

THE IDENTIFICATION OF GUMS BY THE PHENYLHYDRAZINE REACTION.*

BY C. W. BALLARD.

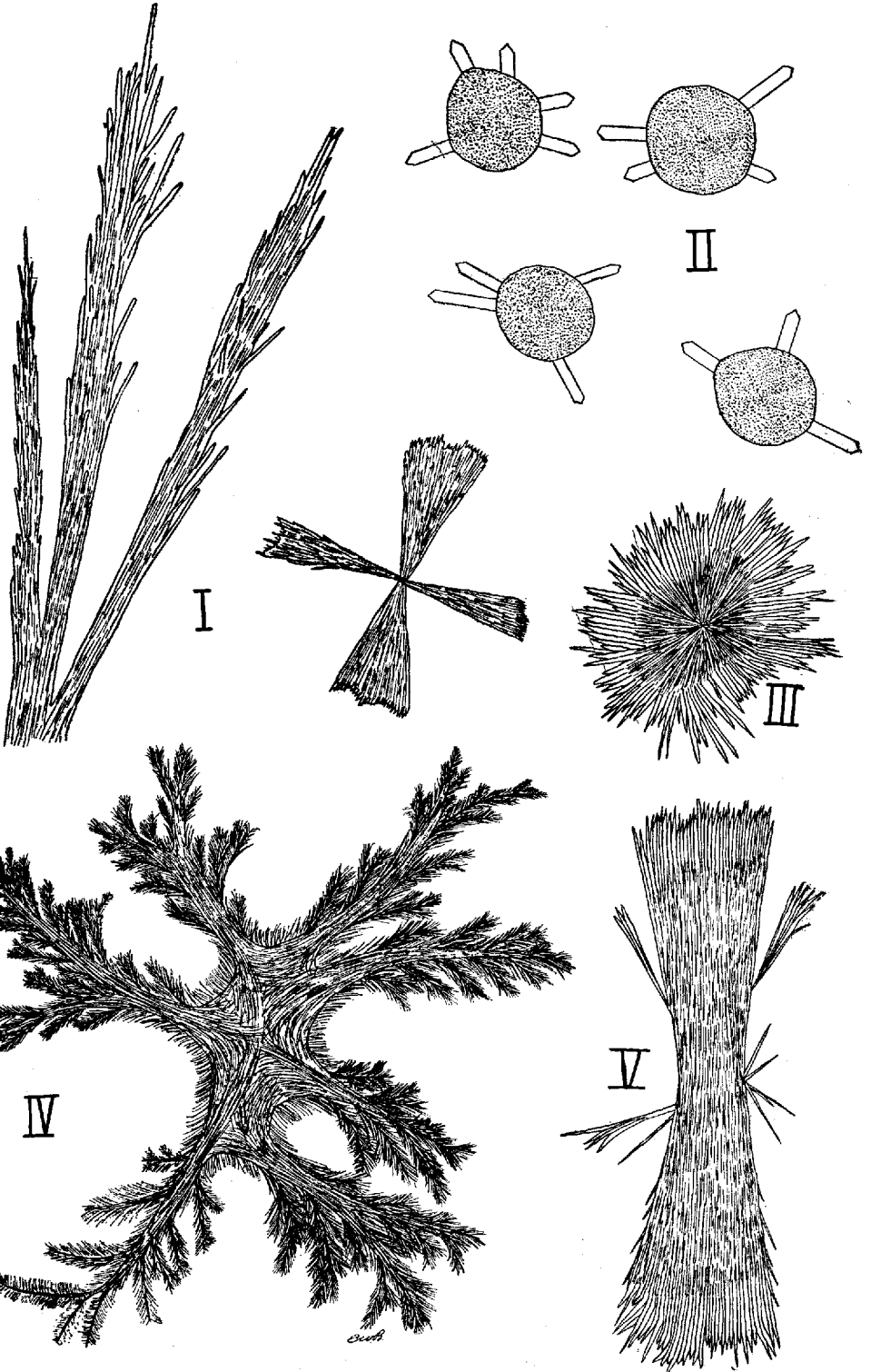
Although the phenylhydrazine test for glucose and other sugars is familiar to those engaged in urinalysis, but little mention is made of the applications of the reaction to other carbohydrates, especially those which may readily be converted into compounds containing an aldehyde radical. Experimental data at hand leads to the conclusion that the test is of value in the differentiation of gums and drugs containing gum and also that it may have practical application in glucosidal work. The field is so extensive that the present contribution is limited to a consideration of the ozones obtainable from a few of the gums and gum containing drugs. Experimental work upon fluidextracts containing glucosides gives promise of interesting results but has not proceeded far enough as yet to justify positive statements regarding the value of this test in its application to water-soluble residues from the evaporation of these preparations.

The preliminary steps in the application of this test to gums consist of extraction or solution of the gum and inversion of the soluble carbohydrate. For extraction or solution purposes it is most convenient to start with about 5 grammes of the material to which is added 100 mils of water, the mixture being kept at gentle heat for about two hours. Water bath or hot plate set at low temperature is necessary as in some instances the solution becomes very viscid and is apt to burn if heated at too high temperature. After cooling the solution is filtered or strained, depending upon the viscosity of the product and water is added through the filter or strainer to make up the original volume. Inversion of the soluble carbohydrate in the filtrate is accomplished by the addition of 50 mils of 5 percent hydrochloric acid and 50 mils of water to the filtrate from extraction or solution. The mixture is then boiled for two hours in a flask fitted with a reflux condenser. After inversion the solution is filtered and the filtrate reserved for the test.

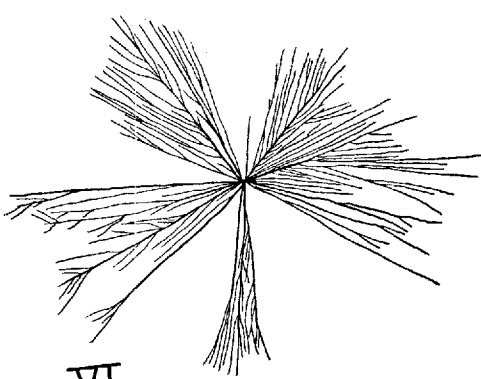
The reagent employed in these tests should be freshly prepared each day and contains phenylhydrazine hydrochloride 1 gramme, sodium acetate 3 grammes, dissolved in 25 mils of water. This solution should be filtered if not entirely clear. For the test equal parts of the filtrate containing the inverted carbohydrate and the freshly prepared phenylhydrazine solution are placed in tubes in a large beaker of boiling water and kept at boiling point for one hour, after which the tubes are allowed to cool slowly. Evidences of a crystalline deposit will often show immediately upon addition of the reagent to the solution but such crystals are imperfect and hardly characteristic. In some instances the precipitate will be voluminous but amorphous in character and it will be necessary to recrystallize. This is best accomplished by removing the precipitate by filtration, dissolving in warm alcohol, adding an equal quantity of water and removing the alcohol by heating upon a water bath.

In conducting check tests with samples of known and unknown identity it is imperative that all conditions throughout the tests be alike, as even slight differences in time or temperature will cause great changes in the character of the crystals produced. Certain gums will not yield a crystalline deposit even upon re-

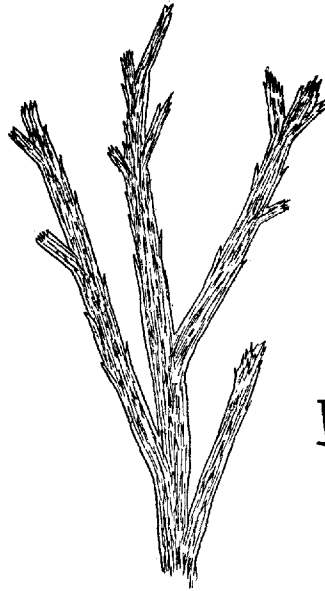
*Read before Scientific Section, A. Ph. A., New York meeting, 1919.



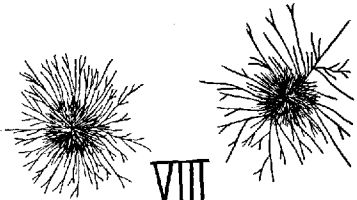
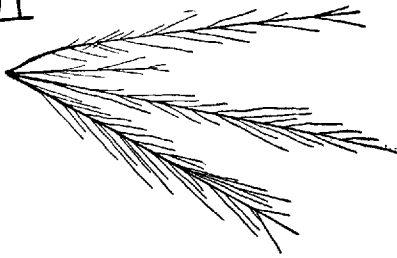
I.—Ozazone from Althaea Root. II.—Ozazone from Peach Kernels. III.—Ozazone from Brown Mustard.
 IV.—Ozazone from Sassafras Pith. V.—Ozazone from Yellow Mustard.



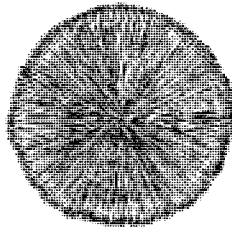
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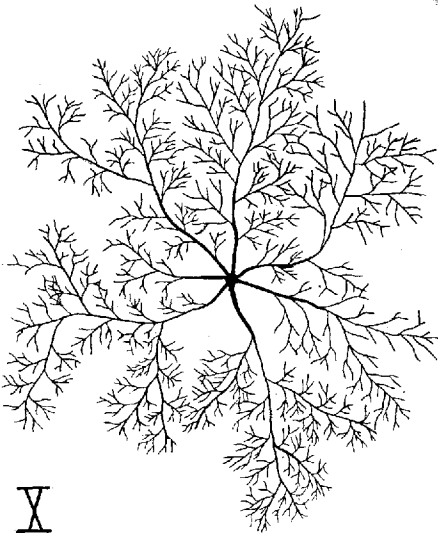
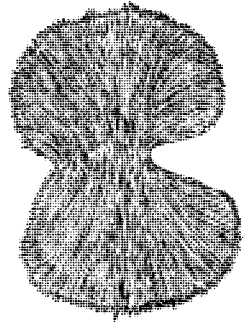
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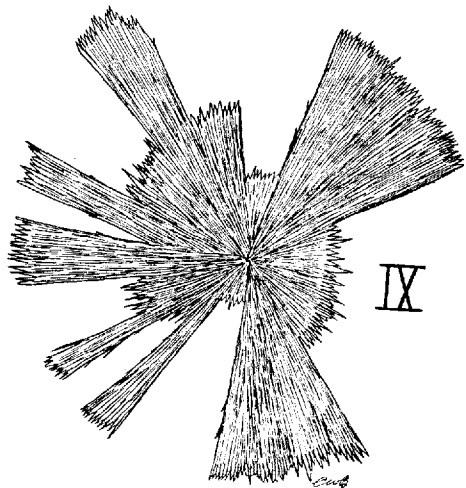
VIII



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X



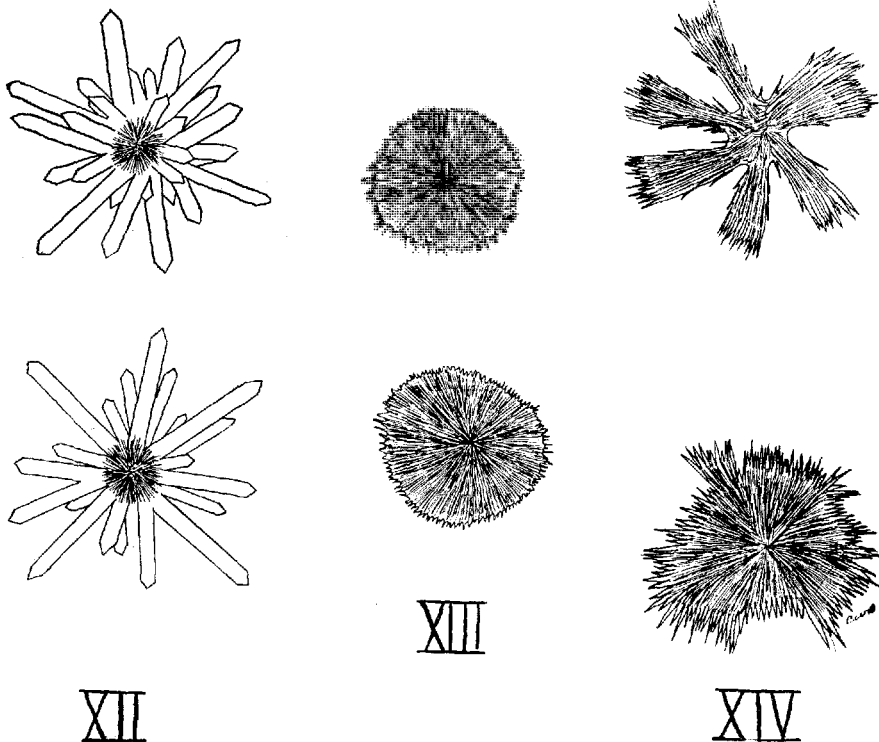
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VI.—Ozazone from Cetraria.
IX.—Ozazone from Elm Bark.

VII.—Ozazone from Apricot Kernels.
X.—Ozazone from Tragacanth.

VIII.—Ozazone from Acacia.
XI.—Ozazone from Quince Seed.

crystallization and this group may be regarded as negative to the phenylhydrazine test. The presence of glucosides with gums in a given substance undoubtedly influences the character of the crystals obtained as two types of crystals were clearly apparent in the ozazones produced from materials containing both gum and glucoside.



XII.—Ozazone from Linseed. XIII.—Ozazone from Indian Gum. XIV.—Ozazone from Bitter Almond Kernels.

In the examination of ozazone crystals an 8 mm. objective with 15 × ocular is most satisfactory as with this combination the preparation may remain uncovered and the magnification is sufficiently great to show even the finer details of crystal structure. The points to be noted in a comparison of ozazone crystals are: Total quantity of precipitate, general form or outline of crystal aggregates, apparent branching of parts of a crystal aggregate and finally the characters of the individual crystals which form the aggregate. The term "branched," as applied to these crystals, is, from the standpoint of crystallography, a misnomer, but it is a convenient expression for purposes of description. Accurate description of crystals as complex in structure as are the ozazones is rather difficult and each of the following descriptions is supplemented by an illustration.

CHARACTERS OF THE CRYSTALLINE PRECIPITATES.

Acacia.—Precipitate voluminous and orange-yellow in color. Individual crystal aggregates are small and spherical with many small branches and a few of larger size. The larger branches are slightly wavy and apparently give rise to small, secondary twigs.

Althæa.—Precipitate voluminous and reddish orange in color. Individual crystal aggregates are often very large with sheaves in form of irregular crosses or six-armed figures. Individual crystals are thin and straight.

Apricot Kernels.—Precipitate small in amount and reddish in color. Individual crystal aggregates are large and in the form of branching sheaves originating from a common center. Individual crystals are thin and straight.

Bitter Almond Kernels.—Precipitate fairly large in amount and bright yellow in color. Individual aggregates are small and in the form of irregularly outlined spheres or five to eight sheaves radiating from a common center. Individual crystals are thin and straight.

Cetraria.—Precipitate voluminous and light yellow in color. Individual aggregates are large and in the form of many rayed figures, the primary rays giving rise to comparatively few but rather large branches. The most conspicuous character is the open arrangement in the branching. Individual crystals are long, straight and thin.

Elm Bark.—Precipitate is voluminous in amount and dark red in color. Crystal aggregates are spherical or twin spheres showing a finely toothed margin with but few projections. The individual crystals arise from a common center and are rather large, thin and straight.

Linseed.—Precipitate voluminous in amount and yellow in color. Individual crystal aggregates are in the form of small spheres from which many broad rays project. The central portion of the aggregate is apparently composed of many small, thin crystals while the outer portion consists of very broad and straight forms.

Indian Gum.—Precipitate is voluminous and of dark orange color. Individual aggregates are spherical and composed of many finely set narrow crystals; a few of the latter projecting beyond the general border of the mass give the margin a ragged appearance. Individual crystals are thin, straight, and all radiate from a common center.

Mustard, brown.—Precipitate is small in amount and reddish yellow in color. Individual aggregates are spherical with very ragged border. Individual crystals are rather broad and nearly straight.

Mustard, yellow.—Precipitate is small in amount and of yellowish orange color. Individual aggregates are in the form of broad sheaves but slightly narrower in the center than at the ends and with but few side branches arising from the aggregate. Individual crystals are fairly large, broad and are nearly straight.

Peach Kernels.—Precipitate is small in amount and the crystals have dark orange centers with light yellow rays. Crystal aggregates are small and spherical with few long and broad projecting rays.

Quince Seed.—Precipitate is voluminous and reddish orange in color. Crystal aggregates are spherical and composed of long and short sheaves radiating from a common center. The edges of the aggregate are ragged. The individual crystals are thin, straight and may be long or short.

Sassafras Pith.—Precipitate is small in amount and reddish yellow in color. Crystal aggregates are large, irregular and show considerable branching. Individual crystals are small, thin and straight. The tree-like branching of this form is decidedly characteristic.

Tragacanth.—Precipitate is fairly voluminous in amount and bright yellow in color. Crystal aggregates are moderately large, irregular and with many small interlacing branches. The individual crystals are small, thin and straight.

Our present tests of identity for gums are not entirely satisfactory as in many instances more reliance is placed upon physical characters than upon chemical properties. While the phenylhydrazine reaction fails to give positive results with all gums it is certain enough to be regarded as another link in the chain of confirmatory tests which might be used to establish the identity of an unknown sample.

SCHOOL OF PHARMACY,
COLUMBIA UNIVERSITY.

OIL OF SANDALWOOD AND ITS ADULTERATION.*

BY AZOR THURSTON.

"A volatile oil distilled from the wood of *Santalum album* Linne (Fam. *Santalaceae*), yielding not less than 90 percent of alcohols, calculated as santalol ($C_{18}H_{26}O = 222.21$)."^{U. S. P.}

The constants for sandalwood oil are as follows:

Specific gravity at 25° C.....	0.965 to 0.980 U. S. P.
Refractive index at 25° C.....	1.498 to 1.508 B. P.
Optical rotation in 100 mm. tube at 25° C.....	—15° to —20° U. S. P.
Santalol not less than.....	90% U. S. P.
Soluble in 5 volumes 70% alcohol.....	U. S. P.

The so-called West India sandalwood oil, cedarwood oil, terpineol, chloroform, castor oil and cottonseed oil are used as adulterants for sandalwood oil. Castor oil and cottonseed oil will decrease the optical rotation and reduce its solubility in 70 percent alcohol; cedarwood oil will increase and West India sandalwood oil will decrease its rotation to the left. Any of these adulterants would reduce the percentage of santalol.

The writer has examined a number of samples of commercial sandalwood oil and the results of analysis are as follows:

No.	Sp. gr.	Ref. ind. at 20°C.	Optical rotation at 25°C.	Santalol.	Remarks.
1.....	0.9687	1.5061	92.28	U. S. P. Standard.
2.....	0.9718	1.5081	—13.3°	88.80	Sol. in 5 vol. 70% alcohol. Below standard in santalol and optical rotation.
†3.....	0.9757	1.5081	—13.3°	92.9	Sol. in 5 vol. 70% alcohol. Below standard in optical rotation.
†4.....	0.9666	1.5033	—11.87°	93.7	Insol. in 5 vol. 70% alcohol. Below standard in optical rotation.

* Read before Scientific Section, A. Ph. A., New York meeting, 1919.

† From Capsules

The following formula is used in calculating the santalol:

$$\text{Percentage of santalol} = \frac{A \times 11.11}{B - (A \times 0.021)}$$

In which A is the result obtained by subtracting the number of mls of half-normal sulphuric acid V. S. required in the titration from the number of mls of half-normal alcoholic potassium hydroxide V. S. originally taken, and B is the weight of acetylated oil taken.