# **Effect of Weather Damage on the Chemical Composition of Soybeans'**

ORLAND A. KROBER and F. I. COLLINS, U. S. Regional Soybean Laboratory, Urbana, III.

O<sup>NE</sup> of the functions of the U.S. Regional<br>Soybean Laboratory is to analyze samples of<br>soybean seed for strains grown by federal and soybean seed for strains grown by federal and and state cooperators to aid in the selection of improved strains for industrial utilization. Samples of soybean seed are sometimes received at this laboratory which are in damaged condition due to unfavorable growing or harvesting conditions. It may be desirable to have an analysis of such samples; however, in evaluating these chemical data, due consideration should be given to the fact that composition may be considerably altered by damage to the seed.

Various studies have been made in this laboratory in an effort to refine the methods of analysis of soybean samples to make possible more accurate evaluation of the strains. The present investigation is concerned primarily with the effect of unfavorable weather conditions during the maturing of the seed and of weather damage of the seed after maturity on its chemical composition.

In a bulletin on weather-damaged soybeans Cartter (1) mentions two types of damage, "green damage" and field damage. When growth is arrested prematurely, soybeans that would be yellow if normally matured are green when harvested, and this condition is popularly known as *"green* damage." These soybeans may be expected to contain about the same amount of oil and protein as normal seed. The oil from such soybeans, however, may contain a somewhat higher percentage of free fatty acid than oil from normally matured, sound seed. If soybeans are not harvested promptly after maturity but are left exposed to rains or damp weather for a time, the seed develops a dark brown color and a mealy or chalky texture and tends to sprout or decay. This is known as weather damage, or field damage. From the standpoint of the processor this type of damage is more objectionable than "green damage."

In a study of the flavor quality of soybean oil Sanders (7) reported that oil from weather-damaged seed was more costly to refine, and even after refin-

<sup>14</sup> Publication by the U.S. Regional Soybean Laboratory, a coopera-<br>tive organization participated in by the Division of Forage Crops and<br>Diseases, Bureau of Plant Industry, Soils, and Agricultural Engineering,<br>Agricultur

ing it was often not of an edible grade. 0il from frost-damaged seed was high in chlorophyll, but this was more easily removed in refining than the red color caused by other field damage (8). Fairbanks, Krider, Catron, and Carroll (2) found that expeller processed meal from frosted-field damaged soybeans was somewhat higher in crude protein, ether extract, and ash than normal meal.

Several investigators have reported effects of damage in storage on chemical composition. Krider, Fairbanks, and Carroll (3) found in a study of binburned soybeans that the damaged meal was somewhat higher in crude protein, ether extract, ash, and crude fiber and lower in nitrogen free extract. O'Kelly and Gieger (6) found that the nitrogen free extract in mature soybeans varied from 17.7 to 30.2% in a large number of determinations. Zeleny (9) found that in stored corn increased fat acidity was associated with heating, and hence with damaging of corn in storage. Milner and Geddes (5) in a study of grain storage found that soybeans lost  $CO<sub>2</sub>$ slowly and at about a constant rate under conditions of low humidity and low moisture content. However, if a critical moisture content of about 14% was exceeded, the loss of CO<sub>2</sub> was greatly accelerated and sugar content of the seed decreased while the acid value of the oil rose rapidly. From these investigations it appears that storage damage to the seed results in loss of carbohydrates and decomposition of the oil, thereby causing an apparent increase in protein and sometimes of the oil although both the latter substances may have been lost but to a lesser extent than the carbohydrates. The partial loss of one substance will therefore alter the percentages of the other substances present in the seed.

## **Experimental Methods**

As a preliminary study, two samples of soybean seed, designated as samples A and B, containing both wrinkled, partially decomposed seed and reasonably sound seed, were divided into damaged and sound portions and analyzed chemically. The results of these analyses are shown in Table 1.

Differences of a few tenths of a per cent in oil content are considered important in the selection of a strain from a group of competing strains. Since changes of that magnitude may be caused by damage



I Calculated **from refractive index according to method of Majors,** K. R., and Milner, R. T. (4).

to the seed as shown in Table 1, the effect of seed quality of samples should be more fully investigated.

Thirty-two samples, averaging about one pound each, were selected from seed samples submitted for analysis from a number of cooperating states. The percentage of damaged seed in the samples ranged from about  $3\%$  to more than  $60\%$ . Each sample was divided by hand-picking into damaged and sound portions as shown in Fig. 1. The sound and damaged portions from each sample were analyzed for ash, moisture, oil, crude protein, non-protein nitrogen, total sugars, reducing sugars, and acid number, Wijs iodine number, and calculated iodine number of the oil. The calculated iodine number was determined from the refractive index of the oil as reported by Majors and Milner (4).

Table 2 shows the deviations in percentage composition of various components of these soybeans showing maximum, average, and minimum values for the damaged portions. The values given in the table are deviations of the damaged portions from the composition of the sound portions, the minus values indicating decreases over the sound portion. The damaged portions were as much as  $4.5\%$  higher than the sound portions in crude protein, averaged 1.8% higher, and in no case were they lower. If the non-protein nitrogen calculated as per cent protein is deducted from the crude protein, the net protein is obtained. The net protein averaged 1.1% higher in the damaged portions but percentages ranged from 2.1% below the corresponding sound portions to 3.8% above. The non-protein nitrogen is much higher in the damaged portions. The marked increase in non-protein nitrogen is presumably due to the decomposition of the protein since there would be no other source of nitrogen. There is evidently a partial loss of protein which is less apparent because of the greater loss of other components.

TABLE 2 The Apparent Gain or Loss of Materials in Damaged Soybeans Compared With Sound Soybeans as Determined by Chemical Analysis of 32 Samples

Constituent	Deviations in Composition of Dam- aged Portion of Seed From That of Sound Portion of Same Sample		
	Maximum	Average	Minimum
Reducing Sugars Non-Protein Nitrogen x 6.25 Iodine Number of Oil (Wiis) Iodine Number of Oil (Calculated	$1.3\%$ 2.9% 4.5% 1.4% 0.1% $3.8\%$ $3.8\%$ 45.3 1.7	$0.3\%$ $0.6\%$ $1.8\%$ 0.2% $-1.8\%$ $0.9\%$ $1.1\%$ 8.9 $-2.0$	$0.0\%$ $-3.3%$ $0.0\%$ $-0.1\%$ $-4.3%$ $0.0\%$ $-2.1\%$ 0.0 $-13.5$
from refractive index of oil)	3.0	$-3.5$	--8.6

The quantity of oil in the damaged portions averaged 0.6% higher than in the sound portions of the samples and varied from  $2.9\%$  higher to  $3.3\%$  lower. Acid numbers of the sound portions ranged from 0.9 to 2.9 and in the damaged portions from 1.5 to 47.9. Iodine numbers of oils (Wijs) and iodine number calculated from the refractive index averaged higher by several units in the sound portions. Iodine numbers by the two methods generally gave closely agreeing results on oil from sound portions but gave results which were seldom in good agreement on oil from the damaged portions.

The damaged portions averaged about 2% lower in non-reducing sugars but slightly higher in re-



FIG. 1. Photograph shows the division of a typical sample into obviously damaged and reasonably sound portions.

dueing sugars, indicating hydrolysis of some of the polysaccharides.

The apparent increase in ash content is probably due to the greater loss of other materials rather than to *any* actual increase in minerals present. If we assume that there was no loss of minerals in the damaging of the beans, we can estimate the total loss of material which would be as much as 20% of the total weight of the seed in some eases. This assumption may be invalidated to some extent by the leaching of some samples with possible loss of minerals, or to a greater tendency for particles of soil to cling to the rougher damaged seed.

Deviations shown in Table 2 are for hand-picked samples and represent extreme eases where all the seed in the damaged sample showed some damage. If a sample contains only half damaged seed, we would expect deviations from the normal composition of the seed to be only half as great as indicated in the table. If the percentage of damaged seed in a sample is low, for example  $5\%$ , the deviations caused would be only one-twentieth that shown in the table and would ordinarily be of little consequence. Likewise, the degree of damage is important. The damaged portions analyzed in the study represent seed in many degrees of damage such as may ordinarily be encountered.

### **Summary**

Soybean samples containing a large proportion of damaged seed were separated into sound and damaged portions and these portions were then analyzed chemically.

Analysis of these samples indicated that damage to the seed caused considerable variation in percentages of oil, protein, ash, and in iodine number and acid of the oil. Sugars in the damaged portions of the soybean samples were generally low when compared with the sound portions.

Weather damaging of soybean seed caused a marked increase in percentage of crude protein. Oil percentages were sometimes higher and sometimes lower in the damaged portions. The iodine number of the oil was usually but slightly affected, and the acid number was higher in the damaged portions.

In order that the chemical analysis of the samples may be representative of the true composition of a strain, the seed analyzed should be of good quality and contain no more than a small proportion of damaged seed.

#### REFERENCES

- 1. Cartter, J. L. U.S.D.A. Bulletin AWI-71 (1943).
- 2. Fairbanks, B. W., Krider, J. L., Catron, Damon, and Carroll.<br>Jour. Agr. Res. 75, 155-159 (1947).
- 3. Krider, J. L., Fairbanks, B. W., and Carroll, W. E. Jour. Agr. *Res. 69,* 383-387 (1944).
- 4. Majors, K. R., and Milner, R. T. Oil and Soap *16,* 228-230 (1939). 5. Milner, Max, **and Geddes,** W. F. Cereal Chem. 23, 225-247
- (1946).
- 6. 0'Kelly, J. F., and Gioger, M. Miss. Agr. Expt. Sta. Tech. Bul. 24, p. 1 (1937). 7. Sanders, J. H. Oil and Soap 21, 357-360 (1944).
	- 8. --- Soybean Digest 6, No. 5, pp. 12, 13 ((1946).

9. Zoleny, Lawrence. Cereal Chemistry *17,* 29-37 (1940).

#### **ABSTRACTS**  ☆ ☆ ☆ ☆ ☆ ☆ **Oils and Fats M. M. PISKUR and MARIANNE KEATING**

THE SYNTHESIS OF UNSATURATED FATTY ACIDS. K. Ahmad and F. M. Strong (Univ. Wisconsin). *J. Am. Chem. Soc. 70,* 1699-1700(1948). A convenient and practical synthesis of mono-unsaturated fatty acids has been suggested. Alkyl acetylenes react with iodochlorides to form acetylenic chlorides which in turn, *via* the nitrile or Grignard reaction and subsequent selective hydrogenation of the triple bond, are converted to the mono-unsaturated fatty acids. The method promises to be of general utility for synthesizing a variety of fatty acids and related long chain aliphatic substances.

FATS, OILS, AND FATTY ACIDS FOR INDUSTRIAL PUR-POSES. Dale V. Stingley (Armour Chem. Div., Chicago). *Inst. Spokesman (Natl. Lubricating Grease Inst.*) 11, No. 10, 6-10(1948). A review covering statistical data, uses, classification, and separation of glycerides by solvent crystallization, liquid-liquid extraction, or fractional distillation. *(Chem. Abs. 42,*  3195.)

REDUCTION OF FATTY ACID ESTERS BY SODIUM. Anon. (Lab. Chevreul, Paris). *Bull. mens. ITERG 1947,*  No. 93-9. The Du Pont process for the manufacture of fat alcohols is amply reviewed. On the basis of previously published theoretical considerations a modification of the process has been worked out by which yields of 94-8% have been obtained in the preparation of oleyl alcohol. The principal source of losses being the saponifying action on the esters of the Na alcoholate formed during the reaction,  $NH<sub>4</sub>Cl$  or  $CO<sub>2</sub>$ is introduced to prevent the Na from combining with the alcohol. The quantity of Na required, however, is 20-40% higher than theory as against only  $5\%$  in the Du Pont process. *(Chem. Abs. 42,* 3310-11.)

COMBINATION DISPERSION OF LIGHT IN FATTY ACIDS AND THE HYDROGEN BOND. M. I. Batuev. *Bull. acad. sci. U.R.S.S. Ser. phys. 11,* 336-9 (1947). Frequencies corresponding to the 0-H bond were observed in the vapor state of acetic and valeric acids. In the liquid state these frequencies were shifted, owing to H bonds. B. assumes that propylic and higher acids have in the fluid state a ring-type association structure, whereas formic and acetic acids show in addition a chain-type association. This can be shown in the behavior of  $C=O$  frequencies of fatty acids when dioxane is added to them. *(Chem. Abs. 42,* 3261.)

SEPARATION OF THE SATURATED STRAIGHT-CHAIN FATTY ACIDS  $C_{11}$  TO  $C_{19}$ . L. L. Ramsey and W. I. Patterson (Federal Security Agency, Washington, D. C.). *J. Assoc. Official Agr. Chemists 31,* 441-52 (1948). A method, based on partition chromatography, is presented for the separation of the straightchain saturated fatty acids  $C_{11}$ -C<sub>19</sub>. The separation of the even-numbered acids from each other and of the odd-numbered members from each other is fairly complete in a single fractionation and recoveries of added acids are essentially quantitative. The fatty acids are separated on a column of silicic acid using a mixture of furfuryl alcohol and 2-aminopyridine as the immobile solvent, and n-hexane as the mobile solvent. The separation is followed by titration of percolate fractions of suitable volume with standard Na ethylate, and the separated acids are determined by titration in 70% alcohol with standard NaOH. Each acid is tentatively identified by its threshold volume, and the identification is confirmed either by a melting point determination or by adding an approximately equal amount of an authentic sample of the suspected acid to the unknown and testing the chromatographic homogeneity of the mixture on a fresh column.

STUDIES ON SYNTHETIC GLYCERIDES. II. LIPOLYTIC HYDROLYSIS OF SYNTHETIC GLYCERIDES WITH FATTY ACIDS OF 8-18 CARBON ATOMS. K. E. Schulte (Univ. Munchen, Germany). *Biochem. Z. 318, 220-6(1947).* Fatty acids were prepared by oxidation of paraffins. Made into glycerides, these have been split by pig pancreas lipase just as natural food glycerides. *(Chem. Abs. 42,* 3007.)

X-RAY INVESTIGATION OF GLYCERIDES. VII. DIFFRAC-TION ANALYSES OF SYNTHETIC 1,3-DIELAIDIN. B. F. Daubert and S. S. Sidhu (Univ. Pittsburgh). J. Am. *Chem. Soc. 70,* 1848-9(1948). The preparation of 1,3 dielaidin by (1) direct synthesis from 1-trityl-2,3 dielaidin, a new compound, and (2) elaidinization of 1,3-diolein is reported. The X-ray and melting