

## Viscous Behavior of Polymerized Vegetable Oils<sup>1,2</sup>

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THE THERMAL POLYMERIZATION of vegetable oils has many characteristics of a polycondensation reaction, one of which is an approximately linear relation between log viscosity and heating time. At high viscosities however, the apparent rate of viscosity increase becomes greater than logarithmic. Two explanations of this phenomenon have been offered. Adams and Powers (1) found that the activation energy of viscous flow varied linearly with the extent of reaction and considered that the increase in viscosity resulted from increase in unit flow. More recently Paschke and Wheeler (6) suggested possible explanations: a square root relation between molecular weight and log viscosity, and the more rapid increase in molecular weight of a bi- or higher functional reactant as extent of reaction increases.

Bulk viscosity has been related to a number of variables. Using unfractionated linseed standoil, Paschke and Wheeler (6) found a general linear relation between bulk viscosity and number average molecular weight, and Sims (9) related bulk viscosity to polymer content. In two studies of standoil fractionation Bernstein (3) and Walker and co-workers (12) separated linseed standoils into fractions and measured viscosity and molecular weight. In the first case, number average molecular weight was measured whereas, in the more recent work, weight average molecular weight was determined. No relations between viscosity and molecular weight were derived however.

By using Walker's data (12), crude integral and differential polymer distribution curves were drawn. They showed the presence of two main sizes of polymer; one of weight average molecular weight of about 15,000 and the other of about 140,000. Small amounts of polymer of intermediate size were also indicated.

Because of the importance of bulk viscosity in vegetable oil polymerization and the strong effect of high molecular weight material on viscosity, fractions of polymerized linseed oil were prepared and studied. In this paper are reported the effect of molecular weight and polymer concentration on activation energy of viscous flow and the results of investigations

to determine whether intrinsic viscosities could be obtained for this type of polymer and whether polymerized linseed oil behaved like other polymer systems well removed from their transition temperatures.

### Materials and Methods

Tung oil, safflower oil, and alkali-refined and bleached linseed oil were polymerized under anaerobic conditions. A sample of heat-bodied linseed oil was subsequently separated into fractions in a specially-designed liquid-liquid extractor (11), using acetone at temperatures increasing from 10 to 55°C. Some properties of the fractions obtained in this way are shown in Table I.

The viscosity of the thermally polymerized oil, its fractions and solutions of polymer in unheated linseed oil, was determined in Ostwald-Fenski pipettes and in Hoeppler and Brookfield viscometers. Density was measured in calibrated pycnometers. In this work, temperature was controlled to  $\pm 0.02^\circ\text{C}$ .

Critical solution temperatures were measured in the manner of Schultz and Flory (7), using acetone as the solvent. Weight average molecular weights were determined by light-scattering in isopropyl ether solution at a wavelength of 365  $\mu$ .

Some of the solutions of polymeric linseed oil in unheated oil were randomized by heating at 165°C. for 5 hrs. in the presence of 5% powdered tin. As control, samples of a 50:50 w/w mixture of tristearin and triolein were also randomized under these conditions. The amount of tristearin remaining after randomization was determined by permanganate oxidation as described by Desnuelle and Naudet (4). A micromolecular still was used to determine weight percentage monomer in the linseed oil mixtures before and after randomization (8).

### Experimental and Results

#### Bulk Viscosity

Initially, log viscosity is a linear function of polymer content (9). However, at greater extents of reaction, the viscosity appears to increase at an accelerated rate. A study was therefore made of the

TABLE I  
Fractionation of Polymerized Linseed Oil with Acetone

Properties	Extraction Temperature, °C.						
	10	20	30	40	50	55	55 <sup>a</sup>
$d_4^{25}$ .....	0.9416	0.9464	0.9558	0.9689	0.9739	0.9657	0.9608
$\nu_{30}$ (stokes).....	3.542	5.592	15.06	80.70	177.3	too viscous	too viscous
M.W. > 900, % <sup>b</sup> .....	36.25	47.75	59.98	68.74	90.83	....	96.89

<sup>a</sup> Insoluble in acetone at 55°C. <sup>b</sup> By molecular distillation (8).  $d$  = refractive index.  $\nu$  = kinematic viscosity.

TABLE II  
Influence of Rate of Shear on Viscosity of Polymerized  
Linseed Oil

R.P.M.	Unheated oil. Spindle No. 1	573 hrs. at 220°C. Spindle No. 2	1,032 hrs. at 220°C. Spindle No. 3
	<i>poise</i>	<i>poise</i>	<i>poise</i>
20.....	0.552	348	452
10.....	0.550	334	460
4.....	0.560	332	458
2.....	0.550	335	460

extent to which this curvature is caused by increased molecular size, to a square root molecular weight relation or to increased activation energy of viscous flow. The effect of rate of shear on viscosity was first investigated.

*Normality of Flow.* The effect of rate of shear on viscosity was investigated at 20°C. and 50°C., using oils of low, medium, and high viscosities. Preliminary investigations, using Ostwald-Fenske pipettes with different flow times and different balls in a Hoespler viscometer, indicated normal Newtonian flow. The data (Table II), obtained with a Brookfield viscometer, confirmed the view that at low rates of shear the flow was normal.

*Effect of Temperature on Viscosity.* Representative data for the variation of viscosity and density with temperature are shown in Table III. Over the range studied, the density varied linearly with temperature in degrees C. As shown in Figure 1, curved plots are obtained when the temperature coefficient of viscosity is determined by using the Arrhenius ( $\log \eta$  vs.  $1/T$ ) or the Andrade plots ( $\log \eta v^{1/2}$  vs.  $1/T$ ) (2). Although the Leaderman (5) line ( $\log \eta$  vs.  $1/T^2$ ) showed less curvature, only the 40, 50 and 60°C. points fell on a straight line and the Arrhenius temperature coefficient was therefore used.

The slopes of the  $d \log \sqrt{v}/dT^{-1}$  plots, measured in the linear region of 40 to 60°C., are shown in Figure 2 as functions of the extent of reaction calculated from polymer content (10). The results indicate that, up to approximately 50% reaction, the rate of increase in activation energy of viscous flow is slow. In the latter stages of reaction however, the temperature coefficient increases rapidly. Because the molecular weight and concentration as the

TABLE III  
Effect of Temperature on the Viscosity and Density  
of Linseed Oil

	Heating time in hours at 320°C.			
	0.0	0.9	2.5	4.2
$d_4^{20}$ .....	0.9279	0.9410	0.9586	0.9704
$V_{20}$ .....	0.4989	2.608	24.46	483.9
$d_4^{30}$ .....	0.9212	0.9343	0.9523	0.9644
$V_{30}$ .....	0.3720	1.727	14.31	250.3
$d_4^{40}$ .....	0.9144	0.9274	0.9455	0.9582
$V_{40}$ .....	0.2677	1.098	7.909	122.5
$d_4^{50}$ .....	0.9076	0.9214	0.9390	0.9518
$V_{50}$ .....	0.2022	0.7405	4.786	65.96
$d_4^{60}$ .....	0.9009	0.9143	0.9329	0.9457
$V_{60}$ .....	0.1556	0.5189	2.979	37.56

$d$  = density.  $v$  = kinematic viscosity.

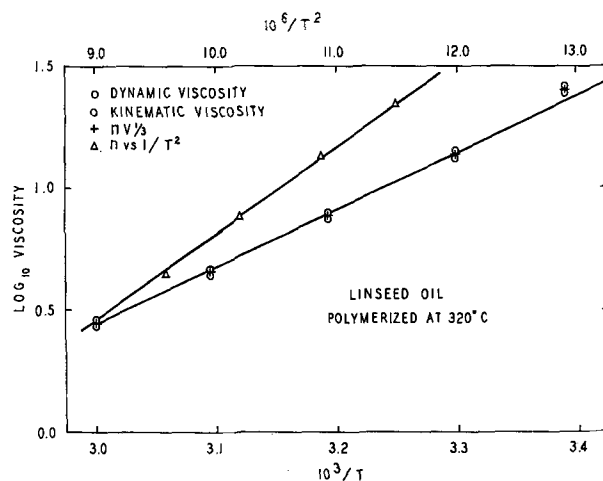


FIG. 1. Log viscosity versus  $1/T$  and  $1/T^2$ . Kinematic viscosity  $v = \eta/d$  where  $\eta$  = dynamic viscosity,  $d$  = density,  $v$  = specific volume.

molecular species present in bodied oil are changing reaction proceeds, an attempt was made to separate the effects of these two factors on viscosity.

*Effect of Concentration on Activation Energy.* The weight average molecular weight of the sample obtained by extraction at 55°C. was found by light-scattering to be 120,000. Solutions of this material were made up in unheated linseed oil over a concentration range of 1 to 60%. Viscosities of these solutions were then measured at 15, 20, 25, 30, and 40°C., and the viscosity temperature coefficients were calculated. A plot of temperature coefficient against polymer content in percentage by weight showed a linear relation with the suggestion of increased slope at concentrations of about 60%, the upper limit tried.

*Effect of Molecular Weight on Activation Energy.* The viscosities of the fractions obtained by liquid-liquid extraction were measured at 20, 30, 40, 50, and 60°C. As before, the linear portion of the Arrhenius

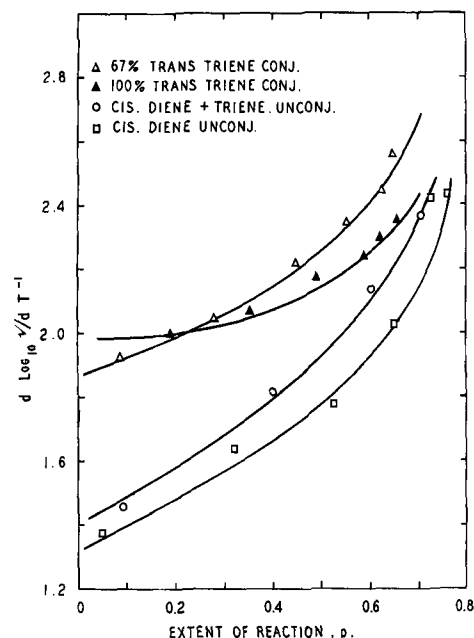


FIG. 2.  $d \log_{10} \sqrt{v}/dT^{-1}$  versus extent of reaction.  $\Delta$  =  $\alpha$ -tung oil,  $\blacktriangle$  =  $\beta$ -tung oil,  $\circ$  = linseed oil,  $\square$  = safflower oil. Activation energy of viscous flow.

TABLE IV  
Effect of Randomization on Polymer Solutions

% Polymer	$d_4^{30}$		$V_{30}$ (stokes)		$\eta_{30}$ (poises)		% Polymer	
	Before	After	Before	After	Before	After	Before	After
0.....	0.9212	0.9218	37.9	39.2	34.9	36.1	1.69	3.63
4.....	0.9241	0.9241	56.8	57.7	52.5	53.3	5.55	8.50
10.....	0.9274	0.9278	117.7	109.5	109.1	101.6	14.1	17.2
20.....	0.9331	0.9332	296.4	283.4	276.6	264.5	20.1	23.8

plot was used to calculate the temperature coefficients. A linear relation with an indication of increase in slope at high viscosities was found to obtain between temperature coefficient and  $\log \eta_{30}$ .

From the molecular weight of the 55°C.-insoluble fraction and an assumed value of 880 for unheated linseed oil, number average and weight average molecular weights were calculated for the various polymer solutions. When temperature coefficient is plotted against weight average molecular weight (Figure 3),

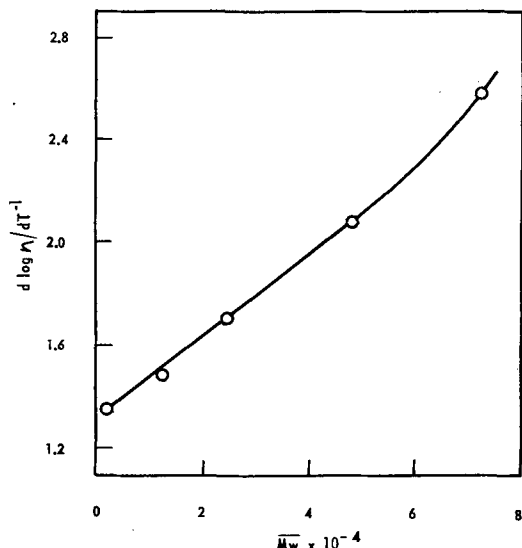


FIG. 3. Viscosity temperature coefficient ( $d \log_{10} \eta / dT^{-1}$ ) versus weight average molecular weight ( $M_w \times 10^{-4}$ ).

the curve increases in slope at molecular weights greater than 40,000. A plot of  $\log \eta$  versus  $\log$  molecular weight shows (Figure 4) marked curvature at approximately the same molecular weight.

**Bulk Viscosity-Molecular Weight Relation.** Using the number average and weight average molecular weights calculated for the solutions of polymer in monomer, a plot was made of  $\log \eta$  versus square root of molecular weight. With number average molecular weights, a linear relation was found to obtain up to a molecular weight of about 2,200. With weight average molecular weights, the plot was curved up to a molecular weight of 40,000, after which  $\log \eta$  varied linearly with the square root of the weight average molecular weight.

The dependence of viscosity on weight average molecular weight is further demonstrated by the data in Table IV. At initial polymer concentrations of 0 and 4%, heating caused an increase in both viscosity and polymer content, presumably because of slight thermal polymerization. Randomization of the 10 and 20% polymer solutions however reduced the viscosity while raising the polymer content.

**Dilute Solution Viscosity**

In an athermal, or indifferent, solvent the heat of mixing of polymer and solvent is zero, and the viscosity-molecular weight relation is unchanged by temperature. A "good" solvent is one with exothermic solvation that helps flexible molecules uncoil and gives a higher intrinsic viscosity to flexible molecules. In a poor solvent the polymer molecules are surrounded by energetically unfavorable solvent and tend to agglomerate if rigid, or coil up if flexible. With thermally polymerized vegetable oils, benzene and ethyl ether are good solvents whereas acetone is a poor one. It was considered that monomer, *i.e.*, unheated oil, might be an athermal solvent and, as such, useful in the evaluation of the constants in the intrinsic viscosity relation.

The behavior of fractionated linseed oil in a known poor solvent was first investigated. Critical solution temperatures of various concentrations of polymer fractions in acetone were measured (Table V) and plotted as functions of solute volume fraction (Figure 5). The results show that material soluble in acetone at 20°C. does not give a sharp peak. The material soluble at 30°C. and at higher temperatures gave definite maxima.

TABLE V  
Critical Solution Temperatures of the 30°C. Fraction.  
Wt. polymer = 0.2058 g.

t°C.	Wt. acetone	$d_4^t$ (acetone)	$d_4^t$ (polymer)	$v_2 / (v_1 + v_2)$
38.6	7.9450	0.7694	0.9475	0.0188
39.5	7.1685	0.7683	0.9470	0.0227
39.9	5.4244	0.7678	0.9467	0.0298
41.8	3.6259	0.7655	0.9456	0.0439
43.8	3.0363	0.7632	0.9444	0.0519
44.3	1.9968	0.7625	0.9440	0.0768
41.8	0.9855	0.7655	0.9458	0.1445

$v_1$  = volume fraction of solvent.  $v_2$  = volume fraction of polymer.

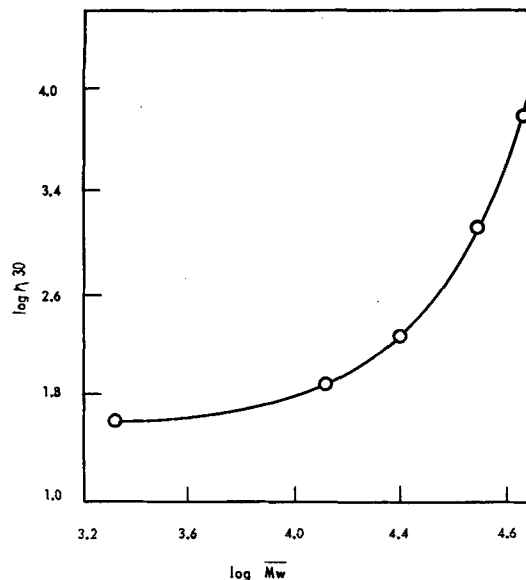


FIG. 4.  $\log \eta$  versus  $\log M_w$ .

Two good solvents, isopropyl ether and unheated linseed oil, were next tried. Preliminary work with unfractionated linseed oil in isopropyl ether gave the following encouraging results:

Sample	Linseed oil heated at 280°C.	
	for 12 hrs.	for 19 hrs.
Conc. (g./100 ml.) .....	1.254	0.7135 1.427
$\eta_{sp}/c$ .....	0.421	0.665 0.665

Molecular weight measurements with solutions of fractionated linseed oil in the same solvent however showed dependence of molecular weight on concentration, indicating that isopropyl ether is not really an athermal solvent for this polymer.

An attempt was then made to determine the intrinsic viscosity of fractions of polymerized linseed oil dissolved in unheated oil. With the fractions obtained at 20, 30, and 40°C., as with unfractionated oil, the plots curved upwards as zero concentration was approached. With material obtained by extraction at 50 and 55°C. however, straight lines were obtained when  $\eta_{sp}/c$  was plotted against concentration. The relations obtained with the 50°C. fraction were as follows:

$$\begin{aligned} \text{at } 25^\circ\text{C.}, \eta_{sp}/c &= 6.10 + 30.13 C \\ \text{at } 40^\circ\text{C.}, \eta_{sp}/c &= 5.64 + 20.33 C. \end{aligned}$$

### Discussion

From the behavior of the various fractions of linseed oil in critical miscibility and bulk and intrinsic viscosity plots, it can be deduced that thermally polymerized linseed oil contains high polymer. This macromolecular behavior was shown most strongly by material that was insoluble in acetone at 30°C. and at higher temperatures. The use of 25°C. as the reference temperature in the American Oil Chemists' Society Acetone Tolerance Test (K11-51) would seem to be well-founded.

As shown in Figure 2, the activation energy of the viscous flow of various thermally polymerized vegetable oils increases rapidly after approximately 50% reaction, suggesting the importance of this factor in their bulk viscosity. However, when the relation between activation energy and polymer concentration was tested with linseed oil fractions, a linear relation was found to obtain up to concentrations as high as 60% polymer. The absence of a sharp rise in activation energy indicates that molecular weight also plays an important role in viscosity increase. In this way thermally polymerized linseed oil resembles polyisobutylene, a polymer that is well removed from its transition temperature.

The relation between viscosity and molecular weight has been shown qualitatively to be strongly dependent on weight average molecular weight. Fractionation data show the presence of appreciable quantities of higher polymer ( $\bar{M}_w > 10^5$ ), a possible reason for the nonlinear relation between bulk viscosity and polymerization time at larger extents of reactions.

The presence of higher polymer makes feasible the determination of intrinsic viscosities. On the basis of the large values for intrinsic viscosity in unheated oil and the negative temperature coefficients for intrinsic viscosity and the slope of the line, monomeric vegetable oil is a "good" solvent for its polymer and not indifferent.

It is felt that this outline of the over-all behavior

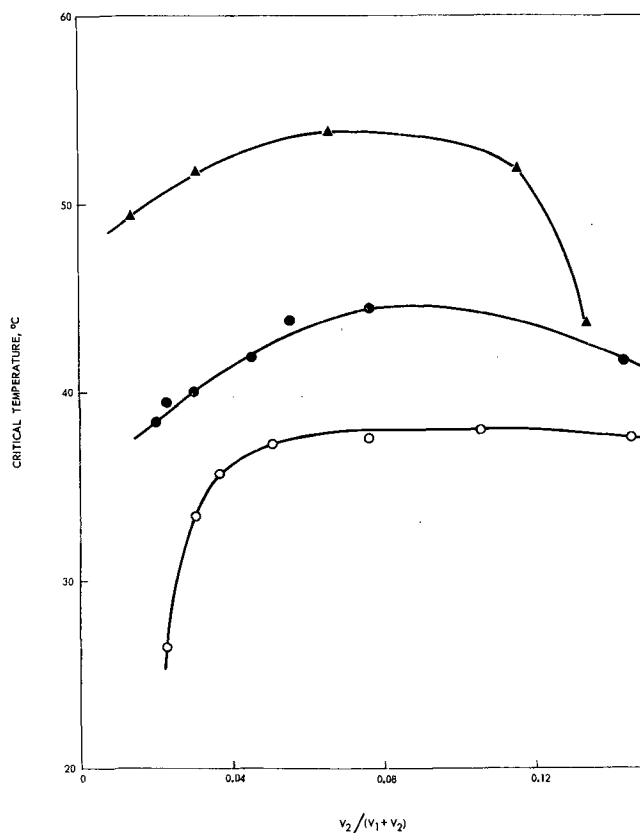


FIG. 5. Critical solution temperatures of polymer fractions.  $\circ$  = 20°C.-soluble material,  $\bullet$  = 30°C.-soluble material,  $\blacktriangle$  = 40°C.-soluble material.

of the system linseed oil polymer-linseed oil monomer indicates the applicability of high polymer techniques to thermally polymerized vegetable oils and the feasibility of establishing relations between viscosity and molecular constitution and molecular weight distribution as has been done with other polymer systems.

### Summary

Extraction of thermally polymerized linseed oil with acetone at various temperatures yielded fractions at higher temperatures that had high molecular weights and gave intrinsic viscosity and critical miscibility plots resembling those of high polymers. Unheated oil was not an indifferent solvent for polymerized oil as judged by the temperature coefficient of intrinsic viscosity.

Molecular weight information obtained with non-randomized samples suggested a linear relation between log viscosity and  $(\bar{M}_n)^{1/2}$  for molecular weights up to 2,500. With weight average molecular weights, a linear relation between log viscosity and  $(\bar{M}_w)^{1/2}$  obtains at molecular weights greater than 40,000. Randomization of the samples decreased their bulk viscosity while increasing polymer content.

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## Spectrophotometric Determination of Total Gossypol in Cottonseed Meal and Cottonseed Meats<sup>1</sup>

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THE NEED for a simple expeditious method for the estimation of total gossypol (bound and free) in cottonseed meal and cottonseed meats has not been adequately fulfilled by previous methods. Such a method would be of considerable benefit to the cottonseed processing industry, to feed manufacturers, and to nutritionists.

Bound gossypol (4), originally designated as D-gossypol (3), was first determined gravimetrically as dianilinogossypol (3; 5). It was extracted by means of hot aniline from cottonseed meal, which had been extracted previously with ether to remove the free gossypol. The extract was concentrated and allowed to stand several days so that crystallization might occur. A modification of this method (8) permitted the extraction of the free and the bound gossypol by a mixture of hot alcohol and aniline. The gossypol in the dianilinogossypol precipitated from the extract was designated as total gossypol. The bound gossypol was determined by subtracting the free gossypol, found by chemical analysis, from the total. More recently total gossypol has been determined spectrophotometrically as the p-anisidine derivative (7). The details of extraction by the p-anisidine method have been modified, and aniline has been substituted for p-anisidine as the coloring agent (6). Aniline has been substituted for p-anisidine in the revised A.O.C.S. Tentative Method Ba 8-55 (1).

The spectrophotometric method presented herein utilizes the reaction of gossypol with aniline and reduces the manipulative operation and time per determination. In this method the sample is treated with 72% alcohol (aqueous) to soften the particles of either cottonseed meats or cottonseed meal and to rupture any residual resin glands containing gossypol (2, 3). Then the sample is heated with aniline, and the dianilinogossypol thus formed is extracted with chloroform and measured spectrophotometrically. This method may be used for cottonseed meals which either contain acidulated cottonseed oil foots or have been aniline-treated.

### Reagents, Materials, and Equipment

Glacial acetic acid: reagent grade.

Ethanol 72% (by weight): dilute 830 ml. of 95% ethanol to 1,000 ml. with distilled water after adding 0.2 ml. of glacial acetic acid (9).

Aniline: freshly distilled, water-white.

Chloroform: U.S.P. grade.

Either pure gossypol or pure dianilinogossypol for standardization: dianilinogossypol may be obtained by extracting cottonseed meats with ether, removing the ether and precipitating dianilinogossypol with aniline. Dianilinogossypol is purified by recrystallization from either boiling benzene or chloroform containing a small amount of aniline. The purified crystals are washed with ether, air-dried, and then dried 12 to 16 hrs. in a vacuum oven at 50°C.

Asbestos: medium fiber.

Glass beads: 6 mm. in diameter.

Hyflo Super-Cel: remove traces of iron, which react with gossypol, by boiling 100 g. of Hyflo Super-Cel with 600 ml. of distilled water and 50 ml. of concentrated hydrochloric acid for 10-15 min. and filter on a large Buchner funnel. Wash well with distilled water. Repeat the process, dry, and pulverize to a powder.

Filter tube: Corning 9480 or similar.

Bell jar: a jar with an aperture in top, Corning 95470, or similar; perforated porcelain disk or plates, diameter 22 mm.

Wash bottle: equipped with a back-pressure check-valve for dispersing chloroform.

Mechanical shaker: conventional type.

A Waring Blendor may be used in place of the shaker for the extraction, small jar with screw cap. Place an aluminum foil liner inside the screw-cap over the regular washer by pulling the foil over the top of the jar and screwing the wet top over it, then fold the edges of the foil over the outside of the lid. Remove the screw-cap containing the liner, and punch a hole approximately 3 mm. in diameter through the center of the cap from the inside to serve as an air vent. The bearing in the jar assembly should be lubricated after about 15 determinations.

Spectrophotometer: A Beckman Model DU was used in this study. Any other good spectrophotometer or photoelectric colorimeter should be satisfactory, after establishing a standard curve for the instrument.

### Standard Calibration Curve

A standard optical-density-concentration curve for pure gossypol as the aniline derivative in chloroform was prepared as follows. First, 25 mg. of pure gossypol were dissolved in chloroform, diluted to 100 ml. with chloroform, and mixed. A 10-ml. aliquot of the standard was transferred to a 100-ml. volumetric

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