ORANGE ESSENCE EVALUATION: A NEW CHEMICAL TEST

R. J. BRADDOCK

IFAS Agricultural Research and Education Center
Lake Alfred
and

D. R. PETRUS

Florida Department of Citrus
Lake Alfred

ABSTRACT

Aqueous orange essences from commercial processors were evaluated by a taste panel for flavor and aroma qualities. A variety of stress conditions designed to decrease the initial quality of the essence was employed to study correlation of taste panel results with a chemical test for malonaldehyde, a compound known to be present in many deteriorating food systems, and shown to be a constituent of commercially processed citrus essences and oils. The quantity of malonaldehyde in essence was found to vary with the abuse given the essence during periods of oxidative deterioration. Results indicate that the measurement of malonaldehyde may prove to be a valuable new analytical method useful in the quality evaluation of commercial aqueous orange essences.

INTRODUCTION

The concentrated aqueous distillate from the commercial production of concentrated orange juice has been termed "essence", in consideration of its use to improve the fresh-orange aroma and flavor of processed juices. Results have been published showing that essence contains a variety of carbonyl and other compounds, some of which may be artifacts formed during the manufacturing process or as a result of adverse storage conditions after processing (Attaway et al., 1962, 1964, 1967).

There is considerable interest from the citrus industry for objective analytical methods to evaluate and determine when the development of off-odors and off-flavors will be a detriment to the quality of processed citrus juices and products. This paper reports the application of a chemical test for malonaldehyde to the measurement of commercial essence quality.

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EXPERIMENTAL

A 2-thiobarbituric acid (TBA) (Eastman) reagent and citrate buffer which proved suitable for reaction with aqueous orange essence was prepared as described by Yu and Sinnhuber (1962). The reaction was performed in test tubes by mixing 2 ml of essence with 4 ml each of buffer and TBA reagent. The tubes were placed in a boiling water bath for 25 minutes, resulting in the formation of a pink-orange complex. Standard curves were obtained by plotting the absorbance at 532 nm versus the concentration of solutions of 1,1,3,3-tetramethoxypropane (TMP) (Aldrich) treated in a similar manner.

Reacted essence samples were removed from the water bath and cooled to room temperature. Then 0.5 gm cellulose powder (Cellulosepulver MN 300 HR, or Avicel, Brinkman) was added to the test tubes and mixed vigorously for 30 sec. A distilled water blank was run simultaneously. After mixing, the contents of the test tubes were transferred quantitatively to a sintered glass funnel and the aqueous portion removed with suction. The firm pad which remained was then washed with 10 ml 0.1 N HCl, discarding the filtrate. Finally, the pad was washed with 9.0 ml 0.1 N NaOH, collecting the filtrate in a clean flask containing 1.0 ml of 1.2 N HCl. If necessary, the volume was adjusted to 10.0 ml with distilled water and the absorbance of the pink solution read at 490 and 532 nm using a Beckman DU with a Gilford photometer attachment. Satisfactory values were also obtained using a Bausch and Lomb Spectronic 20 spectrophotometer.

Other experimental procedures used in this study involved the use of a 12-member trained taste panel and the determination of total essence aldehydes by an N-hydroxybenzenesulfonamide test (Petrus et al., 1970).

Essences were made palatable by dilution with a syrup containing 60 gm sucrose, 4 gm citric acid, 0.5 gm sodium citrate, 0.2 gm pectin and dissolved in 500 ml distilled water. The amount of dilution varied with the concentration of the essence and had to be determined for each essence. For one of the essences used in this study, a typical dilution was as follows: 2 parts essence to 8 parts distilled water and 1 part of this mixture added to 8 parts syrup.

Results and Discussion

The compound, malonaldehyde, has been implicated to be an indicator of autoxidation in many foodstuffs which are susceptible to such deteriorations. This compound has recently been described as a constituent of commercial citrus essences and may prove useful as a quality indicator (Braddock and Petrus, 1971).

Several fresh essences of good quality were obtained from industrial sources and oxidized under controlled conditions. Essence samples were prepared with no metal, 40 ppm Cu and 40 ppm Fe and oxidized by mechanical shaking for various time periods at 50°C in the presence of air. In all experiments, oxidation under these conditions drastically affected the quality of the essences.

Results of oxidation of fresh essences containing no metal ions are summarized in Table 1, signifying decreasing taste panel acceptance and malonaldehyde concentration with increasing oxidation time up to 2 days. Comments of the panelists were unfavorable concerning essences oxidized for 1 and 2 days, but the samples were still identifiable as having a citrus-like aroma. An apparent transition in the flavor profile occurred between 2 and 3 days' oxidation time when the samples lost their identity as citrus essence and were described by the panel as buttery or buttermilk-like. This flavor was more acceptable to the panel than the flavor of samples which had been oxidized for up to 2 days, but was not preferred over fresh, unoxidized essence.

The absorbance ratio, A490/A532, was found to increase rapidly as the oxidation of fresh essence samples containing no metal ions progressed. When this ratio was coupled with the malondehyde concentration, a more reliable indicator of quality was obtained. Most of the fresh, unoxidized essences of good quality had a ratio in the range 0.8 - 1.0. However, the initial ratio and the concentration of malonaldehyde varied from processor to processor with values obtained in the range of from 20 - 100 ppm malonaldehyde. Generally, lower values of from 20 - 40 ppm were associated with the better essences, corresponding to A490/A532 of about 1.0 and a hedonic flavor score of 6-7.

Table 1. The effect of oxidation at 50° C on the quality of aqueous orange essence in the absence of metal ions.

Oxidation (days)	Malonaldehyde. (ppm)	A490/A532	Taste panel
0	20	0.9	7
1	14	3.5	5
2	11	3.9	5
3	10	4.2	6
4	8	5.1	6

Table 2. The effect of oxidation at 50° C on the quality of aqueous orange essence in the presence of 40 ppm Fe.

Oxidation (days)	Malonaldehyde (ppm)	A490/A532	Taste panel
0	20	0.9	6
1	50	1.3	5
2	34	1.6	5
3	24	2.5	4
4	22	2.6	5

The effect of iron and copper upon the oxidation of samples was significant. Data is presented in Table 2 displaying an increase, followed by a decrease of malonaldehyde concentration with oxidation time in the presence of Fe. Again, a taste panel showed a preference for fresh, unoxidized samples. The sudden increase in malonaldehyde concentration after oxidation for 1 day in the presence of Fe is significant, since two commercial essence samples were found to contain up to 5 ppm Fe, a condition not conducive to maintenance of a stable shelf-life. It would be recommended that essence not be brought into contact with ferrous metals, if good quality is to be maintained. Similar conclusions with regard to copper were drawn.

The continued oxidation of essence samples resulted in a loss of total aldehydes in all samples. Data presented in Figure 1 shows a more rapid decrease during the first 2 days in essence samples

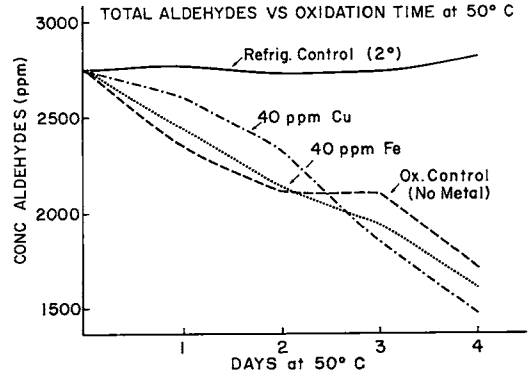

Figure 1.—The effect of oxidation at 50° C on total aldehyde concentration in aqueous orange essence.

to which no metal ions were added. This paralleled the decrease in malonaldehyde concentration in essence samples (Table 1) to which no metal was added. The overall loss of total aldehydes was greater after 4 days' oxidation in samples containing Cu or Fe than for the no metal control, a situation which might result if the metals were catalyzing oxidation of the essence. Since the total amount of aldehydes contributes to the quality and economics when an essence is added back to a concentrated juice, it should be again noted that metal ions such as Fe and Cu and conditions favoring oxidation can be detrimental to essence quality.

Generally speaking, in the initial reaction of the TBA reagent with the essence, if the color of the reaction complex is pink, or mostly pink, the essence is acceptable and has many of the characteristics of fresh juice aroma. If the reaction complex is reddish-orange or -brown, the essence is less acceptable and may have little identity as a citrus essence, probably not significantly improving the flavor and aroma of juice to which it was added. The best commercial essences obtained from various manufacturers contained malonaldehyde concentrations in the range of from 20 - 40 ppm and A490/A532 of approximately 1.0 as mentioned previously. However, there were a few exceptions where the malonaldehyde concentration of acceptable essences exceeded 50 ppm. These essences still maintained the criteria of A490/A532 about 1.0 and TBA-essence reaction complexes which were mostly pink. These results support the author's conclusion that the chemical test for malonaldehyde should be a useful factor when deciding orange essence quality.

It should be pointed out that the total concentration of all compounds present in orange essence is a variable which is affected by processing conditions and the type of essence recovery system, and these vary widely throughout the industry. Each essence processor should evaluate his product for quality and concentration for optimum level of essence addition to orange juice. What may be right for one processor may or may not be for another.

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