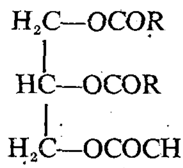
Aceto Glycerides

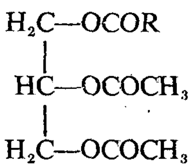
Z. F. LASHKARI*

NATURAL oils and fats are esters of a monocarboxylic acid and a trihydric alcohol viz. glycerol. The acids found in natural fats range from butyric having four carbon atoms to those having as many as twenty-four carbon atoms. Synthetic triglycerides prepared by esterification of glycerol with fatty acids in which one of the acids is acetic acid are called acetoglycerides and are represented by the following structural formulæ :



$$\begin{array}{l} H_2C\text{—}OCOR \\ \quad | \\ HC\text{—}OCOR \\ \quad | \\ H_2C\text{—}OCOCH_3 \end{array}$$

(monoaceto triglyceride)



$$\begin{array}{l} H_2C\text{—}OCOR \\ \quad | \\ HC\text{—}OCOCH_3 \\ \quad | \\ H_2C\text{—}OCOCH_3 \end{array}$$

(diaceto triglyceride),

where R is the fatty acid occurring in natural fats e.g. palmitic, stearic, oleic acids, etc.

The acetoglycerides were first prepared on a commercial basis as early as 1925 by G. L. Schwartz using coconut oil as the primary glycerides. However, they did not gain much importance till fairly recently.

Methods of preparation :

There are two basic methods which could be employed for preparing acetoglycerides :—

(i) Acetylation of mono-or di-glycerides
(ii) Inter-esterification methods

This method involves the initial preparation of the mono-or di-glycerides and the subsequent esterification to give the acetyl derivative.

Preparation of monoglycerides :

Monoglycerides are prepared by controlled esterification of glycerol or by glycerolysis.

To prepare β-monoglycerides, the method of glycerolysis of Eckey and Formo[1] is suitable and has been used for preparing pure acetoglycerides for physical studies. The method consists of mixing the oil with an excess of glycerol in the presence of sodium methoxide in xylene as a catalyst. The reaction is allowed to continue for three days at room temperature after which the product is purified by crystallisation from petroleum ether. In the above method one point to be borne in mind is that the di-glycerides always accompany the mono-glycerides.

Acylation of mono-or di-glycerides :—

The glycerides obtained by the above method may further be esterified by acetic acid in the presence of a catalyst to give acetoglycerides. The catalysts generally used are metallic oxides and chlorides, particularly of tin and zinc, and mineral acids, sulphuric and hydrochloric and phenyl sulfonic acids.

Acylation may also be done using acetyl chloride and acetic anhydride. Acylation with acetyl chloride has been employed by Ward and his coworkers to prepare 1-acetostearin and 1,2-diacetostearin.[2] α-Monostearin is first prepared by esterifying stearic acid with an excess of glycerol in the presence of a small amount of soap. The reaction product is purified by fractional crystallisation. The α-monostearin thus prepared is then acetylated by acetyl chloride in the usual

---

*2nd Year Student, Oils, Fats and Waxes Section.

way and the product is purified by fractional crystallisation from a solvent.

In the acylation with acetic anhydride, monostearin (obtained from completely hydrogenated cotton-seed oil) is reacted with 15-18% by weight of acetic anhydride for one hour at 250°F to give acetostearin.[3] The reaction product is washed and dried. If carefully prepared, the acetostearin has no colour, odour or taste. The amount of acetic anhydride and the grade of monostearin used in the preparation influence the physical properties of the final product. Highly acetylated compounds made from monostearin, tend to melt below the body temperature, and these products have a relatively low film strength at room temperature.

Compounds from technical grade monoglyceride (60% monoglyceride) and compounds from monostearin, acetylated only to a slight extent, have also a relatively low film strength but a melting-point as high as 130°F.

This method of preparation is a very simple one and is used commercially for acetoglycerides intended for non-edible and in some cases even for edible uses.

Experiments have been conducted in U.S.A. with acetylated monoglycerides of castor oil, for use as a plasticiser and stabiliser for polyvinyl resins. In this case it is evident that the acylation takes place with the OH groups in the glycerol as well as in the ricinoleic acid molecule.

(ii) Inter-esterification method : —

This covers two possible methods.

(a) *Acidolysis :*

The preparation of acetoglycerides by acidolysis consists in the replacement of a fatty acid by acetic acid which is carried out in the presence of an acid catalyst which is generally a mineral acid. Acetoglycerides from coconut oil were prepared by Schwartz by reacting acetic acid with neutral coconut oil at 150-170°C in the presence of H_2SO_4. The disadvantage of this method is that the operator has limited control over the composition of the final product due to the random manner in which the interchange of the fatty acid radical occurs. Any specific acid distributes itself impartially between the esterified and free acid portion.

(b) *Ester-ester interchange :*

In the formation of acetoglycerides by ester-ester interchange the methyl or ethyl ester of acetic acid is reacted with the neutral fat. This method is used on a laboratory scale for preparing the acetoglycerides. An important advantage of this method is that relatively pure acetoglycerides are obtained. The presence of a catalyst is essential for reducing the time of reaction. Small proportions of monoglycerides together with a small quantity of an alkaline catalyst are found to have a considerable effect on the speed of the reaction.

Properties :

The specific properties of the acetoglycerides depend on the extent of acetylation carried, so that the final product varies in properties.

All the acetostearin products are unique in that they are non-greasy and quite plastic. In an investigation by Feuge *et al.*[4] on the thermal properties of 1-acetostearin and 1, 2-diacetostearin it was found that the acetylated glycerides possess a unique property of solidifying in a very pliable and stretchable form when cooled under normal conditions. At room temperature several products may be stretched 100% before breaking (parafin wax having a melting-point of 125°F will stretch only 5% under similar conditions).

Other desirable characteristics are a short melting range, a controllable melting-point and an extreme resistance to oxidation and rancidity.

A commercial product, 'Monoacet', has the following properties.[5] It is a solid, white, flexible wax having a melting range of 36-46°C, S.V.$=$345-362, I.V.$<$ 5. It is soluble in certain portions in methanol, toluol, and naphtha at ordinary temperatures. When heated, it is soluble in vegetable and mineral oils, acetone, and ethyl acetate. It is tasteless and bland in odour.

Uses :

(i) For food coatings.

The acetoglycerides attracted attention a few years ago as a prospective food coating compound. The main advantages of their use in this way is found to be due to its impermeability to moisture, which prevents food products from losing moisture (as in the case of cheese) and also from absorbing moisture and becoming sticky as in the case of raisins and purnes. They are used as coatings for cheese, dried nuts, processed meats, fruits and vegetables, frankfurters, fish, candies, and baked goods.[6] Their melting range (36-46°) suggests its use in place of other wax-like products having a similar melting range. It has certain applications as a substitute for cocoa butter, beeswax and partially hydrogenated fats.

(ii) *As a plasticiser and stabiliser*[3]:

One of the first uses to which acetoglycerides were put was as a plasticiser for pyroxylin. The products were relatively impure and did not gain importance.

The fully acetylated product from lard is liquid at room temperatures and is suitable for use with cellulose acetate butyrate for plasticising polymers. It is compatible in all proportions when the butyrate content of the plastic is less than 30% and in most proportions at lower concentrations. At a low polymer content of 20 to 30%, soft but tough films can be formed. Stiffer products exhibiting improved low temperature characteristics result at a higher plastic concentration.

Fully acetylated monoglycerides especially from castor oil are good plasticisers for polyvinyl resins.

In combination with the usual primary plasticisers, the material imparts excellent low temperature characteristics and improved flexibility. A study of polymer-acetoglyceride systems indicates the suitability for use in combination with polystyrene, poly-butyl methacrylate, ethyl cellulose, and methyl cellulose. Higher polymer content of these materials produces viscous solutions showing promise as adhesives.

(iii) *Global edible spreads :*

The Government Regional Research Laboratories of U.S.A., were asked to develop an edible spread, which has a considerable plasticity over a wide range of temperature. By the use of edible counterparts of ethyl sebacates and lithium soaps a wide plasticity range fat was obtained. The disadvantage was poor flavour and oxidative stability and questionable digestibility. Next, the monoglycerides and the acetoglycerides were tried which were found to be suitable.

Aceto-olein has been found to be particularly suitable. Results of tests show that margarine like products may be prepared by acetylating lard, cotton-seed, soyabean and ground-nut oils to an acetyl content of 12-20%. As the acetyl content is increased the consistency characteristics are improved and the plastic range is extended from 15 to 40°C. Small amounts (1-8%) of aceto-olein reduces the hardness of highly hydrogenated cotton-seed oil but the effect decreases with an increase in temperature and a decrease in the degree of hydrogenation of the hard fat.

Simple addition of acetoglycerides to margarine does not result in any improvement but a 50% addition of an acetoglyceride to hard oil mixture improves the plastic range.

It is believed that the spreads become firmer in consistency subsequent to their manufacture, due to the combination of existing aggregates by the slow deposition of monoglycerides.[7]

(iv) *For coating fibres:*

The acetoglycerides have been recommended for special industrial and textile fibre coatings.[5]

Trend of research in acetoglycerides:

The Southern Regional Research Laboratory of U.S.A., is particularly interested in finding new uses for acetoglycerides, and most of the work published so far especially with respect to the edible uses is done in that laboratory.

In the Eastern Regional Research Laboratory work is being done on epoxidised diacetoglycerides in order to improve the suitability as a primary plasticiser for polyvinyl chloride. The results obtained so far, indicate that they are comparable with dioctyl phthalate, including in low temperature flexibility. They are in addition excellent light stabilisers.

Acetoglyceride manufacture in India:

In view of the rather narrow range of uses of acetoglycerides, it is doubtful whether the production and utilisation of the acetoglycerides will be carried out in India in the near future. The best use appears to be for coating edible products either to prevent loss of moisture due to excessive heat in the Indian conditions or to prevent absorption of moisture in the wetter regions of Bombay and Bengal especially during the monsoons. The coating of acetoglycerides may also be used to prevent fungus formation on food products during the monsoon.

REFERENCES :

1. Eckey and Formo, J.Amer.Oil Chem. Soc., 1949, 26, 207.
2. Ward et al., J.Phys.Chem., 1955, 59, 4.
3. J.Ind.Eng.Chem., 1954, 46, 13A.
4. Feuge et al., J.Amer.OilChem. Soc., 1952, 29, 11.
5. Food Manuf., 1954, 29, 291.
6. J.Ind.Eng.Chem., 1951, 43, 13A.
7. Hellman et al., J.Amer.OilChem.Soc., 1955, 32, 110.