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Contributors

Tutin, Frank.
Royal College of Surgeons of England

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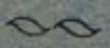
THE PROPOSED METHOD OF MICROSUBLIMATION FOR THE DETECTION OF AESCULIN AND THE IDENTIFICATION OF GELSEMIUM

BY
FRANK TUTIN



THE WELLCOME CHEMICAL RESEARCH LABORATORIES
FREDERICK B. POWER, PH.D., LL.D., *Director*
6, King Street, Snow Hill
LONDON, E.C.

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THE PROPOSED METHOD OF MICRO-SUBLIMATION FOR THE DETECTION OF AESCULIN AND THE IDENTIFICATION OF GELSEMIUM.*

BY

FRANK TUTIN.

In some recent "contributions to applied plant microchemistry," O. Tunmann has proposed a method for the detection of æsculin by microsublimation, which he considers especially adapted for the identification of gelsemium.[1] It is stated that when a small quantity of the ground drug, or a section of the rhizome or root, is placed between two microscope slides, and suitably heated, a characteristic crystalline sublimate of æsculin is obtained. The sublimate is recognised with the aid of the microscope by its appearance, crystalline form, and certain reactions. It is furthermore stated that æsculin, when examined by the micro-chemical method, does not behave as it does under the conditions of an ordinary chemical experiment. Thus, in chemical literature, æsculin is stated to lose its water of crystallisation at about 130°, to melt at 160°, and to decompose, yielding æsculetin and dextrose, at about 230°. Tunmann states, however, that when examined by the microsublimation method, æsculin melts at 49-50°, sublimes readily at 58-60°, and may even be sublimed out of gelsemium at so low a temperature as 40°, no decomposition occurring. The author finally claims that the method

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[1] *Apoth. Zeit.*, 1911, **26**, 812, and this Journal, 1911, **87**, 849.

is of such value that it should be adopted by the Pharmacopœias as a test for the identity of gelsemium.

In view of certain facts, however, it appeared to the present author that the subject required further investigation. In the first place, the suggestion that the chemical and physical properties of a compound can be greatly altered by the conditions under which it is examined cannot be entertained. A small amount of a compound will melt at the same temperature when heated between two microscope slides as when heated in a capillary tube in the ordinary manner, and it will not become more volatile by being examined under a microscope. In the second place, gelsemium does not contain any æsculin, and therefore Tunmann cannot have obtained a sublimate of this compound from the drug in question.

The fluorescent principle in gelsemium has been shown to be scopoletin (æsculetin 5-methyl ether), and not æsculin.[2] Sonnenschein,[3] whose work is referred to by Tunmann, stated that he isolated æsculin from gelsemium, but a consideration of the method employed by him renders it evident that the compound he obtained could not have been the glucoside in question, and must have consisted of scopoletin. Thus Sonnenschein states that the drug was extracted with a mixture of equal parts of alcohol and water, the extract concentrated, and deprived of resin. The liquid was then treated with basic lead acetate, the precipitate collected, suspended in water, and decomposed by means of hydrogen sulphide, the crystalline compound being obtained by extracting the resulting liquid with ether. He also states that a further amount of "æsculin" was obtained from the filtrate from the basic lead acetate precipitate by extraction with ether, after the removal of the lead by means of hydrogen sulphide. Not a trace of æsculin, however, can be removed from its aqueous solution by extraction with ether, whilst scopoletin, on the other hand, may readily be removed by this means. Furthermore, it is stated by Sonnenschein that the "æsculin" obtained by him from gelsemium is identical with the "gelseminic acid" of Wormley,[4] but the latter compound has been shown by Schmidt[5] to be scopoletin.

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2 Moore, *Journ. Chem. Soc.*, 1910, **97**, 2223; 1911, **99**, 1043.
3 *Ber.*, 1876, **9**, 1182.
4 *Amer. Journ. Pharm.*, 1870, **42**, 1.
5 *Arch. Pharm.*, 1898, **236**, 236.

Unfortunately, the statement that æsculin is present in gelsemium now occurs in several standard works, such as Beilstein's 'Handbuch,' but these statements are in every case attributable to the incorrect observation of Sonnenschein.

With consideration of the above facts it was deemed desirable to ascertain the behaviour of anhydrous æsculin, æsculetin, scopoletin, and finely ground gelsemium on heating. Small quantities of the materials in question were placed in small, thin glass tubes, the open end sealed, and the substances then simultaneously heated in a metal bath, the temperature of which was recorded by a thermometer placed in the liquid. At 140° the scopoletin just commenced to sublime, and at 150° a distinctly crystalline sublimate was obtained from it. The temperature was then raised to 170°, at which point it was kept for several hours. The scopoletin then sublimed fairly rapidly, yielding almost colourless, well-formed crystals. The gelsemium also yielded a small sublimate, which was, for the most part, composed of crystals of scopoletin. The æsculin gradually melted, and darkened somewhat, slowly yielding a slight sublimate of tarry matter, containing no crystals, whilst the æsculetin remained unchanged. The temperature was then raised to 210°, and again maintained constant for several hours, when the scopoletin fused, and sublimed rapidly. A further sublimate was obtained from the gelsemium, but was largely of a tarry nature, whilst the æsculetin slowly sublimed in pale yellow crystals. The æsculin suffered gradual decomposition, giving a further sublimate of tarry matter, together with crystals of æsculetin, the identity of which was proved by the melting point (264°).

It is thus evident that the sublimate obtained by Tunmann from gelsemium must have consisted of scopoletin, and not of æsculin, as supposed by him, and that the temperature to which he heated the drug must have been at least 100° higher than he has stated.

In connection with these experiments the melting-point of æsculin has been redetermined. It has been found that the glucoside in question does not melt at so low a temperature as 160°, unless it has become partially decomposed by very slow or prolonged heating. When heated fairly rapidly, in the ordinary manner, fusion occurs at 200-202°.

The observations recorded in this note readily explain why it was that Tunmann failed to obtain any satisfactory

sublimate from the bark of *Æsculus hippocastanum*, which is known to contain a fairly abundant amount of æsculin, but which, so far as known, is devoid of scopoletin.

The detection of scopoletin in gelsemium may, however, prove to be a valuable means of distinguishing this drug from others of a similar appearance, such as that derived from *Gelsemium elegans*, Benth., but it is doubtful whether the sublimation method is the most convenient one. If 0·5 gramme of ground gelsemium be heated in a test tube with chloroform, the mixture filtered, and the filtrate shaken with water to which a few drops of dilute ammonia have been added, the aqueous layer, on separation, will be found to show a distinct, blue fluorescence, thus indicating the presence of scopoletin.