tially eliminates barometric condenser-water disposal problems since this water is relatively free of organic contaminants.

At a nominal cost, which can be economically justified, all deodorizers could be put on a closed-circuit water system. The cooling towers in this system would remain clean and would require little maintenance. The organic materials, which were formerly lost as stream contaminants, would be recovered in a dry form which holds a premium over acidulated soapstock.

This system would prove advantageous to the many processors of fatty products who are currently having waste-water disposal problems or who are operating on closed-circuit water systems, where periodic shutdown, cleaning, and maintenance of the cooling tower are required. The system is a major step toward solving the problems which have been so important in the past few years.

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Long-Chain Unsaturated Alcohols from Jojoba Oil by Sodium Reduction[1]

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JOJOBA OIL is unique in that it is a liquid wax rather than a glyceride oil usually found in oil-bearing vegetable materials; also it is unique in that it is an excellent source of unsaturated C_{20} and C_{22} straight-chain acids and alcohols. These long-chain, monoethylenic components are present as esters and comprise 93% of the jojoba oil, of which 45% are C_{20} acids and alcohols (eicosenoic and eicosenol) and 48% C_{22} acids and alcohols (docosenoic and docosenol).

Jojoba oil is present in the seed of the jojoba plant, which is known botanically as *Simmondsia chinensis* and *Simmondsia californica,* the description of which has been reported in several publications (3, 13). The seeds contain approximately 50% oil, which can be extracted in a remarkably pure state by conventional pressing and solvent-extraction methods commonly used for glyceride vegetable oils. The chemical composition of jojoba oil as reported by McKinney and Jamieson (9) is shown in Table I. Review articles on the composition, properties, and potential uses of jojoba oil have appeared recently (6, 8).

TABLE I
Chemical Composition of Jojoba Oil (9)

Compound	%
Eicosenoic acid	30.30
Docosenoic acid	14.20
Eicosenol	14.60
Docosenol	33.70
Saturated acids	1.64
Palmitoleic acid	0.24
Oleic acid	0.66
Glycerin	0.0
Hexacosenol	2.0

The sodium reduction method has been used commercially to produce alcohols from glyceride esters. Kastens and Peddicord (7) in a staff-industry report show that the best results from the commercial scale reduction of coconut fatty esters were obtained by using molten metallic sodium dispersed in toluene, and a secondary alcohol such as methyl isobutyl carbinol as the reducing alcohol.

Application of the sodium reduction method to jojoba oil was investigated because high yields of alcohol obtained from glyceride esters were reported (4, 7) and because the ethylenic unsaturation was not affected. This paper presents the results of a study of the preparation of long-chain unsaturated alcohols by sodium reduction of the wax fatty esters of jojoba oil on both a laboratory and pilot-plant scale.

Experimental

Equipment. The laboratory reduction and hydrolysis apparatus used in this work is similar to that described and used by Hansley (4). The pilot-plant reduction and hydrolysis units shown in Figure 1 are constructed of stainless steel. The dish-bottomed, jacketed, reduction vessel has an operating capacity of 15 gal. and is equipped with an auxiliary stainless steel stopper which fits flush to the bottom outlet to prevent unreacted metallic sodium from settling in the drain line. The 20-gal. hydrolysis unit is equipped with a condenser and a steam-sparging tube for heating the water for the hydrolysis step.

Materials. The jojoba oil used in this work was prepared by flaking and cold-hydraulic-pressing raw jojoba beans supplied by Boyce Thompson, Southwestern Arboretum, Superior, Ariz. The oil was dried at 220°F. for 30 min. under a vacuum of 27 in. of mercury to remove any traces of moisture present. The oil analyzed as follows: 49.44% unsaponifiables, 0.39% F.F.A., 0.08% hydroxyl, saponification value of 88.7, and iodine value of 83.1. American Oil Chemists' Society methods were used for analyses (1). Commercial grades of methyl isobutyl carbinol, toluene, and metallic sodium were used.

Procedure. The procedures for both the laboratory scale and pilot-plant scale experiments were similar, with the exception of the amounts of materials used. Theoretical proportions of materials required for the sodium reduction reaction are four atoms of sodium

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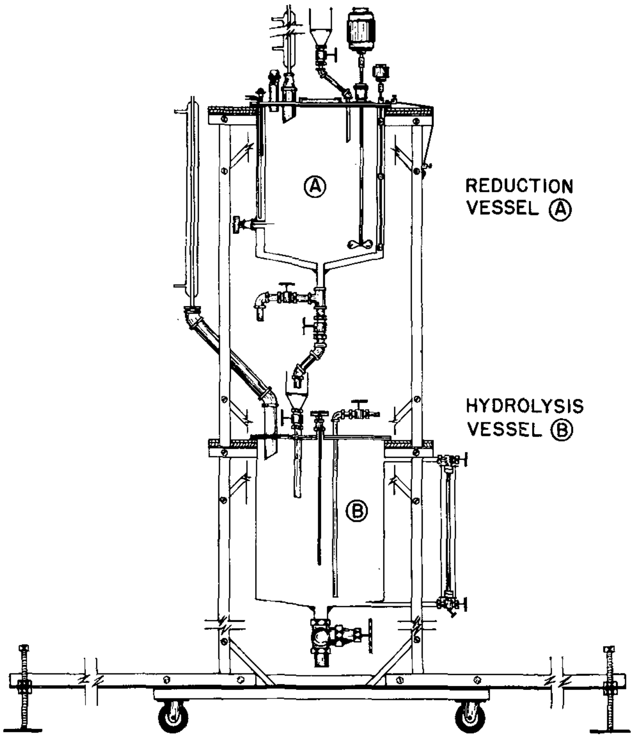

FIG. 1. Pilot-plant sodium reduction and hydrolysis units.

to two moles of reducing alcohol (methyl isobutyl carbinol) to one mole of ester (jojoba oil). About 5% over the theoretical calculations of both alcohol and sodium were used. Toluene served as the inert medium for the reaction and for dispersing the sodium. For the laboratory experiments the weights of the materials used were: jojoba oil 108 g., sodium 18 g., methyl isobutyl carbinol 45 g., and toluene approximately 100 g. In the first pilot-plant run 2,160 g. of jojoba oil, 360 g. of metallic sodium, 900 g. of methyl isobutyl carbinol, and 9,000 g. of toluene were used. In the second run, quantities of all materials except the toluene were doubled. The reduction and hydrolysis reactions are as follows:

$$\mathrm{RCOOCH_2R' + 4\,Na + 2\,R''OH} \longrightarrow$$

$$\underset{\text{Jojoba oil}}{\mathrm{RCH_2ONa + R'CH_2ONa + 2\,R''ONa}} \xrightarrow{\mathrm{H_2O}}$$

$$\underset{\text{Product alcohols}}{\mathrm{RCH_2OH + R'CH_2OH + 2\,R''OH + 2\,NaOH}}$$

The sodium and toluene were placed in a flask, heated to the refluxing temperature of toluene, and agitated to obtain a fine dispersion of molten sodium in toluene. Calculated amounts of jojoba oil and reducing alcohol were then thoroughly mixed in another container, and this reducible mixture was slowly added to the heated sodium and toluene in the reduction flask. The rate of addition of the reducible mixture was governed by the capacity of the reflux condenser. The rate was controlled so that only a slight excess of unreacted ester was present in the reaction flask at any time. This addition of reducible mixture required approximately 30 min. The reaction mixture was stirred an additional 40 min. to ensure complete reduction.

For the hydrolysis operation approximately 1,000 ml. of distilled water were heated to boiling in the hydrolysis flask by bubbling steam through it. The steam was adjusted so that a small amount of water dripped continuously from the condenser into the distillate receiver. The steam served to maintain the required hydrolysis temperature and to saturate the atmosphere within the flask to quench any small unreacted particles of sodium. The hot reacted mixture from the reduction flask was transferred at a slow rate to the water in the hydrolysis flask. An emulsion of long-chain alcohols, water, toluene, and sodium hydroxide was formed. The rate of addition of the reaction mixture was governed by the capacity of the condenser to handle the vapors resulting from the heat generated by the reaction. Total addition time was about 40 min. To ensure complete hydrolysis the mixture was allowed to hydrolyze an additional 45 min. The emulsion was washed with three 1,000-ml. portions of distilled water to remove most of the sodium hydroxide, thereby facilitating breakage of the emulsion. The emulsion was broken with the formation of an organic and aqueous layer by adding 600 ml. of reducing alcohol to change the existing ratio of reducing alcohol to toluene, followed by heating the mixture to approximately 100°C. The aqueous layer was then drawn off, and the organic layer was transferred to a distillation flask, equipped with a short vigreaux-type column to recover the long-chain alcohols (boiling range 155–161°C. at 1 mm. of absolute pressure). The aqueous layer and washings were evaporated to dryness and found to be free of long-chain alcohols.

Infrared absorption curves were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer.

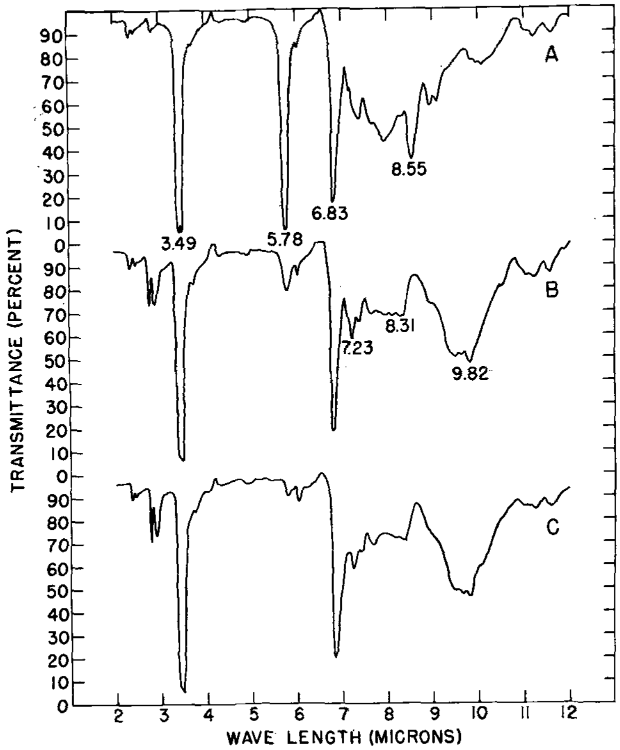

FIG. 2. Infrared absorption spectra
A. cold-hydraulic-pressed jojoba oil
B. product alcohols produced by sodium reduction of jojoba oil purified by washing
C. product alcohols produced by sodium reduction of jojoba oil purified by distillation.

TABLE II

Analysis of Distilled Long-Chain Alcohols

Run No.	F.F.A.	Unsap.	Hydroxyl	Sodium	Iodine value	Yield		Purity
	%	%	%	%		g.	%	%
1	0.07	97.25	5.60	0.00024	83.0	98.6	91.3	98.8
2	0.04	97.74	5.50	0.00096	82.5	98.0	90.7	97.0
3[a]	0.03	98.50	5.62	0.00008	83.1	1785	82.6	98.9
4[a]	0.03	98.62	5.18	0.00006	81.0	3712	85.9	91.4

[a] Pilot-plant runs.

The settings used were: resolution 927, suppression 3, gain 6, response 1, and speed 4. All spectra were obtained as chloroform solutions at concentrations of about 40 g. per liter, with an absorption cell 0.51 mm. in path length. Pure dry chloroform was placed in the reference beam and absorption of chloroform was completely eliminated from the resulting spectra by this differential technique.

Results and Discussion

Analyses of the long-chain alcohols obtained from the two laboratory-scale runs and two pilot-plant runs are shown in Table II. The iodine values of the resulting product alcohols, which varied only from 81 to 83, are comparable to the iodine value of the jojoba oil. This is an indication that the ethylenic unsaturation was not affected by the sodium reduction reaction.

Long-chain alcohol yields of 91% obtained in the two laboratory experiments are comparable to the yields reported (2, 5) for the sodium reduction of glyceride oils. For the pilot-plant runs the yields were somewhat lower. However there is no doubt that, with improvement in handling techniques, these yields could be increased to those obtained in the laboratory-scale experiments.

Purity of long-chain alcohols, as shown in Table II, was based on the analyses of the hydroxyl content of the alcohols as compared to the calculated hydroxyl content of 5.67 for a 50% mixture of pure C_{20} and C_{22} unsaturated alcohols. Therefore the term "purity" as used herein refers to the mixture of long-chain alcohols present. Purity of the long-chain alcohols averaged about 98%. Other indications of the high purity of the product alcohols are the high unsaponifiable values of 98%, which are assumed to be alcohols, and the low free fatty acids (0.03 to 0.07%). The product alcohols were essentially free of soaps as indicated by the very low sodium content.

The infrared spectra are shown in Figure 2A, B, and C. The spectra of the jojoba oil, Figure 2A, reveals some eight to 10 prominent bands, characteristic of long-chain fatty esters (10). A very weak band with maximum at 2.85 μ arises from an O—H stretching vibration. This band appears considerably stronger in the spectra of the alcohols obtained by the sodium reduction. In the spectra of Figure 2B and C two bands appear with well resolved maxima at 2.78 and 2.90 μ, indicating free O—H and bonded O—H . . . . . O groups, respectively.

The spectra of jojoba oil reveals the characteristic strong C—H stretching bands at 3.43–3.49 μ and the weaker C—H bending band at 6.83 μ. As expected, these bands are unchanged in the spectra of the alcohols. The characteristic methyl bending band, at 7.39 μ, in the spectra of the oil apppears at somewhat shorter wavelength in the alcohols (10, 11).

The very strong band at 5.78 μ, in the spectra of the jojoba oil, arises from C=O stretching of the ester group. Weaker bands at 7.93 and 8.55 μ are caused by C—O stretchings of the ester moiety (10). In the spectra of the alcohol purified by washing, Figure 2B, the intensity of the strong C=O stretching 5.78 μ band is considerably reduced, and except for a negligible trace it is absent from the spectra of the alcohols purified by distillation, Figure 2C. The weaker C—O stretching vibrations at 7.93 and 8.55 μ are completely absent in the spectra of the alcohols. Bands at 8.55 and 8.95 μ have been shown to arise, probably from unsymmetrical stretching vibrations of the ester group (10). These bands, observed in the spectra of the oil, are likewise completely absent in the spectra of the alcohols. The absence of these ester bands in the spectra of the alcohols is an indication of the completeness of the sodium reduction and of the purity of the resulting alcohols.

The spectra of the alcohols reveal one additional difference from the spectrum of the jojoba oil. In the region 9.5 to 9.85 μ well-resolved weak bands appear in the spectra of the alcohols which are not observed in the spectra of the oil. These bands arise undoubtedly from C—O stretchings of the C—O—H groups of the alcohols which are too weak to be observed in the spectra of the oil. The infrared spectra exhibit features which might be predicted in the conversion of esters to alcohols and thus confirm the completeness of the reduction and the purity of the resulting alcohols (12).

In Figure 3 the infrared spectrum of the product alcohols from jojoba oil by sodium reduction is com-

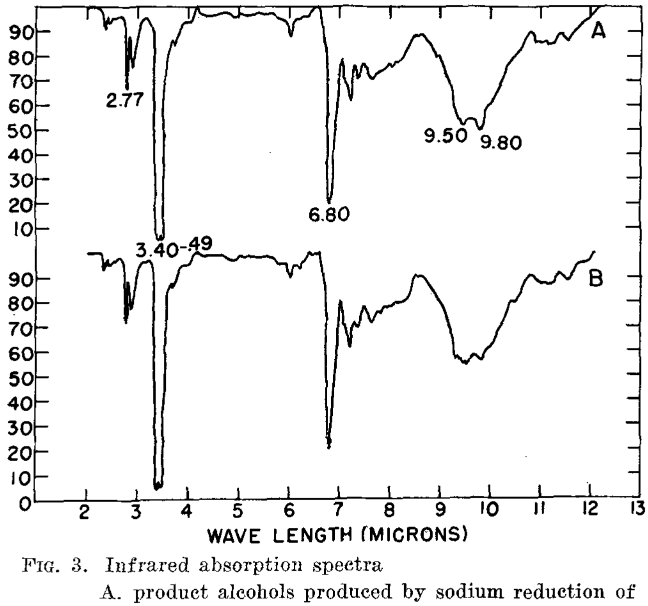

FIG. 3. Infrared absorption spectra
A. product alcohols produced by sodium reduction of jojoba oil
B. pure erucyl alcohol (13-docosene-1-OL).

pared with the spectrum of a pure sample of erucyl alcohol (13-docosene-1-OL). The two spectra are essentially identical, further confirming that the products from the sodium reduction are highly purified long-chain unsaturated alcohols.

Summary

Jojoba oil is a liquid wax composed essentially of C_{20} and C_{22} straight-chain monoethylenic acids and alcohols in the form of esters. Sodium reduction of the wax fatty esters in jojoba oil yielded quantitatively a mixture of unsaturated, long-chain alcohols from the acid moiety of the jojoba oil. Yields of about 91% were obtained in the laboratory-scale experiments and 82 to 86 for the pilot-plant experiments. Analytical data, including detailed infrared spectra information, are given for the resulting product alcohols.

Acknowledgments

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Esters of Hydroxystearic Acids as Primary Low-Temperature Plasticizers for a Vinyl Chloride—Vinyl Acetate Copolymer

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THE USE OF FATTY DERIVATIVES in formulations with vinyl chloride resins has usually been limited to applications utilizing their properties as stabilizers, mold lubricants, or as secondary plasticizers or extenders. The principal exception is the use of alkyl epoxystearates, which may be considered to be primary plasticizers as well as stabilizers (19, 10) since they are highly compatible and efficient, as indicated by their effect on modulus, elongation, and tensile strength.

The literature contains some mention of esters of acyloxystearates as plasticizers and as lubricants. Aliphatic esters of diacetoxystearates (11) and diacetomonoglycerides (16) have been proposed as plasticizers for polyvinyl chloride. The methyl, ethyl, *n*-butyl, and 2-ethylhexyl 12-acetoxystearates have been mentioned as plasticizers for ethyl cellulose (12). A series of alkyl acyloxystearates, in which the alkyl is a branched chain (2-ethylhexyl, isopropyl, or 2-methylpentyl) and the acyloxy group (acetoxy, diethylacetoxy, propionoxy, or butyroxy) is situated at either the 9,10, or 12 position in the chain, has been evaluated as lubricants (18).

Adequate compatibility of a plasticizer with vinyl chloride resins depends on the proper kind, number, and arrangement of polar groups (13). Ester groups are the most effective (15). With dibasic acid esters of mono- or polyhydric alcohols, the compatibility limit is about a total of 26 carbon atoms (8). With phthalates, adipates, and thiodibutyrates, compatibility decreases as the alcohols increase to a chain length of C_9-C_{11}.

In this report it will be shown that many acyloxy and aryloxy compounds prepared from hydroxystearic acids are not only primary plasticizers but impart outstanding low-temperature flexibility when formulated with a vinyl chloride-vinyl acetate copolymer. This has been accomplished without any undesirable changes in modulus and tensile strength, when compared to similar compositions containing di-2-ethylhexyl phthalate.

Experimental

Butyl 12-Acetoxystearate. This was isolated from the commercial product by distillation; b.p. 155°C./0.05 mm.; saponification no. 256; acid no. 3.9; $n^{30/D}$ 1.4436.

Butyl 9,10-Diacetoxystearate. A commercial material prepared from fairly pure 9,10-dihydroxystearic acid was employed as received; saponification no. 329; acid no. 3.5; $n^{30/D}$ 1.4462.

Butyl 9,10,12-Triacetoxystearate. This was isolated from the commercial material by distillation; b.p. 194°C./0.10 mm.; saponification no. 392; acid no. 3.5; $n^{30/D}$ 1.4473.

Methyl 12-Acetoxystearate. Methyl 12-hydroxystearate was heated and stirred for 3 hrs. at 110° with a 100% molar excess of acetic anhydride. Hot water was slowly added to the stirred reaction mixture to hydrolyze the excess acetic anhydride. The aqueous

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