Conjugation of Polyunsaturated Fats with Dimsylsodium

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ABSTRACT

The conjugation of polyunsaturated fatty esters, including soybean oil, trilinolein, soybean methyl esters, and methyl linolenate and linoleate, with the sodium salt of dimethyl sulfoxide (dimsylsodium) as catalyst has been investigated. Methyl esters are ca. 95% conjugated within 2 hr. Glycerides react more slowly but are similarly conjugated within 24 hr. The glyceride linkages are not destroyed as they would be with aqueous or alcoholic alkali. Highly conjugated oils can thus be prepared.

INTRODUCTION

Recently we investigated new catalysts and procedures to conjugate polyunsaturated vegetable oils without destroying the ester linkages (1,2). Our previous work concerned the activity of group VIII metal compounds. Others have studied the conjugation of linseed oil treated with potassium-*n*-butylate in *n*-butanol (3). The rate of conjugation increased whenever dimethyl sulfoxide (DMSO), N,N-dimethylformamide or tetramethylurea was added. Also, the rate of conjugation of linseed methyl esters, if treated with potassium *t*-butylate in diethyl ether, increased when dimethylformamide, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether or tetraethylene glycol dimethyl ether was added as cosolvent (4). The extent of reaction was estimated by comparing extinction coefficients at 234 or 267 nm, or both, of diluted reaction samples after various reaction times. Since products were not further analyzed, no estimation could be made of the various conjugated isomers or whether the ester linkages were retained.

Double bond isomerization of α-olefins catalyzed by dimsylsodium and dimsylpotassium in DMSO was studied by Asinger et al. (5). These investigators found that the dimsyl anion was more active than potassium *t*-butylate in DMSO.

We wish to report a novel method for preparing conjugated soybean oil and a number of polyunsaturated fatty esters at room temperature with dimsylsodium in DMSO alone and in DMSO and other solvents.

EXPERIMENTAL PROCEDURES

Materials

DMSO, tetrahydrofuran, pentane-hexane and bis(2-ethoxyethyl)ether were purchased commercially and purified by distillation. DMSO and pentane-hexane were stored over a molecular sieve (Linde-type 4A, 1/8 in. pellets). The other solvents were stored over sodium. Sodium hydride (Alfa Inorganics) came as a 52% dispersion in mineral oil. Triphenylmethane (TPM, Aldrich) was used as received. Methyl linoleate and linolenate and trilinolein were procured from The Hormel Institute and were 99+% pure. Soybean oil was passed through an alumina column to reduce its acid number to 0.025. Gas chromatographic (GC) analyses of the soybean methyl esters showed: 11% palmitate, 4% stearate, 24% oleate, 55% linoleate and 6% linolenate.

Methods

Dimsylsodium was prepared according to the method of Corey and Chaykovsky (6). Weighings were conducted in a glove box under an atmosphere of dry nitrogen. The sodium hydride was weighed and washed several times with pentane-hexane. The washed hydride was then rinsed with DMSO into a "No-Air" two-necked reaction vessel (Ace Glass) and diluted to 100 ml with additional DMSO. The vessel was sealed and removed from the dry box. The vessel was connected to a vacuum system and partially evacuated. After standing for 18-20 hr, the hydrogen evolution ceased and a grey precipitate settled. Portions (5 ml) of the supernatant solution were titrated with standard acid to determine the normality. Solutions were made to contain ca. 0.05-0.2 N dimsylsodium. Adding a small amount of TPM gives the characteristic deep red of the TPM carbanion; the color serves as a convenient test for the reagent's activity (7).

Small scale conjugation reactions were conducted by first weighing the oil or methyl esters into 10 ml serum vials. Each vial was connected to a vacuum system, alternately evacuated and filled with N_2 several times and finally sealed with a rubber septum. Cosolvents, if used, and dimsylsodium reagent were added with a syringe. The reactions were conducted at room temperature. Glycerides were converted to methyl esters by quenching the reaction by injection of methanol and allowing the mixture to stand several hours. Products were isolated by taking up in hexane, water-partitioning four times, drying and stripping in vacuo.

Larger batches of soybean oil were isomerized and then analyzed to demonstrate that alcohols or acids did not form. Typically, 20 g soybean oil was isomerized at room temperature for 24 hr with 0.13 N dimsylsodium in 70 ml DMSO and 50 ml tetrahydrofuran (THF). Then 2 ml acetic

TABLE I

Conjugation Catalyzed by Dimsylsodium (Room Temperature)

No.	Substrate and concentration		Dimsylsodium concentration	Solvent	Per cent nonconjugated diene reacted, hr 0.5	1	2	6	24
1	Soybean methyl esters	(0.3 M)	0.08 M	1:3, DMSO[a]/bis(2-ethoxyethyl ether)	73	98	98	97	99
2	Methyl linoleate	(0.3 M)	0.08 M	1:3, DMSO/bis(2-ethoxyethyl ether)	79	95	98	99	99
3	Methyl linoleate	(0.3 M)	0.05 M	1:1, DMSO/THF	95	96	96	98	98
4	Soybean oil	(0.1 M)	0.05 M	1:1, DMSO/THF	22	29	49	76	98
5	Trilinolein	(0.15 M)	0.12 M	1:1, DMSO/THF	22	29	42	79	95
6	Soybean oil	(0.15 M)	0.12 M	1:1, DMSO/THF	24	33	55	88	95

[a]DMSO = dimethyl sulfoxide; THF = tetrahydrofuran.

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acid were added and the mixture was poured onto ice. The oil was isolated as described above. Analysis for alcohol groups (8) showed 0.20 meq/g. Titration indicated 0.23 meq acid per gram. Thus alcohol and acid levels were negligible. IR showed no band at 1020 cm^{-1} indicating no sulfoxide. GC of derived methyl esters showed 95% isomerization.

The products were analyzed on a 9 ft x 1/8 in. 10% EGSS-X column in a Model 1625C Varian gas chromatograph. The double bond positions of the highly conjugated samples were determined by the ozonolysis procedure of Kleiman et al. (9). Application of this technique to a sample of pure methyl 9,11-*trans,trans*-octadecadienoate confirmed its validity.

IR spectra were determined with a Beckman IR-8 spectrophotometer.

Solutions of dimsylsodium in DMSO are not stable; they decompose slowly at room temperatures and more rapidly at elevated temperatures (10). The reagent's normality had to be measured before each use. All isomerizations reported here were carried out at room temperature.

RESULTS AND DISCUSSION

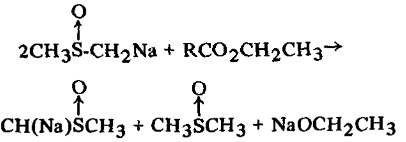
Methyl linoleate and methyl esters of soybean oil were readily conjugated (Table I, nos. 1, 2 and 3). Soybean oil, even though purified, reacted more slowly than methyl linoleate (compare Table I, nos. 3 and 4). Pure trilinolein conjugated at about the same rate as soybean oil (Table I, *nos. 5 and 6*).

The slower rates of conjugation of the glyceride, compared to the methyl esters, may result from a stepwise isomerization of each of the hydrocarbon chains of the glyceride. A carbanion formed on one of the hydrocarbon chains would presumably inhibit formation of a carbanion on another hydrocarbon chain of the same glyceride, and result in the slower reaction noted.

Positions of the double bonds in samples of 99% conjugated dienoates from methyl linoleate were determined by ozonolysis, reduction and GC (9). These analyses showed that the double bonds were equally divided between the 9,11 and 10,12 positions. Only a small amount (ca. 2%) of one other positional isomer (8,10-) was detected.

The conjugated double bonds are principally in the *cis,trans*-configuration with smaller amounts of *cis,cis*-conjugated dienes. Only small amounts of *trans,trans*-conjugated dienes are formed. When soybean oil is isomerized, only traces of conjugated trienes are formed, even though the oil contained ca. 6% linolenate. When pure methyl linolenate is isomerized at 25 C, the ratio of conjugated diene to conjugated triene is ca. 9:1, and conjugation was as rapid as when methyl linoleate was isomerized.

Corey and Chaykovsky (11) reported the reaction of dimsyl ion with certain saturated esters to produce methylsulfinyl ketones:



$$2CH_3\overset{O}{\overset{\uparrow}{S}}\text{-}CH_2Na + RCO_2CH_2CH_3 \rightarrow RCOCH(Na)\overset{O}{\overset{\uparrow}{S}}CH_3 + CH_3\overset{O}{\overset{\uparrow}{S}}CH_3 + NaOCH_2CH_3$$

Although we used only catalytic amounts of dimsyl ion in our reactions, methylsulfinyl ketones may be formed as a byproduct. We examined our products for evidence of methylsulfinyl ketones by IR analysis. The spectra of our reaction product had no band near 1020 cm^{-1} for the methylsulfinyl group. We investigated the sensitivity of the IR method for methylsulfinyl. Heptadecyl methylsulfinyl ketone was prepared by reaction of dimsylsodium with methyl stearate and admixed with methyl stearate. Mixtures containing <4% w/w of the methylsulfinyl ketone did not have a detectable IR band at 1020 cm^{-1}. We also established that polyunsaturated methylsulfinyl ketone could be produced from methyl linoleate by reaction with dimsylsodium. In an experiment, 3 mol dimsylsodium were used per mole of methyl linoleate. IR spectra and thin layer chromatography of the reaction mixture gave clear evidence for a low yield of ketone.

Retention of the glyceride linkage in oils was further established by treating a large quantity of soybean oil with dimsylsodium in THF-DMSO. GC of the methyl esters of the isomerized oil showed 95% of the linoleate had become conjugated. IR indicated no sulfoxide band at 1020 cm^{-1}. Analysis for acid and alcohol groups showed that only negligible hydrolysis occurred.

A useful method has been described for preparing conjugated esters, particularly glycerides, on a laboratory scale. Conjugation is complete in a few hours at room temperature without the formation of appreciable byproducts.

ACKNOWLEDGMENT

Spectra were done by G.E. McManis.

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[Received September 19, 1972]