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Steroids. LXVI¹. Microbiological Hydroxylation of Steroids in Position 21

Following the discovery by PETERSON *et al.*² of the transformation of progesterone into 11 α -hydroxyprogesterone by molds of the Mucorales family, a number of hydroxylations of steroids by microorganisms have been reported. The introduction of the hydroxy group into position 6 β ³, 7 β ⁴, 8 ξ ⁵, 11 α ⁶, 11 β ⁷, 14 α ⁸, 15 ξ ⁹, 16 α ¹⁰, and 17 α ¹¹, has been described.

The recent publication by MEYSTRE, VISCHER, and WETTSTEIN¹² describing the hydroxylation of steroids in position 21 by fungi of the Ophiobolus family has prompted us to report on our own independent work on the introduction of the hydroxy group into position 21, by *Aspergillus niger* ATCC 9142. Progesterone was incubated with a 48 h growth of *Aspergillus niger* ATCC 9142 on a peptone-molasses medium for 96 to 144 h; extraction of the fermentation liquor with chloroform and chromatography on silica gel yielded desoxycorticosterone, identified by its physical constants (m.p. 142-143°, $[\alpha]^{20D} + 185^\circ$ (ethanol) and by its infrared spectrum.

Fermentation of the following steroid substrates with *Aspergillus niger* ATCC 9142 gave the corresponding 21-hydroxy derivatives:

Substrates

- 19-nor-progesterone
- 11-keto-progesterone
- 11 α -hydroxy-progesterone
- 11 β -hydroxy-progesterone
- 6 β -hydroxy-progesterone
- 14 α -hydroxy-progesterone

Conversion Products

- 19-nor-desoxycorticosterone
- 11-dehydrocorticosterone
- 11-epicorticosterone
- corticosterone
- 6 β -hydroxy-desoxycorticosterone
- 14 α -hydroxy-desoxycorticosterone

In all cases, paper chromatography indicated the presence of more polar compounds in addition to the conversion products. The characterization of the oxidation products was based on comparison of chromatographic behavior¹, sulfuric acid chromogen curve², melting point, optical rotation and infrared spectra with those of the known compounds.

A. ZAFFARONI, C. CASAS CAMPILLO,
F. CORDOBA, and G. ROSENKRANZ

*Research Laboratories, Syntex S. A., Mexico D. F.,
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Zusammenfassung

Die Einführung einer Hydroxylgruppe in die 21-Stellung gewisser Pregnanderivate mittels *Aspergillus niger* ATCC 9142 wird beschrieben.

¹ A. ZAFFARONI, Recent Progr. Hormone Res. 8, 51 (1953).

² A. ZAFFARONI, Recent Progr. Hormone Res. 8, 51 (1953); J. Amer. Chem. Soc. 72, 3828 (1950).

Studies on the Action of X-Rays on Aqueous Solutions of Nucleic Acids and Some Nucleotides

It has been known for some time that the action of ionising radiations on desoxyribonucleic acid (D.N.A.) solutions leads to a loss of viscosity¹. The significance of the slow post-irradiation viscosity loss ("after effect") noted by several workers², has been investigated in detail by BUTLER and CONWAY³. These authors concluded that it occurred only if oxygen was present during irradiation and suggested that it may be due to oxidative processes involving hydrogen peroxide and to the slow decomposition of primarily formed hydroperoxides.

We have suggested⁴ that chemical reactions of the free radicals produced by the action of the radiation⁵ can

¹ A. H. SPARROW and F. M. ROSENFELD, Science 104, 245 (1946). - B. TAYLOR, J. P. GREENSTEIN, and A. HOLLANDER, Arch. Biochem. 16, 19 (1948). - G. C. BUTLER, Can. J. Research. B 27, 972 (1949). - D. B. SMITH and G. C. BUTLER, J. Amer. Chem. Soc. 73, 258 (1951). - G. LIMPEROS and W. A. MOSHER, Amer. J. Roentgenol. Radiat. Therapy 63, 681 (1950).

² B. TAYLOR, J. P. GREENSTEIN, and A. HOLLANDER, Arch. Biochem. 16, 19 (1948). - G. C. BUTLER, Can. J. Research. B 27, 972 (1949). - G. LIMPEROS and W. A. MOSHER, Amer. J. Roentgenol. Radiat. Therapy 63, 681 (1950).

³ J. A. V. BUTLER and B. E. CONWAY, J. Chem. Soc. 1950, 3418; 1952, 834.

⁴ G. SCHOLES and J. WEISS, Nature 171, 920 (1953).

⁵ J. WEISS, Nature 153, 748 (1944); Brit. J. Radiol. Suppl. 1, 56 (1947).

¹ Paper LXV, J. IRIARTE, G. ROSENKRANZ, and F. SONDEIMER, J. Org. Chem. (in press).

² D. H. PETERSON and H. C. MURRAY, J. Am. Chem. Soc. 74, 1871 (1952).

³ S. H. EPPSTEIN *et al.*, J. Amer. Chem. Soc. 75, 408 (1953). - H. C. MURRAY and D. H. PETERSON, U. S. Pat. 2,602,769 (July 8, 1952).

⁴ H. C. MURRAY and D. H. PETERSON, U. S. Pat. 2,602,769 (July 8, 1952). - F. W. KAHT *et al.*, Exper. 8, 422 (1952).

⁵ H. C. MURRAY and D. H. PETERSON, U. S. Pat. 2,602,769 (July 8, 1952).

⁶ D. H. PETERSON and H. C. MURRAY, J. Amer. Chem. Soc. 74, 1871 (1952). - S. H. EPPSTEIN *et al.*, J. Amer. Chem. Soc. 75, 408 (1953). - H. C. MURRAY and D. H. PETERSON, U. S. Pat. 2,602,769 (July 8, 1952). - D. H. PETERSON *et al.*, J. Amer. Chem. Soc. 74, 5933 (1952). - P. D. MEISTER *et al.*, J. Amer. Chem. Soc. 75, 55 (1953). - J. FRIED *et al.*, J. Amer. Chem. Soc. 74, 3962 (1952). - O. MANCERA *et al.*, J. Amer. Chem. Soc. 74, 3711 (1952).

⁷ D. R. COLINGSWORTH *et al.*, J. Amer. Chem. Soc. 74, 2381 (1952). - F. R. HANSON *et al.*, J. Amer. Chem. Soc. 75, 5369 (1953). - G. M. SHULL *et al.*, U. S. Pat. 2,658,023 (Nov. 3, 1953).

⁸ P. D. MEISTER *et al.*, Abstr. 123rd Meet. Amer. Chem. Soc., Los Angeles, Calif., March 15-19 (1953), p. 5C.

⁹ J. FRIED *et al.*, Recent Progr. Hormone Res. 10 (in press).

¹⁰ D. PERLMAN *et al.*, J. Amer. Chem. Soc. 74, 2126 (1952). - E. VISCHER *et al.*, Helv. chim. Acta 37, 321 (1954).

¹¹ P. D. MEISTER *et al.*, J. Amer. Chem. Soc. 76, 4050 (1954). - C. MEYSTRE *et al.*, Helv. chim. Acta 37, 1548 (1954).

¹² C. MEYSTRE *et al.*, Helv. chim. Acta 37, 1548 (1954).