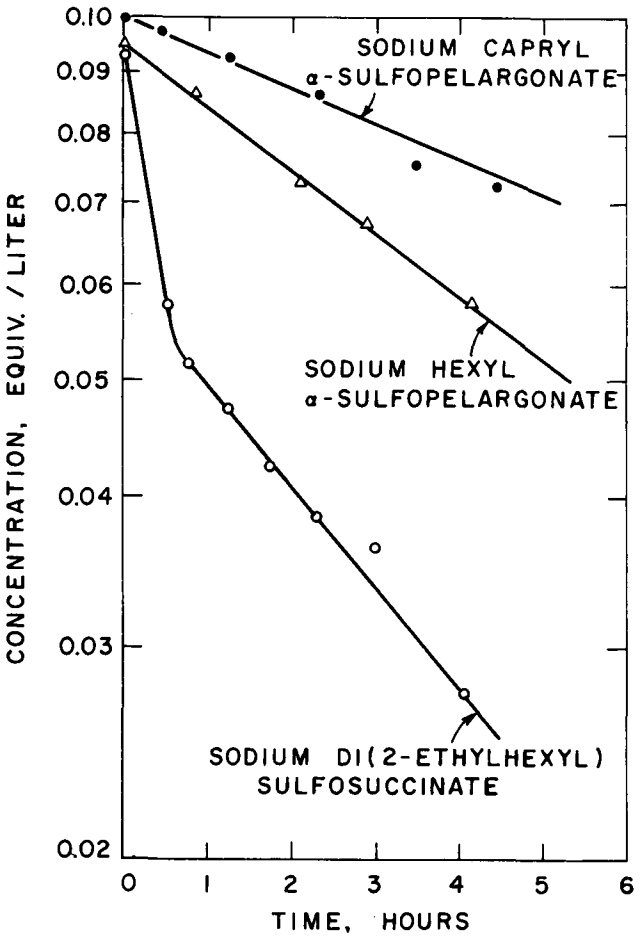

FIG. 2. Acid catalyzed hydrolysis of wetting agents.

α-sulfopelargonate, an ester of a secondary school, is quite resistant both to acid and alkaline hydrolysis.

Differences in the stability of esters are further shown in Table IV. Sodium methyl α-sulfopalmitate has moderate wetting properties which are not destroyed by boiling in 5% H_2SO_4 but are destroyed by boiling in 1% NaOH. Sodium heptyl α-sulfopelargonate has excellent wetting properties in neutral or hot acid solution, but wetting properties are likewise destroyed through hydrolysis in hot alkaline solution. The wetting properties of the capryl ester persist in hot acid and alkaline solution.

Solubility. The sodium alkyl α-sulfopelargonates are easily soluble in water, and also surprisingly soluble in organic solvents and mineral oil. At 25°C. the amyl, hexyl, and 2-ethylhexyl esters are soluble to the extent of 10% or more in absolute ethanol, chloroform, ether, and petroleum ether, and soluble to the extent of about 1% in mineral oil.

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Lysine, Gossypol, and Nitrogen Solubility in Chemically Treated Cottonseed Meals

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The effects of treatment of commercial prepress-solvent extracted and direct-solvent extracted cottonseed marcs with several chemical agents and solvents were studied. The analytical results for "free" and "total" gossypol of the finished meals show that treatment with aliphatic amines, followed by extraction with a suitable solvent, removed large proportions of the "free" as well as "bound" gossypol. This reduction of "free" and "bound" gossypol was accompanied, in some experiments, by an increase in the nitrogen solubility and available lysine, as compared with the results obtained with the untreated air-dried marcs. The available lysine contents of the treated marcs was significantly correlated with the nitrogen solubility in 0.02 *N* aqueous NaOH.

THE NUTRITIVE QUALITY of cottonseed meals for nonruminant animals depends chiefly on the available lysine (lysine with the *epsilon* amino groups free) content of the meals. The available lysine in cottonseed is reduced during the processing of the seed for oil by (a) the actual destruction of lysine (1,2) and (b) by the addition of gossypol to the seed protein through the formation of a Schiff base with the *epsilon* amino groups of lysine. The present study was undertaken to determine the effect of treatment of defatted cottonseed meats with chemicals on the gossypol and available lysine contents of the treated meal.

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Experimental

Commercial prepress-solvent extracted and direct-solvent extracted marcs were used as the sources of material for laboratory treatment with chemicals.

The experimental treatments of the marcs, which consisted of defatted cottonseed flaked meats still damp with adhering commercial hexane, were made

in the laboratory and consisted of one or more of the following unit processes:

1. Slurrying with solvent and/or treating agent.
2. Heating in the presence of solvent and/or treating agent.
   a. Direct live steam heating (drying).
   b. Refluxing with solvent and/or treating agent.
3. Extraction with solvent.

The slurrying was accomplished by simply stirring weighed portions of the marc with appropriate liquid in a glass beaker with a spatula. The steaming was accomplished by spreading the mixture of marc and treating agents on an 8-inch standard 10-mesh brass sieve and passing steam through it for 30 min. Refluxing with solvent was for 30 min. on a steam bath. Extraction was accomplished by successively slurrying the meal with solvent and filtering on a suction funnel five times. All finished meals were spread out exposed to the air for 16 hr., before they were ground to pass through a 20-mesh screen. All experimental treatments were made with 30 to 40 g. of marc containing 25 g. of meal.

Analytical Methods. "Free" and "total" gossypol were determined by the standard A.O.C.S. methods (4) and available lysine by the method of Conkerton and Frampton (5). The percentage of the total nitrogen of the meal that is soluble in 0.02 *N* aqueous NaOH was determined by the method of Lyman *et al.* (6).

The treating agents, methods of treatment, and the results of analyses of the treated meals are listed in Tables I and II.

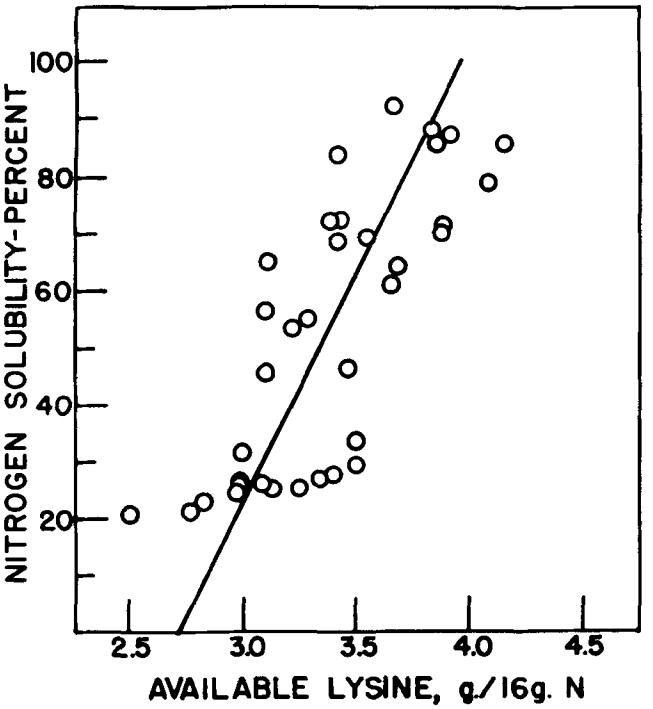

FIG. 1. Relationship between ε-free aminolysine and nitrogen solubility of experimentally treated cottonseed meals.

Results and Discussion

Each treatment reported reduced the "free" and "total" gossypol, but the reduction was greatest when

TABLE I
Results of Treating Commercial Prepress-Solvent Marc with Chemical Agents

Treating agent	Method of treatment	Gossypol (%)			Available lysine g./16 g. *N*	Nitrogen solubility % (0.02 *N* NaOH)
		"Free"	"Total"	Bound		
Original marc	Air dried	0.068	1.36	1.29	3.44	71.6
100 ml. of hexane	Boil off solvent and steam 30 min.	0.029	1.32	1.29	3.10	50.0
100 ml. of acetone	Boil off solvent and steam 30 min.	0.027	1.26	1.23	3.11	45.6
100 ml. of methanol	Boil off solvent and steam 30 min.	0.023	1.27	1.07	3.41	27.2
100 ml. of methanol	Reflux 30 min. and extract with methanol	0.025	1.33	1.30	3.55	69.7
Equal weight of pure octylamine	Let stand for 16 hr. and extract with chloroform	0.013	0.027	.....	3.66	92.0
100 ml. of a 10% soln. of 3-aminopropanol in methanol	Reflux 30 min. and extract with methanol	0.045	0.21	.....	3.87	85.3
100 ml. 50-50 soln. oleylamine in hexane	Reflux 30 min. and extract with hexane	0.035	0.58	.....	3.41	83.8
Pass NH_3 gas through marc for 30 min.	Steam 30 min.	0.018	1.18	1.16	3.51	33.5
Reflux marc with methanol saturated with NH_3 for 30 min.	Boil off solvent and steam 30 min.	0.014	1.05	1.04	3.25	24.9
Reflux marc with methanol saturated with NH_3 for 30 min.	Filter and extract with methanol	0.009	1.19	1.18	3.42	68.2
Equal wt. of soln. of 0.8% NaOH in 80% aqueous methanol	Stir, boil off solvent and steam for 30 min.	0.016	1.18	1.16	2.98	23.9
Equal wt. of soln. of 0.8% NaOH in 80% aqueous methanol	Stir and reflux 30 min., filter and extract with dry methanol	0.024	1.24	1.22	3.10	56.0
0.8 g. NaOH diss. in 20 ml. water; 180 ml. acetone added and the mixture added to 32 g. marc containing 24 g. of meal	Stir, boil off solvent and steam for 30 min.	0.006	0.85	0.84	2.77	21.0
0.8 g. NaOH diss. in 20 ml. water; 180 ml. acetone added and the mixture added to 32 g. marc containing 24 g. of meal	Reflux 30 min., filter and extract with dry acetone	0.031	0.68	0.65	3.11	64.3
Add equal wt. of 0.8% NaOH soln. in 86% aqueous 2-propanol	Stir, boil off solvent and steam for 30 min.	0.020	1.18	1.16	2.99	26.1
Add equal wt. of 0.8% NaOH soln. in 86% aqueous 2-propanol	Reflux 30 min., filter and extract with constant boiling (91%), 2-propanol	0.021	1.26	1.24	3.22	52.7
Equal wt. of 86% aqueous 2-propanol	Filter and extract with c.b., 2-propanol	0.033	1.36	1.33	3.28	54.9
0.2 g. NaOH diss. in 100 ml. methanol	Boil off solvent and steam 30 min.	0.016	1.14	1.12	2.84	22.5
1.4% of $(NH_4)_2HPO_4$ in 10 ml. water	Moisten marc with agent and steam 30 min.	0.026	1.28	1.25	3.00	31.3

TABLE II

Results of Treating Commercial Direct-Solvent Extracted Marc with Chemical Agents

Treating agent	Method of treatment	Gossypol (%)			Available lysine g./16 g. *N*	Nitrogen solubility %(0.02 *N* NaOH)
		"Free"	"Total"	Bound		
Original marc	Air-dried	0.520	0.98	0.46	3.92	87.6
100 ml. 50% soln. oleylamine in hexane	Reflux 30 min. and extract with hexane	0.014	0.079	.....	4.16	85.9
10% octylamine in methanol	Reflux 30 min. and extract with methanol	0.029	0.27	.....	4.08	78.3
10% 3-aminopropanol dissolved in methanol	Reflux 30 min. and extract with methanol	0.015	0.146	.....	3.88	71.5
10% 3-aminopropanol dissolved in methanol	Reflux 30 min. and extract with methanol containing 1% acetic acid	0.014	0.146	.....	3.88	70.3
Methanol saturated with NH_3	Boil off solvent and steam 30 min.	0.013	0.73	0.72	3.51	29.1
Methanol saturated with NH_3	Reflux 30 min. and extract with methanol	0.015	0.95	0.93	3.66	60.3
0.8% NaOH in 25 ml. of 71% aqueous 2-propanol	Boil off solvent and steam 30 min.	0.013	0.77	0.76	3.34	26.2
0.8% NaOH in 25 ml. of 80% aqueous methanol	Reflux 30 min. and extract with methanol	0.037	0.91	0.87	3.47	46.0
0.8% NaOH dissolved in 20 ml. water suspended in 180 ml. acetone	Boil off solvent and steam 30 min.	0.007	0.65	0.64	2.50	20.3
0.8% NaOH dissolved in 20 ml. water suspended in 180 ml. acetone	Reflux 30 min. and extract with acetone	0.039	0.36	0.32	3.39	72.1
0.8% NaOH in 25 ml. of 71% aqueous 2-propanol	Boil off solvent and steam 30 min.	0.011	0.75	0.74	3.08	26.0
0.8% NaOH in 25 ml. of 71% aqueous 2-propanol	Reflux 30 min. and extract with c.b. 2-propanol	0.043	0.93	0.89	3.69	63.9
0.8% NaOH in 100 ml. of methanol	Boil off solvent and steam 30 min.	0.008	0.77	0.76	3.13	24.5

the treatment included contact with any one of the three aliphatic amines used. An increase in the available lysine occurred only when the treatment included contact with the amines. The exception to this observation is found in the marc that was extracted with methyl alcohol. It is probable that the alcohol extracted nonprotein nitrogen. A comparable observation was made by Martinez, Frampton, and Cabell (1) who reported an increase in the available lysine on the extraction of glandless cottonseed meal with 80% aqueous ethyl alcohol.

Treatment with both NaOH and phosphoric acid reduced the available lysine of the marcs.

The data show that addition of gossypol to the seed protein through the formation of a Schiff base with the *epsilon* amino groups of lysine can be driven in the reverse direction by treating the meals with some amines. The amine replaces lysine in the Schiff base, and when the treated meal is extracted with a suitable solvent, it is found that the "free" and "bound" gossypol decrease and the available lysine increases. Thus the data confirm the earlier report by King, Frampton, and Altschul (3) that the treatment of cottonseed meals with amines also reduces the "free" gossypol content of the meals. The residual amines in the several amine-treated meals was not determined. The extraction procedure should have removed all but traces of the amines. It is concluded, on this basis, that the treatment with amines increased the percentage of total nitrogen of the meal that is soluble in 0.02 *N* aqueous NaOH.

One may observe, on examining the data in Tables I and II that in 27 out of 32 instances of reduction or increase in the nitrogen solubility resulting from the treatments, a corresponding decrease or increase in available lysine results. The nitrogen solubilit data are plotted in Fig. 1 against the available lysin The correlation coefficient of 0.76 (with 31 degrees o freedom) indicates that a high degree of correlation exists. This degree of correlation is not good enough, however, to permit the substitution of nitrogen solubility determinations for an estimate of the available lysine in assessing the nutritive quality of a cottonseed meal.

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