stable (2), it is not surprising to find the corresponding acid chloride extremely unstable.

Attempted Preparation of α,β-Dibromopropionyl Salicylic Acid.—5 Gm. salicylic acid was dissolved in 5 Gm. pyridine, and the solution cooled in an ice-salt bath. To this was added slowly, drop by drop, and with stirring, 11 Gm. of α,β-dibromo-propionyl chloride. A gummy mass soon formed, and it became impossible either to continue efficient stirring or to control the temperature. The mass was brown at first, but soon became purple. After all the acid chloride had been added the reaction mixture was heated on the steam-bath for five minutes. There was considerable foaming, accompanied by darkening of the reaction mixture. It was stirred into ice water, and a purple precipitate was obtained. It was isolated as a purple powder weighing 4 Gm. However, it was found to contain considerable water when heated on the steam-bath, and when completely dry was a semi-solid tarry substance. This on cooling solidified into a glassy substance which when powdered, was of a dark purple color. The powder was boiled with benzol, a large part remaining undissolved. The benzol solution was evaporated to dryness, leaving a brown glassy residue. On analysis this substance showed only a trace of bromine. Either the desired compound was not formed, or hydrolyzed in the attempt at purification.

The testing of the bromoalkyl salicylates for toxicity and antipyretic activity was done in the Biological Research Laboratories of E. R. Squibb & Sons and we gratefully acknowledge their assistance.

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A STUDY OF PRECIPITATION IN FLUIDEXTRACT OF UVA URSI I.*[1]

THE CRYSTALLINE NATURE OF THE PRECIPITATE IN FLUIDEXTRACT OF UVA URSI.

BY H. L. TISHER[2] AND C. O. LEE.[3]

INTRODUCTION.

Fluidextracts are a troublesome class of preparations because they precipitate badly upon standing. Years ago Lloyd said, "Physicians object to even muddy fluidextracts. Pharmacists feel annoyed and discouraged when they find their bottles partly filled with sediment, and this trouble (sediment) is the rule and not the exception"(3).

The causes for the formation of precipitates in fluidextracts are many, the chief of which is, perhaps, the fact that they are highly concentrated preparations. The subject has attracted many investigators.

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[1] An abstract of a thesis submitted to the faculty of Purdue University in partial fulfilment of the requirements for the degree of Master of Science by H. L. Tisher.

[2] J. K. Lilly Fellow, Purdue University, School of Pharmacy, 1930–1932.

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FLUIDEXTRACT OF UVA URSI.

The first formula for Fluidextract of Uva Ursi is credited to Maisch (2). His formula, with slight modification, was adopted by the U. S. Pharmacopœia of 1860. It has been retained in the succeeding revisions of the Pharmacopœia, except the last, with slight changes in formulas from time to time. Scoville (5) found that the preparation precipitated badly and in so doing showed a marked loss in astringency. He suggested that tannin-bearing preparations, such as fluidextracts, should be strongly alcoholic.

Fluidextract of Uva Ursi continues to precipitate over long periods of time. For this reason it is among the most troublesome of the fluidextracts; it is not unlikely that this is due to the large amount of tannin in Uva Ursi.

EXPERIMENTAL.

Two lots of Uva Ursi leaves, numbered 21839 and 97169, were furnished by the Eli Lilly Company, Indianapolis. These conformed to the official tests for identity and purity, and were used to prepare the many samples of the fluidextracts which are being reported upon in this study.

Plate I.

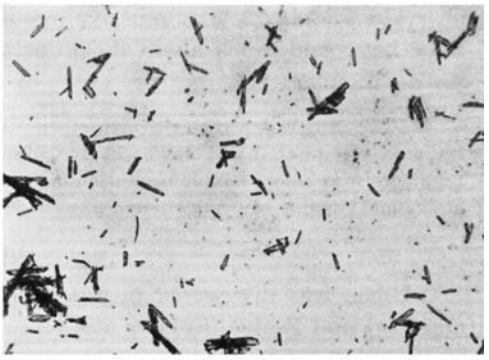

Plate II.

A STUDY OF THE p_H CHANGE IN FLUIDEXTRACT OF UVA URSI.

An official fluidextract was made from uva ursi, Lot 21839. By means of a Leeds and Northrup student potentiometer the p_H of the fluidextract was taken at irregular intervals for about eight months. The changes in p_H were not significant, leading us to conclude that the product which we had observed was a rather stable one in so far as any marked chemical changes were concerned.

CRYSTALLINE CHARACTER OF THE SEDIMENT IN FLUIDEXTRACT OF UVA URSI.

After studying many samples of the fluidextract it was observed that a precipitate occurred regularly in all of the official fluidextracts of uva ursi which we made. It was usually of the same color and appearance and began to show in the bottom of the bottle within a few hours after the preparation was completed. Upon microscopic examination it was found to be largely crystalline. The fluidextract was found to be heavily loaded with suspended crystals similar to the sediment. They were needle-like to boat-shaped in appearance.

Microscopic observations were repeatedly made upon fresh lots of fluidextracts. After about twelve hours the reserve percolates consistently showed small microscopic masses but no crystals. Invariably, after twenty-four hours, however, small needle-like crystals, singly and in tufts, appeared. From this stage on they settled out continuously for long periods and constituted the bulk of the precipitate which formed in the fluidextract.

PROPERTIES OF THE CRYSTALLINE PRECIPITATE IN THE OFFICIAL FLUIDEXTRACT OF UVA URSI.

The crystalline character of the precipitate, which invariably forms in official fluidextracts of uva ursi has never been reported on, so far as we know. It may be described briefly as follows:

(*a*) Color, uniformly light tan to straw.

(*b*) Crystals, needle-like to boat-shaped, appearing singly and in tufts, or sheaves. (Plates I and II q. v.)

(*c*) Practically insoluble in all of the common solvents.

(*d*) Partly soluble in methyl alcohol containing about 20 per cent gaseous hydrochloric acid.

Plate I is a microphotograph of the crystals as commonly observed in the fluidextracts of uva ursi. Plate II is a picture of the crystalline precipitate after it had been treated with methyl alcohol containing 20 per cent gaseous hydrochloric acid and allowed to recrystallize.

INSOLUBLE GUM ISOLATED AND STUDIED.

The presence of a gum in uva ursi has been reported by numerous workers but none have said much about its properties. We were able to obtain it in the following manner.

The drug was percolated with ether. Upon the addition of alcohol to the ether percolate the gum precipitated and was easily coagulated with stirring. It may be described as follows: Light green in color, soluble in acetone and ether, insoluble in alcohol and water, decidedly adhesive and capable of being chewed like chewing gum.

URSON.

Urson was discovered in uva ursi and named by Trommsdorff in 1854 (1). Gintl (4) and Dodge (6) have also reported work upon urson.

We were able to obtain it by evaporating the ether-alcohol solution from which the gum just described, had been removed. Its properties are as follows: A white, amorphous, powder, melting point 240–241°, soluble in ether and alcohol, and insoluble in water.

It would seem that neither urson nor the insoluble gum are to be found, in any amounts, in the fluidextract of uva ursi, both being insoluble in the menstruum. Furthermore, both may be obtained from the exhausted marc. from which the fluidextract has been obtained.

THE EFFECT OF MENSTRUUMS UPON THE CHARACTER OF THE PRECIPITATE.

A series of nineteen fluidextracts was prepared. Nine of these were made with the official menstruums and all showed crystalline precipitates within a day. Nine of the remaining fluidextracts were made with menstruums composed of varying proportions of alcohol and glycerin. The precipitates in each case were non-crystalline. The last of the nineteen fluidextracts was prepared with an unofficial menstruum containing a large proportion of water. The precipitate which formed was crystalline.

From the results of these observations we may conclude, with Scoville, that fluidextracts made from tannin-bearing drugs should be highly alcoholic.

THE PRECIPITATE FROM A MANUFACTURER'S FLUIDEXTRACT.

A quantity of the precipitate of fluidextract of uva ursi was furnished by a manufacturer. It was a black, heavy, non-crystalline, partly liquid mass, and strongly acid to litmus. It gave tests for the presence of arbutin and tannin. Ashed samples gave positive tests for iron, aluminum, sodium and silica.

Quantitative studies indicated the following as being present:

Per cent of volatile substance	31.50
Per cent of ash	3.07
Per cent solubility in water	52.00
Per cent solubility in alcohol	43.10
Per cent solubility in dilute alcohol	58.00
Per cent tannin	4.83
Per cent arbutin	10.67

The tannin was determined according to the method of Löwenthal as given in "Tentative Methods of Analysis" (1930) of the A. O. A. C. (8). The arbutin was determined by the method of Zechner (7). Many of these two assays were made but are not reported here.

SUMMARY.

1. Fluidextract of Uva Ursi has been studied with respect to stability according to changes in p_H.

2. The crystalline character and solubility of the precipitate in official fluidextracts of Uva Ursi have been described.

3. An insoluble gum in Uva Ursi has been obtained and its physical properties studied.

4. Urson has been isolated and studied.

5. The effects of menstruums upon the character of the precipitate have been shown.

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THE WOOD OIL OF DOUGLAS FIR.*

BY CARL H. JOHNSON[1] AND RUSSELL A. CAIN.[2]

The volatile oil from the wood of *Pseudotsuga taxifolia* (Poir.) Britt., commonly known as Douglas fir has been examined by various investigators. The data obtained, however, in most cases is limited to the percentage yield of the oil and a few physical constants.

Frankforter (1) in 1906 extracted from 11.6 to 42.4 per cent of pitch from the wood in which was contained approximately 22 per cent of oil. From the data submitted it was apparent that the terpenes consisted entirely of alpha pinene.

In 1912 Benson (2) steam distilled the wood and obtained a colorless oil which he

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