and the melting point of the hydrochloride as 218°; acid oxalate, m. p. 208°; acid sulphate, m. p. 238° and neutral sulphate, m. p. 220°.

The filtrate from the ammonium hydroxide precipitate was extracted with ether. Upon standing a mixed mass of alkaloid crystals formed. From the mixed crystals a few large crystals were separated out mechanically. These weighed 6 Gm. and melted partially at 100° and finally at 140–142°, with a rotation of  $[\alpha]_{\rm D}^{25} - 272$ . They are probably the same as C.1.

The remainder of the mixed crystal mass, weighing 30 Gm. was treated with hot 95 per cent alcohol which dissolved out the clear crystals and left the round opaque nodules (D.2.).

Alkaloid D.2.—These insoluble nodules weighed 10 Gm., m. p. 197–198°. Recrystallized from chloroform-alcohol they melted at 200–202°. The chloroformic solution was yellow with a green fluorescence. The acid oxalate forms prisms, m. p. 242–243°. This alkaloid is optically inactive and contains no methoxy groups. It is similar to Corydalis C isolated from *C. ambigua* by Chou and which he compares to protopine.

The alcoholic solution from which the insoluble alkaloid D.2. had been filtered did not form any crystals upon standing. After solution in acid and precipitation with alkali the alkaloidal material was dissolved in alcohol and treated with charcoal. After standing several weeks some large crystals formed. These crystals melted at 140–142°. They have an optical rotation of  $[\alpha]_D^{28} - 275$ . The hydrochloride forms columns from hot water, m. p. 260°. A methoxy determination gave 32.7 per cent methoxy groups. This alkaloid is very similar if not identical with alkaloid C.1.

## AN ATTEMPT TO KETONIZE ERGOSTEROL.\*,1

# BY E. MONESS AND W. G. CHRISTIANSEN.

At the Indianapolis meeting of the American Chemical Society in March 1931, Dr. Bills reported on the heat of combustion of ergosterol. From his work he concludes that in the activation of ergosterol there is no absorption of energy, but that the activation depends upon chemical isomerization.

It is known that ergosterol has a complex molecule, part of which is alicyclic and contains an alcoholic hydroxyl group and an ethylenic linkage. Aliphatic ketones are capable of existing in an enolic form, and in some instances the compound is a mixture of the keto and enol forms. The extent to which the compound exists either as the keto or enol form is dependent upon the structure of the compound. Acetyl acetone may be used as an example:

$$\begin{array}{c} CH_{a}C-CH_{2}-C-CH_{a} \longleftrightarrow CH_{a}C-CH = C--CH_{a}\\ \parallel \qquad \parallel \qquad \parallel \qquad \parallel \qquad \parallel \qquad \parallel \\ O \qquad O \qquad O \qquad OH \end{array}$$

When a compound is capable of reacting in both the keto and enol forms it will react entirely in accordance with the ketonic structure or entirely in accordance with the enolic structure, depending on the particular reaction which is being ap-

<sup>\*</sup> Scientific Section, A. PH. A., Washington meeting, 1935. <sup>1</sup> Research Department of the Chemical and Pharmaceutical Laboratories, E. R. Squibb and Sons, Brooklyn, N. Y.

plied. Ergosterol is known in its enolic form but as yet there is no evidence of its existence in the keto form.

If it is true that the activation of ergosterol by ultraviolet light depends upon a chemical isomerization, and if ergosterol could be made to form a keto isomer, such rearrangement should result in a substance possessing anti-rachitic activity, or capable of being activated. The simplest reagent which reacts specifically with ketones is hydroxylamine, and this substance was therefore used in an attempt to form the oxime of ergosterol. We realized, of course, that a possible keto-enol isomerization might not be the explanation of the activation of ergosterol, but in view of Dr. Bills' conclusion that activation is due to chemical isomerization, and in view of the fact that keto-enol isomerism is here theoretically possible, it was of sufficient interest to warrant investigation.

In carrying out the actual experiment we subjected ergosterol to a reaction with hydroxylamine under conditions which were known to give an almost quantitative yield in the formation of the oxime of cyclohexanone. Ergosterol, however, failed to react and was recovered unchanged from the reaction mixture.

#### EXPERIMENTAL.

First, we repeated the work of Bayer (1) in the preparation of the oxime of cyclohexanone, in order to make certain that the conditions of the work were such as to insure a nearly quantitative yield of the oxime. We then proceeded to react ergosterol with hydroxylamine, under the same conditions, as follows:

1.152 Gm. of pure ergosterol, m. p.  $158^{\circ}$  C., were dissolved in 40 cc. of boiling absolute alcohol under reflux. To this solution was added 0.4 Gm. (2 mols.) of hydroxylamine hydrochloride, and 0.6 Gm. (slightly more than 2 mols.) of sodium bicarbonate. The mixture was refluxed for 3 hours. It was then evaporated to dryness and extracted with ether. The ether extract was evaporated to dryness, yielding 0.8 Gm. of a white substance having a melting point of  $157^{\circ}$  C. We had thus recovered most of our ergosterol in an unchanged condition.

## REFERENCE.

(1) Bayer, Ann., 102, 102 (1894).

### OPENING OF THE LEXINGTON FEDERAL NARCOTIC FARM.

The first United States Narcotic Farm, near Lexington, Ky., will open for the reception for admissions on or about May 1st. According to the Journal A. M. A., of February 16th, it will accommodate a maximum of 1000 persons and is designed to accommodate males only. Its object and purposes are to rehabilitate, restore to health and train to be selfsupporting and self-reliant those who are admitted thereto. The control, management and discipline are to be maintained for the safekeeping of the individual and the protection of the community. Experiments are to be carried on to determine the best methods of treatment and research in this field, and the results disseminated to the medical profession and the general public to the end that states may make some provision for establishing a similar policy for helping to solve the problem of drug addiction. The function of the institution at Lexington therefore assumes the character of a treatment and research center and of an educational and rehabilitation center with certain custodial features superimposed.