

THE REESTERIFICATION OF RICE BRAN OIL

CAROLINA R. MEDINA

SUBMITTED TO THE GRADUATE FACULTY OF THE COLLEGE  
OF AGRICULTURE, UNIVERSITY OF THE PHILIPPINES  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF

MASTER OF SCIENCE  
(AGRICULTURAL CHEMISTRY)

DECEMBER, 1972



## BIOGRAPHICAL SKETCH

The author was born on March 6, 1944 in Cabanatuan City. She is the younger of two children born to Ignacio T. Medina and Leonila Rivera.

She studied in Cabanatuan West Central School from 1949 to 1955. In 1955, she enrolled in Nueva Ecija High School, from which she graduated in 1959. She entered the University of the Philippines in 1959 where she took up the degree of Bachelor of Science in Chemistry. She graduated in March 1964. In November of the same year, she took and passed the Board Examination for Chemists.

She joined the staff of Central Luzon State University in Muñoz, Nueva Ecija as an assistant instructor at the Department of Chemistry in June, 1965.

In April, 1970, she was awarded an NSDB training grant for the First Summer Institute for College Teachers of Organic Chemistry held at UP, Diliman.

At present, she is on study leave from CLSU in order to pursue the degree of Master of Science in Agricultural Chemistry. She enrolled for the course in June, 1970 at the Department of Agricultural Chemistry, UPCA, under the UPCA teaching fellowship program.

## ACKNOWLEDGMENT

The author wishes to thank Dr. Julian Banzon, her major adviser and the members of her Guidance Committee, Prof. Lilia S.P. Madamba and Dr. Mariano B. de Ramos for their invaluable help, encouragement and guidance in the course of her work.

She also wishes to thank Central Luzon State University, through its President, Dr. Amado C. Campos, for granting her the opportunity to complete her studies;

Dr. Antonio D. Bustrillos for his support and use of the resources of the Department of Agricultural Chemistry;

Agri-Extracts and Manufacturing, Inc., through ATB Investment and Development, Inc. President Augusto T. Barretto for their interest in the study and for providing all the hexane needed in this study and rice bran for the preliminary work;

The Department of Food Science and Technology for the use of laboratory facilities;

Her friends and all those who made it possible to finish her work.

## TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION . . . . .	1
II. REVIEW OF LITERATURE . . . . .	4
III. MATERIALS AND METHODS . . . . .	8
Extraction of Rice Bran Oil . . . . .	8
General Reesterification Procedure . . . . .	9
Studies on Some Chemical Characteristics of Rice Bran Oil Before and After Reesterification . . . . .	10
IV. RESULTS AND DISCUSSION . . . . .	13
Extraction of Oil from Rice Bran . . . . .	13
Effect of Period of Storage at 10°C of Bran on Per Cent FFA of Rice Bran Oil . . . . .	14
Reesterification Studies . . . . .	14
Effect of Concentration . . . . .	18
Effect of Temperature . . . . .	19
Effect of Reaction Time . . . . .	20
Interaction of Temperature and Concentration . . . . .	21
Interaction of Concentration and Time . . . . .	22
Interaction of Time and Temperature . . . . .	22
Effect of Catalyst . . . . .	24
Glyceride Composition of the Reaction Product . . . . .	25
V. SUMMARY . . . . .	29

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
VI. LITERATURE CITED . . . . .	31
VII. TABLES . . . . .	34
VIII. FIGURES . . . . .	53

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Rate of extraction of oil from rice bran using commercial hexane as solvent .....	34
2	Some physico-chemical properties of rice bran oil .....	35
3	Rate of variation of FFA with period of storage of rice bran at 10°C.....	36
4	Effect of storage of rice bran oil at 0°C on its FFA content .....	37
5	Mean reduction in FFA at 145°C, at varying reaction time and glycerol concentration, using 0.1 per cent SnCl <sub>2</sub> .2H <sub>2</sub> O catalyst .....	38
6	Mean reduction in FFA at 200°C, at varying reaction time and glycerol concentration, using 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O catalyst .....	39
7	Mean reduction in FFA at 220°C, at varying reaction time and glycerol concentration, using 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O catalyst .....	40
8	Summary of effect of glycerol concentration, temperature and period of reaction on the FFA of rice bran oil .....	41
9	The activity of different esterification catalysts at 20 per cent glycerol level (oil weight basis). Reaction conditions: temperature, 200°C; time, 4 hours; catalyst concentration, 0.1% by weight of oil; initial FFA of oil; 183.7 millimoles per 100 grams oil .....	42
10	The activity of different esterification catalysts at 40 per cent glycerol level (oil weight basis). Reaction conditions: temperature, 200°C; time, 4 hours; catalyst concentration, 0.1% by weight of oil; initial FFA of oil, 183.7 millimoles per 100 grams oil .....	43
11	Comparison of different catalysts at 20% glycerol level using Duncan's Multiple Range Test .....	44

List of Tables (Cont'd)

<u>Table</u>		<u>Page</u>
12	Comparison of different catalysts at 40% glycerol level using Duncan's Multiple Range Test .....	45
13	Evaluation of the activity of the different catalysts at 20% glycerol level based on Duncan's Multiple Range Test in Table 11 .....	46
14	Evaluation of the activity of the different catalysts at 40% glycerol level based on Duncan's Multiple Range Test in Table 12. ....	47
15	Listing of catalyst in the order of decreasing activity for reesterification ....	48
16	Chemical characteristics of rice bran oil and of its reesterification product .....	49
17	Glyceride composition of rice bran oil and of its reesterification product. ....	50
18	Analysis of variance for data summarized in Table 8 .....	51
19	Analysis of variance of data in Tables 9 and 10 .....	52

## LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Percentage of oil extracted from rice bran versus extraction time .....	53
2	Reduction in FFA at varying reaction time and glycerol concentration; temperature fixed at 145°C; catalyst 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O.....	54
3	Reduction in FFA at varying reaction time and glycerol concentration; temperature fixed at 200°C; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O...	55
4	Reduction in FFA at varying reaction time and glycerol concentration; temperature fixed at 220°C; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O...	56
5	Reduction in FFA at varying temperature and glycerol concentration; reaction time fixed at 1 hour; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O .....	57
6	Reduction in FFA at varying temperature and glycerol concentration; reaction time fixed at 2 hours; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O .....	58
7	Reduction in FFA at varying temperature and glycerol concentration; reaction time fixed at 4 hours; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O .....	59
8	Reduction in FFA at varying temperature and glycerol concentration; reaction time fixed at 5 hours; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O .....	60
9	Reduction in FFA at varying reaction time and temperature; glycerol concentration fixed at 5%; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O .....	61
10	Reduction in FFA at varying reaction time and temperature; glycerol concentration fixed at 10%; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O.....	62
11	Reduction in FFA at varying reaction time and temperature; glycerol concentration fixed at 20%; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O .....	63

List of Figures (Cont'd)

<u>Figure</u>		<u>Page</u>
12	Reduction in FFA at varying reaction time and temperature; glycerol concentration fixed at 40%; catalyst, 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O.....	64
13	Reduction in FFA with increasing time at different temperatures using 5% glycerol and 0.1% SnCl <sub>2</sub> .2H <sub>2</sub> O catalyst .....	65

## A B S T R A C T

MEDINA, CAROLINA R. University of the Philippines,  
December, 1972. The Reesterification of Rice Bran Oil.

Major Professor: Dr. Julian Banzon.

Studies have been made on the reaction of rice bran oil with added glycerol in order to utilize the reaction as a possible means of lowering the free fatty acid content of high acid oils.

Results show that reesterification is favored by an increase in temperature and an increase in glycerol concentration. Time-temperature-concentration interactions are indicated. Addition of catalysts, notably  $MnO_2$ ,  $ZnCl_2$ , and  $PbO$ , favors reesterification resulting in the significant decrease in free fatty acids. Examination of the reaction product shows that the reaction leads to a change in glyceride composition of the oil.

## LITERATURE CITED

- ARIDA, V. P., F. C. Borlaza, and W. Schmitt. 1967. The ozonolysis of Philippine unsaturated oils. I. Rice bran oil. *Phil. J. Sci.* 96: 249-252.
- BROWNE, C. A. 1903. Contribution to the chemistry of rice oil. *J. Am. Chem. Soc.* 25: 948-954.
- CHOUDHURY, R. B. 1960. The preparation and purification of monoglyceride. I. Glycerolysis of Oils. *J. Am. Oil Chemists Soc.* 37: 483-486.
- COCKS, L. V. and C. Van Rede. 1966. Laboratory handbook for oil and fat analysts. 419 p. London: Academic Press, Inc. Ltd.
- DAVID, J. S., S. K. Rao, S.D.T. Rao, and K. S. Murti. 1965. Quality of bran oil as influenced by the conditions of storage of rice bran. *J. Food Sci. and Tech.* 2: 113-114.
- FEUGE, R. O. 1962. Derivatives of fats for use as foods. *J. Am. Oil Chemists Soc.* 39: 521-559.
- FORMO, M. W. 1954. Ester reactions of fatty materials. *J. Am. Oil Chemists Soc.* 31: 548-559.
- GASTROCK, E. A., et al. 1955. Rice bran oil extraction process. U.S. Patent 2, 727, 914.
- GRACI Jr., A. V., C.G. Reuther Jr., P.H. Eaves, L.J. Molaison and J.J. Spadaro. 1953. Pilot plant application of filtration-extraction to rice bran. *J. Am. Oil Chemists Soc.* 30: 139-143.
- HILDITCH, T.P. 1956. The chemical constitution of natural fats. 3rd ed., 664 p. New York: John Wiley and Sons, Inc.
- HUNTER, I.R., D.F. Houston, and E.B. Kester. 1951. Development of free fatty acids during storage of bran (husked) rice. *Cereal Chem.* 28: 232-239.
- KUBICK, G. 1967. Practical experiences with the rice bran oil extraction. Proceedings of the third meeting on "International Problems of Modern Cereal Processing and Chemistry." I. Milling and rice processing. 1: 152-159.

- LEHMAN, L.W. and E.J. Gauglitz. 1964. Synthesis of tri-glycerides from fish oil fatty acids. J. Am. Oil Chemists Soc. 41: 533-535.
- LOEB, J.R., N.J. Morris, and F.G. Dollear. 1949. Rice bran oil. IV. Storage of the bran as it affects hydrolysis of the oil. J. Am. Oil Chemists Soc. 26: 738-743.
- LUGAY, J.C. and B. O. Juliano. 1964. Fatty acid composition of rice lipids by gas liquid chromatography. J. Am. Oil Chemists Soc. 41: 273-275.
- LYNN, L., G.J. Steen and R.M. Anderson. 1968. New rice oils. Food Tech. 22: 1250-1252.
- MATTIL, K. and R. J. Sims. 1952. The glycerolysis of fat in tertiary aromatic nitrogenous bases to increase monoglyceride yield. J. Am. Oil Chemists Soc. 29: 59-61.
- MEHLENBACHER, V. C. and T.H. Hopper, eds. 1946. Official and tentative methods. 2nd ed., Illinois: American Oil Chemists Society.
- MEHTA, T.N., C.V.N. Rao, V. Laxmikanthan, and S.N. Shah. 1955. Glycerolysis of peanut and mustard oils. J. Am. Oil Chemists Soc. 32: 478-481.
- NODA, M. 1968. Lipids and seeds. III. Enzymatic hydrolysis of rice bran lipids. Nippon Nogei Kagaku Kaishi. 32: 574-580. (Abstracted in the Chem. Abstracts 70: 259059).
- POMINSKI, J., P.H. Eaves, H.L. Vix, and E.A. Gastrock. 1954. Simultaneous recovery of wax and oil from rice bran by filtration-extraction. J. Am. Oil Chemists Soc. 31: 451-455.
- RAO, P., S.A. Ahmed, and S.D.T. Rao. 1967. Factors affecting the free fatty acid change in rice bran. Indian Oil Soap J. 32: 203-210. (Abstracted in Chem. Abstracts 68: 20989m).
- RAO, R. 1955. Possibilities of oil resources from oil mills in India. Oils and Oil Seeds J. 7(9): 14-15. (Abstracted in the Rice J. 58 (13): 27).
- REDDI, P.B., K.S. Murti, and R.O. Feuge. 1948. Rice bran oil. I. Oil obtained by solvent extraction. J. Am. Oil Chemists Soc. 25: 206-211.

- ROTHE, M. 1967. Heat inactivation of enzymes in connection with the stabilization of rice bran. Proceedings of the Third Meeting on "International Problems of Modern Cereal Processing and Chemistry ". 1: 146-150.
- RICE AND CORN RESEARCH PROGRAM. Eighth annual progress report 1965-1966. UPCA Central Experiment Station, College, Laguna.
- SHETH, N. and R. Sivaprasada. 1971. Extraction of rice bran oil. Indian Chem. J. 5 (11): 28-31. (Abstracted in Chem. Abstracts 75: 117183b).
- STIRTON, A. S. 1964. Fat splitting, esterification, and interesterification. In Daniel Swern, ed. 1964. Bailey's Industrial Oil and Fat Products. New York: John Wiley and Sons, Inc.