Selective Hydrogenation of the Cyclopropene Acid Groups in Cottonseed Oil

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Abstract

The cyclopropene acid groups in cottonseed oil can be modified by a light hydrogenation which will not produce large amounts of *trans* isomers or lower the iodine value to a significant extent. Optimum conditions, as indicated by this investigation, are 105–115C, 20 psig hydrogen pressure, 0.1% electrolytic nickel as catalyst, and a low hydrogen-dispersion rate.

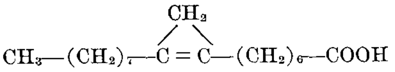
Under milder conditions of hydrogenation the elimination of the cyclopropenes was accompanied by a lower formation of *trans* isomers and a lower hydrogenation of noncyclopropenes, but the time required increased.

In one hydrogenation carried out with commercial nickel catalyst, the 0.4% of malvalic acid groups in the cottonseed oil was hydrogenated completely whereas the iodine value was reduced by only 1.7 units and only 2.1% of *trans* isomers was formed.

Winterization of cottonseed oils which had been hydrogenated to the point of eliminating their response to the Halphen test and in which only small amounts of saturated acid groups and *trans* isomers had been formed gave yields equal to or better than those of the original oil. Hydrogenation actually increased the ease of winterization.

Introduction

THE HALPHEN TEST (1,2) has long been used as a qualitative indication of the presence of cottonseed oil in other oils. About ten years ago the cyclopropene group was shown to be responsible for the color developed in the Halphen test (3). In 1959 it was shown that the cyclopropene acid group occurs in the component fatty acids of cottonseed oil as malvalic acid (8),



$$CH_3—(CH_2)_7—\overset{\overset{CH_2}{/\ \ \backslash}}{C=C}—(CH_2)_6—COOH$$

and more recently sterculic acid, a C_{19} homolog of malvalic acid, has been shown also to occur in cottonseed oil (9).

It has been demonstrated that hydrogenation of cottonseed oil eliminates its response to the Halphen test (4,6,7). It has also been shown that hydrogenation of the cyclopropene group to the cyclopropane nullifies the ability of this group to produce undesirable effects in eggs (5). However, only limited information is available on the amount of hydrogenation required to destroy the response of cottonseed oil or other vegetable oils to the Halphen test. Lowenstein (4) claimed that a negative test was obtained on hydrogenating cottonseed oils to an iodine value of 90–102 under unspecified conditions. Moore et al. (7) reported on one experiment but failed to mention the iodine value of the original oil. Apparently an iodine value drop of at least 7 units and probably more than 10 units was required.

One objective of the investigation was to establish the conditions which would be most selective in hydrogenating the cyclopropene acid groups rather than other unsaturated acid groups.

Another objective was to determine whether or not a cottonseed oil in which the cyclopropene acid groups had been eliminated by hydrogenation could be winterized to produce a salad oil in satisfactory yield.

Experimental Section

Materials

The oil used throughout this investigation was a commercially refined and bleached cottonseed oil with an iodine value of 109.1 and a malvalic acid content of 0.4%, as determined by the Halphen test and the use of a colorimeter.

Two types of catalyst were used. The nickel catalyst, in all except one of the hydrogenations, was a commercial product (Chemetron Corporation) of the supported type prepared by electrolytic precipitation and dry reduction. The other catalyst (Baker and Company Inc.) consisted of 10% by weight of palladium supported on carbon.

Tank hydrogen from a commercial supplier was used as received.

Stainless Steel Hydrogenation Apparatus

Most of the hydrogenations were conducted in a dead-end, 2,000-ml, medium-pressure apparatus (Parr Instrument Company). The bomb was electrically heated, and all parts in contact with the oil were of stainless steel. The effectiveness of the original stirrer which was provided with the apparatus was augmented by the addition of a fixed baffle plate and an additional pair of flat agitator blades. The amount of oil was such that a portion of the flat blades extended above the surface of the oil. To make a run, 500 g of cottonseed oil and the desired amount of catalyst were placed in the stainless steel bomb. A pump attached to the bomb maintained a vacuum over the oil until the operating temperature was reached, usually in about 2 hr. At a steady temperature, hydrogen was introduced rapidly, and the pressure was raised to the desired level. Both the temperature and hydrogen pressure were carefully maintained for the duration of the run. Fifty-ml samples, which were used in determining the point at which the Halphen test became negative by visual examination, were removed from the hydrogenator at five-minute intervals without stopping the hydrogenation reaction. The iodine value and percentage of *trans* bonds were determined on the first sample with a negative Halphen test.

Pressure, temperature, and catalyst concentration were the prime variables in this phase of the investigation. In one of the hydrogenations, palladium-on-carbon was used as catalyst. The agitation rate was kept constant.

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Hydrogenations with 0.1% nickel as catalyst were carried out at three hydrogen pressures: 3, 20, and 40 psig. At each pressure, hydrogenations were made at different temperatures.

To show the effect of varying the concentration of catalyst, hydrogenations were carried out by using 0.05, 0.1, and 0.2% nickel at constant temperature (105C) and hydrogen pressure (20 psig). The comparative hydrogenation, with 0.008% of palladium as the catalyst, was conducted to show the effect of a different type of catalyst.

Glass Hydrogenation Apparatus

A number of hydrogenations were conducted in a 2-liter, 3-neck, round-bottom, glass flask whose sides had been creased vertically at four equally-spaced points to minimize swirling of the oil. A paddle-type stirrer with Teflon blade was inserted in the central neck of the flask and connected through a leak-proof, magnetic coupling to the stirring motor. In some experiments stirring was accomplished through the use of a Teflon-coated, magnetic bar driven by a conventional magnetic stirrer.

To conduct a run, 300 g of oil were placed in the flask, the catalyst was added, the head space of the flask was flushed with hydrogen, the oil and catalyst were quickly heated to the operating temperature, and the stirrer was started. The hydrogen pressure was maintained at just slightly above atmospheric.

In several runs a mixture of hydrogen and nitrogen was used instead of pure hydrogen.

The winterization procedure was patterned after that used in the industrial processing of cottonseed oil. The temperature of each oil sample was lowered slowly over a period of 6 hr from 85F to 55F and held at this temperature for 16 hr. The oil was then slowly cooled to 42F, where it was maintained for 16 hr prior to filtering. Filtration by gravity took place over an additional 24-hr period at this same temperature.

Results and Discussion

Hydrogenations in Stainless Steel Apparatus

To establish the effect of temperature and pressure on the amount of hydrogenation and the time required to eliminate the Halphen response from the cottonseed oil, a series of 15 hydrogenations was conducted with a catalyst concentration of 0.1% electrolytic nickel and a constant rate of hydrogen dispersion (Figures 1 and 2). The percentage of *trans* isomers formed was always low; the lowest was 1.3% for the hydrogenation conducted at 99C and 20 psig. As expected, the percentage of *trans* isomers formed was reduced slightly by an increase in pressure. For a given pressure, the percentage of *trans* isomers increased as the temperature increased, and the rate of increase accelerated as the temperature passed about 115C. The greatest amount of *trans* isomers found was about 3.6%.

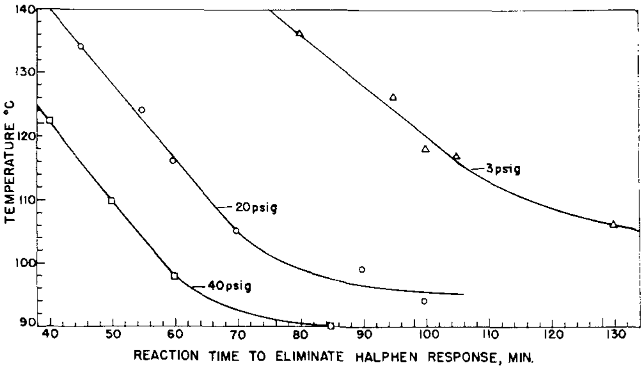

FIG. 1. Reaction time required to eliminate the Halphen response of cottonseed oil by hydrogenation at various temperatures at three different pressures.

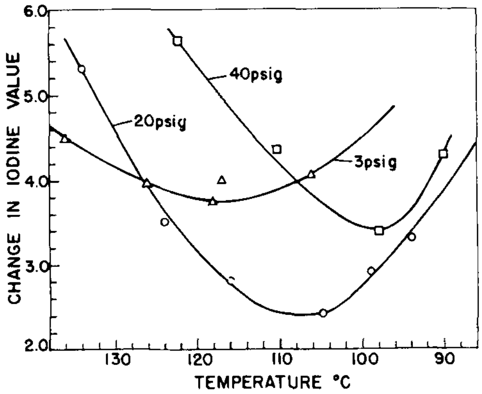

FIG. 2. Reduction in iodine value during hydrogenation of cottonseed oil at various temperatures and three different pressures to eliminate the Halphen response.

As shown in Figure 1, the rate of hydrogenation at a given pressure slowed markedly below a certain temperature. This trend followed the same pattern for each hydrogen pressure. The temperature at which the rate began to change (the breakpoint of the curve) varied inversely with the pressure. Figure 1 also indicates that the effect of pressure decreased rapidly as the pressure increased. At a temperature of about 126C, an increase in pressure from 3 to 20 psig almost halved the time required to obtain a negative Halphen test; an increase from 20 to 40 psig reduced the time required by only about one-quarter.

The effect of temperature and pressure on the degree of hydrogenation required is shown in Figure 2. For each pressure the minimum of the curve is located at or near the breakpoint of the corresponding curve shown in Figure 1. This indicates that, for each pressure, the change in iodine value can be held to a minimum if the temperature is at or slightly above that of the breakpoint of the curve in Figure 1.

The effect of type and concentration of catalyst is illustrated in Table I. The concentration had a marked effect on the length of time required to obtain a negative Halphen test; however both raising and lowering the concentration from 0.1% resulted in greater iodine value reduction. The variation in catalyst concentration caused a change in the formation of *trans* isomers only in the case of the 20 psig hydrogenation, and that change was relatively small. The same effect on the time required for a negative Halphen test caused by the change of catalyst concentration could be achieved by varying the hydrogen pressure. Hydrogenation with a palladium catalyst, even at a very low concentration of the metal,

TABLE I

Effect of Type and Concentration of Catalyst on Time Required to Eliminate Halphen Response from Cottonseed Oil[a]

Catalyst type	Catalyst conc., %	Elapsed time, min	Decrease in iodine value	*trans* Isomers formed, %
Electrolytic nickel	0.05	125	4.0	2.2
Electrolytic nickel	0.10	70	2.5	1.5
Electrolytic nickel	0.20	50	3.5	2.2
Palladium-on-carbon	0.008	40	6.8	9.0

[a] Hydrogen-dispersion-rate constant, 105C, 20 psig H_2 pressure.

produced an oil with a lower iodine value and a higher percentage of *trans* isomers than was obtained in any of the runs with nickel.

The optimum conditions for destroying the cyclopropene acid groups by hydrogenation, as indicated by this series of experiments, were 0.1% nickel, 105–115C, and 20 psig of hydrogen pressure. A temperature range of 97–116C could be used without causing an excessive reduction of iodine value or formation of an objectionable amount of *trans* isomers.

As a final verification of the preferred conditions, 1,000 g of oil were hydrogenated by using 113.5C, 0.1% nickel, and 20 psig hydrogen pressure. Two samples of this oil were withdrawn, one after 65 min and the other after 70 min. After 65 min a slight positive Halphen test was found whereas the 70-min sample gave a negative test. Since the curve from Figure 1 indicated that destruction of the Halphen positive material should have been completed in 63 min, the time may vary somewhat with batch size or may be influenced by the withdrawal of samples during the run. The iodine value of this treated oil was lowered by 3.2 units in 70 min. Only 1.8% *trans* isomers was formed.

Hydrogenations in Glass Apparatus

The optimum conditions for destroying cyclopropene acid groups in preference to hydrogenating other unsaturated acid groups, as determined with the stainless steel apparatus, were used for some hydrogenations in the glass apparatus. The results reconfirmed the well-established fact that hydrogenation is a complex reaction and that similar operating conditions do not produce quite the same results in different hydrogenators. However, by some modification of the operating conditions, the end-products obtained in the glass apparatus could be made equal to or better than those obtained in the stainless steel apparatus.

As least some operating variables did not change the relative reactivity of the cyclopropene acid groups compared with that of the linoleoyl groups. A series of hydrogenations was conducted in which only the rate of agitation was varied. The constants were a catalyst concentration of 0.1% nickel and a reaction temperature of 120C. The time required to reduce the iodine value approximately 2 units, which destroyed the response to the Halphen test in all cases, ranged from 210 min at 300 rpm to 60 min at 500 rpm. The exact decrease in iodine value during the latter hydrogenation was 2.1 units, and the amount of *trans* isomers formed was 1.2%.

The use of mixtures of hydrogen and nitrogen instead of pure hydrogen was tried with the two-fold idea that the technique might increase the preferential hydrogenation of the cyclopropene acid groups and might be employed in plant-scale hydrogenations where slowing of the hydrogenation rate by other means might be inconvenient.

In the first attempts to use a mixture of hydrogen and nitrogen, volume percentages of hydrogen well below 50 were employed but these gave very slow rates. When the hydrogen concentration was increased to 50%, a hydrogenation at 120C with 0.1% nickel catalyst required 360 min to destroy the response of the oil to the Halphen test. However the iodine value decreased only 1.8 units, and only 2.1% *trans* isomers formed.

Winterization

Lowenstein (4) claimed that a slight hydrogenation of cottonseed oil made "the separation of stearin from the oil much easier and more effective" when winterization was carried out for the production of salad oil. He apparently was concerned only with the ease of separating the stearin and made no mention of yields. The authors too found that the slightly hydrogenated oil was winterized much more easily; the filtration rate was greatly improved over that of the unhydrogenated oil. However it also was found that hydrogenation increased the yield of winterized oil. As an example, one hydrogenated oil, in which the iodine value had been reduced 3.2 units and the content of *trans* isomers increased by 1.8%, yielded 80.2% of winterized oil with a cold test of 41 hr whereas the unhydrogenated oil yielded only 68.3% winterized oil with a cold test of 17 hr.

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