Conjugated Hydrogenation of Triglyceride Oil Containing Conjugated Acid

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ABSTRACT

Conjugated hydrogenation of tung oil (fatty acid composition: elaeostearic 57.0%, linoleic 25.8%, oleic 11.2% and saturated 6.0%)[1] has been investigated to ascertain the influence of hydrogen donors, namely primary and secondary alcohols, on rate and selectivity under different operating conditions. 2-Propanol, in general, reflects faster rate and greater degree of reduction but less selectivity towards the reduction of unsaturated acids than ethanol, when tung oil is treated at 200 C, 225 C and 250 C with 2% Ni (optimum catalyst level) and theoretical as well as 100% excess of theoretical amount of the two hydrogen donors to ensure complete hydrogenation of the oil. The rate and degree of reduction with ethanol are less influenced by its amount and amount of catalyst, but with 2-propanol these depend considerably on both the amount of hydrogen donor and amount of catalyst. During conjugated hydrogenation of tung oil, deposition of gel-like mass in minor amount occurs only at the wall of the reaction vessel. This is evidently due to polymerization of the conjugated trienoic acid.

INTRODUCTION

Conjugated hydrogenation is a catalytic hydrogenation-dehydrogenation reaction involving a hydrogen donor and a hydrogen acceptor, usually an unsaturated substance. The process as applied to triglyceride oils was first studied between 1930-38 and then in 1956 by Russian workers

[1]Presented at the IXth ISF Congress, Rotterdam, September 1968.

(1-5). Their studies on some unsaturated oils like cottonseed, sunflower and linseed, with ethanol and n-propanol as hydrogen donors and nickel as principal catalyst at 200-260 C, indicated high selectivity and distinct hydrogenation equilibrium beyond which there was no further reduction. Recently Basu and Chakrabarty (6) investigated the process and observed that secondary alcohols as hydrogen donors enhanced both rate and degree of hydrogenation, in comparison with primary alcohol, but decreased selectivity. Further, with secondary alcohols, rate and selectivity depend on the unsaturations of the oils. Thus safflower oil (iodine value, 144.4) reduced at a faster rate than peanut oil (iodine value, 93.3) under identical operating conditions and exhibited greater selective reduction. According to the reports (1-6) the unsaturated oils stated above could not be reduced below the equilibrium iodine values of 64-71 by this process of hydrogenation, particularly when primary alcohols were used as hydrogen donors. Chakrabarty et al. (7), therefore, took up the study of the conjugated hydrogenation of oils having iodine values already below 64. The authors were able to demonstrate that mahua (*Madhuca latifolia*) oil (iodine value, 60) could be reduced ca. 33% and 94% in iodine values, respectively, by ethanol and 2-propranol as hydrogen donors. Hydrogenation with ethanol was highly selective. Very recently Fukuzumi and Kato (8) investigated this process of hydrogenation with methyl linoleate isomers and claimed higher selectivity with secondary alcohols than with primary alcohols. They further observed that higher pressure increased the rate of hydrogenation but lowered selectivity. They showed that hardly any hydrogenation took place without catalyst except near the autoclave wall.

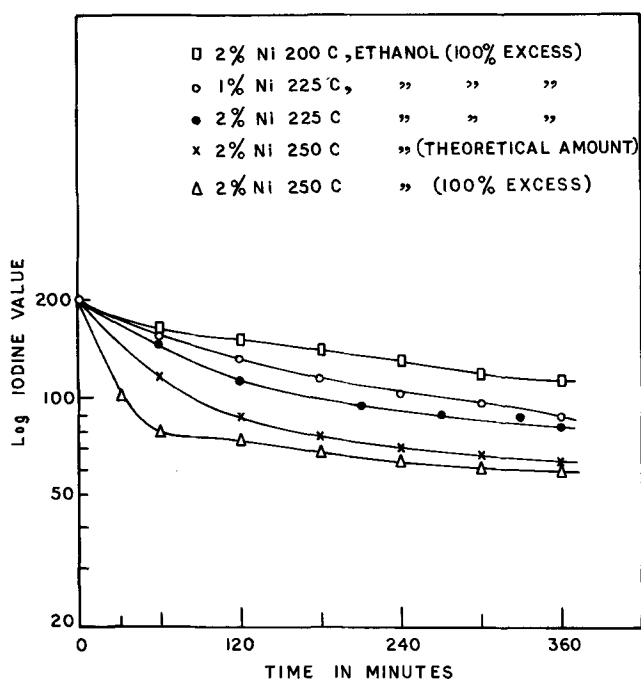The present investigation embodies the study of the

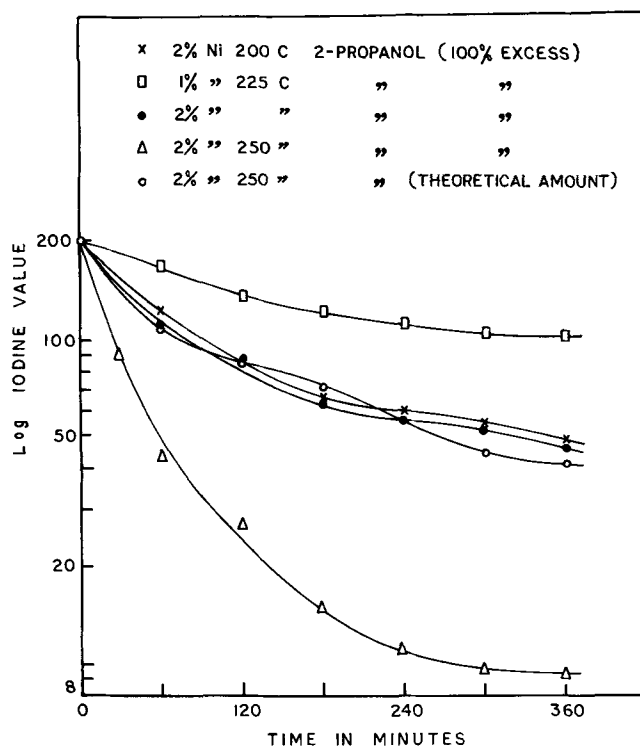FIG. 1. Hydrogenation rate of tung oil with ethanol.

FIG. 2. Hydrogenation rate of tung oil with 2-propanol.

TABLE I

Characteristics of Conjugated Hydrogenation Reaction of Tung Oil with Ethanol as Hydrogen Donor

Catalyst, % Ni	Temperature, C	Pressure, psig	Ethanol, amount	Period of hydrogenation, hr	Theoretical iodine value	Conjugated triene, %	Conjugated diene, %	Total diene, %	Total oleic, %	Saturated, % (Bertram oxidation)	Trans-isomers, % trielaidin
				0	202.0	57.0	---	25.8	11.2	6.0	---
2.0	200	108-117	100% Excess over theoretical amount	1	161.4	29.5	18.0	33.3	31.7	5.5	0.5
				2	151.1	21.8	27.8	37.0	35.5	5.7	4.0
				3	139.5	12.8	33.8	39.9	43.3	5.9	6.8
				4	133.0	10.0	32.1	39.8	44.3	6.4	8.2
				5	116.0	3.1	31.8	36.5	53.2	7.2	9.1
				6	112.8	1.8	28.3	34.9	55.3	8.0	6.2
1.0	225	100-115	100% Excess over theoretical amount	1	155.7	24.5	8.0	37.2	32.2	6.1	2.1
				2	134.0	7.9	29.4	44.6	41.4	6.1	6.5
				3	113.8	2.1	27.7	33.4	58.0	6.5	11.8
				4	103.6	0.7	13.0	24.5	68.5	6.3	18.0
				5	96.7	0.6	4.8	16.5	76.1	6.8	24.7
				6	86.1	0.6	4.7	4.9	88.0	6.5	30.8
2.0	225	110-125	100% Excess over theoretical amount	1	150.0	17.8	34.6	42.9	34.4	5.9	0.7
				2	117.7	2.3	27.7	37.6	54.1	6.0	9.1
				3	95.3	0.8	9.8	14.7	78.5	6.0	32.2
				4	89.8	0.6	3.0	8.7	84.4	6.3	34.2
				5	88.0	0.5	2.9	7.3	84.7	7.5	30.0
				6	81.0	0.3	2.9	3.1	86.1	10.5	30.3
2.0	250	75-120	100% Excess over theoretical amount	0.5	103.3	3.3	37.1	43.7	42.3	10.7	6.5
				1	78.3	---	2.6	9.6	74.5	15.9	30.7
				2	74.6	---	1.0	2.3	81.7	16.0[a]	32.1
				3	68.7	---	1.0	1.2	77.2	21.6[a]	28.0
				4	63.9	---	---	---	67.3	32.7[a]	25.3
				5	60.4	---	---	---	64.8	35.2[a]	24.8
				6	60.0	---	---	---	64.4	35.6[a]	18.4
2.0	250	70-100	Theoretical amount	1	116.4	1.1	28.6	35.5	52.8	10.6	18.0
				2	86.5	0.8	10.2	12.5	72.7	14.0	22.5
				3	76.3	0.5	4.8	7.3	72.2	20.0	25.7
				4	69.9	---	2.7	4.5	70.2	25.3[a]	24.9
				5	67.3	---	2.3	3.9	68.7	27.3[a]	22.3
				6	63.0	---	1.6	2.8	67.4	29.8[a]	20.5

[a]By difference.

conjugated hydrogenation characteristics, hitherto unreported, of tung oil that contains high proportion of conjugated trienoic acid such as elaeostearic acid. The effects of the variables, like the nature of hydrogen donor, the amount of hydrogen donor, temperature and catalyst concentration on the rate, degree of hydrogenation (maximum drop in iodine value) and selective reduction of unsaturated moieties, as well as trans-isomer formation, have been mainly examined.

MATERIALS AND METHODS

Materials used were refined and bleached tung oil, Rufert nickel containing 25% Ni (Harshaw Chemical Co., U.S.A.), ethanol (absolute) and 2-propranol (Merck).

The UV spectrophotometric method of Hilditch et al. (9) was adopted for determinations of elaeostearic acid, conjugated dienoic and total dienoic acids. Trans-isomers as "trielaidins" were determined by the IR spectrophotometric method (10) in a Perkin Elmer Infracord model. For precise determinations of "trielaidins," absorbance due to elaeostearic acid was measured separately with the original oil, and its contribution was deducted from the total absorbances of the hydrogenated samples that contained elaeostearic acid by simple proportions. Total saturated acids were measured by modified Bertram oxidation (11) and also by difference. Total oleic acids were found by difference and in some cases from the iodine values of mixed fatty acids and UV spectrophotometric analysis.

EXPERIMENTAL PROCEDURES

Hydrogenation experiments were carried out, using 10 g of the oil and an appropriate amount of the hydrogen donor, in a high pressure shaking autoclave (Chas. W. Cook and Sons Ltd., England) provided with electric heating and automatic temperature control. The autoclave was agitated at 172 shakes per minute. Nickel catalyst was used in amounts of 1% and 2% on the weight of oil used. The reactions were conducted at 200 C, 225 C and 250 C, and samples were drawn at regular intervals. Products were isolated by first filtration of catalyst aided by Hyflosupercel followed by removal of excess alcohols and carbonyl compounds in nitrogen atmosphere at water bath temperature under vacuum.

RESULTS

Analytical characteristics of hydrogenated products obtained at different conditions are included in Tables I and II and also graphically in Figures 1 and 2.

DISCUSSION

The rate and selectivity of the conjugated hydrogenation of tung oil depend on the nature of hydrogen donor, catalyst amount and temperature. At all operating conditions the hydrogenation attains equilibrium beyond which no further reduction occurs.

Increase in catalyst concentration accelerates the rate of reduction of tung oil when ethanol and 2-propanol are used as hydrogen donors, but the rate is very remarkably improved with 2-propanol. Thus for ethanol, when the catalyst amount is changed from 1% Ni to 2% Ni at 225 C, the rate of reduction especially at the initial stages of hydrogenation markedly improves but attaining ultimately almost comparable rate and degree of reduction. Thus Table I indicates that ca. 8% elaeostearic acid is retained in the hydrogenated product obtained in 2 hr with 1% Ni, compared to ca. 2% elaeostearic with 2% Ni. But the final equilibrium iodine values and fatty acids compositions are nearly the same. With 2-propanol, while 3.6% elaeostearic acid remains in the hydrogenated products even after a 6 hr

run using 1% Ni, there is complete elimination of elaeostearic acid in 3 hr by 2% Ni (Table II). Also the rate and degree of hydrogenation are almost doubled. Table II also indicates that with 1% Ni dienoic and monoenoic acids remain in appreciable amounts, and saturated acid proportion is not increased, whereas with 2% Ni dienoic acids are completely eliminated forming simultaneously ca. 50% of saturated acids.

Increase in catalyst concentration from 2% to 3% does not alter the rate of reduction. Thus at 250 C ethanol with 2% Ni and 3% Ni reduced the iodine value of tung oil to 60.0, and 2-propanol shows iodine values of 9.6 and 8.0, respectively, in 6 hr.

The temperature is an effective variable. Its influence on the rate of hydrogenation depends on the nature of hydrogen donor. At 2% Ni with ethanol, the rate of hydrogenation decreases sharply when the temperature is decreased from 225 C to 200 C, but the rate remains practically unaltered in case of 2-propanol. Thus with ethanol at 225 C (Table I), elaeostearic and dienoic acids are almost wholly reduced to monoenoic acids in 6 hr, whereas hydrogenation at 200 C for 6 hr retains ca. 2% elaeostearic and 35% dienoic acids. Correspondingly hydrogenations at 200 C and 225 C with 2-propanol indicate an almost similar degree of reduction (Table II). But an increase in temperature from 225 C to 250 C increases both rate and degree of hydrogenation irrespective of ethanol and 2-propanol, the latter showing a much faster rate and greater degree of hydrogenation. Thus from Tables I and II it appears that the iodine value of tung oil can be reduced to as low as 60.0 and 9.6, respectively, by ethanol and 2-propanol at 250 C with complete elimination of trienoic and dienoic acids. Further within 1 hr elaeostearic acid is completely reduced.

The plot of logarithm of theoretical iodine values against hydrogenation time in minutes at different temperatures and catalyst concentrations for ethanol and 2-propanol give linear curves as shown in Figures 1 and 2, indicating that the overall hydrogenation is "first order." At 250 C, however, ethanol shows two distinct and different lines instead of one single overall linear curve. This pattern is also displayed by 2-propanol at 250 C. This is probably due to the tremendous increase in rate of reduction of elaeostearic and dienoic acids compared to their rate of reduction at 200 C and 225 C.

Conjugated hydrogenation reaction of tung oil is highly selective with both ethanol and 2-propanol. Ethanol, in general, reflects greater selectivity. Thus it is evident from Tables I and II that the two alcohols at 225 C and 1% Ni reduce only elaeostearic and dienoic acids to monoenoic acids with no concomitant formation of saturated acids. Greater selectivity of ethanol than 2-propanol is also noticeable, since higher content of dienoic acids is obtained than with 2-propanol, which produces more of monoenoic acids before elaeostearic acid is completely reduced. With 2% Ni at 225 C, ethanol displays greater selectivity than 2-propanol. Thus from Tables I and II it appears that, whereas the amount of saturated acids is only slightly increased in the case of ethanol, a considerable amount of saturated acids is formed with 2-propanol before elaeostearic is completely reduced. Further, ethanol forms with 2% Ni less dienoic and more monoenoic acids than with 1% Ni, indicating a fall in selectivity with higher catalyst amount. A similar fall in selectivity with 2-propanol and catalyst increase from 1% Ni to 2% Ni is indicated.

Increase in temperature shows increased selective hydrogenation for ethanol. Thus at 250 C using 2% Ni, ethanol yields in 0.5 hr a product that contains 6.3% elaeostearic acid and 30.0% saturated acids. Tables I and II point out more clearly the difference in selectivity between the two types of alcohols at 250 C. At 200 C and 2% Ni, ethanol again shows more selectivity than 2-propanol. With ethanol

TABLE II

Characteristics of Conjugated Hydrogenation Reaction of Tung Oil with 2-Propanol as Hydrogen Donor

Catalyst, % Ni	Temperature, C	Pressure, psig	2-Propanol, amount	Period of hydrogenation, hr	Theoretical iodine value	Conjugated triene, %	Conjugated diene, %	Total diene, %	Total oleic, %	Saturated, %	Trans-isomers, % trielaidin
				0	202.0	57.0	---	25.8	11.2	6.0[a]	---
2.0	200	112-128	100% Excess over theoretical amount	1	124.1	15.5	13.6	22.4	52.3	9.8[a]	9.7
				2	94.8	5.4	8.1	16.1	61.1	17.3[a]	30.6
				3	65.0	0.2	1.4	2.2	70.2	27.4	28.8
				4	62.2	0.2	1.3	1.7	68.1	30.0	26.9
				5	53.7	0.1	1.2	1.5	58.8	39.6	23.3
				6	47.0	0.1	1.2	1.4	51.3	47.2	19.3
1.0	225	100-122	100% Excess over theoretical amount	1	173.9	40.3	14.5	26.3	27.7	5.7[a]	1.9
				2	136.9	17.2	19.6	30.1	46.8	5.9[a]	5.1
				3	125.5	13.2	19.5	28.7	48.0	6.1[a]	8.0
				4	113.6	6.5	18.2	24.4	62.8	6.3[a]	13.1
				5	106.5	3.8	14.6	21.8	68.0	6.4[a]	20.8
				6	104.6	3.6	14.0	21.0	68.3	7.2[a]	32.8
2.0	225	115-130	100% Excess over theoretical amount	1	111.3	10.5	14.8	22.0	53.3	14.2[a]	13.9
				2	91.1	4.4	8.2	16.9	58.4	20.3[a]	27.3
				3	63.2	0.1	1.5	1.5	69.8	28.6	34.4
				4	56.8	0.1	1.4	1.4	62.7	35.8	35.5
				5	52.0	0.1	1.2	1.2	57.5	41.2	31.8
				6	45.7	0.1	1.1	1.1	50.4	48.4	27.2
2.0	250	80-145	100% Excess over theoretical amount	0.5	92.2	6.3	19.6	25.4	38.1	30.1[a]	13.5
				1	44.2	0.7	1.8	1.8	45.6	48.1[a]	23.6
				2	25.6	---	0.4	0.4	28.8	70.8	22.2
				3	14.9	---	---	---	17.2	82.8	15.3
				4	13.2	---	---	---	15.2	84.8	15.0
				5	9.6	---	---	---	11.1	88.9	10.2
				6	9.6	---	---	---	11.0	89.0	8.2
2.0	250	90-120	Theoretical amount	1	110.9	7.4	22.9	32.0	39.4	21.2[a]	16.2
				2	89.5	0.9	25.1	28.3	45.4	23.6[a]	30.5
				3	71.7	---	3.5	16.1	48.7	35.2	25.3
				4	57.8	---	1.2	2.9	59.1	38.0	23.1
				5	46.7	---	---	1.5	51.0	47.5	20.0
				6	43.5	---	---	0.5	49.3	50.2	18.6

[a]By Bertram oxidation.

there is a very small increase in saturated acids, and only elaeostearic and dienoic acids are reduced to monoenoic acids. At similar conditions 2-propanol produces sufficient saturated acids, in spite of significant amounts of elaeostearic acid being retained. Thus lowering of temperature does not alter selectivity in the case of 2-propanol. This is more readily indicated when the amount of dienoic and monoenoic acids at 200 C and 225 C are compared.

The influence of the amount of hydrogen donor on rate and degree of reduction depends also on the nature of hydrogen donor. It has been observed that 2-propanol in 100% excess over theoretical requirement promotes considerably the rate and degree of reduction. Ethanol also in 100% excess over the theoretical amount promotes rate of reduction but up to certain stages beyond which both rate and degree of reduction are comparable with those of the theoretical amount. Thus ethanol, in theoretical amount and in 100% excess at 250 C in presence of 2% Ni, reduces in 6 hr the iodine value of tung oil from 202.0 to 63.1 and 60.0 (Table I), respectively. But the products of intermediate stages in the case of 100% excess contain much less mono- and dienoic acids than those of the products obtained with theoretical amounts of ethanol. At similar temperature and catalyst concentration, iodine value of tung oil is reduced to 43.5 in 6 hr and 9.6 in 5 hr, respectively, with the theoretical and 100% excess of the theoretical amount of 2-propanol (Table II). In the initial stages also, a notable difference in rate of reduction exists. The unsaturated acids appear to be more selectively reduced with ethanol (Table I).

Substantially high proportions of *trans*-isomers are also formed by this process of hydrogenation. Catalyst amount and nature of hydrogen donor have very little effect on the formation of *trans*-isomers. Thus an increase in catalyst concentration from 1% Ni to 2% Ni at 225 C hardly makes any difference in trielaidin content when ethanol and 2-propanol are used as hydrogen donors (Tables I and II). Trielaidin formations depend largely on temperature employed. At 200 C and 2% Ni the quantity of trielaidin formed in the case of both ethanol and 2-propanol is much less than that at 225 C and 2% Ni. At 250 C, trielaidin quantity increases further for both hydrogen donors. The amount of hydrogen donor, primary or secondary, has no significant influence on the formation of *trans*-isomers.

A gel-like mass in small amount appears to be formed only at the wall of the reaction vessel presumably due to polymerization of the conjugated trienoic acid.

ACKNOWLEDGMENT

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