

Rate of Isomerization of 1,2-diolein

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1,2- and 1,3-diglycerides form an equilibrium mixture containing respectively 42 and 58 %^{1,2} 1,2-Diglycerides are important intermediates in the biological hydrolysis and synthesis of triglycerides and their rate of isomerization at physiological conditions is of apparent interest. It has been reported that in aqueous dispersion at 40° for 30 min 1,2- and 1,3-diolein is rather stable over the pH range of 6–8.³ The present investigation was undertaken to study more systematically the effect of pH on the rate of isomerization of 1,2-diolein at 37°. The diglyceride was dispersed in dilute isotropic solution in mixed mono-olein bile salt micelles.

Experimental. Racemic 1,2-dioleoyl-1-¹⁴C-glycerol was synthesized as previously described.⁴ 10 μ equiv. of the labeled diolein and 40 μ equiv. 1-mono-olein were transferred in heptane to a test tube. The solvent was evaporated at a temperature not exceeding room temperature and 10 ml solution of 6 mM sodium taurodeoxycholate in 0.15 M buffers of desired pH was added. On brief shaking the glyceride solution became clear and the test tube was incubated at 37°. 1 ml samples were removed at zero time and at suitable intervals up to 72 h depending on the pH of the solution. The 1 ml samples were transferred to test tubes containing 1 ml each of heptane, diethylether and ethanol. After shaking the upper phases were removed and aliquots chromatographed on thin-layer silicic acid plates. The separation of the 1,2- and 1,3-diglycerides and their determination by liquid scintillation counting was as earlier described.⁴ The zero time samples contained 3 %, as a mean, of 1,3-isomer, which was subtracted from the 1,3-diglyceride figures obtained after

Table 1. Effect of pH on $T/2$ of 1,2-diolein in mono-bile salt solution at 37° (see text).

pH	$T/2$	
3.4 (citrate-HCl)	8700	hours
5.8	296	»
6.3	175	»
7.0 (phosphate)	60	»
8.0	6.0	»
9.0 (borate-NaOH)	1.3	»
12.0 (NaOH)	0.057	» (3.42 min)

the incubations. The values for 1,3-diglycerides formed were plotted in a semilogarithmic scale and the $T/2$ calculated from the initial straight line of the curves obtained for each pH value. The $T/2$ values are given in Table 1.

The conditions of the experiments were chosen similar to those occurring under physiological conditions, *i.e.* in intestinal content during digestion or in experiments with cell preparations. Under these conditions — slightly acid or neutral pH-values — diglycerides with long chain fatty acids are stable enough to allow experiments over at least a few hours without any appreciable isomerization occurring. Diolein is relatively more stable than is 2-mono-olein under these conditions.⁵

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