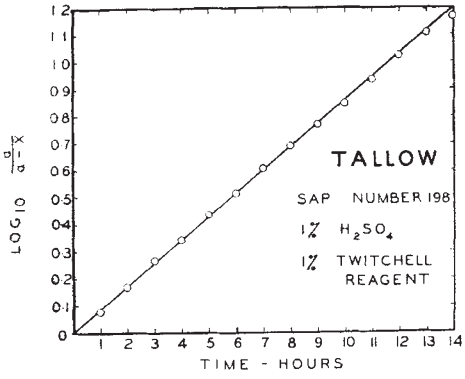
Kinetics of the Twitchell Hydrolysis

THE hydrolysis of fats in a dilute sulphuric acid medium using a catalyst commonly known as Twitchell reagent has been believed for nearly half a century[1] to take place at the interface of oil and water, the reagent fulfilling the function of an efficient emulsifier. Recently, however, Lascaray[2] suggested that the reaction is essentially homogeneous and is carried out in the oil phase under the influence of water dissolved in this phase. Convincing as his arguments are, he did not consider the kinetic order of the reaction, the study of which proved valuable in elucidating the related fat hydrolysis by acidification[3]. This omission was probably due to the existence of an induction period in the Twitchell process which tends to obscure its kinetics.

Kinetic measurements of the Twitchell hydrolysis carried out in this Laboratory on a number of fats and with various reagents showed that the reaction is of the first order throughout, if started in the presence of 1 per cent by weight (calculated on the fat) of sulphuric acid in the form of 10 per cent aqueous solution. In order to approach industrial practice, this was followed by a continuous addition of water (up to 100 per cent by weight of the fat) as the hydrolysis proceeded, the mixture being kept at 100° C. A run conducted under these conditions is shown in the accompanying graph in which $\log \frac{a}{a-x}$ (a is saponification number, x is acid value) plotted against time gives a straight line, an indication of a first-order reaction. This kinetic order can be accounted for in the simplest way by assuming that the reaction takes place in the oil phase, which seems to confirm Lascaray's views. A heterogeneous reaction would be less likely to give a consistent kinetic order in view of the gradual addition of water and the accompanying changes in the interfacial surface, while hydrolysis in the water phase would probably result in zero-order kinetics.



At the same time, it appears that the initial concentration of sulphuric acid given above, which is higher than that usually employed, assists the hydrolysis by eliminating the induction period and therefore has a potential application in practice. Other consequences arising therefrom, such as the possibility of a continuous Twitchell process, will be discussed elsewhere.

L. HARTMAN

Fats Research Laboratory,
Department of Scientific and Industrial Research,
Wellington, New Zealand. Sept. 8.

[1] Lewkowitsch, J., *J. Soc. Chem. Indust.*, **22**, 67 (1903).
[2] Lascaray, L., *Indust. Eng. Chem.*, **41**, 786 (1949).
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Influence of Œstrogenic Hormones on the Reticulo-Endothelial System in the Guinea Pig

FEW observations have been recorded on the action of œstrogens on the reticulo-endothelial system, and there is considerable disagreement concerning their action upon the histiocytes. Fluhmann, working with the rabbit[1], and Nicol with the guinea pig[2], showed that injection of œstrogenic hormones stimulated the appearance and activity of phagocytic cells in the endometrium of the uterus, as evidenced by the capacity of the cells to take up trypan blue. This was associated with growth and enlargement of the uterus. They considered these cells to belong to the reticulo-endothelial system. Nicol believed they were derived partly via the blood stream and partly from the connective tissue of the endometrium, and that the activity of these cells in some manner prepared the endometrium for the subsequent action of the luteal hormone. Fluhmann regarded these cells as scavengers.

Leites and Riabow[3] stated that splenectomy combined with ovariectomy creates the optimum condition for the experimental blockade of the reticulo-endothelial system, while Haendel and Malet[4] pointed out that ovarian extracts stimulated the reticulo-endothelial cells. Mosinger[5] states that, in the guinea pig, prolonged administration of œstrogens for two to three months produces reticulo-endotheliosis, followed by sclerosis; but his results are not supported by photomicrographs.

At the present time, œstrogens are used in the treatment of prostatic carcinoma, in cancer of the breast, urinary bladder and other organs, with striking results, especially in the prostate. In the case of the prostate, the evidence at present points to the fact that the œstrogens act mainly through the anterior lobe of the pituitary, since similar results can be obtained by deep X-ray of the pituitary and by castration. The beneficial action is accompanied by fibrosis[6-8]; but no definite explanation has yet been found which explains the manner in which the response of the affected tissues is brought about[9]. The present research was designed to study this problem.

For the present investigations the effect of varying doses (0·1–5 mgm. daily for six days) of natural and synthetic œstrogens (œstradiol benzoate, œstrone, stilbœstrol and stilbœstrol dipropionate, D.B.E. (di-*P*-ethoxyphenyl-*B*-phenylbromo-ethylene), and dienœstrol, given intramuscularly or by mouth) on the reticulo-endothelial system in the spleen, liver, uterine horn, lymph nodes, skin and subcutaneous tissue, bone marrow and adrenal glands, was studied histologically on 79 double-ovariectomized sexually mature virgin guinea pigs injected with a 1 per cent solution of trypan blue in distilled water at the rate of 0·8 c.c. per 100 gm. body-weight. Of these animals, six were used as controls and received only injections of trypan blue subcutaneously. The remainder of the animals were divided into six groups, each of which received for six days a different daily dose of œstrogen and also a daily dose of trypan blue.

The effect was measured by the number of dye-bearing cells and the intensity of the vital-staining in the various organs and tissues examined. To ensure reliable comparison, the animals used were killed on what would have been the fifteenth day of the œstrous cycle had the ovaries been present.

It was found that the œstrogenic hormones produce hyperplasia and stimulation of the macrophages in