TABLE I

Gossypol Content[a]

Exp. No.	Weight %[b]	Peak area %[c]	Weight % / Peak area %
1	10.31	13.51	1.310
2	23.97	23.80	.993
3	32.17	31.91	.992
4	36.75	38.46	1.047
5	42.85	43.86	1.024
6	60.59	60.98	1.006
7	70.52	70.09	.994
8	74.76	75.76	1.013

[a] Average of two replicates in each case.

[b] $\text{Weight } \% = \dfrac{\text{wt. of gossypol}}{\text{wt. of tricaprin} + \text{wt. of gossypol}} \times 100$

[c] $\text{Peak Area } \% = \dfrac{\text{area of peak b of TMS-gossypol}}{\text{area of tricaprin} + \text{area of peak b of TMS-gossypol}} \times 100$

Application of GLC to the quantitative determination of gossypol requires the use of an internal standard. Among the various compounds tested for this purpose, tricaprin was chosen since it is eluted quantitatively from the column and its retention time under the conditions for the analysis was approximately one-half that of gossypol. Also the compound is available commercially in pure form (Applied Science Laboratories). Standard mixtures with various quantities of gossypol and tricaprin by weight were prepared and analyzed by GLC. The results of these analyses are shown in Table I. The peak areas were calculated by triangulation; only the area of peak b of gossypol was computed. It can be seen that, if one considers all three peaks (a, b, and c), then the area percentage of gossypol will be greater than its weight percentage. This is to be expected in view of the fact that up to eight trimethylsilyl groups may have been added to the molecule. However the relatively constant nature of the factor obtained by dividing the weight percentage of gossypol by its area percentage indicates that this method can be used for quantitative determinations.

As a practical application of this method to pigments in cottonseed products, uncooked cottonseed flakes were extracted by the official method (2) for determining free gossypol. An aliquot of this aqueous acetone extract was reduced to dryness on a flash evaporator at 30C, and carbon disulfide and the silylating reagent were added. It was observed that,

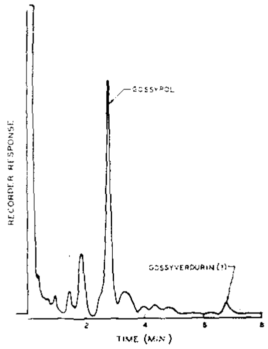

FIG. 3. GLC analysis of the aqueous acetone extract of uncooked, flaked cottonseed meats for gossypol as the TMS derivative. Temperature 240–300C programmed at 4 C/min. Other conditions the same as in Figure 1.

in addition to the normal gossypol peaks, several other smaller peaks were obtained (Figure 3). The last peak in Figure 3 was found to have the same retention time as the TMS derivative of an authentic sample of gossyverdurin. It is known that there are other gossypol-like pigments present in cottonseed which probably account for the other minor peaks. Identification of these peaks and investigation of the extension of this method to pigments in other cottonseed products are in progress.

ACKNOWLEDGMENT

The authors thank Don Brasseaux for making available the Aerograph 1520B Gas Chromatograph. This work was supported by USPHS Grant AM-06011 and the Cotton Research Committee of Texas.

P. K. RAJU
Department of Biochemistry and Biophysics
CARL M. CATER
Texas Engineering Experiment Station and
Department of Biochemistry and Biophysics
Texas A&M University
College Station, Texas

REFERENCES

1. Pons, W. A. Jr., and J. D. Guthrie, JAOCS *26*, 671 (1949).
2. "Official and Tentative Methods of the American Oil Chemists' Society," Official Method Ba 7–58.
3. Pons, W. A. Jr., C. L. Hoffpauir and R. T. O'Connor, JAOCS *27*, 390 (1950).
4. Pons, W. A. Jr., J. Pominski, W. H. King, J. A. Harris and T. H. Hopper, JAOCS *36*, 328 (1959).

[Received April 17, 1967]

• *Letters to the Editor*

Calculation of the Linolenic Selectivity Ratios of Hydrogenation Catalysts

THE CALCULATION of the selectivity ratios or ratios of the reaction rates of the various reactions that occur during the hydrogenation of unsaturated oils may be made by using an analog computer (Butterfield et al., JAOCS *41*, 29, 1964) or may be estimated graphically (Albright, JAOCS *42*, 250, 1965). Since an analog computer is not always available, the graphical method has wider utility. However the present graphical method does not provide for the calculation of the linolenic selectivity ratio, which is the ratio of the reaction rates of the hydrogenation of linolenic to linoleic and linoleic to oleic.

Since the selective reduction of the linolenic in soybean oil is a desirable characteristic (Koritala and Dutton, JAOCS *43*, 556, 1966) of some catalysts, this report describes a method of calculation of the Linolenic SR so catalysts may be classified by this criterion.

Essentially the same method of calculation from the equations described by Albright was used. A GE-265 Time Sharing Computer system was programmed with the first order, nonreversible, kinetic equations of the reaction sequence

$$\text{linolenic} \xrightarrow{K_1} \text{linoleic} \xrightarrow{K_2} \text{oleic}$$

and the compositions were calculated over a range of values of K_1 of 0.5 to 10. A K_2 value of 0.5 was arbitrarily assigned, and time values of 0.1 to 5 were used in the equations. Thus the composition of the products resulting from the hydrogenation of oils containing linolenic acid were calculated for Linolenic Selectivity ratios ($\text{Ln SR} = \frac{K_1}{K_2}$) of 1 to 20.

The composition of the starting oil which was used for the calculations was an average composition of soybean oil: 22% oleic, 55% linoleic, and 8% linolenic. However the results of the calculation were graphed (Figure 1) so that the selectivity of the hydrogenation of oils which have fatty acid composition different from soybean oil could be calculated from the same graph. The ratio of the starting and ending linolenic ($\frac{\text{Ln}}{\text{Ln}_0}$) was plotted against the ratio of the final linoleic (L) and against the sum of the starting linoleic plus 1.2 times the amount of linolenic that had been changed to linoleic ($L_0 + 1.2\ (\text{Ln}_0 - \text{Ln})$. By the addition of the linolenic that had been changed to linoleic ($\text{Ln}_0 - \text{Ln}$) in the calculation of the ratio of starting and ending linoleic, the effect of a high initial linolenic content is minimized. This is necessary if the graph is to be used for other compositions than the one used in the calculations. The error caused by varying the initial linolenic content is also reduced if the formed linoleic (ΔLn) is multiplied by the constant 1.2. This brings the calculated Ln SR lines of several starting compositions to coincidence at about the point of half hydrogenation of the linolenic. This constant was calculated from data obtained by using high and low initial linolenic at several selectivity ratios.

Table I shows the linoleic ratios of two different compositions calculated by both methods for a linolenic selectivity of 2. As shown, if the ratio L/L_0 had been used to prepare the graph for hydrogenation of 8% linolenic and 55% linoleic, the Ln SR calculated from data which were obtained by using 50% linoleic, 50% linolenic would have a large error. However, in using $L/L_0 + 1.2\Delta\text{Ln}$, the error is small if the high linolenic data are used to calculate the Ln SR from the graph.

The composition of soybean oil was used in the calculations to prepare the graph because it is the composition believed most likely to be used in Ln SR tests.

TABLE I

Ln/Ln_0	$\frac{L}{L_0}$ I	$\frac{L}{L_0}$ II	$\frac{L}{L_0 + 1.2(\text{Ln}_0 - \text{Ln})}$ I	$\frac{L}{L_0 + 1.2(\text{Ln}_0 - \text{Ln})}$ II
0.819	1.077	0.929	0.885	0.901
0.670	1.116	0.862	0.799	0.815
0.549	1.125	0.796	0.730	0.739
0.449	1.112	0.734	0.670	0.670
0.368	1.084	0.676	0.616	0.605
0.135	0.833	0.435	0.409	0.378

Composition of I, 50% linoleic, 50% linolenic; of II, 55% linoleic, 8% linolenic.

TABLE II

	Ln	L
Unhydrogenated	8.0	54.4
Hydrogenated	1.7	47.4

$$\text{Ln}/\text{Ln}_0 = \frac{1.7}{8.0} = .21$$

$$\frac{L}{L_0 + 1.2(\text{Ln}_0 - \text{Ln})} = \frac{47.4}{54.4 + 1.2(8.0 - 1.7)} = \frac{47.4}{61.9} = 0.76$$

From graph, Ln SR = 6 compared to 6.2 as calculated by Koritala, using an analog computer.

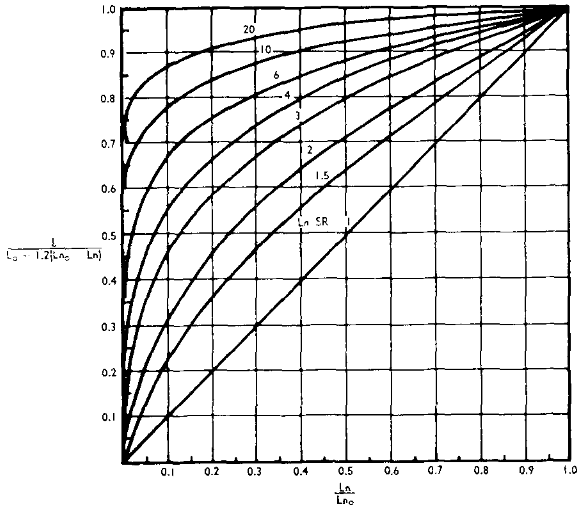

FIG. 1. Calculated Ln SR during hydrogenation.

Application of Graph (Figure 1)

Determine the fatty acid composition of the oil before and after hydrogenation. Calculate Ln/Ln_0 by division of the linolenic content of the hydrogenated oil by the linolenic content of the original oil.

Calculate $L/L_0 + 1.2\Delta\text{Ln}$ by division of the linoleic content of the hydrogenated oil by the sum of the starting linoleic plus 1.2 times the difference in the starting and ending linolenic. Read the Linolenic Selectivity (Ln SR) from the graph shown in Figure 1.

For example, data from the work of Koritala and Dutton are shown in Table II.

ROBERT R. ALLEN
Foods Division
Anderson, Clayton and Company
Sherman, Texas

ACKNOWLEDGMENT

Computer programming by D. C. Stone.

[Received May 1, 1967]