EFFECT OF WATER ON METHYL KETONE FORMATION IN BUTTEROIL

The existence in heated butteroil of a series of odd-numbered methyl ketones from C_5 through C_{15} has been well documented by Langler and Day (1). The isolation from butteroil of a corresponding series of β-keto esters as their pyrazolones was accomplished by Van der Ven et al. (5). Shortly afterwards, Parks et al. (2) succeeded in isolating as a group the glycerides containing the β-keto acids directly from butteroil and showed them to give rise to the methyl ketones upon heating in the presence of water. The greater stability of β-keto esters relative to unesterified β-keto acids indicates that hydrolysis takes place prior to methyl ketone formation and that a relationship should exist, within limits, between water concentration in the oil at the temperature at which the oil is heated and the concentration of methyl ketones formed.

Van der Ven et al. (5) were the first to show that methyl ketone formation could be inhibited by drying the oil prior to heating. Langler and Day (1) confirmed their observation and, in addition, demonstrated the accelerating effect of added water.

Prior to publication of those two papers, studies on the effect of a water gradient added to chemically dried butteroil was undertaken. Since this approach differed in several respects, the data should be of further usefulness to those interested in the methyl ketone problem.

PREPARATION OF BUTTEROIL

Freshly pasteurized cream was churned in an electric drink mixer, the butter isolated, melted at 52 C, and stored overnight at 4 C. The butter was remelted at 63 C and the buttermilk removed. The fat phase was centrifuged at 5,000 rpm (International Centrifuge, Size 1, Type SB)[1] and the clear oil pipetted off.

DRYING OF BUTTEROIL

Three hundred milliliters of butteroil was stirred magnetically with 8 g of finely powdered CaH_2 for 3 hr in a 500-ml ground-glass Erlenmeyer flask fitted with a $CaCl_2$ drying tube. The temperature of the oil was maintained just above the melting point of the fat. The suspension of CaH_2 in butteroil was transferred to two dry 200-ml centrifuge bottles fitted with tight rubber stoppers containing a self-sealing hole. The bottles were centrifuged for 15 min at 5,000 rpm.

GENERAL PROCEDURE

The clear butteroil was removed from the bottles with a 50-ml hypodermic syringe fitted with a 14-gauge 4-in. hypodermic needle and quickly transferred to clean 15-ml ampoules containing various amounts of distilled water. The ampoules were filled to a mark made at a point just above the juncture on the tapered portion of the neck, equivalent to 13 ml of butteroil. Dry nitrogen gas was carefully bubbled through the oil for 7 min, the ampoules sealed and incubated at 101 C for 6 hr in a constant-temperature oven. Preliminary trials had established that this particular oil afforded maximal ketone formation when incubated for 6 hr in the presence of enough water to saturate the oil at 101 C.

Carbonyls in the oil were assayed as their 2,4-dinitrophenylhydrazones following the procedures of Schwartz et al. (3). Preliminary trials showed that over 95% of the carbonyls formed under these conditions were methyl ketones. Consequently, class separation of the hydrazones was deemed unnecessary and the increase in the monocarbonyl content over that of an unheated sample was taken as methyl ketones formed.

RESULTS AND DISCUSSION

The effect of a water gradient on methyl ketone formation in the predried butteroil is shown in Figure 1. The data clearly show the dependence of ketone formation on the water content of the sample. Higher incubation temperatures would require shorter, and lower incubation temperatures longer, times to reach maximal ketone formation (4). A net of approximately 6.5 μmoles per 10 g of oil was the maximum potential of this particular sample. Other analyses (1, 4) have shown two to

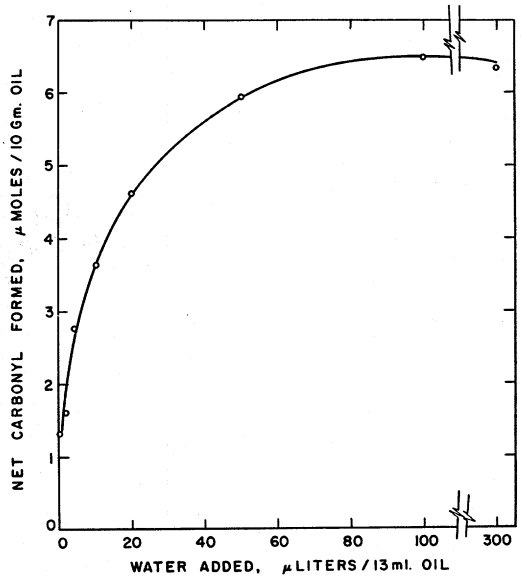

FIG. 1. Effect of water on methyl ketone formation in butteroil.

[1] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

three times this amount, so that one may expect a wide variation in the potential of different samples of butteroil.

A slight amount of ketone was produced at "zero" water concentration. In subsequent trials it was possible to dry the oil as described above so that no detectable ketone was produced even after heating for 24 hr at 101 C, and only a relatively small amount of carbonyls was produced after nine days.

A sample of the original butteroil not dried but otherwise treated exactly the same afforded a net value of 4.3 μmoles of ketone per 10 g, or approximately 66% of the maximum potential.

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