Oil Fixation in Cottonseed Meals[1]

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Abstract

A fraction of the lipid material in cottonseed is fixed in the meal during processing in an oil mill and cannot be extracted with petroleum ether. This relatively unknown and unrecognized "fixed oil" fraction may vary in quantity in different meals. A procedure is described for the quantitative estimation of the fatty acids from this fraction in previously extracted cottonseed meal.

Introduction

A number of complaints have been voiced within the past decade about the difficulty of making an accurate determination of the oil content of cottonseed and other oil-bearing meals (1–6). Incomplete recovery of the residual oil in cottonseed meals by petroleum ether extraction as recommended by the Official AOCS Method (7) was suggested as a possible source of error (1). In 1956 Miller proposed saponification of the extracted meal residue followed by acidification and wet extraction of the fatty acids with ether to isolate and recover the fatty acids from the fixed oil fraction (1). This excellent proposal was eventually abandoned because of difficulties caused by formation of emulsions during the ether extraction step (2).

In 1961, Hopper reported recovery of part of the fixed oil fraction by employing longer than usual periods of extraction (6). By extracting the meal for 17 instead of the customary 3 or 4 hr, he was able to gain an additional 0.8 to 1.0% of oil from some meals.

Indirect evidence of oil fixation in cottonseed meals coming from screw press oil mills, as compared to hydraulic press mills, was furnished by Brawner, who compiled data on oil production from many oil mills for over five seasons (2).

Shuey et al. have stated that in wheat flour the oil-binding capacity increases with increased protein content and that chlorine bleaching of the flour also increases the oil-binding capacity (8).

This paper reports a procedure for the quantitative determination of fatty acids derived from the fixed oils in cottonseed meals.

Experimental

Cottonseed meals left after petroleum ether extraction, according to the Official AOCS Method (7,9), were used throughout for the determinations. The sample (5 g) was saponified with 6% alcoholic potassium hydroxide (50 ml) for 1 hr on a hot water bath in a 400 ml beaker with occasional stirring. Water (10–20 ml) was added to prevent bumping and the mixture evaporated to dryness. The residue was suspended in 250 ml water and stirred with warming until most of the residue dissolved. The beaker was cooled, the contents acidified with an excess of hydrochloric acid, warmed on a hot water bath an additional hour and placed overnight in a refrigerator to solidify the fatty acids.

The mixture was filtered through a Whatman No. 5 filter paper. The precipitate and filter paper were dried in air for 24 hr or longer at room temp. Oven drying at this point rendered part of the fatty acids nonextractable in the next step. The filter paper and contents were placed in another No. 5 paper, inserted into a Butt tube and extracted with petroleum ether, boiling point range 35–60C, for 8 hr. The solvent was then removed and the extraction flask placed in a 100C forced draft oven for an hour, cooled in a desiccator and weighed. Blank runs were made with filter paper and small wads of cotton as used during the extraction and corrections made for the amount of impurities extracted in the blanks.

For more accurate results, the extracted precipitate remaining in the Butt tube and the inner filter paper were removed and placed in a 400 ml beaker for a second saponification as outlined above until a second, smaller fraction of fatty acids was also recovered and weighed.

The factor 1.045 was then applied to the recorded wt of the recovered fatty acids, reporting the results as oleic triglyceride. No assumption was intended that the fatty acids were in the triglyceride form before saponification. The conversion to triglyceride is made solely for the purpose of making quantitative comparisons of small fractions of fatty acids recovered in this procedure with the bulk of the oil removed from the seed previously and predominantly triglyceride in form.

Results and Discussion

Single samples of commercial cottonseed meals of various types taken at random yielded the following quantities of fixed oil:

Direct solvent	1.2%
Prepress solvent	1.5%
Prepress solvent	1.9%
Screw press	1.9%
Expeller	1.9%

Further work was done on the cottonseed input and the cottonseed meal (protein) fraction of the output in a screw press mill for a period of 14 weeks.

Input

The residues remaining after analysis of whole cottonseed for oil by the Official AOCS Method (9) were analyzed for fixed oil by the new procedure. The 14-week average for fixed oil was 1.37%, equivalent to 1.06% when recalculated on a whole seed basis or 21.2 lb of fixed oil per ton of seed. The values for ammonia were also determined and found to be 5.36%, equivalent to 4.16% when recalculated on a whole seed basis. The average ammonia content of the whole seed determined previously from daily routine determinations had been found to be 4.17% indicating practically complete retention of ammonia by the meal residue after the oil extraction.

Output

The cottonseed meal produced in the oil mill during the same 14-week period had an average fixed oil content of 2.14% on a residual oil free basis. When recalculated to the original whole seed basis this value

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was equivalent to 20.1 lb of fixed oil per ton of seed.

The meal residue used for the input fixed oil analysis consisted essentially of the whole seed with only two seed constituents removed besides the foreign matter: 3.3% as moisture and 19.0% as oil. Approximately 77% of the wt of the original seed including all of the ammonia or protein was present in the residue for input fixed oil analysis.

The cottonseed meal used for fixed oil analysis of the output had more seed constituents removed in the form of moisture, linters, hulls, a small protein fraction and oil leaving only approximately 47% by wt of the original seed for output fixed oil analysis.

The fatty acids from the fixed lipids of the two meals are directly proportional to their protein contents. Shuey et al. found a similar relationship in their work on the oil-binding capacity of wheat flour.

The quality of the fixed oil fatty acids was examined. Samples of residual oil in cottonseed meal representing ca 4% of the wt of the meal were obtained by petroleum ether extraction. The residual oil was hydrolyzed, methylated and the fatty acid composition determined by gas chromatography. The fatty acids derived from the fixed oil in the same meals were also methylated and their composition determined by gas chromatography. The two were essentially the same. The neutralization equivalents of the fatty acids from the fixed oil were determined by very slow titration in a carbon dioxide free atmosphere to give values approaching 278 and in the range observed for fatty acids from cottonseed oil.

When tested for cyclopropenoid fatty acids by the Halphen test (10) the fatty acids from the fixed oil fraction of screw press cottonseed meal gave a value of 0.15%, lower than is usually found in cottonseed oil. On the other hand, a sample of fatty acids derived from the fixed oil of the whole seed residues prepared in the laboratory (9) gave a value of 0.36%, which is about normal for cottonseed oil.

In their work on the processing of cottonseed meats Eaves et al. (11) found that during solvent extraction of raw cottonseed meats phosphorus-containing compounds are extracted with the oil in significant amts. They also found that cooking of the meats hindered the extraction of these phosphorus compounds. It would appear therefore that apart from an insignificant fraction most of the phospholipids present in the cottonseed are fixed in the meal as a result of cooking of the cottonseed meats when processed in an oil mill. The phospholipids present in the meal after petroleum ether extraction (7,9) also contribute their share to the fatty acids in the fixed oil determination.

The greatest significance of the fixed oil fraction is that any material balance for oil in an oil mill when made without taking into account the fixed oil fraction present in input and output meals is necessarily incomplete. A superior and more accurate material balance for oil may be obtained provided the results from determinations for fixed oil are used to supplement the results of analyses for oil by the Official AOCS Method (7,9). A valid material balance for oil should include the significant item of milling loss of oil which is not even recognized in the present state of affairs.

The Halphen-positive cyclopropenoid fatty acid constituents of the fixed oil are also of practical interest in expanding the use of cottonseed meal for poultry rations. Satisfactory quantitative estimation of the levels of these compounds present in given cottonseed meals can be made only by determination and study of the neglected, unknown fixed oil quantity in addition to the known and readily obtainable total oil in seed and residual oil in meals.

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• *Letters to the Editor*

Gas Chromatographic Analysis of Tall Oil Rosin Acids

A RAPID ANALYTICAL method which would provide a reasonably quantitative measure of rosin acid isomers was desired for our continuing study of rosin composition. Historically, methods of isomer analysis have been very time-consuming. Recently the gas chromatography of rosin acid methyl esters (1,2), prepared with diazomethane (3), has allowed rapid analysis. A drawback to this method lies in the hazards associated with diazomethane. Other methods of esterification, using acid catalysis, are excluded since the sterically hindered rosin acids esterify slowly and the labile double bond systems rearrange rapidly. A potential chromatographic method for rosin acids was suggested by a paper of Robb and Westbrook (4) who prepared methyl esters of fatty acids by decomposition of their tetramethylammonium salts.

Our work on the pyrolysis of the tetramethylammonium salts of rosin acids to methyl esters demonstrates that this approach can be used to provide a rapid, safe and accurate method for the determination of rosin acid isomer content. Tetramethylammonium salts are prepared by titration. Pyrolysis of these salts in the inlet port of the gas chromatograph conveniently forms the methyl esters which then separate on the chromatographic column.

Tetramethylammonium chloride (5) 2.7 g (24.6 mmoles) was dissolved in about 30 ml of anhydrous methanol. Silver oxide 5.8 g (25.1 mmoles) was added and the mixture stirred under anhydrous