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THE DISTINCTION OF TRUE EXTRACT OF VANILLA FROM
LIQUID PREPARATIONS OF VANILLIN.

BY WILLIAM H. HESS.

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AN "extract of vanilla" can not be made artificially that will duplicate the one made from the bean itself, either in respect to chemical behavior, or with regard to usefulness as a flavoring agent. During the sweating process in preparing the vanilla bean for market, chemical changes of unknown nature take place, and as a result of these changes, the aroma is much improved. The importance of this process is well known, and those conditions which produce the best flavor are carefully studied.¹ To provide the various ingredients of the vanilla bean artificially and so treat them that the delicate aroma incorporated in an alcoholic tincture shall equal that acquired from the bean is a hopeless task, and it is quite as difficult to deceive the analyst by such a product. The vanillin that is synthesized and put upon the market, is identical with the vanillin extracted from the bean itself. There are other constituents as tannin, gum, and organic acids which might be duplicated, and whose origin could not be easily proved. There is one important constituent, however, which will be extremely difficult to replace, and that is the

¹ See article by Prof. H. H. Rusby, Merck's Report, Feb. 1, 1898, p. 74.

resin. This resin behaves so differently from other resins that its separation and identification is a most valuable means of proving the origin of "vanilla extract."

Vanilla beans contain from four to eleven per cent. of this resin. It is of a dark red to brown color. The coloring-matter furnished by this resin constitutes about one-half of the color of the tincture of vanilla. Since manufacturers desire a deeply colored product, they are careful to get all the resin in solution. This resin is soluble in fifty per cent. alcohol so that in the "extract" of high grade where plenty of alcohol is used, all the resin is kept in solution. In cheap extracts where as little as twenty per cent. of alcohol by volume is sometimes used, an alkali, usually potassium bicarbonate, is added to aid in getting resin, gum, etc., in solution, and also for the purpose of preventing subsequent turbidity. The color is thus deepened very materially. As vanillin is acidic in character and decomposes carbonates to form salts, the delicate flavor is impaired to a considerable extent by the addition of an alkaline carbonate, and a foreign odor is thereby introduced that is quite disagreeable and not difficult to recognize.

In testing preparations of vanilla it is well to make a pharmacopoeial tincture to be used in parallel tests, along with the sample of unknown purity. The following simple tests have been found useful:

I. DILUTION TEST.

Place a few cc. of the alcoholic tincture in a test-tube and add water slowly to three times the original volume and shake. If no alkali has been used in making the extract, a flocculent reddish brown precipitate will separate out. There should be but a slight turbidity. A milky solution would indicate foreign resin. Now add hydrochloric acid, a drop at a time, to a portion of the diluted sample. Turbidity results at once, due to extracted matter held in solution by the plant bases, as well as by alkali purposely added. The turbidity produced on acidifying should be slight (absence of foreign resin). Some practice with this simple test will enable an inspector to judge somewhat of the character of a "vanilla extract." If alkali have been used,

the turbidity increases considerably, and the *color* will fade when acid is added.

2. SEPARATION AND IDENTIFICATION OF THE RESIN.

Place 25 cc. of the "extract" to be examined in an evaporating dish and drive off the alcohol on a water-bath. When the alcohol is all gone, make up to about the original volume with water. If alkali have not been used in the manufacture of the "extract," the resin will appear as an amorphous, flocculent, red to brown residue. Acidify the cool solution with a few drops of hydrochloric acid to free the resin from bases, and the whole of the resin will separate out leaving a partly decolorized and clear supernatant liquid, after standing a short time. If it is desirable to weigh the resin for a quantitative determination, several hours are necessary for its complete separation. Collect the resin on a filter, wash with water, and reserve the filtrate for further tests.

Place a piece of the filter with the resin attached in a few cc. of dilute caustic potash. The resin dissolves to a deep red solution. On acidifying, the resin is reprecipitated.

Make a solution of the resin in alcohol. To one portion of this alcoholic tincture add a few drops of ferric chloride. No striking coloration is produced. To another portion of the alcoholic tincture add some hydrochloric acid, and again there is little change in color. Most resins give color reaction with ferric chloride or hydrochloric acid in alcoholic solution.

3. TESTS OF COLORING-MATTER.

(a) *For caramel.*—Concentrate a portion of the filtrate obtained from the resin in an evaporating dish on a water-bath until the depth of color is approximately that of the original tincture. Now add a few drops more of strong hydrochloric acid (nitric or dilute sulphuric acid will also serve), and heat gently. If caramel be present a yellowish red, flocculent precipitate is formed, very much resembling a precipitate of iron hydroxide in color and texture. Cool and filter out this precipitate, and wash it with water. It is insoluble in water, strong alcohol, or ether. It is soluble in dilute caustic potash, in gla-

cial acetic acid, and in dilute alcohol. About one half the color of caramel is thus removed.¹

(b) *For an azo dye.*—To a small portion of the filtrate add some ammonia. With a natural product the color is very much deepened. Now add some zinc dust and let it digest. The color should not fade entirely even on heating, but the solution will assume a tint about as deep as it was before adding ammonia. If the coloring be due to an azo dye it will fade to a colorless solution, the azo being reduced to the hydrazo compound. Pour some of the decolorized product into an open dish so as to expose considerable surface of liquid to the oxygen of the air. In case an hydrazo group has been formed, it will be slowly oxidized back to the colored azo compound. The oxidation may be hastened by adding some hydrogen peroxide, and the color will return at once. Other reducing agents as stannous chloride and hydrochloric acid, will also serve.

Test a portion of the original solution from the resin for tannin. This substance is present in small quantity only, and should not be found in great excess.

To another portion of the sample add a few drops of lead acetate solution. A bulky flocculent precipitate should form, showing the presence of organic acids and extractives in considerable quantity. This test should be the first, and absence of a precipitate condemns the sample. This precipitate will carry with it nearly all the coloring-matter left in the filtrate from the resin.

Vanilla extract is frequently adulterated with the "Extract of Tonka." The sophistication is best detected by ascertaining the presence of coumarin, the odoriferous constituent of the tonka bean. For a quick method of detecting coumarin in presence of vanillin, see a previous paper from this laboratory.²

¹ For further tests for caramel see Author in *Zitschy. anal. Chem.* (1885), p. 30. The following method for caramel and resin will be found most convenient and satisfactory in examining commercial extracts. If the solution, free from alcohol, is acidified slightly with hydrochloric acid and digested a few minutes on a water-bath, both the resin and caramel will be precipitated. Now filter, wash well with water to remove all sugar, and dry the precipitate and filter-paper at a low temperature. Treat the precipitate with absolute alcohol as long as any color is washed out. This removes the resin and leaves the caramel on the filter. The alcohol may be evaporated from the resin and the latter may then be treated as above. The residue is easily proved to be caramel by dissolving it in hot dilute acetic acid and adding phenylhydrazine to the solution, when a reddish brown precipitate will form which is characteristic at this point.

² This Journal, 21, 255 (1899); *Pharm. Review*, 17 (Jan., 1899).

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A SIMPLIFIED REDUCTOR.

BY P. W. SHIMER.

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FOR the reduction of iron and phosphomolybdate solutions, I have been using, for some time, a form of reductor which is simple, convenient, and effective. The reductor tube is a plain glass tube three-eighths inch in internal diameter and twenty inches long, drawn-out and cut off at the lower end. It is filled by placing a few small pieces of broken glass in the drawn-out portion and on this about an inch of well-cleaned sand. The tube is then filled with amalgamated zinc of as nearly uniform twenty mesh size as possible. About eighty grams are required. No asbestos or glass wool is used. The sand prevents particles of zinc from falling through, and it does not become clogged by use. Should any error arise on account of the omission of a more perfect filter, it would show in the blank, which is, however, uniformly very small, not more than 0.05 to 0.10 cc. permanganate.

The use of amalgamated zinc, as proposed by A. G. McKenna, makes a small reductor possible. The consumption of zinc is very small, and when the column has settled about one inch, a little fresh zinc can easily be poured in above. The reductor tube is united with a four-inch funnel by means of rubber tubing, well tightened with wire. Between the funnel and reductor is a Hoffman clamp. The lower end of the tube passes through a soft two-hole stopper so far as to reach half way to the bottom of a heavy-walled pint gas-bottle. The gas-bottle is connected with a filter-pump through an intermediate safety-bottle and valve. The funnel is clamped to a retort stand in such a

