# CHAPTER II

## CHEMISTRY OF METHYL RICINOLEATE

Methyl ricinoleate is a methyl ester of ricinoleic acid, fatty acids of Castor oil derived from the bean of the castor plant (Ricinus communis L., of the family Euphorbiaceae). The castor plant occurs in practically all tropical and subtropical countries, either wild or cultivated. Castor oil is also known as Ricinus oil, ail of Palma christi, tangantangan oil and Nealoid.

Castor oil is obtained by pressing, or pressing followed by solvent extraction. Pharmaecutical grade oil is high quality oil derived solely from the first pressing of beans and accounts for only a very small percentage of total sales. Technical grade castor oil obtained by pressing, repeated pressing and solvent extraction has an extremely wide range of uses because of its very exceptional chemical and physical characteristics which relate to its uniquely high content of an unsaturated hydroxy fatty acid, cis 9, 12 hydroxy octadecenoic acid, commonly known as ricinoleic acid (2)

### 2.1. Fatty Acids Composition of Castor Oil

The composition of fatty acid in castor oil derived from analysis of the methyl ester of castor oil fatty acid with gas chronmatographic method is given in Table 2.1 (2,3).

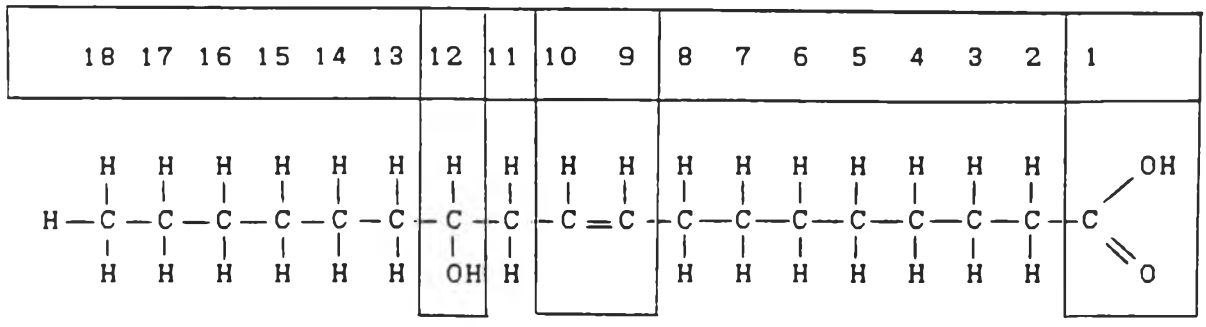
Table 2.1 Fatty acids composition of castor oil.

| Fatty acid | | Percentage |
|---|---|---|
| Type | Name | |
| C 16 : 0 | Palmitic acid | 0.9 - 1.2 |
| C 18 : 0 | Stearic acid | 0.7 - 1.2 |
| : 1 | Oleic acid | 3.2 - 3.3 |
| : 2 | Linoleic acid | 3.4 - 3.7 |
| : 3 | Linoleic acid | 0.2 |
| C 18 : 1 9, - OH 12 | Ricinoleic acid | 89.0 - 89.4 |
| C 18 : - OH 9, 10 | Dihydroxy stearic acid | 1.3 - 1.4 |

Various sources have reported a range in ricinoleic acid content of 80-95%. The structure of the glycerides of castor oil has been ascertained with approximately 68% tri-ricinolein, 28% di-ricinolein, 3% mono-ricinolein and 1% ricinoleic acid. It is therefore evident that heredity, environmental and the limitations of sampling end analysis (4).

## 2.2. Characteristic of Methyl Ricinoleate

Scinentifically 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 back-bone, with a hydroxyl group on the 12 carbon atom and a cis double bond between carbons 9 and 10 which structure is shown in Figure 2.1 (4).




ricinoleic acid

Figure 2.1 Structure of ricinoleic acid

It is this particular juxtaposition, that gives the acid its usual versatility.

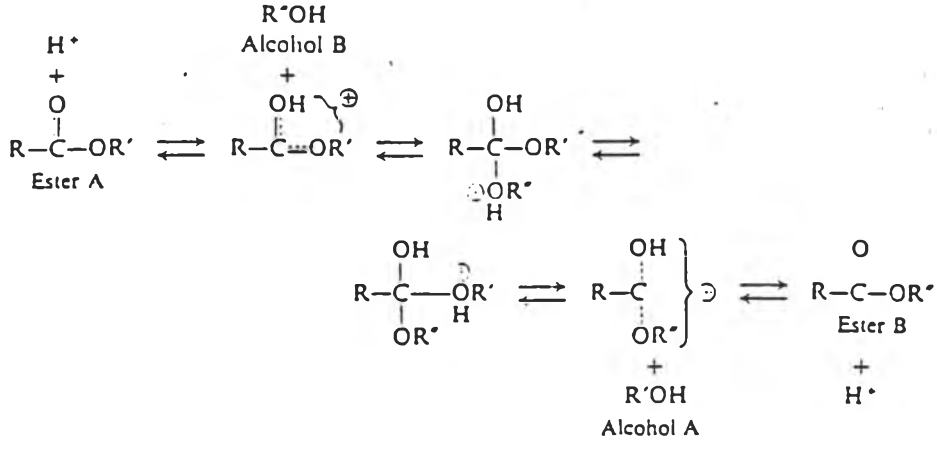
Methyl ricinoleate is the methyl ester of ricinoleic acid. This ester is prepared by esterification of ricinoleic acid or alcoholysis of castor oil (5).

In the esterifieation of an acid or alcoholysis of fat, an alcohol acts as a neucleophilic reagent ; as hydrolysis of an ester, an alcohol is displaced by a neucleophilic reagent. Knowing this, we are not surprised to find that are alcohol is capable of displacing another alcohol from an ester. This alcoholysis (cleavage by an alcohol) of an ester is called Transesterification.

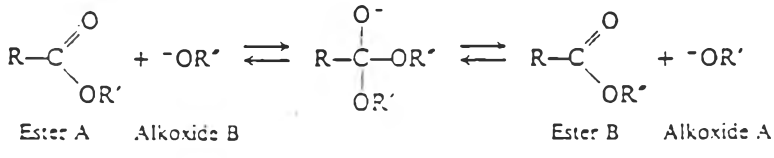
$$RCOOR' + R''OH \underset{}{\overset{H^+ \text{ or } R^-}{\rightleftharpoons}} RCOOR'' + R'OH$$

Transesterification is catalyzed by acid ($H_2SO_4$ or dry HCl) or base(usually alkoxide ion). The mechanisms of these two reactions are exactly analogous to those we have already studied.

For acid-catalyzed trasesterification :




For base-catalyzed trasesterification:




Transesterification is an equilibrium reaction. To shift the equilibrium to the right, it is necessary to use a large excess of the alcohol whose ester we wish to make, or else to remove one of the products from the reaction mixture. The second approach is the better one when feasible, since in this way the reaction can be driven to completion (6).

Transesterification with a monohydroxy aliphatic alcohol of low molecular weight such as methanol or ethanol may be catalyzed by either acid or alkali, but the alkali-catalyzed reaction is generally superice in speed,

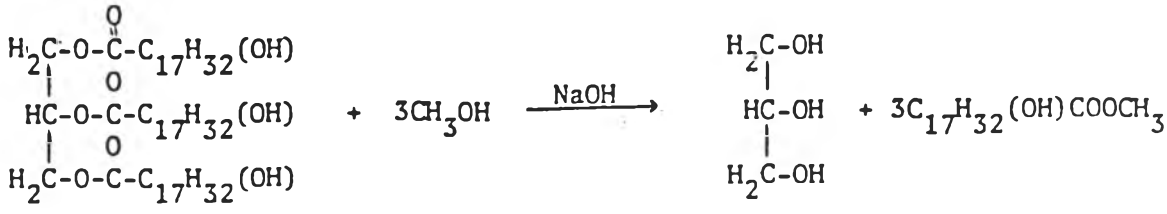
completeness and the relatively low tenperature at which it can be effected.

The fat must be clean, dry and substantially neutral. It is heated to about 80 °C (176 °F), and to it is added commercial anhydrous (99.7%) methyl alcohol in which is dissolved 0.1-0.5% sodiums or potassium hydroxide. The quantity of alcohol recommended is about 1.6 times that theoretically required for the reaction, although the alcohol may be reduced to as little as 1.2 times theoretical, if the operation is carried out in three stop. Alcohol amounting to more than 1.75 times the theoretical quantity does not materially accelerate the reaction and interferes with subsequent gravity separation of the glycerol.

After addition of the alcohol, the mixture is stirred for a few minutes and is then allowed to stand, the glycerol begins to separate almost immediately ; since it is virtually anhydrous and much heavier than the other liquids. It readily settles to form a layer at the bottom of the tank. Conversion of the oil to methyl ester is usually 98% complete at the end of an hour.

The lower layer of glycerol contains not less than 90% of the glycerol originally present in the fat, the upper layer consists of the methyl esters, most of the unreacted alcohol and alkali, the remainder of the glycerol, and a small amount of sope. These impurities are removed from the esters by successive washes with small amounts of warm water.

Transesterication of castor oil with methanol in the presence of a basic catalyst occurs according to the following reaction (7).



A glyceride of ricinoleic acid | Glycerol | Methyl ricinolcate

Methyl ricinoleate is colorless liquid, insoluble in water, soluble in alcohol and ether. It is combustible and low toxicity. The following characteristic is given in Table 2.2 (5).

Methyl ricinoleate uses as low-temperature plasticizer for rubber polymers, lubricant-plasticizer in phenolic molding resins, plasticizer for epoxy resin sytems, cutting oil additive and wetting agent (8).

The plasticizing effect of ricinoleate or hydroxy stearate plasticizers is generally characterized by :

1. Excellent softening and flexibilizing action. Invinyls, they are said to improve "hard" or "drape". In nitrocellulose leather finishes the ricinoleate plasticizer provides better "feel" in contrast to the "boardy" characteristic of phthalate and phosphate plasticizers.

2. Good low temperature plasticizing, specifically recommended for rabber and plastics where the compare favoralde to adipic and sebacic acid plasticizers.

3. Excellent lubricants. The lubricating effect is advantageous for vinyl calendering and extrusions, plate release in leather finishing,

4. Excellent pigment wetting. They are highly recommended for the production of pigment dispersions, or for incorporation in elastomeric or plastic compositions containing pigments or fillers.

5. Good electrical properties. Low dissipation factor, and high valume resistivity and dielectric constant.

Table 2.2 Characteristics of methyl ricinoleate

| | |
|---|---|
| Specific gravity (25 °C/25 °C) | 0.925 |
| Refractive index $nD^{20}$ | 1.4628 |
| Saponification value | 173 to 178 |
| Iodine value | 83 to 85 |
| Hydroxyl value | minimum 160 |
| Viscosity (Stockes @ 25 °C) | 0.3 poise |
| Boiling point | 245 °C |

## 2.3. Chemical Reaction of Methyl Ricinoleate

Because of the hydroxyl groups, double bonds and ester linkages in methyl ricinoleate provide similarly reaction sites for the preparation of many useful derivatives as castor oil used.

For castor oil, chemical reactions commercially used to create important derivatives are as follow (8) :

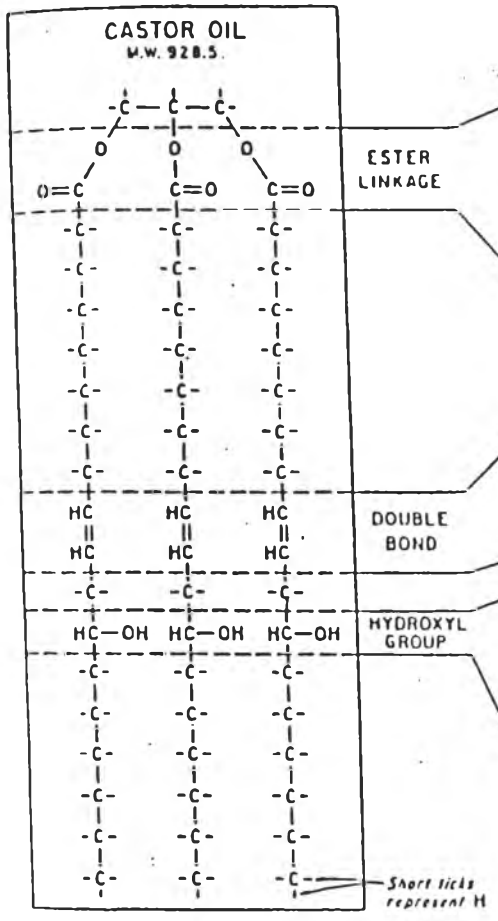
| | | |
|---|---|---|
| Acetylation | Epoxidation | Pyrolysis |
| Alkoxylation | Esterification | Saponification |
| Amination | Hydrogenation | Sulfation |
| Caustic Fusion | Isocyanate Reaction | |
| Chemical Dehydration | Oxidative Polymerization | |

The diagram which shows the fundamental structure of castor oil and its functions in these reaction is shown in Figure 2.2 (8).

Addition of hydrogen to the double bond of ricinoleate ester (hydroxystearate) yields improving stability to oxidation and resistance to ultraviolet light. The saturated ricinoleate esters are medium-range melting wax like solids exhibiting oil- and water-resistance. With properties similar to several of the natural waxes, the hydroxystearate esters may be employed in wax blends and cosmetics for their dye and pigment wetting characteristics. They can also serve as coupling agents for incompatible mixtures of polar and non-polar materials in hot-melt compositions.

Methyl hydroxystearate is specially used in; internal lubricant and processing aid for reduction of surface tack in butyl rabber, excellent mold release, firming agent in cosmetics and specialty inks, and source of hydroxystearic acid for glycerine-free multi-purpose lithium grease (8).

Methyl 12-lydroxystearate ($C_{17}H_{34}OHCOOCH_3$) is white waxy solid ; melting point 48 °C ; acid value 4 ; iodine value 5; insoluble in water,limited solubility in organic solvents; combustible ; and low toxicity. It is used in Adhesives ; inks, cosmetic ; and greases (5).




CHEMICAL REACTIONS OF CASTOR OIL

| NATURE OF REACTION | ADDED REACTANTS | TYPE OF PRODUCTS |
|---|---|---|
| (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 | Na reduction | Alcohols |
| (6) Amidation | Alkyl amines, alkanolamines, etc. | Amine salts Amides |
| (7) Halogenation | $SOCl_2$ | Fatty acid halogens |
| (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 |
| (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 |

Figure 2.2 Chemical reactions of castor oil