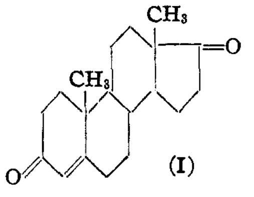
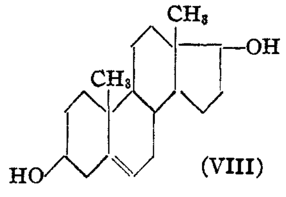
constitution which exhibits the relationship between rat-tests and capon-test potency characteristic of testicular extracts. The natural expectation that this observation would prove significant in the elucidation of the constitution of the testicular hormone was fulfilled with surprising promptitude.

Laqueur, *et al.* [*Z. physiol. Chem.*, **233,** 281 (1935), appearing on June 7] described the isolation of a testicular hormone of unknown constitution (m. p. 154°), with a capon activity of about 10 γ, which was called testosterone (VI). Although (VI) showed the characteristic difference in capon-test and rat-test effectiveness, the published figures do not permit a rigorous comparison with (I).

At London, Laqueur expressed the opinion, based on chemical evidence, that (VI) is an isoandrosterone. The physiological activity of (I) suggested further investigation of (VI) and we have recently learned by private communication from Prof. Laqueur that (VI) yields (I) upon oxidation. Therefore it appears highly probable that formula (II) is that of testosterone (VI).

In pursuance of the program outlined in our paper (*loc. cit.*) we reduced androstene-3-ol-17-one (VII) with sodium and alcohol to androstene-3,17-diol (VIII), m. p. 175–178° corr. Utilizing the greater reactivity of the 3-substituent we partially oxidized the dibromide of (VIII) to produce (II) upon subsequent debromination. We also partially saponified the diacetate of (VIII) to produce the 17-monoacetate, which, upon oxidation of its dibromide and debromination, should yield the acetate of (II).


(I)


(VIII)

Further details will be published elsewhere, and we hope that the previous announcement of our research program (*loc. cit.*), together with the work initiated before the isolation of testosterone, may serve as a reservation of this project.

Footnote (*Sept. 7*).—At the time this note was written the author was unaware that testosterone (androstene-3-one-17-ol) had already been synthesized in his laboratory in Zürich by his assistants. The substance was made by partially saponifying the unsaturated diol diacetate and oxidation of the monoacetate dibromide.

GEORGE HERBERT JONES LABORATORY L. RUZICKA
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

RECEIVED AUGUST 20, 1935

EXPERIMENTS ON THE CONSTITUTION AND PREPARATION OF THE TESTICULAR HORMONE

Sir:

In the preceding Communication of L. Ruzicka it is evident from the dates given that the publication of his experiments on the preparation of androstendione-3,17 antedates the publication of our experiments on the preparation of this same compound. However, we would like to state that the particular issue of the *Helv. Chim. Acta* to which reference is made was not received in our library until August 8, three days after the publication of our experiments, and that a sample of dehydroandrosterone prepared by our method (received by THIS JOURNAL, June 4) was sent to Professor Butenandt on May 20. We were unaware, therefore, of Professor Ruzicka's experiments, and our suggestion as to the constitution of the testicular hormone and our experiments on its preparation were made independently. At the time of the appearance of his article in the *Helv. Chim. Acta* we were engaged in the preparation of 17-hydroxy-androsten-one-3, and we had succeeded in preparing androstendiol (m. p. 175°), and its diacetate (m. p. 159°) by the reduction of our synthetically prepared dehydroandrosterone when the above Communication reached us. In view of Professor Ruzicka's Communication, and of his request that this project be reserved we are discontinuing our work in this particular direction.

FRICK CHEMICAL LABORATORY EVERETT S. WALLIS
PRINCETON UNIVERSITY E. FERNHOLZ
PRINCETON, N. J.

RECEIVED SEPTEMBER 23, 1935

THE PREPARATION OF β-CHLOROVINYLARSINE SULFIDE

Sir:

β-Chlorovinylarsine sulfide was first described by Lewis and Stiegler [THIS JOURNAL, **47,** 2546 (1925)] as a clear, amber-colored plastic mass insoluble in the usual solvents other than carbon disulfide and possessing an extraordinarily irritating and noxious odor.

We have succeeded in obtaining this substance, β-chlorovinylarsine sulfide, in a crystalline condition by the following procedure. Hydrogen sulfide was conducted for two hours through a solution of 45 g. of β-chlorovinyldichloroarsine (b. p. 78° at 12 mm.) in 50 cc. of alcohol. The solution became noticeably warmer and a yellow viscous oil gradually separated out. After two hours separation ceased and this was taken as the end of the reaction. The resulting product was an amber-yellow viscous oil which adhered to the walls of the flask. The alcoholic solution was poured off, the oil washed repeatedly with alcohol and then dissolved with warming in carbon disulfide. After cooling and distilling off part of the solvent, the substance separated in crystalline form. In order to obtain a more complete separation an equal volume of benzene may be added to the solution; yield 20 g. or 51% of the theoretical. After recrystallization from benzene and drying in a vacuum desiccator, the melting point was 114°.

Anal. Calcd. for C_2H_2ClSAs: As, 44.49; Cl, 21.05; S, 19.03. Found: As, 44.55; Cl, 21.06; S, 19.27.

β-Chlorovinylarsine sulfide crystallizes in cubes, possesses a pale yellow color and a weak, not unpleasant, odor; is easily soluble in carbon disulfide, less so in benzene and ether and insoluble in water. Under the influence of sunlight the substance acquires an orange color.

MOSCOW, U. S. S. R. S. L. WARSCHAWSKI

RECEIVED JULY 17, 1935

THE ISOLATION OF CROTYL AND METHYLVINYLCARBINYL BROMIDES

Sir:

The composition of bromide mixtures arising from the action of hydrogen bromide and phosphorus tribromide on crotyl alcohol or methylvinylcarbinol has been the subject of much discussion. Some claim that pure products [Charon, *Ann. chim. phys.*, [7] **17,** 216 (1899); Prévost, *Ann. chim.*, **10,** 113 (1928); Claisen and Tietze, *Ber.*, **59B,** 2344 (1926); Juvala, *Ber.*, **63B,** 1989 (1930)] are obtained from alcohols of this type while others report the formation of mixtures of bromides but have not separated them [Baudrenghien, *Bull soc. chim. Belg.*, **31,** 160 (1922); Meisenheimer and Link, *Ann.*, **479,** 211 (1930); Young and Prater, This Journal, **54,** 404 (1932); Gredy and Piaux, *Bull. soc. chim.*, [5] **1,** 1481 (1934)]. The bromides obtained in this Laboratory have always been mixtures. We have recently separated these mixtures into the primary (crotyl bromide) and secondary (methylvinylcarbinyl bromide) isomers by fractional distillation at 0°. The properties are $n^{23}\text{D}$ 1.4805 and 1.4612; $d^{25}{}_4$ 1.3335 and 1.2998; b. p. 49° and 31.0° at 93 mm., >107° and 86.5° at 760 mm., and +2.0° at 5 mm. and −2.0° at 14 mm. for the primary and secondary isomers, respectively. Mixtures of these bromides may be analyzed from density or refractive index measurements since these properties are linear functions of the composition.

Both of the pure bromides rearranged to an equilibrium mixture of 14% secondary and 86% primary in a few days at room temperature, in less than one hour at 75° and in less than five minutes at 100°. If a mixture of the bromides is subjected to slow distillation at atmospheric pressure through a 100-cm. packed column, almost pure secondary bromide is obtained as a distillate. Equilibrium is so rapidly established in the boiler that the secondary bromide is replaced as fast as it is removed from the top of the column.

It is now evident that the bromides reported by Juvala, Baudrenghien and Gredy and Piaux having $n^{23}\text{D}$ 1.4750 to 1.4759 contained from 24–29% of secondary bromide. Their compositions were dependent on the method of distillation and had nothing to do with the method of preparation. The bromides used by Gredy and Piaux must have gone to equilibrium after the refractive index was taken and before the Raman spectra were measured, since their analysis of 90% primary and 10% secondary is qualitatively in agreement with the equilibrium composition and not with the composition calculated from the refractive index.

In the light of these developments, crotyl alcohol and methylvinylcarbinol are being converted into bromide mixtures by various reagents under conditions designed to avoid rearrangement of the product. The composition of these mixtures will be reported in the near future.

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RECEIVED AUGUST 12, 1935