23. The Acyl Wandering and the Racemization of Glycerides.

By Bunsuke SUZUKI and Yoshiyuki INOUE.

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One of the authors (S)¹⁾ had separated from the oils of marine animals various glycerides which have the non symmetrical constitutions but as far as they have been observed, all were optically inactive. The natural fats and oils, in general, are also either inactive or very slightly active but the activity is commonly attributed to the presence of some other active substances such as lecithin &c. The inactive state of the glycerides of natural fats and oils should be accounted for on one of the following bases, that is: that the glycerides occur in living tissues a priori as racemic bodies; that the active glycerides of the tissues are racemized in the ordinary sense of the term, or that the glycerides are inactivated and racemized by the acyl wandering during the preparation and the preservation.

The fact that the acyl groups of glycerides may, sometimes, wander²⁾ will be seen in our following experiments of obtaining $\alpha\alpha'$ -di-p-nitrobenzoyl glycerin instead of $\alpha\beta$ -di-p-nitrobenzoyl glycerin even though the process follows the course of forming the latter. Di-p-nitrobenzoyl methyl glycerin formed by the reactions a and b were identical while that prepared by the reaction c differed

If there had occurred no rearrangement of p-nitrobenzoyl group in the reaction a, the product would have been II, in reality, however, $\alpha\alpha'$ -

1) Proc. **3** (1927), 526-532; **4** (1928), 161-168; **5** (1929), 265-271.

2) Ber. **53** (1920), 1621, 1634.

1) J. Am. Chem. Soc. **51** (1929), 302.

fairly rapidly, one example (the solvent: chloroform) being shown in Table 2 and Fig. 1. The change is more rapid in acidic solutions, thus making it more difficult to prepare the free ester in optically pure state.

The similar decrease of rotation had been observed (Table 3) with the chloroform solution of the strychnin salt of α -phthalyl acetone glycerin which was prepared as,

The salt was fractionated in chloroform and a fraction the $[\alpha]_D^{19}$ of which was -20.77 , was obtained. The constitution of acetone glycerin is definite¹⁾ and well fixed so that we cannot assume an easy wandering of the phthalyl group. The racemization, therefore, must be due to other causes. Whatever the causes may be it is evident that the atoms or atomic groups of these glycerin derivatives are in a mobile state and are easily susceptible to the rearrangement of their positions in space.

TABLE 3.

Days	
0	-20.77
4	-18.57
8	-10.35
12	-10.35

In the case of the experiment of Table 2, the acyl wanderings in three ways are possible as shown in Fig. 2, if we assume that they occur freely. The wandering 3 will form an inactive and utterly different body, while 1 and 2 will form the racemic bodies of the same constitutions with the starting material. In case the wandering 3 runs we must expect that the original rotation (-8.87) is not recovered, contrary to the experimental result. In this case there is no reason to suppose that the wanderings 1 and 2 take place preferably. We assume, therefore, that the racemization has been caused by the changes of the spacial positions of atoms or atomic groups around the asymmetrical carbon.

Fig. 2.

If the glycerides of fatty acids likewise undergo the change we can understand why the specimens of natural fats and oils which we usually handle are inactive. As there are the possibilities of racemization, the estimation of rotation must be carried out as rapidly as possible after the preparation. Castor bean oil and pea nut oil have been prepared as hastily as possible by macerating the seeds with ether in a cold place. The ethereal solution was filtered and dried by adding an unusual amount of anhydrous sodium sulfate. Ether was

1) Ber. **53** (1920), 1606.

evaporated off, the observation tubes were filled directly with oils and the estimation made.

The magnitude of the rotation in both cases has been twice as great as ordinary value found in literature¹⁾ but it decreased in time, attaining in the end the constant and ordinary value.

The experiments with an old preparation of castor bean oil (J. Ph. IV) were carried out simultaneously but no change of the rotation was observed for a considerable length of time.

The natural fats and oils are the mixtures of various organic substances, so that our observations are not direct and definite concerning the glycerides but taking into consideration the facts proved with the synthesized glycerides as above mentioned, we take it as very probable that the inactivity of the ordinary preparations of natural fats and oils do not show necessarily that the glycerides preexist in living tissues in racemized state. On the contrary, it is more probable that the glycerides of non symmetrical constructions are active as other organic constituents of organisms are but that they lose the activity during the preparation as well as the preservation. In the long run, specially on certain conditions, the inactivation or the racemization by acyl wanderings among different carbon atoms may occur but the racemization which proceeds in comparatively short time is mainly due to that of the ordinary sense of the term.

TABLE 4.
(pea nut oil)

Time (h)	Rotation (100 mm)
0	-0.149
45	-0.084
53	-0.079
72	-0.065
81	-0.065
120	-0.065

TABLE 5.
(castor bean oil)

Time (h)	Rotation (50 mm)
0	+1.970
43	+1.915
67	+1.845
73	+1.833
91	+1.748
99	+1.732
114	+1.682
125	+1.666
142	+1.629
166	+1.584
213	+1.525
221	+1.510
237	+1.505
245	+1.501
261	+1.503
269	+1.502

Fig. 3.

1) Abderhalden: Handb. Biolog. Arbeitsmeth. Abt. I, Teil 6 S. 371.