per kg., it follows that $554 - 229 = 325$ mg. per kg. must be in an insoluble form.

As stated above, this amount must be well within the truth. If any considerable amount of the tin of the liquor is insoluble, the insoluble tin of the drained solids must be considerably more than 325 mg. per kg. The remaining figures in the column marked "Insoluble tin in drained solids" were all calculated in the same manner, using average figures for the weight and water content of drained solids and liquor as the individual determinations were not made.

The column headed "Insoluble tin in drained solids" is of particular interest although, as stated above, it is believed that the figures in this column are somewhat less than the truth; the relative amount reported as insoluble tin in samples of different ages shows that the process of hydrolyzation is a continuous one.

The figures given in the last column headed "Soluble tin in total sample" were obtained by adding together the figures in the columns headed "Milligrams tin per kilogram liquor" and "Soluble tin in drained solids," after calculating these respective figures to milligrams of tin per kilogram of tin of original sample. It is interesting to note that the figures in this column are almost identical with the figures in the column headed "Milligrams tin per kilogram liquor." It is probable, therefore, that an approximate idea of the amount of soluble tin in a sample of canned food can be obtained by determining the amount of tin in the liquor of the food, although the figure so obtained will obviously include any insoluble tin which may be present in the liquor in a finely divided state and also any tin that may be present in colloidal form.

Recent workers agree that the ideas of the earlier writers on the toxicity of tin were erroneous. It is now known that the toxicity of soluble tin compounds is at least very much less than it was formerly supposed to be. It is evident, however, that the results obtained in the study of soluble tin salts cannot be used as a criterion on which to judge the toxicity of tin in canned foods. Whatever the insoluble combination in which tin occurs in canned foods it is in all probability less likely to be absorbed from the intestinal tract than soluble tin compounds. The same is true, perhaps to a less extent, of tin in colloidal form. At any rate, the need of experimental work on the toxicity of tin as it occurs in canned foods is obvious.

NATIONAL CANNERS' ASSOCIATION, WASHINGTON

THE EFFECT OF CURING ON THE AROMATIC CONSTITUENTS OF VANILLA BEANS¹

By FRANK RABAK

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The fruit of vanilla has long been used as a flavoring agent. The plant is native to Mexico, where it is at present extensively cultivated for the production of the vanilla beans of commerce. It has been introduced into a number of other tropical and subtropical countries where it is also profitably cultivated. Among the other sources are South America (Guadaloupe),

¹ Published by permission of the Secretary of Agriculture.

Tahiti, Reunion, Madagascar, Comores, Seychelles, and Mauritius.

Vanilla beans as found on the market are described by the United States Pharmacopoeia¹ as the "cured, full grown, but immature, fruit of *Vanilla planifolia*, Andrews. (Family *orchidaceae*)."

Vanilla is used for flavoring purposes in the form of the so-called extract or tincture of vanilla, which is prepared by extracting the coarsely comminuted beans with a hydroalcoholic menstruum varying in strength from 45 to 65 per cent.

The aroma of vanilla, to which the flavor is attributed, does not preëxist in the beans but is formed by a chemical reaction induced during the drying or curing process to which the beans are subjected after harvesting.

Behrens² states that ripe vanilla beans have little or no odor but become strong in odor by curing,

COMMERCIAL VANILLA BEANS

due to the splitting up of an existing glucoside with the formation of the compound vanillin. The above statement regarding the odor of vanilla was confirmed by Busse,³ who states that vanillin is formed from a nonodorous body partaking of the nature of a glucoside.

In an extensive research with vanilla, Lecomte⁴ found that the fruit of vanilla contained, besides the glucoside coniferin, two ferments, one an oxidase and the other a hydrolyzing agent. The latter con-

¹ United States Pharmacopoeia, Eighth Decennial Revision, 1900, 497.

² J. Behrens, "Ueber das Vorkommen des Vanillins in der Vanille," *Der Tropenpflanzer*, 3 (1899), 299.

³ W. Busse, "Vanille—Chemie der vanille Frucht. Arbeiten aus dem Kaiserlichen Gesundheitsamte," Berlin, XV, 1898 bis 1899, p. 101.

⁴ H. Lecomte, "Sur la formation du parfum de la vanille," *Compt. rend.*, 133 (1901), 745.

verts the glucoside coniferin into coniferyl alcohol and glucose, the former oxidizing this alcohol into vanillin.

Later investigations have shown that the agreeable aroma of vanilla is not due alone to the compound vanillin but is strongly influenced by other substances of entirely different character.

Walbaum¹ states that the value of vanilla beans does not depend solely on the vanillin content. The oleoresinous constituents of the beans were examined and found to contain anisaldehyde and anisic alcohol besides other compounds which could not be identified, but which possessed a characteristic agreeable odor.

The presence of other odorous constituents in vanilla beans is also mentioned by Iserman,² who states that

agents which are known to impart much of the pleasant flavor to the cured beans.

CURING OF BEANS

As has been previously stated, the flavor of vanilla beans is brought about by a curing process with a consequent development of the true flavor upon which the efficacy of the beans as a flavoring material depends.

The curing process varies somewhat according to the source of the beans, the prime object, namely, the evaporation of the moisture and the formation of the flavoring constituents, being attained in every case. This is accomplished in a general way by a process of heating and subsequent sweating, the details of which vary in the different producing countries.

Two general methods are in vogue for the curing

LABORATORY CURED VANILLA BEANS

the special aroma and taste is probably due to vanilla resins. Busse³ states that vanillin is present in the living fruits only in insignificant quantities and is mainly produced in the process of curing. Vanillin is not the sole criterion of quality and does not represent the natural aroma of the fruit. Besides vanillin there is present in the beans vanillic acid, resin, oil, sugar, mucilage, and tannin.

Up to the present time attention has been largely directed towards the vanillin content of the beans, only bare mention being made of the resinous consti-

of vanilla beans, the dry and the hot water methods.

The dry method, in use in Mexico, consists essentially of placing the freshly gathered beans in the sun for several hours, after which they are wrapped in woolen cloths to promote sweating, and the process of heating and sweating is continued for several days until most of the moisture has evaporated. The final drying is usually completed in the shade. In unfavorable weather a drying oven is employed, in which the beans are sweated at a temperature of 60° C. The curing process is continued until the beans are soft and supple and have acquired a chocolate-brown color, the complete length of time required being frequently as long as 5 mos.

The hot water method, used in Reunion, consists in placing the beans in hot water (90 to 100° C.)

¹ H. Walbaum, "Das Vorkommen von Anisalkohol und Anisaldehyde in der Früchten der Tahiti-vanille. Festschrift, Otto Wallach. Zur Erinnerung an seine Forschungen auf dem Gebiete der Terpene in den Jahren 1884-1909," p. 649.

² S. Iserman, "Vanilla Beans: Chemistry and Character of Constituents," *Western Druggist*, July, 1910, 358-362.

³ H. Busse, "Studien ueber die Vanille," *Apoth. Zeit.*, 13 (1898), 894.

for 10 to 30 secs., after which they are wrapped in woolen blankets or placed in a box lined with blankets, where the sweating process takes place. Subsequently the beans are exposed to the sun and later the curing is completed in a drying room until the finished beans have the proper color and texture. This process requires from 1 to 2 mos. for completion.

The curing process is difficult and precarious, calling for a high degree of skill and experience. Weather conditions also have much to do with the rapidity and success of the process. The exact details of the two methods differ greatly according to locality. The general method of procedure for both processes is considerably modified in the minor details, the one object being to produce finished beans which will have the maximum amount of flavor of superior quality and at the same time will have had removed

curing vanilla beans were made. It was also desired to ascertain whether the long-continued curing as now practiced is absolutely necessary for the production of beans of commerce and whether shorter time of curing noticeably affects the percentage of vanillin in the cured beans.

A comparison of the efficacy of the two general methods of curing, namely, the dry method and the hot water method, and the effect of temperature upon the curing was sought. Furthermore, it was desired to study the effect of the various curing methods upon the formation of the oleoresins of vanilla which are present in all cured beans and which agreeably modify the flavor of the beans.

LABORATORY CURING EXPERIMENTS

A small quantity of green beans was obtained from

TABLE I—TREATMENT, LOSS IN WEIGHT AND CURING OF VANILLA BEANS AT ROOM TEMPERATURE AND IN THE WATER OVEN
Immersion in water three successive times at temperature given, for periods indicated, at intervals noted

BEANS CURED AT ROOM TEMPERATURE					BEANS CURED IN WATER OVEN (40-60° C.)				
TREATMENT	No.	Per cent Loss in Weight	Curing Period Days	REMARKS	No.	Per cent Loss in Weight	Curing Period Days	REMARKS	
None	1	53.0 66.4	14 24	Curing progressed slowly for 7 days after which color developed rapidly to uniform brown; beans well cured in 14 days. At end of this time, however, beans were wrapped in wax paper and allowed to dry. Cured beans were dark brown in color, soft, pliable and possessed fine aroma.	2	32.5 67.0	8 33	Beans became uniformly brown in 6 days, sweating continuous until 8th day when beans were wrapped in waxed paper and allowed to dry until soft and pliable. Beans possessed characteristic but mild aroma.	
Temp., 40° C. Period, 30 sec. Interval, 1 min.	7	39.3 68.5	14 46	Curing proceeded about same as No. 1. After subjecting to sweating process for 14 days beans were uniformly brown in color. Beans wrapped in waxed paper and allowed to dry until they presented a wrinkled appearance and proper pliability. Beans possessed very fine aroma.	8	49.6 66.6	8 28	Beans all brownish color in 5 days with good odor developing. After 8 days' sweating in water oven beans were wrapped in waxed paper and allowed to dry slowly until proper texture was attained. Odor was fine vanilla-like characteristic but not especially strong.	
Temp., 60° C. Period, 20 sec. Interval, 1 min.	5	36.5 66.0	11 33	Beans became yellowish green after third day. After 11 days all were uniformly brown in color and had characteristic wrinkled appearance. Beans wrapped in waxed paper and allowed to dry to proper flexibility. Beans characterized by strong and exceptionally fine odor.	6	41.4 66.2	8 33	After 5 days beans were uniformly brown in color with pronounced odor and apparently curing rapidly. After 8 days' sweating beans were treated as above and dried to proper pliability. Odor was strong, vanilla-like.	
Temp., 80° C. Period, 10 sec. Interval, 1/2 min.	3	40.7 66.2	12 24	Beans assumed brown color and developed odor more rapidly than any of above. After 12 days' sweating beans wrapped in waxed paper and set aside to dry. After 12 days of drying beans possessed a most exquisite aroma, deep brown color and fine texture.	4	31.2 64.0	8 29	Uniformly brown after 4 days' sweating, curing more rapidly than any of above and becoming soft and pliable. After sweating 8 days beans treated as above. Final appearance excellent both as regards color and pliability. Odor strong.	
Temp., 90° C. Period, 10 sec. Interval, 1/2 min.	9	23.3 66.1	10 28	Beans were all pliable, wrinkled and brown in 10 days with odor fairly strongly developed. Allowed to dry in air for 18 days. Beans pliable and wrinkled with only faint odor and pale brown color.	10	30.0 66.3	3 25	Beans possessed a uniform dark brown color in 2 days with prominent odor developing. After 3 days' sweating beans were exposed to air and dried until proper degree of pliability was reached. Strong but unpleasant odor noted.	
Temp., 100° C. Period, 10 sec. Interval, 1/2 min.	11	35.2 64.0	10 18	Beans became light brown and soft on third day. Taken from towel on 10th day and allowed to dry in air for 8 days. Odor prominent but not strong. Color pale brown.	12	44.0 69.0	3 17	Beans uniformly brown but pale after 1 day's sweating. Odor only fair and color pale brown after 3 days. Beans allowed to dry sufficiently, the cured beans being very light in color with faint odor.	

from them sufficient moisture to prevent molding when the beans are finally packed for the market. As a general rule from 5 to 7 lbs. of the fresh beans are required to produce 1 lb. of cured beans.

It is stated by Ellis¹ that the temperature of the water into which the pods are dipped before curing has much to do with the successful curing of vanilla.

Treatment with hot water supposedly kills the pods and prevents dehiscence. It is, however, essential that the temperature be not sufficiently high to destroy the action of the oxidase which is present in the pericarp. A destruction of the oxidase would seriously interfere with the formation of the odorous constituents of the cured beans.

The object of this investigation was twofold. A number of modifications of the process now used in

¹ F. R. Ellis, "Vanilla," *The Chemist and Druggist*, 67 (1905), 593.

Mexico through a prominent manufacturer of vanilla extract. The small ends of the beans were very slightly yellow but were practically devoid of odor.

The curing experiments were conducted with twelve lots of beans, one-half of which were cured at room temperature and the other half in a water oven at somewhat higher temperature. Each of the six lots cured at room temperature were given different treatment prior to the sweating and drying. The treatment consisted in dipping the green beans into water at various temperatures up to the boiling point. Each lot was kept wrapped in a soft towel and placed on the laboratory shelf to undergo the sweating and drying process.

The duplicate lots of beans cured in the water oven at a temperature of 40–55° C. received exactly the same treatment as those cured at room temperature.

A description of the treatment, loss in weight, and time of curing of the green beans at room temperature and in the water oven is given in Table I.

The general treatment in the curing at room temperature and in the water oven was similar to that employed in the commercial curing of the beans. The processes of sweating and drying were applied, however, under very different conditions than those obtaining at localities where the beans are cured commercially. During the sweating process the beans were wrapped in soft towels and later in waxed paper to complete the drying.

The treatment of the two sets of samples was identical in that one sample in each set was cured without previous treatment, while the remaining five samples were subjected to the action of hot water at increasing temperatures up to the boiling point. The subsequent treatment of each sample was identical in every case.

It will be noted that the time of sweating or the length of time required to produce the brown color and the characteristic odor of the cured beans de-

waxed paper, placed in tight containers, and allowed to stand for a period of 2 mos. After this time the samples were carefully examined and compared with regard to average weight and length, also color, odor, and general appearance, with several commercial samples of cured beans, and the results tabulated, as shown in Table II.

The average weight and length of the laboratory cured beans compare very favorably with the commercially cured samples. In color and odor several of the laboratory samples were superior to the commercial samples. The presence of crystals of vanillin on the surface of the beans usually occurs when beans with high content of this constituent are kept in a confined space for a period of time. Crystals of vanillin were observed to be most prevalent in the samples cured at room temperature, an entire absence of crystals being noted in the samples cured in the water oven with one exception, that of Sample 2, on which a few crystals were observed.

A decided red-brown color was apparent in the cross section of the beans cured at room tempera-

TABLE II—GENERAL COMPARISON OF LABORATORY CURED AND COMMERCIAL CURED VANILLA BEANS

SAMPLE	CURED BEANS		BROWN COLOR	ODOR	DESCRIPTION OF WHOLE BEANS	DESCRIPTION OF CUT BEANS (CROSS SECTION)
	Av. G.	Av. Length Mm.				
1	4.1	19	Chocolate	Fragrant, vanilla-like	Uniformly colored, soft, pliable. A few small vanillin crystals on surface	Uniformly red-brown, inner portion redder than surface
7	5.1	19.5	Pale	Fine, fragrant	Soft and pliable, wrinkled. No crystals	Reddish brown, inner portion redder than surface
5	4.9	18	Chocolate	Fine, mild	Pliable and wrinkled. A few crystals on surface	Reddish brown, inner portion redder than surface
3	5.1	19.5	Dark	Especially fine	Nearly covered with vanillin crystals	Dark brown, somewhat lighter than surface
9	4.4	19	Light chocolate	Very mild	No crystals	Uniformly brown
11	5.2	19.5	Reddish	Lacking fineness	Not uniformly colored. A few crystals at ends	Lighter but uniformly brown
2	5.2	19.5	Dark	Good, strong	A few crystals at one end	Inner portion lighter brown than surface. Charred odor
8	5.1	20	Chocolate	Mild, fragrant	Uniformly colored. No crystals	Uniformly chocolate-brown
6	5.6	20	Pale	Prune-like	No crystals	Uniformly pale brown
4	4.7	19	Chocolate	Good, but lacking bouquet	No crystals	Inner portion paler than surface
10	4.8	18.5	Chocolate	Very mild	Not uniformly colored. No crystals	Lighter in cross section
12	4.8	18	Pale	Prune-like	Not uniformly colored. No crystals	Uniformly brown
Mex. A	5.1	23	Dark	Strong, not agreeable	Pliable, sticky. No crystals	Much lighter brown than surface. Odor somewhat tobacco-like
Tahiti	3.2	18	Dark	Strong	Conspicuous pale, longitudinal stripes	Uniformly brown. Odor somewhat tobacco-like
S. Amer.	3.9	20	Very pale	Mild, sweet	Not pliable. A few crystals	Inner portion reddish brown
Bourbon	2.7	17	Almost black	Pleasant	Very pliable. No crystals	Inner portion lighter brown than surface
Old (a)	2.5	16	Pale	Very faint	Nearly dry. No crystals	Uniformly pale brown

(a) Beans several years old.

creases with the increase in temperature of the water in which the green beans were immersed. Indications, therefore, point to increased activity of the oxidases which supposedly bring about the changes. Whether this increased activity is favorable or detrimental to the production of color and odor will be apparent later.

After the sweating process, the time required for drying to the proper appearance and texture varied somewhat according to the previous treatment with hot water. The beans were dried until the proper pliability was obtained, or until the loss of moisture was from 64 to 69 per cent. In a general way the drying increased in rapidity as the temperature to which the beans were originally subjected was increased.

The formation of the brown color as well as the vanilla odor was seemingly most rapid in the samples subjected to the hottest water. These changes were also most marked and rapid in the samples sweated in the water oven at a temperature ranging from 40 to 60° C.

The various lots of cured beans were wrapped in

ture, with a decreasing tendency as the temperature of the water increased into which the beans were immersed.

Physical tests being insufficient and inadequate to determine accurately the quality of beans cured by the various modifications of the methods, a chemical examination was necessary. Not only was it desired to ascertain the respective qualities of the beans with regard to vanillin content, but also the oleoresin content, which is considered an important adjunct to the flavor of the beans.

PREPARATION AND PROPERTIES OF EXTRACTS

In order more advantageously to judge the quality of the cured beans and to make a thorough comparison of the various samples with the commercial beans, extracts were made from the samples according to the directions in the United States Pharmacopoeia¹ for the preparation of tincture of vanilla. The resulting extracts afforded an excellent means for com-

¹ United States Pharmacopoeia, Eighth Decennial Revision, 1900, 484.

paring the general physical and chemical properties of the individual samples with those prepared from commercial vanilla beans. These comparisons are shown in Table III.

The general physical properties of the extracts from the samples cured at room temperature were superior to those cured in the water oven at somewhat higher temperature. The colors of the former were distinctly more red and brownish red than the latter. All the laboratory extracts were more attractive in color than the extracts from the commercial beans. The deeper color of the extracts from the laboratory cured beans was perhaps due to the presence of vanilla resins which possess a color of deep red to brown.

The odor and taste of the extracts from the beans cured at room temperature were superior to those from the oven cured beans. The presence of a distinct flowery or fruity odor and taste was apparent. Extracts from the commercial beans seemed lacking in this respect.

In vanillin content less difference is noted between the extracts from the commercial beans and the laboratory cured beans. The extracts from the beans cured at room temperature assayed considerably higher in

ples were next in order, followed by the Tahiti and the old sample.

In order partly to obtain more expert judgment and partly to verify the writer's judgment of the samples, a sample of each extract was submitted to a prominent manufacturer of flavoring extracts, who, without having any knowledge of the identity of any of the 18 samples submitted, made the following report on the color, odor, and taste:

COLOR—South American, the best.

ODOR—Nos. 3, 5, 1 and 7 ranked highest; Tahiti, No. 11, and South American, next; Mexican A, Nos. 9, 8, and 2, Bourbon, 4, 6, 10, and 12, Mexican B and old sample follow in order.

TASTE—Nos. 1, 2 and 3 ranked first; South American, Nos. 11, 7, 9, and 8, were next in rank, followed by Tahiti, Mexican A, No. 2, Bourbon, Nos. 4, 6 and 10; No. 12, Mexican B, and old sample were stated to contain a foreign taste.

According to the report the color of the extract from the South American beans was considered best. This is in close accordance with the colors as described in Table III. Extracts 1 and 3 possessed about the same color as the South American, namely, a bright wine-red, while Nos. 5 and 7 were slightly darker. The remainder of the laboratory extracts possessed an admixture of brown, this color being more prominent in some than in others.

TABLE III—PHYSICAL AND CHEMICAL COMPARISON OF VANILLA EXTRACTS FROM LABORATORY CURED AND COMMERCIAL BEANS

SAMPLE	PHYSICAL PROPERTIES OF EXTRACTS			PER CENT VANILLIN
	COLOR	ODOR	TASTE	
1	Wine-red	Pleasant, fruity, very fragrant	Very agreeable, fruity, lasting	0.255
7	Deep wine-red	Pleasant, fruity	Agreeable, vanilla-like	0.253
5	Very deep wine-red	Pleasant, less fruity	Mild, characteristic, pleasant	0.210
3	Wine-red	Very pleasant, flowery	Very pleasant, fruity	0.317
9	Wine-red, slight brownish tint	Pleasant, vanilla-like	Agreeable, not fruity	0.212
11	Wine-red, slight brownish tint	Mild, pleasant	Agreeable, slight	0.212
2	Wine-red	Pleasant, agreeable	Mild and pleasant	0.215
8	Brown with reddish tint	Strong, pleasant	Strong, lasting	0.252
6	Light wine-red, brownish tint	Mild, lacking fragrance	Characteristic, pleasant	0.228
4	Brown with only trace of red	Pleasant, fragrance lacking	Pleasant, lasting	0.201
10	Wine-red, distinct brownish tint	Mild, characteristic	Characteristic, less agreeable	0.239
12	Wine-red, distinct brownish tint	Mild, agreeable	Pleasant, slightly prune-like	0.225
Mex. A	Light brown	Pleasant, characteristic	Agreeable, not fruity	0.259
Mex. B	Wine-red, with brownish tint	Strong, vanilla-like, lacking fragrance	Strong, harsh, not fruity	0.291
Tahiti	Very pale brown	Strong, extract-like, lacking fragrance	Strong, unpleasant, licorice-like	0.200
S. Amer.	Wine-red	Pleasant, agreeable, vanilla-like	Strong, agreeable, vanilla-like	0.268
Bourbon	Wine-red, with brownish tint	Pleasant, agreeable, vanilla-like	Characteristic, not fruity	0.248
Old	Brown	Mild, vanilla-like	Mild, not agreeable	0.196

general average than from the beans cured at higher temperatures.

Considerable variation in vanillin content exists, however, in samples prepared from the beans which had received the hot water treatment before curing. It is very probable that the effect of this treatment as regards composition of the beans will be more pronounced in other constituents than in the vanillin.

To the writer the laboratory cured beans and also the extracts appeared to possess a better odor and taste than any of the commercial beans or extracts. The color of the extracts in every case also distinctly excelled in color those from the beans cured at higher temperatures.

Judging from a purely physical standpoint of color, odor, and taste, the extracts from Samples 1 and 3 were considered the finest, followed by Samples 5, 7, 9 and 11. Samples 2, 8, 6, 4, 10 and 12 were all lower in color estimation and slightly inferior in odor and taste. Of the extracts from the commercial beans, the South American sample was distinctly superior to the others in every respect and more nearly corresponded to Samples 1 and 3 of the laboratory cured beans. The Bourbon and Mexican sam-

Not only was the rating of the various samples by the manufacturer with respect to odor and taste in close accordance with the writer's selections, but it is a singular fact that three of the laboratory cured samples were stated to excel in point of odor and taste the extracts from the commercial beans and in nearly all cases the beans cured at room temperature were superior to those cured in the water oven.

In order to ascertain whether the various modifications of the curing process produced any effect upon the composition of the beans, an analysis of the residues remaining from the preparation of the extracts was examined.

EXTRACTION OF THE RESINS

Since it is generally conceded that resins or oleo-resins tend strongly to modify the agreeable odor of vanilla beans, it is very probable that the superior aroma and flavor of several of the cured samples of beans were due to the presence of these odorous resinous substances. These substances are for the most part soluble in alcohol, to a less extent, however, in hydroalcoholic solutions. In preparing the extracts described 65 per cent alcohol was used. Not all of the resinous constituents of the beans were dis-

solved by alcohol of this strength but it is assumed that approximately the same percentage of these constituents was extracted from each sample. Provided that more resinous constituents were present in some samples than in others, and granting that the 65 per cent alcohol extracted only a small portion of these constituents, the residues from the preparation of the extracts still contained much of the unextracted resinous substances.

These residues were therefore subjected to extraction with 94 per cent alcohol in order to obtain the residual resins. The residues remaining from the alcohol extraction were further extracted with ether. The percentages of alcohol and ether extracts, and descriptions of each, are given in Table IV.

The quantity of alcohol-soluble constituents remaining in the beans after the preparation of the extracts is considerable. While a number of constituents are no doubt present in these extracts, a large portion probably consists of vanilla resins, together with some vanillin.

The percentage of alcohol extracts from the samples of beans cured in the laboratory at room temperature is uniformly higher than from those cured in

EXAMINATION OF RESINS EXTRACTED WITH ALCOHOL

In order to obtain further knowledge of the alcohol extracts obtained from the residues, the chemical constants, acid, ester, and saponification numbers were determined. The results are shown in Table IV.

Considerable variation exists in the acid, ester, and saponification values of the alcohol extracts obtained from the residues of the laboratory cured beans. The general average of these constants is higher than that of the commercial beans, as was also the percentage of extract. The content of free acid constituents of the resinous extracts is high in nearly all instances, signifying the presence of considerable resin acids. The ester values are likewise high, showing the presence of saponifiable resinous compounds. The resin acids and the combined saponifiable resins seem to have been formed to a greater extent in the beans cured in the laboratory than in the commercially cured samples. Provided these substances tend to add fragrance to the odor of the vanilla bean and therefore also to the extract made from the beans, it would seem that methods which would insure a high percentage of these resinous substances should be preferred. Doubtless a certain percentage of these

TABLE IV—ALCOHOL AND ETHER EXTRACTS FROM VANILLA RESIDUES

SAMPLE	ALCOHOL EXTRACT OF VANILLA RESIDUES				CHEMICAL CONSTANTS OF ALCOHOL EXTRACT OF RESIDUES				ETHER EXTRACT OF VANILLA RESIDUES			
	Per cent	COLOR	STATE	VANILLA ODOR	Acid Value	Ester Value	Sapon. Value	Per cent	COLOR	STATE	ODOR	
1	19.23	Dark red	Semi-solid	Fine	13.4	170.5	183.9	4.14	Red-brown	Oily	Fatty	
7	27.25	Brownish red	Nearly solid	Fine	27.0	182.3	209.3	4.50	Brownish red	Oily	Balsamic	
5	18.22	Brownish red	Nearly solid	Fine	14.3	169.0	183.3	5.34	Pale brown	Oily	Fatty(a)	
3	20.80	Reddish brown	Semi-solid	Mild	14.6	180.0	194.6	3.73	Pale brown	Oily	Fatty(a)	
9	21.41	Reddish brown	Semi-solid	Pronounced	39.0	161.4	200.4	3.71	Pale yellow	Oily	Slight fatty	
11	16.07	Brownish red	Nearly solid	Fine	36.0	167.5	203.5	3.88	Pale brownish red	Oily	Mild, pleasant	
2	23.19	Pale brownish red	Partly liquid	Yes	34.3	124.6	158.9	4.86	Pale brown	Oily	Slight balsamic	
8	13.30	Reddish brown	Nearly solid	Pronounced	34.0	132.0	166.0	3.33	Brownish red	Oily	Slight vanilla	
6	17.18	Brownish	Semi-solid	Faint, agreeable	60.1	126.1	186.2	4.99	Pale brown	Oily	Nearly odorless	
4	21.28	Pale brown	Nearly solid	Mild	48.3	134.5	182.8	4.33	Pale yellow	Oily	Faint vanilla	
10	13.11	Brownish	Semi-solid	Faint	53.2	127.3	180.5	4.38	Pale brown	Oily	Faint	
12	15.50	Brown	Partly liquid	Faint	40.0	142.2	182.2	3.70	Pale brown	Oily	Faint	
Mex. A	19.60	Brown	Liquid	Faint, fatty	25.8	145.6	171.4	4.01	Red-brown	Oily	Fatty(a)	
Mex. B	12.76	Brown	Semi-solid	Yes	12.9	155.3	168.2	4.11	Dark brown	Oily	Fatty	
Tahiti	6.43	Pale brown	Solid	Faint	39.7			6.03	Dark red-brown	Oily	Faint balsamic	
S. Amer.	27.20	Dark red-brown	Semi-solid	Pleasant	8.4	85.0	93.4	2.81	Dark brown	Oily	Slight vanilla	
Bourbon	19.75	Dark brown	Nearly solid	Good	38.2	155.0	193.2	4.46	Yellow	Oily	Faint	
Old	13.35				28.2	134.2	162.4	4.22	Pale brownish	Oily	Faint	

(a) Fatty taste as well as odor.

the water oven. Likewise those extracts were considerably deeper and richer in color. It would seem, therefore, that curing at room temperature is more conducive to the formation of vanilla resins and coloring matter.

The highest percentage of alcohol extract (vanilla resins) in the commercial beans was in the South American sample. This sample also produced a vanilla extract with the deepest color. The residues from the Mexican and Bourbon beans also contained a high percentage of alcohol-soluble substances, and likewise a highly colored extract. These facts are significant of the effect of curing upon the color of prepared extracts and also of the comparatively large quantity of flavoring resins which remain in the residues.

The ether extracts were found to consist largely of fatty oil and were nearly devoid of odor. Some of the less soluble resinous constituents are doubtless present in these extracts. The percentages of ether extract seem to bear no direct relationship as regards treatment during curing. Some variation is apparent, however, among the samples from different sources.

substances are extracted by the hydroalcoholic menstruum used in preparing the extracts of commerce, the quantity in solution depending largely upon the strength of the alcohol employed.

CONCLUSIONS

From the results reported herein it may be said in general that the curing process as at present commercially applied to vanilla beans is unnecessarily long and extended, requiring on an average several months for the transformation of the green to the cured beans.

In the laboratory experiment conducted it has been shown that the beans can be cured in a much shorter time by means of a much less tedious process. It has further been demonstrated that the process is simplified to the advantage rather than to the detriment of the aromatic constituents. In order to produce uniformity in the composition of the beans, and thereby insure more uniform extracts, the importation and curing of the green beans are suggested.

While the amount of vanillin in the beans was not increased appreciably, as compared with commercial beans, it may be stated with assurance that the beans

cured in the laboratory were in most cases superior in vanilla resins and coloring matter. This is significant since vanilla resins and coloring matter are considered important adjuncts to the quality of vanilla beans. The superior flavor of the extracts prepared from the laboratory cured beans may therefore be ascribed to the resinous constituents. A considerable proportion of the vanilla resins are left unextracted when the menstruum is less than 65 per cent alcoholic strength.

Curing the green beans at room temperature either without previous treatment or after treatment with water up to 90° C. for a short period of time apparently produces beans of the best quality, as judged by the flavoring extracts prepared from the samples.

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A STUDY OF THE STEREO-ISOMERISM OF A FERMENTATION LACTIC ACID

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Investigations of the isomerism of lactic acid soon followed Pasteur's famous work with tartaric acid. In 1890, Lewkowitsch¹ showed that ammonium lactate when exposed to the action of *Penicillium glaucum* for several weeks became optically active. In 1892, Professor T. Purdie proved, by direct analytical evidence, that commercial lactic acid can be resolved into two oppositely active isomeric acids.² The results of experiments of various writers on the kind of lactic acid formed in naturally soured milk do not agree. Some found inactive acid, some dextro-, and some laevo-rotatory acid. Dr. P. G. Heinemann cleared up most of this conflicting testimony by showing that different bacteria produce different kinds of acid. As a summary to an excellent paper on the subject, he says: "Racemic lactic acid is the result of the formation of pure dextro acid and pure laevo acid by at least two different species of microorganisms. Racemic (inactive) lactic acid is not known to be the product of one species only."³

The object of this paper is to discuss the kind of lactic acid present in Matzoon, an Armenian artificially soured milk, and to give the results of an investigation of its optical powers.

Matzoon is a beverage prepared from cows' milk with the aid of an appropriate ferment. From this ferment, or "starter," the author isolated a bacillus, a streptococcus, and a yeast. The bacillus was determined as a member of the *B. bulgaricus* group, corresponding more closely to *B. caucasicus* (Flügge) than to any other member. The streptococcus isolated was *Str. kefir* (Kuntze), a member of the *Str. lebanis*⁴ group. The yeast was determined as *Saccharomyces kefir*: this organism is unable to ferment milk or lactose, excepting a slight production of alcohol.

Lactic acid was discovered by Scheele. It exists

in sour milk, human gastric juice and in muscle. It has been found in the vegetable kingdom in the peduncles of *Solanum dulcamara*.¹ There are four lactic acids, three having the formula $\text{CH}_3\text{CHOH}\cdot\text{COOH}$, and one the formula $\text{CH}_2\text{OH}\cdot\text{CH}_2\text{COOH}$. Inactive or ethylidene lactic acid (α -hydroxy propionic acid) may be prepared by treating α -chloropropionic acid with potassium hydroxide: it forms a zinc lactate that crystallizes with three molecules of water of crystallization. Sarco- or dextro-lactic acid ($\text{CH}_3\text{CHOH}\cdot\text{COOH}$) is found in meat: the zinc lactate made from this acid crystallizes with two molecules of water of crystallization.

Laevo-lactic acid ($\text{CH}_3\text{CHOH}\cdot\text{COOH}$) differs from the dextro acid only in its optical powers: its zinc lactate crystallizes with two molecules of water of crystallization.

Beta hydroxy propionic acid (hydracrylic or ethylene lactic acid) has the formula $\text{CH}_2\text{OHCH}_2\text{COOH}$. When heated it liberates water and forms an unsaturated acid, acrylic acid, CH_2CHCOOH .

Thus we have three lactic acids having the same structural formula but different properties. This is known as stereo-isomerism, physical isomerism, or optical isomerism. Ethylene lactic acid, $\text{CH}_2\text{OHCH}_2\text{COOH}$, is inactive under all circumstances. Ethylidene lactic acid, $\text{CH}_3\text{CHOHCOOH}$, on the other hand, may exhibit optical activity. On close examination the latter is found to contain a carbon atom in its molecule which holds four other atoms or groups of atoms, all different from each other. Optically active substances, without exception, contain one or more such carbon atoms in their molecules, and the property of turning the plane of polarization bears a close relation to the structure of a substance. Optical activity is, therefore, due to the presence of a carbon atom in a molecule which holds four dissimilar groups with its four bonds. Such a carbon atom is known as an asymmetric carbon atom. Furthermore, an optically active substance may show dextro-rotation, that is, turn the plane of polarization to the right; or laevo-rotation, that is, turn the plane of polarization to the left. A closer examination of the lactic acid molecule may show why the acid exhibits both dextro-rotation and laevo-rotation.

Let us now examine the lactic acid molecule. If we attempt to draw a picture of the molecule in space we may have:

The difference between these formulae is only that of an object and its image in a mirror. If *b* be superimposed upon *a*, we will find that the OH group

¹ Ber., 16, 2720.

² J. Chem. Soc., 1892, 754.

³ J. Biol. Chem., 2, 612.

⁴ Freudenreich, Landw. Jahrb. d. Schweiz., 10 (1896), 1.

¹ Standard Dispensatory.