TABLE I

Migration of the Double Bonds of Methyl Linoleate During Isomerization with Palladium on Carbon Catalyst
(Temperature, 200 ± 5°C.; 5% of 10% Pd/C by weight)

Sample No.	Reaction time	Distillation temperature	Pressure	Yield	Refractive index 25°C.	% Conjugation	Hydrogen iodine value [a]	Composition of long chain dicarboxylic acids from ozonization, mole %							
								C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}[b]
1	0.5 hr.	120–123°C.	0.1 mm.	95%	1.4613	11.4	170	—	7	10	60	12	2	1.5	7
2	22 hrs.	118–120°C.	0.1 mm.	95%	1.4634	21.0	133	0.3	12	13	39	13	7	6	9
3	46 hrs.	118–120°C.	0.1 mm.	70%	1.4660	15.8	120	0.5	7	14	33	12	11	8	13

[a] Theoretical value for methyl linoleate used: 170.
[b] Includes higher unidentified acids.

one another and giving rise to conjugated dienes, and others moving away to structures wherein the olefinic bonds are further apart. Indeed chromatographic studies of the acids obtained from the oxidative cleavage of isomerized methyl linoleate substantiated this. Ultraviolet absorption spectra did not indicate the presence of any cyclized, aromatic components even after 46 hrs. of heating at 200°C. but showed the formation of aromatics at 250°C.

Results of chromatographic work are summarized in Table I. The origin of the C_{12} and C_{13} dicarboxylic acids (and probably part of the C_{11}) is presumed to be a result of partial hydrogenation of the olefinic bond closer to the carboxyl group. The activity of Pd/C as a hydrogenation-dehydrogenation catalyst introduces to these experiments some resemblance to the partial hydrogenation work of previous investigators. It is therefore not surprising that the dicarboxylic acids found here are, in general, those previously reported.

The analysis of monobasic acids obtained from the oxidation of isomerized linoleate was incomplete. Only two monobasic acids were identified, caproic (C_6) and heptylic (C_7).

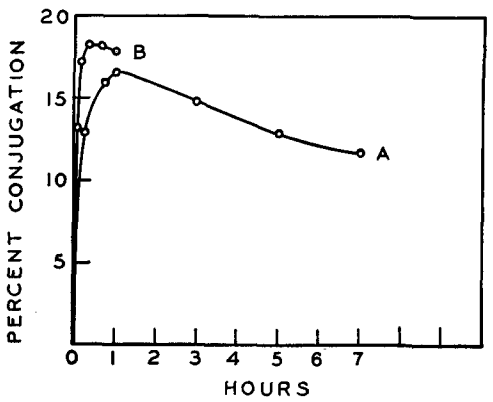

FIG. 3. Isomerization of methyl linoleate—250 ± 5°C.
A— 4% catalyst.
B— 10% catalyst.

Summary

The isomerization of methyl linoleate by heating with palladium on carbon catalyst gave an initial rapid rise in the degree of conjugation which reached a maximum and then gradually decreased. The maximum conjugation obtained was about 24% after 4 hrs. of heating at 200 ± 5°C. with 25% by weight of catalyst. Ultraviolet absorption spectra did not indicate the presence of any cyclized aromatic components even after 46 hrs. of heating at 200°C. but showed the formation of aromatics at 250°C. The limit of conjugation obtained is a result of random migration of the olefinic bonds rather than dimerization or polymerization reactions.

Acknowledgments

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Conductivity Method for the Control of a Soap Dryer

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THE USUAL LABORATORY METHODS for determining fatty acid contents of dried soaps containing 80 to 85% fatty acids are too time-consuming for adequate automatic control of the drying process. However a method based on the measurement of the electrical conductivity of compressed soap makes possible effective control of the soap-drying process.

Soap entering the vacuum dryer has a fatty acid content of 62 to 65%. Depending on end-use, such as soap flakes or toilet soap, the fatty acid content of the soap base is specified as minimum 80.0, 82.0%,

etc. A close adherence to these specifications is necessary for economic reasons, storability, and later processing of the soap base.

Conductivity Measurements

Schönfeld (1) cited the work of many investigators who measured the electrical conductivity of soap solutions in determining the colloidal character at different concentrations. Vold and Heldman (2) studied phase transitions by measuring the conductivity of more concentrated soaps (0 to 13% moisture) at high temperatures. Gonick (3) found a relationship between specific conductivity and concentration in the region of minimum equivalent conductivity of the soap solutions.

Generally the conductivity of a soap solution increases with the temperature, and the temperature coefficient falls with increasing concentration (1). Addition of electrolytes suppresses hydrolysis of the soap; sufficiently large additions reduce the conductivity of the mixture below that of the pure electrolyte because of ion-adsorption or reduction of the free cross-section for ion-transport. At a fatty acid content of 80 to 85% (corresponding to 87 to 92% soap) the free cross-section will be the dominating factor when the electrolyte content of the soap is within the usual range (0 to 0.10% NaOH, 0.40 to 0.80% NaCl). In other words, the conductivity will depend on the amount of electrolyte solution, and accordingly the conductivity will depend on the content of fatty acid in the soap.

As the soap is dried, both the fatty acid and electrolyte concentrations increase. For relative measurements this factor is not important since there is a correlation between conductivity and electrolyte concentration. But before a conductivity method can be used for the absolute determination of fatty acid contents, one must determine that the conductivity is not materially affected by the electrolyte concentration or other variables. The most important sources of variation are as follows:

a) *Between soap batches:* composition of fats, contents of glycerine, alkali, salt, and other substances.
b) *Within a soap batch:* drying conditions, length of storage, and fatty acid content.
c) *Between samples* (which are prepared by compressing the dried soap granules in a hydraulic press or by milling and plodding with the ordinary equipment for making soaps): degree of compression, mechanical treatment (milling), and temperatures during milling.
d) *Sampling and measuring errors:* sample age, evaporation from the sample, homogeneity, orientation, and temperature of the sample, and instrumental errors.

The conditions of drying, storage history, degree of compression, and temperature during milling are particularly important factors because they cause changes in soap structure (2, 4) which may affect the conductivity.

In order to determine the relationship between fatty acid percentage and conductivity, four experiments were made in which the regression of fatty acid percentage upon conductivity, the temperature coefficient, and the magnitude of errors were determined.

Apparatus and Procedure

Measurements of the conductivity were made with a Radiometer conductivity meter, Type CDM2 with an oscillator for supplying alternating current of 3,000 cycles to minimize polarization effects. The principle of the conductivity meter very much resembles that of an ohmmeter except that the meter scale is calibrated in reciprocal ohms, *i.e.*, Siemens (S), and that the test voltage is alternating. The test voltage is adjusted with a built-in potentiometer.

The conductivity meter has built-in resistances for different measuring ranges. In the tests described in this paper the conductivity was measured in milli Siemens (mS); 1 mS = 1 millimho, corresponding to 1,000 ohms.

The instrument is shown in Figure 3. Instead of the usual cell the electrodes were made from two pointed piano-wires, 18 mm. long and 1.5 mm. in diameter, placed 18 mm. apart in a socket. The measurement was made by inserting the electrodes into a piece of soap to rest against the socket, and then reading the instrument deflection in milli Siemens (mS).

Most of the sources of variation listed above were avoided by the following procedure. A 700-kg. sample, representing a 45-min. continuous production of dried soap, was homogenized and then stored in 30-kg. closed containers for 8 days at constant temperature. For each experimental batch five containers were taken at random. Thus each batch weighed between 150 and 160 kg.

Four batches with increasing contents of water were prepared by mixing the dried granulated 84% soap with increasing quantities of 5% electrolyte-free CMC solution for 15 min. in an amalgamator. The homogeneous batch was milled and plodded like a toilet soap for 40 min. As the bar of soap was pressed from the plodder nose, it was cut into pieces weighing approximately 100 g. Thus about 1,500 pieces were made from each batch. For conductivity measurements about 140 pieces evenly distributed over the batch were taken in subgroups of seven consecutive pieces each.

In each sub-group conductivity was immediately determined in five pieces, and temperature in the sixth by inserting a thermometer into the center of the piece. The seventh piece was used for fatty acid analysis. All samples from a given batch were ground and blended prior to the fatty acid determination. Because previous experiments had shown distinct orientation in the soap bar, conductivity was always measured across the bar in the front cut. If measured lengthwise of the bar the conductivity was higher.

As these experiments were made on a single batch of dried soap, variations between batches were avoided. Samples were prepared successively with constant load of mill and plodder. Measurements were made immediately after samples left the plodder nose. Thus variation between samples was minimized.

Results

The symbols used in the statistical treatment of the results are those in general use: $\bar{X}$ for mean, R for range, b for regression coefficient, r for correlation coefficient, etc. Factors for computing control limits were taken from reference 5. These values are summarized in Table I.

Temperature readings having an accuracy of 0.1° C. showed that the temperatures of the sub-groups varied by $\pm$ 3° around the mean temperature for a

batch. Data summarized in Table I showed that there was a linear relationship between conductivity, L, and temperature, t, according to the equation

$$L - \bar{L} = b\,(t - \bar{t})$$

wherein the regression coefficient, b, was determined by the method of least squares (6).

The temperature correction, p, as percentage of conductivity at 33°C., was found to fit the formula

$$p = 3.2 - 2.5/L_{33°}$$

As expected, the temperature coefficient decreased with increasing soap concentration (declining conductivity). From the conductivity L_t at a given temperature, t, the conductivity at the selected standard temperature 33°C. can now be found by the equation

$$L_t = L_{33°} + (t - 33)\, L_{33°}\, p/100$$

Relation Between Fatty Acid Percentage and Conductivity

Fatty acid contents were determined with a refractometer, according to the method of Steinchen (7). The analyses showed an average deviation of 0.20% corresponding to a standard deviation of the mean of 0.13% for a duplicate determination. Data in Tables I and II show that the fatty acid percentage fell in direct ratio to the square root of the conductivity according to the equation

$$\%\ \text{F.A.} = 86.86 - 3.80\ \sqrt{L_{33°}}$$

This curve is shown graphically in Figure 1. The

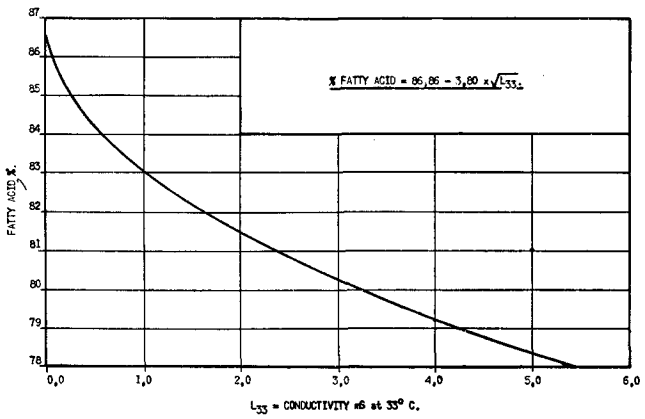


FIG. 1. Relation between fatty acid content and conductivity.

standard error for the deviation between fatty acid content calculated by this formula and the result of the analyses was about 0.13% abs. As shown in Table II, there was excellent agreement between calculated and measured fatty acid contents.

TABLE II

Fatty Acid Contents in Dried Soaps as Determined by Conductivity and Refractometric Methods

Batch	I	II	III	IV
Mean temperature, °C	33.20	34.40	32.85	32.55
Mean conductivity, mS	1.34	2.13	3.79	5.41
Corrected conductivity, L_{33}, mS	1.34	2.07	3.80	5.48
Fatty acid content, %				
Calculated	82.46	81.39	79.45	77.96
Found[a]	82.5	81.6	79.1	78.2

[a] Determined by refractometric method according to Steinchen (7).

Thus it appears that the measurement of conductivity is a quick and accurate method for controlling

TABLE I

Mean, Range, and Temperature Coefficient of Conductivity of Dried Soaps

Batch	I	II	III	IV
Number of samples in sub-group	5	5	5	5
Number of sub-groups	20	20	16	18
Mean of conductivity, $\bar{X}$, mS	1.34	2.13	3.79	5.41
Mean of temperature, $\bar{T}$, °C	33.2	34.4	32.85	32.55
Mean of range, $\bar{R}$, mS	0.11	0.12	0.26	0.30
Standard deviation, σX, mS	0.05	0.05	0.11	0.13
Standard deviation, $\sigma\bar{X}$, mS	0.02	0.02	0.05	0.06
Temperature regression coefficient b	0.019	0.043	0.090	0.149
Temperature correlation coefficient	0.65	0.51	0.80	0.73

relative variations in the fatty acid contents of dried soaps. The mean of five measurements by conductivity method had a standard deviation of about 0.05% abs., and the measurements could be made in about one minute.

In Figure 2 are shown the results of controlling the operation of a dryer by means of the $\bar{X}$-R chart. In this case the conductivity was determined on compressed bricks of soap from the dryer. These bricks measured 40 x 40 x 40 mm. and were prepared at a compression pressure of 10 atm. The standard deviation of a single measurement was here about 0.14 mS. Whether the pressure was 5 or 40 atm. had no significant effect upon the conductivity. It will be seen that, by the present method, the plant was under control except when adjustments in velocity were made as indicated by the arrows.

A control instrument was accordingly constructed, consisting of a small plodder for automatic sampling and a Radiometer conductivity meter with recorder for continuous reading. The plodder is connected with the screw conveyor from the dryer as shown in Figure 4. The electrodes are placed in the plodder

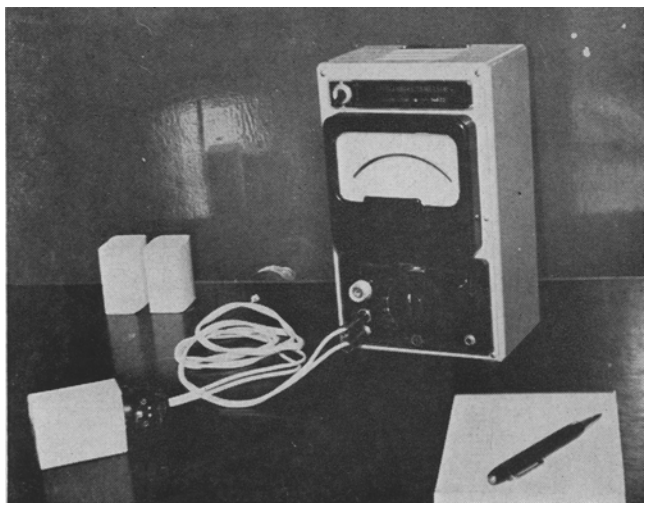
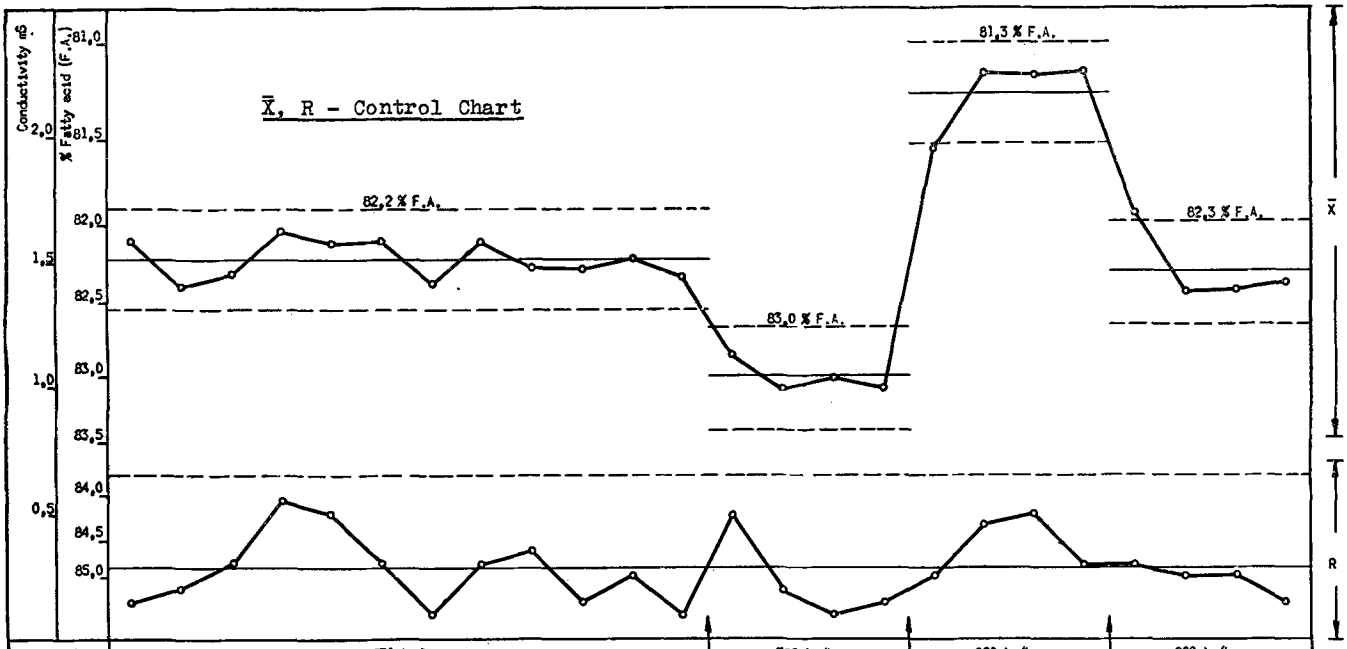


FIG. 3.

nose, and the conductivity is continuously indicated on the control panel as shown in Figure 5. The measuring is very precise (standard deviation only 0.05 mS), and variations in drying conditions are immediately indicated. The instrument has thus proved valuable to the operator of the plant.



Soap kg/hr.	870 kg/hr.												780 kg/hr.				960 kg/hr.				860 kg/hr.			
Nr.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
X_1	1,52	1,35	1,30	1,34	1,27	1,50	1,37	1,73	1,64	1,48	1,42	1,44	1,40	1,08	0,99	1,09	2,10	2,45	1,92	2,20	1,75	1,34	1,29	1,44
X_2	1,52	1,50	1,60	1,49	1,52	1,65	1,42	1,65	1,54	1,48	1,47	1,39	1,20	1,03	1,04	0,99	1,95	2,35	2,22	2,40	1,50	1,44	1,39	1,49
X_3	1,67	1,30	1,40	1,74	1,72	1,45	1,37	1,53	1,44	1,38	1,67	1,44	0,90	0,98	1,04	0,99	1,85	2,20	2,42	2,10	1,70	1,49	1,34	1,34
X_4	1,67	1,45	1,50	1,89	1,77	1,75	1,47	1,43	1,29	1,53	1,52	1,49	1,00	0,88	1,09	0,94	1,90	2,00	2,42	2,35	1,80	1,24	1,54	1,38
$\bar{X}$	1,59	1,40	1,45	1,62	1,57	1,59	1,41	1,59	1,48	1,47	1,52	1,44	1,13	0,99	1,04	1,00	1,95	2,25	2,24	2,26	1,69	1,38	1,39	1,41
R	0,15	0,20	0,30	0,55	0,50	0,30	0,10	0,30	0,35	0,15	0,25	0,10	0,50	0,20	0,10	0,15	0,25	0,45	0,50	0,30	0,30	0,25	0,25	0,15

$\bar{R} = 6,65/24 = 0,28$; $D_4\bar{R} = 2,28 \times 0,28 = 0,64$; $UCL_R = 0,64$; $LCL_R = 0$; $A_2\bar{R} = 0,729 \times 0,28 = 0,20$; $\bar{\bar{X}} = 1,51$; $UCL_{\bar{X}} = 1,71$; $LCL_{\bar{X}} = 1,31$

$\bar{\bar{X}} = 1,04$; $UCL_{\bar{X}} = 1,24$; $LCL_{\bar{X}} = 0,84$

$\bar{\bar{X}} = 2,18$; $UCL_{\bar{X}} = 2,38$; $LCL_{\bar{X}} = 1,98$

$\bar{\bar{X}} = 1,47$; $UCL_{\bar{X}} = 1,67$; $LCL_{\bar{X}} = 1,27$

FIG. 2. Control chart for soap dryer. Effect of change in velocity on percentage of fatty acid in soap.

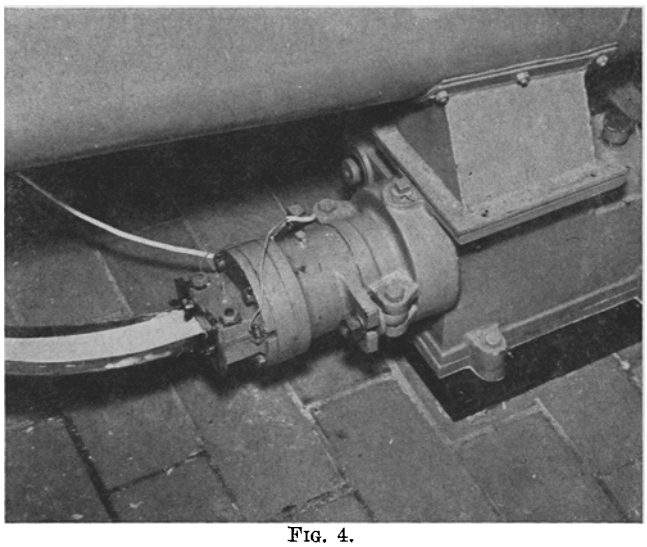


FIG. 4.

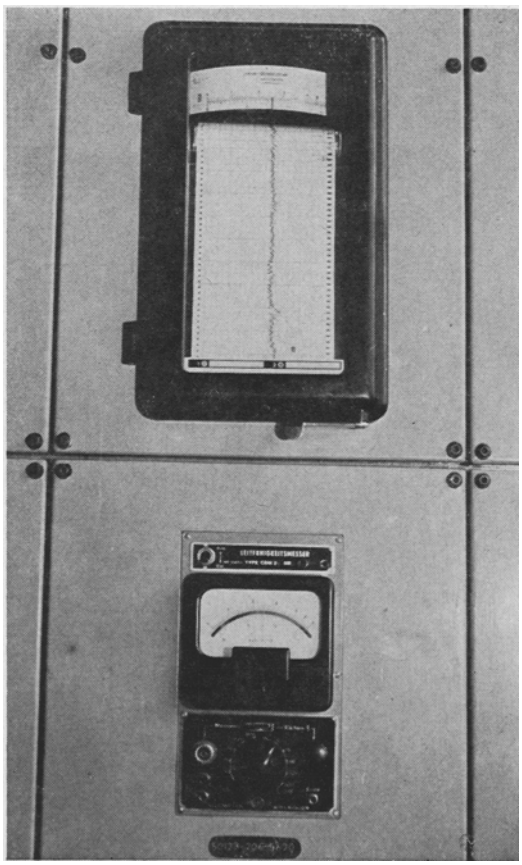


FIG. 5.

Preliminary data have shown no significant deviation betwen computed and analyzed fatty acid percentages in spite of varying fat composition and varying electrolyte concentration between 0.05–0.12% NaOH, 0.35–0.50% NaCl. The apparent independence of the electrolyte concentration may be due to its relatively high level in soap (10–30%, based on "free water."). Conductivity measurements with the described electrode pair in pure sodium chloride solution showed a steady increase in conductivity with concentration up to about 10% sodium chloride solu-

tion. Above that level, conductivity was relatively constant.

Conclusion

Data reported in this paper show that a conductivity method may be used for the computation of fatty acid contents of soap in the range of 78 to 83%. The method is adaptable to the control of soap dryers.

Acknowledgment

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Preliminary Report on the Nutritional Significance of Bound Gossypol in Cottonseed Meal

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A NUMBER OF INVESTIGATORS have shown that the nutritional value of different samples of cottonseed meal varies over a wide range (5, 12, 14, 20). The work of Lyman *et al.* (12, 13), Haddon *et al.* (7), and Chang *et al.* (5) indicates that processing conditions are of major importance in connection with these variations. Two distinct nutritional factors are involved. The first is the necessity of reducing the content of free gossypol to low levels in order to avoid the unfavorable physiological effects of this compound. The second factor concerns the quality of the protein as modified by processing methods and other variables. During an investigation designed to develop laboratory methods for estimating protein quality in cottonseed meal Lyman, Chang, and Couch (12) found a relationship between protein quality and bound or inactivated gossypol. This relationship between protein quality and bound gossypol was given further consideration during the course of a cooperative survey of the nutritional value of prepress solvent cottonseed meals (5). Four different investigators studied the same group of meals in chick growth tests. The correlation coefficients between chick growth rate and total gossypol (essentially bound gossypol) were —0.899, —0.791, —0.805, and —0.140. All of these coefficients were significant at the 1% level except the last. In a rat protein-repletion test the correlation between protein quality and total gossypol was —0.682. This value is significant at the 1% level.

Such a relationship between the nutritional value of the protein in cottonseed meal and bound gossypol would be predicted on the basis of previous postulates concerning the chemical nature of bound gossypol. A number of years ago Clark (6) proposed the concept that, during the processing of cottonseed meal, free gossypol, which is toxic in guinea pigs, rabbits, and pigs, is converted into an insoluble, inert gossypol-protein complex. It is known that gossypol in this form has lost its harmful properties. In the laboratory gossypol-protein complexes have been prepared by Hale and Lyman (8) and Castillon and Altschul (3). Gossypol is known to combine with amino groups. Chang (4) prepared a lysine-gossypol compound and fed this to rats. Essentially all of the lysine as well as the gossypol were recovered in the feces. These findings and others suggest that gossypol may be bound to protein through an amino group.

Kuiken and Lyman (11) reported that the availability of lysine in a sample of cottonseed flour was only 64.5% whereas in wheat and peanut flour it was about 95%. The formation of a gossypol-protein complex could account for this decreased lysine availability and resulting lowered nutritional value of the cottonseed protein. The importance of lysine availability in cottonseed meal is further indicated by the reports of Sherwood and Couch (19) and Richardson and Blaylock (16, 17), who showed that the addition of lysine to the diet increased the growth of chicks when cottonseed meal was used as the source of protein.

As a part of an evaluation of the general concept concerning the nature of bound gossypol and its significance in the utilization of cottonseed meal protein, the purpose of the present communication is 1) to describe a procedure by which bound gossypol can be removed from samples of cottonseed meal without subjecting the material to heat; 2) to report the results of tests designed to determine whether the removal of bound gossypol results in improvement of the nutritional value of the protein; and 3) to report the change in nutritional value of purified cottonseed protein which takes place when the protein combines with gossypol.

Experimental

Description of Cottonseed Meal Sample. The meal used in this study was a commercial prepress solvent meal. It was selected for study solely on the basis of its high bound gossypol content.

Treatment to Remove Free Gossypol. Three liters of 70% acetone were added to 2,000 g. of meal, and the mixture was stirred vigorously with a mechanical stirrer for 6 hrs. The mixture was allowed to stand for 24 hrs. at room temperature, then filtered, and washed three times with acetone and finally once with ethyl ether. The treated meal was spread on paper in thin layers to dry.

Treatment to Remove Bound Gossypol. a) To 2,000 g. of cottonseed meal 450 g. of redistilled aniline