specimen of biosynthetic *l*-menthol glucuronide[6] (see table).

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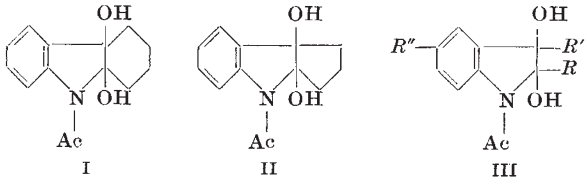
[1] Bergmann, M., and Wolff, W. W., *Ber. dtsch. chem. Ges.*, **56**, 1060 (1923).
[2] Smolenski, K., *Roczniki Chemji*, **3**, 153 (1923); *Chem. Zent.*, **2**, 317 (1924).
[3] Hardegger, E., and Spitz, D., *Helv. Chim. Acta*, **32**, 2165 (1949).
[4] Hardegger, E., and Spitz, D., *Helv. Chim. Acta*, **33**, 337 (1950).
[5] Fernandez-Garcia, R., Amoros, L., Blay, H., Santiago, E., Soltero-Diaz, H., and Colon, A. A., *El Crisol*, **4**, 40 (1950); *Chem. Abs.*, **45**, 555 (1951).
[6] Quick, A. J., *J. Biol. Chem.*, **61**, 667 (1924).

Perhydroxylation of Indole Derivatives by Osmium Tetroxide

THE very various transformations undergone by 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole (I) have recently aroused some interest[1]. The related compound (II) does not undergo Wagner–Meerwein rearrangements like those given by (I)[2]. Witkop[1a] has satisfactorily explained this failure by pointing out that such rearrangement of (II) would involve the formation of a four-membered ring compound. While this suggestion is convincing, it seemed worth while to confirm that the diols (I) and (II) possess similar configurations, for the Wagner–Meerwein change is markedly affected by the *cis*- or *trans*-configuration of the compound involved, only the *cis*-diols becoming readily rearranged[3]. Further, (I) and (II) have hitherto been prepared by rather different methods.



Most of the small number of known diols of type (III) have been obtained by Perkin, Plant and their associates[4], by the action of nitric acid in acetic acid upon the acylated indoles. We have now prepared such compounds by treating various N-acetylindoles with osmium tetroxide and pyridine in benzene solution, and afterwards hydrolysing the highly crystalline, fawn-coloured esters which were formed. Thus, N-acetyltetrahydrocarbazole gave (I) (found: C, 68·3; H, 7·1; calc. for $C_{14}H_{17}O_3N$: C, 68·0; H, 6·9 per cent), melting point 203–204° alone and mixed with an authentic specimen; and (II) (found: C, 66·7; H, 6·6; calc. for $C_{13}H_{15}O_3N$: C, 66·9; H, 6·5 per cent), melting point 149–151°, identical with the preparation of Plant and Tomlinson[2], was obtained similarly.

Other examples, obtained from the appropriate indoles, which might be mentioned, are (III; $R=R'=$ Ph; $R''=$ H), melting point 206–208° (found: C, 76·8; H, 5·6; $C_{22}H_{19}O_3N$ requires C, 76·5; H, 5·5 per cent), and (III; $R=R'=R''=$Me), melting point 102–108° (found: C, 66·3; H, 7·4; $C_{13}H_{17}O_3N$ requires C, 66·3; H, 7·3 per cent). Likewise, N-acetyl-2 : 3-dimethylindole gave a product of melting point 130–133° (Plant and Whitaker[5] give melting point 132–134° for (III; $R=R'=$Me; $R''=$H)).

The method of preparation of these compounds proves conclusively that they possess the *cis*-configuration[6].

A more detailed and extended description of these and other experiments in perhydroxylation of indoles will be given later. We are greatly indebted to Dr. Plant and Dr. Tomlinson, who kindly provided specimens of their preparations of (I) and (II).

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[1] (*a*) Witkop, *J. Amer. Chem. Soc.*, **72**, 614 (1950). (*b*) Patrick and Witkop, *ibid.*, p. 633. (*c*) Witkop and Patrick, *Experientia*, **6**, 183 (1950) and later publications. (*d*) Plant and Robinson, *Nature*, **165**, 36 (1950). (*e*) Plant and Tomlinson, *J. Chem. Soc.*, 2127 (1950).
[2] Plant and Tomlinson, *J. Chem. Soc.*, 298 (1933).
[3] Whcland, "Advanced Organic Chemistry", 519 (2nd edit., New York, 1949).
[4] This work is summarized by Schofield, *Quart. Rev. Chem. Soc.*, **4**, 391 (1950).
[5] Plant and Whitaker, *J. Chem. Soc.*, 283 (1940).
[6] Criegee, *Annalen*, **522**, 75 (1936).

Estimation of Deoxycorticosterone by a Modified Hagedorn–Jensen Procedure

Heard, Sobel and Venning[1] demonstrated that estimation of the reducing powers of lipid-soluble extracts prepared from urine provides a measure of the corticosteroid content of such extracts. The value of the method depends upon the presence of characteristic reducing groups in the corticosteroid molecules, making it possible to utilize oxidation reactions similar to those used in the estimation of sugars. Various methods based on this principle have been reviewed by Sprechler[2].

It is of interest in this connexion to report some experimental findings on a convenient and rapid procedure which we have recently developed for the estimation of pure deoxycorticosterone and its acetate in aqueous methyl alcohol solution, based on a modification of the Hagedorn–Jensen blood sugar method[3]. This modification was made possible by employing the reaction which takes place when ammonium molybdate solution is added to potassium ferrocyanide solution in presence of strong acetic acid. The intensity of the brown coloration produced is a direct measure of the amount of ferrocyanide present and may be estimated by a colorimetric or absorptiometric method, thereby avoiding the necessity for the thiosulphate titration.

The standard procedure adopted was as follows: 1 ml. of 50 per cent aqueous methyl alcohol containing deoxycorticosterone or its acetate was measured into a tube, treated with 2 ml. of the Hagedorn–Jensen[3] alkaline ferricyanide reagent, and the tube immersed in a boiling water-bath for 3 min. A blank estimation on 1 ml. of 50 per cent aqueous methyl alcohol was carried out simultaneously. After heating, the tubes were rapidly cooled and the contents made up to 6 ml. with distilled water. 1 ml. of 10 per cent ammonium molybdate solution was added, followed by 5 ml. glacial acetic acid, and, after mixing, the colours (which are stable up to at least 1 hr.) were read on a Spekker photoelectric absorptiometer, using Ilford violet filters.