PINE TREE SUGAR.

By Harvey W. Wiley.

Pine tree sugar is derived from an exudation from the *Pinus lambertiana.* The resin or sap of the tree collects in cavities made with an ax or by fire, and on drying forms masses of impure sugar. These crude samples have a very sweet taste and a somewhat peculiar one, due to the resin which they contain, but would at once be pronounced sugar from the taste alone.

Pinus lambertiana occurs in the Oregon Cascade and Coast ranges, from the head of the Mackenzie River and the valley of the Roque River, south along the western flank of the California Sierras, through the Coast ranges to the Santa Lucia Mountains and in the San Bernardino and Cuyamaca Mountains. It is a large tree 46 to 92 metres high, 3 to 7 metres in diameter. It is most common and reaches its greatest development upon the Sierras of Central and Northern California, between 4,000and 8,000 feet elevation. In Oregon it descends to 1,000 feet.

In 1887 some members of the Geological Survey collected a small quantity of this exudation from the sugar pines and this was sent to me by Mr. H. M. Wilson.* The quantity of material was sufficient for a preliminary study, which showed that it was a sugar having a specific rotatory power of about 65, unacted on by Fehling solution either before or after treatment with hydrochloric acid, and possessing a composition which was represented approximately by the formula $C_7 H_{14} O_6$.† In searching through the literature on this subject I found that pine tree sugar had been examined by Berthelot and described in "Annales de Chimie,"

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*Received Feb. 6, 1888. Examined March. 1889.

†Means of three combustions. C=41.51%. H=7.47%.

3d series, Vol. 46, 1856, p. 76. Following is an abstract of Berthelot's paper :

" M. Boursier de la Riviere, consular agent of France in California, in 1856 took with him to France a saccharine substance produced by the *Pinus lambertiana.* This material was given to M. Berthelot for analysis. M. Boursier collected this substance from cavities near the base of trees. The exudation from the tree is at first resinous and semi-liquid. It gradually becomes dry and forms irregular masses, consisting mostly of sugar. The natives of the country eat it: Pure pinite is prepared by dissolving the crude sugar in water, filtering through animal boneblack, and leaving to spontaneous evaporation. Several weeks are required for the formation of the proper crystals. These were re-crystallized twice, and the pure pinite obtained subjected to analysis. The analysis gave the following percentages of carbon and hydrogen :

Carbon	43.4%
Hydrogen	7.8%

The second combustion gave :

Carbon	43.5%
Hydrogen	7.3%

These numbers led to the formula $C_6 H_{12} O_5$ or $C_{12} H_{24} O_{10}$ in which the percentages of carbon and hydrogen completed are as follows :

Carbon	43.9%
Hydrogen	7.2%

The combustion of pinite is very difficult. It is necessary to mix it intimately with oxide of copper and to end the combustion in a long current of oxygen at a temperature near that of the fusion of the glass. Treated with ammoniacal lead acetate, pinite afforded a substance which, on analysis, gave the following numbers ;

Carbon	12.5%
Hydrogen	2.1%
$Pb O$	72.8%

Showing the following composition: $C_6 H_{12} O_5 2 Pb O$, corresponding to:

Carbon	11.8%
Hydrogen	2.0%
PbO	72.8%

Whence it is concluded that pinite is isomeric with anhydrous mannite and possesses the same composition and formula as quercite.

The specific gravity of pinite was found to be equal to 1.52. Pinite is dextro-gyratory. $a_j = 58^\circ.6$. Treated with strong hydrochloric acid and heated to 100° for 10 minutes its rotatory power is not appreciably altered.

Pinite does not ferment, either before or after treatment, with hydrochloric acid. Pinite does not reduce Fehling solution."

The difference between the behavior of the sample examined by Berthelot and called by him pinite, and the sample sent to me was of such a marked nature that I determined to secure, if possible, a larger quantity of the material in order to make a more thorough study of its properties. The chief differences, as will be noticed, were in the specific rotatory power and the percentage composition. The sample examined by Berthelot had a much lower specific rotatory power than the one examined by me and had the composition of the ordinary glucoses; my sample had a much higher rotatory power and the composition of a hepta-glucose.

During the Summer of 1889, therefore, I made arrangements with the Director of the Geological Survey to employ one of his men in California for two weeks in collecting samples of this sugar, and, as a result of this work, I received, in the Autumn of 1889, about fifty pounds of a very good article of crude sugar. After the reception of this sample in my laboratory, but before I had commenced to work on it, M. Maquenne published a paper on "A New Sugar With an Aromatic Nucleus," which he named *Beta pinite* and which he claimed was obtained from the *Pinus lambertiana* growing in Nebraska. Inasmuch as this tree does not grow in Nebraska, M. Maquenne was evidently mistaken in regard to the origin of the sugar. He found the specific rotatory power and percentage composition of the sugar, which he called *Beta pinite*, the same as I found it for the pinite obtained from California. M. Maquenne's paper anticipated in a large degree the work which I had proposed to do on this sample and it is of such interest that the following abstract of it is given :

* "At present only two sugars are known derived from benzine, viz., inosite and quercite, both of which are changed by the action of hydrodic acid into definite aromatic compounds. The relations of inosite and benzine are more intimate than those of quercite, since by oxidation this latter substance gives a fatty derivative, trioxyglutaric acid, instead of quinones or phenols. *Beta pinite* is another of these aromatic sugars derived, according to Maquenne, from the *Pinus lambertiana* from Nebraska (?).

Beta pinite melts at 186° to 187°, and is strongly dextrogyrous. Its specific rotatory power is $(a)_D = 65^\circ.51$. (Berthelot, pinite $(a)_j = 58^\circ.6$). These characters are exactly those of sennite. *Beta pinite* and sennite are probably identical. The analysis of *Beta pinite* gives a formula between $C_7 H_{14} O_6$ and $C_8 H_{16} O_7$. Heated for some minutes to boiling with hydroiodic acid it is decomposed with disengagement of methyl. It represents, therefore, a methylic ether like the sugars of caoutchouc discovered by Girard, and without doubt isomeric with bornesite. If the residue be evaporated to a sirup and alcohol added, there is produced without agitation a crystalline precipitate, which, to the microscope is shown to be made up of small tetrahedra. This new sugar, purified by a second crystallization from weak alcohol, melts at 246°. It is very soluble in water, almost insoluble in alcohol (strong), wholly insoluble in ether. Its composition corresponds exactly to the glucoses. Its molecular weight appears to be the same as the glucoses, as determined by Raoult's method. Heated in the sand bath to complete decomposition with nitric acid, rutilant vapors are set free and a white residue is left which, in contact with a solution of sodium carbonate in weak alcohol, precipitates immediately crystals of a black reddish color of sodium rhodizonate. It is

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* C. R.. 109, 812.

thus assured for the identification of the salt that it is transformed into tetraoxyquinone under the action of hydrochloric acid and that it gives a red precipitate with barium chloride. The product of the dedoubling of the *Beta pinite* by the hydroiodic acid is certainly an aromatic derivative, very probably an addition product of benzine itself, and consequently an isomer of inosite. It is proposed to designate it by the term *Beta inosite.* It would be interesting to submit the true pinite to the action of hydroiodic acid and to compare it in this respect with *Beta pinite.* For this purpose Berthelot has kindly given me some of his original material, and I have thus been able to notice that this substance is converted, like *Beta pinite,* when it is boiled with hydroiodic acid, into a sugar which melts at 245° and presents all the characters of *Beta inosite,* being converted by nitric acid into rhodizonic acid and into tetraoxyquinone. There is produced at the same time a lively effervescence, due without doubt to the escape of methyl iodide. In general the two pinites, and probably sennite, are in close relation with the aromatic series. They form ethers derived from a new principle isomeric with the glucoses and which appear to have the same formula as inosite."

From a careful comparison of the work of Berthelot and Maquenne with the work which I have done on this sugar, I think it is evident at once that there is only one variety of sugar, viz., pinite, and that Berthelot, in the sample which he originally received, was mistaken in assigning it so low a specific rotatory power. It will be noticed that in a portion of Berthelot's original sample, which he sent to Maquenne, the same characteristics were noticed, in so far as they were compared, and which are described by Maquenne in the *Beta pinite.* There is, therefore, little doubt of the fact that what Maquenne calls *Beta pinite* should simply be called pinite and it is important that this mistake of giving the same sugar two different names should be rectified before it has found a permanent place in chemical literature.

The method pursued by me in purifying the crude product was as follows :

The crude sugar contains a considerable quantity of resinous and coloring matter. Its aqueous solution is almost black and has a pleasant piney odor. The crude sugar was finely powdered and treated with successive portions of boiling 95% alcohol until all the coloring matter soluble therein was removed. After removal of the alcohol the dry sugar was dissolved in water, making a concentrated solution. This solution was still highly colored. It was filtered through boneblack in a hot jacketed filter, by which process the greater part of the coloring matter was removed.

The solution was next treated with a slight excess of basic lead acetate, the precipitate removed by filtration and the excess of lead removed with H_2S. The filtered solution was then evaporated slowly over a steam bath until the crystallizing point was almost reached and again filtered through hot boneblack.

The solution thus obtained was almost colorless. Two methods of procedure were followed both, of which yielded excellent results.

First Method.—The clear solution was evaporated to the crystallizing point, quite a coloration resulting. It was stirred while cooling and a fine mass of small crystals was thus obtained. The concentration should be such that the mass should have a pastry consistence when crystallization is fully accomplished, which requires from two to four days. The crystals are washed with 95% alcohol on a filter until the filtrate shows no further color. The washing is then continued with absolute alcohol until the 95% alcohol is all displaced. The final washings are with ether. The sugar is dried at a very gentle heat (not above 50°) and then placed on filter paper over H_2SO_4 until constant weight is obtained.

Second Method.—The sirup is evaporated to near the point of crystallization and placed in a large jar of which it does not occupy more than one-fourth. The jar is placed on ice, and to the sirup, with constant stirring, three to three and one-half volumes of absolute alcohol are added. The thorough mixture of the alcohol with the sirup is finally conveniently accomplished by blowing through a tube or pipette. The mixture is stirred from time to time to insure small crystals. The deposition of sugar is complete in from ten to fifteen hours. The sugar is washed and dried as before.

The sugar thus obtained is a pure white powder. Twenty-five grains of it occupy a volume of 16.3 cc.; whence its absolute specific gravity is 1.5338. Its specific rotatory power, in varying concentration, is shown by the following data:

Grms. in 100 cc.	Angular Rotation.	$(\alpha)_D$
5	6.57	65.05
20	25.98	64.95
25	32.48	64.96
30	39.05	65.08

From the above it is noticed that the rotatory power appears to be independent of the concentration and is almost exactly 65 as a mean of all the results.* Distilled with sulphuric acid, according to the method used for the production of furfuramide only a trace of this substance was noticed. Oxidized with nitric acid some peculiar reactions were observed as follows:

When the oxidation was carried on in the usual way and stopped at a certain time, large quantities of white rhodozonic acid are produced. Treated with strong nitric acid in an open dish, however, and evaporated to dryness, a peculiar tarry mass is produced, of which the barium salt forms a reddish brown mass the composition of which has not been accurately determined.

From the work of Maquenne, already quoted, it is probable that this substance may be barium rhodizonate. In addition to this a yellowish substance was noticed in small quantities, which is probably due to the formation of picric or croconic acid. Treated with phenylhydrazin in the usual way, pinite gives no osozone; pinite treated with a solution of barium hydrate solution produces an amorphous precipitate, a part of which on standing becomes crystalline. The same is true when treated with calcium and strontium hydrates. Attempts to form the polybasic salts have been only partially successful.

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*Increasing temperature appears to diminish the rotatory power. A solution which at 5° gave an angular deviation of 14° 32′ gave at 82° only 13° 00′. Allowing for the expansion of the solution the reading should have been nearly 14°.

The separation of pinite into two bodies by Maquenne, as indicated in the abstract of the paper given, has been followed by him by a study of these separate bodies, of which the following is an abstract :

*"The *Beta inosite* produced by heating *Beta pinite* to 120° with an excess of hydroiodic acid, as stated in a previous communication, yields a molecule of methyl iodide and a molecule of *Beta inosite.*

Saturated hydroiodic acid, in the presence of a little red phosphorous, easily reduces the *Beta inosite* at 160° to 170°. There are formed some brown products of a tarry nature and also a substance having the odor of phenol which remains dissolved in the liquid acid. For the determination of this last body, it is converted by the action of iodine, and of potassium in excess, into an insoluble iodine derivative. The body thus obtained is yellow, crystallizable in alcohol or chloroform, in fine needles, fusible at 159°, soluble in alkalies and insoluble in water and dilute acids.

Under the influence of boiling nitric acid, this body is transformed into picric acid, easily recognized by its bitter taste and the characteristic aspect of its potassium salt. It is therefore identical with the phenol iodide which before has been obtained from inosite. This result, in addition to the production of quinones in the oxidation of *Beta inosite,* shows that this substance has the formula $C_6 H_{12} 0_6$, characteristic of ordinary inosite.

The study of its ethereal combinations proves that it possesses also with inosite the function of an hexatomic alcohol. Moreover, *Beta inosite* is without action on Fehling solution and upon the phenylhydrazin acetate, which excludes from its molecule the presence of aldhydic or acetonic carbonyls. The method of preparing hexacetyl-beta-inosite and hexabenzoyl-beta-inosite is also given.

Rotatory Power.—Beta inosite is strongly right handed. A 10% solution examined in a 220 mm. tube gave a deviation of 14°.3 which corresponds to the formula $(a)_D = 65°$. It is remarkable that the rotatory power is very sensibly the same as that which has been found for *Beta pinite.* In general *Beta inosite* possesses all the chemical properties of the inosite derived from muscles or from leaves. It constitutes, therefore, as that does, an addition product from

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*C. R., Vol. 109, p. 968.

benzine, a derivative from hexamethylene $C_6 H_{12}$. It differs from inosite physically by a much greater solubility, by its higher melting point, by its crystallizing form, and by its ethers, which do not resemble any corresponding combinations of inosite : and finally, by its action on polarized light. The latter property would seem to indicate that a molecule of *Beta inosite* is assymmetrical in its constitution, which may possibly be due to its containing two oxhydryls attached to the same atom of carbon.

Beta inosite is distinguished from the product recently obtained by Tanret in the action of hydroiodic acid on quebrachite by its point of fusion—it is a little higher, viz., 247 in place of 238 ;—by its crystallizing form, which is much less marked ; by its rotatory power, which is to the right, while the inosite of Tanret is strongly left handed.

Beta inosite is also different from the matezodambose of Girard, the rotatory power of which is very small, viz., 6°.

As a result of these researches, it follows that pinite constitutes the mononiethyline of *Beta inosite* and that its formula is $C_7 H_{14} 0_6$. This important principle is, therefore, an isomer of bornesite and of quebrachite, that is to say, it is a body absolutely distinguished in its composition and its chemical function from quercite."

Girard has shown, however, that the *Beta pinite* and the *Beta inosite* described by Maquenne, are identical with the sugar obtained by him from caoutchouc and which he calls matezite ; and that the *Beta inosite* is identical with another sugar called matezodambose. The abstract of the work of Girard showing these analogies follows ;

*"Girard has abstracted from the juice of the caoutchouc of Madagascar, a sugar which he has named matezite. Treating this substance by hydroiodic acid in a concentrated state, and at the boiling temperature, it is broken up into the iodide of methyl and a sugar isomeric with the glucoses, namely, matezodambose. Shortly after, there was found in commerce, under the name of pinite, a sugar extracted from the *Pinus lambertiana* which Maquenne calls *Beta pinite* to distinguish it from the pinite of Berthelot. When this sugar is treated with hydroiodic acid it is

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*C. R. Vol. 110. p. 46.

broken up into methyl iodide and into a sugar which resembles inosite, which is called *Beta inosite*. Struck with the analogies of this substance with the caoutchouc sugar, Combes has identified *Beta pinite* and matezite as the same sugar, and *Beta inosite* and matezodamzite as the same sugar." The following is a table of the physical constants of the various substances :

	Matezite.	B. Pinite.	Matezodambose.	B. Inosite.
Melting point......	187°	186°.5	246°	246°
Rotatory power.....	66°	65°.7	67°.6	68°.4

The rotatory powers are determined by solutions containing 2% of the material. From what precedes, it is evident that *Beta pinite* and *Beta inosite* are not new chemical compounds.

It is seen from the above data that we have in this exudation of the *Pinus lambertiana* a chemical body of the most remarkable and interesting properties. It is evident that the study of these properties has only been well commenced, and with the large quantities of material which are now at my disposal I hope at a subsequent time to add something more to our knowledge concerning it.

ANALYSIS OF A PEKOE CEYLON TEA.

By Joseph F. Geisler

This sample of tea would be considered a curiosity by most people, inasmuch as its appearance is so different from that of the usual varieties of teas met with in commerce. It is a fine Pekoe Ceylon Tea, and its appearance shows it to consist of a mixture of small dark and yellow leaves, the latter predominating. These small leaves are tightly rolled into coils varying from $\frac{1}{4}$ to $\frac{1}{2}$ inch in length, the greater portion being about $\frac{5}{16}$ inch long, with an average diameter of about $\frac{1}{32}$ inch. The small, light, yellowish colored coils are completely covered with hair, giving some a silvery appearance.