SYMPOSIUM: NOVEL USES OF AGRICULTURAL OILS

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Production, Chemistry, and Commercial Applications of Various Chemicals from Castor Oil[1]

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ABSTRACT

The presence of a hydroxyl group, in addition to an olefinic linkage, in the predominating fatty acid of castor oil gives this vegetable oil many unique and interesting properties. Castor oil consists largely of glycerides of ricinoleic acid or 12-hydroxy octadecenoic acid. The chemical reactions of castor oil, undecylenic acid, 12-hydroxylstearic acid, sebacic acid, and nylon 11, depict the uniqueness of this agricultural oil. By dehydration, castor oil is converted to a conjugated acid oil similar to tung or

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oiticica oil. The catalytic dehydration results in the formation of a new double bond in the fatty acid chain. The dehydrated castor oil imparts good flexibility, rapid dry, excellent color retention, and water resistance to protective coatings. The pyrolysis of castor oil cleaves the molecule to produce undecylenic acid and heptaldehyde. The pyrolysis of the methyl ester at 450-550 C results in the formation of methyl 10-undecylenate. Hydrolysis of the methyl ester gives 10-undecylenic acid. Hydrogen bromide is added to form 11-bromo undecanoic, which is ammoniated and condensed to form a nylon polymer. When castor oil is added slowly to an 80% caustic solution, the sodium ricinoleate formed splits to form sodium sebacate and capryl alcohol. Sebacic acid is condensed with hexamethylene diamine to form nylon 6,10. The commercial application of castor oil derivatives in urethanes, starch gel modifiers, medium chain triglycerides, and thixotropic additives is reviewed briefly.

INTRODUCTION

Castor oil has long been known as an article of commerce and has been reported as a constituent of the embalming fluid used by the ancient Egyptians. Although it has developed a reputation for its medicinal use, castor oil now finds extensive use as an industrial oil. Castor oil is unique in consisting largely of glycerides of ricinoleic acid

TABLE I

Composition of Castor Oil Fatty Acids

Fatty acid	Percentage
Ricinoleic acid (12-hydroxy oleic)	89.5
Linoleic acid	4.2
Oleic acid	3.0
Stearic acid	1.0
Palmitic acid	1.0
Dihydroxystearic acid	0.7
Eicosanoic acid	0.3
Linolenic acid	0.3

CHEMICAL REACTIONS OF CASTOR OIL

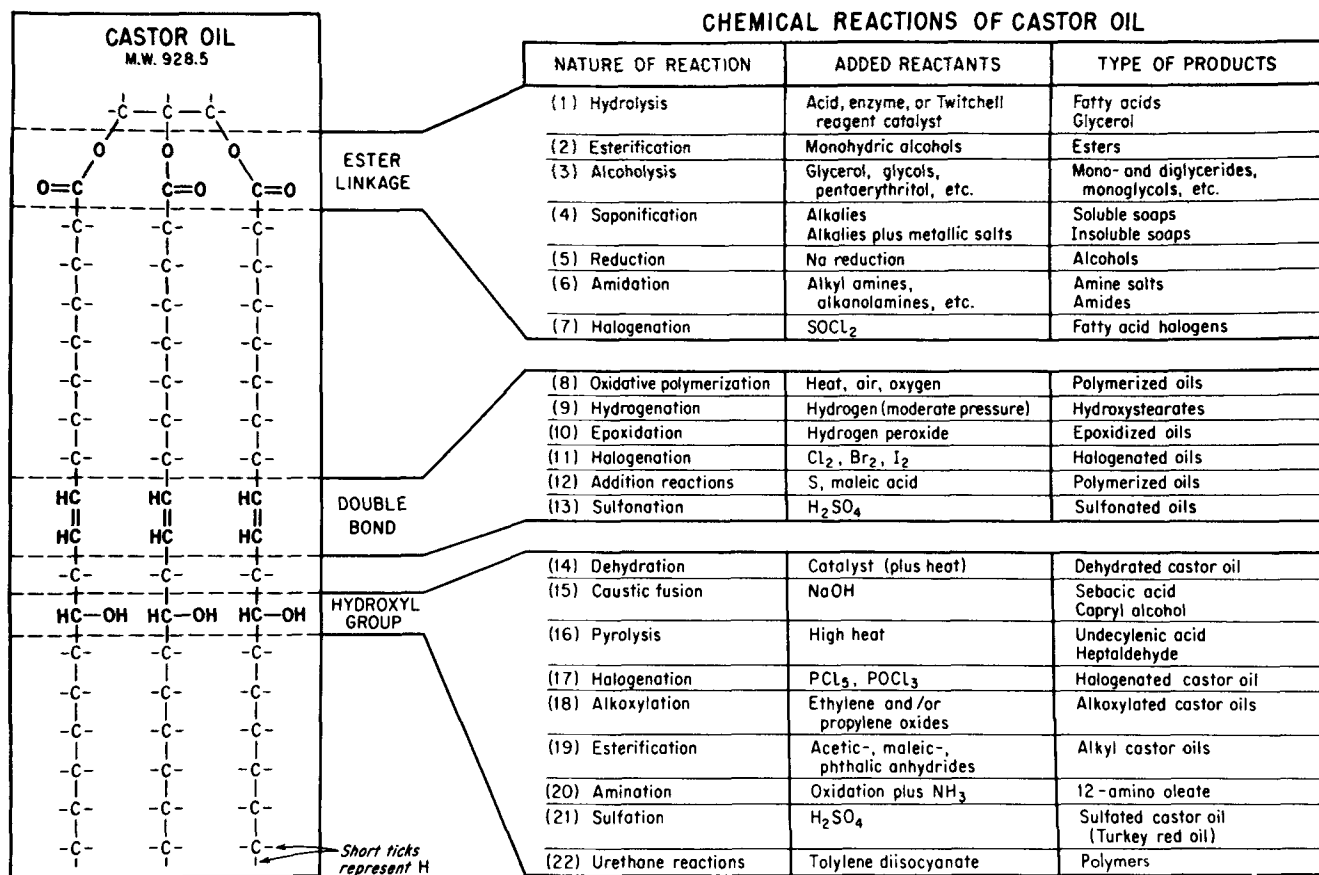|	NATURE OF REACTION	ADDED REACTANTS	TYPE OF PRODUCTS
ESTER LINKAGE	(1) Hydrolysis	Acid, enzyme, or Twitchell reagent catalyst	Fatty acids Glycerol
	(2) Esterification	Monohydric alcohols	Esters
	(3) Alcoholysis	Glycerol, glycols, pentaerythritol, etc.	Mono- and diglycerides, monoglycols, etc.
	(4) Saponification	Alkalies Alkalies plus metallic salts	Soluble soaps Insoluble soaps
	(5) Reduction	No reduction	Alcohols
	(6) Amidation	Alkyl amines, alkanolamines, etc.	Amine salts Amides
	(7) Halogenation	$SOCl_2$	Fatty acid halogens
DOUBLE BOND	(8) Oxidative polymerization	Heat, air, oxygen	Polymerized oils
	(9) Hydrogenation	Hydrogen (moderate pressure)	Hydroxystearates
	(10) Epoxidation	Hydrogen peroxide	Epoxidized oils
	(11) Halogenation	Cl_2, Br_2, I_2	Halogenated oils
	(12) Addition reactions	S, maleic acid	Polymerized oils
	(13) Sulfonation	H_2SO_4	Sulfonated oils
HYDROXYL GROUP	(14) Dehydration	Catalyst (plus heat)	Dehydrated castor oil
	(15) Caustic fusion	NaOH	Sebacic acid Capryl alcohol
	(16) Pyrolysis	High heat	Undecylenic acid Heptaldehyde
	(17) Halogenation	PCl_5, $POCl_3$	Halogenated castor oil
	(18) Alkoxylation	Ethylene and/or propylene oxides	Alkoxylated castor oils
	(19) Esterification	Acetic-, maleic-, phthalic anhydrides	Alkyl castor oils
	(20) Amination	Oxidation plus NH_3	12-amino oleate
	(21) Sulfation	H_2SO_4	Sulfated castor oil (Turkey red oil)
	(22) Urethane reactions	Tolylene diisocyanate	Polymers

FIG. 1. Chemical reactions at three basic points of functionality in castor oil. (Copyright 1970 Baker Castor Oil Co.)

or 12-hydroxyoctadecenoic acid. Castor oil is one of the few naturally occurring glycerides that approaches being a pure compound and is the only major vegetable oil that is composed of nine-tenths of the glyceride of a hydroxy acid. The composition of castor oil fatty acids is as shown in Table I.

Ricinoleic acid (12-hydroxy-9-octadecenoic acid), $CH_3(CH_2)_5$ CHOH $CH_2CH:CH(CH_2)_7COOH$, has an 18 carbon backbone, with one hydroxy group on the 12 carbon atom and a cis-double bond between the 9 and 10 carbon atoms. The formula wt is 298.46, the neutralization value 188.0, and the molecule strongly dextrorotory because of the asymmetric carbon atom in the 12 position. The presence of ricinoleic acid gives castor oil its unique properties and unusual versatility. Castor oil differs from other oils by its high acetyl or hydroxyl value and from oils of comparable iodine value by its high viscosity and specific gravity. Unlike other oils, it is miscible with alcohol, but only slightly soluble in petroleum ether at room temperature.

At the present time, two grades of castor oil are recognized in the U.S. Depending upon source and grade, the physical and chemical properties are usually within the limits shown in Table II for no. 1 and no. 3 oils.

TABLE II

Characteristics of Grades of Castor Oil

Property	No. 1 oil	No. 3 oil
Color, gardner	1-2	5-6
Acid value	2-3	5-8
Specific gravity 25 C/25 C	0.957-0.961	0.957-0.961
Viscosity, stokes @ 25 C	6.5-8.5	6.5-8.5
Iodine value	82-88	80-88
Hydroxyl value	160-168	158-168
Saponification value	179-185	177-182

The hydroxyl group, double bonds, and ester linkages in castor oil provide reaction sites for the preparation of many useful industrial derivatives. The chemical reactions at the three basic points of functionality are depicted in Figure 1.

The functionality may be modified at the carboxyl position through a wide range of esterifications. The unsaturation can be modified by hydrogenation, epoxidation, polymerization, or addition reactions. The hydroxyl group can be readily acetylated and alkoxylated. The hydroxyl group can be eliminated by dehydration to increase the unsaturation of the molecule.

DEHYDRATION OF CASTOR OIL

The chemical dehydration of castor oil consists of the removal of the hydroxyl group and an adjacent hydrogen atom in the ricinoleic acid portion of the triglyceride (1). In the proposed mechanism (2) for this reaction in the presence of sulfuric acid catalyst, carbonium ions are formed by electrophilic attack upon the unshared pair of electrons of the hydroxyl oxygen atom via formation of the hydroxonium ion (Fig. 2). Further reaction yields both conjugated and nonconjugated diene forms (Fig. 3).

Catalysts for the dehydration of castor oil may be any of a variety of inorganic or organic acids, salts, clays, resins, or oxides (1,3,4). The dehyration process and catalysts used therein have been the subject of numerous patents (1,4-9). The most widely used catalysts are sulfuric acid or phosphoric acid, sodium bisulfate, and acid-activated clays. Of the many factors involved in the dehydration of castor oil, the choice of catalyst is most important in governing process conditions, as well as the color, viscosity, and side reactions. The catalytic dehydration of ricinoleic acid also may involve the loss of water by reaction of the hydroxyl groups with carboxyl groups to form estolides or polyricinoleates.

Higher degrees of diene conjugation are possible by the

$$H_2SO_4 + H_2O \rightleftarrows HSO_4^{\ominus} + H_3O^{\oplus}$$

$$H SO_4^{\ominus} + H_2O \rightleftarrows SO_4^{\ominus\ominus} + H_3O^{\oplus}$$

- -

$$R—\underset{\underset{OH}{|}}{C}HCH_2CH=CH- \quad +H_3O^{\oplus} \longrightarrow R—\underset{\underset{OH_2}{|}{\oplus}}{C}H—CH_2—CH=CH— \quad +H_2O$$

HYDROXONIUM ION

$$R—\underset{\oplus}{C}H—CH_2CH=CH— \quad +H_2O \longleftarrow |$$
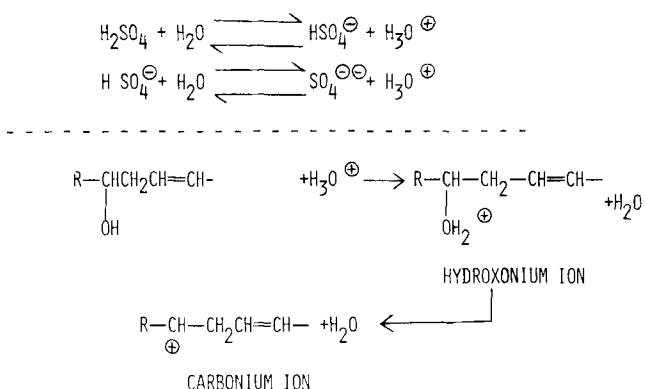
CARBONIUM ION

FIG. 2. Carbonium ion formation during dehydration of castor oil (see ref. 2).

estoliding route. Condensation of the carboxyl end of one ricinoleic acid molecule with the hydroxyl group of another gives a build-up of estolide formation, as depicted in Figure 4. Estolide formation is accelerated by heat and can undergo various reactions (10,11). Breakdown of the estolides yields acids with ca. 50% diene conjugation.

The commercial dehydration of castor oil is carried out in stainless steel, inconel, monel, or glass lined reactors. The reactors generally are equipped with steam-jet ejectors or other vacuum sources and efficient agitation. Temperatures of 230-280 C are required, and considerable heat input is necessary. Dowtherm or electrical heating ordinarily are employed. Systems for continuous dehydration have been patented and described in various literature (12,13). Analytical changes which take place during the dehydration are utilized for process control. As the hydroxyl group is removed during the course of the reaction, the viscosity decreases, the iodine value increases, and the refractive index changes, allowing these analyses to be utilized to control the degree of dehydration and polymerization. It is interesting to note that maximum iodine value occurs at or near the point of minimum viscosity. Beyond this point, polymerization is initiated with a consequent drop in iodine value. Dehydrated castor oil is available in viscosities ranging from that of the unpolymerized product at 1.5-2.0 poise at 25 C to polymerized oils from 40-50 poise at 25 C.

Dehydrated castor oil (DCO) is noted for nonyellowing and outstanding color retention characteristics in protective coatings. Varnishes, alkyds, and coating resin systems based upon DCO are noted for high speed dry, flexibility, excellent chemical resistance, adhesion, gloss, and water proofness. The penetrating property of the DCO based additives, combined with low mol wt and low viscosity, diffuses the μ size chalk particles on a painted surface and establishes contact with the substrate to secure adhesion. Latex paints reinforced with DCO additives prevent grain cracking. checking, or stripping of the paint film by reducing liquid moisture transmission (14).

PRODUCTION OF NYLON 11
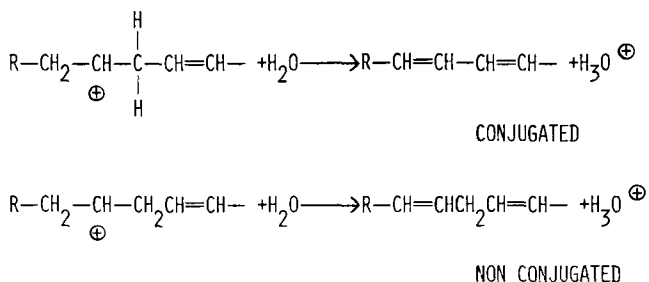
In the production of nylon 11, castor oil is alcoholyzed

$$R—CH_2—CH—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{\underset{\oplus}{C}}}—CH=CH— \quad +H_2O \longrightarrow R—CH=CH—CH=CH— \quad +H_3O^{\oplus}$$

CONJUGATED

$$R—CH_2—CH—CH_2CH=CH— \quad +H_2O \longrightarrow R—CH=CHCH_2CH=CH— \quad +H_3O^{\oplus}$$

NON CONJUGATED

FIG. 3. Formation of alternative dienoic products from dehydration of castor oil.

$$CH_3(CH_2)_5\underset{\underset{OH}{|}}{C}HCH_2CH=CH(CH_2)_7COOH$$

$$HO \; OC(CH_2)_7CH=CHCH_2\underset{\underset{OH}{|}}{C}H(CH_2)_5CH_3$$

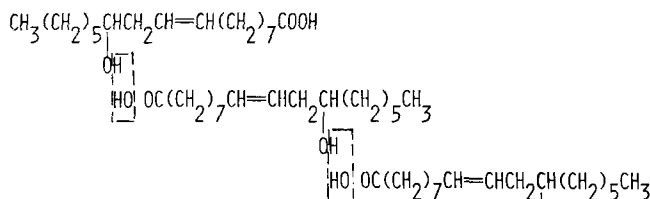$$HO \; OC(CH_2)_7CH=CHCH_2\underset{\underset{|}{}}{C}H(CH_2)_5CH_3$$

FIG. 4. Estolide formation from ricinoleic acid.

with methyl alcohol to form methyl ricinoleate and glycerol. The pyrolysis of methyl ricinoleate is accomplished at ca. 450-500 C to form methyl 10-undecylenate and heptaldehyde. Hydrolysis of the methyl ester gives 10-undecylenic acid. Hydrogen bromide is added to this molecule in the presence of peroxides to form 11-amino-undecanoic acid, known as RILSAN monomer (15). Heating the molten monomer gives the polymer by condensation. The chemical equations representing this synthesis are shown in Figure 5.

Nylon 11 polyamide has mp of ca. 186-190 C facilitating high speed uniform processing. Nylon 11 has the advantage of having a cold impact, no rupture temperature of -40 F (and, thereby, better than nylon 6 type derivatives), low moisture sensitivity, and superior zinc chloride resistance. In a 50% solution of zinc chloride, it showed no attack after several thousand hr of testing. Nylon 6 and 6,6 showed attack in ca. 20 min and nylon 6,10 was attacked in 20 hr. The excellent chemical resistance and stability in contact with all types of fuels, along with vibration and shock resistance, have led to the use of nylon 11 in the automotive industry.

Monofilament fabricated from nylon 11 is used as a covering for braided cable coverings and in industrial

METHYL RICINOLEATE

$$CH_3(CH_2)_5CHOHCH_2CH=CH(CH_2)_7COOCH_3$$

↓ PYROLYSIS

$$CH_2=CH \; (CH_2)_8COOCH_3 + CH_3(CH_2)_5CHO$$

METHYL UNDECYLENATE   HEPTALDEHYDE

↓ HYDROLYSIS

$$CH_2=CH(CH_2)_8COOH \quad (10\text{-UNDECYLENIC ACID})$$

↓ HBR

$$BrCH_2(CH_2)_9COOH \quad (11\text{-BROMOUNDECANOIC ACID})$$

↓ NH_3

$$NH_2CH_2(CH_2)_9COOH \quad (11\text{-AMINOUNDECANOIC ACID})$$

↓ CONDENSATION

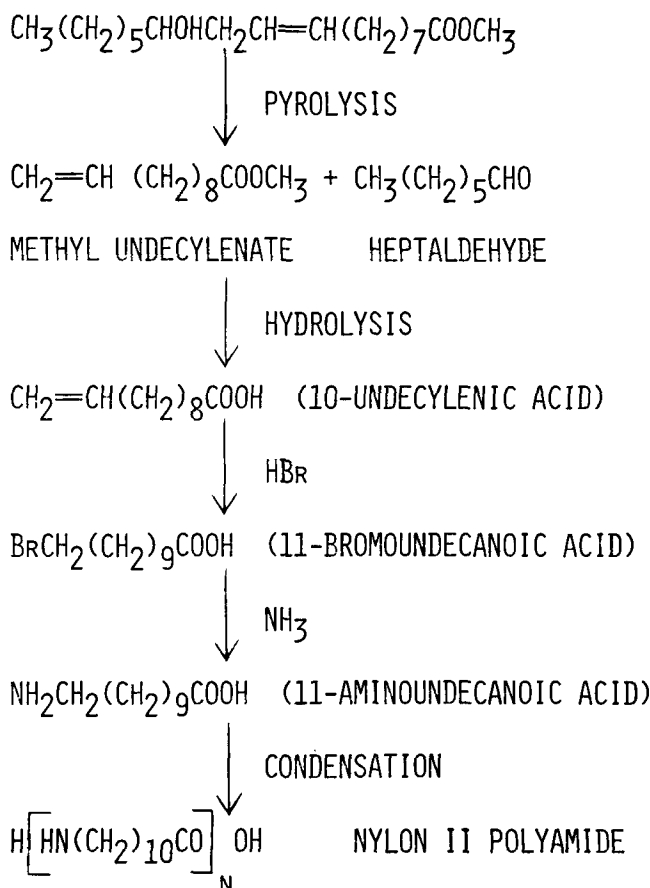$$H\left[HN(CH_2)_{10}CO\right]_N OH \quad \text{NYLON 11 POLYAMIDE}$$

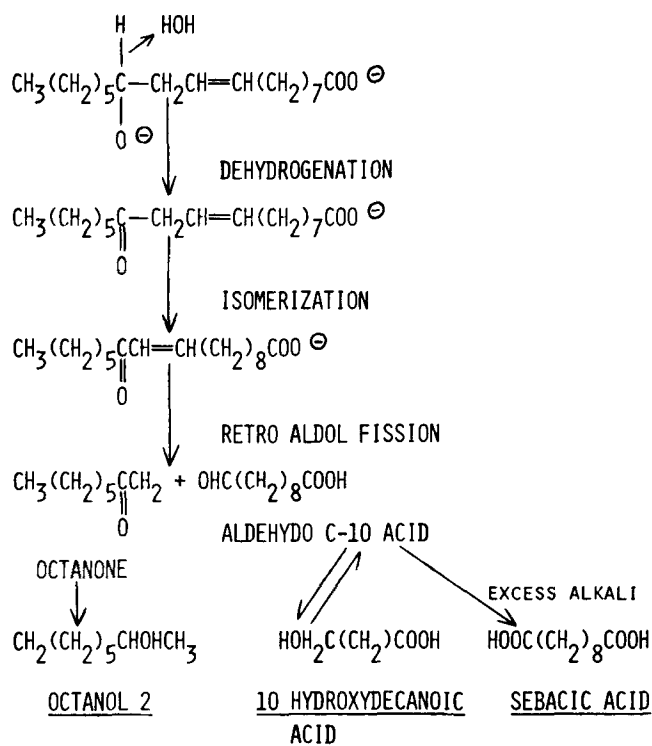FIG. 5. Synthesis of nylon 11 polyamide.

FIG. 6. Alkali fusion of ricinoleate.

fabrics, such as filter cloth, bags, netting, flexible fishing lines, and a variety of brush applications where toughness and durability are required. A variety of bearings and rollers in conveyor systems are fabricated by machining. Flat and tubular film is used in difficult to solve packaging problems demanding superior quality nylon. Molded nylon 11 parts are used in the automotive field in the fuel system, brackets for steering gear columns and hand-brakes, carburetor linkage, filters, etc. Glass reinforced nylon 11 provides an appreciable increase in rigidity and improvement in compressive strength and resistance to cold flow under load.

The use of nylon 11 for powder coatings or dry coatings has been developed by a commercial firm to overcome growing concern for the environment (16). As nylon 11 is insoluble in commercial solvents and is nonemulsifiable, liquid techniques are virtually impossible, and powder must be used for conventional coating application. Electrostatic deposition of nylon 11 allows thin films to be applied to metal substrates. Since it is thermoplastic, no cure is required. When the powder has been applied, it must be melted and coalesced into continuous plastic film. Forced draft ovens or IR radiant ovens are used for fusion; and, since no polymerization or cross-linkage are required for curing, coated objects can be processed quickly and air-cooled.

Nylon 11 has a long history in providing durable and totally functional coatings in Europe. It has been used for wear resistance and impact on centrifugal pumps; conveyors; fan impellers; textile, printing, and paper machine roll coverings; automotive springs; and marine hardware. Applications for resistance to hostile environments, such as hot water, detergents, and thermal cycling, have led to the use of nylon 11 in dishwashers, washing machines, heat exchangers, channel buoys, refrigerators, water softeners, and internal pipe and fittings for chemical transport.

PYROLYTIC DECOMPOSITION OF CASTOR OIL

The pyrolytic decomposition of castor oil at temperatures 650-750 F splits the ricinoleate molecule at the hydroxyl group to form heptaldehyde and undecylenic acids. Heptaldehyde, a seven carbon aldehyde, is used in the

manufacture of synthetic flavors and fragrances. It also is converted to heptanoic acid by various oxidation techniques and to heptyl alcohol by catalytic hydrogenation. When heptaldehyde is reacted with benzaldehyde by the aldol reaction, amyl cinnamic aldehyde is produced. Undecylenic acid, a C_{11} fatty acid having terminal unsaturation, is used primarily for its fungicidal and bactericidal properties, which continue through its derivatives. A combination of undecylenic acid and zinc undecylenate is used in the treatment of athlete's foot infections. The copper salt has been compounded into ointments used in treating facial and body infections.

The alkali fusion of castor oil is accomplished with sodium hydroxide or potassium hydroxide at elevated temperatures and in the presence of catalysts to split the ricinoleate molecule (17,18). Dependent upon reaction conditions, two different end products can be achieved. At lower reaction temperatures of 180-200 C, methyl hexyl ketone and 10-hydroxydecanoic acid are prepared using one molecular proportion of alkali. This reaction is favored by the presence of primary or secondary alcohols, such as 1 or 2-octanol (19). The increase to two moles of alkali/mole ricinoleate with an increased temperature range of 250-275 C and a shorter reaction cycle produces capryl alcohol and sebacic acid.

An interesting reaction mechanism (Fig. 6) has been proposed to describe the above reactions (20). During the alkali fusion, ricinoleic acid is converted into the β,γ unsaturated keto acid which isomerizes in alkaline media to the α,β keto acid. The α,β ketone undergoes a retroaldol fission to yield a ketone and the C_{10} aldehydo acid. As the reaction continues, the aldehydo acid can react irreversibly to the dicarboxylic sebacic acid; or it can accept hydrogen from ricinoleic acid and convert it to the β,γ keto acid, which recycles into the system, and gives rise to the 10-hydroxydecanoic acid.

The 10-hydroxydecanoic acid is formed in good yield when castor oil or methyl ricinoleate is fused with alkali in the presence of a high boiling unhindered primary or secondary alcohol at 180-200 C (21). Hydroxydecanoic acid has been used to synthesize acryloxy aliphatic acyl chlorides to prepare graft polymers with long side chains containing acyl chloride terminal groups. The active polymers were applied to wool fabrics and found to impart shrink resistance. The treatment also gave a soft hand or feel to the wool due to internal plasticization of the polymer coating (22).

The alkali fusion of castor oil at 250-275 C in the presence of excess alkali and catalyst produces sebacic acid, capryl alcohol, and hydrogen. Sebacic acid is used in the manufacture of nylon 6,10 by reaction with hexamethylenediamine. Of the polyamides made by condensation of dibasic acids with diamines, the nylon 6,10 type has better molding properties and resistance to moisture than adipic acid based nylon. The nylon 6,10 polyamide finds major usage in moldings, extrusions, filaments, and bristles and some textile fiber applications. A variety of sebacic acid esters is prepared and used as plasticizers and as lubricants for jet engines. Bis(2-ethylhexyl) sebacate has been found satisfactory for wide temperature range performance encountered by jet engines, demonstrating outstanding ability to maintain lubricity under severe operating conditions.

HYDROGENATION OF CASTOR OIL

The hydrogenation of castor oil can be performed in a number of ways to produce unique derivatives (Fig. 7).

Since castor oil contains unsaturated ricinoleic acid, hydrogen can be added to the double bond to yield a saturated acid of higher mp. Simple double bond hydrogenation produces tri-12-hydroxyoctadecanoin. Commercial preparation is accomplished by careful introduction of

hydrogen at temperatures in the order of 300 F and in the presence of nickel catalyst. Care is necessary to avoid decomposition of the sensitive hydroxyl group. The repeated use of Raney-type nickel with replenishment of 10% fresh catalyst for each successive hydrogenation has been reported (23,24). The product of complete hydrogenation, essentially tri-12-hydroxyoctadecanoin, is a hard high melting wax with mp of 86 C. This synthetic wax is used commercially in waxes, polishes, cosmetics and paper coatings. Although it lacks the gloss of some high melting natural waxes, it is preferred in specific applications where its ability to impart grease-proofness is required. The largest use for hydrogenated castor oil is in the manufacture of multipurpose greases. High pressure lithium-based greases derived from hydrogenated castor oil are used as the gelling agent which imparts improved performance. Such greases have a higher drop point, more resistance to water and a greater lubrication required for automotive and military use.

Conversion of castor oil or the methyl ester to the fatty alcohol can be accomplished by sodium reduction or high pressure hydrogenation. Quantitative reduction to ricinoleyl alcohol is achieved using a secondary reducing alcohol in the presence of sodium suspensions in refluxing xylene. Hydrogenation of ricinoleic acid with a copper-cadmium catalyst at 220 C and 3800 psi yields 70% ricinoleyl alcohol with wax esters and fission products (25).

The preparation of methyl 12-ketostearate from methyl/12-ketostearate has been accomplished using copper chromite catalyst and less efficiently with Raney nickel. The ketostearate also can be prepared from methyl ricinoleate in a two step process using Raney nickel. The first step is a rapid hydrogenation to methyl 12-hydroxystearate, the hydrogen coming from the catalyst, followed by a slower dehydrogenation to product (26,27).

The preparation of the stearate (Fig. 7) can be theoretically accomplished by dehydrating hydrogenated castor oil or by dehydration of castor oil followed by full hydrogenation of the diene intermediate (28). These processes are not economically feasible on a commercial basis to convert ricinoleic glycerides to stearic or stearic-oleic glycerides.

Partial hydrogenation of castor oil results in waxes of modified chemical properties. The hardness, flexibility, mp, and iodine value of the finished products are controlled by degree of hydrogenation. Esters of castor oil are changed by hydrogenation from fluid products to soft waxes with mp of 45-65 C. These products are used in leather coatings requiring oil resistance and water imperviousness, in roll leaf foils because of their alcohol solubility and excellent wetting and adhesion to metallic particles.

Sulfonated castor oil, also known as turkey-red oil, represents one of the earliest chemical derivatives of castor oil. The traditional method of preparing turkey-red oil is to add concentrated sulfuric acid to castor oil over a period of several hr while cooling the reaction mass. Constant cooling and agitation are required with controlled rates of acid addition, to maintain a temperature of 25-30 C. Upon complete addition of the desired amount of sulfuric acid, the reaction mass is washed to remove surplus acid and then neutralized with such alkalis as sodium hydroxide solution, potassium hydroxide solution, ammonia, or an amine, such as ethanolamine.

SULFONATION OF CASTOR OIL

Sulfonation of castor oil with sulfuric acid results largely in a sulfuric acid ester, in which the hydroxyl group of ricinoleic acid has been esterified. However, many reactions can take place during the sulfuric acid treatment and subsequent washing and neutralization (29). Aside from sulfation of the hydroxyl group, the double bond can be attacked to produce an ester or the hydroxy-sulfonic acid.

$$CASTOR\ OIL \xrightarrow{H_2} R'CH-(CH_2)_{10}COOR$$
$$\underset{OH}{|}$$

12 HYDROXYSTEARATE

$$\xrightarrow{+2H_2} R'CHCH_2CH=CH(CH_2)_7CH_2OH$$
$$\underset{OH}{|}$$

RICINOLEYL ALCOHOL

$$\xrightarrow{+H_2,-H_2} R'C-(CH_2)_{10}COOR$$
$$\underset{O}{\|}$$

12 KETOSTEARATE

$$\xrightarrow{-H_2O,+2H_2} R'-CH_2CH_2CH_2CH_2(CH_2)_7COOR$$

STEARATE
RICINOLEATE HYDROGENATIONS

FIG. 7. Hydrogenations.

Hydrolysis of the sulfuric acid esters occurs during the reaction and subsequent treatment to form hydroxy acids and sulfuric acid. The hydroxy acids can be further sulfated at the OH group. Saponification of the glycerides can occur on neutralization with the formation of mono- and diglycerides and free fatty acids. The mono- and diglycerides produced can be sulfated at the hydroxyl group and the fatty acids can form lactones, lactides, and estolides by interreactions and loss of water. Despite the many side reactions and complex mixture obtained by the sulfuric acid treatment of castor oil, most commercial products seem to be similar in properties. Commercially sulfated castor oil contains ca. 8.0-8.5% combined SO_3, indicating that its surfactant properties are due to the sulfation of only one of the reactive points in the unsaturated, hydroxy bearing triglyceride. The addition of the sulfate group as a hydrophile at the hydroxyl position imparts excellent wetting, emulsification, and dispersing characteristics to castor oil. The anion-active product is used in the textile industry for fiber wetting ability and as dye agent to obtain bright, clear colors.

Sulfonation of castor oil with anhydrous SO_3 produces a product which has better hydrolytic stability (30). The organically combined SO_3 is low compared to the amount of SO_3 introduced to the reaction. When two moles of SO_3 (17%) were added to the oil, the final product was found to contain only 8.0-8.5% combined SO_3. The sulfonation with SO_3 is carried out at temperatures higher than the sulfuric acid sulfation. The finished product contains less inorganic salts and free fatty acids, and the stability in acid media is improved.

The reaction between a diisocyanate and an alcohol to form a urethane polymer is well known. Castor oil, with a pendant hydroxyl group on each ricinoleate chain, has an average of 2.7 hydroxyl groups/molecule and is considered a reactive polyol for urethane reactions (31-33). Ricinoleate polyols of varying functionality have been designed to allow usage in specific areas, such as the electronics and coating industries. The moisture resistance of urethane polymers of ricinoleate polyols as compared to those of polyesters or polyethers has led to widespread usage in molding, casting, and spray coating applications where

encapsulation is desired in encapsulation casting. Viscosity and the tolerance in the proportioning of the resin and curing agents are prime considerations. Lower viscosities allow faster dispensing cycles, simpler filling and less possibility of voids. Equal or nearly equal wt ratios of polyols and prepolymers, together with a substantial tolerance in proportioning, allow for better metering accuracy and processing safety. Epoxy resins used in encapsulation have been replaced by ricinoleate urethane systems having initial viscosities in the 600-800 centipoise range. Ricinoleate polymers based upon polyurethane resins of low viscosity are achieved without the excessive use of toxic tolylene diisocyanate or nonreactive plasticized or solvent as diluents. The end product requires no heating for processing and possesses superior heat aging characteristics. Gel time and cure rate of encapsulating casting compounds are of critical importance. Ricinoleate-based casting compounds can be formulated easily to cure either at room temperature or at elevated temperatures. Some electronic components are extremely heat sensitive and require resins that cure at low temperatures with little exotherm. Ricinoleate polyol-based polyurethanes that cure at room temperature with low exotherm are used in electronic component encapsulation of toroidal coils, inductors, and selenium rectifiers, where heat sensitivity and freedom from mechanical distortion are required to avoid stresses that cause variations in performance. The polyurethane systems also offer good flexibility, low shrinkage, and high shock absorbency. The ricinoleate polyols are inherently water repellent and offer a desirable combination of low dielectric constant and dissipation factors along with high volume resistivity. Ricinoleate urethanes have found new uses and wide acceptance in potting and encapsulation, elastomers, cast and molded goods, adhesives, sealants, and coatings (34).

DERIVATIVES FOR FOOD ADDITIVES

The potential use of castor oil derivatives for use as food additives has been considered. Castor oil itself has been used as a frying oil in China and, in India, as an adulterant of various edible oils. No adverse effects were noted when rats were fed 1% hydrogenated castor oil diets over a period of 16 weeks. It has been shown that neither hydrogenated castor oil nor 12-hydroxystearic acid possess cathartic activity. The hydroxystearates are nontoxic, based upon rat feeding studies performed at the Western Regional Research Laboratory, U.S. Department of Agriculture (35,36). Foods that contain other hydroxy fatty acids include milk, as well as such items as apples and pears. It appears then that derivatives of 12-hydroxystearic acid may be satisfactory as food additives from a safety standpoint.

A series of nonionic surfactants was synthesized from 12-hydroxystearic acid and compared with the corresponding stearate esters with regard to their effect upon the gelatinization characteristics of starch. The hydroxystearates induced an unusually high paste viscosity. The high viscosity imparted to starch pastes by the hydroxystearates indicates advantages in puddings and pie fillings, where thicker hot pastes serve to keep fruit or nuts suspended (37). The thickening action of hydroxystearates also was evaluated in peanut butter. The use of tri-12-hydroxyoctadecanoin or 12-hydroxystearic acid at a level of 0.5-1.0% in unhardened peanut butter resulted in a product indistinguishable from commercial, hardened peanut butter. The behavior of monostearin, stearic acid, tripalmitin, and related ricinoleates was evaluated. The hydroxystearates formed gelatinous crystalline matrixes in contrast to the nonhydroxy derivatives which either formed no crystals at all or the crystals of which were not held in suspension and did not produce significant thickening. Formation of satisfactory gels was restricted to the hydroxystearates. An

evalution panel was unable to discriminate between peanut butter containing hydroxystearate additive and a standard commercial control (38).

Medium chain triglycerides have been studied in lipid physiology for a number of years. Synthetically prepared medium chain triglycerides were substituted for C-18 triglycerides in animal testing. The medium chain glycerides were absorbed easily into the blood, whereas the longer chain natural fats were absorbed only after emulsification with the aid of bile acids, etc.

It is well known that fats provide the primary reserve supply of body energy, due to the oxidative conversion through acetic acid. The fatty acids are degraded by successful removal of two carbon units from the molecule. This mechanism has been called β oxidation and is the major pathway for fatty acid oxidation in cells. With odd numbered fatty acids, a three carbon propionate residue is formed. Thus, using a C_{11} triglyceride, such as triundecanoin, the β-oxidation route will yield a three carbon fragment for nutritional study. The use of C_{11} undecylic triglyceride in animal studies showed the fatty acids derived therefrom could be stored in the adipose tissue of rats and dogs. It was found that rats with odd number fatty acids stored in the adipose tissue endured stress situations, such as starvation, much better than rats with normal even numbered adipose tissue. The physiological response to starvation is to mobilize liver glycogen, which is relatively small, but a readily available energy store. Following this, fat is mobilized and provides additional energy. Mobilization of odd carbon fatty acids yields propionyl residues that are potentially glucogenic. Experimental work showed terminal C_3 units to provide enough carbohydrate to starved animals so that their depletion of liver glycogen and drop in blood glucose were dramatically less than with even numbered fatty acids (39). From the experimental work performed thus far, it would appear that the C_{11} acids derived from castor oil may have a potential for stress relief in human beings.

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