

# Chemical Derivatives of Castor Oil<sup>1</sup>

K.T. ACHAYA, Regional Research Laboratory, Hyderabad-9, India

## Abstract

The chemistry of castor oil and its derivatives is reviewed with particular reference to work done in India in general and at the Regional Research Laboratory in Hyderabad in particular. Topics covered are the structure of castor oil, preparation of ricinoleic acid and its glycerides, monoglycerides, surfactants from castor oil, diverse hydrogenations, dehydration, preparation and properties of estolides, alkali fusion or oxidation to dibasic acids, hydroxylation and acetoxy-epoxies, urethanes and polymerisable monomers.

## Introduction

The work on castor oil by scientists in India, particularly the work conducted at the Regional Research Laboratory in Hyderabad for two decades will be reviewed. Although the many contributions of scientists from the USA, UK and East and West Germany shall be referred to, the coverage and bibliography of this presentation will remain selective.

When I was a boy, black Sunday came about once in six months. A teaspoonful of warm castor oil, flavored with a few drops of lemon juice to make the medicine go down, was poured into our unwilling throats to a waiting empty stomach below. The induction period was short; the rest of the day was disastrous. Little did I imagine that I was to have so close an association subsequently with castor oil.

## Fatty Acids and Glycerides

Scientifically castor oil is a material with a diversity of uses shared by no other natural fat. Castor oil is unique not only in carrying overwhelmingly a single fatty acid, but in that this acid is a very special one. Ricinoleic acid has an 18-carbon backbone, with a hydroxy group on the 12 carbon atom and a *cis* double bond between carbons 9 and 10 (Fig. 1). It is this particular juxtaposition that gives the acid its unusual versatility. Ricinoleic acid makes up 90% of the mixed acids of castor oil. The remaining 10% consists of about 4% each of oleic and linoleic acids and 1% or less each of palmitic, stearic and dihydroxystearic acids (1,2). The reactions of castor oil are essentially those of a glyceride of

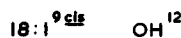
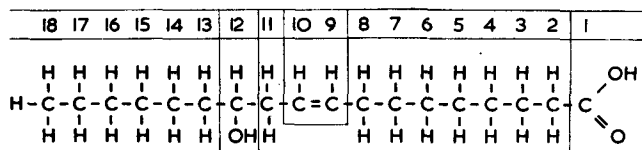
ricinoleic acid. The actual glycerides have been determined (1) by countercurrent distribution between 90% ethanol and hexane. Triricinolein amounts to 68%, and is thus slightly less than the random proportion of about 72%; diricinoleins constitute 28%, which is slightly more than the random proportion of about 24%. There are 3% monoricinoleins, and slightly under 1% glycerides containing no ricinoleic groups at all. Short term pancreatic lipolysis of the total oil, or of the pure di- and monoricinoleins isolated from it by repeated preparative thin layer chromatography, gave erroneous results or computation (showing, for example, the presence of considerable triricinolein in the purified diricinolein concentrate), suggesting that such calculations are not applicable to the analysis of types in glycerides which carry ricinoleic acid. Extraction of commercial castor oil with aromatic-free light petroleum concentrates the triricinolein (3); the residual product contains 94% ricinoleic acid and does not precipitate on holding at -10 C for 10 days, an important consideration in its use as an aircraft brake fluid ingredient. To obtain ricinoleic acid, the mixed fatty acids from this triricinolein concentrate can be first adducted with urea to remove normal acids, and the solubles then taken up in ethyl acetate to precipitate dihydroxystearic acid; the main impurity remaining thereafter is about 1.5% linoleic acid (3). Alternatively the mixed acids of castor oil can be partitioned by Gunstone's well-known procedure between 80% methanol and hexane. From the alcoholic extract, removal of dihydroxystearic acid by ethyl acetate crystallisation yields 85% of ricinoleic acid of high purity (4). Ricinoleic acid tends to self-polymerise on keeping, and must be made afresh in the quantities needed.

## Monoglycerides

The monoglycerides of castor oil, as of other oils, are generally made commercially by the alkali-catalysed glycerolysis reaction. The monoglyceride content of the product does not exceed 50% and Choudhury (5) has shown that this is because of the limited solubility of glycerol in the fat phase, which limits the forward reaction and results in an equilibrium. Molecular distillation can of course raise the monoglyceride content, but is an expensive operation.

Alternatively, and less expensively, the reactants can be refluxed together in a mutual solvent, such as phenol, pyridine, or others more easily handled, using about 2.5% of sodium bicarbonate as a catalyst. If proper solvent removal can be achieved without encouraging the reverse reaction, the product contains up to 95% of monoglycerides. Much less glycerol is required than in the usual glycerolysis reaction, and excess glycerol and solvent can both be recovered and reused (6).

Monoricinolein of high purity can also be made synthetically. A simple procedure has been worked out for this purpose (7,8). Isopropylidene glycerol, itself obtained by condensation of glycerol with acetone, is interesterified with methyl ricinoleate in the presence of sodium methoxide as a catalyst, the



ricinoleic acid

Fig. 1. Structure of ricinoleic acid.

<sup>1</sup> Presented at the Plenary Session of the ISF-AOCS World Congress, Chicago, September 1970.

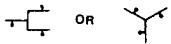
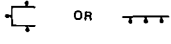
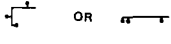
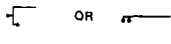
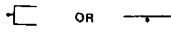
SULFATE SALT	STRUCTURE	SULFATE GROUPS		
		TOTAL	SECONDARY	PRIMARY
TRIRICINOLEIN		3	3	-
DIRICINOLEIN		3	3	-
MONORICINOLEIN		3	2	1
MONOACETOXYRICINOLEIN		2	1	1
DIACETOXYRICINOLEIN		1	1	-

FIG. 2. Ricinoleo glycerides examined for surfactance as sulfate salts.

methanol formed in the reaction being distilled away continuously. This procedure could even be commercially attractive since the methyl esters of castor oil (which are of course 90% methyl ricinoleate) can be made simply by stirring the oil with two parts of methanol in the presence of an alkaline catalyst, either at room temperature overnight, or at 30 C for 2 hr, the glycerol which separates as a layer being simply tapped off (9).

For what end use is a high monoglyceride content important? Monoglycerides of normal oils obviously have a higher emulsifier action than corresponding di- or triglycerides. With castor oil, in which the mono-, di- and triricinoleins each carry three hydroxyl groups, the position is not so clear. A study has been made (10) of the surfactant properties of the neutralised sulphated salts of various glycerides of ricinoleic acid, some of which were also acetylated. Perusal of the structures in Figure 2 shows that the only two products among them carrying primary hydroxyl groups are monoricinolein and monoacetoxyricinolein. It is of interest that only the sulphated salts from these two products show a high deterative ability, although the emulsifying power of the sulphated salts of all the products studied was almost uniformly good.

**Other Surfactants**

From the days of Turkey Red Oil, the first synthetic nonsoap surfactant, castor oil has been a natural choice as a raw material for surfactant manufacture. The early products were obtained simply by treatment of castor oil with concentrated sulphuric acid or oleum. A later development was the introduction of castor fatty acids into the reaction mass at some point in the manufacture to give products of improved stability, the so-called Monopol oils or soaps. Soon after came the sulphated esters of ricinoleic acid with lower alcohols, which are even today rated as outstanding for their excellent fibre rewetting ability. A

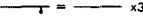
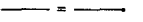
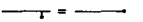
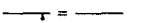
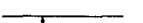

PRODUCT	SKELETON	UNSATURATION	SULFATE
TRIRICINOLEIN	 x3	CENTRAL	CENTRAL
OLEYL SULFATE		CENTRAL	TERMINAL
RICINOLEYL DISULFATE		CENTRAL	CENTRAL & TERMINAL
METHYL SULFATOOLEATE		CENTRAL	CENTRAL
METHYL SULFATOSTEARATE		NONE	CENTRAL
STEARYL SULFATE		NONE	TERMINAL

FIG. 3. Structures of fatty products examined for surfactance as sulfate salts.

recent systematic study (11) has shown that of various lower alcohol esters of ricinoleate, the hexyl ester after sulfation exhibited the lowest critical micelle concentration; saturation of the double bond of the ricinoleate moiety raised the critical micelle concentration considerably. The sulfated ricinoleic amides have also been examined (12). The di-*n*-butyl amide showed the highest surface tension lowering ability and detergent power, and in this instance the corresponding saturated product was even better in these respects.

The surfactant properties of salts of various sulfated fatty derivatives, chosen for structural variety as shown in Figure 3, have been examined (13). As expected, terminally sulfated oleyl sulfate showed good detersion and foaming, and centrally sulfated methyl sulfatooleate, good wetting and emulsifying ability; saturation of the double bond in either product diminished their particular qualities, particularly in oleyl sulphate. Foaming ability is very low in ricinoleyl disulfate, which carries both a central and a terminal hydrophile in the chain, as well as a high unsaturation; wetting, detersion and emulsifying power are all very good. In another study (14), progressive reduction of the unsaturation in ricinoleyl disulphate was found to adversely affect the wetting power and detersion, while enhancing slightly the emulsifying ability.

Another comparative evaluation also (15) concerned similar fat-based products with terminal or central hydrophiles, or both, and carrying unsaturation or otherwise. In one series, these hydrophiles were sulfate groups, and in the other they were sulfonate groups. In every instance the sulfate excelled the corresponding sulfonate of an otherwise identical structure in the major surfactant manifestations of wetting, emulsification and detergency. In aliphatic products therefore the sulfate group as a hydrophile is more effective than the sulfonate group. The position of the hydrophile in the center of the chain had an unexpectedly strong effect; a hydrophile located at the twelfth carbon atom in an 18-carbon aliphatic chain conferred better surfactance than one located at the ninth or tenth carbon atom.

A well known pyrolysis product of castor oil is 10-undecenoic acid with a terminal double bond. Coupling its methyl ester with either benzene or toluene by a Friedel-Crafts reaction gave mixed alkyl aryl products with the structures shown in Figure 4.

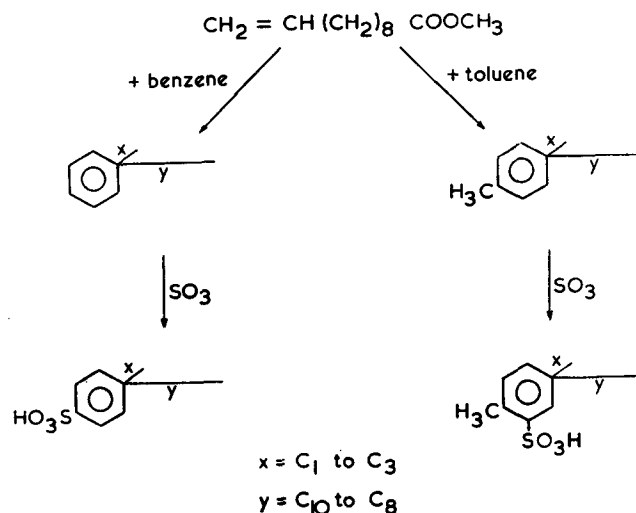


FIG. 4. Alkyl aryl surfactants derived from methyl undecenoate.

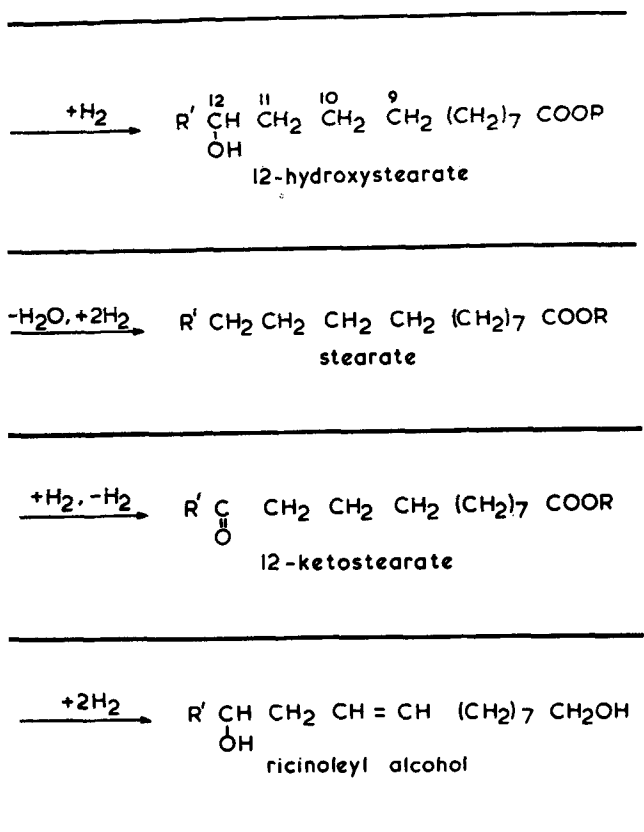


FIG. 5. Various hydrogenations of ricinoleate.

Further sulfonation yielded *para* sulfonates from the benzene-coupled product and *meta* sulfonates from the toluene-coupled product. The sodium salt of the former had considerably better detergency than that of the latter, but inferior emulsifying and suspending ability (16). This study is of interest since *meta* sulfonates have rarely been examined for their surfactant quality, being rather difficult to prepare.

### Hydrogenation

Castor oil or methyl ricinoleate can be hydrogenated in a number of ways, and four products which result are shown in Figure 5. Simple double-bond hydrogenation to give glycerides of 12-hydroxystearic acid can be commercially achieved using 2% of a Raney-type nickel catalyst at 150 C and 150 psi hydrogen pressure. The catalyst can be repeatedly reused if 10% of fresh catalyst is added before each run (17,18). The resulting waxy-looking product has a high melting point of 85 C, and is used to make high pressure lithium-based greases and as a suspending agent for pigments in paints.

Conversion of ricinoleic glycerides to stearic (or stearic-oleic) glycerides can, of course, be done in two stages: initial dehydration to diene products, and total saturation of the latter. It is possible to combine the two steps, and use a mixed catalyst consisting of dehydrating (sodium bisulfate) and hydrogenating (Rufert nickel) components (19). Subjecting commercial castor oil to this mixed catalyst at 200 C at atmospheric hydrogen pressure yielded, after 6 hr, a product of low hydroxyl value (below 10), low acid value (6-8) and iodine value ca. 40. This is useful for making soap in countries like India where hard animal fats are scarce. Another approach is to dehydrate fully hydrogenated castor oil; the

product of iodine value 66 has 40% *trans* and 30% *cis* monoenoic acids, the balance being stearic acid (20).

The conversion of ricinoleate to 12-ketostearate has been studied (21,22) at the Western Regional Research Laboratory, Albany, California. The overall reaction involves no net loss of hydrogen atoms. However the hydrogenation reaction is separate from the dehydrogenation; hydrogen to saturate the double bond comes from the catalyst surface and this reaction occurs rapidly, followed by a separate slow and overlapping dehydrogenation of the CHOH to a keto group. In fact the reaction proceeds best with a saturated product like methyl 12-hydroxystearate, which is cleanly reduced to 12-ketostearate using 1% Adkins copper chromite catalyst at 180-260 C. This catalyst is preferred to the somewhat erratic Raney nickel. With castor oil or even hydrogenated castor oil, the reaction does not proceed smoothly.

The fourth type of hydrogenation is the reduction of the terminal carboxy or carbalkoxy group to an alcohol function. Of course either castor oil or its methyl esters can be quantitatively reduced to the fatty (ricinoleyl) alcohol using a secondary reducing alcohol and suspensions of sodium in refluxing xylene by Hansley's well known modification (23) of the classical Bouveault-Blanc procedure. High pressure hydrogenation can also be employed if the twin problems of preserving the hydroxyl group and protecting the unsaturation can be overcome. This has been done (24) by batch hydrogenation of freshly prepared ricinoleic acid at 220 C and 3800 psi hydrogen pressure using 5% of a 3:1 copper-cadmium catalyst employed in the form of the ricinoleate soaps. The yield of the alcohol is about 70%; the remainder consists of lower fission products and wax esters. If the ratio of copper to cadmium in the catalyst is reversed without altering the total quantity used, the main product is the wax ester, ricinoleyl ricinoleate (24,25).

### Dehydration

Dehydration of castor oil gives a product called dehydrated castor oil (DCO) containing a fair proportion of conjugated diene and therefore useful as a surface-coating material. The mechanism of the reaction, shown in Figure 6, involves no complex

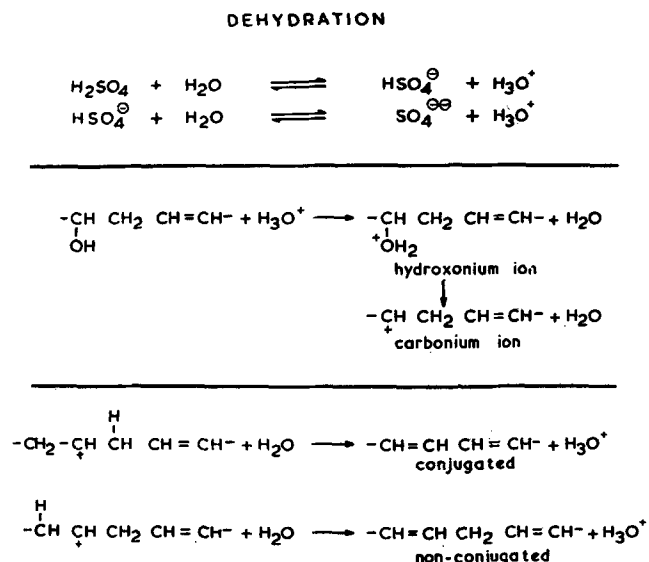


FIG. 6. Dehydration mechanism.



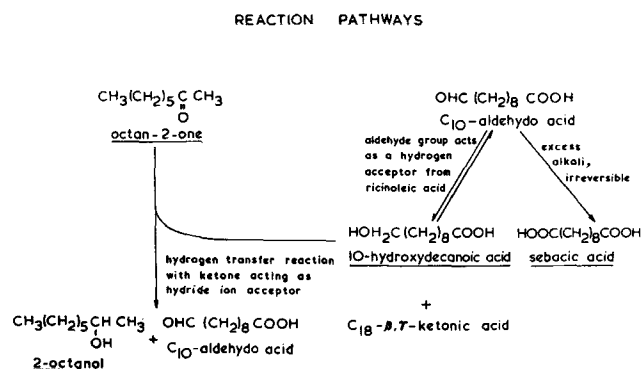


FIG. 9. Alkali fusion reactions of ricinoleate, later stages.

The other and better known alkali fusion reaction of castor oil gives rise to sebacic acid, 2-octanol and hydrogen. At Hyderabad a continuous process is being evolved using either solutions or pastes. The reaction requires 2 moles of alkali per mole of ricinoleate, temperatures of the order of 240 C and short reaction times of 1-2 hr, and is favored by the presence of ketones or aldehydic acids.

To explain both reactions, the interesting reaction mechanism shown in Figure 8 has been proposed (33). Ricinoleic acid, in presence of alkali, is converted into the corresponding  $\beta,\gamma$  unsaturated-keto acid which isomerises to the  $\alpha,\beta$ -keto acid. This undergoes a "retro-aldol" fission to yield a ketone and an aldehyde acid. These products become starting points for a complex series of reactions (Figure 9). The aldehyde acid can react in one of two ways: it can go irreversibly to sebacic acid, or it can accept hydrogen from ricinoleic acid, converting it to the  $\beta,\gamma$ -keto acid, which recycles into the system, meanwhile giving rise itself to 10-hydroxydecanoic acid. The end products of the two reactions are shown underlined in the figure.

Another interesting reaction which has been evaluated is the oxidation of fully hydrogenated castor

oil with nitric acid to give an equimolar mixture of C<sub>11</sub> and C<sub>12</sub> dibasic acids (34). Normal oxidative cleavage of ricinoleic acid will, of course, cause scission of the double bond to azelaic acid. Hence castor oil can give rise directly to one of four dibasic acids, C<sub>9</sub>, C<sub>10</sub>, C<sub>11</sub> or C<sub>12</sub>, depending upon the conditions of fission. With no other oil is this possible.

### Hydroxy Derivatives

An isolated double bond is amenable to hydroxylation particularly with peracids, and that in castor oil is no exception. A series of fully hydroxylated (saturated) products have been prepared at Hyderabad (35) both from ricinoleic acid and its derivatives like the triglyceride and the fatty alcohol, and from 10-undecenoic acid and its derivatives like the 1-monoglyceride and the fatty alcohol. The utility of these products, both C<sub>18</sub> and C<sub>11</sub>, in alkyd formulations (36) was examined. The 1,10,11-trihydroxy product (obtained by hydroxylation of 10-undecenyl alcohol) yielded quick drying alkyds, while fully hydroxylated castor oil itself showed alkyd formulation potential. There were indications that adjacent hydroxy groups, such as are introduced by peracid hydroxylation, are not fully utilised for cross-linking, perhaps because of steric hindrance.

The same hydroxy derivatives were also sulfated and the neutralised materials examined as surfactants (36). The sulfate salt of the 11-carbon saturated alcohol, undecanyl, closely resembled that of lauryl alcohol in its properties, and the 18-carbon polysulfate salts were all good emulsifying agents.

### Acetoxy-epoxy Derivatives

Where unsaturation and hydroxy groups both occur, as in castor oil or its derivatives, the former can be epoxidised using appropriate reagents, such as anhydrous peracids under nonacidic conditions, and the latter can then be acetylated with acetic anhydride and pyridine. In PVC resins, the products obtained may be expected to exhibit both a stabilising function, by reason of the epoxy groups present, and a plasticising function, by reason of the acetoxy groups. Some studies in this direction have been made. At the Hyderabad laboratory, castor oil alone or in admixture with various proportions of linseed oil has been epoxidised and then acetylated to give a range of products with varying epoxy-acetoxy ratios (37). At the Shri Ram Institute for Industrial Research in Delhi, several series of products have been evaluated. When monoricinolein was acylated at all the three hydroxyl groups with various fatty acids from one to six carbon atoms in length, the hexyl triester was found to show the best plasticising properties (38). When various diols and higher polyols were esterified with ricinoleic acid, the ricinoleate diester of pentaerythritol showed excellent plasticiser properties (39).

At the Southern Regional Research Laboratory in New Orleans, good plasticising properties have been shown by the morpholide esters of ricinoleic acid and of cyanoethylated ricinoleic acid (40,41).

### Urethanes

Urethanes are products of reaction of an alcohol with an isocyanate group. If excess isocyanate is present, and this is then reacted with water, an amine and carbon dioxide result and escape of the latter

#### MONOMERS

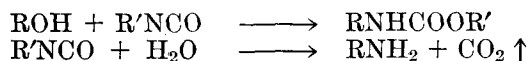
VINYL	$\left\{ \begin{array}{l} \text{Esters} \\ \text{Ethers} \end{array} \right.$	$\text{CH}_2 = \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{R}$
		$\text{CH}_2 = \text{CH} \cdot \text{O} \cdot \text{R}$
ALLYL	$\left\{ \begin{array}{l} \text{Esters} \\ \text{Ethers} \end{array} \right.$	$\text{CH}_2 = \text{CHCH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{R}$
		$\text{CH}_2 = \text{CHCH}_2 \cdot \text{O} \cdot \text{R}$
ACRYLIC	Esters	$\text{CH}_2 = \text{CH} \cdot \text{CO} \cdot \text{O} \cdot \text{R}$
METHACRYLIC	Esters	$\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} \cdot \text{CO} \cdot \text{O} \cdot \text{R}$

where R is

undecenoate	ricinoleate
undecanoate	hydroxystearate
11-substituted undecanoates (Br, Cl, I, OH, OCH <sub>3</sub> , φ)	acetoxystearate
10,11-disubstituted undecanoates	ketostearate
1,11-disubstituted undecanoates	

FIG. 10. Polymerizable monomers prepared.

through the reaction mass gives rise to a cellular or foam structure:



A great deal of work has established that when castor oil is the alcohol component, the foams produced are of the rigid or semirigid type which find use for insulation and structural support (42,43).

The published work of the Defence Laboratories in India may be cited (44). Castor oil is treated with slightly less than half its weight of triethanolamine at 150 C for 2.5 hr under nitrogen. The amount of triethanolamine is controlled to give a pH of 8.6 to 9.5 in the final product, which is important for subsequent balanced urethane formation. The resinous reaction mass, which is a complex mixture of triethanolamine ricinoleate with mono-, di- and triglycerides of castor oil, is stirred at high speed with small amounts of surfactant and water, and the isocyanate (4,4'-diphenylmethyldiisocyanate) added all at once, when an instant reaction occurs. Both the density (2.5–4.4 lb/ft<sup>3</sup>) and compressive strength (ca. 50 psi) of the foams are high, and the proportion of open cells low (15–20%). To obtain fireretardancy, which is increasingly important in the riot and arson prone world of today, a retardant like tri-β-chloroethylphosphite can be incorporated. Brominated and chlorinated derivatives of castor oil have been employed for the same purpose in America (42,43).

Castor oil can be used for production of other types of urethanes called elastomers, which are hard yet resilient and malleable products used, for example, to make trolley wheels. In work at the National Chemical Laboratory in Poona, India (45), castor oil is first made difunctional by blocking one of the three hydroxyl groups of triricinolein with phenyl isocyanate. Further reaction with one equivalent of ethylene glycol and three equivalents of 4,4'-diphenylmethyldiisocyanate gives the elastomer, which is cured with sulfur, peroxide or radiation. The product is reported to have a high Shore hardness of 90, a tensile strength of 3500 psi and an elongation of 100%.

### Monomers Capable of Polymerization

Coupling of fatty materials with acids and alcohols carrying terminal unsaturation yields esters and ethers which are capable of polymerization. A series of such products have been prepared in a high degree of purity at Hyderabad (46,47). The fatty portion was either ricinoleic acid or its derivatives (e.g., hydroxystearic, acetoxystearic and ketostearic acids), or undecenoic acid or its derivatives (such as undecanoic acid, 11-substituted undecanoic acid including halo-, hydroxy-, methoxy- and phenyl-substituted materials, 10,11-disubstituted products and 1,11-disubstituted products). These were coupled with vinyl and allyl alcohols to give esters or ethers, or with acrylic and methacrylic acids to give the esters (Fig. 10). Several new or improved preparative methods were developed. Thus in the preparation of vinyl esters by the interchange reaction between fatty acid and vinyl acetate, 40% hydrofluoric acid was used in place of strong sulfuric acid. In preparing the acrylate esters of secondary alcohols, acrylic acid was added to the secondary alcohol

alternately with a tertiary base, the latter being added in quantities just enough to fix the liberated hydrogen chloride which otherwise causes a substantial lowering of the yield.

Polymerisation of some of the materials has been examined. The homopolymers were not useful. The copolymers were more promising (48,49). Thus an equimolar mixture of methyl 12-acryloxystearate and vinyl acetate or chloride, when polymerized by a free radical or a redox system, yielded polymers with potential in the manufacture of adhesive tape. Potential paint vehicles with drying qualities resulted when vinyl 10,11-epoxyundecanoate was copolymerised with vinyl chloride using a redox system.

### REFERENCES

- Achaya, K.T., B.M. Craig and C.G. Youngs, *JAOCS* 41: 783 (1964).
- Binder, R.G., T.H. Applewhite, G.O. Kohler and L.A. Goldblatt, *ibid.* 39: 513 (1962).
- Phaiip, K.J., P. Venkatarao and K.T. Achaya, *Indian J. Technol.* 1: 427 (1963).
- Subbarao, M.R., N.S. Rajagopal, M.M. Paulose, R. Subbarao, M.W. Roomi and K.T. Achaya, *J. Sci. Food Agr.* 15: 645 (1964).
- Choudhury, R.B.R., *JAOCS* 37: 483 (1960) and 39: 345 (1961).
- Ashraf, S.M., and H. Shripathi Rao, "Annual Report," Regional Research Laboratory, Hyderabad, India, 1967–68, p. 73.
- Gadgoli, H.G., and J.G. Kane, *Indian J. Chem.* 4: 289 (1966).
- Chandran, D.V., and R.K. Bhatnagar, *JAOCS* 45: 581 (1968).
- Belihal, S.S., and J.G. Kane, *Indian Oil Soap J.* 26: 219 (1961).
- Subrahmanyam, V.V.R., and K.T. Achaya, *J. Chem. Eng. Data* 6: 548 (1961).
- Bertsch, H., H. Reinheckel and G. Czichocki, *Fette Seifen Anstrich.* 67: 677 (1965).
- Bertsch, H., H. Reinheckel and G. Czichocki, *Ibid.* 68: 817, 1002 (1966).
- Subrahmanyam, V.V.R., and K.T. Achaya, *J. Chem. Eng. Data* 6: 38 (1961).
- Pantulu, A.J., and K.T. Achaya, *Fette Seifen Anstrichm.* in press.
- Upendra Rao, A., *Ibid.*, in press.
- Achaya, K.T., and P.K. Saraswathy Amma, *Indian J. Chem.* 5: 109 (1967).
- Shripathi Rao, H., K.S. Chari and J.S. Aggarwal, *J. Sci. Ind. Res.* 21D: 89 (1962).
- Shripathi Rao, H., P. Narasimham, K.S. Chari and J.S. Aggarwal, *Indian J. Technol.* 1: 320 (1963) and 2: 21 (1964); *Res. Ind.* 8: 125 (1963).
- Laxma Reddy, G., H. Shripathi Rao and J.S. Aggarwal, *Chem. Proc. Eng. Suppl.* 3: 68 (1968).
- Modak, S.N., and J.G. Kane, *JAOCS* 42: 428 (1965); *Indian J. Technol.* 2: 352 (1964).
- Freedman, B., and T.H. Applewhite, *JAOCS* 43: 125, 342 (1966).
- Freedman, B., J.S. Nelson, R.G. Binder and T.H. Applewhite, *Ibid.* 42: 340 (1965).
- Hansley, V.L., *Ind. Eng. Chem.* 39: 55 (1947).
- Pantulu, A.J., and K.T. Achaya, *JAOCS* 41: 511 (1964).
- Pantulu, A.J., and K.T. Achaya, *Fette Seifen Anstrichm.*, in press.
- Toyama, Y., and K. Takaoka, *Ibid.* 71: 195 (1969).
- Sivasamban, M.A., S.A. Saletore and S.H. Zaheer, *J. Sci. Ind. Res.* 13B: 349 (1954); *Indian Patents* 46,457 (1952) and 55,423 (1956).
- Waheeduddin, M., and M.A. Sivasamban, *Paintindia* 16(5): 24 (1966).
- Rheineck, A.E., and D.D. Zimmerman, *Fette Seifen Anstrichm.* 71: 869 (1969).
- Hawke, F., and E.A. Kohll, *J. S. Afr. Chem. Inst.* 12: 1, 17 (1959).
- Venkatesan, T.K., V.V.R. Subrahmanyam and J.G. Kane, *Indian J. Technol.* 2: 351 (1964).
- Diamond, M.J., R.G. Binder and T.H. Applewhite, *JAOCS* 42: 882 (1965).
- Dyntham, R.A., and B.C.L. Weedon, *Tetrahedron* 8: 246 (1960) and 9: 246 (1961).
- Steadman, T.R., and J.O.H. Peterson, *Ind. Eng. Chem.* 50: 59 (1958).
- Subbarao, R., and K.T. Achaya, *J. Sci. Ind. Res.* 19B: 482 (1960) and 21D: 446 (1962).
- Subbarao, R., and K.T. Achaya, *Indian J. Technol.* 4: 53 (1966).
- Upendra Rao, A., and T. Chandrasekhara Rao, *Fette Seifen Anstrichm.* in press.
- Jain, A.K., and R.K. Bhatnagar, *J. Oil Technol. Ass. India* 2(1): 12 (1970).
- Jain, A.K., and R.K. Bhatnagar, *Indian J. Technol.* 8: 62 (1970).
- Dupuy, H.P., R.T. O'Connor and L.A. Goldblatt, *JAOCS* 35: 99 (1958).
- Dupuy, H.P., R. Calderon, E.R. McCall, R.T. O'Connor and L.A. Goldblatt, *Ibid.* 36: 659 (1959).
- Lyon, C.K., and T.H. Applewhite, *J. Cell. Plast.* 1967(2): 1.
- Lyon, C.K., and G. Fuller, *Ind. Eng. Chem. Prod. Res. Develop* 8: 63 (1969).
- Venkataramani, B., and C.D. Pande, *Indian J. Technol.* 7: 289 (1969).
- Phadke, V.B., and N.G. Ghatge, *CSIR News* 19: 31 (1969).
- Kulkarni, N.G., N. Krishnamurti, P.C. Chatterjee and J.S. Aggarwal, *JAOCS* 45: 465 (1968); *Ibid.* 46: 396 (1969).
- Chatterjee, P.C., H. Dakshinamurthy and J.S. Aggarwal, *Indian J. Technol.* 2: 335 (1964); *Ibid.* 4: 173 (1966).
- Sowa, J., and C.S. Marvel, *J. Polymer Sci.* 5: 1501 (1967).
- Chow, R.C.L., and C.S. Marvel, *Ibid.* 5: 2949 (1967).

[Received February 26, 1971]

