10. *Natural and Synthetic Indican.*

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THOUGH a specimen of natural indican was not available when the synthesis of this glucoside was achieved (J., 1927, 1937), the characteristic properties of the synthetic material left no doubt that it was identical with the natural glucoside. We have repeated the synthesis and found that synthetic indican, anhydrous material, m. p. 176°, $[\alpha]_{5461}^{19°}$ — 77·64° in water (c, 1·0), and trihydrate, m. p. 58°, $[\alpha]_{5461}^{19°}$ — 65·63° in water (c, 1·0), was identical with a natural specimen (Perkin and Bloxam, J., 1907, **91**, 1715), anhydrous material, m. p. 176°, $[\alpha]_{5461}^{19°}$ — 77·75° in water (c, 0·6), and trihydrate, m. p. 57°. Both the natural and the synthetic compound were hydrolysed by emulsin (cf. Beyerinck, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 101).

Penta-acetylindican.—The simultaneous acetylation and decarboxylation of 3-β-glucosidoxyindole-2-carboxylic acid had given rise to a penta-acetylindican (A) (*loc. cit.*) which separated from MeOH or EtOH in needles, m. p. 148°, $[\alpha]_{5461}^{20°}$ — 47·93° in acetone (c, 0·4). Acetylation of indican (synthetic) with hot Ac_2O (5 c.c.) and NaOAc (0·5 g.) has now furnished an almost theo. yield of a second form (B) of the penta-acetate, which crystallised from MeOH in squat prisms, m. p. 112°, $[\alpha]_{5461}^{18°}$ — 47·11° in acetone (c, 0·6) (Found : C, 57·0; H, 5·6. Calc. for $C_{24}H_{27}O_{11}N$: C, 57·0; H, 5·4%). On being heated above its m. p., (B) solidified and changed at 120—130° into (A), which then melted at 147°. A mixture of (A) and (B) had m. p. 147—148°.

In a similar manner the acetylation of the natural glucoside yielded the penta-acetate, m. p. 112°, $[\alpha]_{5461}^{18°}$ — 47·20° in acetone (c, 0·6), which had properties identical with those of (B) derived from synthetic indican (Found : C, 57·0; H, 5·6%).

The interconversion of the forms (A) and (B) was also effected as follows : A hot alc. solution of (B) was cooled to 50°, a crystal of (A) added, and the glucoside pptd. by the gradual addition of H_2O. Next day the compound was collected and dissolved in warm 70% MeOH, and on being nucleated the solution deposited (A) in needles, m. p. 147°, which had m. p. and mixed m. p. 148° after recrystn. from EtOH. When a trace of (B) was added to a solution of (A) in EtOH at 50° and the mixture kept at room temp., the whole of the penta-acetate separated in the form (B), m. p. 112°, in the course of several hours.

The rotations of the following compounds used in the synthesis of indican (*loc. cit.*) are now recorded : methyl 3-*O*-tetra-acetyl-β-glucosidoxyindole-2-carboxylate, $[\alpha]_{5461}^{18°}$ — 47·67° in acetone (c, 0·7); potassium 3-β-glucosidoxyindole-2-carboxylate, $[\alpha]_{5461}^{18°}$ — 48·41° in H_2O (c, 0·6).

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