

CCCXXXI.—*A Synthesis of 2-Hydroxy-4 : 5-dimethoxybenzoic Acid.*

By FRANK S. H. HEAD and ALEXANDER ROBERTSON.

By the oxidation of dehydrodeguelin with potassium permanganate, Clark (*J. Amer. Chem. Soc.*, 1931, **53**, 2007) has isolated a hydroxy-dimethoxybenzoic acid, giving a blue ferric chloride reaction and considered to be 2-hydroxy-4 : 5-dimethoxybenzoic acid; we have prepared this acid from 2-hydroxy-4 : 5-dimethoxybenzaldehyde (*J.*, 1930, 2434).

2-Acetoxy-4 : 5-dimethoxybenzaldehyde.—On repeated crystallisation from methyl alcohol, 2-hydroxy-4 : 5-dimethoxybenzaldehyde (*loc. cit.*) formed straw-coloured, thick plates, m. p. 107°. Acetylation of the aldehyde (4 g.) by means of acetic anhydride (12 c.c.) and pyridine (4 c.c.) at 37° for 16 hours afforded the *acetate*, which crystallised from dilute alcohol as a voluminous mass of hair-like needles (4 g.), m. p. 95° (Found: C, 58.6; H, 5.5. $C_{11}H_{12}O_5$

requires C, 58.9; H, 5.4%). The compound is readily soluble in acetic acid and acetone and does not give a ferric chloride reaction.

2-Hydroxy-4 : 5-dimethoxybenzoic Acid.—Potassium permanganate (2.5 g.), dissolved in water (60 c.c.), was gradually added to a solution of 2-acetoxy-4 : 5-dimethoxybenzaldehyde (2 g.) in acetone (50 c.c.) maintained at 50°. After 15 minutes, the reaction mixture, cooled to 0°, was cleared with sulphur dioxide, and on slow evaporation of the acetone, 2-acetoxy-4 : 5-dimethoxybenzoic acid crystallised. A solution of the compound in saturated aqueous sodium bicarbonate (15 c.c.) was filtered from a trace of unchanged aldehyde and acidified with 15% hydrochloric acid. The acid, thus precipitated, crystallised from dilute acetone in colourless needles (1.6 g.), m. p. 166° (Found : C, 55.0; H, 5.1. $C_{11}H_{12}O_6$ requires C, 55.0; H, 5.0%). It is readily soluble in alcohol or acetic acid and sparingly soluble in water.

A solution of the acetyl derivative (1 g.) in 10% aqueous potassium hydroxide (10 c.c.) was kept at room temperature for 2 hours. Acidification of the solution with dilute hydrochloric acid gave 2-hydroxy-4 : 5-dimethoxybenzoic acid, which crystallised from dilute acetone in clusters of almost colourless, rhombic prisms (0.5 g.) showing characteristic twinning, m. p. 213—214° (decomp.) [Found : C, 54.3; H, 5.4; OMe, 30.7. Calc. for $C_7H_4O_3(OMe)_2$: C, 54.5; H, 5.1; OMe, 31.3%]. The acid is readily soluble in warm alcohol or acetone and sparingly soluble in warm water. It separates from alcohol in clusters of squat prisms, from dilute acetic acid in aggregates of irregular plates, and from a solution in aqueous sodium bicarbonate on acidification in colourless needles. With alcoholic ferric chloride the compound gives an intense blue coloration which assumes a faint tinge of purple on dilution with water.

LONDON SCHOOL OF HYGIENE AND
TROPICAL MEDICINE,
UNIVERSITY OF LONDON.

EAST LONDON COLLEGE.

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