rapid change in temperature is apparently related to the violence of the reaction. Curve B indicates the entire lack of violence found in the acetic acid modification. In Curve C, representing the curve obtained in the ferrous sulfate modification, the rise of temperature after the evolution of bubbles can be seen to approximate 15° within one-half minute. In Curve D, which represents the data from the boric acid modification, the rise of temperature is approximately one-half of that found in Curve C and, as will be noted by the slopes of the two curves, the rise is more gradual.

Summary

1. It has been found possible to decrease the violence of the reaction of the ferrous sulfate modification of the Skraup quinoline synthesis by the addition of boric acid.
2. The yield of quinoline has been increased by the addition of the boric acid.
3. A comparison of the vigor of the reactions has been obtained.

DENVER, COLORADO

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY]

THE STEROLS OF ERGOT. II. THE OCCURRENCE OF DIHYDRO-ERGOSTEROL

BY FREDERICK W. HEYL AND ORLO F. SWOAP[1]

RECEIVED JUNE 9, 1930 PUBLISHED SEPTEMBER 5, 1930

Recently[2] we briefly described the preliminary fractionation of "ergosterol" from ergot fat. Crude ergosterol was prepared from an ether solution of the unsaponifiable fraction by precipitation with petroleum ether. We have now studied this ether–petroleum ether filtrate. Originally our expectation was that fungisterol might be found there in such proportion that its isolation would be somewhat more readily accomplished. In this study we have incidentally isolated pure α-dihydro-ergosterol, which was first described by Windaus and Brunken.[3] They report a specific rotation of −19.3°, and a melting point of 173–174°. The acetate melts at 180–181° and for $[\alpha]_D$ they found −21.0° Heilbron, Johnstone and Spring[4] report that the melting point of α-dihydro-ergosterol acetate varies from 179–180 to 173°, depending upon the duration of the acetylation process. The rotation, $[\alpha]_{5461}^{21}$, varied from −25.3 to −30.3°.

---

[1] Holder of the Upjohn Coöperative Fellowship at Kalamazoo College (1929–1930). This paper is based upon the thesis presented by Mr. Swoap to the Faculty of Kalamazoo College, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Hart and Heyl, THIS JOURNAL, **52**, 2013 (1930).

[3] Windaus and Brunken, *Ann.*, **460**, 232 (1928).

[4] Heilbron, Johnstone and Spring, *J. Chem. Soc.*, 2248 (1929).

α-Dihydro-ergosterol, isolated from ergot fat, melted at 172.5–175°, gave an acetate melting at 176–177° and for $[\alpha]_D^{26}$ we found −20.6°. The benzoate melted at 153–155° and the color tests agreed with those known for this substance.

This result is what one might expect since Anderson has repeatedly shown that sitosterol is accompanied by dihydrositosterol in corn oil,[5] wheat embryo,[6] and rice bran.[7] Consequently a mixture of very closely related alcohols in various stages of saturation might be anticipated in the unsaponifiable matter of ergot fat.

Experimental

A quantity of petroleum ether–ether filtrates from ergosterol had separated a quantity of crystalline material upon long standing. This was filtered off and lightly washed with petroleum ether. A quantity (74 g.) was fractionally crystallized from ethyl acetate. The top fraction melted at 158.5–160°; intermediate fractions showed a series of melting points of about 121–125°, and the bottom fractions melted below 100°. A further quantity (312 g.) of the crude material was fractionally crystallized in the same way and separated into 33 fractions after an elaborate system of recrystallizations.

Fractions 6, 7 and 8, aggregating about 5 g., showed rotations of −22.5, −22.5 and −19.1°, respectively, and from these, by further elaborate fractional crystallization from alcohol, α-dihydro-ergosterol was isolated. For example, the fractionation of fraction 8 (2.3 g.) yielded the following fractions:

Fraction no.	Weight, g.	M. p., °C.	$[\alpha]_D$
8A	0.45	165–167	−25.0
8B	.14	159–164	−25.4
8C	.24	161–164	−22.66
8D	.08	156–159	−12.4
8E	.15	137–150	− 9.5

Of these, A, B and C were acetylated separately:

Fraction no.	Weight, g.	M. p., °C.	$[\alpha]_D$
Acetate 8A	0.26	171–173	−19.75
8B	.10	169–173	−19.0
8C	.20	167–173	−18.1

8A, 8B and 8C were combined with acetate fraction 7C (m. p. 167–170°; $[\alpha]_D$ −17.0). The acetate was recrystallized several times from ethyl alcohol, when it melted at 176–177°.

Anal. Calcd. for $C_{27}H_{43}OCOCH_3$: C, 81.60; H, 10.87. Found: C, 82.02; H, 10.60.

The above acetate was saponified with 3% methyl alcoholic potash and the recovered alcohol was crystallized three times from methyl alcohol. Pure α-dihydro-ergosterol as leafy needles melting at 172.5–175° and $[\alpha]_D^{26}$ − 20.6 was isolated.

Anal. Calcd. for $C_{27}H_{43}OH$: C, 84.30; H, 11.54. Found: C, 84.52; H, 11.54.

Color Tests of α-Dihydro-ergosterol.—With the Rosenheim trichloro-acetic acid, a

---

[5] Anderson, This Journal, **46**, 1450 (1924).

[6] Anderson and Nabenhauer, *ibid.*, **46**, 1717 (1924).

[7] Nabenhauer and Anderson, *ibid.*, **48**, 2972 (1926).

completely negative test resulted. With Salkowski test, the chloroform was colorless and the sulfuric acid layer orange-yellow. With the Liebermann-Burchard test the color transitions were as follows: very slight pink, transitory lavender, deep blue, slowly to green.

α-Dihydro-ergosterol Benzoate.—The alcohol (0.1 g.) was dissolved in pyridine (2 cc.) and 2 drops of benzoyl chloride added. The benzoate precipitated and after long standing was filtered off and recrystallized from alcohol. It melted at 153–155°.

Anal. Calcd. for $C_{27}H_{43}OCOC_6H_5$: C, 83.55; H, 9.90. Found: C, 83.10; H, 10.33.

The benzoate gave the same color reactions described above and in addition gave a positive reaction to the Heilbron and Spring[8] modification of the Tortelli–Jaffe reaction.

Reduction to α-Ergostenol.—Three-tenths of a gram of the acetate was reduced with Adams' platinum oxide catalyst as previously described[9] and a top fraction of α-ergostenol acetate melting at 110–111° was obtained. Upon saponification with 3% methyl alcoholic potash, α-ergostenol melting at 133° was obtained.

Summary

From the unsaponifiable fraction of ergot fat, α-dihydro-ergosterol has been isolated. The alcohol itself melted at 172.5–175° and gave $[\alpha]_D^{26}$ $-20.6°$. The acetate of α-dihydro-ergosterol melted at 176–177° and the benzoate at 153–155°. The color reactions agree exactly with those described by Windaus and Brunken, and by Heilbron and Spring.

KALAMAZOO, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ORGANIC GERMANIUM DERIVATIVES. III. DIPHENYL GERMANIUM DIHALIDES AND DIPHENYL GERMANIUM IMINE

BY CHARLES A. KRAUS AND CECIL L. BROWN

RECEIVED JUNE 12, 1930 PUBLISHED SEPTEMBER 5, 1930

I. Introduction

The present is one of a series of papers relating to the chemistry of the typical amphoteric elements. It may be considered that all the elements from the first to the seventh groups inclusive, which have a deficiency of from seven to one electrons with respect to the rare gas type, are amphoteric. The elements that have a deficiency of only one or two electrons are strongly electronegative and their amphoteric tendencies are not marked. On the other hand, those elements that have a deficiency of five, six or seven electrons usually act electropositively and their electronegative characteristics are not pronounced. Amphoteric properties are most marked in the elements of the fourth group, which have a deficiency of four electrons. In the case of carbon, this property is well illustrated by triphenylmethyl. The triphenylmethyl group combines, on the one hand, with negative

---

[8] Heilbron and Spring, *Biochem. J.*, **24**, 133 (1930).

[9] Hart, Speer and Heyl, THIS JOURNAL, **52**, 2017 (1930).