Estimation of Unsaturation. It has been shown in Part I of this work (17) that the Standard Wijs method employed at 15–20°C. gives an accurate measure of the total unsaturation of the methyl esters of castor oil and can be used in calculating the fatty acid composition. A comparative study of the iodine values of hydrogenated castor oil, its mixed methyl esters, and acetylated hydrogenated castor oil has shown (Table IV) that the same method can be applied with certainty to the methyl esters of hydrogenated castor oil. This has therefore been employed in calculating the fatty acid composition of various samples of hydrogenated castor oil, as given in Table V. The high uncorrected iodine value by the bromometric method shows that substitution predominates in hydrogenated castor oil. In such an oil there is an excess of hydroxyl groups over double bonds with the result that a greater quantity and higher concentration of halogens are available for side reactions than in castor oil.

Summary

1. Products of low iodine value (<10.0) and hydroxyl value (35–40) can be readily obtained by hydrogenating castor oil at atmospheric pressure and at temperatures of the order of 220°, using 1.0% Raney nickel.

2. Dehydration of ricinoleic acid and subsequent hydrogenation of the resulting double bond as also simple saturation of ricinoleic acid are the main reactions occurring during the hydrogenation of castor oil under ordinary conditions.

3. Increase in the amount of catalyst favors more the hydrogenation of double bond at lower temperatures and both dehydration and hydrogenation at about 220°, which seems to be the optimum temperature for the maximum conversion of ricinoleic acid into nonhydroxy acids with both Raney and dry-reduced nickel at atmospheric pressures.

4. Higher proportions of catalyst, addition of catalyst stepwise, and higher temperature of hydrogenation cause considerable splitting and estolide formation.

5. When hydrogenation is carried out at room temperature, under a pressure of 40 p.s.i. with alcohol as solvent, a product rich in monohydroxy stearic acid is obtained.

6. True unsaturation of hydrogenated castor oil is measured by the Wijs method at 15–20°C.

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Reactions of Unsaturated Fatty Alcohols. III. Viscosity and Molecular Weight Studies on Some Vinyl Ether Polymers[1]

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Recent work at this laboratory on the preparation and polymerization of vinyl alkyl ethers derived from fatty alcohols has resulted in the initiation of molecular weight studies on these materials. Although several of the higher vinyl ether polymers have been known for a number of years, no molecular weight information appears to have been published. Investigators working with the higher alkyl vinyl ether polymers have referred to viscosity measurements to get comparisons of the degree of polymerization of their products. It seemed to us that a relationship between molecular weight and intrinsic viscosity for the higher alkyl vinyl ethers would be valuable. This paper reports the results of our studies on stearyl, soybean, and linseed vinyl ether polymers.

Molecular Weight Studies

In a previous paper of this series (9) preliminary experiments on the polymerization of vinyl ethers prepared from stearyl alcohol and several unsaturated fatty alcohols were described. Molecular weight data obtained by boiling-point elevation studies in benzene gave molecular weights ranging from 1,000–5,000. However the method was not considered satisfactory for our purposes because improved polymerization conditions were giving polymers of higher molecular weight and the relatively small boiling-point elevation in benzene reduced the accuracy of the determination. Isothermal distillation methods for determining molecular weights seemed a possible solution. The method of Parrette (6), using a modified Signer tube agitated by a rocking device, was tried, but attainment of equilibrium was too slow for our purposes. Cyclohexane has a rather large molal depression constant (K_f), and since our polymers were readily soluble in this solvent, a cryoscopic method was worked out. The apparatus used was simple in design and was similar to the conventional apparatus used for this work (1). A Beckman thermometer was used to measure freezing-point depressions. Constant stirring was accomplished by coupling an automobile

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[1] Presented at fall meeting, American Oil Chemists' Society, September 23–26, 1956, Chicago, Ill.

windshield wiper to the ring stirrer. The cooling bath was crushed ice.

Pure anhydrous cyclohexane was used in initial calibration work, but a satisfactory freezing point could not be obtained because of absorption of water during the determination. This difficulty was resolved by equilibrating the solvent with water at room temperature. Freezing points obtained after this treatment argeed within ± 0.005°C. The amount of supercooling of the cyclohexane ranged from 0.1 and 0.2°C. in all determinations. Freezing-point readings obtained when more than 0.2°C. supercooling occurred were discarded. It was generally not possible to obtain less than 0.1°C. supercooling with our materials.

Since a small amount of water was present in the cyclohexane, a new molal depression constant (K_f) was obtained on the equilibrated solvent. Pure azobenzene was used as a standard. A new K_f of 18.3 was obtained by using the Van't Hoff equation

$$K_f = \frac{M \times G \times \Delta T_f}{1{,}000 \times g} \qquad (1)$$

where M is the molecular weight of the solute, G and g are the weight of the solvent and solute, respectively, and ΔT_f is the freezing point depression in °C. Stearyl, soybean, and linseed vinyl ether polymers were submitted for molecular weight studies. These polymers were prepared with ionic catalysts according to a procedure described in a previous paper (8). Products varying in degree of polymerization were prepared by altering the conditions of polymerization slightly. Any monomeric material in the polymers was removed by extracting three times with hot methanol. Molecular weight determinations were performed on these preparations without further fractionation. Molecular weights were measured at three concentrations and a plot of 1/M *vs.* concentration (percentage by weight) gave a linear relationship that could be extrapolated to zero concentration.

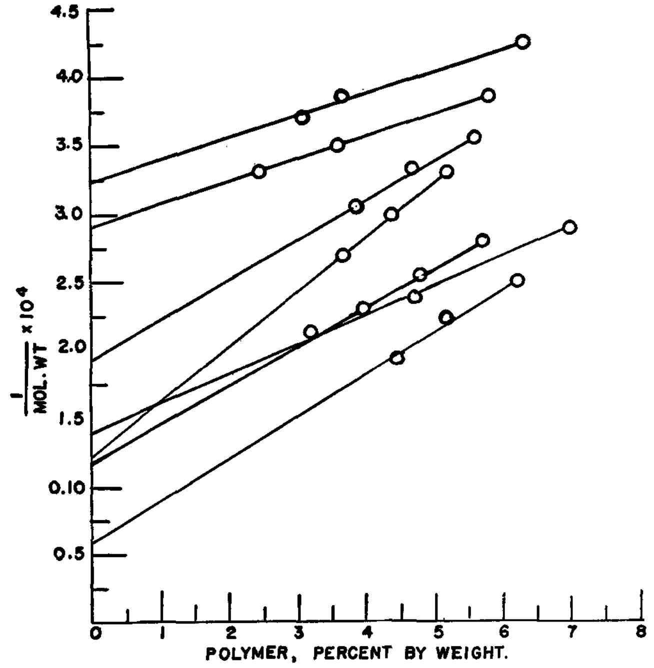


FIG. 1. Molecular weight of soybean vinyl ether polymers determined cryoscopically in cyclohexane.

A typical family of curves obtained for soybean polymers is shown in Fig. 1 with number-average molecular weights ranging from 3,000 to 15,000. Sample weights of the highest molecular weight polymers were selected so that a ΔT_f of 0.15°C. was obtained at the lowest concentration measured. Since the freezing point could be determined to ± 0.005°C., a maximum error of ± 3% was possible with dilute solutions of the higher polymers. Figure 1 shows that the most dilute solution measured for the sample having the highest molecular weight polymer was 4.5% by weight. This leaves a large concentration range to extrapolate across so that an error of ± 3% in locating the final point would lead to a larger error in the extrapolated value for the molecular weight. This effect is somewhat compensated for by the more precise points obtained at higher concentrations.

Intrinsic Viscosity Measurements

Viscosities were measured in an Ostwald-Cannon-Fenske viscometer, using benzene as the solvent. The viscometer was immersed in a water bath kept at 25°C. ± 0.05°C. Specific viscosities, η_{sp}, were obtained from

$$\eta_{sp} = \frac{T_2}{T_1} - 1$$

where T_2 is the flow time in seconds of the solvent containing polymer at concentration, C, and T_1 is the flow time in seconds of the pure solvent. The reduced viscosity (η_{sp}/C) was calculated at three different concentrations, and the intrinsic viscosity $[\eta]$ was determined from the intercept of a curve drawn through these points to zero concentration. A typical family of curves obtained with soybean vinyl ether polymers is shown in Figure 2. For clarity only a few curves in this figure correspond to molecular weight curves shown in Figure 1. The polymers with higher viscosity show a considerable change of η_{sp}/C with concentration (curves D, M, K, A). The slope of the curves increases as the molecular weight increases, and the polymers represented by curves D, M, K, and A appear to obey the Huggins relationship (4)

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C \qquad (2)$$

which normally describes the concentration dependence for high polymers. The values for k' are shown in Table I. Curves T and P also have a k' reasonably close to that obtained for high molecular weight polymers. However, with the lower molecular weight polymers, the slope of the η_{sp}/C *vs.* C curve is small, and the difference between η_{sp}/C and $[\eta]$ becomes slight. This results in an uncertain value for k' for low molecular weight polymers. Equation (2) was derived from a study of high molecular weight polymers, and it appears from the data in Table I that the soybean polymers start to obey this relationship

TABLE I

Value of M and k' in the Relationship $\eta_{sp}/C = [\eta] + k'[\eta]^2C$ for Soybean Polymers

Polymer curve	$[\eta]$	k'	Mol. Wt.
Y	0.050	0.26	1,000
P	0.081	0.51	3.500
T	0.110	0.42	8,500
F	0.142	0.33	17,500
A	0.159	0.48	24,000
K	0.172	0.48	31,000
M	0.191	0.54	40,000
D	0.250	0.45	90,000

TABLE II

Values of K' and a in the Mark-Houwink Relationship for Several Vinyl Ether Polymers

Vinyl ether polymer	K'	a
Stearyl	1.7×10^{-3}	0.47
Soybean	5.1×10^{-3}	0.34
Linseed	11.5×10^{-3}	0.25

when the intrinsic viscosity is at least 0.16. This viscosity represents a molecular weight of about 25,000 or about 85 monomer units in the polymer chain.

Similar viscosity data were obtained on stearyl and linseed vinyl ether polymers. A family of curves resembling the curves shown in Figure 2 was obtained.

Intrinsic Viscosity-Molecular Weight Relationships

The relationship between intrinsic viscosity and molecular weight has been worked out for many of the more important polymers. Most polymer systems encountered have shown that the intrinsic viscosity is related in some fashion to the size and shape of polymer molecules; hence most polymer systems show a relationship between intrinsic viscosity and molecular weight. This relationship can be described by the general formula of Mark and Houwink (5)

$$[\eta] = K'M^a \qquad (3)$$

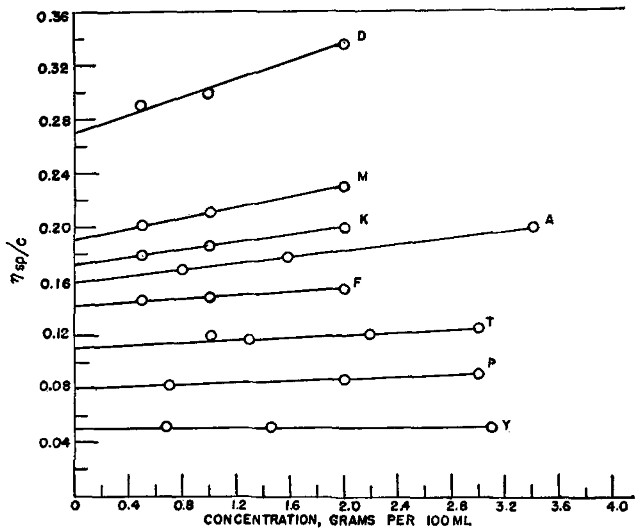


FIG. 2. Intrinsic viscosity of soybean vinyl ether polymers in benzene.

where K' and a are constants determined, respectively, by the intercept and slope of a plot of log $[\eta]$ *vs.* log M. Theoretically the value of a can vary from zero for Einstein's impenetrable spheres to two for a system whose molecules are shaped like rigid rods. Only a few systems are known where $a = 0$ (2, 3). Most high polymers have a value of a between 0.5 and 0.8, and recent studies by many investigators picture the majority of polymer molecules in solution as a random coil, a configuration intermediate between spheres and rigid rods.

The intrinsic viscosity and molecular weight data obtained on stearyl, soybean, and linseed vinyl ether polymers are plotted in Figures 3, 4, and 5. These fatty vinyl ether polymers prepared in this study conform to the Mark-Houwink equation (Formula 3).

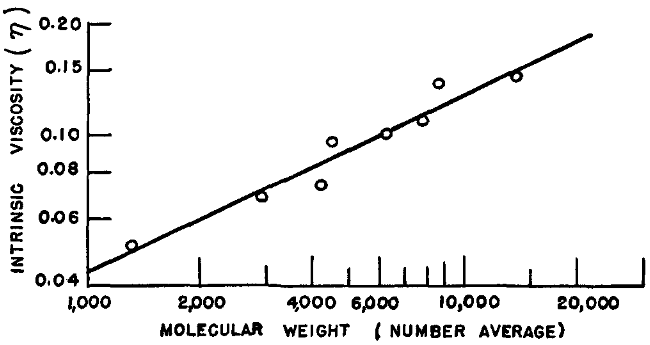
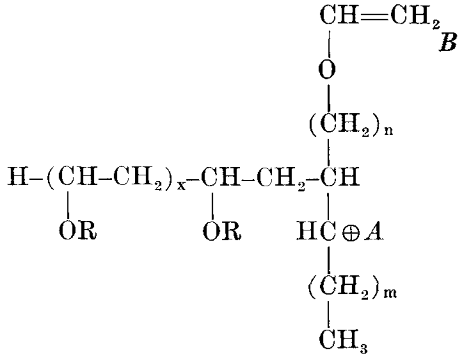


FIG. 3. Intrinsic viscosity-molecular weight relationship of stearyl vinyl ether polymers.

The values of a and K' were evaluated from the corresponding plots of log M *vs.* log $[\eta]$ for each polymer family. These values are shown in Table II. The value of a obtained for stearyl polymers is near that usually obtained for linear vinyl polymers. However, with soybean and linseed vinyl ether polymers, the value for a is considerably lower than that expected for systems of this type. This fact leads one to suspect that soybean and linseed polymers may not be entirely linear, and possibly some cross-linking or branching of the polymer chain results from the participation of the unsaturated side groups in the polymerization. A possible intermediate can be represented by the general formula:



$$\begin{array}{lll} & & CH{=}CH_2 \quad B \\ & & \,| \\ & & O \\ & & \,| \\ & & (CH_2)_n \\ & & \,| \\ H\text{-}(CH\text{-}CH_2)_x\text{-} & CH\text{-}CH_2\text{-} & CH \\ \;\;| & \;| & \,| \\ \;\;OR & \;OR & HC\oplus A \\ & & \,| \\ & & (CH_2)_m \\ & & \,| \\ & & CH_3 \end{array}$$

in which the ionic charge on carbon atom A can react with water or some other chain terminator. Further polymerization can then continue through the vinyl group at B to produce a semi-branched chain in the molecule. On the other hand, the polymerization can continue at both points (A and B) to produce a branched polymer molecule. A reduction in the

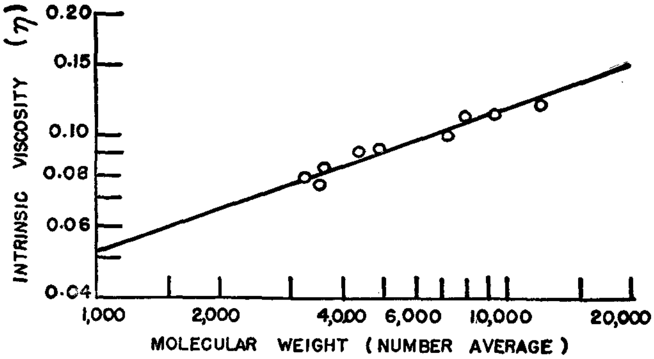


FIG. 4. Intrinsic viscosity-molecular weight relationship of soybean vinyl ether polymers.

amount of diene conjugation and in the iodine value in going from the monomer to the polymer is evidence for the participation of the unsaturated side chain in the polymerization. Information on this point is contained in a previous paper (8).

Figures 3, 4, and 5 can be used to determine the number average molecular weight of these vinyl ether polymers once the intrinsic viscosity has been determined. A number of polymers obtained during this study had intrinsic viscosities up to a value of 0.27 (Figure 3, curve D). The limitations of the cryoscopic method for determining molecular weight do not permit the measurement of *M* of a polymer in this range. However, if the relationship of log M *vs.* log $[\eta]$ is linear up to this point, molecular weights of the order of 100,000 have been obtained for soybean vinyl ether polymers. With stearyl vinyl ether polymers the molecular weights obtained thus far do not exceed 25,000. There is evidence in the case of polystyrene that the value of *K* and *a* in the Mark-Houwink relation which describe high polymers (mol. wt. of 1 to 2 million) continue to hold for low molecular polystyrenes (mol. wt. of 1 to 10 thousand) (7).

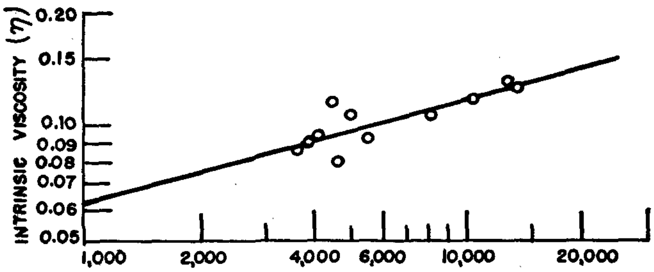


FIG. 5. Intrinsic viscosity-molecular weight relationship of linseed vinyl ether polymers.

Summary

Molecular weights of the polymers of the vinyl ethers of stearyl, soybean, and linseed fatty alcohols were measured cryoscopically in cyclohexane at three different concentrations. Corrected number-average molecular weights were obtained by extrapolation to zero concentration. For each family of polymers a series of preparations varying in degree of polymerization were studied with number-average molecular weights ranging from 1,500 to 15,000 or higher.

Reduced viscosity measurements at 25°C. were made on benzene solutions of each polymer preparation at three different concentrations. Intrinsic viscosities were obtained by extrapolating to zero concentration. Intrinsic viscosities for the polymers range from 0.05 to 0.20.

Logarithmic plots of molecular weight *vs.* intrinsic viscosity gave linear relationships for stearyl, soybean, and linseed polymers. Values for *K'* and *a* in the equation of Mark and Houwink were obtained from these plots.

Acknowledgment

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Analysis of Corn Oil for Total Tocopherols[1, 2]

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ALTHOUGH A NUMBER of the vegetable oils can be analyzed for their tocopherol content satisfactorily by the Parker-McFarlane treatment with sulfuric acid (9) and the subsequent Emmerie-Engel reaction with iron-dipyridyl (3), corn oil is well known to give low and erratic results by the procedure (6, 9). The nature of the interfering substance is unknown, and no suitable method for its elimination from the oil has been reported. This is unfortunate because of the widespread use of corn and its products in the animal diet and the consequent importance of a knowledge of the levels of tocopherol present in the whole grain.

Other procedures which have been applied to corn oil include saponification and adsorption of the unsaponifiable fraction (4); molecular distillation and subsequent hydrogenation (11); and paper chromatography (2). In the chromatographic experiments only *gamma*- and *alpha*-tocopherols were found in corn oils, and these were in an approximate ratio of 90% *gamma* to 10% of the *alpha* form (2, 5). However none of the procedures is suitable for use as a routine method for small samples (one gram or less) with ordinary laboratory equipment.

In the present study efforts were made to learn about the properties of the substance in corn oil which interferes with the Emmerie-Engel procedure and to develop a method for its removal.

Experimental

Reagents and Apparatus. Gamma-tocopherol, natural product (Distillation Products Industries), was used for all standardization and recovery experiments.

Alpha, alpha'-Dipyridyl (Matheson, Coleman, and Bell Division, Matheson Company). A solution of 0.25 g. in 100 ml. of ethanol was prepared fresh every two days.

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[2] Journal Paper No. 1051 of the Purdue University Agricultural Experiment Station, Lafayette, Indiana.