Hydrogenation of Conjugated Fatty Acids with Hydrazine[1]

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Abstract

The reduction of α- and β-eleostearic acids with hydrazine has been studied. GLC analysis of the products coupled with oxidative degradation using permanganate-periodate reagent showed an initial attack mainly at the 9,10 and 13,14 bonds in the triene without change in configuration. The method should be useful in structural studies on conjugated fatty acids.

Introduction

AYLWARD AND CO-WORKERS (2–7) studied the hydrogenation of a number of unsaturated fatty acids and other ethylenic compounds using hydrazine. Further studies by Rao (14) and Scholfield (16) showed that no shifts in double bond position occurred during reductions with hydrazine. More recently Dutton et al. (13) have proposed hydrazine reduction of linolenic acid for the production of C_9, C_{12} and C_{15} dicarboxylic acids by oxidation of the resultant monoethenoid acids. Most of the studies on hydrazine reduction have been on methylene interrupted systems although Aylward and Rao (4) also studied the reduction of eleostearic acid using iodine values, UV and IR spectra and melting points for analysis of the products. These analytical results did not permit a conclusive evaluation of hydrazine reduction of conjugated systems.

The present study used GLC and oxidative scission with permanganate-periodate to follow the course of hydrazine reduction of conjugated fatty acids and to determine the resulting products.

Materials and Methods

The α- and β-eleostearic acids were prepared from tung oil by recrystallization of the fatty acids according to the procedure outlined by Crombie and Jacklin (12). The conjugated trienoic acids were found to be 95% pure by GLC; the methyl eleostearate was a mixture of α- and β-isomers in the ratio of 81:19.

The reductions were carried out by adding the fatty acids to a 10% solution of hydrazine in a water-ethanol mixture. Molar ratios of reactants varied from 1:3–1:10. The reactions were carried out at 50C using a magnetic stirrer; excess hydrazine was removed at the end of the reaction time by washing with dilute hydrochloric acid.

The mixture of hydrogenated acids was converted to methyl esters with 2% H_2SO_4-methanol at room temp for 16 hr under a nitrogen atmosphere.

A conventional GLC apparatus with T/C detector was used for analyses of the methyl esters. The column was 8 ft x 3/16 in. OD copper containing *o*-phthalic ethylene glycol polyester (10) on 60–80 mesh C-22 acid washed firebrick (1:4.5 w/w).

Permanganate-periodate oxidations were carried out according to the procedure of von Rudloff (15) as modified by Youngs (18) and the scission products were analyzed by GLC of the methyl esters (11).

Results

GLC analysis of the partially hydrogenated α- and β-eleostearic acids (Fig. 1) showed peaks corresponding in emergence times to methyl stearate (peak 1), octadecenoate (peak 2), conjugated octadecadienoates (peaks 4,5), conjugated octadecatrienoates (peaks 6, 7), and a trace of unconjugated octadecadienoate (peak 3). The partial reduction of α-eleostearic acid gave two conjugated dienoic acids (Fig. 1A); the first emerging peak (peak 6) was assigned a *cis,trans* and the second (peak 7) a *trans,trans* configuration. The similar reduction of the β-eleostearic acid gave only one conjugated dienoic acid, the *trans,trans* isomer (Fig. 1B).

The mixture of acids in the partially reduced products of α- and β-eleostearic acid (A and B respectively) were oxidized with permanganate-periodate and the resultant dicarboxylic acids were analyzed by GLC. The results (Table I) showed that in both products C_9, C_{11} and C_{13} were the major dicarboxylic acids.

Sufficient quantities of the partially reduced β-eleostearate were separated on a column of silicone grease on Celite 545 to obtain individual samples of the dienoate and the mixture of stearate and monoenoate. Each sample was oxidized and the results are given in Table II. The conjugated dienoate gave rise to equimolar proportions of C_9 and C_{11} dicarboxylic acids whereas the monoethenoid gave approx a 1:2:1 ratio of C_9, C_{11} and C_{13} dicarboxylic acids.

The course of the hydrazine reduction of β-eleostearic acid was followed by GLC analysis using methyl palmitate as an internal standard. The reduction was carried out at 50C with a molar ratio of 1:6 and small samples were removed at time intervals up

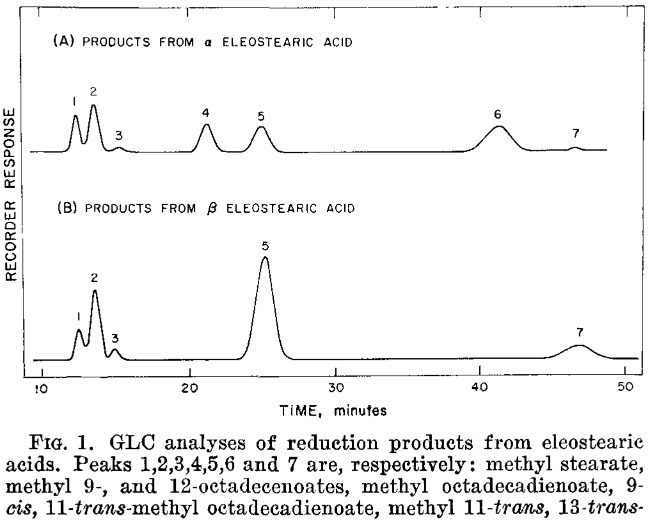

FIG. 1. GLC analyses of reduction products from eleostearic acids. Peaks 1,2,3,4,5,6 and 7 are, respectively: methyl stearate, methyl 9-, and 12-octadecenoates, methyl octadecadienoate, 9-*cis*, 11-*trans*-methyl octadecadienoate, methyl 11-*trans*, 13-*trans*-octadecadienoate, methyl α-eleostearate and methyl β-eleostearate.

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TABLE I

Dicarboxylic Acids Produced by Oxidation of Partially Reduced α- and β-Eleostearic Acids

Reduced product	Carbon number of dicarboxylic acid						
	Mole %	8	9	10	11	12	13
α-Eleostearic acid (A)............		1.8	57.0	0.9	32.8	....	7.5
β-Eleostearic acid (B)...........		2.4	61.5	1.6	27.4	....	7.1

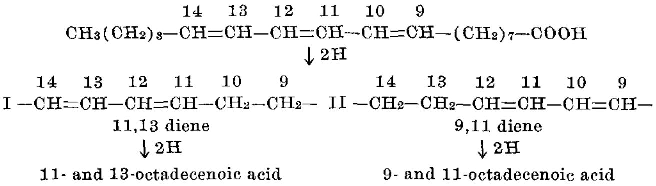
to 160 min. Results show in Figure 2 as area ratios relative to methyl palmitate.

Discussion

Boeseken (8,9) studied the catalytic hydrogenation of conjugated trienes and proposed that the reduction proceeded by a 1,6 addition to the triene followed by a 1,4 addition to the diene. The isolation of vaccenic acid (*trans*,11-octadecenoic acid) in good yield from the hydrogenation of tung oil (9) was offered as proof for the mechanism. Allen and Kiess (1) hydrogenated methyl eleostearate catalytically and found equal molar proportions of 9-,10-,11-,12- and 13-octadecenoates. They concluded that the first mole of hydrogen added equally at all possible positions and that double bond shifts also occurred resulting in six different dienes. The addition of the second mole of hydrogen produced the five monoenoic esters. These workers suggested that the double bond shifts were confined to the six carbon atoms which made up the conjugated triene structure.

The data in the present study with hydrazine reduction confirm the previous findings (14,16) that no significant shift in double bond positions occurs during the reaction. The oxidation of the partially reduced trienes (Table I) and of the isolated dienes and monoenes (Table II) show C_9, C_{11} and C_{13} dicarboxylic acids as major products.

The GLC data (Fig. 1) show only trace amt of the unconjugated diene acid produced during hydrogenation. This acid would arise from reduction of the 11,12 bond in the conjugated triene. Hence the reduction must occur mainly at the 9,11 and 13,14 bonds in the conjugated triene structure according to the following sequence:



$$\begin{array}{c}
CH_3(CH_2)_3-\overset{14}{C}H=\overset{13}{C}H-\overset{12}{C}H=\overset{11}{C}H-\overset{10}{C}H=\overset{9}{C}H-(CH_2)_7-COOH \\
\downarrow 2H
\end{array}$$

$$\begin{array}{cc}
\text{I } -\overset{14}{C}H=\overset{13}{C}H-\overset{12}{C}H=\overset{11}{C}H-\overset{10}{C}H_2-\overset{9}{C}H_2- & \text{II } -\overset{14}{C}H_2-\overset{13}{C}H_2-\overset{12}{C}H=\overset{11}{C}H-\overset{10}{C}H=\overset{9}{C}H- \\
\text{11,13 diene} & \text{9,11 diene} \\
\downarrow 2H & \downarrow 2H \\
\text{11- and 13-octadecenoic acid} & \text{9- and 11-octadecenoic acid}
\end{array}$$

In agreement with this sequence reduction of the all-*trans* system (β-eleostearic acid) gave equal proportions of the 11,13 and 9,11 conjugated dienes as shown by the equal proportions of 9 and 11 dicarboxylic acids produced by oxidation of the isolated conjugated dienoic acid (Table II). Also, the isolated monoenoic acids with double bonds in the 9,11 and 13 positions show a ratio of approx 1:2:1, respectively. The results in Table II could suggest that less reduction of the 9,10 bond occurred in the dienes, but values of similar magnitude were not found for reduction of the trienes. In the same manner, the data in Table I suggest that the *cis* bond at the 9 position in the α-eleostearic is hydrogenated somewhat more readily than the corresponding *trans* bond in the β-eleostearic acid. Thus, the difference (ca. 5%) in yield of C_9 dicarboxylic acids derived from the *cis* double bond in α-eleostearic (Table I) is of the same order as that between C_9 and C_{13} dicarboxylic acids (Table II) on reduction of the C_9 and C_{13} double bond of dienes to monoenes.

TABLE II

Oxidation Products of Conjugated Diethenoid and Monoethenoid Acids Isolated from Reduced β-Eleostearic Acid

	Number of C atoms in dicarboxylic acid						
	Mole %	8	9	10	11	12	13
Diethenoid...............................		1.3	49.5	0.9	48.3	....	....
Monoethenoid...........................		trace	28.7	0.9	46.7	....	23.7

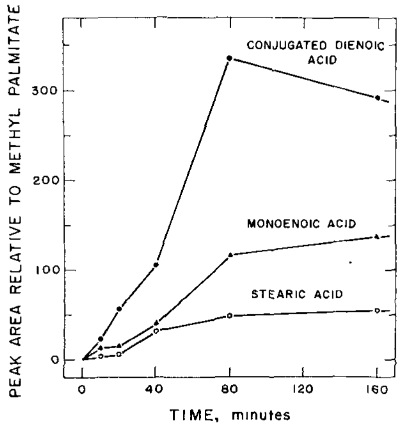


FIG. 2. Production of saturated, monoene and conjugated diene acids by hydrazine reduction.

Figure 1 shows that the *cis* bond configuration is retained in the reduction of triene to diene. The reduction of the 13,14 bond in α-eleostearic acid would give rise to 9-*cis*,11-*trans*-octadecadienoic acid (peak 4), whereas reduction of the 9,10 bond would yield the 11-*trans*,13-*trans*-octadecadienoic acid (peak 5). Since β-eleostearic acid possesses an all-*trans* structure, only one diene peak results on the GLC chart. The course of the reaction (Fig. 2) followed by GLC using methyl palmitate as an internal standard, shows a rapid increase in formation of the conjugated dienoic acids to a max value at 80 min followed by a gradual decrease.

The partial reduction of conjugated trienoic acids with hydrazine could be a useful technique for structural studies. The initial attack at the bond on either end of the system produces a conjugated dienoic product in which there is no shift in double bond position and no apparent conversion of *cis* to *trans* structures. Further studies would be required to determine equal attack at all unsaturated systems.

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