

The Recovery of Methyl Anthranilate in Concord Grape Essence

SUMMARY

The making of a full-flavor dehydrated Concord grape juice requires a relatively high-fold essence. Essences on the order of 600- to 1000-fold produced by ordinary continuous distillation techniques showed very high losses of methyl anthranilate, which is considered a major characteristic of Concord grape flavor. These losses could be attributed to losses in the bottoms stream from the distillation column as well as unaccountable losses over the system. Data are presented to show the mechanisms involved in the recovery of methyl anthranilate by distillation. This important constituent, with a boiling point of 512°F, can be removed from bottoms in an aqueous system because it is not completely miscible with water in all proportions. When making high-fold essence, however, the ethanol concentration becomes so high in the enriching section of the distillation column as to render methyl anthranilate completely miscible in all proportions. This prevents methyl anthranilate from rising above this point in the tower. A good essence is produced by combining a side stream high in methyl anthranilate and an overhead product high in volatile esters and ethanol but deplete in methyl anthranilate.

THE DEVELOPMENT by Turkot *et al.* (1956) of a continuous process for full-flavor fruit-juice powders emphasized the need of recovering the volatile flavor constituents of the juice efficiently in a highly concentrated essence. The Eastern Utilization Research and Development Division, over 15 years ago, first reported work on a process to recover volatile aromas from apple juice (Milleville and Eskew, 1944). Much work has since been published on producing 75- to 150-fold^c essences used to restore natural aromas to 4-fold concentrates (Eskew *et al.*, 1952) and to 7-fold concentrates (Eskew *et al.*, 1952) of Concord grape juice. The essence recovery process (Claffey *et al.*, 1958) consists essentially of a rapid atmospheric evaporator and a distillation column. The distilling column concentrates the vapor from the evaporator, containing most of the volatile flavor constituents of the juice, to 75 or 150 times the original concentration in the juice. Adding back the essence to the concentrate restores the natural flavors and aromas.

Returning natural flavors to a dehydrated product without adding excessive liquid, however, requires a much higher-fold essence, on the order of 1000-fold. Highly concentrated essences of about 1000-fold have

been produced by redistilling a low-fold essence in a small continuous distillation column. For apple, cherry and strawberry essence results have been quite good. When the technique was applied to Concord grape essence, however, the typical Concord grape character was noticeably lacking.

Analysis of the normal 150-fold Concord grape essences used to restore aromas to 7-fold concentrates has shown that recoveries of methyl anthranilate, long known to be a constituent of Concord grape flavor (Sale and Wilson, 1926) and a basis for military purchases of Concord grape products (Military Specification, 1952), were only about 50% of that in the feed. Recoveries have been much lower in high-fold essences on the order of 1000-fold. It was hoped that an improvement in the recovery of this constituent would considerably improve the quality of the essence.

This paper reports a study of the distillation of methyl anthranilate in a complex system obtained from partial vaporization of Concord grape juice.

MATERIALS AND ANALYTICAL PROCEDURES

The methyl anthranilate and ethyl acetate used for analytical procedures and in the making of synthetic essences for distillation studies were obtained from Eastman Organic Chemicals Distillation Products Industries,^d Rochester, New York. The methyl anthranilate was assumed to be 100%, and the assay for ethyl acetate was listed on the package as 99%. The ethanol used was 95% U.S.P. grade. All analyses were made with clear solutions. Analyses of juice and colored solutions were done on clear aliquots obtained from a quantitative distillation of the juice.

Methyl anthranilate analysis. Methyl anthranilate concentrations were estimated by the method prescribed in military specifications for Concord grape-juice concentrate for beverage use (Military Specification, 1952) except that the potassium salt of alpha-naphthol-2-sulfonic acid was used instead of the prescribed sodium salt.

This is a spectrophotometric method that depends on the color developed when the methyl anthranilate is coupled with the naphthol. The absorbance of the solution was measured at 490 μ with a Model B Beckman spectrophotometer. The concentration of methyl anthranilate was determined by comparing the absorbance obtained with that of a standard solution or by interpolation from a previously prepared standard curve.

Volatile-esters analysis. The volatile esters were determined by an adaptation of the method of Thompson (1950) used by Walker *et al.* in work on strawberry juice (Walker *et al.*, 1954). By this method the esters are converted to the corresponding hydroxamic acids by reacting with alkaline hydroxylamine and then treating with ferric chloride in acid solution. This gives colored ferric complexes of hydroxamic acids. The absorbance of the colored solution is measured at 540 μ and compared to a standard.

Ethanol analysis. Ethanol was determined by a colorimetric method described by Reid and Truelove (1952). The method depends on the color produced by the reaction of ceric ammonium nitrate with the alcohols. The absorbance of the un-

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^c Fold is the volumetric ratio of the juice feed to the recovered essence, i.e., one gallon of essence obtained from 150 gal. of juice would be 150-fold.

^d Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

known sample at 500 $m\mu$ is compared with that of a standard solution, or the concentration is determined by interpolation from a standard curve. The method is most applicable when alcohol concentrations are low and when only a single alcohol is present. The latter requirement is not a serious problem in the analysis of grape juice or essence, because practically all of the alcohol is ethanol.

EXPERIMENTAL DATA AND DISCUSSION

Commercial Concord grape juice expressed from heat-treated grapes and detartrated by the usual settling methods contains 2–3 ppm of methyl anthranilate and about 50 ppm of volatile esters determined as ethyl acetate. The ethanol concentration generally ranges from 0.05 to 0.10% but may be higher, depending on the history of the grapes. Ethyl acetate is 95% of the esters, and ethanol is 90% of the total organics. Various workers have reported traces of acetone, organic acids, higher alcohols, and some aldehydes, all of which no doubt contribute something to the over-all flavor (Holley *et al.*, 1955).

Methyl anthranilate, the methyl ester of ortho-amino-benzoic acid, is a colorless liquid. When dissolved in ethanol and water, the solution has a blue fluorescent tinge. It boils at 266°C (512°F) at one atmosphere (Perry, 1950), and is only very slightly soluble in water. Chemically, it is quite stable, though solutions in ethanol and water take on a brownish cast if exposed to strong sunlight for long periods.

Because of its high boiling point it is surprising that methyl anthranilate is concentrated in the distillate rather than found in the bottoms or waste products of the distilling column. However, methyl anthranilate is only partially miscible in water, and, as with all partially miscible systems, a heterogeneous minimum boiling azeotrope with a boiling point below that of water is formed when a mixture of the two liquid phases is vaporized.

Fig. 1 shows a typical boiling-point composition diagram for immiscible liquids. The upper solid lines show the vapor composition, and the lower lines the liquid. Point A represents the normal boiling point of pure methyl anthranilate at 512°F, and point B that of pure water at 212°F. The region between points a and b represents compositions forming two

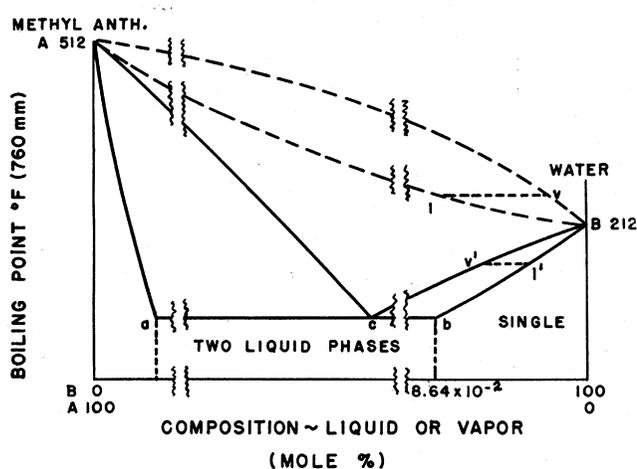


Fig. 1. Typical boiling-point composition curve for immiscible liquids. (Only Points A, B, and b are known for a methyl anthranilate-water system.)

liquid phases, while the areas to the left of a and to the right of b are regions of a single liquid phase. The composition at point b is about 8.6×10^{-2} mole per cent, or 7200 ppm of methyl anthranilate by weight. Starting with juice at 3 ppm, a 1000-fold essence might be as high as 3000 ppm, or about $\frac{1}{2}$ the saturation concentration. Thus, in our distillations, considering only the two components methyl anthranilate and water, we are always working to the right of b and never encounter the two liquid phase region. The vapor-liquid equilibrium involved in this work, then, is only that portion of the curve to the right of b.

Considering a liquid of composition l' on boiling, at some temperature below 212°F, a vapor will be formed having composition v' . If this vapor is removed from contact with the liquid and condensed, a liquid will be produced with a higher methyl anthranilate concentration than the starting liquid. Repeating this process, as is done in a continuous distillation column, and starting with a liquid whose composition lies to the right of b, it is theoretically possible to produce pure water as bottoms and a mixture of composition c as a distillate. The practicality, however, of stripping the methyl anthranilate from the bottoms must be determined from knowledge of the vapor-liquid equilibrium of the binary solution.

Vapor-liquid equilibria for methyl anthranilate and water in the miscible concentration range. The miscible concentration range of a solution of methyl anthranilate and water at 178°F is less than 8.5×10^{-4} mole fraction of methyl anthranilate. In these extremely dilute solutions it can be expected that the concentrations of vapor in equilibrium with the liquid will follow Henry's law. The equation describing the equilibrium relationship can be written as

$$Y_a = k X_a$$

in which

Y_a = mole fraction of the methyl anthranilate in the vapor

X_a = mole fraction of the methyl anthranilate in the liquid

k = proportionality constant

To avoid confusion it should be explained at this point that in this concentration range the high-boiling component acts as the low-boiler because the azeotrope has a higher vapor pressure than either of the pure components. The system could be thought of as a two-component system consisting in this case of pure water and the lower-boiling azeotrope (Fig. 1).

In the case of immiscible liquids the value of "k" must be obtained experimentally by obtaining vapor-liquid equilibrium values in the desired range of concentration.

This was done with an Othmer equilibrium still (Othmer, 1928). The still was charged with about 250 ml of a water solution containing 300 ppm (3.56×10^{-5} mole fraction) of methyl anthranilate. Boiling was continued for 1 hr before sampling at an evaporation rate equal to twice the volume of the sampling section, allowing the establishment of equilibrium between the vapor sample and the main

body of liquid. Samples of the condensed vapor and of the liquid from the still were taken almost simultaneously. Subsequent samples of lower liquid concentrations were obtained by draining off one quarter of the volume of liquid in the body of the still and replacing it with distilled water.

The still was heated by immersing the glass heating-loop attached to the still in an oil bath held at about 160°C. The upper part of the still was covered with asbestos paper and wrapped with an electrically heated mantle to maintain the outer glass jacket at $100.0 \pm 0.5^\circ\text{C}$. Condenser water at 85°C minimized the sensible heat required to raise the condensate return to the boiling point. The temperatures of the vapors leaving the still were 99.6–99.9°C, corrected to 760 mm, and were measured with a calibrated thermometer graduated to 0.1°C. The changes were so slight that they were considered beyond the accuracy of the experimental techniques, since slight superheating of the vapors could have occurred. The boiling point of these solutions was very close to that of water, and temperatures of 99.60–99.95 were observed.

Fig. 2^o is a log-log plot of the vapor-liquid equilibrium. Log-log paper was used because the data cover such a wide range of concentrations, i.e., from 3×10^{-7} mole fraction to $3,570 \times 10^{-7}$ mole fraction.

The resulting straight line (Fig. 2) may be written as the function

$$\log Y = m \log X + \log k$$

Since the slope is unity, m is one, and, taking anti-logs, the equation becomes:

$$Y = k X$$

which is a form of Henry's law. This is the expected for such systems. The value of k that equals the value of Y when X is one on the log-log plot, is 3.33. This agrees with the average of the ratios of the composition of vapor and liquid. A value of 3.33 for k means that a distillation column operating at total reflux can effect a stripping of more than 97% of the methyl anthranilate from water in three theoretical steps.

Other problems in the recovery of methyl anthranilate. The work up to this point shows only that methyl anthranilate can be removed from the waste stream of the essence column by providing adequate stripping. Only part of the problem is solved, however. Some material balances over a 1000-fold column, starting with a 75-fold essence, showed unaccountable losses of methyl anthranilate as high as 50% of the feed. In other cases the high-fold product showed a concentration lower than that of the feed.

To investigate these conditions, work was continued with a model system consisting of an aqueous solution of methyl anthranilate and ethanol. The solution used as feed to the high-fold continuous distillation tower approximated a 75-fold Concord grape essence and contained 60 ppm of methyl anthranilate and 50 g/L of ethanol. The tower, a 1-in. ID glass tube packed with protruded stainless-steel packing, size 0.16 x 0.16 in., purchased from the Scientific Develop-

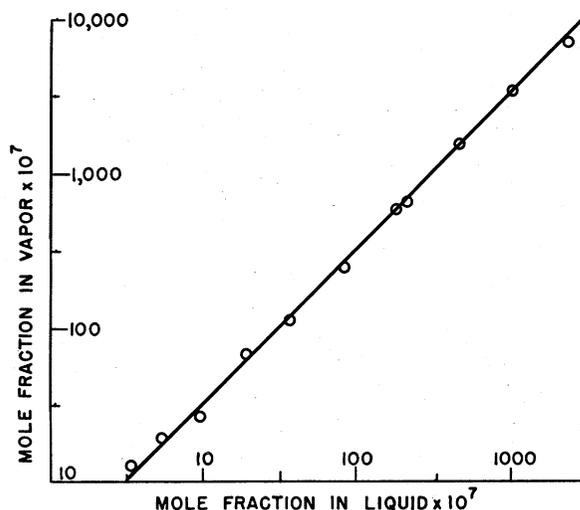


Fig. 2. Vapor-liquid equilibrium, methyl anthranilate and water.

ment Company, State College, Pennsylvania, was fed liquid at the boiling point at about 15 ml/min. The electrically heated reboiler was operated to vaporize 15 ml/min (equal to the feed rate) while an overhead product was removed at about 1–1.5 ml/min. Several runs were made under the same conditions except that the overhead product rate was varied in order to change the fold of the "essence." The fold ranged from 650 to 1120 and resulted in distillates of varying ethanol concentrations. It was noted that accompanying low ethanol concentrations in the overhead was a rather high methyl anthranilate recovery, while high ethanol concentrations resulted in very poor recoveries. Fig. 3 is an arithmetic plot of the recoveries of methyl anthranilate against the ethanol concentration of the essence. Below 50–55% ethanol concentration, methyl anthranilate recovery was rather high and probably limited only by the efficiency of the stripping section of the column. With ethanol concentrations above 60%, however, the recovery of methyl anthranilate decreased rapidly. These data suggest a discontinuous function. Apparently, two independent physical laws are represented. Going back to Fig. 1, the boiling-point composition diagram for methyl anthranilate and water, and recalling that methyl anthranilate can be expected to rise in a

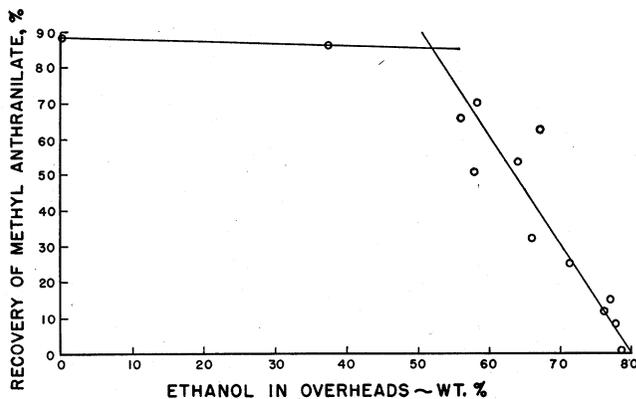


Fig. 3. Recovery of methyl anthranilate versus ethanol concentrations.

^o Tables of data for all plots are available on request.

distillation column only because it is miscible in the solvent at certain concentrations, it seems logical to assume that, should the methyl anthranilate encounter concentrations of ethanol and water in which it is completely miscible in all portions, the boiling point composition curve would follow a normal temperature composition diagram represented by the dotted lines in Fig. 1. This being the case, if a liquid of concentration "1" is boiled, then the composition of the vapor would be represented by v, which is less concentrated in methyl anthranilate. Therefore, under these conditions, the methyl anthranilate, with its high boiling point, would quickly diminish in the rising vapor in the column above the point where miscibility in the solvent is complete. Since the methyl anthranilate is stripped from the bottoms, and since at high ethanol concentrations it cannot leave the top of the tower, it must then be trapped in the enriching section of the column. Because the concentrations of methyl anthranilate involved are so minute, the loss would be too slight to be noticed by an over-all material balance. Only the methyl anthranilate balance would be affected.

Determination of the binodal curve for the system methyl anthranilate, ethanol and water. To prove this thesis and to throw further light on the physical properties of the system, the solubility of methyl anthranilate in ethanol-water solutions was determined at 81°C. This temperature was selected on the basis of Fig. 3. It is the boiling point of a 55% ethanol-water solution that seems to be the approximate concentration in which methyl anthranilate is completely miscible in all proportions. The data were obtained by alternately titrating water and ethanol into a weighed quantity of methyl anthranilate using the resulting cloudy and clear solutions as end points. About 50 g of methyl anthranilate were placed in a large test tube fitted with a three-hole rubber stopper. A thermometer graduated into 0.1°C was immersed in the solution and was surrounded by a glass stirring rod that could be raised and lowered to agitate the solution. The third hole was used to insert the tip of either the water- or ethanol-containing burette for titration. The test tube was placed in a constant-temperature water bath and held to 81.0 ± 0.1°C. By alternately adding water until a slightly cloudy solution remained and then adding ethanol until a clear solution resulted, the binodal curve for the system was traced. After each end point was reached, an excess of the liquid was added to obtain a new point by back-titrating to the cloudy or clear end point, whichever was the case. This resulted in points on both sides of the curve, thereby compensating for errors for each type of end point. The points at zero ethanol concentration were obtained from a mixture of distilled water and methyl anthranilate. After holding this mixture in the water bath for several hours with intermittent agitation to establish equilibrium between the lower methyl anthranilate phase and the upper water phase, samples were taken of each layer. The water phase was analyzed for methyl anthranilate by the standard method, and the water

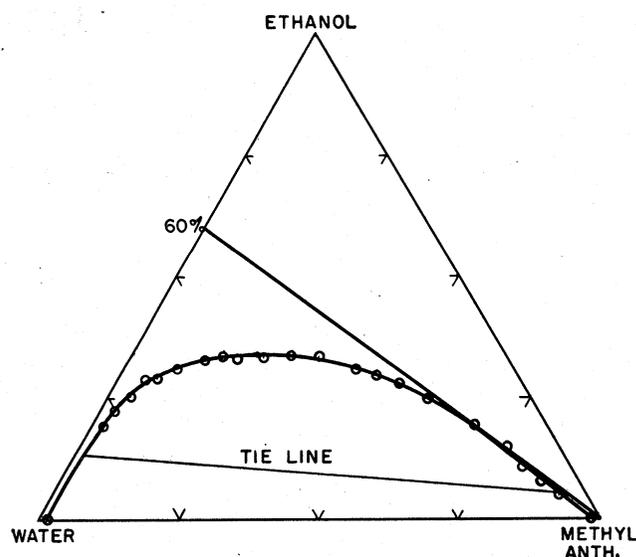


Fig. 4. Solubility of methyl anthranilate in ethanol and water at 81°C.

content of the methyl anthranilate layer was obtained by the Karl Fisher method. Similarly, as a check on the curve itself, a tie line was obtained by analysis of the upper water layer and lower methyl anthranilate layer of a mixture of methyl anthranilate, water, and ethanol whose composition was within the binodal curve.

Fig. 4 is a three-component diagram showing the binodal curve for the system. The tie line, determined independently as a check on the curve, is also shown. The region within the curve represents compositions of the three components that form two liquid phases. The compositions of solvent (ethanol and water) in which methyl anthranilate is completely miscible in all proportions lies on any line that passes through the apex representing pure methyl anthranilate and does not touch the two-phase region bounded by the binodal curve. The minimum composition of ethanol and water for complete miscibility in all proportions is determined, then, by the line passing through the pure methyl anthranilate point and an infinitesimal value above the tangent to the binodal curve. This line, drawn in Fig. 4, shows that the minimum ethanol-water concentration for complete miscibility in all proportions is about 60% ethanol.

Recovery of methyl anthranilate by distillation. With this knowledge in mind, the small, 1-in. glass tower packed with protruded stainless-steel packing, described earlier, was modified by providing a side-stream drawoff at a point 10 in. of packing below the top of the tower (Fig. 5). The column now had a stripping section of 56 in. of packing, and an enriching section of 29 in.

Trial runs were quite successful with a synthetic 75-fold essence containing 57 mg/L of methyl anthranilate and 5% by weight of ethanol. The methyl anthranilate balance over the tower was greatly improved. By withdrawing a side-stream, methyl anthranilate concentrations were collected as high as 1500 mg/L, a concentration that had never been at-

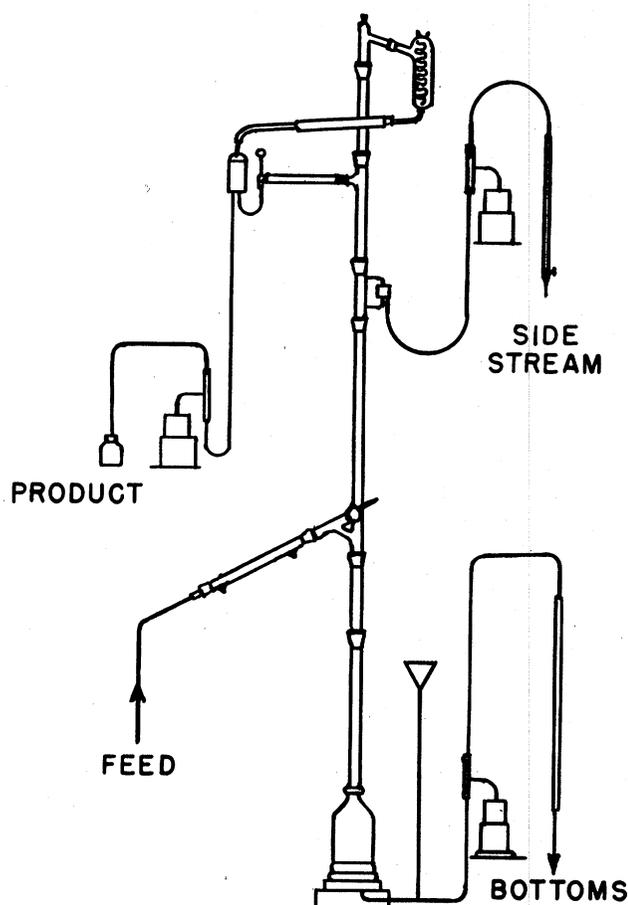


Fig. 5. High-fold distillation apparatus.

tained previously with Concord grape essence. The methyl anthranilate concentration in the overheads was quite low. High ethanol concentration on the order of 90% in the overhead product reduced the methyl anthranilate concentration to a mere trace, sometimes too low for accurate analysis.

These runs showed a recovery of 70–75% of the methyl anthranilate in the combined side stream and overhead of the column, with 20–25% remaining in the bottoms.

With this success the production of a 1000-fold natural essence was attempted with a 75-fold essence produced from an essence recovery unit (Eskew *et al.*, 1959). This essence was particularly good in that it contained 175 mg/L of methyl anthranilate, 3000 mg/L of volatile esters, and 4% ethanol. The feed rate to the column was 15 ml/min, the side stream was removed at 0.75 ml/min, and the overhead was collected at 0.25 ml/min.

With this technique, 70% of the methyl anthranilate was found in the side stream, and only 2% in the overhead product. The side stream contained 35% ethanol and 2400 mg/L of methyl anthranilate. As would be expected, each stream separately lacked the full character of the Concord grape flavor; a noticeable improvement resulted when the two streams were mixed to give the 1000-fold essence.

In this case the over-all yield to the 1000-fold essence was 60% of the methyl anthranilate in the single-strength juice. With 14% remaining in the concentrate, the reconstituted juice contained 74% of the methyl anthranilate in the juice. There was a 20% loss to the bottoms of both the 75-fold and 1000-fold tower. The 6% remaining is unaccounted for and includes errors and handling losses.

These data show the importance of stripping efficiency in both the essence-recovery unit-distillation column and the high-fold tower. In the usual production of 75- or 150-fold essence now being produced commercially, the methyl anthranilate should be readily recovered as overhead product since the ethanol concentration is always far below the critical concentration of 55–60% by weight. The losses experienced are thus due only to the inefficiency of the stripping section of the column.

It is interesting to note that the case of the volatile esters seems quite different. In the overhead product of the high-fold tower for this run, 74% of the volatile esters were collected, with a concentration of 85,000 mg/L, whereas the side stream had only 2%, with a concentration of 1744 mg/L. The over-all recovery of the volatile ester is about the same as the methyl anthranilate. Again, losses seem to be due only to inefficient stripping in both the low-fold and the high-fold columns. It should be pointed out that the volatile esters are also solvents for methyl anthranilate and doubtless have the same effect in the high-fold tower as the ethanol. For this reason the critical ethanol concentration may vary in the multi-component system represented by natural juice essence from the 60% determined with the model three-component system.

CONCLUSIONS

This study shows the importance of ethanol concentration in recovery of the volatile constituents of Concord grape juice by distillation techniques. Methyl anthranilate, a high-boiling component of Concord grape juice that gives it much of the characteristic flavor, can be recovered by distillation because it is not miscible in all proportions with water. When making low-fold essences, where ethanol concentrations are always far below the critical range, losses are due only to low stripping efficiency of the essence column. When higher-fold essences are produced, however, the ethanol concentration increases to the point where the methyl anthranilate becomes completely miscible with the essence, and under these conditions the methyl anthranilate must be removed from the column by withdrawing a side stream from the enriching section of the tower.

ACKNOWLEDGMENT

The author expresses his thanks to Joseph A. Connelly of the Plant Products Laboratory for his invaluable assistance with analytical procedures.

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