Two-Step Homogeneous Conjugation and Hydrogenation of Methyl Esters of Unsaturated Fatty Acids

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ABSTRACT

A new approach to the selective hydrogenation of unsaturated fatty acids is suggested. It consists of a two step process. The first is a selective conjugation of the double bonds, while the second consists of the hydrogenation reaction using a catalyst which is specific to conjugated systems. Potassium *t*-butoxide was used as a conjugation catalyst and its activity and selectivity were tested at various concentrations, different molar ratios of catalyst to oil, and in various solvents. Phenanthrene chromium tricarbonyl was used as the hydrogenation catalyst and its activity tested at various concentrations, temperatures and in various solvents.

INTRODUCTION

Many investigators associate the poor keeping properties of soybean oil, butter oil, beef tallow and others with their linolenic acid content. The oxidation products of linolenic acid seem to consist mainly of unsaturated aldehydes which cause flavor reversion even when present in quantities of ppm. The high linoleic content of soybean oil may be desirable nutritionally because linoleic acid is an essential fatty acid. Therefore it is important to find an economical process for selective elimination of linolenic acid in soybean oil. As soybean oil is a complex mixture of triglycerides containing various fatty acids, several selectivities are concerned with the hydrogenation of this oil, as other modifications of the oil may occur during the hydrogenation.

Various investigators have studied different approaches to the selective hydrogenation reaction. While one approach was directed toward selective heterogeneous hydrogenation (1), the other was toward selective homogeneous hydrogenation (2,3). Recent work shows that during homogeneous catalytic conjugation of unsaturated fatty acids with arene-chromium carbonyl the shifted double bond becomes

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TABLE I

Conjugation of Linoleate-Linolenate Methyl Ester Mixture (1:1) With Potassium *t*-Butoxide

Solvent[a]	N Catalyst	Moles catalyst per moles esters	Time, min	Linolenate activity	Selectivity
DMF	0.44	1/10	1	57.2	3.9
			4	61.5	2.4
			15	64.2	2.1
DMF	0.47[b]	1/10	1	38.8	3.2
			4	49.1	4.0
			15	56.0	3.5
DMF	0.47[b]	1/15	15	13.6	0.2
DMF	0.88	1/10	1	27.2	2.5
			4	50.0	3.3
			15	57.6	2.6
DMF	0.88	1/5	1	57.5	2.8
			4	68.2	1.6
			15	73.7	1.1
DMSO	0.3	1/10	1	60.1	0.9
			4	60.0	0.8
			15	59.4	0.7
DMSO	0.3	1/20	1	47.6	4.9
			4	50.0	2.9
			15	50.7	3.3
DMSO	0.1	1/10	15	15.0	4.6
Et_2O	0.3	1/10	15	0	---
Dioxane	0.3	1/10	15	0	---
DME	0.3	1/10	15	12.6	16.8
Tetraglyme	0.4	1/10	1	45.2	16.5
			4	62.2	1.7
			15	68.8	1.3
Tetraglyme	0.3	1/20	15	0	---
Tetraglyme	0.2	1/10	1	25.2	∞
			4	31.4	∞
			15	31.1	∞

[a]DMSO = dimethyl sulfoxide, Et_2O = diethyl ether, DME = dimethoxyethane, tetraglyme = tetraethyleneglycol dimethyl ether, and DMF = dimethylformamide.

[b]Catalyst was K,*t*-BuOH; all other catalysts were Fluka catalysts.

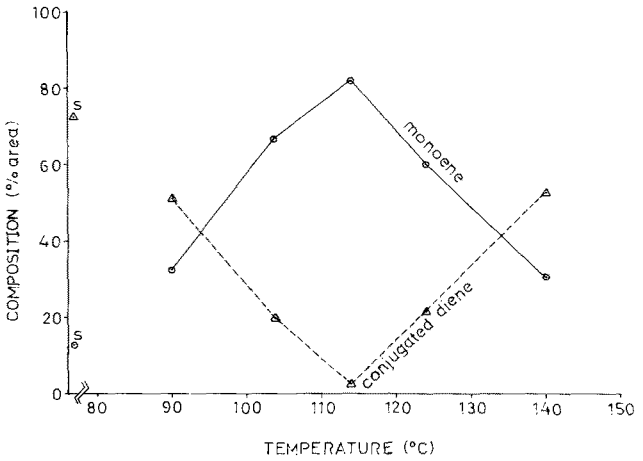

FIG. 1. Hydrogenation of conjugated safflower methyl esters in isopropyl alcohol at various temperatures. Only the amounts of conjugated dienes and monoenes is shown at the end of 1 hr of the reaction (80 mg ph-Cr(CO)$_3$ 3 g esters, 30 ml solvent). S indicates the amounts present in the starting material.

trans, but that the finally hydrogenated product has 90-95% *cis* configuration (2,3).

In this investigation we proposed to conjugate linolenic acid selectively without conjugating linoleic acid, and to hydrogenate the conjugated acid selectively under mild conditions. This report describes the conjugation of linoleate-linolenate methyl esters by potassium *t*-butoxide and the hydrogenation of methyl esters of conjugated fatty acids by phenanthrene chromium tricarbonyl complexes.

EXPERIMENTAL PROCEDURES

Materials and Methods

Potassium *t*-butoxide was either the practical grade of Fluka or was prepared by the reaction of potassium in excess *t*-butyl alcohol. After removal of excess alcohol by distillation, titration of catalyst solution in various solvents showed that some complexing of the catalyst with excess *t*-butyl alcohol had occurred (in a ratio of ca. 4:1).

Methyl esters of fatty acid mixtures were prepared by conventional methods (4). Immediately before use the methyl esters for conjugation were passed through an active basic aluminum oxide column. For hydrogenation, methyl esters of safflower oil were fully conjugated with excess potassium *t*-butoxide in dimethylformamide (DMF). The conjugated methyl esters were distilled at reduced pressure and passed through a basic aluminum oxide column.

Phenanthrene chromium tricarbonyl was prepared according to a published general procedure (5). All solvents were distilled immediately before use.

Reactions were monitored with a dual-column Packard gas chromatograph, as described elsewhere (6).

Conjugation

The starting material for these reactions was a mixture of linseed methyl esters and safflower methyl esters (6:4), that contains a ca. 1:1 ratio of methyl linoleate to methyl linolenate.

The methyl ester mixture (0.73 g, 0.0025 mole) was placed in a 25 ml round-bottom flask, equipped with a rubber septum over the neck and a glass tube side arm. Throughout the reaction an atmosphere of nitrogen was maintained. The catalyst solution was introduced through the rubber septum from a syringe. The reaction mixture was shaken quickly. Samples were withdrawn with a second syringe and injected into a small test tube containing 1 ml water to quench the reaction. The product was extracted into cyclohexane for injection into the gas liquid chromatography (GLC) apparatus.

Hydrogenation

The apparatus consisted of a 60 ml Carius Tube (7), equipped with a rectilinearly activated Teflon stirrer and enclosed in a stirred glycerol bath.

The catalyst was introduced into the Carius Tube with the aid of 10 ml solvent, followed by the methyl esters in 20 ml solvent. The apparatus was flushed three times with hydrogen, each time introducing the gas to 500 psi and then evacuating to 50 psi. The bath was heated to the desired temperature without stirring at 100 psi hydrogen pressure (.75-1 hr required). Hydrogen was then introduced to 500 psi, and stirring was then begun at a rate of one stroke per second. At the end of the reaction, the glycerol was removed from the bath, the apparatus was allowed to cool to room temperature (1-1.5 hr required), and the hydrogen was removed.

RESULTS AND DISCUSSION

In conjugations with potassium *t*-butoxide we have examined the effect of the source of catalyst, concentration of catalyst solution, molar ratio of catalyst to mixture of methyl esters, and time of reaction and solvent.

Results are expressed in terms of activity and selectivity as follows:

$$\text{conjugation activity (linolenate)} = \frac{\text{(18:3 conj) time } t}{\text{(18:3) 0 time}} \times 100$$

$$\text{conjugation activity (linoleate)} = \frac{\text{(18:2 conj) time } t}{\text{(18:2) 0 time}} \times 100 =$$

$$\frac{\text{(18:2) 0 time - (18:2) time } t}{\text{(18:2) 0 time}} \times 100$$

$$\text{conjugation selectivity} = \frac{\text{activity (linolenate)}}{\text{activity (linoleate)}}$$

The amount of conjugated linoleate at time *t* is

TABLE II

Hydrogenation of Conjugated Safflower Methyl Esters in Isopropyl Alcohol[a]

Methyl ester mixture	Composition of esters					
	16:0	18:0	18:1	18:2	18:2 conj.	Other
Starting material	8.3	2.4	13.8	2.3	72.1	1.1
Product 40 mg catalyst per 3.0 g esters (molar ratio 1:80)	7.5	2.6	16.4	3.6	66.9	3.0
Product 80 mg catalyst per 3.0 g esters (molar ratio 1:40)	7.5	2.0	83.0	4.0	3.5	0
Product 160 mg catalyst per 3.0 g esters (molar ratio 1:20)	6.9	1.9	71.9	7.8	7.8	3.7

[a]At 114 C for 1 hr.

TABLE III

Hydrogenation of Conjugated Safflower Methyl Esters[a,b]

Methyl ester mixture	Composition of esters				
	16:0	18:0	18:1	18:2	18:2 conj.
Starting material	8.0	1.3	17.4	Traces	73.3
Methanol	8.0	1.8	25.3	Traces	64.9
Ethanol	8.6	3.1	53.1	2.5	32.7
n-Butanol	8.3	2.4	67.9	1.7	19.7
n-Octanol	9.0	3.3	23.8	1.2	62.5
Methoxyethanol	8.7	2.9	28.4	Traces	60.0
Isopropyl alcohol	7.9	1.2	78.4	3.3	9.3
Cyclohexanol	8.7	2.7	60.5	3.0	25.1
t-Butyl alcohol	7.9	1.8	82.1	0.9	7.3
Acetone	9.7	2.4	26.4	0.9	60.6
Acetonitrile	8.3	1.7	18.0	Traces	71.7
Tetrahydrofuran	9.5	3.2	33.4	1.4	52.6
DMF	8.2	3.6	19.9	Traces	67.5
Triglyme[c]	10.2	2.7	19.9	1.3	65.9
Cyclohexane	8.3	1.1	86.0	3.1	1.4

[a]At 114 C for 1 hr in various solvents.

[b]Eighty milligrams catalyst per 3.0 g esters (molar ratio 1:40).

[c]Triethyleneglycol dimethyl ether.

measured indirectly, because of the fortuitous overlap of the peaks due to unconjugated linolenate and conjugated linoleate in the GLC.

The conjugation results with potassium *t*-butoxide are shown in Table I. As can be seen from Table I, the source of catalyst does not seem to be an important factor. The normality of the catalyst solutions was determined by titration. When comparing reactions at 1:10 molar ratio of catalyst to methyl esters, it was found that the more concentrated solution (0.88 N) led to decreased linolenate activity. This was apparently due to the limited solubility of potassium *t*-butoxide in DMF. Yet when the molar ratio was doubled at constant normality, increased linolenate activity resulted as expected. In general with DMF a maximum selectivity of 2-4 was obtained when linolenate activity approached 50-60%.

Reactions in nonpolar solvents, such as diethyl ether and dioxane, failed. The lack of solubility of catalyst prevented experiments at higher concentrations. With dimethyl sulfoxide (DMSO) the best results were obtained at a catalyst normality of 0.3 N and molar ratio of catalyst to methyl esters of 1:20. At higher molar ratio, linolenate activity was increased but selectivity was completely lost. At a lower catalyst normality activity was greatly decreased, although selectivity was preserved.

However a far superior result was obtained with tetraglyme. Linolenate conjugation of up to 30% was obtained with infinite selectivity (no linoleate conjugation occurred). Based on the relatively high selectivity obtained in tetraglyme, the hydrogenation work proceeded.

Of the known arene-$Cr(CO)_3$ complexes (8), phenanthrene chromium tricarbonyl was used as a hydrogenation catalyst in all the hydrogenation experiments. Initial experiments were directed at the question of optimal temperature of the hydrogenation reaction of the conjugated safflower methyl esters in isopropyl alcohol.

Figure 1 indicates that at temperatures above 114 C the rate of catalyst decomposition became competitive with the rate of homogeneous hydrogenation. However at lower temperatures the reaction proceeded to completion at a decreased rate.

Next the effect of varying catalyst to substrate ratio was investigated (Table II). Halving the molar ratio led to greatly reduced reactivity.

After establishing the optimal conditions in isopropyl alcohol, solvent effect was examined by maintaining the previously established conditions constant (Table III). As can be seen from results presented in Table III, the order of reactivity with alcoholic solvents is as follows: isopropyl alcohol, *t*-butyl alcohol > *n*-butanol, cyclohexanol, ethanol > methoxyethanol, methanol, *n*-octanol. Since cyclohexane was shown to be the most appropriate solvent among those tested, it was investigated further and shown that even after 15 min the reaction was 80% complete.

This work with methyl esters demonstrates that a two step (conjugation-hydrogenation) approach to selective reduction of unsaturated oils might be effective. Furthermore homogeneous hydrogenation reactions with arene-$Cr(CO)_3$ complexes can be carried out at relatively low temperatures. Investigation is being directed toward the search for more active and selective conjugation and hydrogenation catalysts.

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