Changes in Total Volatile Aldehyde Content with Storage of Deglet Noor Dates

Content of total volatile aldehydes in fresh and stored dates was measured for the first time, and acetaldehyde was the major constituent. In fresh dates, the concentration of volatile aldehydes, on a dry weight basis, averaged 125 ppm. Total volatile aldehydes decreased progressively as storage time outdoors increased from 0–5 months. Further studies are recommended to determine if total aldehyde assay could be used for quality indexing of dates.

Dates undergo certain chemical changes during storage and slowly deteriorate. Inversion of sucrose in Deglet Noor dates has been observed in dates during processing and storage (Vinson, 1911; Maier and Metzler, 1961; Coggins et al., 1968). Other chemical changes during storage include a decrease in the total amino acid concentration (Rinderknecht, 1959) and the formation of new polyphenols with decrease in others (Maier and Metzler, 1965). Maier and Schiller (1960, 1961a,b) demonstrated that both oxidative enzymatic and nonoxidative nonenzymatic browning take place in dates during deterioration; and they developed a method for evaluating darkening. They suggested that one possible pathway of nonenzymatic browning in dates might be the condensation of amino acids with reducing sugars, which yields volatile carbonyl compounds (El'Odé, 1966).

In commercial practice, dates are stored outdoors in stacks of bins covered with black polyethylene film for several weeks or months and later moved to refrigerated storage. Occasionally bins of dates are put directly into refrigerated storage. Cold storage temperatures in commercial facilities range from below 0 to 7 °C. A 12-month test was completed to study changes in date quality under actual commercial conditions of refrigerated storage and a combination of outdoor and refrigerated storage. In these studies (Norman et al., 1975, 1976), the soluble pigment content of dates held outdoors up to 5 months increased steadily, and some sucrose inverted, but none of the chemical tests performed indicated the extent of deterioration that was observed visually. More sensitive tests are needed to enable the evaluation of quality changes during storage. Total aldehyde content is useful for the quality evaluation of citrus essence and citrus products (Petrus et al., 1970), unblanched frozen peas (Whitefield and Shipton, 1966), poultry (Dimmick and MacNeil, 1970), and peanuts (Brown et al., 1973). To the authors' knowledge, aldehydes in dates have not been studied. More information on the chemical reactions that cause deterioration of dates would aid in the development of criteria to evaluate quality and of methods to preserve dates.

A method by Ismail and Wolford (1970) for the estimation of total aldehydes (including saturated, unsaturated, and aromatic aldehydes) in aqueous orange essence was adapted for our study of total volatile aldehydes of date tissue. We measured total aldehydes of fresh dates and dates stored for 0–5 months outdoors, then 7–12 months in cold storage. The major volatile aldehyde was isolated and identified.

MATERIALS AND METHODS

Date Samples. Deglet Noor dates were from a 12-month study just terminated. All storage was at Indio, Calif. Eighteen bins of dates harvested in January, 1975, had been stored outdoors 0–5 months and then placed in cold storage for 7–12 months at −3 to 4 °C. During the 5-month outdoor storage period, air temperature ranged from 2–27 °C in the first, 2–28 °C in the second, 9–22 °C in the third, 7–30 °C in the fourth, and 17–42 °C in the fifth month. The test bins stored outdoors were stacked and the entire block enclosed in black polyethylene film. Initially, three bins were put in cold storage and the remaining bins were stored outdoors. Then, each month, three bins were transferred from outdoor to indoor storage until all 18 bins were in cold storage. At the end of the 12-month storage, ungraded samples from each bin were analyzed for total aldehyde content. Fresh date samples from the 1976 harvest were obtained from commercial sources and compared with the stored samples. The fresh dates were stored at −23 °C and analyzed within a few days after harvest. The Cal-Date Company, Indio, Calif., furnished the dates used in the test.

Volatile Aldehyde Distillation Procedure. Dates (200 g) and water (350 mL) were homogenized with a Brinkman Model PT-45/2 Polytron in a 1-L graduated cylinder (cut off and fire polished at the 700-mL mark). The homogenate was quantitatively transferred to a 2-L round-bottom distillation flask, and 650 mL of water, a few drops of silicone antifoam, and a boiling chip were added. The flask was connected to a Friedrichs condenser, and 100 mL of distillate was collected in an ice-cooled volumetric flask. For evaluation of the distillation procedure, second and third 100-mL fractions were also collected. The stoppered flasks were stored at 7 °C.

Colorimetric Estimation of Total Aldehydes. Water (5 mL) and 0.5% *N*-hydroxybenzenesulfonamide in 95% EtOH (1 mL) were added to 5 mL of the distillate or standard. Then, N KOH (1 mL) was added. After 10 min, 1 mL of 1% $FeCl_3$ was added and 5 min allowed for color stabilization. The absorbance of the solution was read on a Beckman Acta M IV spectrophotometer at 505 nm.

Aldehyde Standard Solution. Ismail and Wolford (1970) used a mixture of 1-octanal and *trans*-2-hexanal as a standard because of their presence in orange essences. Acetaldehyde was found to be the major aldehyde in the date distillate and was therefore used as a standard at 200 mg/L water.

Pigment Content. Soluble pigment content was estimated from the absorption of 80% EtOH solutions of date tissue at 400 nm on a Beckman Model Acta M IV spectrophotometer. Absorbance readings were converted to mg/g dry weight by use of the extinction coefficient 0.650 mL/(mg)(cm) given by Maier and Schiller (1960) for date pigment.

2,4-Dinitrophenylhydrozones (DNPH's). A saturated solution of 2,4-dinitrophenylhydrazine in 6 N HCl (50 mL) was added to each 100-mL distillate. The solution was held overnight at 7 °C; then the precipitate was filtered, washed, dried, and weighed. Reference DNPH's were prepared from commercially available carbonyls and recrystallized from 95% EtOH.

Regeneration of DNPH's. The carbonyls were regenerated from the hydrazones with levulinic acid–2 N HCl (9+1) according to Keeney (1957) but were not extracted from the aqueous distillate.

Thin-Layer Chromatography (TLC). The DNPH derivatives were separated on silica gel G plates (E M Laboratories No. 5539) with benzene, benzene–ethyl

Table I. Total Volatile Aldehyde Content[a] of Three Distillation Fractions of Four Field Grades of Fresh Deglet Noor Dates

Grade	Distillation fractions: First 100 mL, ppm	Second 100 mL, ppm	Third 100 mL, ppm
Natural	155	20	7
Waxy	115	16	8
No. 1 dry	120	15	8
No. 2 dry	120	12	2

[a] Values represent the average of duplicate analyses and are expressed in ppm on a dry weight basis.

acetate (97:3), and benzene–tetrahydrofuran (95:5) and on Seasorb 43-Celite 545 plates (prepared according to Schwartz et al., 1964) with acetone–benzene–MeOH (75:23:2 and 75:20:5) and chloroform–hexane (85:15).

Gas Chromatography (GC). The DNPH derivatives were also separated with a Varian Model 2800 gas chromatograph equipped with dual hydrogen flame detectors. All columns were stainless steel, $^1/_8$ in. × 6 ft. Flow rates were: nitrogen, 40 mL/min; hydrogen, 30 mL/min; and air, 400 mL/min. The DNPH's were separated on OV-17 (3% on Chromosorb WHP 100/120 mesh), with stop-flow injection of ethyl acetate solutions. The regenerated carbonyls were separated on Carbowax 20M-TPA (10% on Chromosorb WHP 100/120 mesh), with injection of headspaces of the aqueous distillate, and on Chromosorb 101 (80/100 mesh), with injection of the aqueous distillate. Temperature programming was as follows: OV-17, 170–300 °C at 7.5 °C/min; Carbowax 20M-TPA, 50–145 °C at 5 °C/min; and Chromosorb 101, 170–220 °C at 2 °C/min.

RESULTS AND DISCUSSION

Isolation and Identification of Acetaldehyde. DNPH derivatives from 3.6 kg of dates weighed 0.74 g. The DNPH's were dissolved in boiling 95% EtOH and held overnight at −17 °C. Yellow crystals formed; the yield was 0.54 g or 73% of the total DNPH derivatives. The yellow crystals were dissolved in ethyl acetate and analyzed by TLC and GC. TLC revealed a single spot with the same R_f as authentic acetaldehyde DNPH with three solvent systems on silica gel G and Seasorb-Celite plates. A brown color characteristic of aliphatic aldehydes was obtained on Seasorb-Celite plates and with ethanolamine on silica gel plates. The GC retention times were the same for authentic acetaldehyde DNPH and the unknown DNPH on OV-17 and for the regenerated aldehydes on Carbowax 20M-TPA and Chromosorb 101. The UV–visible spectra of the unknown DNPH were as follows: $\epsilon = 2.2 \times 10^4$, λ_{max} 355 nm, 242, 260, 425 in $CHCl_3$; $\epsilon = 2.1 \times 10^4$, λ_{max} 430 nm, 237, 520 in 0.25 N ethanolic NaOH containing 10% $CHCl_3$. These spectra were identical with those of authentic acetaldehyde DNPH and agree with those reported by Jones et al. (1956). The melting point range (uncorrected) was 166–168 °C for the unknown DNPH, the authentic acetaldehyde DNPH, and a mixture of the two. These data establish that more than 73% of the volatile carbonyls of dates was one compound, acetaldehyde. Because of the methods used, the amount of acetaldehyde cannot be considered quantitative.

Acetaldehyde is not an unexpected component of dates since it is a constituent of many fruits, vegetables, and plants. Several minor carbonyl components in the DNPH mother liquor were detected by TLC and GC. As yet, we have not identified them.

Distillation Efficiency. Total aldehydes in three 100-mL fractions collected from each distillation of four grades of fresh dates were measured so that we could determine the amount of distillate to collect. Recoveries were, respectively, 83–89, 10–12, and 2–6% of the total volatile aldehydes in the first, second, and third 100-mL distillates from 200 g of dates (Table I). The volume we chose to collect for the remainder of the study was the first 100 mL. Although continuing the distillation increased recovery, aldehyde dilution was increased and the probability for the formation of volatiles by thermal degradation was increased.

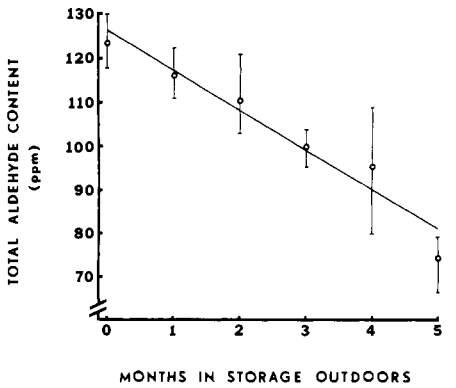

Figure 1. Changes in content of total volatile aldehydes, in ppm on a dry weight basis, of Deglet Noor dates that had been stored outdoors for 0–5 months, then held in cold storage for 7–12 months.

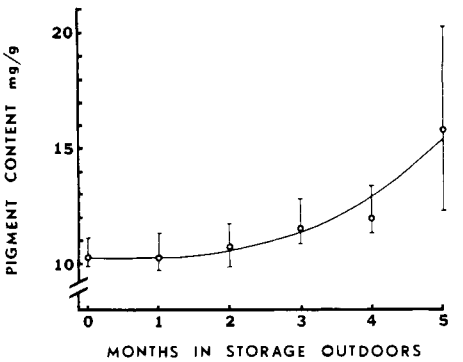

Figure 2. Changes in soluble pigment content, in mg/g on a dry weight basis, of Deglet Noor dates that had been stored outdoors for 0–5 months, then held in cold storage for 7–12 months.

Total Volatile Aldehydes of Dates. The total aldehyde content of four grades of fresh dates analyzed in duplicate averaged 125 ppm on a dry weight basis (Table I). Natural dates contained the most and No. 2 dry dates the least total aldehydes.

The content, on a dry weight basis, of total volatile aldehydes of dates decreased progressively as the storage time outdoors increased (Figure 1). A linear regression line was fitted to the data. The mean and range values for each three-bin sample were determined at the end of the 12-month storage period but are plotted against the number of months the samples had been stored outdoors. The total aldehyde content decreased from 126 ppm after 12 months in cold storage (zero months outdoors) to about 81 ppm after 5 months outdoors plus 7 months in cold storage. This decrease probably reflects changes in acetaldehyde since it constituted about 73% of the total volatile carbonyls. A decrease in acetaldehyde content during storage would indicate that it is not a product of the amino acid–sugar browning pathway in dates. We do not know whether any of the aldehydes present in minor concentrations increased or decreased in concentration during storage.

Table II. Dates Found Marketable as Fresh Fruit, Products, and Culls[a] by Packinghouse Grading of Deglet Noor Dates Stored 0-5 Months Outdoors then Held 7-12 Months in Cold Storage

	Months in storage outdoors					
Dates marketable	0	1	2	3	4	5
Fresh fruit, %	89	85	53	29	5	25
Products, %	5	6	35	59	84	49
Culls, %	6	7	12	12	11	26

[a] Values represent the average of three bins of dates and are expressed in percent by weight.

Browning took place in the dates during storage, as shown by the regression line of soluble pigment measurements (Figure 2). Browning was more obvious visually than is indicated by the soluble pigment values. Dates held outdoors 5 months were very dark. We concluded from visual observations of all the treatments that dates should not be stored outdoors for more than 1 month if optimum color and quality of dates are to be maintained.

We also measured certain other changes that took place in the dates during storage. Those held zero months outdoors contained 10.9% fructose, 11.4% glucose, and 59.3% sucrose, on a dry weight basis, at the end of the test. Sucrose inverted to fructose and glucose during outdoor storage; at the end of the test, 1, 9, 11, 15, and 34% of the sucrose had inverted in dates stored outdoors for 1, 2, 3, 4, and 5 months, respectively. The average moisture content of the dates was 17.1 ± 2.1% before storage and 15.7 ± 0.4% after storage.

All the bins of dates were graded (Norman et al., 1976) in the packinghouse at the end of the test for determination of the quantities marketable as fresh fruit, products, and culls (Table II). Marketability was about the same for dates stored outdoors 0 and 1 month but decreased markedly for those stored outdoors 2 months. The amount of dates marketable as fresh fruit was lower for dates that had been stored outdoors 2 and 5 months than for dates not stored outdoors by 36 and 64 percentage points, respectively.

These results are preliminary in our study to determine if total aldehyde assay could be used for quality indexing. Further studies with adequate replication of different storage conditions and quality measurements are required to fully relate total aldehyde content to quality changes of dates. Individual carbonyl compounds need to be studied so that we can determine whether particular components increase or decrease with deterioration of dates.

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Received for review November 15, 1976. Accepted February 1, 1977. Mention of a proprietary product in this paper does not constitute a recommendation or an endorsement of the product by the U. S. Department of Agriculture.

An Enzymic Assay for Ammonia in Waste Matter

An enzymic method for ammonia analyses has been shown to compare favorably with the standard method, Nesslerization. Favorable comparison was found for accuracy, simplicity, and cost. The enzymic method was shown to be about three times as sensitive as Nesslerization and more directly applicable with physiological samples. Samples that contained considerable color negated the use of the Nessler procedure whereas this presented no problems for the enzymic method.

The application of the enzyme, glutamate dehydrogenase (GDH) (EC 1.4.1.2), to the analysis of ammonia levels in serum has been shown to be an extremely sensitive method (Mondzac et al., 1965). The exploitation of the fluorescence of nicotinamide adenine dinucleotide (NADH) makes this method the most sensitive of any method in use. The measurement of the radiation adsorption of NADH, while less sensitive, is more generally useful in most laboratories. Thus, we have chosen to compare the enzymic reaction by absorption spectroscopy with standard methods in the determination of ammonia levels in water samples and solutions containing animal wastes. This method is of interest to scientists concerned with pollution of water supplies and those interested in the use of animal