

THE ANALYSIS OF VANILLA EXTRACT.

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Vanilla extract is defined by the U. S. Department of Agriculture standards as "the flavoring extract prepared from the vanilla bean, with or without sugar or glycerin and contains in 100 cc. the soluble matters from not less than 10 gm. of the vanilla bean."

The vanilla bean is, according to the same authority, "the dried cured fruit of *Vanilla planifolia*."

The tincture of vanilla of the U. S. P. is a preparation conforming to the foregoing standards and the process described in that work is taken as a type process for the preparation of a standard preparation for purposes of comparison by many authorities. Inasmuch as there is nothing said in the standards about the grade or geographical origin of the vanilla beans, it logically follows that a multitude of sins are committed under the name of vanilla extract. The only commercial variety of vanilla bean which is not derived from the *Vanilla planifolia* is the inferior Tahiti bean which comes from a species called *Vanilla pompona*, so that the manufacturer may legally use any grade of Mexican, Bourbon or other variety of bean and make an extract true to the name "vanilla extract," and, to tell the real truth of the matter, there is no way of telling from the composition of the finished article what kind or grade of beans have been used, except by the flavor and aroma, characters not determinable by analytical procedure. Even the inferior Tahiti beans may be used without fear of detection, so the judging of a vanilla extract, after all, depends largely upon the exercise of the critical faculties of taste and smell.

There are certain factors, however, which, when ascertained, aid in arriving at a conclusion as to the genuineness of the product, and give some idea as to its quality. Of these, the principal ones commonly taken into account in judging of an extract are:

- 1 Percentage of alcohol.
- 2 Percentage of residue upon evaporation.
- 3 Percentage of ash.
- 4 Percentage of vanillin.
- 5 Percentage or relative amount of resins and character of same.
- 6 Character of color.
- 7 Presence or absence of such foreign substances as coumarin, acetanilide, etc.

The percentage of alcohol is of importance on account of the fact that if too little be used in extracting the beans the product is deficient in resins and consequently inferior in its flavoring value and aroma. Too much alcohol is also productive of an inferior product. The 60 percent alcoholic menstruum of the U. S. P. tincture is about the upper limit for a first class product and by far the greater number of manufacturers use a 50 percent. alcohol or even slightly lower. The percentage of alcohol in the finished product therefore ranges in high grade extracts from 35 to 55 percent. by volume and the majority are in the neighborhood of 40 percent. Some few commercial extracts of wide reputation are slightly below 35 percent., but they are always more or less turbid from the partial precipitation of resinous matter.

The alcohol may be readily estimated by taking a measured volume of 25 cc. of the extract and diluting it with about 60 cc. of water, placing it in an Erlenmeyer flask connected with a well cooled condenser and distilling off exactly 50 cc. for determination of the alcoholic strength by taking its specific gravity and referring to the appropriate table in the appendix of the U. S. P.

The percentage of residue upon evaporation is usually determined in routine practice more for the sake of observing the character of the residue and for purposes of comparison than for any real value which it possesses as there is no restriction as to the amount of sugar or glycerin which may be used, either of which, of course, increases the amount of residue in proportion to the amount present. It is customary to estimate the residue in 5 cc. of the extract by drying to constant weight upon the water bath.

The percentage of ash, which may readily be ascertained by igniting the residue after its determination, is of value in detecting the use of fixed alkali such as sodium or potassium carbonates or hydroxides, which are sometimes though rarely used to aid in extracting the resinous matter from the beans with a lower percentage of alcohol than would be otherwise possible. The percentage of ash varies somewhat in genuine extracts but we have never seen one which contained more than 0.50 percent by weight.

The percentage of vanillin may vary from 0.10 percent to 0.25 percent in a genuine vanilla extract, which is quite a wide variation when one takes time to consider it. As the value of the extract is largely dependent upon the amount of this constituent present it is customary to estimate it, which can be very readily done by a shaking out process.

The official method of the A. O. A. C. provides for the dealcoholizing of the extract as a preliminary step by repeatedly evaporating to a small volume at a temperature below 70° C. In a large number of analyses made by this method and also by a method simply based upon the removal of the alcohol at water bath temperature, we have been unable to detect any appreciable difference in the results and believe that the amount of vanillin lost by volatilization during concentration is negligible. A simple and satisfactory method is as follows —:

Measure 25 cc. of the extract into a shallow evaporating dish and concentrate to about one third of its volume upon the water bath. Add hot water to make up the original volume and observe the character and amount of resinous matter which precipitates at this stage of the procedure. Then add lead acetate T. S., drop by drop, until no further precipitation is produced. Filter while still warm through a plaited filter into a separatory funnel, washing the residue on the filter with small portions of hot water, being careful not have more than 50 cc. of total filtrate. Add to the liquid in the separatory funnel 25 cc. of ether and agitate thoroughly. When the liquids have separated, draw off the lower aqueous portion and transfer the ether (now containing most of the vanillin) to a tared glass capsule.

Place the aqueous liquid again in the separator, add a fresh portion of 25 cc of ether and repeat the operation, adding the ether to that in the glass capsule. Repeat this procedure a third time, using 15 cc. of ether for the final extraction. The combined ether extractions, when evaporated to dryness at room temperature, leave a varnish like film of nearly colorless vanillin, which upon standing

for a few hours, usually crystallizes in fan shaped radiating crystalline masses throughout the film.

The percentage of vanillin by this method in a high grade extract will be in the neighborhood of 0.20 percent. An extract containing over 0.30 percent is looked upon with suspicion as containing added vanillin. Some cheap extracts contain over 1 percent of vanillin to make up for the deficiency in aroma due to resins, etc. It sometimes happens that when a single bottle of extract of vanilla (holding about 1 fl. oz.) is the only sample available, the procedure as above outlined for alcohol, vanillin, etc., must be modified. Excellent comparative results, agreeing within 0.01 percent as a rule, in the vanillin estimation, have been obtained by the following procedure:

Estimate the alcohol as previously directed, using an asbestos mat between the burner and the flask. Allow the residue from the alcoholic determination to cool in the flask. Then transfer it to the separator without filtering, using water to rinse out the flask. Shake out the liquid in the separator with two portions of 25 cc. each of chloroform and evaporate the chloroform in a tared glass capsule. The residue will be almost pure vanillin, agreeing closely with the results obtained by the use of the official method or the modification previously described.

After shaking out with chloroform, the liquid in the separator may be transferred to a graduated cylinder and an aliquot portion taken for the determination of the residue and the balance used for the tests of the resins to be subsequently described. Thus all of the principal characters may be ascertained in a 30 cc. sample, using 25 cc. for the alcohol, vanillin, resins and residue. The remaining 5 cc. may be used for the caramel test also subsequently described in this article.

The percentage of resins is rarely determined on account of the difficulty of collecting them upon a filter. However, upon dealcoholizing and diluting as directed under determination of vanillin and then passing through a filter, the portion which adheres to the filter may be used for certain identifying tests for the detection of foreign resins, such as color reactions with acids, specific tests for rosin, etc.

An arbitrary factor called the lead number, which is largely influenced by the percentage of normal resins present, is sometimes ascertained by estimating the amount of lead acetate precipitated from a solution of known strength under carefully standardized conditions.

This is a complicated and tedious operation, only of value in doubtful cases and will not be described here.

The character of the color is an important factor. Any caramel color at all is evidence of fraud. The former tests for caramel, such as fullers' earth test, paraldehyde test, amyl alcohol test, etc., were all unsatisfactory. A test which has recently appeared in literature and which upon careful investigation has been found to be extremely reliable is given herewith. Prepare a reagent as follows:

Tannic acid.....	5.00 gm.
Sulphuric acid.....	3.75 cc.
Water q. s. to make.....	250.00 cc.

Take equal parts of the above reagent and of extract of vanilla in a test tube

and heat the mixture to boiling. Stand it aside for 12 hours or over night and observe the character of the precipitated residue at the end of that time. A genuine extract of vanilla will show a flocculent, brownish precipitate which shows no tendency to adhere to the bottom of the test tube. Any caramel present will be indicated by a blackish brown sediment adherent to the bottom of the test tube. In applying this test the best results are obtained when specimens of known composition (of both genuine and caramel colored goods) are simultaneously tested.

Coumarin, the odorous principle of the tonka bean, is frequently present in cheap or imitation vanilla extracts, either through tonka beans having been used or by the addition of coumarin itself. The odor of coumarin is so distinctive, even when present in small proportions in combination with vanillin, that it is not always necessary to test for it. Where its presence is suspected it may readily be detected by redissolving the previously estimated vanillin in ether, transferring to a separatory funnel and shaking out with three or four portions of 2 percent ammonia water. This shaking out removes the vanillin completely and upon again evaporating the ethereal solution in a glass capsule any coumarin present will be left as a residue and may be weighed and identified by its color and its melting point of 67° C. (vanillin has a melting point of 80° C.).

Acetanilide, which has sometimes been found as an adulterant of vanillin, would also be left as a residue from this second ethereal solution with the coumarin, and it may easily be detected by treating the coumarin residue with petroleum benzine, which entirely dissolves coumarin but leaves behind any acetanilide, which in its turn may be identified by its characteristic chemical tests and its melting point of 112° C.

While there is little that is new or original in the foregoing communication apart from the procedure directed for the examination of the sample where only a limited amount is available, it is offered as being of interest to many pharmacists who have neither the time nor opportunity to familiarize themselves with the analytical procedures described in works on food analysis but who would eagerly avail themselves of points offered in an article of this kind.

OREGON BALSAM.

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Since the time that Dowzard expressed his opinion that Oregon Balsam was a mixture of colophony and oil of turpentine, the question of its origin has been frequently asked.

Mr. Rabak, a pupil of Professor Kremer's, of the University of Wisconsin, undertook to determine the actual source of this oleoresin. His investigation proved quite conclusively that Oregon Balsam was collected from a species of fir or possibly several species. Samples of twigs and cones yielding this product were identified officially as *Pseudotsuga mucronata* (Sudworth) and, as to synonym, *Pseudotsuga Douglasii* (Carrière). For details concerning the examination of the resin, the author's paper must be consulted (*Pharm. Rev.*, Aug., 1904, 293-299).