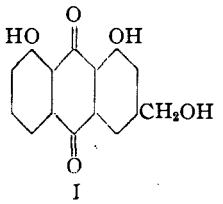
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Anthrone Series. V. The Structure of the So-called Aglycone of Aloin[1]

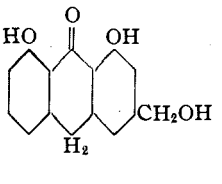
BY THOMAS F. McDONNELL WITH JOHN H. GARDNER

The structure of aloin has been the subject of numerous investigations. It has been shown that on hydrolysis with hydrochloric acid, it yields 1,8-dihydroxyanthraquinone-3-carbinol (I, aloe-emodin)[2] and *d*-arabinose.[3] Because of these facts, aloin was long regarded by most workers as a *d*-arabinoside of aloe-emodin. Recently, Hauser[4] pointed out that a solution of aloin and borax becomes deep red on heating and gives a green fluorescence, reactions which are characteristic of anthrones.[5] On heating the borax solution for some time and acidifying, Hauser obtained a product which he regarded as an aloe-emodin anthrone and which, on oxidation, yielded aloe-emodin. Cahn and Simonsen[6] repeated Hauser's work and found that methyl alcohol as well as the anthrone was formed on the borax hydrolysis of aloin. They explained this by formulating aloin as a tetrahydroanthraquinone derivative.

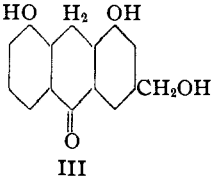
There are two possible anthrones derivable from aloe-emodin, the 9-anthrone (II) and the 10-anthrone (III). The determination of the structure of the product obtained by Hauser's method is of importance in the elucidation of the structure of aloin and is the object of this investigation.



I



II



III

On reducing the anthrone obtained by the borax hydrolysis of aloin there was obtained a product which was found to be identical with chrysophanic acid-9-anthrone (1,8-dihydroxy-3-methyl-9-anthrone), which had been prepared previously by Naylor and Gardner.[7] The identity was confirmed by conversion of the reduction product to the acetate, which was identical with chrysophanic acid-9-anthranol acetate, and by oxidation to chrysophanic acid (1,8-dihydroxy-3-methylanthraquinone). It can therefore be regarded as proved that aloin yields aloe-emodin-9-anthrone (1,8-dihydroxy-9-anthrone-3-carbinol, II) on hydrolysis with borax solution.

Experimental

Aloe-emodin-9-anthrone.—Aloin from Curacao aloes was hydrolyzed by the method of Hauser. The anthrone was purified by crystallization from toluene and then from 75% acetic acid; m. p. 201.0–202.5°.[8] Hauser gives m. p. 194–195°.[4]

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.47; H, 4.56.

Acetate of Aloe-emodin-9-anthranol.—Aloe-emodin-9-anthrone was acetylated in the usual way with acetic anhydride and sodium acetate; yellow needles from glacial acetic acid followed by 75% acetic acid, m. p. 197.2–197.8°.

Anal. Calcd. for $C_{23}H_{20}O_8$: C, 65.08; H, 4.75. Found: C, 64.69; H, 4.62.

Reduction of Aloe-emodin-9-anthrone.—A boiling solution of 0.4 g. of aloe-emodin-9-anthrone in 35 cc. of glacial acetic acid was treated with 16 g. of stannous chloride in 30 cc. of hot concd. hydrochloric acid. After boiling for one hour, 5 g. of 20-mesh tin was added, followed by 20 cc. of concd. hydrochloric acid in small portions during four hours, with continuous boiling. On diluting with hot water and cooling there was obtained a yellow solid; yield, 0.27 g. after crystallization from alcohol. It was finally purified by crystallization from glacial acetic acid; m. p. 202.5–203.8°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 74.99; H, 4.77.

A mixture of equal parts of this product and chrysophanic acid-9-anthrone prepared by the method of Naylor and Gardner,[7] m. p. 203–204°, melted at 202–204°, proving that the compounds were identical.

Acetate of Chrysophanic Acid-9-anthranol.—On acetylating with acetic anhydride and sodium acetate there were obtained yellow prisms, m. p. 238.2–238.8°, from glacial acetic acid.

(1) Based upon a portion of a thesis submitted by Thomas F. McDonnell in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1933.

(2) Oesterle, *Arch. Pharm.*, **237**, 81 (1898).

(3) Leger, *Compt. rend.*, **150**, 1695 (1910).

(4) Hauser, *Pharm. Acta Helv.*, **6**, 79 (1931).

(5) Schoneten, *Jahresber. Pharm.*, **112** (1892); cited by Hauser, Ref. 4.

(6) Cahn and Simonsen, *J. Chem. Soc.*, 2573 (1932).

(7) Naylor and Gardner, THIS JOURNAL, **53**, 4114 (1931).

(8) All melting points in this paper are corrected.

Anal. Calcd. for $C_{21}H_{18}O_6$: C, 68.85; H, 4.92. Found: C, 68.53; H, 4.90.

A mixture of equal parts of this substance and the acetate of chrysophanic acid-9-anthranol obtained from chrysarobin,[7] m. p. 239.6–240°, melted at 237.8–238.2°, showing that the compounds were identical.

Chrysophanic Acid.—A solution of 0.065 g. of chrysophanic acid-9-anthrone, obtained from aloe-emodin-9-anthrone, in 4 cc. of glacial acetic acid was treated with 0.036 g. of chromic acid in a little water. The mixture was warmed on the steam-bath for a half hour, diluted with water and cooled; yield, 0.02 g. of orange powder, m. p. 190.5–192°, from alcohol, using "Norit."

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 70.87; H, 3.94. Found: C, 71.29; H, 3.80.

A mixture of equal parts of this substance and chrysophanic acid prepared from chrysarobin, m. p. 193–194°, melted at 191–192.5°, proving that the compounds were identical.

Summary

The product obtained from aloin by hydrolysis with an aqueous solution of borax is 1,8-dihydroxy-9-anthrone-3-carbinol.

ST. LOUIS, MISSOURI RECEIVED FEBRUARY 26, 1934

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

Lonchocarpic Acid, a New Compound from a Species of Lonchocarpus

BY HOWARD A. JONES

In the course of an investigation of plants for their rotenone content numerous species of *Derris* and *Lonchocarpus* have been studied in the Insecticide Division. A recent sample of root material of an unknown species of *Lonchocarpus* from Venezuela gave no qualitative color test for rotenone.[1] When subjected to the usual carbon tetrachloride extraction used in determining rotenone,[2] about 2.3% of crystalline material readily separated from the extract. This material, purified by recrystallization from acetone and carbon tetrachloride, had a melting point of 201° and a methoxyl content of 7.0%.

A larger sample of the same root was then obtained from the same source, and the bark and inner portion of the root were separated. These portions were extracted separately with acetone, the extracts were evaporated to small volume, and the material was caused to crystallize by the addition of carbon tetrachloride and subsequent cooling. The bark yielded 3.7% crystalline material and 7.2% total extractives, while the inner portion of the root gave 1.5% crystalline material and 2.4% total extractives. The average for the whole root based on the proportion of bark to inner portion was 2.1% crystalline material and 3.7% total extractives. The crystalline material separated more readily and in an apparently purer state from the extract of the bark than from that of the inner portion of the root.

The crystalline material from the inner portion of the root was recrystallized, but could not be obtained in a satisfactorily pure condition. The melting point of the recrystallized material was 197°.

The crystalline material from the bark as first separated had a melting point of 199°. It was recrystallized once from acetone and carbon tetrachloride and then from acetone alone. A melting point of 201.5° was obtained on this purified material. (The compound also occasionally exhibited a melting point of 220–221°, probably indicating dimorphism.) A further recrystallization from amyl acetate did not change the melting point.

The pure material is readily soluble in acetone and chloroform, sparingly soluble in benzene and amyl acetate, and only slightly soluble in carbon tetrachloride and petroleum ether. It is optically inactive in chloroform solution. It contains no nitrogen. The analytical figures for carbon, hydrogen and methoxyl together with the results of the titration of the material with alkali indicate an empirical formula of $C_{26}H_{26}O_6$, on the assumption that the compound is a monocarboxylic acid with one methoxyl group. The name "lonchocarpic acid" has been given to the compound.

Experimental

Preparation of Lonchocarpic Acid.—Five hundred grams of ground root of *Lonchocarpus sp.* was extracted with acetone. The extract was evaporated to about 300 cc. and carbon tetrachloride added while hot until precipitation began. The extract was then cooled in the refrigerator for several days. The crystalline material was separated, the filtrate evaporated to about one-half the volume and again cooled. A second crop of crystals was obtained.

(1) Jones and Smith, *Ind. Eng. Chem., Anal. Ed.*, **5**, 75 (1933).
(2) Jones, *ibid.*, **5**, 23 (1933).