

NOTES.

Some Dissociation Constants. By ALEXANDER G. OGSTON.

CERTAIN dissociation constants, most of which have not hitherto been determined, are now reported. They were measured by a potentiometric technique—those of the phenols by the methods described by Ogston and Brown (*Trans. Faraday Soc.*, 1935, **31**, 166) and Ogston (*J.*, 1935, 1376), and the others by the micro-method of Ogston and Peters (*Biochem. J.*, 1936, **30**, 736), a fuller description of which will be published elsewhere. In accordance with the estimated accuracy of these methods, the values of p_K are recorded to the nearest 0.1 unit.

Phenols (at 17–18°).

	p_K .		Δp_K .		p_K , in MeOH.
	In H ₂ O.	In MeOH.			
Trichlorophenol	5.5	9.7	4.2	Pentachlorophenol	8.2
Tribromophenol	5.9	11.0	5.1	Pentabromophenol	8.0

The values of Δp_K suggest that, if tautomerism is impossible, phenols show a change between water and methyl alcohol of the same order as that shown by carboxylic acids. Tiessens (*Rec. trav. chim.*, 1929, **48**, 1066) obtained conductimetrically a p_K of 6.4 for trichlorophenol in water, but this method is very much more sensitive to the presence of impurities than is the potentiometric method. The solubility of tribromophenol in water was found to be 2.3×10^{-4} mol./l.

Purines (in water at 25°). These substances were supplied by Dr. J. M. Gulland.

	p_K .		p_K .
Hypoxanthine.....	8.7	Inosine (hypoxanthine riboside)	8.7
7-Methylhypoxanthine	8.8	Adenine	4.1
9-Methylhypoxanthine	8.9	Adenosine (adenine riboside)	3.6

α -Bromopropionyltyrosine (in water at 25°). This was prepared by Mr. E. R. Holiday. p_{K_1} (carboxyl group), 3.6; p_{K_2} (phenolic group), 10.3. The value of p_{K_2} is a little uncertain. Tyramine (in water at 25°). p_{K_1} (amino-group), 9.3; p_{K_2} (phenolic group), 10.9.

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Synthesis of 4' : 5-Dihydroxyflavone. By I. Z. SYED and T. S. WHEELER.

AN intimate mixture of 2 : 6-dihydroxyacetophenone (2 g.) (Limaye, *Ber.*, 1934, **67**, 12; Baker, J., 1934, 1954), *p*-anisic anhydride (20 g.), and sodium *p*-anisate (5 g.) was heated for 5 hours (oil-bath) at 180—190°, and alcohol (90 c.c.) added. The mixture was boiled under reflux for 2 hours, and again for 30 minutes after addition of a solution of potassium hydroxide (15 g.) in water (20 c.c.). Evaporation under reduced pressure left a brownish viscous residue, which was treated with water; the resulting yellow amorphous solid (1.5 g.) was boiled with excess of acetic anhydride and a few drops of pyridine for 1½ hours and poured on ice. The precipitated 5-acetoxy-4'-methoxyflavone separated from alcohol (charcoal) in white needles, m. p. 171—172° (Found : C, 69.6; H, 4.7. $C_{18}H_{14}O_6$ requires C, 69.7; H, 4.5%).

A solution of the acetyl derivative (0.5 g.) in glacial acetic acid (16 c.c.) and concentrated hydrochloric acid (25 c.c.) was heated at 100° for 45 minutes and diluted with water. The resulting precipitate of 5-hydroxy-4'-methoxyflavone separated from alcohol (charcoal) in pale yellow needles, m. p. 155—156°, which gave an orange-yellow coloration with magnesium and hydrochloric acid and a dark red-brown coloration with alcoholic ferric chloride (Found : C, 71.6; H, 4.5. $C_{18}H_{12}O_4$ requires C, 71.6; H, 4.5%).

5-Hydroxy-4'-methoxyflavone (0.5 g.), acetic anhydride (5 c.c.), and hydriodic acid (redistilled; *d*, 1.5; 3 c.c.) were heated together under reflux for 45 minutes and poured into sodium hydrogen sulphite solution at 0°. The dried precipitate was boiled with excess of acetic anhydride and a few drops of pyridine for 2 hours and poured on ice. The resulting precipitate of 4' : 5-diacetoxyflavone separated from alcohol (charcoal) in white needles, m. p. 179—180° (Found : C, 67.1; H, 4.1. $C_{18}H_{14}O_6$ requires C, 67.4; H, 4.1%).

The diacetyl derivative was hydrolysed in the same manner as 5-acetoxy-4'-methoxyflavone. 4' : 5-Dihydroxyflavone crystallised from alcohol in yellow needles, m. p. 237—240°, which gave an orange-yellow coloration with magnesium and hydrochloric acid and a dark red-brown coloration with alcoholic ferric chloride (Found : C, 70.4; H, 4.2. $C_{18}H_{10}O_4$ requires C, 70.9; H, 3.9%).

3-Anisoylation in the fusion is precluded by the analytical results.

All the analyses are micro-analyses by Dr. Schoeller.—ROYAL INSTITUTE OF SCIENCE, BOMBAY. [Received, July 10th, 1936.]
