

3. It has been found that none of these compounds rearranges into substituted phenols in a manner similar to the allyl-phenyl ethers.

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### PROSO MILLET INVESTIGATIONS—ANALYSIS OF THE OIL—A CHARACTERISTIC ALCOHOL.

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While engaged in an exhaustive examination of the grain of the proso millet, with a view to its employment as a commercial food source, certain peculiarities of the ether extract from the finely divided grain came to our attention. These unusual features led to the following series of investigations, which, while as yet open to further work, have brought out several interesting details, when viewed from the standpoint of the cereal analyst.

This variety of millet, termed *proso* from the Russian name for the "true millet," was denominated by Linnaeus, *panicum miliacum*. It is extensively cultivated in the region of the Altai Mountains in Siberia, in Southern Russia, and in the semi-arid areas of eastern and southern Asia, where it constitutes a staple foodstuff for both man and the lower animals. Its botanical name suggests its productivity, which is marked, even in regions where other common grains do not thrive by reason of aridity of climate. Our first undertaking was merely one involving the analysis of the grain to determine its nutritive factors and, particularly, its gluten and gliadin content, as affecting its adaptability as a breadstuff, and so to throw light upon its possibilities as a food crop for our semi-arid regions west of the Missouri River.

The grain upon which we undertook our studies was raised upon the farms of this institution, from specially selected white seed derived by selection from mother seed obtained in Russia by Professor N. E. Hansen, of this college. Two analyses were made upon the seed, the first upon a coarsely ground meal, unbolted, and the second upon bolted flour from the same grade of grain. The former sample consisted of the hulled grain, ground to pass through a 70-mesh sieve but without further treatment. In the second case, the grain, hulled and pulverized, was passed through the ordinary No. 60 mill screen, so producing a flour similar in fineness to the so-called "Red Dog" grade of wheat flour. By this process, the crude fiber content was materially reduced and the percentage of starch was largely increased, as compared with like data from the coarser samples first taken from the unbolted meal. The following table is presented to show in percentages the analytical results from

unbolted meal, bolted flour, and an average comparable analysis of patent wheat flour, according to Leach's tables.<sup>1</sup>

	Ash.	Mois- ture.	Cr. Fib.	Cr. Prot.	Eth. Extr.	N- Free.	Starch.	Total.
Proso meal.....	2.86	12.80	6.25	15.86	5.07	57.16	59.65	100.00
Proso flour bolted.....	1.45	10.09	0.80	14.90	3.32	69.44	69.15	100.00
Patent wheat flour.....	0.44	12.77	0.21	10.55	1.02	74.90	...	99.89

According to the above data, we note that aside from the inferences which our original problem led us to form as to the food value of the grain, its oil content is low as compared with that of many other common oil-bearing seeds now in use as oil sources of commercial moment, but it was found that, by extraction of the coarser material for a 16-hour period, we could depend upon a constant 5% extract, and we have used such means in obtaining the quantity of oil needed for our special work upon the oil.

To prepare the oil for this work, we proceeded as follows. The selected hulled seed was ground through a common laboratory hand mill, keeping the crushers tight. The product passed through a 40-mesh sieve. This meal was extracted in a specially constructed apparatus, consisting essentially of a large glass cylinder, constricted at both ends, about 125 cm. in length, and surmounted by a Liebig condenser in position for refluxing. The cylinder was furnished with an inner tube which passed from a point below the lower end of the cylinder, through a cork inserted in this end, up through the meal to be extracted and above the surface of the charge, which consisted of about 1.8 kg. of meal. Between the cork stopper, which was perforated with small glass tubes to permit egress of oil-saturated ether, and the charge was placed a 2-inch layer of glass wool. An aluminum cone was suspended from the lower end of the reflux condenser, to distribute the return flow of condensed ether. The whole was connected, as usual, with a boiling flask of 2 liters capacity and the extraction continued for 16 hours per charge. As the quantity of oil sought for the work precluded the use of expensive ethyl ether, we made use of petroleum ether, which we found, upon trial, to be almost as efficient as anhydrous ether both in point of amount of yield of oil, and in quality of the product. The extraction was considered to be complete when the medium issued from the cylinder practically water-white and left but the slightest trace of oil upon evaporation of 50 cc. The oil so extracted, upon distilling off the solvent, was at first of a medium straw color, changing, upon standing, to a light golden yellow, the oil being quite mobile, with an odor distinctly characteristic of this product. The oil, so extracted, was the subject of the following experimentation, after filtering out, through coarse linen, a peculiar mass of crystals which

<sup>1</sup> "Food Inspn. and Analysis," 1904, p. 236.

were noticed as collecting in the oil after it had stood out of contact with air for several hours. These crystals were of lustrous appearance, pearly white and in the form of thin plates. After several unsuccessful attempts to separate the oil by the use of solvents, we removed them as mentioned above, washed them free from oil by means of cold ethyl ether, in which the crystals were but very slightly soluble, rewashed them in 95% alcohol, cold, and dried them at 100°, after recrystallization from hot 95% alcohol. The crystal-mass, when so purified, crystallizes in 6-sided pearly plates, closely resembling those of phytosterol, but in other respects markedly differing from the latter, particularly in their melting point, which was sharp at 279°, corrected. These crystals were set aside for further examination, which will be reviewed at a later point in this report.

**Physical Characteristics of the Oil.**—The oil of proso millet is a semi-drying oil having a specific gravity of 0.9228 at 22.5°, as determined by the pycnometer. It has a refractive index, as determined by the Abbé Refractometer, of 1.4745. These values correspond well with the semi-drying nature of the oil. It is insoluble in 95% alcohol up to 35 volumes and is insoluble in absolute alcohol up to 25 volumes, showing it to be composed very largely of fixed oils, as confirmed by succeeding tests.

**Chemical Constants.**—The saponification value was 181.5, indicating a possible composition similar to that of peanut oil as to the nature of the acid groups involved, and pointing to its quality as a semi-drying oil. Its iodine value, determined by the Hubl method, was 92.3, showing it to be high in relative amount of unsaturated acids. In point of free fatty acids, the constant was high, corresponding to 119 mg. of oleic acid per g. of oil. This number would, therefore, preclude the use of the oil as a lubricant. The acetyl value was high, 39.23 mg. of potassium hydroxide being required to neutralize the acetic acid produced from hydrolysis of the acetylated fat, per g. This value corresponds, by calculation, to 10.9% of alcohols and hydroxy acids in the original oil, a characteristic of semi-drying oils. The Reichert-Meissl value was fairly large, *viz.*, 2.5. Unsaponifiable matter, as determined by the method of Allen and Thompson, was found to be 2.52 parts per hundred, by weight. It was found to consist of resins, in the main, but in insufficient quantity for exact determination as to type. The elaidin test, conducted according to the method of Andes,<sup>1</sup> gave us, at first, a foamy, orange-yellow, buttery mass, which, after 2 hours, assumed a red-brown and semi-liquid character. These results presume the oil to lie midway between oils like rapeseed, sesame and cottonseed and the more strictly drying oils such as hempseed and linseed. To assure ourselves regarding this point,

<sup>1</sup> "Drying Oils," 1901, 3-4, 574 (1889).

we oxygenated the oil according to the method of Livache,<sup>1</sup> with the following results:

Time of exposure. Days.	Gain. % of O by weight.
1.....	0.60
2.....	0.74
3.....	0.92
4.....	1.20
5.....	1.64
6.....	2.00
7.....	2.60
14.....	3.10
21.....	3.18

These results would rank the oil with the group represented by rape-seed oil, as to its drying properties.

The Lewkowitsch method for determination of crude glycerol,<sup>2</sup> resulted in a low value, *viz.*, 3.31%. While this small percentage may be partially due to loss through volatility of glycerol in steam during the frequent evaporations involved in the acetin method, such low value was to be expected when the high, free acid value and rather moderate saponification number were taken into consideration.

Phytosterol was determined by the A. O. A. C. method and the product obtained, upon its evaporation and recrystallization from hot alcohol, gave us the characteristic needle-tufts to the amount of 0.63% by weight of original oil. Their melting point was 134°, corrected, and their identity so established.

All tests for phenol bodies were negative, and the Schiff test for aldehydes gave but a very faint coloration after the mixture had stood for 2 hours, indicating that aldehydes, if present, are of negligible amount.

As calculated from saponification value, the mean molecular weight of the fatty acids is 296.

**Volatile Acids.**—56.7 g. of the oil was saponified by alcoholic potash, evaporated to free the soaps from alcohol, the soaps neutralized with excess of sulfuric acid, and warmed to complete the separation of insoluble acids. The acid cake was separated and the residual liquor distilled until distillate gave no reaction with litmus. This distillate was titrated against 0.1 *N* sodium hydroxide solution and 0.36% of volatile acids found, as calculated to formic acid. A slight acetic acid content was found to form a part of this small percentage, through resort to the method of Ducleaux, as modified by Dyer,<sup>3</sup> this conclusion arising from parallelism of graphs, charted according to the above method.

**Insoluble Fatty Acids.**—The caked acids, obtained as above, were

<sup>1</sup> *J. Soc. Chem. Ind.*, 6, 494 (1886).

<sup>2</sup> Lewkowitsch, 9.

<sup>3</sup> *J. Biol. Chem.*, 28, 445 (1917).

washed, recaked, and found to constitute 89.8% of the oil. This combined mass of saturated and unsaturated acids of higher carbon content gave the following constants: saponification value, 195.9; iodine value, 96.6; mean molecular weight, 286.

**Saturated Acids.**—44.4 g. of the oil was subjected to the lead salt method of Gussarow-Varrentrapp, with Tortelli's modifications,<sup>1</sup> to separate unsaturated from saturated acids. By this process, we found that, of the total insoluble acids 85.3% were unsaturated and 14.7% saturated. The 2 types were examined as to their chemical constants, with following results: solid acids, iodine value, 24.4; neutralization value, 187.3; unsaturated acids, iodine value, 123.8; neutralization value, 314.

An attempt was made to separate the individual solid acids by a fractional precipitation through use of barium and magnesium salts, and through the use of lead acetate in alcoholic solution, but, after repeated trials, these methods were abandoned as affording little prospect of any definite approach to a quantitative separation. We finally accomplished this separation by first dissolving the solid acids in absolute alcohol, using least possible volume, and successively lowering our alcohol concentration, by the admixture of water, to conditions which induced the next sign of precipitation. By this method 3 fairly distinct fractions were obtained, all crystallized as fine needles, whose melting and solidifying points were found to be as follows:

Fraction.	% Alcohol in solvent.	Melting point. (Corr.)	Solidifying point. (Corr.)
A	70.0	68-73	64-65
B	60.0	59-64	55-57
C	50.0	52-57	51-51.5

Fractions A, B and C were refractionated by the same process as mentioned above, with the following results:

Sub-fraction.	% Alcohol by vol.	Melting point. (Corr.)	Neutralization equiv.
A <sub>1</sub>	70.0	72.2	366
A <sub>2</sub>	50.0	Fraction too small for accurate determination	
B <sub>1</sub>	70.0	62.8	254
B <sub>2</sub>	65.0	62.5	...
B <sub>3</sub>	60.0	62.4	...
B <sub>4</sub>	50.0	62.6	...
C <sub>1</sub>	50.0	56.7	273
C <sub>2</sub>	40.0	Fraction too small for detn.	

Fractions B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>, B<sub>4</sub> were combined, recrystallized from 70.0% alcohol, and a melting point of 62.7°, and the above neutralization value of 254, determined from this product. From above data and from usual solubility tests, the crystals were identified as those of palmitic acid, which constitutes approximately 80% of the entire amount of solid acids.

<sup>1</sup> *J. Ind. Eng. Chem.*, 9, 542 (1917).

Fraction A<sub>1</sub> was converted into its lead salt, which had a melting point of 113°, uncorrected, and was insoluble in ether. These facts, together with the neutralization value of the acid, raised a presumption that it might be carnaubic acid. The acid was analyzed, with the following results:

Calc. for C<sub>24</sub>H<sub>48</sub>O<sub>2</sub>: C, 78.26; H, 13.04. Found: C, 78.37; H, 13.19.

The lead salt of fraction C<sub>1</sub> was made and its melting point fixed at 105.5°. This, with the melting point of the acid itself, 56.7°, pointed to daturic acid, and this conclusion was confirmed by combustion.

Calc. for C<sub>17</sub>H<sub>34</sub>O<sub>2</sub>: C, 75.56; H, 12.59. Found: C, 75.42; H, 12.70.

As no other crops of crystals, appreciable in amount, were observed, our solid acids were presumed to be composed of a comparatively large amount of palmitic acid, with less quantities of carnaubic and daturic acids.

**Unsaturated Acids.**—These acids were prepared by the lead precipitation method, whereby we obtained a voluminous nearly white oil-mass, whose iodine number was 124, and mean molecular weight 314.

In order to determine the individual acids of this mass, we had recourse at first to the method of bromination. But, even after our samples had stood for 24 hours in contact with the brominating mixture and in the cold, we found but slight traces of a solid product. We inferred, by reference to the work of Jacobson and Holmes,<sup>1</sup> who assert that this method secures satisfactory results only in case of linolenic acid, when applied to such mixtures as we were investigating, that we have here no considerable amount of linolenic acid.

We then resorted to the well-known method of Hazura.<sup>2</sup> 24 g. of the unsaturated acids was saponified and the resulting soaps were oxidized by the above method, when a heavy precipitate of the hydroxy acids settled out on standing in the cold overnight. This mass, on filtering it out and allowing it to dry spontaneously to constant weight, gave us a dry product of 9.3 g. The filtrate, which might contain hexahydroxystearic acid as an oxidation product of linolenic or isolinolenic acid, was evaporated to a small volume and acidified with sulfuric acid. The resulting brown flocculent mass was extracted with ether and the only product which we could obtain was that embodied in the extract, which gave us a very small quantity of crystals in the form of flat, rhombic plates, obtruncated. We lacked material to obtain its major characteristics, but concluded from our meager data, that we had a small amount of the iso type of linolenic acid in our oil.

The main precipitate of hydroxy acids, washed with ether, was exhausted with 4000 cc. of ether, and from the ethereal solution we obtained,

<sup>1</sup> *Am. Chem. J.*, 38, 482 (1907).

<sup>2</sup> *Monatsh.*, 8, 260 (1887).

by evaporation to 150 cc. and cooling, 4.8 g. of crystals which were rhombic in shape. These crystals were found to have a melting point of  $139.4^{\circ}$  (corr.), concordant through 6 trials, and a neutralization equivalent of 318. Dihydroxystearic acid was thus identified. By calculation to oleic acid, it was evident that of our total oxidized unsaturated acids, 51.6% consisted of oleic acid. We found that this hydroxylated acid was insoluble in cold water and cold alcohol, but readily soluble in hot alcohol, which was used for all recrystallizations.

The solid remaining after extraction of the above fraction with ether was boiled out repeatedly with much hot water, each time filtered while hot, and allowed to deposit crystals on slow cooling. In this manner we obtained a final separation of the whole mass of crystals, into 7 fractions, which were filtered, dried at  $100^{\circ}$  to constant weight, and subjected to test as to melting point and neutralization value, as follows:

Fractions	I.	II.	III.	IV.	V.	VI.	VII.
Melting pt. (Corr.)....	$158.3^{\circ}$	$158.0^{\circ}$	$159.3^{\circ}$	$173.7^{\circ}$	$173.9^{\circ}$	$173.7^{\circ}$	$173.6^{\circ}$
Neutral. value.....	351	355	353	347	348	346	344

Fractions I, II, III were combined, as were Fractions IV, V, VI, VII, and each recrystallized from hot water, their constants being determined as before and as follows:

Fraction	I-II-III.	IV-V-VI-VII.
Melting pt. (Corr.).....	$159.9^{\circ}$	$173.4^{\circ}$
Neutral. value.....	354	349

The first combined fractions (I, II, III), when recrystallized, separated in leaflets which were long, oppositely truncated parallelograms. The second combined series of fractions gave, on recrystallization, silky needles, when deposited from the hot water medium. The fraction melting at  $173.4^{\circ}$  was thus easily identified as tetraoxystearic acid, from original linolic acid, and its amount, 1.9 g., indicated that, of the unsaturated acids which we succeeded in oxidizing, 20.4% was in the form of linolic acid.

The second combined fraction, with neutralization value so close to that of the tetrahydroxy acid above mentioned, but markedly differing in melting point, we considered to be an isomeric form of the tetra acid, and its amount, 2.2 g., indicated that 23.7% of the original oxidized acids was an iso-linolic acid.

We, therefore, conclude that our unsaturated acids are composed largely of oleic, linolic and an iso form of linolic acid.

**Unknown Solid.**—We examined the white crystalline solid, mentioned elsewhere in this paper as being allied in several particulars to a phytosterol but radically differing from this class of substances in its extremely high melting point, which was found to be unvarying at  $279^{\circ}$ , corrected. The substance contains only carbon, hydrogen and oxygen.

The fuchsine test for aldehydes gave negative results, pointing neither to the presence of aldehyde grouping nor to any polymerized form thereof.

The product was carefully tested for the presence of acid, carbohydrate, phenol, ester, anhydride, lactone and ketone grouping. In none of these tests did we derive any positive results, excepting the application of the hydroxylamine method for ketones, where we obtained a slight test for the ketone structure, unsatisfactory in its intensity and amount of precipitate, but nevertheless positive.

We applied the usual acetylation test for the presence of alcoholic radicals, and obtained positive and satisfactory proof that the substance under examination is an alcohol.

The product was analyzed with the following results:

Analyses	I.	II.	III.	IV.	Average.
Carbon-%.....	80.52	80.71	80.86	81.10	80.8
Hydrogen-%.....	10.16	10.39	10.00	9.90	10.1

By calculation from above data, we derive an empirical formula of  $C_{12}H_{18}O$ .

Using chloroform as solvent, we obtained molecular weight data as follows, employing the Liebig method:

Analysis	I.	II.	III.	IV.	Average.
Mol. wt.....	372	354	350	349	356

The product was also examined by the Menzies method of vapor density, to determine its molecular weight, as follows:

Analysis	I.	II.	III.	Average.
Mol. wt.....	378	362	367	369

In the latter manipulations, we used carbon disulfide as solvent, finding that other usual solvents gave us unconcordant results, evidently due to association.

We would, therefore, assign to this product a tentative molecular formula of  $C_{24}H_{36}O_2$ .

The product is soluble in hot ether, hot alcohol, chloroform, carbon disulfide, carbon tetrachloride, xylene, benzene, and slowly soluble in pyridine, acetic anhydride, and ethyl acetate. It is insoluble in water or cold alcohol. With a mixture of one cc. of acetic anhydride and 2 drops of conc. sulfuric acid, it assumes a purple coloration, which rapidly deepens to wine-red.

Some light was thrown upon its structure by the fact that when an amount of the purified product corresponding to its apparent molecular weight as determined above, was treated with theoretical amounts of the proper reagents, a substance was obtained which we identified as fluorescein. This would indicate that two side chains, in *ortho* position to a nuclear ring, are to be found in the structure.



So far as we have been able to gain access to the literature, we find no product which corresponds to this substance to have been noted. We, therefore, venture to claim that this oil carries an alcohol-ketone, in several respects allied to the phytosterols, in other regards differing markedly from such types, and have named this solid product, pending its further examination, "Prosol."

#### Summary.

The oil of proso millet is a semi-drying oil, capable of classification in this regard, with oils of sesame, rape and peanut.

It is essentially composed of glycerides of the following fatty acids: palmitic, oleic, linolic, iso-linolic, and, in smaller percentages, carnaubic and daturic.

The solid acids from such an oil can best be separated through their fractional precipitation from a series of varying concentrations of alcohol in water, with fairly constant differences between successive concentrations.

The bromination method seems inadequate for the satisfactory separation of individual members of the unsaturated fatty acids from similar oils.

A ketone alcohol, insoluble in water, soluble in certain organic solvents, and possessing certain properties similar to those of a phytosterol, is a by-product in the preparation of this oil, as the authors prepared it for analysis. So far as they have been able to ascertain, this product has not been discussed in the literature pertaining to plant products.

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#### NEW BOOKS.

**Verdampfen, Kondensieren und Kühlen.** By E. HAUSBRAND. 6th Edition. 1918. 53 figure, 5113 tables. 540 + xix pp. Julius Springer, Berlin. 16 Mk.

This edition contains much new material, formulas, tables, and examples, from investigations prior to 1918 which should be helpful in the design, construction and operation of apparatus for evaporating, condensing or cooling. It contains 37 more tables and 140 more pages than the second English edition of 1916. Much of the book has been rewritten with new material in almost every chapter. A number of tables have been changed to conform with later investigations. Noteworthy are the additions on heat transfer in liquid and vapor cocurrent and counter current systems; in heat interchangers, and preheaters; in evaporators using hot liquids; in still steam through cold tubes; and in systems using air, gases, and superheated water vapor. The section on multiple effect evaporators has been entirely recast to show more clearly the function of each unit in the multiple system. Most of the new data have been taken from German engineering publications.

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