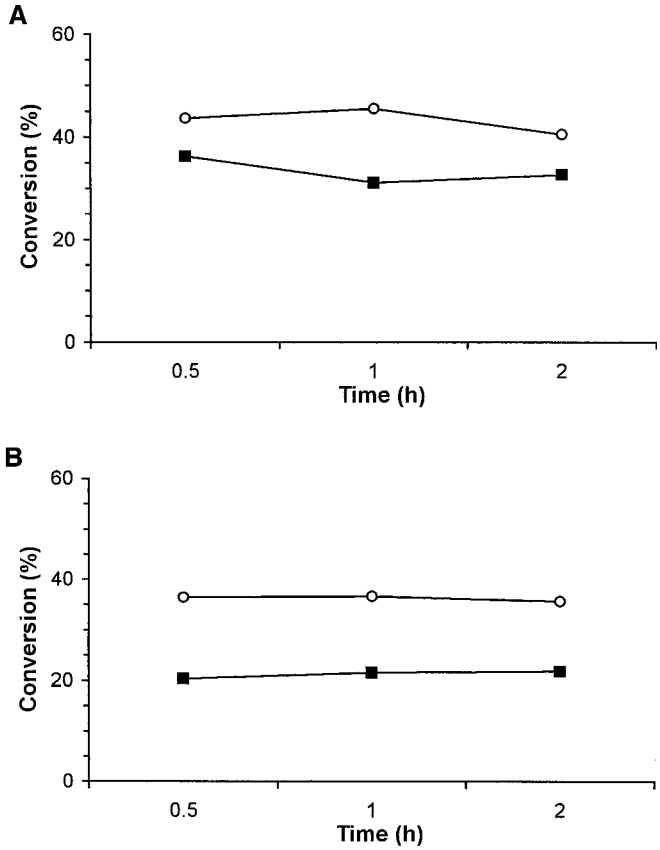

FIG. 4. Time course of potassium hydroxide-catalyzed alcoholysis of (A) crambe oil and (B) camelina oil with crambe alcohols (○) and camelina alcohols (■) (molar ratio of triacylglycerols/alcohol = 1:3).

crambe alcohols and camelina alcohols are *ca*. 20 to 30% lower than the conversions of these oils with oleyl alcohol (Fig. 1). Furthermore, the conversions of both oils are about 10–15% higher in alcoholysis with crambe alcohols than with camelina alcohols (Fig. 4 A,B).

The compositions of wax esters formed from crambe oil and camelina oil by potassium hydroxide-catalyzed alcoholysis with crambe alcohols and camelina alcohols are compared with the wax ester composition of jojoba oil in Figure 5. The wax esters obtained by alcoholysis of camelina oil with camelina alcohols contain products with carbon atoms C36 (≈50%), C38 (≈30%), and C34 as well as C40 (both ≈10%). The corresponding esters from crambe oil and crambe alcohols constitute a product of mainly C40 (≈40%), C44 (≈35%), and C36 as well as C42 (both ≈10 %) chain lengths. If crambe oil is transesterified with camelina alcohols, the wax esters in the products consist of C40 (≈40%), C36 (≈20%), and C38 as well as C42 (both ≈15%) (Fig. 5). Products of similar chain-length distribution are obtained if camelina oil is transesterified with crambe alcohols (data not shown). The last two products show compositions that are closest to the wax ester composition of jojoba oil (Fig. 5). The main wax ester constituents of jojoba oil are those with chain lengths C42 (≈50%), C40 (≈30%), and C44 (≈10 %).

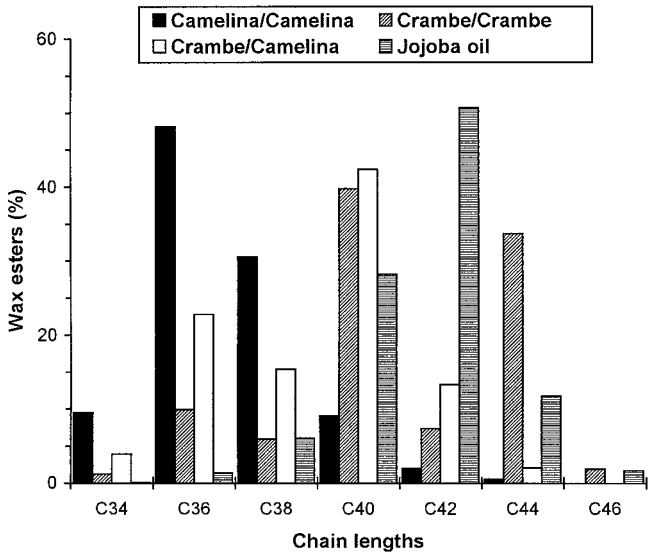

FIG. 5. Composition of the wax esters formed by potassium hydroxide-catalyzed alcoholysis of crambe oil and camelina oil with crambe alcohols and camelina alcohols in comparison to wax esters of jojoba oil (molar ratio of triacylglycerols/alcohol = 1:3, time of reaction = 3 h).

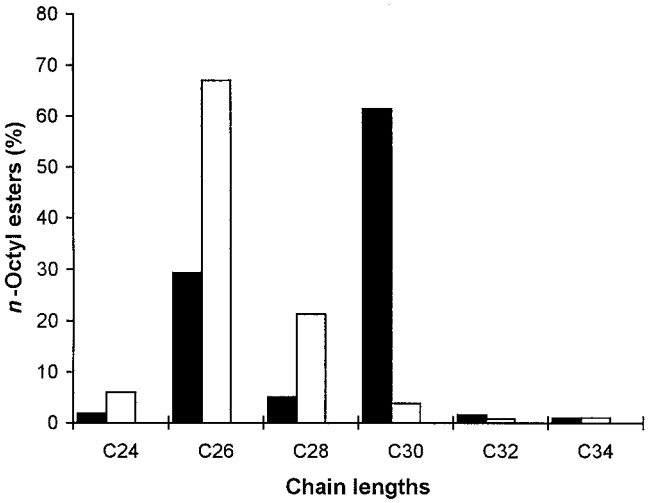

FIG. 7. Composition of the *n*-octyl ester formed by potassium hydroxide-catalyzed alcoholysis of crambe oil (solid bar) and camelina oil (open bar) with *n*-octanol (molar ratio of triacylglycerols/alcohol = 1:3, time of reaction = 3 h).

Alcoholysis of crambe oil and camelina oil with n*-octanol.* The time course of conversions in the potassium hydroxide-catalyzed alcoholysis of crambe oil and camelina oil with *n*-octanol is shown Figure 6. The alcoholysis of crambe oil with *n*-octanol leads to conversions of 70–85% whereas camelina oil yields only 40–55% *n*-octyl esters. These results are inverse to those obtained in the alcoholysis of crambe oil and camelina oil with oleyl alcohol (Fig. 1), in which the conversion of crambe oil is higher than that of camelina oil. This might be due to different mutual solubilities of the two sets of reactants. The alcoholysis with *n*-octanol also levels off after about 2 h (Fig. 6).

The compositions of the *n*-octyl esters formed by potassium hydroxide-catalyzed alcoholysis of crambe oil and camelina oil with *n*-octanol are shown in Figure 7. The *n*-octyl esters of crambe oil are predominated by chain lengths of C26 (*ca.* 30%) and C30 (*ca*. 60%). The alcoholysis of camelina oil with *n*-octanol leads to alkyl esters of mainly C26 (about 70%) and C28 (about 20%) chain lengths (Fig. 7).

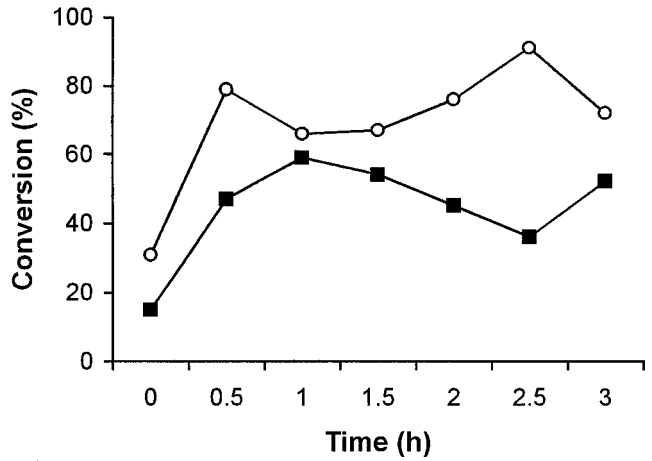

FIG. 6. Time course of potassium hydroxide-catalyzed alcoholysis of crambe oil (○) and camelina oil (■) with *n*-octanol (molar ratio of triacylglycerols/alcohol = 1:3).

Figure 8 shows the effect of the molar ratio of reactants on the conversion to *n*-octyl esters in potassium hydroxide-catalyzed alcoholysis of crambe oil and camelina oil with *n*-octanol. As in the alcoholysis of crambe oil and camelina oil with oleyl alcohol (Fig. 3) the conversions increase with increasing molar excess of the alcohol (Fig. 8). The conversion of crambe oil with *n*-octanol to *n*-octyl esters increases, respectively, from 5–10 to *ca*. 25%, and finally to >95% if the molar ratio of oil to *n*-octanol is raised from 1:3 to 1:6, and finally to 1:10 (Fig. 8A). The increase of the conversions with the increasing molar ratio of oil to *n*-octanol in the alcoholysis of camelina oil is not as dramatic as with crambe oil. Increasing the molar ratio of camelina oil to *n*-octanol from 1:3 to 1:6 and finally to 1:10 raises the conversions to alkyl esters from around 10 to 15–20% and to 30–35%. After 1 h reaction the conversion reaches almost 60% at a molar ratio of 1:10; however, after 2 h reaction the conversion drops to about 20%, obviously owing to the reverse reaction, i.e., hydrolysis (Fig. 8B).

Alcoholysis of crambe oil and camelina oil with isopropanol. Under the conditions employed, only traces of isopropyl esters are formed when crambe oil and camelina oil are subjected to alcoholysis with isopropanol, catalyzed by potassium hydroxide.

Our studies show that wax esters for lubricants and cosmetics as well as alkyl esters comparable to enzymatically prepared medium-chain esters (14) are conveniently prepared from crambe oil and camelina oil by potassium hydroxide-catalyzed alcoholysis with long-chain alcohols, such as oleyl alcohol or alcohols derived from crambe oil and camelina oil, and *n*-octanol. The conversions increase with increasing

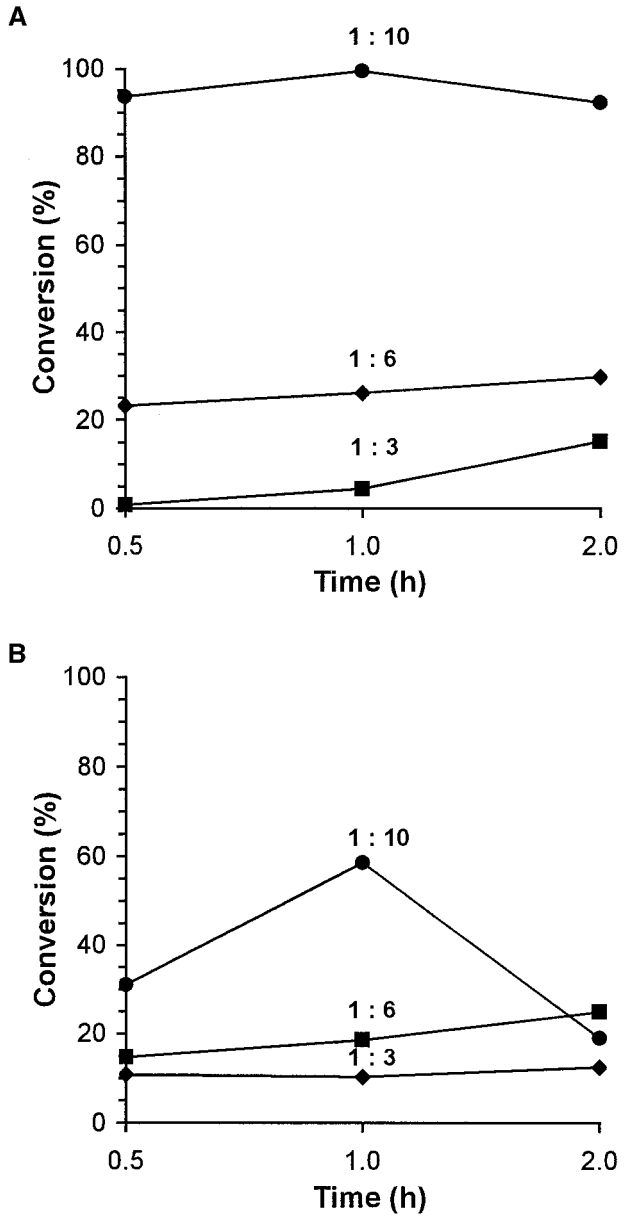

FIG. 8. Time course of potassium hydroxide-catalyzed alcoholysis of (A) crambe oil and (B) camelina oil with *n*-octanol at different molar ratios of triacylglycerols/alcohol.

molar excess of the alcohol over crambe oil and camelina oil. The conversions in alcoholysis with oleyl alcohol (≈50–70%) as well as with *n*-octanol (≈40–85%) are quite high, whereas with alcohols derived from crambe oil and camelina oil only moderate conversions (≈20–45%) are obtained. Isopropyl esters are not formed by alkali-catalyzed alcoholysis of crambe and camelina oils.

Lipase-catalyzed alcoholysis of triacylglycerols with different alcohols to prepare alkyl esters is also possible (15–18). The results of the lipase-catalyzed transesterification of crambe oil and camelina oil with long-chain, medium-chain, and short-chain alcohols as substrates are shown in the following paper (19).

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