

Dehydration of Lesquerella Oil

SHELBY F. THAMES,* HAIBIN YU, MIN D. WANG, and THOMAS P. SCHUMAN

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

SYNOPSIS

The dehydration of lesquerella oil has been accomplished for the first time. Dehydration was performed using sulfuric acid, sulfates and phosphates, acidic clay, and aluminum oxide as dehydration catalysts. Dehydration products were characterized by infrared (FTIR), ultraviolet (UV), and proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopies. Color grades, acid values, hydroxyl values, and iodine values were obtained by established ASTM methods. Dehydration of either lesquerolic or ricinoleic acids creates slightly more conjugated diene than nonconjugated diene. Product mole ratios of conjugated to nonconjugated diene versus catalyst type varied from 1.1 to 1.6. Dehydrated lesquerella oil containing about 28 mol % conjugated (77.8 mol % total) diene has an iodine value of 147. Drying properties were also examined. Dehydration converts nondrying lesquerella oil into a drying oil with a drying velocity equivalent to a commercially dehydrated castor oil. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Domestic lesquerella oil (LO) contains 55–60% 14-hydroxy-*cis*-11-eicosenoic (lesquerolic) acid. Lesquerolic acid is a 20 carbon homolog of ricinoleic acid (C_{18}), currently obtained from imported castor oil¹ and the only commercial source of hydroxy fatty acid. Since the early 1970s, all castor oil used in the United States has been imported, ranging from 29,347 to 64,351 metric tons per year.² Preliminary analyses have compared LO and castor oils.³ Castor oil contains about 90% of ricinoleic acid; LO contains about 55% lesquerolic acid. Both ricinoleic acid and lesquerolic acid have a β , γ -unsaturated hydroxyl group the same distance away from the methyl end of the fatty acid molecule. The comparable chemical structure means that analogous yet different products may be derived from them.²

Many products are developed from castor oil. Among a variety of applications, dehydrated castor oil (DCO) and dehydrated castor oil fatty acid are listed third in order of importance among many products from castor oil.^{1,4} The accepted mechanism of the dehydration reaction of hydroxy fatty acid is shown in Figure 1.⁵ The first intermediate is the

protonated hydroxyl group on the fatty acid, which then loses water to form a carbonium ion. Further reaction produces both conjugated and nonconjugated diene forms with loss of hydrogen from carbon **a** or carbon **b**. Nondrying castor oil is thus converted into a drying oil. Changes in molecular structure, loss of hydroxyl group, and formation of another double bond can be evidenced by spectroscopic methods.

As dehydration of hydroxy fatty acid can produce either a conjugated or a nonconjugated diene, the question as to which of these two products prevails is of interest, since it has been believed that the drying speed of an oil is largely determined by its content of conjugated double bonds.¹⁴ Initially, when Scheiber studied dehydration, he believed that 90% of the fatty acids obtained consisted of conjugated isomer.⁹ However, the use of maleic anhydride for the quantitative determination of conjugated double bonds in oils and fatty acids became the basis of analytical methods by Kaufmann and Baltes and by Ellis and Jones.¹⁵ Using the Kaufmann method, Priest found conjugated diene content in DCO ranged only from 17.3 to 25.4 mol %¹⁶ and Achaya found a conjugated diene content of only 35% by gas chromatographic (GC) analysis.¹⁷ Both results proved Scheiber's assumption erroneous. The conjugated diene content of DCO reported by other researchers generally falls into the range of 30 to 45 mol %.^{4,7}

* To whom correspondence should be addressed.

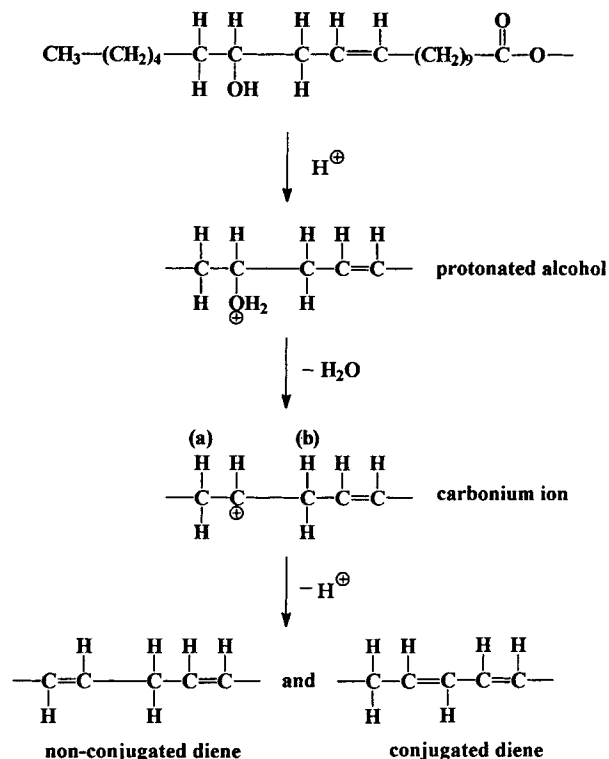


Figure 1 Mechanism of LO dehydration.

The practical dehydration process is the subject of hundreds of patents, concerned with either increasing the diene content, with giving a product of light color, or with reducing the degree of after-tack shown on drying.⁶ Of many factors involved in the dehydration process, the choice of catalyst is most important in governing process conditions as well as color, viscosity, and side reactions. Catalysts tested include a variety of inorganic or organic acids, salts, clays, resins, and oxides.⁶ The most widely used catalysts are sulfuric acid, phosphorous acid, sodium or potassium hydrogen sulfate, and acid-activated clay.^{5,6} Commercially, DCO is light in color with drying speed equal to or faster than linseed oil, but slower than tung oil. Much of the unsaturation is linoleic acid, a good portion of which (about 33%) is conjugated.^{4,7} We are conducting research to compare LO, castor oil, and their derivatives by defining chemical structure/property relationships. Results of LO research are directed into, specifically, potential products for commercialization. The present work reports the study of the dehydration of LO.

EXPERIMENTAL

Materials

Lesquerella oil (LO, refined from *Lesquerella fendleri*) was purchased from International Flora Tech-

nology, LTD. Castung 103 G-H, a commercially dehydrated castor oil of Gardner-Holdt viscosity range G-H, was obtained from CasChem, Inc. Sulfuric acid, ammonium dihydrogen phosphate, potassium dihydrogen phosphate, and cupric sulfate were purchased from Fisher Chemical Company. Deuterated chloroform, sodium bisulfate, potassium bisulfate, acidic-activated aluminum oxide (Al_2O_3), and activated carbon black were purchased from Aldrich Chemical Company. Materials purchased from Fisher and Aldrich Chemical Companies were ACS reagent grade except the deuterated chloroform. Linoleic and conjugated linoleic acid methyl ester were purchased from Sigma Chemical Company. Clay 452 was supplied by American Colloid Company. Nuodex cobalt 10% and Nuodex zirconium 12% were produced by Nuodex, Inc. All chemical materials were used as received.

Dehydration of Lesquerella Oil

To a four-neck, 100-mL round bottom flask equipped with a mechanical stirrer, nitrogen inlet, and thermometer were added catalyst and 50 g LO. The stirred flask contents under nitrogen atmosphere were then heated to 240°C. A 2-mL aliquot was withdrawn every 15 min into a vial and quenched immediately by cooling with an ice bath. The oil was filtered through a 4- to 4.5- μm glass frit Buchner funnel to remove solids.

Analytical Procedure

FTIR spectra of LO and dehydrated lesquerella oil (DLO) were obtained on a Nicolet Systems IR42 FTIR spectrometer. Analytical sample films were cast from chloroform onto polished sodium chloride discs which were then dried for 2 h *in vacuo*. UV absorbance spectra were run from 190 to 450 nm in redistilled hexane on a Perkin Elmer 544 UV/Vis spectrometer. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were obtained on a Bruker AC-200 200 MHz NMR spectrometer using deuterated chloroform solvent spiked with tetramethylsilane (TMS) for internal reference.

Gardner color, iodine value, hydroxy value, and acid value were determined by ASTM methods #D-1544, #D-1541, #D-1957, and #D-1980, respectively. Viscosity was measured on a Brookfield digital viscometer with a #18 spindle at 6 rpm and 25°C. Drying time was recorded by a Gardner circular drying time recorder using the combination catalyst system 0.06% Nuodex cobalt (10%) and 0.12% Nuodex zirconium (12%) in 2 mil wet film at 20°C. The wet film was produced by draw bar of 2 mil gap.

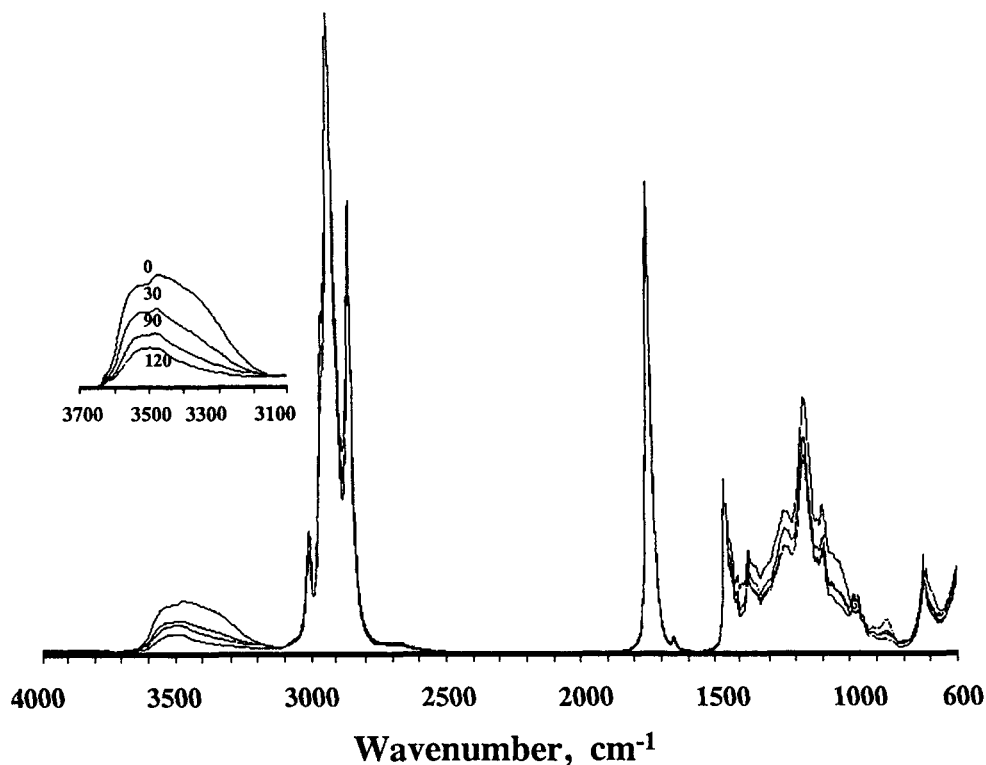


Figure 2 Infrared spectra of LO dehydration product obtained with 1% KHSO_4 at 240°C taken at 0, 30, 90, and 120 min.

RESULTS AND DISCUSSION

The FTIR spectra of LO show a characteristic hydroxyl absorption, centered at 3468 cm^{-1} (Fig. 2). Evidence for loss of hydroxyl functionality can be determined from a comparison of IR spectra in Figure 2 taken of aliquots at different reaction times, which confirms decreased hydroxyl absorption.

The UV absorption peaks of fatty acids containing isolated double bonds, and two and three con-

jugated double bonds are located at 203, 232, and 270 nm, respectively.⁸ Pure LO does not contain fatty acids of conjugated bonds.³ Comparing the spectrum of LO which has one absorption peak at 203 nm with the UV spectrum of DLO (Fig. 3), formation of conjugated diene is proved by the ap-

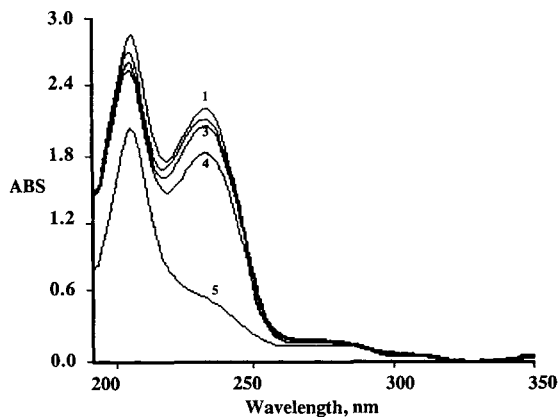


Figure 3 UV spectra of LO dehydration product obtained with 1% NaHSO_4 at 240°C at (1) 90, (2) 60, (3) 30, (4) 15, and (5) 0 min.

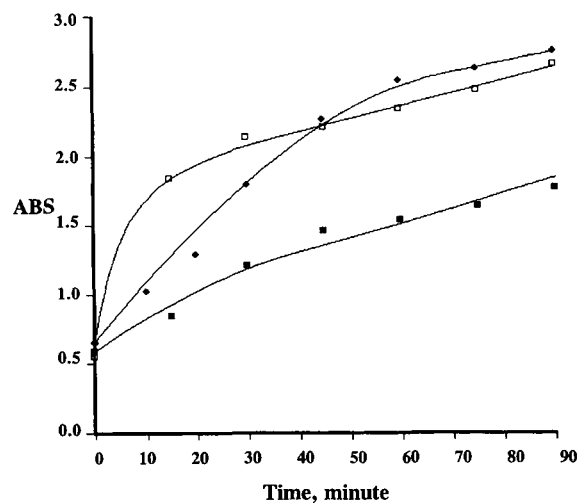


Figure 4 Intensity of UV absorption at 232 nm of LO dehydration aliquots from catalytic reactions (■) 1% KHSO_4 , (◆) 1% CuSO_4 , and (□) 1% NaHSO_4 at 240°C versus reaction time.

pearance of a peak at 232 nm for DLO samples. Curve 5 of Figure 3 has a slight shoulder indicating some conjugated diene in unreacted LO. We attribute the presence of conjugated diene to, but have not confirmed, possible isomerization of crude LO during processing.

Figure 4 shows variation of absorptive peak intensity at 232 nm versus reaction time for three dehydration processes. Peak intensity for the NaHSO_4 catalyst system increases quickly to 68% conversion in approximately 15 min and then increases > 25% conversion over the next 75 min; however, absorption at 232 nm for the KHSO_4 -catalyzed reaction increases rather continuously yet more slowly than NaHSO_4 catalysis to 75% total conversion at 90 min. For CuSO_4 catalysis, intensity grows at a rate intermediate to NaHSO_4 and KHSO_4 processes for the first 35 min, and maintains that rate of conversion through 60 min to 91% conversion and then approaches 100% conversion, as noted by NMR analysis, over the ensuing 30 min period. These variations in conversion are likely a result of differing catalyst efficiencies. The final DLO product in a CuSO_4 process has the strongest UV absorption

Table I Spectral Assignment to Fatty Acid $^1\text{H-NMR}$ Absorbances

Peak	Chemical Shift (ppm)	Assignment
a	3.6	$-\text{CH}(\text{OH})-$
b	2.78	$-\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}-$
c1-c4	6.28, 5.91 5.60, 5.25	$-\text{CH}=\text{CHCH}=\text{CH}-$
d	5.48	$-\text{CH}=\text{CH}-$
m	0.9	$-\text{CH}_3$

at 232 nm and therefore the most conjugated diene content among the three.

The degree of LO dehydration and percentage conjugated double bond produced can be determined by established methods such as UV spectroscopy, titration, and GC.⁸⁻¹⁰ These methods are time consuming. In this paper, these important values are calculated by $^1\text{H-NMR}$ semiquantitative analysis. The $^1\text{H-NMR}$ spectra of LO and DLO together with conjugated and nonconjugated linoleic acid methyl esters are shown in Figure 5. Assignment of the

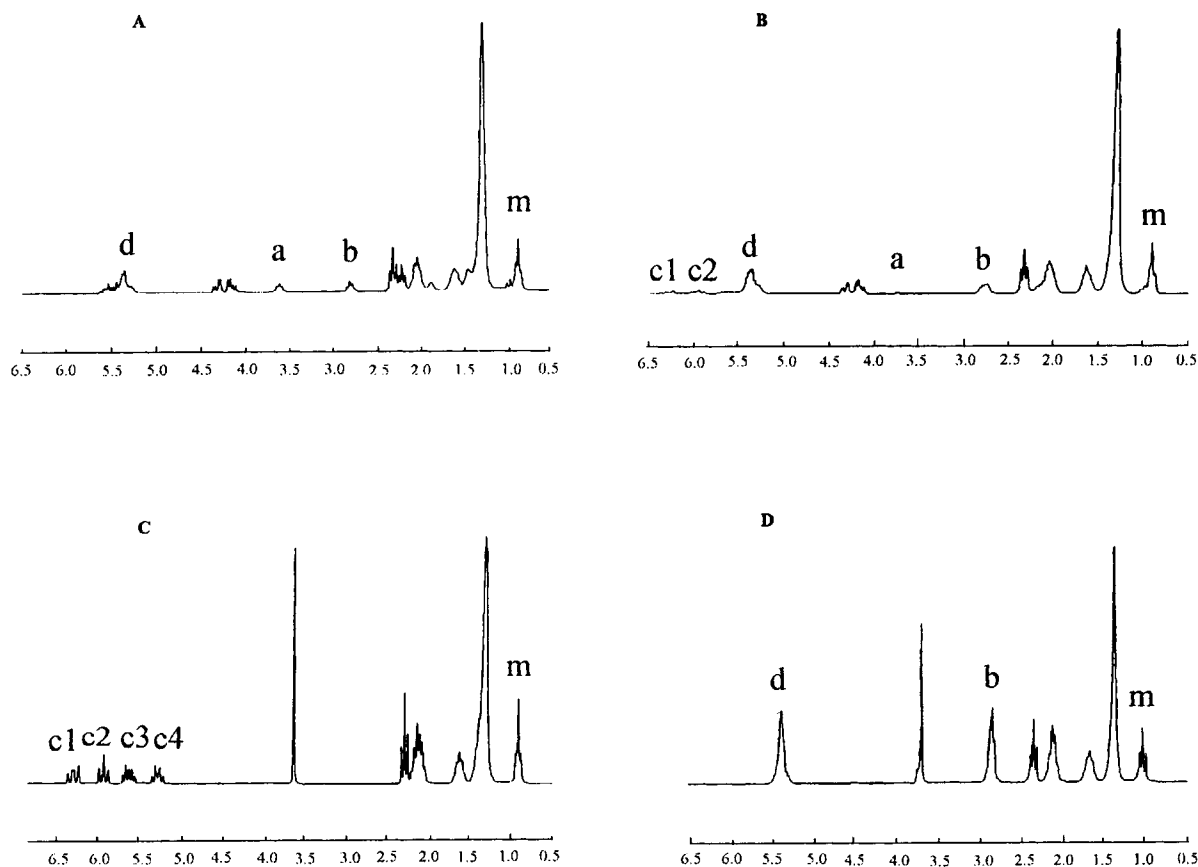


Figure 5 $^1\text{H-NMR}$ spectra of (A) LO, (B) DLO, (C) conjugated methyl linoleate, and (D) nonconjugated methyl linoleate.

Table II Measurements of Hydroxy Value and Degree of Dehydration for Variable Dehydration Conditions

No.	Experiment	Hydroxy Value (mg KOH/g)	Degree of Dehydration	
			NMR	Titration
—	LO	103.0	—	—
—	CO	163.0	—	—
1	LO + 1% NaHSO ₄ 240°C, 90 min	8.8	93.1	92.0
2	LO + 1% KHSO ₄ 240°C, 120 min	31.3	75.3	72.3
3	LO + 1% CuSO ₄ 240°C, 120 min	8.3	99.6	92.0
4	LO + 5% clay 452 240°C, 90 min	37.6	71.5	73.5
5	LO + 20% Al ₂ O ₃ 280°C, 240 min	—	76.5	—
6	LO + 2% KHSO ₄ 280°C, 30 min	26.9	71.0	73.1
7	LO + 1% KHSO ₄ 280°C, 60 min	6.5	93.3	93.7
8	LO + 2% NH ₄ H ₂ SO ₄ 280°C, 120 min	—	68.7	—
9	LO + 2% KH ₂ PO ₄ 280°C, 90 min	6.2	97.4	94.0
10	LO + 0.5% H ₂ SO ₄ 240°C, < 5 min	18.4	84.0	82.1
11	CO + 1% NaHSO ₄ 240°C, 45 min	18.8	87.1	86.7

peaks of interest are collected in Table I.¹¹⁻¹³ The peaks of the methyl group [CH_3 —, **m**, Fig. 5(A)–(D)] at each fatty acid chain end and the hydroxyl carbon proton [— $\text{CH}(\text{OH})$ —, **a**, Fig. 5(A) and (B)] of lesquerolic acid are positioned at 0.92 and 3.56 ppm, respectively. These peaks are well resolved for quantitative calculation. Peaks in Figure 5(C) and (D) at approximately 3.6 ppm correspond to the protons of the methyl ester (— COOCH_3). The degree of dehydration at time t , therefore, can be calculated according to eqs. (1) and (2):

$$H = \frac{3A_h}{A_m} \quad (1)$$

$$P_t = \frac{H_0 - H_t}{H_0} \quad (2)$$

where H is the percentage of hydroxy fatty acid, A_h is peak area of the hydroxyl carbon proton, A_m is peak area of protons in the terminal methyl group of fatty acids, H_0 and H_t are the percentages of hydroxy fatty acid in pure LO and DLO at time t , and P_t is the percent degree of dehydration of available hydroxy fatty acids at time t .

The degrees of dehydration, obtained from ¹H-NMR spectra as well as hydroxy value titration (ASTM #D-1957), are listed in Table II. These two tests produce similar results, shown by a data set correlation coefficient of 0.969. Sulfuric acid was the most active catalyst, 84% dehydration of LO occurring in less than 5 min. Catalysts such as acid-activated alumina and ammonium dihydrogen phosphate were not investigated further as even long reaction times yielded relatively poor conversions to diene. Increasing temperature accelerates the dehydration process. For the 1% KHSO₄ system at 240°C, 75.3% conversion occurred while at 280°C the conversion was 93.3%.

Figure 6 shows degree of dehydration versus reaction time for selected catalytic reactions. Catalytic efficiency, based on minimum time necessary to achieve high degrees of dehydration, increases in the order KHSO₄ < clay 452 < CuSO₄ < NaHSO₄, which is the order similar to that observed with castor oil.⁶ Figure 6 also includes a castor oil dehydration using 1% NaHSO₄ at 240°C, indicating that LO reacts slightly slower than castor oil under identical reaction conditions.

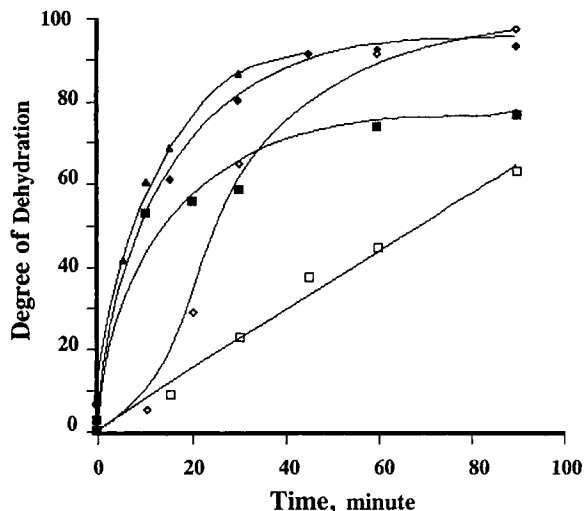


Figure 6 Degree of dehydration of LO, by aliquot from catalytic reactions (\square) 1% KHSO_4 , (\diamond) 1% CuSO_4 , (\blacksquare) 2% clay 452, (\blacklozenge) 1% NaHSO_4 , and (\blacktriangle) CO 1% NaHSO_4 at 240°C , versus time.

Raw LO contains the unsaturated C_{18} acids, 18 : 1 (16.9%), 18 : 2 (7.6%), and 18 : 3 (13.2%) besides lesquerolic acid.³ Dehydration of lesquerolic fatty acid produces conjugated diene acid (20 : 2) analogous to conjugated linoleic acid (18 : 2). The methylene ($-\text{CH}_2-$) between unconjugated double bonds appears at 2.78 ppm and is also well resolved [**b**, Fig. 5(A) and (B)]. Four multiplet peaks at 5.26, 5.60, 5.91, and 6.27 ppm with 1 : 1 : 1 : 1 area ratios in the NMR spectrum of conjugated linoleic acid [**c1-c4**, Fig. 5(C)] correspond to the four unsaturated protons ($-\text{CH}=\text{}$). Although the peaks at 5.26 and 5.60 ppm overlap with proton absorption due to protons of isolated double bonds [Fig. 5(D), **d**, 5.34 ppm], the peaks at 5.91 and 6.27 ppm resolve well enough for quantitative analysis [Fig. 5(B)]. Thus the respective percentages of conjugated and nonconjugated acids can be analyzed.

For this study, the percentages of conjugated and nonconjugated fatty acids are obtained using eqs. (3) and (4):

$$C_t = \frac{3D_t}{2A_m} \quad (3)$$

$$N_t = \frac{3M_t}{2A_m} \quad (4)$$

where C_t is the percent of conjugated acid at time t , D_t is the area sum of diene peaks at 5.91 and 6.27 ppm at time t , A_m is peak area of protons in the chain terminal methyl group, N_t is the percent of nonconjugated double bonds at time t , and M_t is the

peak area at 2.78 ppm at time t . LO does not contain conjugated fatty acids, therefore C_t also represents conjugated diene produced during dehydration. N_t is dependent on the initial oil composition giving total nonconjugated diene content.³ Thus the amount of nonconjugated diene produced, N_{pt} , is given by eq. (5):

$$N_{\text{pt}} = N_t - N_0 \quad (5)$$

where N_0 is the percent unconjugated acid in the raw oil.

The dehydration results of LO and castor oil are listed in Table III. Test results show the dehydration process produces more conjugated than unconjugated diene, approximately 14% more conjugated than nonconjugated diene is created. The observed ratio of conjugated to non-conjugated diene (C_t/N_{pt}) varies from 1.1 to 1.6. Figure 7 shows the variation of conjugated diene and unconjugated diene versus time of dehydration.

The values expressed in Table III indicate total diene composition before and after dehydration. These results can be converted into the percent yield of conjugated and nonconjugated oil produced from available hydroxy fatty acid (see Table IV). The relative percent yield of conjugated (P) and nonconjugated (U) products is given by eqs. (6) and (7):

$$P = \frac{C_\infty}{P_\infty H_0} \quad (6)$$

$$U = \frac{N_{\text{pt}\infty}}{P_\infty H_0} \quad (7)$$

Table III Composition of Lesquerella Oil Dehydrated under Variable Conditions^a

Sample	C_t	N_t	N_{pt}	C_t/N_{pt}
1	26.46	51.36	20.25	1.3
2	22.44	50.35	19.25	1.1
3	28.88	51.77	20.66	1.4
4	20.43	33.51	12.40	1.6
5	19.19	44.82	13.71	1.4
6	11.41	38.10	6.99	1.6
7	24.46	50.74	20.64	1.2
8	21.42	45.39	14.28	1.5
9	25.30	50.75	19.64	1.3
10	22.29	50.37	20.26	1.1
11	36.31	36.32	33.67	1.1

^a C_t , conjugated diene content; N_t , total nonconjugated diene content; N_{pt} , nonconjugated diene content produced by the dehydration reaction; (C_t/N_{pt}), ratio of conjugated diene to nonconjugated diene produced. Values for neat LO: $C_t = 0$, $N_t = 31.11$; values for Castung: $C_t = 0$, $N_t = 2.65$.

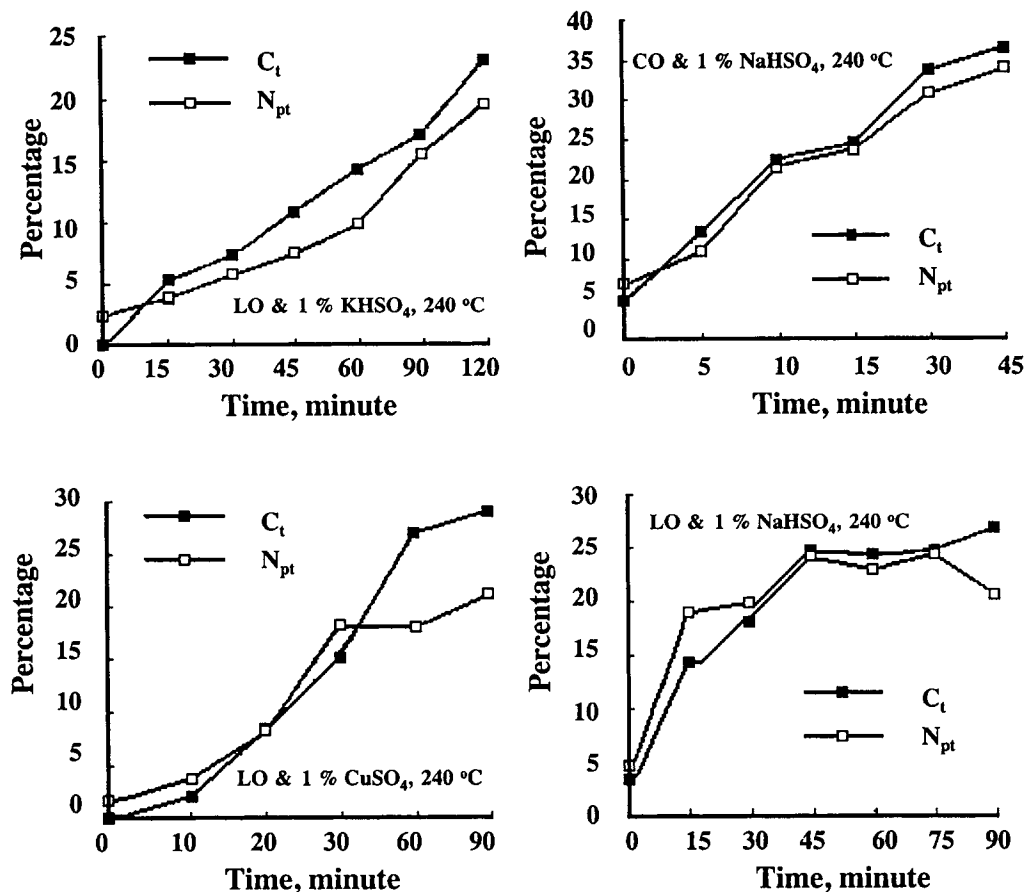


Figure 7 Percentage in oils of conjugated, C_t , and nonconjugated, N_{pt} , diene produced during dehydration versus time.

where C_α and $N_{p\alpha}$ are the conjugated and nonconjugated diene produced, respectively, at P_α degree of dehydration. Without side reactions, the sum percents of P , U , and remaining hydroxyl for each experiment should be unity (100%).

Dehydration of LO yields approximately 1.5 times more conjugated than nonconjugated product. In contrast, dehydration of castor oil produces nearly equal amounts of conjugated and nonconjugated products, with a ratio (C_t/N_{pt}) of 1.1. The conjugated diene content is comparable to the result of Achaya (35%) obtained by GC analysis.¹⁷ CO is observed to exhibit no dehydration selectivity.⁵

The physical properties of DLO are shown in Table V. The choice of catalyst affects both the operating conditions and properties of DLO. Among the catalysts examined, the catalytic efficiencies of acidic aluminum oxide and ammonium dihydrogen phosphate are low. LO achieves a high degree of dehydration with sulfuric acid in a few minutes, but the dehydrated product is consistently dark brown in color and of high acid value suggesting competing sulfonation. Cupric sulfate results a highly conjugated diene which possesses good drying velocity; however, the color of the oil was > 18 Gardner grade even after bleaching with activated carbon. Clay 452

Table IV Percent Yield of Conjugated (P) and Unconjugated (U) Diene Produced by Dehydration of LO under Various Conditions^a

Sample	1	2	3	4	5	6	7	8	9	10	11
P	51.32	54.61	52.33	61.02	45.30	29.00	47.27	56.16	46.83	44.28	46.67
U	39.27	46.54	37.73	37.04	32.30	17.74	39.61	37.44	36.50	40.26	43.00

^a Sample number indicates reaction conditions (see Table II).

Table V Measured Physical and Chemical Properties of Dehydrated Oils

No.	Color (Gardner)	Acid Value	Viscosity (cP)	Iodine Value	Drying Time (h)
LO	6	1.13	240	107	Nondrying
1	11	2.08	181	147	2.5
2	09	6.71	194	139	4.5
3	>18	4.04	187	144	2.5
4	8	6.77	—	135	5.0
5	8	—	210	123	4.0
7	10	5.62	164	139	2.5
8	13	—	185	125	4.0
9	9	4.96	210	133	3.0
10	12	8.01	192	128	3.5
11	10	3.66	—	142	4.0
Castung	6	5.92	—	138	2.5

generates a product of light color, but was not efficient.

Nondrying LO is converted into a drying oil during dehydration. DLO with an iodine value of 139 or better exhibits a drying time of approximately 2.5 h comparable to a commercial DCO, Castung, with an iodine value of 138. Therefore, LO is a promising substitute for CO as an alternative source of drying oil. Using only 1% NaHSO₄ (Expt. 1, Table II), LO can be dehydrated to over 90% in about 45 min, where the resulting oil has a color of 11 Gardner grade, an acid value of 2.08, an iodine value of 147, and dries in just 2.5 h.

CONCLUSION

Dehydration of LO was performed with several catalysts at various reaction conditions. The depletion of hydroxyl groups and formation of double bonds were confirmed by FTIR, UV, and ¹H-NMR analysis. The choice of catalyst affects the rate, conversion amount, and the properties of the DLO product. Sodium bisulfate is determined to be the best catalyst among the reagents examined. Dehydration of lesquerolic acid produces more conjugated diene than nonconjugated isomer, where the mole ratios of conjugated to nonconjugated diene produced ranges from 1.1 to 1.6. Further, experiment confirms

that LO can be converted into a drying oil with properties comparable to a commercial DCO.

This material is based upon work supported by the Cooperative State Research Service, U.S. Department of Agriculture, under Cooperative Agreement Number 93-COOP-1-9529. Our thanks to Drs. Harry Parker and Daniel E. Kugler and Mrs. Carmela Bailey for their time and support.

REFERENCES

1. C. R. Smith, Jr., T. L. Wilson, T. K. Miwa, H. Zobel, R. L. Lomar, and I. A. Wolff, *J. Org. Chem.*, **26**, 2903 (1961).
2. United States Department of Agriculture, *Growing Industrial Materials Series, Lesquerella as a Source of Hydroxy Fatty Acids for Industrial Products*, October 1991.
3. K. D. Carlson, A. Chaudry, and M. O. Bagby, *JAACS*, **67**, 438 (1990).
4. *The Chemistry of Castor Oil and Its Derivatives and Their Applications*, International Castor Oil Association, Westfield, NJ, 1992.
5. A. E. Rheineck and R. O. Austin, in *Treatise on Coatings, Film Forming Compositions, Part II*, Vol. 1, R. R. Myers and J. S. Long, Eds., Marcel Dekker, New York, 1968, pp. 212–220.
6. W. C. Forbes and H. A. Neville, *Ind. Eng. Chem.*, **36**, 555 (1940).
7. D. S. Bolley, *JAACS*, **36**, 518 (1959).
8. T. F. Bradley and D. Richardson, *Ind. Eng. Chem.*, **34**, 237 (1942).
9. G. W. Priest and J. D. von Mikuson, in *Protective and Decorative Coatings*, Vol. 1, J. J. Mattiello, Ed., John Wiley, New York, 1943, p. 431.
10. V. Spitzer, F. Marx, J. G. S. Maia, and K. Pfeilsticker, *JAACS*, **68**, 183 (1991).
11. V. Rutar, *J. Agric. Food Chem.*, **37**, 67 (1989).
12. K. Wollenberg, *JAACS*, **68**, 391 (1991).
13. K. D. Carison, A. Chaudry, R. E. Peterson, and M. O. Bagby, *JAACS*, **67**, 495 (1990).
14. L. A. Jordan, *J. Oil Colour Chemists Assoc.*, **35**, 577 (1952).
15. B. A. Ellis and R. A. Jones, *Analyst*, **61**, 812 (1936).
16. G. W. Priest and J. D. von Mikuson, *Ind. Eng. Chem.*, **32**, 131 (1940).
17. K. T. Achaya, *JAACS*, **48**, 758 (1971).

Received October 1, 1994

Accepted April 8, 1995