# The Decomposition of Secondary Esters of Castor Oil with Fatty Acids

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**In this study, thermal splitting of secondary fatty acid esters of castor oil was investigated to determine the reaction kinetics under various conditions. Zinc oxide, *p*-toluenesulfonic acid and sulfuric acid were used as catalysts. Reactions were carried out at 260, 270, and 280°C. Experimental data fitted the first-order rate equation for the catalyzed and noncatalyzed reactions. In addition to the kinetic investigation, the splitting (pyrolysis) mixture was evaluated in the preparation of a synthetic drying oil. For this purpose, the mixed fatty acids of linseed, sunflower and *Ecballium elaterium* seed oils were used in the esterification stage of the process. Pyrolysis mixtures were converted to drying oils by combining the liberated acids with equivalent amounts of glycerol. The oils thus obtained show good drying oil properties.**

KEY WORDS: Castor oil, decomposition, *Ecballium elaterium*, kinetics, linseed oil, pyrolysis, sunflower oil.

Castor oil consists largely of glycerides of ricinoleic acid (12-hydroxy octadecenoic acid). The presence of a hydroxyl group in addition to an olefinic linkage in this predominating fatty acid provides castor oil many reaction possibilities (1,2). Among these reactions, esterification occupies an important place in the manufacture of industrially useful materials. For instance, in the manufacture of non-drying alkyd resin, castor oil is esterified with phthalic anhydride (3). Secondary esters of castor oil formed with drying oil fatty acids were evaluated as a material with drying oil properties (4). The kinetics of the esterification reaction between castor oil and oleic acid was also investigated (5). Another reaction applicable for technical purposes is the splitting of secondary esters of castor oil. In this splitting (pyrolysis) process, conjugated double bonds are formed on the ricinoleic acid chain. Therefore, the decomposition mixture has potential in the preparation of a synthetic drying oil with conjugated diene. Secondary fatty acid esters of castor oil as well as acetylated castor oil were reported earlier as the starting materials for the manufacture of dehydrated castor oil (6,7). Closely related to the decomposition of secondary esters of castor oil is the breakdown of estolides obtained by the condensation reaction between ricinoleic acid molecules (8). Decomposition of estolides as well as of acetylated castor oil was reported to be a first-order reaction (7,8). On the other hand, the preparation of dehydrated castor oil alkyd by the well-known *in-situ* process is also based on the splitting of secondary ester linkages formed by phthalic anhydride (9–11).

The purpose of the present study is to develop the rate equations for splitting secondary esters of castor oil and to evaluate the splitting mixture in the preparation of a drying oil. The splitting process was carried out at 260, 270, and 280°C with and without catalyst. The catalysts used were zinc oxide, *p*-toluenesulfonic acid monohydrate and sulfuric acid. For the preparation of drying oils, mixed fatty acids of linseed, sunflower and *Ecballium elaterium* seed oils were used as the acid components in the esterification stage of the process.

## EXPERIMENTAL PROCEDURES

*Materials.* Castor oil was obtained by cold pressing the seeds of Turkish origin. *Ecballium elaterium* (L.)A. Rich. from the family cucurbitaceae, for which the English name is Squirting Cucumber seed oil was also obtained in the laboratory from the seeds of Turkish origin. Linseed and sunflower oils were commercially purchased. Main characteristics of the oils are presented in Table 1. The oleic acid used was analytical grade from Riedel deHaen with an acid value of 200 and an iodine value of 92. Mixed fatty acids were obtained by alkali saponification of oils followed by acidification with dilute sulfuric acid. Other reagents were analytical grade from Merck (Darmstadt, Germany).

*Experimental setup.* Esterification and ester splitting reactions were carried out in a four-necked flask equipped with a stirrer, a thermometer, an inert gas inlet tube and an air condenser.

*Esterification of castor oil with fatty acids.* Esterification reactions were conducted in concentrated solution by using equivalent proportions of the reactants. Castor oil and fatty acid were placed into the reaction flask and heated to 250°C. The temperature was kept constant at 250°C until the acid value was decreased to a low value. No catalyst was used in this reaction.

*Splitting of castor oil ester and drying oil preparation.* Castor oil ester was placed into the reaction flask and heated under the inert gas atmosphere at the given splitting temperature. For the catalyzed decomposition, 0.1% of catalyst based on ester product was added. During the heating process, no material was removed from the reaction medium. Samples were withdrawn at the predetermined time intervals and their acid and saponification values were determined (14). A correction for catalyst, if

TABLE 1

**Main Characteristics of the Oils Used in the Study**[a]

| Oil | Refractive index, $n_D^{20}$ | Acid value | Saponification value | Iodine value[b] | Hydroxyl value |
|---|---|---|---|---|---|
| Sunflower oil | 1.4750 | 0.6 | 188.3 | 121.5 | — |
| Linseed oil | 1.4811 | 1.0 | 192.4 | 173.6 | — |
| Castor oil | 1.4780 | 2.1 | 178.0 | 84.6 | 166.4 |
| *Ecballium elaterium* seed oil | 1.4898 | 3.9 | 189.6 | 159.0[c] | — |

[a] Analytical methods were taken from Reference 14 unless otherwise stated.
[b] Hanus (Ref. 12).
[c] Woburn (Ref. 13).

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necessary, was applied to each sample. The ester value, corresponding to secondary ricinolyl ester groups, was determined by calculation. In drying oil synthesis, splitting was continued until almost a constant acid value was reached. That was in the range of 75–80. To convert the decomposition mixture to a drying oil, liberated fatty acids were esterified with equivalent amounts of glycerol at 225°C until a low acid value was reached.

## RESULTS AND DISCUSSION

In the kinetic studies, the secondary ester of castor oil with oleic acid was used. Castor oil esters formed with mixed fatty acids of linseed, sunflower and *E. elaterium* seed oils were evaluated in the preparation of drying oils.

In the thermal decomposition, secondary ester groups, *i.e.*, ricinolyl groups, are split mainly, because the glyceryl ester linkages are more thermally stable (6,7). Considering that the thermal decomposition reaction is first order, the following rate equation 1 was used (15):

$$\ln c_0/c = kt \qquad [1]$$

where $c_0$ and c are the concentrations of ricinolyl ester groups at the beginning and at time t, respectively.

To test the above rate equation, ln c was plotted against t. In this procedure, the ester value corresponding to ricinolyl ester linkages was used as concentration because $c_0/c$ is a ratio of concentration and its value is independent of units provided that the same units are used for both $c_0$ and c. In fitting a straight line to the experimental data, least square approximation was applied, and in each case the standard error of estimate (s) and the coefficient of determination ($r^2$) were calculated (16). The obtained results are shown in Figures 1–4. As can be seen, the reaction followed first order kinetics under the applied conditions.

Rate constants determined from the slopes of straight lines and energies of activation are presented in Table 2.

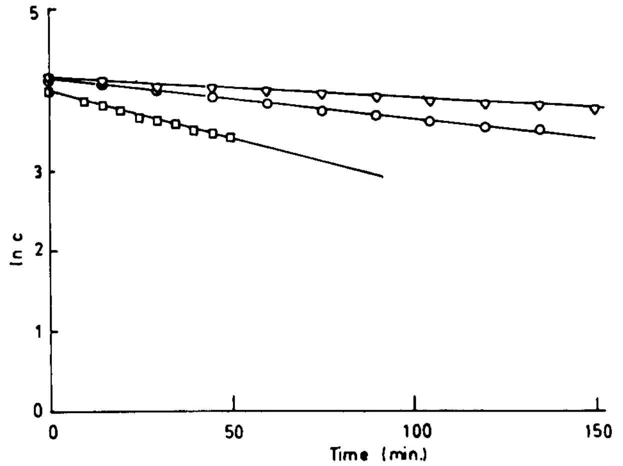

**FIG. 1. Rate of uncatalyzed decomposition of secondary ester of castor oil with oleic acid: ▽, 260°C, s (standard error of estimate) = $1.1402 \times 10^{-2}$, $r^2$ (coefficient of determination) = 0.9928; ○, 270°C, s = $1.7635 \times 10^{-2}$, $r^2$ = 0.9949; □, 280°C, s = $1.1966 \times 10^{-2}$, $r^2$ = 0.9963.**

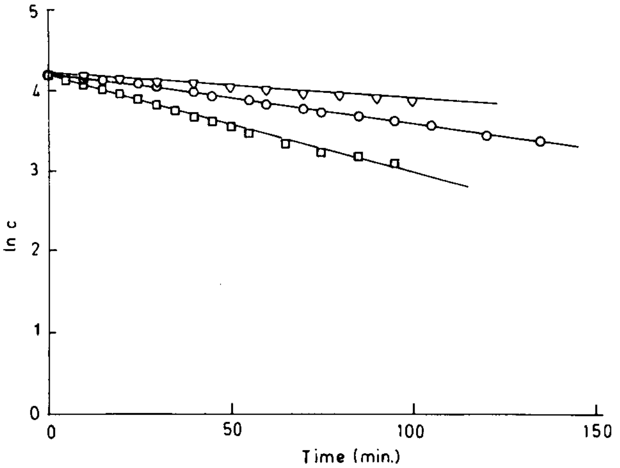

**FIG. 2. Rate of zinc oxide-catalyzed decomposition of secondary ester of castor oil with oleic acid: ▽, 260°C, s (standard error of estimate) = $6.7460 \times 10^{-3}$, $r^2$ (coefficient of determination) = 0.9962; ○, 270°C, s = $1.6730 \times 10^{-2}$, $r^2$ = 0.9962; □, 280°C, s = $3.0042 \times 10^{-2}$, $r^2$ = 0.9930.**

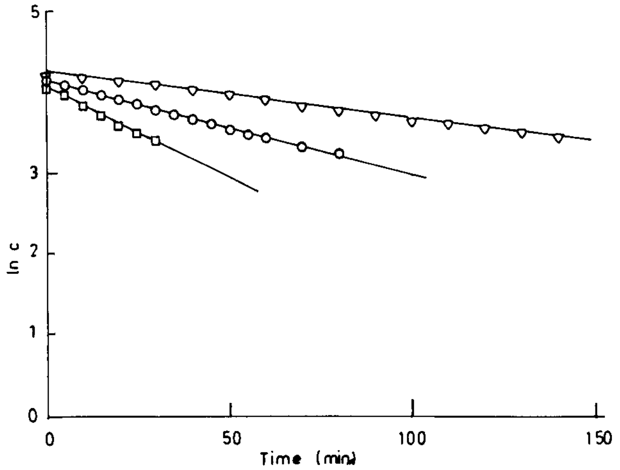

**FIG. 3. Rate of *p*-toluenesulfonic acid-catalyzed decomposition of secondary ester of castor oil with oleic acid: ▽, 260°C, s (standard error of estimate) = $1.5618 \times 10^{-2}$, $r^2$ (coefficient of determination) = 0.9965; ○, 270°C, s = $1.1656 \times 10^{-2}$, $r^2$ = 0.9984; □, 280°C, s = $1.5241 \times 10^{-2}$, $r^2$ = 0.9967.**

By evaluating rate constants, it can be seen that *p*-toluenesulfonic acid is the most effective splitting catalyst.

In the preparation of drying oils from decomposition mixtures, besides linseed and sunflower oils, *E. elaterium* seed oil was included as a mixed fatty acids source for the esterification stage. *Ecballium elaterium* seed oil contains a conjugated trienoic acid, called punicic acid (17–19).

Since conjugated dienes are also formed during the splitting process, conjugated dienoic and trienoic acid contents of the decomposition mixture were determined to evaluate the effect of catalysts on conjugation. For this purpose, ultraviolet absorption analysis was applied with a Beckman (Munchen, Germany) UV Spectrophotometer model DB-GT (20). The dienoic acid contents of the

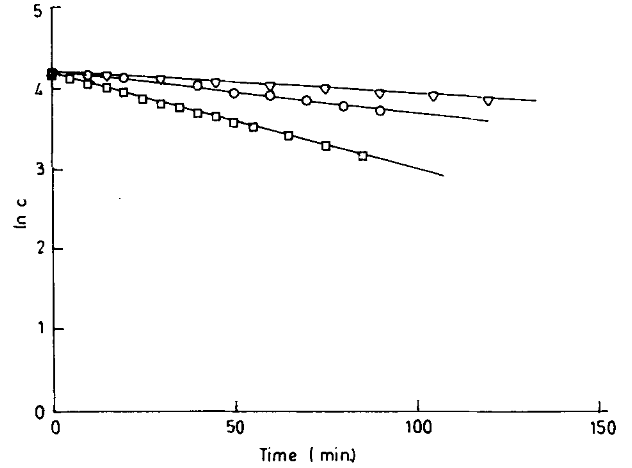

**FIG. 4. Rate of sulfuric acid-catalyzed decomposition of secondary ester of castor oil with oleic acid: ∇, 260°C, s (standard error of estimate) = 8.8058 × $10^{-3}$, $r^2$ (coefficient of determination) = 0.9950; ○, 270°C, s = 2.3649 × $10^{-2}$, $r^2$ = 0.9815; □, 280°C, s = 7.2710 × $10^{-3}$, $r^2$ = 0.9995.**

samples were found in the range 15.9–17.6. These results show that there is no superiority of any catalyst in forming conjugated bonds. However, because *p*-toluenesulfonic acid appeared to be the most effective splitting catalyst, it was used in the decomposition step of drying oil synthesis.

Some characteristics of the synthetic oils obtained are given in Table 3. Drying times of the samples with various amounts of driers are presented in Table 4. As can be seen, it is possible to obtain an oil with good drying properties even with sunflower oil. Almost the same drying times were obtained when linseed and *E. elaterium* seed oil fatty acids were used. Although *E. elaterium* seed oil contains about 20% punicic acid, it does not contain linolenic acid. Therefore, mixed fatty acids of *E. elaterium* seed oil impart the same effect on drying time as those of linseed oil.

## ACKNOWLEDGMENT

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TABLE 2

**Rate Constants and Activation Energies for the Decomposition of the Secondary Ester of Castor Oil with Oleic Acid**

| Catalyst used in the reaction | Rate constant, k, (min.$^{-1}$) | | | Activation energy, E, kcal/mole |
|---|---|---|---|---|
| | 260°C | 270°C | 280°C | |
| None | $2.55 \times 10^{-3}$ | $5.12 \times 10^{-3}$ | $1.15 \times 10^{-2}$ | 44.13 |
| *p*-toluenesulfonic acid | $5.69 \times 10^{-3}$ | $1.15 \times 10^{-2}$ | $2.23 \times 10^{-2}$ | 39.9 |
| Sulfuric acid | $2.82 \times 10^{-3}$ | $5.37 \times 10^{-3}$ | $1.19 \times 10^{-2}$ | 42.19 |
| Zinc oxide | $3.14 \times 10^{-3}$ | $6.48 \times 10^{-3}$ | $1.21 \times 10^{-2}$ | 39.47 |

TABLE 3

**Some Properties of the Synthetic Oil Samples Prepared in this Study**

| | Synthetic oil sample prepared with the mixed fatty acids of | | |
|---|---|---|---|
| Characteristics | Sunflower oil | Linseed oil | *Ecballium elaterium* seed oil |
| Refractive index, $n_D^{20}$ | 1.4828 | 1.4890 | 1.4879 |
| Acid value | 13.84 | 18.42 | 15.00 |
| Saponification value | 186.08 | 190.66 | 192.42 |
| Iodine value (Woburn) | 143.57 | 172.42 | 166.22 |
| Conjugated dienoic acid (%) | 18.1 | 16.9 | 17.1 |
| Conjugated trienoic acid (%) | Trace | 1.26 | 2.1 |
| Viscosity, cP(25°C) | 186.5 | 522.8 | 472.7 |

TABLE 4

**Drying Times (Set-to-touch) of the Synthetic Oils Prepared in this Study[a] (21,22)**

| Naphthenate driers contents[b] | Drying time (min) of the sample prepared with mixed fatty acids of | | |
|---|---|---|---|
| | Sunflower oil | Linseed oil | *Ecballium elaterium* seed oil |
| 0.5% Pb + 0.03% Co | 210 | 170 | 185 |
| 0.5% Pb + 0.05% Co | 180 | 150 | 160 |
| 0.8% Pb + 0.08% Co | 142 | 130 | 137 |

[a] At 20°C and 70% relative humidity. [b] As metal based on oil.

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