and Hinshelwood, are given in *Chemistry and Industry*[2], where full references are to be found. An extension of the measurements to the bromination of ethers in 50 and 75 per cent acetic acid indicates that, within the range so far examined, change in medium and/or reagent is accompanied by a change in the activation energy such that $E_1 = mE_2$, where m is a constant independent of the constitution of the ether. Details of these measurements will be published later.

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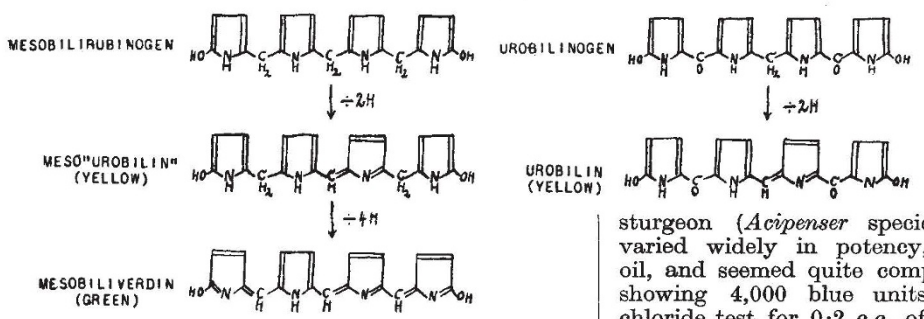
[1] *J. Chem. Soc.*, 1079; 1934.
[2] *Chem. and Ind.*, 254; 1932.

Urobilinogen

SINCE Fischer and Meyer-Betz isolated crystals of mesobilirubinogen from a pathological urine[1], it has been generally assumed that urobilinogen and mesobilirubinogen are identical. However, Watson[2] was unable to reduce crystalline urobilin from fæces or urine to crystals of mesobilirubinogen.

My experiments give further evidence of the non-identity of the two chromogens. Natural urobilin and 'urobilin' from mesobilirubinogen show a very slight, but definite, difference in the position of their absorption maxima in acid alcohol (490·9 and 493·2 mμ respectively in the Hartridge reversion spectroscope). With ferric chloride, mesobilirubinogen and also its 'urobilin' are dehydrogenated to mesobiliverdin and mesobiliviolin, whereas urobilinogen from normal urine and fæces and from pathological urine (splenic anæmia) is only changed into urobilin[3]; the latter is completely stable against ferric chloride. It makes no difference whether urobilinogen is obtained directly from urine or fæces or by reduction of urobilin with sodium amalgam; nor is mesobilirubinogen changed into urobilin, if subjected to the procedures involved in the preparation of the latter from fæces or urine.

These observations prove that the two chromogens differ in their skeletal system, not (or besides) in the side chains. For the deep colour of the green and violet pigments is caused by a chain of conjugated



double bonds going through the system of the four pyrrole rings. The assumption of two carbonyl groups standing between the pyrrole rings I and II and between III and IV in urobilinogen instead of two CH_2-groups in mesobilirubinogen would appear to be in agreement with the analytical findings of Watson for urobilin and would explain the impossibility of further dehydrogenation beyond the urobilin state. In the above formulæ the side chains have been left out. Experiments to prove the carbonyl groups and to reduce them to CH_2-groups are being made.

Thus urobilinogen is not a simple product of reduction of bilirubin by the intestinal bacteria, but a product of dismutation or oxidation of bilirubin. That the bile pigment is subjected to such processes in the intestine is shown by the presence of mesobiliviolin in the fæces (Watson). This contains four hydrogen atoms more than bilirubin in the side chains (two ethyl groups instead of two vinyls), but as I found recently, four atoms of hydrogen less than bilirubin in the skeletal system.

It seems extremely improbable, however, that Fischer was mistaken in the isolation and identification of his mesobilirubinogen. The only remaining explanation is that in some pathological cases (that of Fischer was one of liver cirrhosis[4]) mesobilirubinogen may occur instead of urobilinogen[5]. It seems not impossible that in cases of extensive liver damage, bilirubin is reduced by the liver, perhaps an infected liver, to mesobilirubinogen and that this reaches the kidney without passing the intestine[6]. The differentiation of the two urobilinogens is therefore of importance in clinical diagnosis. It should be mentioned that there is no reason for the clinician, who bases his determinations of urobilin directly or indirectly on the mesobilirubinogen standard, to get alarmed. There is apparently no difference between the two chromogens as regards their standard value for the Terwen—Ehrlich estimation.

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[1] Fischer and Meyer-Betz, *Z. physiol. Chem.*, **75**, 232; 1911.
[2] Watson, *Z. physiol. Chem.*, **204**, 57; 1932. **208**, 101; 1932. **221**, 145; 1933. *Proc. Exp. Biol. and Med.*, **30**, 1207, 1210; 1933.
[3] Lemberg, *Chem. and Ind.*, **53**, 179; 1934.
[4] Fischer, *Z. f. Biol.*, **65**, 163; 1915.
[5] Hoesch (*Biochem. Z.*, **187**, 107; 1926) observed that some urines gave violin bands with ferric chloride, whereas others did not.
[6] Lichtenstein, *Münchener mediz. Wochenschr.*, **72**, 1962; 1925. Weiss, *Biochem. Z.*, **207**, 151; 1929.

Fish Liver Oils Rich in Vitamin A

THE outstandingly high vitamin A content of the liver of the halibut (*Hippoglossus hippoglossus*) has led to considerable commercial interest in any species giving a liver oil of a potency comparable with halibut liver oil. In the same family as the halibut, several of the larger species give rich oils, but they are not of the same order of potency as good halibut oils. Samples of sturgeon (*Acipenser* species) liver oils examined varied widely in potency, as with halibut liver oil, and seemed quite comparable, the best sample showing 4,000 blue units in the antimony trichloride test for 0·2 c.c. of a 20 per cent solution. Recently, the liver oil of the tunny fish (*Thunnus thynnus*) has been examined. The oil was rich in vitamin A, the blue values for three samples being 1,927, 1,993 and 2,724. The livers contained about 20–25 per cent of oil. The particular fish used were caught off Scarborough.

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