Bromine Retention by Cottonseed and Cottonseed Products After Fumigation of the Seed With Methyl Bromide

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THE Bureau of Entomology and Plant Quarantine began studies in 1945 to explore the possibilities of fumigating cottonseed with methyl bromide to destroy larvae of the pink bollworm as a supplement to the heat treatment long in use. This made it necessary to determine to what extent bromine is retained by the fumigated seed and especially by the oil obtained from such seed by hydraulic pressing.

The present investigation shows that cottonseed after fumigation with methyl bromide retains 70 to 180 parts per million of total bromine. This is found in the linters, hulls, and meats. When the seed is hulled and the oil pressed from the meats by hydraulic pressing, all of the bromine compounds are found in the press cake and none in the oil.

Fumigation

Cottonseed with a moisture content of 5.2% was subjected to three different fumigant treatments at El Paso, Texas, each treatment being duplicated in separate fumigations designated as A and B. A sample of untreated seed was retained as a control. The details of each fumigation follow:

Treatment No. 1. Fumigated on June 6, 1946, with 5 lb. of methyl bromide per 1000 cu. ft. A 10-lb. sample was taken from fumigation A and a 200-lb. sample from fumigation B.

Treatment No. 2. Fumigated on May 28, 1946, with 10% methyl bromide in 90% carbon tetrachloride by volume at the rate of 5 gallons per 1000 cu. ft. A 10-lb. sample was taken from fumigation A and a 200-lb. sample from fumigation B.

Treatment No. 3. Fumigated on May 29, 1946, with 10% methyl bromide in 90% ethylene dibromide by volume at the rate of 5 gallons per 1000 cu. ft. A 10-lb. sample was taken from fumigation A and a 200-lb. sample from fumigation B.

The cottonseed was fumigated in a metal-lined chamber of 200 cu. ft. capacity (5x5x8 feet). In each instance, a full load of 2 tons of cottonseed was used, with the experimental sample buried in the center of the load. In treatment No. 1, the methyl bromide was applied as a gas above the cottonseed. In treatments Nos. 2 and 3 the fumigant solution was sprayed on the top of the load of seed. The dosages of fumigant used were at least twice those found necessary in preliminary tests for complete mortality of larvae.

Processing

The 200-lb. samples (B), representing the control and seed from each of the three fumigant treatments, were processed through small-scaled standard oil mill equipment at the Southern Regional Research Laboratory, using standard mill procedures for cleaning, delinting, hulling, and separating of the meats, and for flaking, cooking, and hydraulic pressing of the meats. The 2-stack jacketed cooker, cake former, and 6-box hydraulic press for 8"x18" cakes used are illustrated in Figure 1.

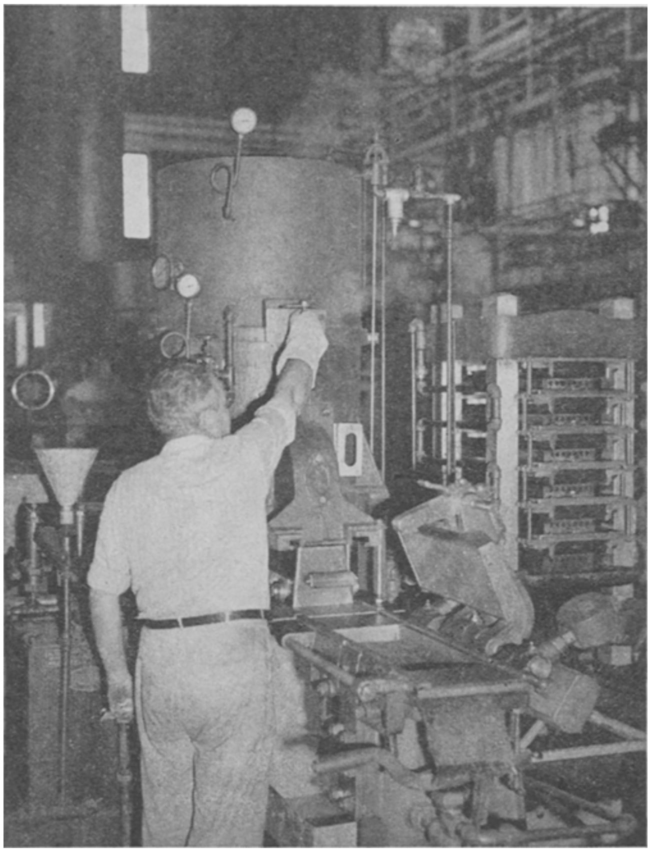

FIG. 1.

One lot was processed each day starting on June 17, 1946. To insure against contamination each sample was divided into two equal portions and each portion completely processed separately. The first half portion of each sample served to clean the equipment and was discarded. In addition, the equipment was thor-

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TABLE I.

Total Bromine Content of Cottonseed After Fumigation With Methyl Bromide. Values in Parts per Million on a Moisture-Free Basis.

Treatment	Whole Seed	Hulls with Linters	Linters	Hulls	Meats	Cake	Oil
Control							
B (200 lb. seed)							
(1)	0	0	0	......	trace	trace	0
(2)[1]	0	......	......	......	......	......	......
No. 1.—Methyl bromide							
A (10 lb. seed)							
(1)	169	211	......	......	132	......	......
(2)[1]	176	......	......	......	......	......	......
B (200 lb. seed)	82[3]	......	74	110	83[2]	117	0
No. 2.—Methyl bromide in carbon tetrachloride							
A (10 lb. seed)							
(1)	138	154	......	......	103	......	......
(2)[1]	133	......	......	......	......	......	......
B (200 lb. seed)	113	130	100	......	86	130	0
No. 3.—Methyl bromide in ethylene dibromide							
A (10 lb. seed)							
(1)	74	76	......	......	58	......	......
(2)[1]	68	......	......	......	......	......	......
B (200 lb. seed)	107	126	78	......	83	137	0

[1] Analyzed 50 days later than (1) [2] Sample taken during processing. [3] Calculated from values found for constituent portions of the seed.

oughly cleaned by hand after each processing. The second half of each sample was used for analysis.

Owing to the low moisture content of the cottonseed it was necessary to add sufficient water to the meats prior to cooking (1 hour up to 235° F.) to produce a normal or average press cake. The correct amount of water was determined in the cooking of the first half of each sample. No processing differences or difficulties were encountered, and no quality impairment was noted with any of the treated samples.

Samples of linters, hulls, meats, cake, and oil were taken during the processing and reserved for analysis for total bromine.

Method of Analysis

A portion of each A and B sample from each fumigation treatment was ground for analysis without separation into hulls and meats. Another portion of each A and B sample was separated by use of a Bauer mill and screening into meats and hulls with linters. The meats were ground through a Wiley mill prior to analysis.

All samples were analyzed by the method described by Dudley (1). This procedure was checked by adding known amounts of potassium bromide to untreated cottonseed. Quantitative recovery was obtained.

Because of the special interest in the possible retention of bromine compounds in the oil obtained by commercial processing of fumigated seed, the oil samples were ashed in three different ways prior to final analysis by the Dudley method:

(a) One hundred ml. of 1% potassium hydroxide in 95% ethyl alcohol was added to 18-g. samples of the oil and the mixture allowed to stand in a porcelain dish overnight. The alcohol was evaporated and the sample heated on a hot plate at low heat until foaming ceased. The oil was then ignited with a flame and allowed to burn off lamp-fashion. The ignition was completed in a muffle furnace at 500° C. and the analysis completed as specified in the Dudley method.

(b) Sufficient 10% potassium hydroxide in 95% ethyl alcohol was added to 18-g. samples of the oil to saponify the samples. The mixture was allowed to stand overnight and then dried on a hot plate at low heat. The sample was ignited in a muffle furnace and the analysis completed by the Dudley method.

(c) The oil was burned in a Parr oxygen bomb in small portions until 10 g. were consumed. To facilitate absorption and reduction of the bromine 8 ml. of 1.0 N potassium hydroxide and one drop of 85% hydrazine hydrate were placed in the bottom of the bomb. The combustion capsules were washed with 0.1 N potassium hydroxide containing some hydrazine hydrate and the washings combined with those from the bomb. These washings were evaporated to dryness and the bromine was determined by the Dudley method.

The bromine values reported for the oils were obtained by procedures (a) and (b). They were confirmed by the use of procedure (c).

Results

The bromine values obtained are summarized in Table I. It is of special significance that the oils obtained by hydraulic pressing from the cottonseed and fumigated with methyl bromide contained no bromine. Although methyl bromide has been reported to be soluble in olive oil and sesame oil (2), it is not retained tenaciously by vegetable oils. In an experiment on this point, 200 mg. of methyl bromide was introduced into 30 g. of the control sample of cottonseed oil. After standing for 3 days about half of the methyl bromide had been lost from the oil. On agitation of the oil by use of a mechanical shaker and weighing at intervals, the rest of the methyl bromide was removed and the original weight of the oil was attained. This indicated little or no retention of methyl bromide by the oil.

The quantitative calculations given in Table II indicate that the bromine in cottonseed meats appears almost quantitatively in the press cake. These data further substantiate the conclusion that bromine com-

TABLE II.

Recovery in the Press Cake of Total Bromine Present in the Meats.

Fumigation Treatment	Weight of Meats. Dry Basis	Yield of Cake. Dry Basis	Bromine Content of Meats	Bromine Found in Press Cake
	lbs.	*lbs.*	*grams*	*grams*
Control	39.0	26.5	Trace	Trace
1-B	42.1	28.6	1.53	1.52
2-B	39.6	26.6	1.54	1.57
3-B	40.8	26.8	1.54	1.66

pounds are not present in the oil obtained by hydraulic pressing of cottonseed fumigated with methyl bromide. The results also indicate that the methyl bromide has reacted to produce nonvolatile bromine compounds, presumably inorganic bromides (3), which do not enter the oil. The observation recorded in Table I, that the fumigated cottonseed stored in burlap bags did not lose bromine over a period of 50 days, is further indication that methyl bromide decomposes or reacts in the seed to yield nonvolatile bromine compounds.

Acknowledgments

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Abstracts

Oils and Fats

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SOLVENT EXTRACTION PROCESS APPLIED TO COTTONSEED. N. H. Moore (Delta Products Co., Wilson, Ark.). *Food Industries 19,* 471-3 (1947). Results of pilot plant operations at Wilson, Ark., indicate increased yield of cottonseed oil by solvent extraction, as compared with hydraulic process. New plant starts soon with operating capacity of 200 tons daily.

THE MIXED UNSATURATED GLYCERIDES OF LIQUID FATS. VI. LOW-TEMPERATURE CRYSTALLIZATION OF RAPE OIL. T. P. Hilditch, P. A. Laurent, and M. L. Meara (Univ. Liverpool). *J. Soc. Chem. Ind. 66,* 19-22 (1947). The mixed glycerides of rape oil were separated by systematic crystallization from acetone at low temperatures into 3 fractions. The component acids of each fraction were determined. Spectrographic analysis of alkali-isomerized acids from selected ester-fractions showed the presence of more linolenic acid than had hitherto been reported, and also of small amounts of a docosadienoic acid, $C_{22}H_{40}O_2$.

SOME UNSAPONIFIABLE CONSTITUENTS OF THE DEODORIZATION DISTILLATES OF VEGETABLE OILS. H. Jasperson and R. Jones (J. Bibby & Sons, Ltd., Liverpool). *J. Soc. Chem. Ind. 66,* 13-17 (1947). An examination has been made of some of the unsaponifiable constituents of the deodorization distillates of coconut oil, palm kernel oil, palm oil, peanut oil, cottonseed oil, and sunflower seed oil. The presence of large amounts of Me ketones, chiefly Me-nonyl-ketone, has been confirmed in the case of coconut oil and palm kernel oil distillates, and small amounts have been demonstrated in those of palm, peanut, cottonseed, and sunflower seed oils. The presence of carbinols corresponding to some of the ketones has been confirmed in the distillates of coconut and palm kernel oils. The predominant type of hydrocarbon was shown to be terpenoid, exhibiting strong absorption at λ maximum 230 mμ and possessing strong odor and a nauseating flavor. The mean unsaturation (Wijs, 30 minutes) of the terpenes examined from each distillate were as follows: palm oil 130, peanut oil 46, cottonseed oil 36, sunflower seed oil 68, palm kernel oil 41, and coconut oil 22.

THE PIGMENTS OF COTTONSEED. II. GOSSYCAERULIN, A BLUE QUINONOID GOSSYPOL DERIVATIVE OCCURRING IN COOKED COTTONSEED. C. H. Boatner, C. S. Samuels, C. M. Hall, and M. C. Curet (Southern Regional Research Lab., New Orleans, La.). *J. Am. Chem. Soc. 69,* 668-72 (1947). A blue pigment, gossycaerulin, has been prepared by heating acidified solutions of gossypol, and reaction conditions which favor the formation of this pigment have been determined. The properties of purified gossycaerulin have shown it to be a polar, α-hydroxy, quinonoid, oxidation product of gossypol. A yellow pigment has been detected as a byproduct formed from gossypol during its conversion to gossycaerulin. A purple compound resulting from the reaction of gossycaerulin with H_2SO_4 has been shown to exhibit the reactions of a quinonoid compound. Gossycaerulin has been detected in cooked cottonseed, and the extent of its formation has been shown to be correlated with the disappearance of gossypol, the length of heating, and the pH developed during heating of the seed.

HARDENING OF FAT WITH RANEY NICKEL. S. Schmidt-Nielsen and E. Spillum. *Kgl. Norske Videnskab. Selskabs Forh. 17,* No. 31, 122-5 (1944). To determine the effect of the Ni content of the alloy, 7 alloys containing 15-60% Ni and 3.6-3.8% of Al were prepared, and 0.5% of each catalyst was used with (a) 100 g. of refined and (b) 100 g. of crude herring oil at 75° and 100° atmosphere for 60 minutes. The selective effect of the Raney-Ni catalysts is the strongest for the catalyst with the weakest action, decreasing with the progress of the process. To determine the intermetallic compounds known to form in Al-Ni alloys, an alloy with 28% Ni was treated with diluted HCl (30 g./l.); there was obtained a mass of needle-shaped crystals of the color of metallic Ni of a compound corresponding to $NiAl_3$. Treatment of the crystals with NaOH gave a very active catalyst of 3.7% Al; this shows the importance of the remaining of part of the Al in the catalyst. (*Chem. Abs. 41,* 115-6.)

CHANGES OF CATALYST IN POISONING. A. D. Khvatov (Moscow State Univ.). *J. Gen. Chem.* (U.S.S.R.) *16,* 407-14 (1946). Confirmation was secured for the supposition that, on poisoning of Ni catalyst by CO, there occurs not only an intensive topochemical change of the surface but also the change of structure of the components of the catalyst which changes the basic course of the reaction. The change in Ni is apparently the determining factor in the changes of the other catalyst components. The greatest drop of activity corresponds to the greatest change of disperse nature of the catalyst and a minimum amount of removed metal. The control reaction used was the