CHEMICAL EXAMINATION OF PROSO OIL.

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While engaged in an exhaustive analysis of the grain of the Proso Millet, looking toward its employment as a commercial foodstuff, certain peculiarities of the ether extract of the grain were noted. These unusual features led to the present series of experimental researches, which have as yet progressed only so far as to establish the common constants of the oil. This paper will, therefore, be in the nature of a partial and introductory report of these investigations, which we propose to continue in the near future.

Proso, which is the Russian name for true millet, was denominated by Linnaeus, Panicum Miliaceum, in reference to its productiveness. It has been extensively cultivated in the region of the Altai Mountains in Siberia, and in southern Russia, as well as in the dry areas of eastern and southern Asia, where it constitutes a staple foodstuff for both man and the lower animals. As its botanical name would suggest, it is very productive, even in regions where other grains cannot thrive by reason of arid conditions. Hence, in first undertaking the analysis of the grain, our purpose was to determine its nutritive properties and hence its adaptability to our semi-arid regions of America as a cereal food crop.

The grain analyzed was raised on the Brookings plots, from specially selected white seed originally brought from Russia by Professor N. E. Hansen, of this college. The seed was hulled and ground to a coarse flour which was fine enough to pass through the ordinary No. 60 mill screen,

which produced a flour similar to Red Dog. By this process the crude fiber content was materially reduced from its percentage as found in the case of the coarser meal that had previously been analyzed in the station at Brookings. This flour gave the following analysis:

Ash	1.45%
Moisture	10.09%
Crude Fiber	0.80%
Crude Protein	14.90%
Ethel Extract	3.22%
Nitrogen Free Extract	69.44%
Total	100.00%
Starch	69.15%

According to the above data, the ether extract appears low as compared with many of the common oil-bearing seeds now in use, but it was found that by using for our oil source a coarser meal, the oil content increased to an average of 4.0%. Hence, for our work of examining the oil of Proso, we selected a meal that we could prepare by simply grinding the cleaned white seed through a common laboratory hand-mill, keeping the crushers tight. This meal would pass through a forty-mesh sieve.

The meal so prepared was extracted in a specially prepared apparatus which would serve for the extraction of four or five pounds of the meal at each charge. This apparatus consisted essentially of a large glass cylinder surmounted by a Liebig condenser, inverted, and furnished with a large inner tube through which the vapor of the exhausting medium might pass, to be recondensed and returned over a large aluminum cone for distribution to the charge. As the quantity of oil demanded for the experiments precluded the use of the more expensive ethyl ether as a medium of extraction, we made use of petroleum ether, which was found to be almost as efficient as anhydrous ether in point of amount and quality of yield. The extraction was considered complete when the medium issued without color and left but the slightest trace of residue upon evaporation. The extract so produced was of a medium straw color, but,

upon evaporation of the solvent, this color changed to a light golden yellow, the oil being quite mobile, with an odor distinctly peculiar to this product. The oil so produced is the subject of the following series of experiments.

Upon standing out of contact with air, we noted the formation in this oil-mass of a large quantity of lustrous crystals. After several unsuccessful attempts to separate these crystals by the use of solvents, they were removed by filtration through coarse linen, washed free from oil by cold 95% ethyl alcohol, and dried at 100°, after recrystallation from hot 95% alcohol. This product, purified, crystallizes in six-sided pearly laminae, closely resembling those of cholesterol, but markedly differing from the latter in melting point, which was found to be 273°-276°, uncorrected. These crystals are soluble in ether, hot alcohol, chloroform, carbon tetrachlorid, xylene, benzol, carbon bisulfid, and partially soluble in pyridine, insoluble in water, cold alcohol, acetic anhydride and ethyl acetate. With a mixture of 1 cc. acetic anhydride and two drops of concentrated sulfuric acid, it gave a purple color, which became rapidly a deep wine red. While we have not as yet identified these crystals, their properties as well as the high acetyl value of the oil, as hereinafter stated, point to one of the higher alcohols or to a polymerized aldehyde. Their identification will form the subject of further study.

The oil is a semi-drying oil having a specific gravity of .9228, as determined by the pycnometer method, under temperature conditions of 22.5°. It has a refractive index, as determined by the Abbe Refractometer, of 1.4745. These values correspond well with the semi-drying nature of the oil.

The oil was found to be insoluble in 95% alcohol up to 35 volumes, and was insoluble in absolute alcohol until we reached 25 volumes, showing it to be composed very largely of fixed oils.

The saponification value was 181.5 and again points to the fact that this is an oil of the semi-drying group, and of a possible composition similar to that of peanut oil as to the nature of the acids involved.

The Iodine value, determined by the method of Hubl as outlined in the A. O. A. C. procedure, was 92.3. The oil is therefore not extremely high in amount of unsaturated acids.

Free Fatty Acids—This constant was high, corresponding to 119 mg. of oleic acid per gram of oil. This number would therefore preclude the use of the oil as a source of lubricants.

Acetyl Value—This value, indicating the value of the alcohols and hyroxylated fatty acids contained in the oil, was high, it requiring 39.23 mg. of KOH to neutralize the acetic acid produced by hydrolysis of the acetylated fat. This number corresponds, by calculation, to 10.87% of alcohols and hydroxy-acids in the original oil. This high value is characteristic of the semi-drying oils.

Reichert-Meisel Value which indicates the amount of volatile fatty acids present, was fairly large, it being 2.5. The number given is again characteristic on the average, of many of the semi-drying oils obtained from vegetable sources.

Unsaponifiable Matter, as determined by the method of Allen and Thompson, was found to be 2.52 parts per one hundred, by weight. This probably consists of resins and waxes in the main.

The Elaidin Test, under the well-known Potassium Nitrite Method of Andes (Drying Oils, 1901, pp. 3-4), showed, at first, a foamy, orange-yellow, buttery mass. After 120 minutes the elaidin assumed a red-brown color and became a semi-liquid body. This test conforms to those usually found in cases of semi-drying oils such as rapeseed, sesame and cottonwood oils. On the other hand, it inclines toward the more drying oils such as hempseed and linseed oils. We may, accordingly, presume it to lie midway between the two classes of oils.

The oil was caused to undergo the oxygenation test of Lavache (J. S. C. I., 1886, p. 494). Results were as follows:

After 1 day a gain of .6 parts per 100.
After 2 days a gain of .74 parts per 100.
After 3 days a gain of .92 parts per 100.

After 4 days a gain of 1.2 parts per 100.
After 5 days a gain of 1.64 parts per 100.
After 6 days a gain of 2.0 parts per 100.
After 7 days a gain of 2.6 parts per 100.
After 2 weeks a gain of 0.00 parts per 100.
After 3 weeks a gain of 0.00 parts per 100.

This test indicates that this oil will rank with peanut, sesame, rape and in oxygen-absorption effect, again showing the marks of a semi-drying oil.

Glycerol, while inconclusive, by reason of the many opportunities of loss through the volatility of glycerol in steam during the frequent evaporations involved in the process, was determined by the Acotin method, wherein crude glycerol is first obtained from a weighed quantity of the oil, and this product acetylated by prolonged treatment with acetic anhydrid, according to Lewkowitsch (J. S. C. I., 1889, p. 574). Upon determination of the acetic acid from a hydrolyzed portion of this acetylated product, and by calculation from these results, we found the glycerol content of the oil to be 3.61%. This value is partially explained, as being comparatively low, by the high free acid value and rather moderate saponification value.

The oil was examined for the presence of Phytosterol, an alcohol often found in vegetable oils, of formula $C_{26}H_{43}OH$, by the method outlined in Bulletin No. 107, published by the U. S. Department of Agriculture. Upon evaporation and crystallization of the product from hot alcohol, the characteristic tufts of needle-shaped crystals were obtained in amount of 0.63% by weight of original oil. Their melting point was found to be 133°-135°C, uncorrected, so establishing their identity.

Phenols—The oil was tested for the presence of Phenol bodies, by the common Ferric Chlorid test. No phenols were observed.

Aldehydes—When subjected to the Schiff Reagent test for Aldehydes, a distinctly purple color developed after the mixture had stood for two hours. Aldehydes are therefore present in amounts yet to be determined quantitatively.

Conclusions.

The oil of Proso Millet is a semi-drying oil, to be classed in this particular with oil of sesame, rape and peanuts.

Proso yields approximately 35 bushels per acre. The legal weight per bushel in South Dakota is 50 pounds. But this variety easily runs 56 pounds per bushel, making an average yield per acre of 78 pounds of the oil. Hence, by comparison with the value, commercially speaking, of other commonly used oils, this oil should be found to be capable of hydrogenation to an edible fat. Its value, together with the high protein and carbohydrate content of the resulting oil-press-cake, should make it of very considerable commercial value, since it can be easily and profitably produced in cold and semi-arid regions. During the present period of food stress, it would seem, therefore, that Proso might be made one of our most valuable food crops, since its fat and protein content, as given above exceeds that of patent wheat flour and its starch content is practically the same as that of wheat flour.

We propose to continue our investigations along the lines of the isolation and identification of the acids found in this oil, of the crystalline product mentioned as of extremely high melting point in the above description of our work, of the products to be obtained through commercial hydrogenation of the oil, and, in general, of the possible use of this oil as a source of edible products.