methyl esters by refluxing for 2½ hours with anhydrous methanol (2 ml./g.), containing 1.6 g. of naphthalene-2-sulfonic acid as catalyst. The isolated methyl esters, which weighed 90 g., were distilled from an alembic flask under high vacuum, yielding the following fractions:

Fraction	*B.P., °C./mm.*	*Weight, g.*	*Iodine No.*	*Hydroxyl Oxygen, %*	*Appearance*
1	113-132/0.05	9	73	3.3	Yellow liquid
2	133/0.04	15	63	5.6	Yellow liquid
3	154/0.05	7	43	7.0	Semi-solid
4	158/0.05	21	9	9.2	White solid
Residue	......	27	79	1.9	Black tar

Fraction 2 analyzed as methyl monohydroxyoctadecenoate, mainly, and Fraction 4 as methyl dihydroxystearate. The residue was probably mainly linoleate polymers. An α-glycol analysis on Fraction 4 showed the absence of adjacent hydroxyl groups.

An alternative procedure for the isolation of the dihydroxystearic acid fraction was to crystallize the saponified and acidified reaction product from ether-petroleum naphtha at 0°. In this way 25-30 g. of crude dihydroxystearic acids, m.p. 66-77° and hydroxyl oxygen, 8.4-9.2%, was obtained. Recrystallization from 95% ethanol at —20° yielded 12-15 g. of dihydroxystearic acids, m.p. 77-80°, and iodine number, 12.

Secondary Hexyl Formates. One hundred grams (1.19 moles) of 1-hexene, 200 ml. of anhydrous formic acid, and 1 ml. of 70% perchloric acid were mixed and refluxed for 15 minutes at the highest reflux temperature of the mixture (96°). The catalyst was neutralized with sodium bicarbonate, and the reaction mixture was fractionally distilled. After the recovery of 160 g. of formic acid, b.p. 51-57°/125, 94 g. (55% yield) of mixed hexyl formates, b.p. 87.5-95°/125 and saponification number 394-412, was obtained. Hydrolysis of these esters and fractional distillation of the resulting hexanols through a highly efficient column indicated that the formates consisted of about two-thirds 2-hexyl formate and one-third 3-hexyl formate. No 1-isomer could be identified.

Addition of Anhydrous Formic Acid to Soybean Oil. The relatively low solubility of glycerides in formic acid, compared to the other compounds studied, required that a small amount of mutual cosolvent be used. In the absence of a cosolvent substantially no addition of formic acid to the double bond was noted.

Ten grams of soybean oil, iodine number, 135, and saponification number, 191, 20 ml. of anhydrous formic acid, 0.1 ml. of 70% perchloric acid, and 5 ml. of butyl acetate were refluxed for 15 minutes after homogeneity was attained (total reaction time was usually between two and three hours). The reaction solution was poured into water and the upper layer was dissolved in ether and washed with water until acid-free. Evaporation of the ether yielded 9.5-10 g. of formylated soybean oil, iodine number 60-62, saponification number 295-302, and acid number 35-50.

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Summary

A new method for hydroxylating long-chain unsaturated compounds is described which involves addition of formic acid at its boiling point to the double bond followed by hydrolysis of the intermediate formate esters. The addition reaction proceeds slowly in the absence of catalysts, but strongly acidic substances, such as perchloric acid, sulfuric acid, and boron fluoride-acetic acid complex, speed up the addition tremendously.

Monohydroxystearic acids can be prepared in good yield by addition of 90-100% formic acid to the double bond of oleic or elaidic acids, methyl oleate, or the unreacted olefinic material separated from the hydrolyzed reaction product of oleic acid with formic acid, followed by hydrolysis. Similarly prepared are dihydroxyoctadecanes from oleyl alcohol, monohydroxyoctadecenoic and dihydroxystearic acids from linoleic acid, monohydroxyhendecanoic acids (isolated as methyl esters) from 10-hendecenoic (undecylenic) acid, and secondary hexanols from 1-hexene. Triglycerides are readily formylated if a small amount of mutual cosolvent is employed.

Acetic acid in the presence of acidic catalysts also adds to the double bond at its normal boiling point, but yields are lower than with formic acid.

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A Micromolecular Still[1]

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THE analysis of fatty methyl esters for monomer, dimer, and trimer (plus higher polymers) has been useful in following the kinetics of polymerization of methyl esters and drying oils. With nonconjugated and diene conjugated esters, the alembic pot distillation method has been satisfactory (1, 2, 3). When this method was considered for analysis of methyl eleostearate, it was soon evident that the time and temperature involved caused considerable polymerization of the monomer during the analysis. Also a method which would require less material for analysis was desirable when working with highly pure esters which are difficult to prepare.

The method of Booy and Waterman (4) appeared

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to meet the requirements. Their apparatus consisted of a shallow pan suspended from a glass helical spring, enclosed in a highly evacuated glass vessel. Heat was supplied by infrared lamps outside the vessel, adjusted so as to first distill monomer only, and then dimer. They showed an accuracy of 1% on known mixtures of monomer, dimer, and residual polymer.

The apparatus to be described is a modification which is easier to control and manipulate. The principal modifications are as follows: a) Heating is done by a thermostatically controlled aluminum block surrounding the distillation area. This gives reproducible and easy control of distillation temperature. b) The sample is dispersed on a small bale of glass wool suspended from a quartz helix. The glass wool prevents spattering and gives a large distillation surface. c) Arrangements have been made to collect the distillate in sealed ampoules when desired.

This apparatus has been in use at this laboratory since the middle of 1951 and has been useful in analyzing polymerized methyl eleostearates (5) as well as commercial dimerized fatty acids.

A recent abstract of a paper by Sims (6) describes an apparatus similar to the present one. The paper[2] has not been published to the present time, but a drawing kindly furnished by Sims indicates that he uses an internal heating coil and a glass pan.

Description of Apparatus

The apparatus is shown in the figure. The quartz helix is approximately 10 cm. long, is 1.5 cm. in diameter, and has 60 turns. The sensitivity is 2.92 cm. displacement per gm. load. A crosshair below the helix is blackened with India ink to facilitate reading. The helix was furnished by Microchemical Specialties Company, Berkeley, Calif. The crosshair is read against a scale mounted on the outside wall of the containing vessel. Any suitable linear scale may be used, such as the scale from a broken Beckman thermometer.

The reading of the crosshair against the scale is made by any suitable method which will avoid parallax. In the present apparatus a cathetometer was used at a distance of five feet.

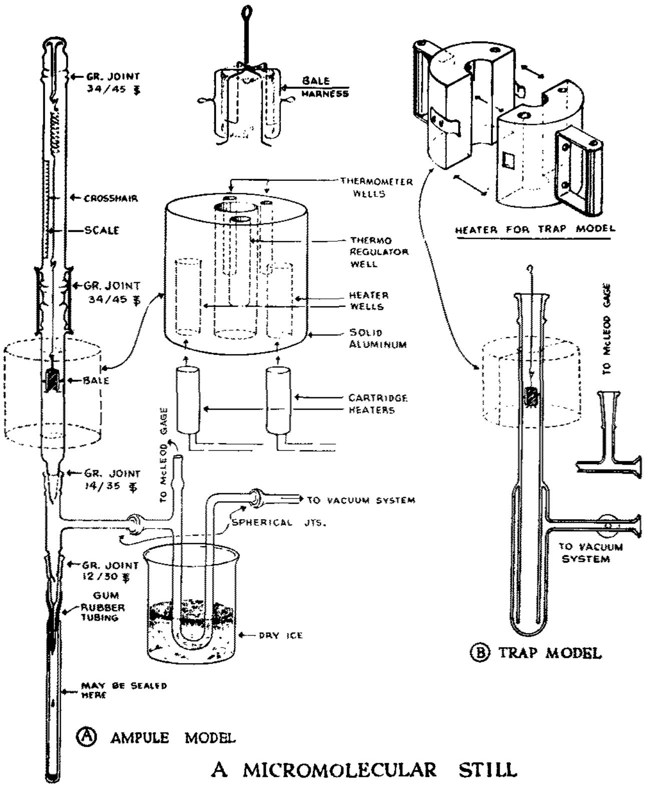
The bale of glass wool, in its harness, is suspended from a hook on the end of the fibre from the quartz helix by a suitable glass fibre extension with hooks on each end. The distillation vessel is made of 3.0 cm. i.d. glass tubing, with ground joints as indicated in the figure, to facilitate assembly and cleaning. The tube extends 2-3 cm. below the bottom of the heating block before constriction by the 14/35 joint. This affords a free path to this condensing zone, which is cooled by a jet of air. The ampoule model is fitted with a device so that the monomeric distillate may be sealed off under vacuum without interrupting the distillation. If a pure dimer fraction is desired, the apparatus is cooled down after monomer has distilled and is disassembled. The monomer is washed from the walls of the vessel below the middle 34/45 glass joint before reassembly and distillation of dimer. Otherwise the dimer would be contaminated by monomer draining from the walls.

The trap model is used for routine analysis where isolation of monomer and dimer is not necessary. The receiver and dry ice trap are combined, and a split heating block is used as shown in the figure.

The bale of glass wool is made by wrapping thin glass wool sheets around a thin glass rod until a roll 1.5 to 2 cm. is formed. The glass rod is removed, and sections are cut off with scissors as needed. For charges of about 0.5 gm. the bale is suitably about 2 cm. long. Longer bales may be used with larger charges. The bale is placed in the harness and passed through a flame to melt down any loose fibres which may project from the carrier and which would interfere with free suspension or might carry material from the bale to the walls of the vessel.

The heating block is aluminum, with a central hole to fit the distillation vessel. It is heated and controlled by any suitable method. The present model uses two cartridge heaters (150 watt, Chromalox) in suitable wells. Wells for thermometer and regulator are also provided, as shown. Any suitable regulator may be used, such as a Thermocap Relay on a mercury thermometer (Niagara Electron Laboratories, Andover, N. Y.); permanently set, vacuum-sealed bimetallic regulators (type D8-2A, Thomas A. Edison Company, Instrument Division, West Orange, N. J.); or Gardsman J. E. Series Controlling Pyrometer (West Instrument Company, Chicago, Ill.). The last mentioned is being used at present. The outside of the heating block is covered with asbestos paper insulation.

The harness for carrying the bale of glass wool is made of fine Nichrome wire (Fig. 1). It consists of six legs which are twisted together at the top to form a loop for suspension on the glass fibre extension. The legs are bent to form a cage-like holder. Four of the legs have short outward projections at the base. The other two, opposite one another, have outward



A MICROMOLECULAR STILL

Fig. 1.

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[2] Now published, *Vacuum 2*, 245 (1953).

projecting loops near the bottom and short inward projections at their base. These inward projections hold the bale of glass wool while the outward projections prevent the glass wool from touching the walls of the apparatus. The harness is ca. 1.5 cm. in diameter and 2 cm. long.

In the ampoule model a small dry ice trap is placed between the still and the mercury diffusion pump, which is backed up by a mechanical pump. A swing type McLeod gage is attached to the system between the trap and the still. Pressures were 1-5 μ during distillation.

Calibration of Instrument for Cut-off Temperatures

Known mixtures of monomer, dimer, and residual trimer were used to determine the proper temperatures for distillation of monomer and dimer. Methyl eleostearate was used for monomer since it is very sensitive to heat polymerization and would show any polymerization during distillation of monomer.

The dimer used was a center cut from molecular distillation of the methyl ester of alkali conjugated linoleic acid, fractionally distilled in a falling film type of molecular still. Trimer was a residue from a similar distillation. At a block temperature of 150° C. monomer was essentially completely distilled, but dimer distilled at a negligible rate. Similarly 250°C. was a suitable temperature for distillation of dimer. Normally distillation was complete 30 minutes after these block temperatures were reached.

Some measurements made with a thermocouple in the bale of glass wool showed that it was within a few degrees of block temperature after distillation had stopped. The bulk of the monomer distilled at a bale temperature of 80° to 105°, and the dimer at 180° to 200°. These are comparable to the temperatures at which monomers and dimers distill in falling film or centrifugal molecular stills.

Comparisons were also made on polymerized methyl esters which had been analyzed by the alembic pot method (1, 2, 3). Table I shows these results.

TABLE I

Polymerized methyl ester		% Monomer	% Dimer	% Trimer
I. 10,12-t,t-linoleate	Previous method	37.8	58.8	3.1
3 hours at 270°C.	Present method	38.9	60.2	1.9
II. Alkali conj. linoleate	Previous method	74.3	19.6	6.3
12 hours at 270°C.	Present method	76.0	20.5	3.5
III. Linolenate	Previous method	57.4	31.9	9.9
6 hours at 290°C.	Present method	61.9	29.9	8.2
IV. Linolenate	Previous method	29.8	40.1	29.3
24 hours at 290°C.	Present method	34.8	42.6	22.6

The agreement is within 1-3% in most cases. The % trimer is lower in all cases by the present method. The present method is probably more accurate than the previous method since incomplete drainage in the previous method would give a higher % trimer. The differences in % monomer and % dimer are greatest with linolenate, where thermal cracking leads to fractions of intermediate molecular weight and makes the cut-off point by either method less definite. The present method gave sharp cut-offs with polymerized methyl eleostearate. Pure alpha and beta methyl eleostearate showed 99.7% and 99.5% monomer by the method, and very little conversion of one to the other.

Operational Procedure

The apparatus is assembled with the empty bale as shown, and a reading taken (Reading O). Approximately 0.5 gm. of sample is added to the bale of glass wool, and a second reading is taken (Reading F). The mechanical pump is started. This will result in no change of reading if volatile material, such as solvent, is absent. When the pressure is 100 μ or less, the vapor pump is started. Heating is started when the pressure is 8 μ or less. After about 30 minutes at 150° block temperature, when distillation of monomer has practically stopped, a third reading, M, is taken. The block is then heated to 250°, and a fourth reading D is taken after 30 minutes and reasonable cessation of distillation.

$$\%\ \text{Monomer} = \frac{\text{M}-\text{F}}{\text{O}-\text{F}} \times 100$$

$$\%\ \text{Dimer} = \frac{\text{D}-\text{M}}{\text{O}-\text{F}} \times 100$$

$$\%\ \text{Residual Trimer} = \frac{\text{O}-\text{D}}{\text{O}-\text{F}} \times 100.$$

If distilled monomer sample is desired, the sample tube is sealed off before distillation of dimer. If distilled dimer sample is desired, the still must be cleaned after monomer distillation, as previously mentioned.

Discussion

The method has proven useful in following the rate of polymerization of the methyl eleostearates (5) and in following the kinetics of the dimerization of methyl linoleate by di-t-butyl peroxide (7, 8). In both of these cases alembic pot distillation was unsatisfactory. With the eleostearates, additional polymerization occurred during distillation. With the conjugated dimers formed by di-t-butyl peroxide, intramolecular reaction apparently occurred since the distilled dimers showed less conjugation ($k = 28.4$ at 235 mμ) than those distilled by the present method ($k = 41.6$ at 235 mμ) or in a centrifugal molecular still.

The method would probably be less satisfactory if appreciable quantities of material were present of molecular weight intermediate between monomer and dimer or between dimer and trimer. For instance, when pure methyl oleate was polymerized at 300° for 48 hours, distillation by the alembic pot method showed a plateau midway between monomer and dimer as well as a dimer plateau (by plotting refractive index *vs.* percentage of distilled) (2). Such a "one-and-one-half-mer" would undoubtedly make the monomer-dimer cutoff very obscure in the present method.

However on normal polymers the present method has the advantages of using small samples, minimum heat damage, provision to collect monomer and dimer, and ease and speed of operation.

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