TABLE V

Total Unsaturation of Conjugated Soybean Fatty Acids
[Theoretical total iodine number 138.0, Wijs iodine number (390% excess) 117.5]

Weight of sample, grams	Excess reagent, % (Time, 1 hour)	Iodine number
0.0598	640	137.8
0.0893	386	138.6
0.1183	268	139.0
0.1196	265	138.5
0.1786	148	137.2
0.2366	94	131.8

depending upon sample weight and excess reagent. Such a procedure gives true iodine numbers and has been investigated for various tung oils, oiticica oil, isomerized fatty acids, and dehydrated castor oil.

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Extraction and Evaluation of Oil From Dried Brewers' Grains[1]

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THE principal by-product of the brewing operation is brewers' grains, which consist of the insoluble material remaining after mashing of the malt and adjuncts. The average analysis for these grains is as follows: moisture, 10%; protein (N × 6.25), 27.0%; crude fiber, 15.5%; ash, 3.5%; crude lipids, 7.0%.

Although the oil content of dried brewers' grains is relatively low, it was thought that these grains might serve as a commercial source of vegetable oils. In order to determine the chemical characteristics of this oil and the feasibility of extracting and refining it, the work reported herein was undertaken.

The first problem considered was the effect on the feeding value in dairy cattle rations if the grains were relatively fat-free. Evidence in the literature is somewhat contradictory on this point. For example, Monroe, *et al.* (1), concluded, "under the conditions of these trials no significant differences were observed in the production of milk, butterfat, or 4% milk, or in the general health of milking cows from the feeding of practical grain mixtures ranging in average fat percentage from 4.89 to 2.69." Maynard, *et al.* (2), reported a somewhat different view, namely, "in a continuous experiment involving two groups of eight cows each, the group fed the high-fat mixture (7% fat) produced 4.4% more milk, 2.0% more fat, and 4.1% more fat-corrected milk than did the group fed the concentrate mixture containing only 3% fat." Inasmuch as the proposed extraction of oil from dried brewers' grains could be expected to lower the fat content of the mixed feed ration by an average of only 0.9%, it was felt that the decrease would not significantly affect the feeding value of the mixed feed ration. Furthermore modern tendency is towards extraction in the oilseed industry, and a variety of extracted oilseed meals are now being accepted by feed manufacturers.

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An analysis of the oil from spent barley malt has been reported by Täufel and Rusch in 1929 (3), but this work was performed on a European spent barley malt which contained no adjuncts. The present work was performed on spent grains derived from a mixture of American barley malt and rice. It is obvious that the analyses of the oil extracted from such residues will vary somewhat from brewery to brewery because of the use of different adjuncts, such as corn grits, corn flakes, corn syrup, milo maize, wheat flakes, and others. Since most breweries use a high ratio of barley malt to adjunct, the differences in the analyses of the oil from spent grains should not be pronounced.

Our work on this oil was roughly divided into three catefories, namely: a) methods of extraction, b) chemical analysis, and c) refining, which will be discussed in this order.

Methods of Extraction

It has been found in our laboratories that the average crude fat (that is, diethyl ether extractable by A.O.A.C. procedure) (4) of spent barley malt is 7.0% (as is basis), with a minimum of 5% and a maximum of 9%. The only practical way to recover this fat is by solvent extraction. For this purpose commercial hexane (boiling range 143° to 158°F.) was employed because of its wide use in the vegetable oil extraction industry.

Pilot studies were run on two continuous countercurrent extractors, namely, a horizontal and vertical type. The former type has been described by Lerman, *et al.* (5). The grains enter at one end of the extractor and are conveyed from section to section by impeller blades; the solvent enters at the other end and is pumped to the end that the grains entered.

The vertical extractor embodies the same principle of countercurrent extraction, that is, the fresh solvent is in contact with extracted marc, while the

most concentrated miscella is in contact with the fresh grains.

Two runs were made on the horizontal extractor, the essential difference being that in the first run no preparation was given to the grains while in the second run the grains were given one pass through smooth flaking rolls set at 0.0". Both the marc and the miscella were handled in the conventional manner to recover the solvent-free grains and oil. Table I gives pertinent data from the horizontal extractor runs.

TABLE I

Extraction Data—Horizontal Extractor

	Run 1	Run 2
Rate dried grains fed to extraction system (pounds per hour)	4.8	4.9
Total weight dried grains extracted (lbs.)	33.6	181
Solvent feed temperature (°F.)	75	78
Extractor temperature (°F.)	129	130
Preparation of feed before extraction	None	Smooth flaking rolls set at 0.0"
Solvent used	*n*-Hexane	*n*-Hexane
Solvent ratio	2.1	2.5
Retention time in extraction system (min.)	45	45
Feed in miscella (% of incoming grains)	.02	.05
Oil in miscella (%)	3.9	6.7
Average moisture of incoming grains (%)	7.6	6.4
Average oil content of incoming grains (% dry basis)	8.7	8.2
Average oil content of extracted grains (% dry basis)	1.5	.46

The primary purpose of the pilot run on the vertical extractor was to furnish a sufficient quantity of oil for laboratory experimental purposes. This pilot plant had about 25 times the capacity of the horizontal pilot extractor. Steaming or flaking equipment was not available for pretreatment of the grains. Table II is a summary of the data obtained with the vertical extractor when operating with dried brewers' grains.

TABLE II

Extraction Data—Vertical Extractor

Rate dried grains fed to extraction system (pounds per hour)	115
Total weight dried grains extracted (pounds)	1500
Temperature grains to extractor (°F.)	110
Solvent inlet temperature (°F.)	150
Extraction zone temperature range (°F.)	130-143
Preparation of feed before extraction	None
Solvent used	*n*-Hexane
Solvent ratio	1.85
Retention time in extraction system (minutes)	50
Filter cleaning cycle	None
Average moisture of incoming grains (%)	7.04
Average oil content of incoming grains (% dry basis)	7.7
Average oil content of extracted grains (% dry basis)	4.68

The pilot tests with these two extraction systems indicate that both systems would probably be satisfactory for commercial extraction, but that pretreatment by flaking is required for efficient operation. Flaking is required because dried brewers' grains are composed largely of hulls enclosing small, dark brown, and impervious particles, which contain most of the protein and oil of the dried brewers' grains. Flaking tends to break the hulls and to some extent may also break the hard particles.

Chemical Analysis

Table III gives representative analytical data for the oil recovered from dried brewers' grains in comparison with similar data reported by Täufel and Rusch (3) on *Treberfett*, which is an oil extracted from a European spent barley malt. Wherever possible, A.O.C.S. methods were employed.

TABLE III

Comparison of Analyses of Dried Brewers' Grains Oil and *Treberfett*

	Dried Brewers' Grains Oil		*Treberfett*
	Average	Range	
Specific gravity at 25°C./25°C.	0.932	0.929- 0.935	0.9659
Acid number	42.1	39.0 - 46.5	40.3
Saponification number	180	168 -188	172.3
Iodine number	110	106 -114	104.9
Unsaponifiable (%)	4.6	3.5 - 5.5	7.7
Acetone-insoluble "phosphatides" (%)	5.37	2.11 - 9.23	.....
Titre acids (°C.)	30.6	29.5 - 32.2	.....
Total fatty acids (%)	89.2	83.3 - 93.2	79.6
Solid fatty acids (% T.F.A.)	22.7	21.2 - 24.0	20.4
Stearic acid	4.4*	.....	10.9
Palmitic acid	16.7*	.....	9.5
Iso-oleic acid	1.6**	.....	.....
Liquid fatty acids (%T.F.A.)	74.9	72.6 - 77.2	79.68
Oleic acid	28.2	27.5 - 29.0	24.0
Linoleic acid	42.8	41.6 - 44.0	55.1
Higher unsaturated acids	2.8	2.0 - 3.5	0.58

* Estimated.
** Calculated from iodine value of solid fatty acid portion.

It may be seen from Table III that the differences in the analyses of oil from dried brewers' grains composed of barley malt and rice residue and those of *Treberfett*, the oil from a European barley malt residue, are not pronounced. This would indicate that the analyses of the oil from the dried brewers' grains of any brewery are probably similar.

Identification of the components of the unsaponifiable fraction was unsuccessful. Repeated fractionations yielded a substance with melting point in the range 81° to 84°C., which corresponds to a similar fraction reported by Nabenhauer and Anderson (6) and identified by them as myricyl alcohol.

Refining

The oil extracted from dried brewers' grains is dark yellow-brown in color and has very high free fatty acid and unsaponifiable fractions, as well as a pleasant but strong malt-like odor. In order properly to refine the oil for edible purposes it would be necessary to remove the free fatty acids by neutralization, followed by centrifugation to remove the soap stock, to bleach, and finally to steam-distill under vacuum to deodorize it, and to remove at least part of the unsaponifiable material by winterization.

Conventional methods for removal of the free fatty acids by neutralization with sodium carbonate or caustic soda, followed by centrifugation, proved impractical because of the high oil loss due to emulsification of the oil with the soap stock.

The free fatty acids could possibly be selectively extracted with liquid propane using the Solexol process (7), but the small quantities of oil involved would not justify the expenditure for the Solexol process.

For use as a soap stock or source of fatty acids, it is desirable to have a low concentration of phosphatides and unsaponifiable material. For this reason, high speed centrifugation tests were run on the oil,

TABLE IV

Centrifugal Clarification Data

	Acetone-insoluble,	Unsaponifiable,	Yield,*
	%	%	%
Original oil	9.23	5.46	100.00
Clarified oil by straight clarification	7.96	4.97	89.19
Clarified oil, 5% water added	5.02	4.80	82.95
Solids obtained by straight clarification	19.7	8.63	10.81
Solids obtained with 5% water added	29.7	8.06	17.05

* Calculated by a material balance of acetone-insoluble fraction.

both straight clarification and clarification with 5% water, in an effort to substantially reduce the phosphatide and unsaponifiable fractions. Table IV gives the results of this test.

The data in Table IV indicate that neither straight centrifugal clarification, nor clarification with 5% water, is completely effective in removing the acetone-insoluble or unsaponifiable fractions from the oil and that the loss of oil is significant in both cases.

Because the oil could not be satisfactorily neutralized without excessive oil loss in separating the soap stock, no bleaching or steam deodorization tests were run.

Discussion of Results

Possible uses for this oil appeared to be splitting and distillation to recover the various fatty acids and glycerin, and splitting for use as a soap stock. Edible oil uses are ruled out because of difficulties in refining the oil.

As a source of fatty acids, because of the high unsaponifiable fraction (3.5 to 5.5%) and dark color, this oil would be classified with vegetable oil foots. As a soap stock the oil does not appear promising because of the high unsaponifiable fraction and dark color. No investigation has been made of what applications, if any, the unsaponifiable and acetone-insoluble fractions may have.

Conclusion

The oil extracted from dried brewers' grains from a brewery using rice as an adjunct is somewhat similar in its fatty acid composition to cottonseed oil, but its dark color, high free fatty acid (19.6 to 23.2%), high unsaponifiable fraction (3.5 to 5.5%), and high acetone-insoluble fraction (2.11 to 9.23%) lessen the value of this oil. Since conventional methods of refining did not prove satisfactory, this oil appears to be of value only as a source of fatty acids and would therefore have to be classified with vegetable oil foots.

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The Production and Standardization of a Detergent Soil[1]

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A STANDARD is a defined measure of quantity, value, or quality, or by general consent is an example or test. One of the difficult parts of any standard is attainment of the general consent. A standard must possess some degree of reproducibility, and this factor is one of the reasons for delay in the acceptance of "standard" soils or soiled fabrics. High standards are not easy to attain, and such materials as common chemicals must be subjected to considerable purification and subsequent analysis before they become recognized as standards. Evidence of lack of analytical or statistical control of soils is one of the deficiencies to be noted in much data published on this subject.

One of the main reasons for lack of an accepted standard soil or soiled fabric is feeling that the laboratory soiled fabrics and washing methods show little or no correlation with actual practice. However the need for an artificially soiled fabric which could serve to screen the literally thousands of synthetic detergents or their multitudinous combinations with each other and with other detergent aids is readily understood. From the tone of publications on detergency, the methods of washing and the so-called standard soils appear to be the result of the then rather recent research. No indication is given as to their suitability over prolonged periods of usage. Standardization of soil by preliminary tests seems to be the exception rather than the rule, and of the many papers published few provide such necessary data (5). A notable exception to this generalization is the published information on recently available power-laundry soiled fabric (3). This paper is presented to give the results of 12 years continued experience with one type of soiled fabric and records the many variables which must be controlled to standardize it.

Soil has been aptly described as matter out of place, and this description adequately covers the multitude of materials which it is expected a detergent will aid in removing. To limit the discussion, the removal of soil in this instance is confined to removal from textile fabrics, but even then the affinity of soiling materials for various fibers presents a complicated picture, to say the least. As a further limit, since it represents a large proportion of the garments repeatedly and frequently washed, cotton will be the fiber discussed.

Investigation of the effects of the various individual soils and their further complex mixtures upon cotton could be the work of a lifetime. However a

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