

(c) The activity of various cardiac drugs on cardiac muscle and other tissues.

(d) The development of a method of biological assay for the standardization of the cardiac group of drugs.

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PHYTOCHEMICAL NOTES.*¹No. 112. PRELIMINARY CHEMICAL EXAMINATION OF *CORYDALIS AUREA*.

BY HAROLD EPPSON.

Thirty-five kilograms of air-dried herb collected in full bloom near Laramie, Wyoming, at an altitude of about 7400 ft. were percolated with alcohol in a Lloyd extractor, yielding 8920 Gm. of extractive, calculated on a moisture-free basis.

The alcoholic extract was extracted with petroleum ether, yielding an oily extract that weighed 1382 Gm. This was saponified with alcoholic KOH in the usual manner.

Isolation of Dimyristylcarbinol.—The saponified petroleum-ether extract was heated to remove the alcohol. Upon cooling a solid, waxy, yellow-red material formed on the surface. Additional similar material was obtained from the ether extract of the saponified fat. After repeated recrystallization from alcohol and methyl alcohol a light cream-colored material was obtained which melted at 81–82°. The acetylated product, after two recrystallizations from alcohol, melted at 44–45°. Elementary analyses yielded the following results:

	I.	II.	Computed for $C_{29}H_{48}O_2$.
C	79.4%	79.5%	79.3%
H	13.3%	13.4%	13.3%

Upon saponification the acetate yielded as saponification values, 124, 119 and 120, respectively. The regenerated alcohol, after recrystallization from both methyl and ethyl alcohol, melted at 81–82°. Elementary analyses yielded the following results:

	I.	II.	Computed for $C_{27}H_{44}O$.
C	81.6%	81.8%	81.7%
H	14.2%	14.2%	14.2%

* Scientific Section, A. PH. A., Madison meeting, 1933.

¹ From the laboratory of Edward Kremers.

According to Kipping,¹ dimyristylcarbinol melts at 80.5–81° and its acetate at 45–45.5°. Sando² records the melting point of the alcohol at 81.5–82°.

The total amount of non-saponifiable material obtained by shaking the saponified mixture with ether amounted to 340 Gm.

The saponified fat, after removal of the non-saponifiable material, was treated with sulphuric acid to liberate the free fatty acids. The free acids were treated according to the Twitchel³ method, with slight modifications and thereby separated into 180 Gm. of solid fatty acids and 234 Gm. of liquid fatty acids.

The main alcoholic extract after extraction with petroleum ether was diluted with water and acetic acid to about 33 liters, sufficient acetic acid being added to make it about one per cent acid. After standing for two and one-half days the precipitated resinous fraction, weighing about 540 Gm. air dry, was filtered off. The filtrate was made alkaline with ammonium hydroxide. A flocculent gray-green precipitate formed and was filtered off.

Alkaloid C.1.—This gray-green precipitate was extracted with ether while still moist. It was then dried somewhat and extracted with ether made alkaline with ammonium hydroxide. Upon standing in an open beaker, the ether extract deposited a mass of nodular crystals weighing 53.5 Gm., and colored green from contaminating chlorophyll.

By fractional crystallization 22 Gm. of alkaloid, m. p. 135–138° and 31 Gm. of alkaloid, m. p. 135–139° were obtained, called alkaloid C.1. This alkaloid is colorless in concentrated H₂SO₄ and gives immediate red color with concentrated HNO₃. It is optically active, $[\alpha]_D^{20} -265$ (in chloroform or absolute alcohol). Upon recrystallization the m. p. was 138–140° and $[\alpha]_D^{25} -271$. Determination of the methoxy groups gave 33.47 and 32.7 per cent, respectively.

Upon cooling the HI mixture from the methoxy determination a precipitate formed. This was filtered off and washed with water, giving a cream-colored powder, m. p. 278–280° with decomposition.

Alkaloid C.2.—The ammonium hydroxide precipitate after extraction with ether was dried and powdered and, further extracted with ether, made alkaline with ammonium hydroxide. This ether upon evaporation deposited some needle-like crystals of alkaloid C.2. These were recrystallized from alcohol when they formed as flat shiny plates, melting at 148–149°. They gave a yellow color instantly with concentrated HNO₃.

This alkaloid is optically inactive. The hydrochloride forms needles, recrystallized from hot water, melting at 238–239°. A methoxy determination run by the Hewitt and Moore modification of the Zeisel method gave 33.7 and 34 per cent, respectively. From the formula given below by Chou this shows the presence of four methoxyl groups. The demethylated product recovered from the HI reaction mixture formed a cream-colored crystalline precipitate, m. p. gradually darkens, decomposes 278–280°.

This alkaloid is probably the same as that isolated from *Corydalis aurea* by Heyl⁴ and from *C. ambigua* by Chou.⁵ Chou gives the formula as C₂₀H₂₃O₄N

¹ *J. Chem. Soc.*, 63, 459 (1893).

² *J. Biol. Chem.*, 56, 457 (1927).

³ *Ind. Eng. Chem.*, 13, 806 (1921).

⁴ *Apoth. Ztg.*, 25, 137 (1910).

⁵ *Chinese J. Physiol.*, 2, 203 (1928); 3, 69 (1929).

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 $[\alpha]_D^{25} - 272$. 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.

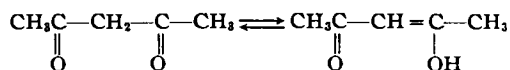
The alcoholic solution from which the insoluble alkaloid D.2. had been filtered did not form any crystals upon standing. After solution in acid and precipitation with alkali the alkaloidal material was dissolved in alcohol and treated with charcoal. After standing several weeks some large crystals formed. 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:



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-

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