

a similar procedure and shown to be identical with the higher-melting isomer B from streptomycin B by melting point (161–162°, no depression on admixture of isomer B), rotation ($[\alpha]^{25D} -65^\circ$ (*c*, 1.1 in chloroform)), and analysis (C, 49.19; H, 5.98; S, 8.41; CH₃CO, 44.7). The dextrorotatory isomer A from streptomycin B presumably represents the previously unknown anomeric α -thioethyl-tetracetyl-D-mannoside.

Dihydrostreptomycin B trihydrochloride¹, m. p. 194–5° (cor. dec.), $[\alpha]^{25D} -55^\circ$ (*c*, 0.9 in water), on treatment with 3% methanolic hydrogen chloride for forty hours at room temperature and subsequent acetylation yielded α -methyl pentaacetyl dihydrostreptobiosaminide^{4,5} m. p. 192–3° (cor.), $[\alpha]^{25D} -119^\circ$ (*c*, 0.49 in chloroform) and β -methyl tetraacetyl D-mannopyranoside, $[\alpha]^{25D} -50^\circ$ (*c*, 0.69 in chloroform), m. p. 160–161° (cor.), unchanged on admixture of an authentic specimen.

Anal. Calcd. for C₁₅H₂₂O₁₀: C, 49.72; H, 6.12; OCH₃, 8.56; CH₃CO, 47.5. Found: C, 49.61; H, 6.08; OCH₃, 8.35; CH₃CO, 48.5.

These results together with analytical data previously reported¹ for the reineckate¹ and hydrochloride of streptomycin B indicate that streptomycin B is made up of streptidine, streptobiosamine and D-mannose joined glycosidically to form a triacidic base of the composition C₂₇H₄₉O₁₇N₇.

Anal. Calcd. for C₂₇H₄₉O₁₇N₇·3HCr[(NH₃)₂(SCN)₄]·2H₂O: C, 26.97; H, 4.29; N, 20.15; S, 22.11; Cr, 8.98. Found¹ (after drying *in vacuo* at 80° for two hours): C, 26.89; H, 4.24; N, 20.1; S, 22.2; Cr, 8.70. Calcd. for C₂₇H₄₉O₁₇N₇·3HCl·H₂O: C, 37.26; H, 6.24; N, 11.25; Cl, 12.23. Found (after drying *in vacuo* at 140° for two hours): C, 36.85; H, 6.11; N, 11.3; Cl, 12.83.

(4) J. Fried and O. Wintersteiner, *THIS JOURNAL*, **69**, 79 (1947).

(5) Q. R. Bartz, J. Controulis, H. M. Crooks, Jr., and M. C. Rebstock, *ibid.*, **68**, 2163 (1946).

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THE REACTION OF IODONIUM SALTS WITH THIOL COMPOUNDS

Sir:

In the interesting paper by Freedlander and French¹ on the chemotherapy of certain iodonium compounds, they have suggested tentatively that the activity of the iodonium compounds may, in some cases, be due to a reaction with certain thiol groups essential to the microorganisms.

For some time we have been engaged in the study of the reactions which occur between iodonium salts and sulfhydryl compounds. We have found, for example, that diphenyliodonium chloride reacts in an aqueous solution with thioglycolic

acid (kept neutral with sodium carbonate) to produce phenyl iodide and S-phenylthioglycolic acid (21% yield), m. p. 58–60° (lit. 61–63°²); sparingly soluble in water, soluble in benzene. This reaction is a rapid one at the boiling point of the solution. It also proceeds at room temperature but at a reduced rate. When thioglycolic acid dissolved in water is shaken with diphenyliodonium chloride, sodium carbonate, tellurium and ether at room temperature, diphenyltellurium is formed. The latter compound can be isolated from the ether layer as the yellow dibromide, m. p. 199–200°. The reaction with tellurium is an interesting one because of the possibility of a free radical mechanism, although other interpretations are possible.³

It has also been found that diphenyliodonium chloride reacts with other thiol compounds, such as thiophenol and cysteine. In the latter case the product is S-phenylcysteine, m. p. 200° (lit. 201–202°)⁴; calcd. for C₉H₁₁O₂SN: S, 16.3. Found: S, 16.2. All the iodonium reactions show a characteristic transient yellow color or precipitate.

The above reactions should be of interest from the standpoint of enzyme studies. Further work is in progress and we hope to communicate full details at a later date. We are very grateful to the Alberta Branch of the Canadian Cancer Society for financial aid in support of this work.

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(2) Gilman and Webb, *THIS JOURNAL*, **62**, 987 (1940).

(3) Sandin, McClure and Irwin, *THIS JOURNAL*, **61**, 2944 (1939); Sandin and Brown, unpublished work.

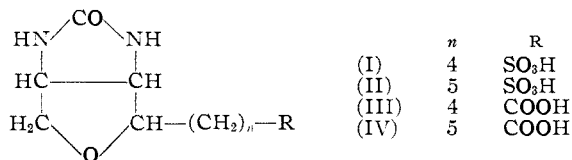
(4) Clarke and Inouye, *J. Biol. Chem.*, **94**, 541 (1931).

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FURAN AND TETRAHYDROFURAN DERIVATIVES. VIII. THE SYNTHESIS OF THE SULFONIC ACID ANALOGS OF OXYBIOTIN AND HOMOOXYBIOTIN

Sir:

In connection with our studies on the relationships of chemical structure and biological activity in the biotin and oxybiotin series,¹ we became interested in *dl*-oxybiotin sulfonic acid (I) and *dl*-homoöxybiotin sulfonic acid (II), the sulfonic acid analogs of *dl*-oxybiotin (III) and *dl*-homoöxybiotin (IV), respectively. In this communication we wish to record the synthesis of these two compounds.



(1) Hofmann, Chen, Bridgwater and Axelrod, *THIS JOURNAL*, **69**, 191 (1947).

(1) Freedlander and French, *Proc. Soc. Exptl. Biol. Med.*, **63**, 319 (1946); *C. A.*, **41**, 2115 (1947).