Mineral Drugs of the Pharmacopoeia of the United States

Stibnite

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A Thesis submitted for the degree of Bachelor of Science (Pharmacy)

The University of Wisconsin

1934

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In attempting to define a mineral drug for the purposes of this thesis it seemed desirable to define the term mineral according to modern scientific usage. Definitions were, accordingly, selected from two modern dictionaries in general use, and two treatises on mineralogy, the classical work of Dana and the briefer survey of Kraus.

Webster's New International Dictionary defines a mineral as follows: A mineral is any chemical element or compound occuring naturally as a product of inorganic processes. Minerals are usually solids. Except in rare instances they have a definite molecular structure which manifests itself in crystal form, optical properties, etc. Rocks, except certain glassy forms are either simple minerals, or more frequently aggregates of two or more minerals.[1]

According to Murray's New English Dictionary, a mineral is any substance which is obtained by mining; a product of the bowels of the earth. In the early and modern technical use, the ore (of a metal).[2]

A material substance that is neither animal nor vegetable; a substance belonging to the "mineral kingdom".

Dana's Manual of Mineralogy and Petrography says, "Minerals are the materials of which the earth consists, and plants and animals the living beings over the surface of the mineral made globe. A few rocks, like limestone and quartize consist of a

1. Webster's New International Dictionary.
2. Murray's New English Dictionary.

single mineral in more or less pure state, but the most of them are mixtures of two or more minerals. Through rocks of each kind various other minerals are often distributed, either in scattered way or in veins and cavities. Gems are the minerals of jewelry; and ores, those important for the metal they contain. Water is a mineral, but generally in an impure state from the presence of other minerals in solution. Even fossils are minerals in composition. This is true of coal which has come from buried plant beds, and amber from the buried resin of ancient trees, as well as of fossil shells and corals.[3]

"It is sometimes said that minerals belong to the mineral Kingdom, and animals to the animal Kingdom. Substituting the term inorganic for mineral, the statement is right; for, as there are the two kingdoms of life, so there is in nature what may be called a Kingdom, or grand division, including all species not made through the organizing principle of life. But this inorganic Kingdom is not restricted to minerals, it embraces all species made by inorganic forces; those of the earth's crust or surface, and, also, whatever may form under the manipulations of the chemist. The laws of composition and structure, exemplified in the constitution of rocks, are those also of the laboratory. A species made by art, as we term it, is not a product of art, but a result solely of the fundamental laws of composition which are at the basis of all material existence; and the chemist only

3. Manual of Mineralogy and Petrography--Dana. 1888

supplies the favorable conditions for the action of those laws. Mineral species are, then, but a very small part of those which make up the inorganic Kingdom or division of nature."[4]

A more recent definition is that of Dean H. E. Kraus of the College of Pharmacy of the University of Michigan. In defining a mineral, Dean Kraus says, "A mineral, then may be defined as a substance occuring in nature with a characteristic chemical composition and usually possessing a definite crystalline structure, which is sometimes expressed in external geometrical forms or outlines. Characteristic of a mineral is its occurence in nature. The same chemical substance, for example Ca SO_4, may be found in nature, or it may be prepared in the chemical laboratory. When found in nature it is designated as a mineral and hydride. When prepared in the laboratory it cannot be interpreted as a mineral and is usually referred to as calcium sulphate. In order to be classified as a mineral, therefore a substance must be the product of nature and not the result of processes carried on in the laboratory. Most minerals are inorganic in character and are either chemical elements or combinations of such elements; that is, chemical compounds. Some substance of an organic nature such as coal, amber, petroleum, asphalt, etc. are frequently included as indicated, a few minerals are very simple in composition, such as sulphur, silver, copper, and gold. These are elements."

From these few definitions it becomes apparent that the au-

4. An Introduction to the Study of Minerals and Crystals. By Henry Edward Kraus.

thorities do not agree among themselves as to what constitutes a mineral. Dana, for example, rules out inorganic material not formed by nature but includes such substances as coal, petroleum and amber. Murray's New English Dictionary, tells us that "a mineral is anything obtained by mining, a product from the bowels of the earth," and in the next few lines excludes everything that is animal or vegetable including, apparently not only amber and coal, but calcium phosphate deposits from the bones of animals. It also excludes, by implications these substances which would otherwise be regarded as minerals which occur at the surface of the earth and do not require mining operations for their production.

Kraus, in his brief treatise, defines as minerals all substances occuring in nature with a characteristic chemical composition and, usually, a definite crystalline structure. If applied closely this definition would include any crystalline substance, organic or inorganic, which occurs naturally either in the earth itself or in animal or plant organisms, for example, gall stones, or camphor and calcium oxalate crystals deposited in the tissues of the plant.

Webster's New International Dictionary classifies as minerals only those substances occuring naturally as the result of inorganic processes. This definition, strictly applied, excludes not only coal and the so-called minerals oils, but calcium phosphate and coral which result at least in part, from organic processes.

It is, therefore, somewhat difficult to strictly define the

concept mineral, a step which appears to be necessary in defining a mineral drug.

In Gould's Medical Dictionary we find the term mineral and drug defined as: "A mineral is any inorganic chemical compound found in nature. The word is usually limited to the solid inorganic compounds."[5]

The term drug is defined as, "a substance simple or compound, natural or prepared, single or mixed with other substances used as a medicine." Combining the two we arrive at the following definition for a mineral drug:-Any solid inorganic compound or substance found in nature which is used as a medicine.[6]

For the purposes of this paper, then, it will be sufficient to consider as a mineral drug any inorganic compound or substance found in nature and used in medicine in its unaltered native form.

The Mineral drugs of the United States Pharmacopoeia have been few in number. Some of these few have been dropped altogether, some others no longer appear in their unchanged native condition but in physically, if not chemically, modified form. For example, while native forms of calcium carbonate, marble and chalk, appeared in the earlier editions, these forms have been replaced by prepared chalk and precipitated calcium carbonate which can not be considered as minerals. Still others, kaolin and talcum, which did not appear in the earlier editions but were introduced in the form of the mineral in 1900, have later been supplant-

5. Illustrated Dictionary of Medicine--Gould.
6. Ibid.

ed by purified forms of the minerals.

The drug under consideration, antimony trisulphide, appeared first, in the Pharmacopoeia of 1830 in the unchanged mineralogical form of stibnite. In later editions, 1840-1890, it appeared as the native sulphide of antimony purified by fusion, a form which would scarcely be considered as a mineral, as would much less the purified antimony tri sulphide of the editions of 1880 and 1890 and the National Formulary III, though the product included in all these various editions presents very much the same appearance as when it first appeared as the native stibnite.

Whether or not stibnite has been included in its unchanged native form in any of our modern pharmacopoeias, it was known to the ancients and was used by them as a medicine and a cosmetic. In the Vulyate edition of the Bible, several references are made to the use of stibium for painting the eyes, for example, (Ezekiel 23,40) "to lavisti et circum linsti stibio occulos tuos," (II Kings 9,30)"Jezebel depinxit oculos suos stibio;" also (Jeremiah 4,30) "tu pixeris stibio oculos tuos". The quotation from Ezekiel, to be sure, as translated from the Hebrew Bible by Rabbi Madnick, "thou didst wash thyself, paint thine eyes; and deck thyself with ornaments," contains no reference to stibium, nevertheless the Latin version shows that, at the time it was written, stibium was the material used for this purpose.

Dioscorides in the first century A. D. described stibium or stimmi. He attributed to it the power to build skin, to act as an astringent and to stop wild growth of the skin, also to clean

the eyes from dirt.[7] (Berendes--Die arzneimittellehre der Drorkuss des, Buch 5, Cap. 99). Pliny at about the same time in his Historia Naturales (33, 34) described stimmi and seven remedies derived from it. He spoke of two kinds of stimmi, also called stibium, which were regarded respectively as male and female. Some commentatus have considered that antimony trisulphide and native antimony denoted respectively the male and the female.[8] (J. W. Mellor-A Comprehensive Treatise of Inorganic and Theoretical Chemistry.)

Caius Julius Callistrus who wrote under the name of Scribonius Largus, also in the first century (43-48 A. D.) includes Stibium or Stibi as number 34 in his list of mineral drugs.[9]

Basil Valentine who wrote somewhere from the 11th to the 14th century, knew antimony in various forms, combinations and colors, probably principally as the sulphide. In his Triumphal Chariot of Antimony in which he extols its medicinal virtues, he says: The Arabs to whom this metal has long been known, called it Asinot; the Chaldeans designated it Stibium; its usual name among the Latins is Antimony; the German name (Spiesglas) reflects one of the peculiarities of the metal, viz. the streaks by which it is distinguished. This variety of names teaches us two things: first that antimony was known to the Arabs, Chaldeans,

7. Berendes--Die arzneimittellehre der Drorkuss--Buch 5. Cap. 99
8. J. W. Mellor--A Comprehensive Treatise of Inorganic and Theoretical Chemistry
9. Das Receptbuch des Scribonius Largus, translated into German by Filix Renne (Hist. Sendies by Kobert)

Latins and Germans, and, second that its virtues were held in the highest estimation among them."[10]

In another place he tells how lead, "the lead of the sages" may be prepared from antimony.[11]

Agricola, in his De Re Metallica published in 1556 described Stibi or Stibium, which was no doubt the sulphide of antimony in much the same way as Dioscorides did 1500 years before. The following extract from an historic note on the metallurgy of antimony in the very excellent translation, by Herbert Clark and Lou Harvey Hoover, of De Re Metallica summarizes the early history of this mineral as follows: "The Egyptologists have adopted the term antimony for certain cosmetics found in the Egyptian homes from a very early period. We have, however, failed to find any reliable analyses which warrant this assumption, and we believe that it is based on the knowledge that antimony was used as a base for eye ointments in Greek and Roman times and not on proper chemical investigation. It may be that the ideograph which is interpreted as antimony may really mean that substance, but we only pretend that the chemist should have been called in long since. In St. Jeramie's translation of the Bible, the cosmetics used by Jezebel (II. Kings lx.30) and by the lady mentioned by Ezekiel (xxiii, 40) "who didst wash thyself and painted thine eyes" is specifically given as stibio. Our modern translation gives no hint of the composition of the cosmetic and whether some of the Greek and

10. The Triumphal Chariot of Antimony (Kerckringus) p. 57
11. Ibid. p. 170

Hebrew manuscripts do furnish a basis for such translation we cannot say. The Hebrew term for this mineral is Kohl which subsequently passed into "alhol" and "alcohol" in other languages and appears in the Spanish Bible in the above passage in Ezekiel as alcoholasti. The term antimonium seems to have been first used in Latin editions of Feber published in the latter part of the 15th century. In any event the metal is clearly mentioned by Dioscorides (1st century) who calls it stimmi, and by Pliny who calls it stibium, and they leave no doubt that it was used as a cosmetic for painting the eyebrows and dilating the eyes. Dioscorides (V. 59) says; "The best stimmi is very brilliant and radiant. When broken it divides into layers with no part earthy or dirty. It is brittle. Some call it stimmi, others platyophthalmon (wide eyes), others larbason, others gynaekeion feminine."[12]

Pliny states (xxxiii, 33 and 34) "in the same mines in which silver is found, properly speaking there is a stone froth, it is white and shining, not transparent; is called stimmi or stibi, or alabastrum and larbasis xxxxxit is astringent and refrigerative and its principal use is for the eyes x x x x x
Above all in roasting it care should be taken that it does not turn to lead.

12. Agricola De re Metallica 1556. Translated by the Hoovers-1912. p. 428

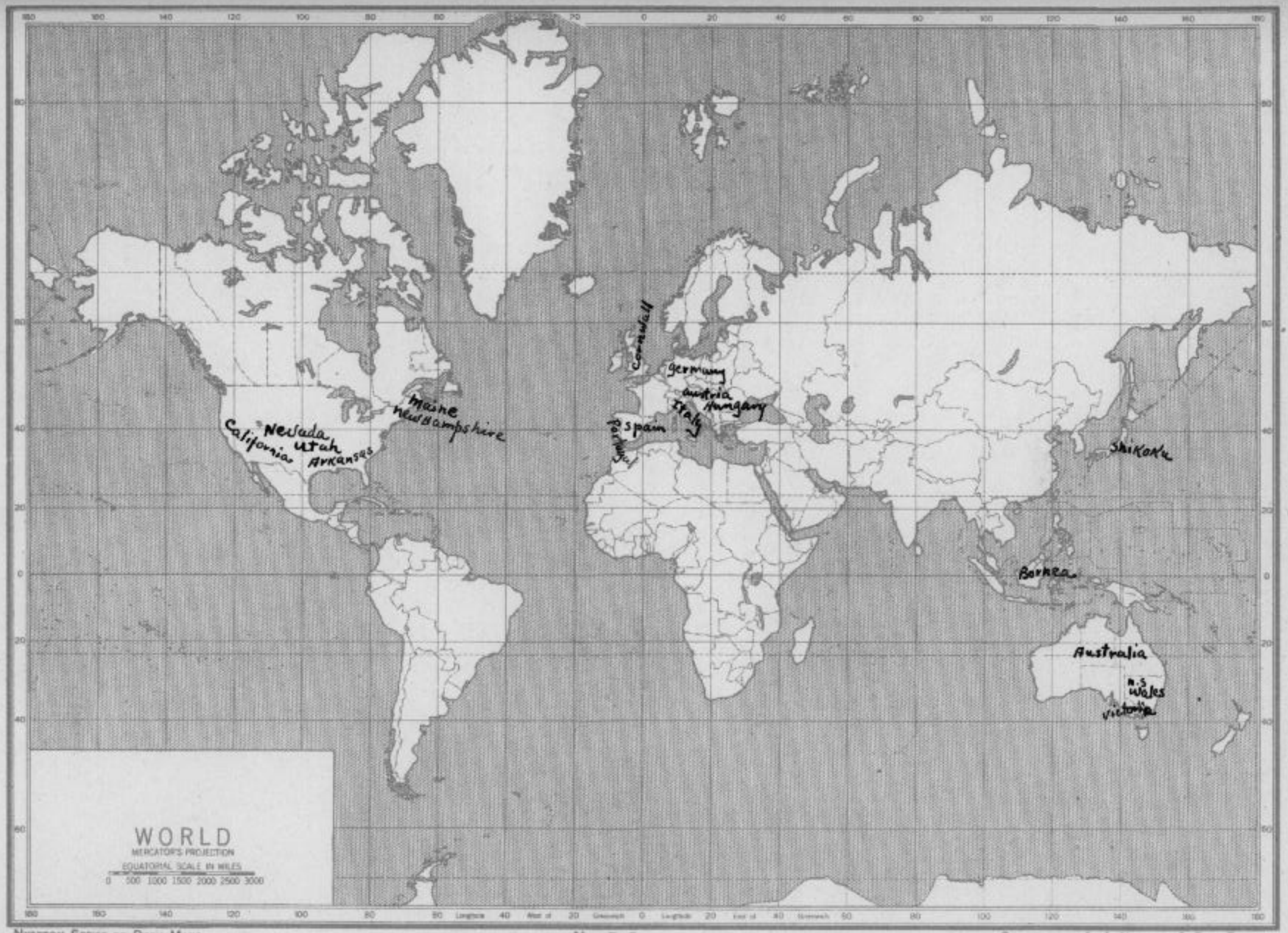
Stibnite Occurence

Stibnite occurs in prismatic or needle like crystals which are orthorombic and usually elongated. The sides are striated and the ends have low pyramids on them. Sometimes the long crystals are curved or even twisted.[13]

It occurs in veins in combination with ores of silver, lead, zinc, or iron, and is often associated with barite, spathic iron, or quartz. It is widely distributed being produced in Hungary; Germany, France, England, Spain, Portugal, Italy, Japan, and Australia. In the United States it occurs at Carmel, Me. and Lyme, N. H.[14] It is sparingly abundant in various parts of California. It is also found in Arkansas, Nevada and Utah. The occurence of this mineral is shown on the accompanying map.

13. Dana--Manual of Mineralogy and Petrography. page 112
14. Loomis--Field Book of Common Rocks and Minerals. page 81

Occurence of Antimony Sulphide (Stibnite).



Stibnite in Pharmacy and Medicine--Pharmacopoeias of the United States

Stibnite has been official in seven editions of the United States Pharmacopoeia. It first appeared in the New York edition of 1830 as Antimonii Sulphuretum. It was described as follows: "in conical loaves, surface dark gray, when broken presenting a striated crystalline structure and a lustre resembling that of lead; powder bluish gray or black; insoluble."

The Pharmacopoeia of 1840 describes Antimonii Sulphuretum as follows: "Native sesquisulphide of antimony purified by fusion--In striated masses totally dissolved by chlorohydric acid with the aid of heat, sulphohydric acid gas being evolved. Its solution in chlorohydric acid yields a white precipitate when added to distilled water; and the resulting liquid after filtration, yields an orange colored precipitate with sulphohydric acid."

The editions of the 1850, 1860 and 1870 pharmacopoeias describe stibnite in identically the same way as the edition of 1840.

In 1880 stibnite appeared with a change in the official Latinized title, the English title and the synonym. It was described as follows: "Native sulphide of antimony purified by fusion and as nearly free from arsenic as possible--steel gray masses of a metallic lustre and striated crystalline fracture forming a grayish black, lustreless powder, without odor or taste and insolube in water or alcohol. When heated it fuses at a temperature below red heat. One part of the powdered sul-

phide when boiled with ten parts of hydrochloric acid dissolves without leaving more than a slight residue."

In 1890 stibnite appeared as Antimonii Sulphidum with the change of the official synonym of Antimonii Sulphuretum Pharm. 1870, to Antimony Trisulphide. The drug is described in the same manner as the pharmacopoeia of 1880 described it.

Purified Antimony Sulphide

The purified form of Antimony Sulphide has been official in three United States pharmacopoeias. Purified Sulphide of antimony was described in 1880 as follows: "A dark powder, odorless and tasteless and insoluble in water or alcohol. It fuses at a temperature below red heat. When boiled with ten parts of hydrochloric acid it is nearly all dissolved, hydrosulphuric acid being evolved. The solution when added to water yields a white precipitate which is soluble in solution of tartaric acid, after separation of the precipitate by filtration, the filtrate gives an orange-red precipitate with hydrosulphuric acid."

In 1890 Purified Sulphide of Antimony appeared with a change in the English title and the synonym. It was described as follows: "A heavy grayish black lustreless powder, without odor or taste and permanent in the air. Insoluble in water or alcohol, but soluble in hydrochloric acid with the evolution of hydrogen sulphide."

In 1900 Purified Antimony Sulphide appeared in the National Formulary, the third edition. The drug was not described as to its physical appearance and properties.

Stibnite in Foreign Pharmacopoeias

British

No mention of stibnite was found in the local pharmacopoeias which, for so long a period preceded in the British Pharmacopoeia, the London, Edinburg, and Dublin Pharmacopoeias.

In the first edition of the British Pharmacopoeia, that of 1864, there is included a Prepared Sulphuret of Antimony. This is followed, in 1867, by the item Antimonii Nigrum, Black Antimony, Prepared Sulphuret of Antimony, 1864. It is described as the native sulphide of antimony, purified from siliceous matter by fusion and, afterward, reduced to a fine powder.

Neither stibnite nor antimony sulphide is mentioned in later editions of the British Pharmacopoeia.

Purified Antimony Sulphide

The purified antimony sulphide has been official in three British Pharmacopoeias. In 1885 Antimonium Nigrum Purificatum, Purifed Black Antimony was described as follows: "Native sulphide of antimony purified from siliceous matter by fusion, reduced to fine powder, and if, on testing any soluble salt of arsenic is present, is purified by the following process--macerate the sulphide of antimony with a solution of ammonia for five days, stirring frequently. Then allow the powder to subside, pour off the supernatant liquid and thoroughly wash the residue with water. Dry powder by the aid of heat."

In 1898 Antimonium Nigrum Purificatum, Antimonious Sulphide

was described as follows: "Native Antimonious sulphide from which siliceous matter has been removed by fusion, reduced to a fine powder, and if any of arsenium be present, is purified by digestion with half its weight of solution of ammonia for several days, washing and drying. It is a grayish black crystalline powder decomposed on boiling with hydrochloric acid, an almost clear solution being formed of hydrogen sulphide escaping."

In 1907 Antimonii Nigrum Purificatum, Antimonious Sulphide Black Antimony was described as follows: "Antimonious Sulphide is the natural substance freed from siliceous matter and arsenium, by fusion and subsequent digestion of powdered sulphide with ammonia. It occurs as a nearly black crystalline powder, insoluble in water, but almost entirely soluble in hot hydrochloric acid with the evolution of hydrogen sulphide. It should contain more than traces of arsenic."

<u>French</u>

The first mention of Antimony Sulphide found in the French pharmacopoeia is of purified antimony sulphide in 1839 where it appears under the title Sulphuretum Stibicum Depuratum.

In the edition of 1866 we find the native sulphide of Antimony under the title Sulphuratum Stibicum, with the French title Sulfure D' Antimoine. The following is a free translation of its description: "It exists in long prisms which has a gray metallic luster. It fuses very easily and is soluble in hydrochloric acid giving off hydrogen sulphide in the air. It should be free from arsenic."

The item does not appear until the edition of 1908 where purified antimony sulphide is found with the following titles and descriptions: "Stibium Sufuratum Nigrum Depuratum, Antimoine (Trisulfure D'), Sulfure D'Antimoine Purife. It is soluble in potassium hydroxide and hydrochloric acid with the evolution of hydrogen sulphide."

German

Native sulphide of Antimony, stibnite, is included in all editions of both the Pharmacopoeia Germaniae and the Pharmacopoeia Germanica. The following are the titles, synonyms and descriptions freely translated, employed:

"1848, Stibium Sulphuratum Nigrum; Schwarzes Schwefelspiessglanz; Sulphuretum stibinigrum, statt des antimonium crudum, Grauspiessglanzers, Schwefelspieszglanz. It is a black grayish mass, coating the fingers with a metallic luster. It glows in the air and becomes oxidized and passes into the air with a white smoke. It consists of antimony and sulfur and ought to be free from arsenic, lead and copper."

"1857, Stibium Sulphuratum Nigrum; Antimonium Sulphuratum Nigrum; Sulphuretum stibi nigrum, antimonium crudum, antimoine Sulfure, Protosulfure d'antimoine, Gray Antimony Ore, Sulphuret of antimony, Protosulphide of Antimony, Silver glance, antimon Sulfur, Schwefelspieszglanz. It is ia grayish black mass which stains the fingers with a metallic luster. It consists of antimony and sulfur and is produced in chemical laboratories. It should be free of arsenic, lead and copper."

"1872, Stibium Sulfuratum; Schwelelspiessglanz; Antimonium

Crudum. It is a heavy, dark gray, shining mass. It should be free of arsenic, lead and copper."

"1926, Stibium Sulfuratum Nigrum; Spieszglanz; Antimon Trisulfid. It is a grayish black powder which was used by the Hebrew and Grecian women as a paint for their eyebrows."

Names and Synonyms

1. Antimoine cru
2. Antimoine sulfure
3. Antimonii sulphidum
4. Antimonii sulphuretum
5. Antimonio crudo
6. Antimonium crudum
7. Antimonium nigrum
8. Antimonous sulphide
9. Antimony needle
10. Antimony sulphide
11. Antimony trisulphide
12. Artificial sulphuret of Antimony
13. Black antimony
14. Black (crude) antimony
15. Black or crude antimony
16. Japanese antimony
17. Prepared Sulphuret of Antimony
18. Schwefelantimon
19. Schwefelspiessglantz
20. Stibium Sulfuratum crudum
21. Stibium sulfuratum crudum et laevigatum
22. Stibicum Sulfuratum nigrum
23. Sulfuratum nigrum
24. Sufure d'antimoine
25. Sulfure d'antimoine cru

Names and Synonyms

26. Sulfure d'antimoine du commerce
27. Sulfure
28. Sulfuro de antimonio (sp.)
29. Sulfuretum stibicum
30. Sulphuret of antimony
31. Trisulfuro di antimonio

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10. Ibid
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12. The Dispensatory of U. S. A.--20th ed.
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Approved

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May 28, 1934