

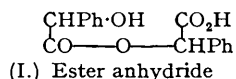
NOTE

The Effect of Heat on Mandelic Acid. By W. ROGIE ANGUS and R. P. OWEN.

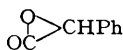
It has been observed that the m. p.'s and f. p.'s of *l*-mandelic acid are progressively and considerably lowered after each successive heating, and in order to ensure that this was not due to racemisation or incomplete resolution, *r*-mandelic acid has been similarly studied and found to exhibit the same behaviour. Since this work is only incidental to that reported in this vol., p. 227, however, it has not been pursued beyond the stage now reported, which has established that mandelic acid undergoes some change in structure and composition on being melted, and proved that the f. p. curve of mixtures of *r*- and *l*-mandelic acids cannot be determined by the usual methods. The lowering of the m. p. is reproducible and appears to be a function of the temperature and time of heating. When mandelic acid is esterified or acylated, this behaviour is not encountered, indicating that the phenomenon is due to some reaction involving either or both the hydroxyl and the carboxyl group, probably internal ester formation. The property of forming internal esters on heating is characteristic of α -hydroxy-acids, *e.g.*, lactic acid, and it is conceivable, therefore, that the behaviour of liquid (fused) mandelic acid will be analogous. Kishner (*J. Russ. Phys. Chem. Soc.*, 1925, **56**, 15) reported that when *r*-mandelic acid is heated alone to 130°, or in a sealed tube with water, the m. p. is lowered from 118° to 105–106°.

The first fusion gave a m. p. of 118° and a f. p. of 114.4° , the maximum temperature attained by the fused acid being 120° . The second fusion gave an arrest in the cooling curve at $112-114.8^{\circ}$, and after heating to 125° the subsequent cooling curve showed a f. p. of 108.4° . After further heating to 133° , the cooling curve showed the new f. p. to be 102.2° . The acid was kept at 133° for 30 mins., and the resulting compound showed no definite f. p. but passed gradually into a semi-solid state on cooling. When *r*-mandelic acid (m. p. 118°) was kept in a sealed glass tube at $120^{\circ} \pm 1^{\circ}$ for 6 days it became a yellow oil, cooling to a thick syrup which, with 2 : 4-dinitrophenylhydrazine, gave no indication of the presence of an aldehyde. Sodium carbonate completely removed the syrup from an ethereal solution, and on standing yielded a white precipitate (insoluble in hydrochloric acid) which, after two recrystallisations from alcohol and one from benzene, had m. p. 136° . As water seemed to be given off during the heating, the experiment was repeated except that the tube containing the mandelic acid was fitted with side tubes containing phosphoric anhydride. Water distilled into these side tubes. After being heated for 7 days, the resulting oil, on cooling, solidified into a transparent glass (m. p. $73-75^{\circ}$); this was easily soluble in acetone, chloroform, and alcohol, but only slightly soluble in ether, from which it could be extracted by cold sodium carbonate solution. On standing, the extract deposited a white, semi-liquid mass. The supernatant liquid was decanted, and the semi-liquid shaken with alcohol; a white precipitate was obtained which had no definite m. p. and was the sodium salt of some acid. Hydrolysis with hydrochloric acid gave a white precipitate, which, after repeated recrystallisation from alcohol, had m. p. 130° . Analysis of the glassy material obtained on heating gave C, 64.7, 64.5, 64.6; H, 4.6, 4.7, 4.8%, but no acceptable empirical formula can be derived from these results.

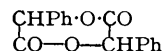
Bischoff and Walden (*Annalen*, 1894, **279**, 118) found that when mandelic acid was heated to $200-205^{\circ}$, water and benzaldehyde were given off and a glassy material (m. p. 60°) remained; this showed no reaction with sodium carbonate solution, and, from analysis, appeared to be a mixture of (I), (II), and (III). By comparing the analytical data now



(I.) Ester anhydride



(II.) Lactone



(III.) Double inner anhydride

obtained with those of Bischoff and Walden and with the values calculated for these condensation products, it becomes evident that the present results cannot be reconciled with their interpretation.

	C, %.	H, %.
Present results	64.6	4.7
B. & W.	69.7	4.8
Ester anhydride (I)	67.1	4.9
Lactone (II) and inner anhydride (III)	71.6	4.5

The conditions of heating in the two investigations were widely different and, although the condensation products would appear to be almost certainly a mixture, the low value for carbon now obtained casts doubt on the possibility of (I), (II), or (III) having been formed under the present experimental conditions. It would appear, therefore, that the extent to which condensation occurs and the products of condensation are governed by the temperature to which the acid is heated and by the method of heating.—UNIVERSITY COLLEGE OF N. WALES, BANGOR. [Received, January 5th, 1943.]