

Epoxidation of the dimethyl ester of the acrylic acid adduct with hydrogen peroxide and an ion-exchange resin as catalyst required minor modifications of the published procedure (3). Conditions yielding products representing 80% or more of epoxidation are listed in Table III.

Summary

Adducts of dienophiles and alkali-conjugated safflower fatty acids containing conjugated muoleic acid in the *cis,trans* form were prepared by heating the reactants in the presence of selenium as a catalyst. The products appeared to be identical to those prepared from *trans,trans* conjugated linoleic acid so that isomerization of *cis-trans* to *trans,trans* acids is eliminated as a separate step. Although yields of pure product were lower than desired because of difficulties in removing selenium, yields of crude adducts ranged from 64–82%. The adducts obtained could be epoxidized with hydrogen peroxide and an ion-exchange resin as catalyst in 80–93% yield or with peracetic acid in 89–98% yield.

Acknowledgment

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The Effect of Gamma Radiation on the Hydrogenation of Cottonseed Oil

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GAMMA RADIATION has been found to affect the rates of certain reactions. This radiation on interacting with atoms of the materials through which it is passing has the ability to eject electrons which may produce ions or free radicals, depending on the substances involved. The ions or free radicals may promote desired reactions or may cause reactions which would not occur otherwise.

Gamma radiation significantly increases the rates of polymerization of ethylene (12, 13) and styrene (3). The common feature of these addition-type of polymerizations is that they all have a free radical mechanism. The reaction between chlorine plus benzene to produce benzene hexachloride also has a free radical mechanism. *Gamma* radiation as well as actinic light vigorously increases the rate of this reaction (10). The radiation presumably forms chlorine atoms from the chlorine molecule.

When the linear-type of polymers are exposed to *gamma* radiation, the properties of the polymers frequently change. In the case of polyethylene (7, 11) the tensile strength and hardness increase and hydrogen gas is released. Apparently some of the hydrogen atoms are knocked off of the polymer chain, and cross-linkage between the chains results. In the case of polymethylmethacrylate however tensile strength decreases rapidly with irradiation (7). Depolymerization and chain cleavage are probably the main reactions. Both cross-linking and depolymerization occur in the polymers, but the dominant reaction depends on the polymer.

Atomic hydrogen is an effective hydrogenation agent for hexadecene-1 and linseed oil even in the absence of a catalyst (4). Some polymerization also

occurs, indicating that the atomic hydrogen reacts at the double bond to form a free radical. This radical can react with another hydrogen atom to complete the hydrogenation, or it can react with another radical to form a dimer.

Burton (6) bombarded oleic acid with deuterons. The irradiated material contained 1.7% stearic acid, proving that hydrogenation occurred. In addition, 52.5% of the oleic acid was converted to polymerized acid. Apparently the reactions involved were similar to those with atomic hydrogen. Earlier Sheppard and Burton (16) and Breger and Burton (5) demonstrated that paraffinic compounds were produced by the irradiation of fatty acids with *alpha* particles and deuterons.

The effect of *gamma* radiation from Cobalt 60 was determined for the oxidation reaction between oleic acid or methyl oleate and oxygen (8). Radiation significantly increased the rates of peroxide and carbonyl formation. Long and Proctor (14) utilized high-energy cathode rays to produce monocarbonyl compounds from several vegetable oils. Radiation also decreased the amounts of triene groups. The presence of oxygen did not seem to have any significant effect on the production of monocarbonyls. Antioxidants tended in some cases however to suppress the monocarbonyl formation. The mechanism of the reaction was not determined, but it appears to be a complicated free radical type. Recently Pan, Goldblith, and Proctor (15) studied the effect of ionizing radiation on the *trans*-isomerization of oleic acid and potassium oleate.

No reference was found concerning the effect of *gamma* radiation on the hydrogenation of triglycerides. The results of such an investigation are reported here.

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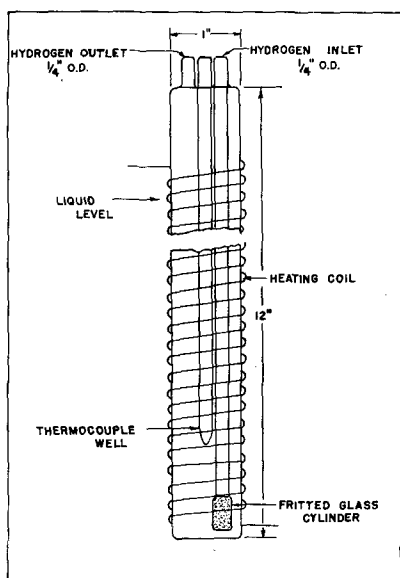


Fig. 1. Reactor detail.

Equipment and Operating Procedure

The hydrogenation reactor (Fig. 1) was constructed of Pyrex glass tubing about 12 in. long with an inside diameter of about 1 in. The reactor was filled for each hydrogenation run with 60 cc. of cottonseed oil by pouring the liquid through the hydrogen outlet line. The inlet line was used to introduce the hydrogen below the surface of the oil through which it bubbled. The hydrogen flow for each run was adjusted to 0.05 cu. ft. per minute, at which flow the oil was agitated vigorously without blowing the oil out of the reactor. A wet-test meter was used to measure the hydrogen flow-rate.

The reactor temperature was controlled manually by means of a Variac connected to No. 4 Nichrome wire, wound around the reactor and sandwiched between asbestos insulation. A thermocouple that could be read to within 1°C. was inserted in the well of the reactor.

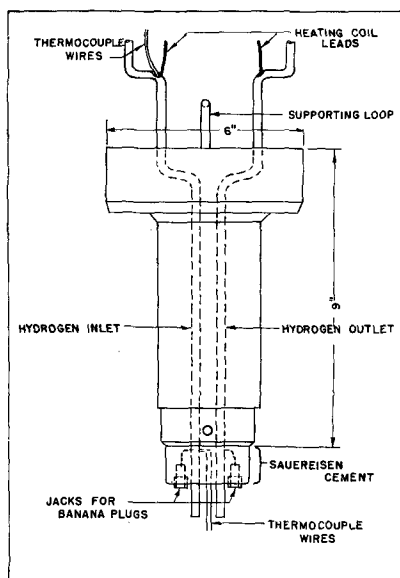


Fig. 2. Plug detail.

The Cobalt-60 source, nominally rated at 900 curies, was in the form of a hollow cylinder and was encapsulated in an aluminum shell 13.5 in. long with an inside diameter of 1.78 in. The source was contained inside a 4,000-lb. steel-jacketed lead "pig," which reduced the radiation escaping to the room to about one milliroentgen per hour. The intensity of radiation inside the reactor was 265,000 roentgens per hour.

A removable lead plug (Figure 2) was used to close the top opening of the lead "pig" shown in Figure 3 and so reduced the radiation levels above the pig to a relatively low level. Teflon tubing was employed to connect the hydrogenation reactor to the steel tubes that passed through the plug. The thermocouple wires and heating coil leads were passed through the tubes in the plug. Sauerisen cement was used to seal the electrical leads in the openings through the tube walls. An aluminum canister was

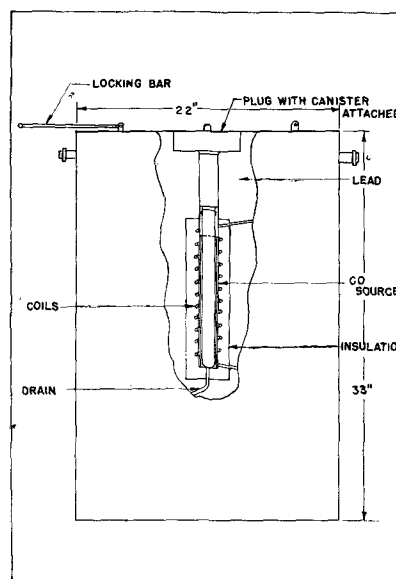


Fig. 3. Sectional view of Co-60 "Pig."

then slipped over the reactor and attached to the plug. The entire assemblage (plug, reactor, and canister) could then be lowered into the Cobalt-60 source, when desired. Tygon tubing served to connect the hydrogen cylinder and the wet-test meter to the inlet and outlet lines of the plug, respectively.

Refined and bleached cottonseed oil was used in this investigation, and its analyses are shown in Tables I and II as Samples 5 and 37. The oil was stored in a cold room at 40°F. prior to hydrogenation in order to minimize composition changes with time. Rufert catalyst flakes containing 24.5% nickel were mixed with the oil before adding it to the reactor. Electrolytic hydrogen was supplied from cylinders.

The hydrogenated oil upon completion of a run was removed from the reactor and filtered to remove the catalyst. Samples were then analyzed for polyunsaturated acid groups by the ultraviolet absorption method, for *trans* isomers by the infrared absorption method, for iodine value by the conventional Wijs solution method, unsaponifiables by Method Da 11-42 (Official Methods of American Oil Chemists' Society), and carbonyls by a Procter and Gamble Company method.

TABLE I
 Analyses of Triglyceride Samples^a

Sample	Temperature	Ni catalyst	Time oil in source before hydrogenate	Hydrogenate in source	Time of hydrogenation	I.V.	Saturated	Oleic	Linoleic	Linolenic
	°C.	%	min.		min.		%	%	%	%
5.....	0.00	0	111.2	25.7	17.1	52.4	0.30
37.....	0.00	0	108.7	28.1	15.1	52.2	0.19
3.....	25	0.00	2880	110.0	23.9	21.8	49.75	0.11
38.....	25	0.00	1380	109.2	27.8	14.9	52.7	0.21
22.....	190	0.00	0	yes	90	111.0	23.0	22.4	50.0	0.20
29.....	20	0.07	0	yes	1440	112.2	22.58	21.98	51.02	0.02
20.....	25	0.70	0	yes	60	109.4	25.5	19.5	50.3	0.29
12.....	190	0.70	0	no	30	24.9	68.2	27.2	0.13	0.08
27.....	190	0.70	0	yes	30	33.9	58.0	37.5	0.08	0.00
15.....	190	0.70	0	no	60	1.7	93.8	1.8	0.08	0.00
13.....	190	0.70	0	no	90	1.5	94.2	1.3	0.12	0.03
34.....	190	0.07	0	no	10	86.7	23.6	47.9	24.1	0.00
17.....	190	0.07	0	no	30	51.6	38.4	57.1	0.41	0.00
18.....	190	0.07	0	no	60	28.3	64.5	30.7	0.40	0.00
19.....	190	0.07	0	no	90	17.8	75.9	19.6	0.08	0.00
33.....	190	0.07	0	yes	10	95.1	26.6	32.7	36.3	0.00
21.....	190	0.07	0	yes	15	78.1	20.9	62.6	12.1	0.00
25.....	190	0.07	0	yes	30	54.8	35.0	60.4	0.19	0.00
24.....	190	0.07	0	yes	60	33.2	59.1	36.1	0.01	0.42
31.....	190	0.07	1260	yes	60	62.7	26.5	68.0	1.1	0.00
32.....	190	0.07	1260	yes	60	65.0	25.3	68.2	2.1	0.00
36.....	190	0.07	1380	no	60	43.8	46.7	48.6	0.3	0.01
28.....	190	0.07	0	yes	90	37.9	53.8	41.6	0.24	0.00
11.....	170	0.70	0	no	30	50.3	40.0	55.3	0.23	0.04
26.....	170	0.70	0	yes	30	51.6	38.4	57.1	0.14	0.00
10.....	170	0.70	0	no	60	10.7	83.9	11.6	0.12	0.01
14.....	170	0.70	0	no	90	1.4	94.3	1.1	0.16	0.06
16.....	150	0.70	0	no	90	5.3	90.1	5.4	0.09	0.00

^a The arachidonic analyses for all samples was 0.00.

Discussion of Results

The results of the hydrogenation runs of this investigation are shown in Tables I and II. Temperature reported was the average temperature as measured by the thermocouple inserted in the well of the reactor. Temperature control during a run was maintained to within $\pm 3^\circ\text{C}$. of that reported. The amounts of cottonseed oil and catalyst used for a run were measured with sufficient precision so that the catalyst concentration was accurate to within 2% on a relative basis.

Several preliminary hydrogenation runs were made in the Cobalt-60 source to determine if any significant changes of operating conditions occurred because of the γ radiation. Hydrogenation runs (Samples 20 and 29), using nickel catalyst, were made at 25°C . in the presence of γ radiation. No significant

changes in the iodine value occurred because of this treatment, which appears to indicate that neither hydrogenation nor polymerization was significant. A hydrogenation run (Sample 22) was made at 190°C . in the Cobalt-60 source, but no catalyst was used. The analyses of the product indicate that for this case also no appreciable hydrogenation or polymerization occurred.

Figure 4 is a comparison of three series of runs that indicate the effect of γ radiation on the rate of hydrogenation. In all cases the runs made in the Cobalt-60 source hydrogenated slower than those runs out of the source. The relative difference in the reaction rates between the irradiated and nonirradiated runs increased as the time of reaction increased. The fastest rates of hydrogenation occurred for the runs at 190°C . with a high catalyst concentration (0.70% nickel). For the runs at 190°C . with low (0.07%) nickel concentration the reaction rates were slowest while the runs at 170°C . and 0.70% nickel had intermediate rates. The relative rates of reactions for the three series of runs were as would be expected from previous results, such as those of Bailey (2) and Eldib and Albright (9). The general slope of the curves of the logarithm of the iodine value versus the time of reaction is also similar to that reported previously.

Figure 5, a plot of the saturated acid content versus the iodine value, indicates that the degree of selectivity was essentially identical for all runs of this investigation regardless of the temperature, catalyst concentration, or γ radiation. Selectivity is defined here as the preferential hydrogenation of linoleic acid groups as compared to oleic acid groups. It is of interest to note that the saturated acid content decreased slightly during the initial period of hydrogenation. Whether such a decrease of the saturated acid actually occurred or whether the analyses were erroneous is not known. The data of Eldib and Albright (9) for nonirradiated hydrogenation runs however indicate a similar phenomenon. Plots were made, but are not shown here, of the linoleic and total

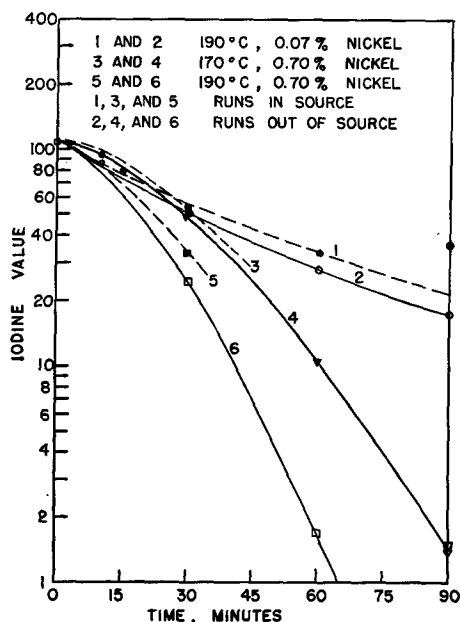


FIG. 4. Rate of hydrogenation.

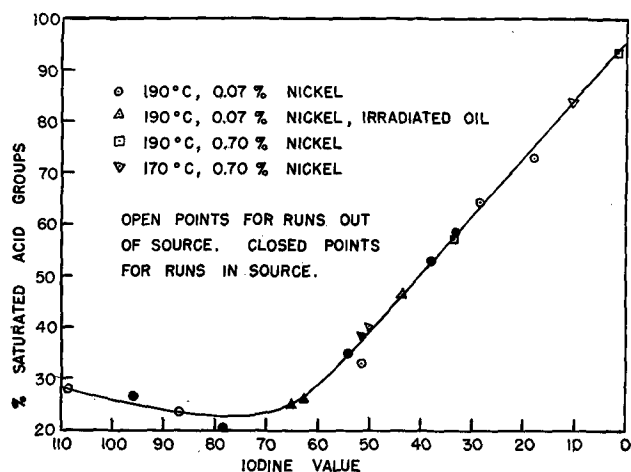


FIG. 5. Saturated acid content of hydrogenated oils.

oleic acid groups as a function of the iodine value. A single smooth curve was also found to represent data on each plot, which further verifies that *gamma* radiation does not affect selectivity.

Previously (1, 2) it was reported that selectivity and *cis-trans* isomerization are affected by the same operating variables. Eldib and Albright (9) theorized that each depends primarily on the concentration of reactants at the surface of the catalyst. Figure 6 indicates, as would then be expected, that the degrees of isomerization for all runs of this study were also identical.

Since the rates of hydrogenation decreased in the presence of *gamma* radiation, apparently the radiation affected at least one of the following items: a) reactor, b) hydrogen gas, c) cottonseed oil, or d) the catalyst. The glass reactor turned a light shade of brown upon exposure to *gamma* radiation. Repeat runs in the reactor however gave relatively good reproducibility, and there were no indications that adverse reactor properties occurred because of the *gamma* radiation. It seems improbable that changes in the reactor caused the slower reaction rates.

TABLE II
Analyses of Triglyceride Samples (Cont.)

Sample	Trans acid	Conjugated diene	FFA	Unsaponifiable	Carbonyl value ^a
	%	%	%	%	
5.....	0.7
37.....	1.0	0.32	0.061	0.63	2.5
3.....	1.3
38.....	1.3	0.63	0.246	0.79	1.2
22.....	2.2	0.98	0.100	0.87	4.6
29.....	0.3	1.11
20.....	0.6	1.06
12.....	19.4
27.....	25.4	0.05
15.....	0.0
13.....	0.2
34.....	17.2	0.57
17.....	36.2	0.05
18.....	20.8	0.05
19.....	13.0	0.03
33.....	10.7	0.51
21.....	24.5	0.56
25.....	37.6	0.07
24.....	24.8	0.05	0.035	1.5
31.....	35.6	0.19	0.167	1.8
32.....	35.0	0.19	0.190	1.7
36.....	32.4	0.08	0.224	2.1
28.....	27.5	0.06
11.....	36.3
26.....	35.0	0.07
10.....	7.3
14.....	0.0
16.....	3.0	0.03

^a The carbonyl value was determined by a Procter and Gamble Company method.

Radiation may split the hydrogen molecule into atoms even though the energy required to produce atomic hydrogen is high. Hydrogen however is quite transparent to *gamma* radiation and would absorb a negligible amount of energy during the exposure time available. If atomic hydrogen were produced, the rates of hydrogenation would probably be increased (4). Since the rates were decreased, it is improbable that appreciable amounts of atomic hydrogen were produced and probably *gamma* radiation has little effect on the hydrogen.

A previous study (14) showed that triglyceride oils upon exposure to radiation are chemically changed to produce carbonyls or degradation products which might be catalyst poisons. A series of runs was made to test this hypothesis. Cottonseed oil was irradiated in the Cobalt-60 source for 1,260–1,380 minutes (21–23 hrs.) before hydrogenation. The irradiated oil was then hydrogenated both in and out of the source. The runs (Samples 31, 32, and 36) with the irradiated oil hydrogenated slower than comparable runs with nonirradiated oil. Apparently catalyst poisons were

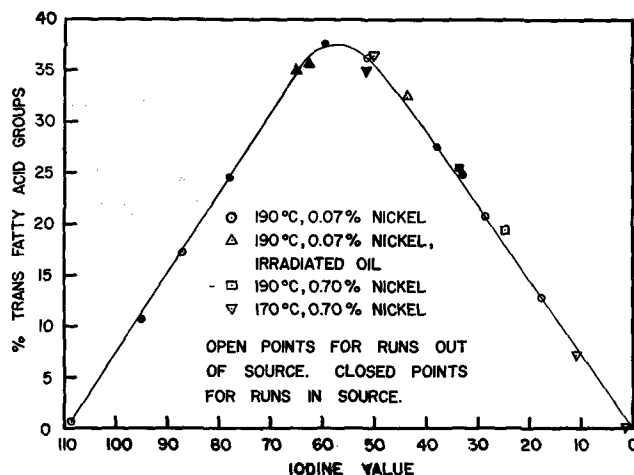


FIG. 6. Trans fatty acid content of hydrogenated oils.

formed which reduced the amount of effective catalyst, which would, of course, decrease the rate of hydrogenation. Since selectivity and isomerization did not change with radiation, the activity of the unpoisoned catalyst probably did not change.

The analyses of irradiated cottonseed oil (Samples 3 and 38) were compared to those of nonirradiated oil (Samples 5 and 37). No significant changes of the iodine value occurred. The radiation caused small but probably significant increases of the conjugated dienes and the *trans* isomers, indicating some hydrogen rearrangement. The free fatty acid content also was higher for those runs in which irradiated oil was used. The analyses for unsaponifiables indicated no significant increase. The comparison of samples 37 and 38 indicates that the carbonyl content of the oil was decreased by radiation, but a comparison of Samples 24, 31, and 32 indicates that the reverse was true. Further investigations appear necessary to determine the effect of *gamma* radiation on the carbonyl content. Free fatty acids are known (2) to be catalyst poisons, and presumably they were the main cause of the slower reactions in the case of *gamma* radiation. Carbonyls however might also have been involved.

Summary and Conclusions

Hydrogenation of cottonseed oil occurred at slower rates of reaction in a *gamma* radiation field of Cobalt 60 than comparable nonirradiated runs. The *gamma* radiation apparently degraded the triglycerides to form poisons for the nickel catalyst. Free fatty acids and possible carbonyls were probably the poisons produced. The degree of selectivity and *cis-trans* isomerization that occurred during hydrogenation were unaffected by the *gamma* radiation.

Acknowledgment

The refined and bleached cottonseed oil was furnished by Anderson, Clayton and Company. The Procter and Gamble Company performed the analyses. H. K. Hawley of the Procter and Gamble Company made suggestions concerning the analytical phases of this investigation.

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Solubility of Cottonseed Proteins in Hydrochloric Acid

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THE MARKED VARIABILITY in the growth response of nonruminants to cottonseed meals, fed as a protein supplement, has created the need for grading cottonseed meals intended for use for this purpose. The problem of developing specifications for cottonseed meals for mixed feeds for poultry and swine has been approached empirically by several investigators. Some progress has been made in the development of such specifications. For example, a correlation has been noted between the solvent power for cottonseed proteins (*e.g.*, the fraction of the total meal nitrogen that will dissolve in a specified period of time) of 0.02 Normal aqueous NaOH and the growth response of chicks fed cottonseed meal as a protein supplement (1, 2). A correlation has been noted also between the comparable solvent power of 0.5 Normal aqueous NaCl and the growth of chicks (1, 3).

A correlation is reported in this paper between the solvent power of a 6 Normal aqueous HCl for cottonseed meal proteins and the growth response of chicks fed the cottonseed meals as a protein supplement. The correlation obtained with the acid solution is as good as those obtained with the two solvents mentioned above.

Experimental

Determinations of the Fraction of the Total Meal Nitrogen-Soluble in HCl Solution. Cottonseed meal samples containing 600 milligrams of nitrogen were weighed into flat-bottom, screw-capped glass bottles. Glass beads and 200 milliliters of constantly boiling hydrochloric acid solution were added to each of the bottles. The capped bottles were shaken vigorously, then clamped on to a rotating shaft in a water bath

maintained at 37.5°C. Bottles containing the resulting suspensions were withdrawn for analyses at successive intervals of time. The samples were cooled quickly to room temperature and immediately centrifuged. The supernatant liquid was filtered, and determinations for nitrogen, using the Kjeldahl procedure, were carried out on the clear filtrates.

Determinations of the Fraction of the Total Meal Nitrogen-Soluble in 0.02 Normal NaOH and in 0.5 Normal NaCl Solutions. The methods used for these determinations were the same as those described in other investigations (1, 2, 3).

Determination of Amino Nitrogen. The procedure described by Pope and Stevens (4) was followed in determining the amino nitrogen in the clear filtrates, *vide supra*. It was advantageous, in this study, to double the concentrations recommended by Pope and Stevens for the CuCl₂ and Na₃PO₄ solutions. It was necessary, for consistent results, that the suspension of cupric phosphate be prepared daily.

Determinations were carried out on the filtrates before and after the addition of trichloroacetic acid in order to estimate the extent of protein hydrolyses.

Results

Data which are typical of the effect of time on the fraction of the total nitrogen soluble in 6 Normal HCl are recorded in Figure 1. It may be noted that the fraction increases with time; the kinetics of this dispersion of the protein into 6N HCl are not simple however.

Included in Table I are the data for the fraction of the total meal nitrogen found in the 6N HCl after 1 hr. of exposure. Included also are reproductions of the data for the fractions of the total nitrogen of cottonseed meals dispersed in 0.5 Normal NaCl, and in 0.02 Normal NaOH, as recorded by Chang *et al.* (1). The data for the nutritional response of chicks

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