

THE REESTERIFICATION OF RICE BRAN OIL

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BIOGRAPHICAL SKETCH

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A B S T R A C T

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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 triglycerides 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.