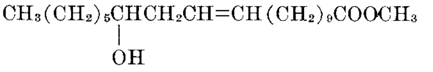
Distillation is an unsuitable method for purification of methyl dimorphecolate owing to its tendency to decompose on heating. Hence, three other purification methods were investigated. Column chromatography with silicic acid yielded pure samples but is suitable only for small quantities of material. Fractional crystallization at dry-ice temp could be performed on bulk quantities, but the operation is inconvenient and gave low yields. Multiple-stage liquid-liquid extraction could be used on bulk quantities, and completion of only 3 steps of the scheme with combination of the principal fractions from the identical solvent gave high yields of methyl dimorphecolate suitable for use in synthetic reactions. Acetonitrile-commercial pentane was a more effective solvent system for this purpose than aqueous methanol-commercial pentane.

Anhydrous anion exchange resin-catalyzed methanolysis of *Lesquerella* oil effectively produces methyl lesquerolate, [3].



$$\mathrm{CH_3(CH_2)_5\underset{\underset{OH}{|}}{C}HCH_2CH{=}CH(CH_2)_9COOCH_3}$$

[3]

However, since the solubility of *Lesquerella* oil is relatively low, only 5.6 g/100 ml methanol, supplementary addition of a hydrocarbon solvent is necessary to obtain homogenous solutions. A residence time of 2.5 hr is sufficient to convert at least 85% of the glyceride to methyl ester as judged by wt of glycerol recovered. Since methyl lesquerolate is not as sensitive to thermal decomposition as methyl dimorphecolate, the former can be purified more conveniently by distillation *in vacuo* rather than by liquid-liquid extraction, but prolonged heating of methyl lesquerolate at temp above 220C must be avoided in order to prevent formation of dienes.

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Suggestions regarding the preparation of the anhydrous ion exchange resins from T. H. Applewhite; elemental analyses by L. M. White and G. E. Secor; and general assistance in some of the experimental work from A. R. Gramps.

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Vibration-Stirred Microhydrogenation

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Abstract

A reaction vessel assembly suitable for small-scale catalytic hydrogenations is described. A specially-shaped, vibrating stirrer is used produce vigorous agitation of the reaction mixture.

Introduction

EXPERIMENTS DESIGNED to investigate fundamental catalytic hydrogenation mechanisms generally require highly-purified, well-defined materials. The high cost and limited availability of some specific isomers used as reactants then dictate miniaturization of equipment so that the quantities of costly materials used are small. This, however, aggravates the difficulty of some techniques, particularly that of stirring the reaction mixture: the gas, liquid, and solid phase must be in intimate contact so that mass-transfer problems are minimized. Adequate stirring of small-scale hydrogenation mixtures can be accompished by a vibrating stirrer.

Some devices using reciprocating stirring motion have been described (1–4), but are of limited utility. Stirrer motion of such devices is generally slow, resulting in limited mixing. Violent agitation of a reaction mixture can be produced by vibratory motion of a stirrer such as A of Figure 1, driven at 60 cycle/sec by a vibrator (in this case, a Wen sabre saw). Violent turbulance of the reaction mixture occurs if the amplitude of stirrer motion, controllable by varying the voltage input to the vibrator, exceeds about 1 mm. Small gas bubbles are sucked into the liquid, and jets of reaction mixture are forced through the peripheral holes of the stirrer, as shown schematically in Figure 1. Stirrers having cross-sections (B, Figure 1) produce varying degrees of agitation, but cause splattering.

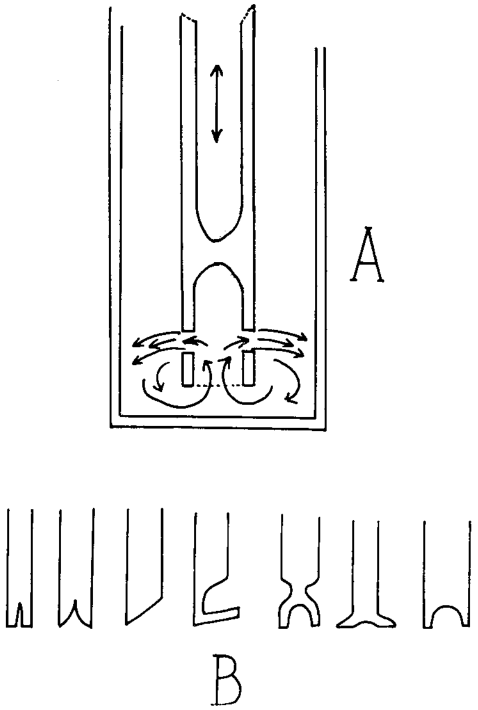

FIG. 1.

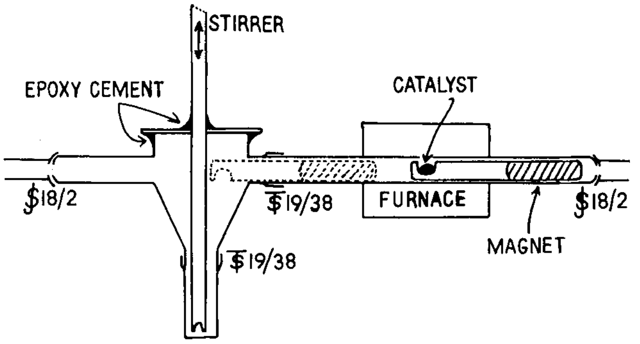

FIG. 2.

Stirrer A is made by collapsing a Pyrex tube, blowing three or four equally-spaced peripheral holes 2 or 3 mm below the cavity top, and then cutting the tube about 2 mm below the holes. The degree of agitation produced depends on hole diam and on the viscosity of the reaction mixture as well as on amplitude: jet formation and turbulence occur in water with holes of ca. 1 mm diam, but 2-mm holes are required with methyl linoleate. A stirrer of 0.6 mm I.D. produces satisfactory agitation of 0.2–0.5 ml liquid in a 1-cm I.D. vessel. Smaller quantities can be stirred by reducing the size of both stirrer and vessel.

The essentials of the reaction vessel assembly show in Figure 2. A gas-tight seal is made with epoxy cement between stirrer shaft and a $\frac{1}{8}$-in. thick Neoprene disc and between the latter and the reaction vessel "head." Catalyst is placed in a depression in a movable tube within a side-arm of the head. The reactant in the vessels is degassed, saturated with hydrogen, and the catalyst is reduced. The catalyst tube is then moved from the furnace zone by use of an external magnet. The side-arm, and consequently the rod within it, is then rotated, so that the catalyst drops into the reaction vessel. The apparatus, in conjunction with conventional burette and gas-handling systems, is being used to study the selective hydrogenation of methyl linolenate.

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Nutritional Studies of Polyglycerol Esters[1]

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Abstract

Palatable polyglycerol esters of various mol wt were prepared with fatty acids from cottonseed and peanut oils. The wt gains of weanling male rats fed 1 g/day polyglycerol esters in 5 g of a basic diet were compared with those of matching rats fed 1 g, 0.5 g, and no lard in 5 g basic diet. After three weeks, all rats were given free access to diets containing 8% polyglycerol esters or lard. The polyglycerol esters were utilized as well as lard for wt gain. Intestinal absorption of the fatty acids from the polyglycerol esters was the same as with lard. Autopsies and histological examination of the tissues revealed no abnormalities attributable to the consumption of these materials. Appearance of the animals was normal throughout the experiment. The epididymal fat of the animals was similar regardless of the polyglycerol structure fed. No polyglycerols were detected in the body fat. From these results, it is concluded that the polyglycerol esters of both low and high mol wt were nutritionally similar to naturally occurring fats and that they were nontoxic.

Introduction

POLYGLYCEROL ESTERS have been of considerable interest to the food technologist for may years. Heretofore, only very limited application has been achieved owing to the inability of prior processing techniques to remove the unfavorable color, flavor, and odor of these compounds.

Polyglycerol esters of suitable color, flavor and odor have now been developed by utilizing improved processing techniques. Because their apparent and potential utilization in diversified food application has received wide attention, an investigation of the nutritional properties of these esters was undertaken.

Previously, Bodansky and co-workers (1) demonstrated that the lower mol wt polyglycerol esters were completely harmless when fed at high levels in the diet, even during continued long-term feeding of these compounds. The present study is designed to extend the scope of their study by including the higher mol wt polyglycerol esters.

Both the lower and higher mol wt polyglycerol esters were examined for their capacity to be utilized for energy during caloric restriction and for growth during ad libitum feeding; for the extent to which they are absorbed under restricted and ad libitum feeding; and for their effects on the fatty acid composition, wt and pathology of certain organs.

Experimental Procedures

Briefly, the polyglycerol esters were produced as follows: glycerol was polymerized with a suitable catalyst, utilizing newly developed processing techniques, to form the desired polyglycerol ranging from a diglycerol (2 glyceryl radicals) to a triacontaglycerol (30 glyceryl radicals). Subsequent esterification with the appropriate fat, oil or fatty acid yielded the desired polyglycerol ester.

The polyglycerol esters studied and the analytical values obtained for these esters show in Table I.

Weanling male rats of the Sherman Strain, born

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[1] Presented at the AOCS Meeting, Atlanta, 1963.

[2] Deceased.