OILS RECOVERED FROM CELERY PACKINGHOUSE WASTE

E. D. LUND, C. J. WAGNER, JR., and W. L. BRYAN

U.S. Citrus and Subtropical Products Laboratory[1]
Winter Haven, Florida

Abstract. **Distilled oil with fresh-celery aroma was recovered from celery packinghouse waste at yields up to 200 ppm. Compositions were determined by glc and the relative contributions of individual components to celery aroma were assessed from results of odor threshold and preference tests. Components estimated to contribute most to celery quality were sedanolide and β-selinene, with minor contributions from 3-n-butyl phthalide and hexahydro-3-n-butylphthalide. Yields of these components were higher from celery waste containing more leaves than stalks, but were largely unaffected by growing season (winter or spring) or variety ("Utah 5270" or "Flormart"). Oil yield from the Flormart variety was 4-fold that from Utah 5270, but concentration of celery-like components in the d-limonene carrier were lower in Flormart oil. Distilled oils darkened with aging or heating but did not lose celery aroma.**

Fresh celery packinghouse trimmings, produced in large quantities in the major celery processing areas of Florida and California, are estimated in Florida alone to be more than 100 million lbs. annually (6). This mixture of leaves and stalks is either hauled away for disposal or spread on the fields and plowed under, at some expense to the producer.

Processes to economically dispose of celery waste while recovering salable by-products have been studied in our laboratory (2). These processes reduce costs of present disposal practices and the value of by-products might produce an overall profit. In this case the large quantity of "tops" field-trimmed during mechanical harvesting might also be profitably recovered. One by-product of high potential value is celery oil steam distilled from juice expressed from celery waste.

Previous studies in our laboratory demonstrated that oil with fresh celery aroma could be recovered in low yield by steam distilling pureed whole celery (7). Components responsible for the characteristic celery aroma of seed and leaf oil have been summarized elsewhere (4). These have been useful in assessing the relationship between oils from different sources. d-Limonene was present in largest amount while other terpenes and several sesquiterpenes were isolated in lesser quantities (9). The contribution to celery flavor of the hydrocarbons, except for the sesquiterpene β-selinene, was considered to be small. Among the oxygenated components, celery-like odor was associated only with the "carbonyl" fraction (10). The phthalides 3-n-butyl phthalide and sedanolide of the carbonyl fraction had strong celery aromas, and hexahydro-3-n-butyl phthalide contributed to a lesser extent. These three phthalides are high boiling, chemically related lactones whose structures differ only in the number of double bonds. Sedanolide (B.P. of 185°C at 17 mm Hg) is the most complex, with one double bond in its six-membered ring, and would probably be the most difficult to synthesize.

This paper extends previous work and relates source of celery waste to yield and composition of oil. Another objective was to determine quantitatively the relative contributions of major oil components toward celery-like aroma in order to better assess relative quality of oils from different sources.

Materials and Methods

Celery Waste Sources

Celery waste trimmings or stalks were obtained from the Zellwood area of Florida during November 1972, and April and July 1973, to show seasonal and varietal differences. The "Utah 5270" and late maturing "Flormart" were studied, and the waste consisted of mixtures of leaves and stalks. Flormart waste was obtained in July after the Utah 5270 variety had been harvested. Stalks were studied separately in one experiment to determine relative distribution of celery-like components.

Oil Recovery Process

Waste celery was ground in a hammer mill with 1/2 inch screen openings and the slurry pressed in a 6-inch diameter horizontal screw

---

[1]One of the laboratories of the Southern Region, Agricultural Research Service, U. S. Department of Agriculture.

References to specific commercial products do not constitute endorsement.

The authors acknowledge the assistance of L. J. Swift, O. W. Bissett, and C. W. Wilson, III, U. S. Citrus & Subtropical Products Laboratory.

press with 0.020-inch diameter holes (Rietz Manufacturing Company, Santa Rosa, Calif.) to remove most of the juice (up to 90 lbs. juice/100 lbs. celery waste). Oil was steam distilled from the juice and concentrated by distillation, as described elsewhere (Figure 1) (2). The juice first was preheated to about 80°C in a tubular heat exchanger at 0.3 gpm (45 sec residence time) and fed to the bottom of a vertical tube contactor (2-inch i.d. x 91-inch height) with steam injected at the base to give about 10% vaporization. Oil vaporized by the steam during two-phase co-current flow up the contactor was concentrated in a packed distillation column (3-inch i.d. x 60-inch height). Condensed oil (15°C) was separated in a trap and the aqueous distillate returned to the rectification section of the column as reflux, thereby concentrating the more water-soluble components and increasing their concentrations in the oil product.

Analytical

Volatile oil content of ground celery was determined by the "Bromate Titration Method" (5) as equivalent d-limonene, the most prevalent component of both citrus and celery oils.

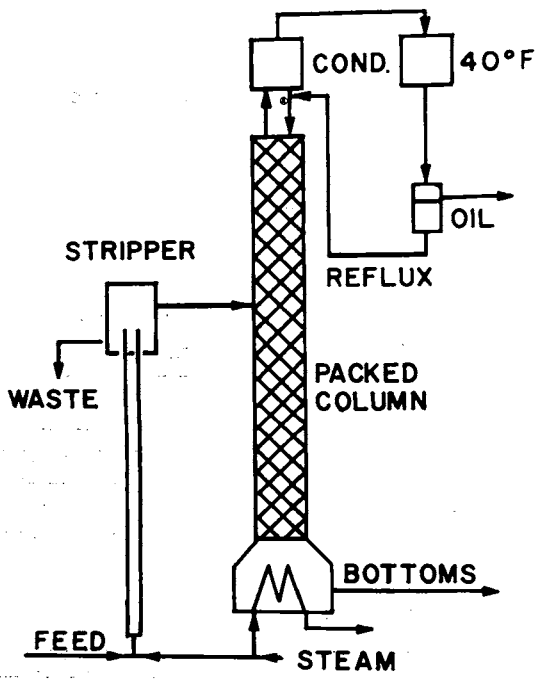

Fig. 1. Oil recovery system (schematic diagram of steam stripping and distillation equipment) (2).

Preparative isolation of components for analysis was accomplished by separating a 200-300 μl sample on a preparative glc column (9-ft by 1/4-inch S.S. column, packed with 20% Carbowax 20M on 60/80 gas Chrom P). The helium carrier gas flow was 200 ml/min and the temperature was programmed from 80-220°C. Detection was by means of a 30:1 splitter and a flame ionization detector. The injection port, detector, and exit port temperatures were 220°C. The larger peaks were collected in traps immersed in liquid nitrogen for analyses by infrared and mass spectra.

Oil components were analyzed quantitatively by an analytical glc column (15-ft x 1/8-inch S.S. column packed with 5% Carbowax 20M on 70/80 Anakrom ABS). Samples (2 μl) were injected with 37 ml/min helium carrier gas flow. Injection port and detector block were at 220°C, column temperature was programmed from 80-220°C, and a flame ionization detector was used. The column was calibrated with cis-3-hexene-1-ol and component concentrations were determined from peak areas and corrected by means of a peak area response factor (3).

Aqueous samples were analyzed by saturating the aqueous solutions with sodium sulfate, extracting with methylene chloride (11) and concentrating the solution by fractionally distilling the methylene chloride through a Vigreux column. Samples of the concentrated extract (2 μl) were injected into the analytical glc column.

Odor Evaluations

Odor differences between two solutions were determined by triangular tests (1) with 12 panelists, each evaluating two sets of three samples in open 5-ml vials. All samples contained 0.1-0.5% ethanol used to dissolve the celery oil components in water at levels up to 80 ppm for odor evaluation.

Threshold concentrations were obtained by first familiarizing each panelist with the characteristic odor of the component, then carrying out successive triangular evaluations at lower concentrations. The threshold was defined as "the lowest concentration distinguishable from water at the 95% confidence level." Each pure component had been separated from the oils on the preparative glc column.

Relative contributions of β-selinene and the three known phthalides to celery odor were also evaluated by the panel. Four vials containing

these celery-like components at 10 x threshold concentrations in water were presented. Each panelist rated the vials on a 1 to 5 hedonic scale, where 5 represented the nearest to fresh celery odor.

Oil Stabilizing Treatments

Various treatments to improve oil stability toward darkening during storage at 40°F were tried: 1) addition of butylated hydroxy tolulene (BHT) antioxidant at 100 ppm; 2) addition of distomaceous silica adsorbent and filtering; 3) extraction with 10% aqueous sodium bicarbonate to neutralize acidity followed by rinse water, and 4) addition of excess tartaric acid chelating agent followed by extraction with $NaHCO_3$ solution and water.

Results and Discussion

Yield

The amount of oil recovered by distillation, as ppm in celery slurry fed to the process, varied with celery source (Table 1). As reported by Wilson (8), oil yield was much lower from stalks than from waste which contained a large fraction of leaves. Oil yield was also much higher from the Flormart variety waste than from Utah 5270.

Percent recovery of oil varied from 22 to 54% of oil in the ground feed slurry, based on bromate titration. Thus, a large fraction of the oil (up to 30%) remained in the presscake; other losses were from incomplete recovery during steam stripping and distillation. Generally, per-

Table 1. Yield and composition of Florida celery oils

Variety	Utah 5270			Flormart
Month processed (1972-73)	November		April	July
Type feed	Stalks	Waste	Waste	Waste
Oil Recovery				
as ppm of feed	8	59	27	203
as % of oil in feed	22	41	47	54
Concentration in oil, wt %				
β-pinene	2.83	1.10	0.97	0.39
d-Limonene	72	84	-	-
Cis-3-hexene-1-ol	0.06	2.13	0.26	0.21
Caryophyllene	3.38	0.62	1.50	0.57
Humulene	0.47	0.15	0.17	0.09
β-Selinene[z]	5.10	4.00	3.67	0.99
Unidentified compound (mw = 204)	0.40	0.73	1.59	0.10
Hexahydro-3-n-butyl phthalide[z]	0.09	0.17	0.07	0.04
3-n-Butyl phthalide[z]	0.05	0.09	-	-
Sedanolide[z]	0.99	3.09	2.68	0.97
Unidentified compound[z]	0.17	0.05	0.12	0.03
Unidentified compound[z]	0.07	0.09	0.07	0.04
Other (total)	14	4	-	-

[z]Components with celery-like odor.

cent recovery increased with volatile oil content in the celery waste, suggesting constant sources of loss during the various process steps. In commercial operation, such losses could be substantially reduced through process optimization.

Oil Composition

Celery source greatly influenced composition of oils, as shown in Table 1 where components of four oils are tabulated in order of retention times in the glc column along with their respective contentrations in wt %. Components identified by footnote in Table 1 had distinct celery-like odors detected during preparative glc analyses. The last two detectable compounds emitted from the glc column were unknown compounds with celery aromas. Their infrared spectra were similar to those of the phthalides.

Oils recovered from stalks and waste had significantly different compositions (columns 1 and 2, Table 1). Stalk oil had significantly higher concentrations of the hydrocarbons, caryophyllene and humulene, than waste (predominantly leaves), but only 1/3 the concentration of sedanolide and about 3% as much cis-3-hexene-1-ol (leaf alcohol). The lower levels of the latter two components in stalk oil were caused in part by disproportionate losses of these components in the bottoms from the distillation column. This was shown by material balance calculations which indicated loss of more water-soluble compoonds was higher during recovery of stalk oil. The relative concentrations of components in the original feed slurries are only approximately indicated by the compositions of recovered oils.

Results of the November 1972 and April 1973 tests suggest little seasonal variation in oil composition from Utah 5270 celery. This was tentatively concluded because April waste contained a higher proportion of stalks than the November waste, yet concentrations of many components were intermediate between November stalk and waste oils.

Concentrations of all celery-like components were significantly lower in oil distilled from Flormart celery than in oil from Utah 5270 variety. The higher total oil yield offset the lower concentrations however, and, based on original celery waste, the total amounts of these components recovered were about the same from both varieties.

Odor Evaluation

All distilled oils had strong celery aromas. Those from celery waste, particularly the November oil, also had an aroma of green leaves, thought to be caused mainly by cis-3-hexene-1-ol (leaf alcohol). The relative values of the oils for celery flavoring purposes were assessed from the concentrations, odor thresholds, and preference ratings of the four individual components with most celery-like odor.

Odor thresholds for the four known celery-like components in water ranged from 1 ppm for sedanolide and β-selinene to 10 ppm for 3-n-butyl phthalide, (Table 2). Based on odor threshold, sedanolide might, therefore, be rated ten times as potent as 3-n-butyl phthalide. Sedanolide was also rated most characteristic of celery odor at 10 x its threshold concentration (10 ppm) with a rating of 4.7 on a 5-point hedonic scale. 3-n-Butyl phthalide was also rated quite celery-like, but at a much higher concentration (100 ppm). The odors of β-selinene and hexahydro-3-n-butyl phthalide were not rated as celery-like as those of the other components, but their presence in celery oil might contribute synergistically to fresh celery odor.

The results of Table 2 show that sedanolide contributed most to celery-like quality of the distilled oils, followed by β-selinene. Oil from November waste celery had the highest concentrations of these components and should be highest in celery-like flavor, unless flavor was masked by the high concentration of cis-3-hexene-1-ol. Stalk oil, with about 1/3 the sedanolide content of oil from the waste, should be considerably

Table 2. Odor evaluations of celery-like components.

Compound	Threshold ppm[z]	Preference rating[y]
Sedanolide	1	4.7
3-n-Butyl phthalide	10	3.6
β-Selinene	1	1.6
Hexahydro-3-n-butyl phthalide	2	1.2

[z]In water, 95% confidence level.
[y]Evaluated at 10 times threshold level, 1-5 hedonic scale, standard deviation = ± 0.6.

lower in flavoring strength, in spite of the 25% higher β-selinene concentration. April oil would probably be somewhat less in flavor strength than November waste oil and Flormart oil would be rated lowest in celery flavor based on the results of Tables 1 and 2.

Oil Stability

Freshly distilled celery oils were slightly yellow or orange, and aqueous extracts of the oils were slightly acidic (pH=6). The oils darkened noticeably overnight at 40°F and continued to darken during storage at 35°F, becoming almost black within a few months. A black precipitate often formed in aged samples. The colored components were not adsorbed on diatomaceous silica. Neutralization of acidic components with sodium bicarbonate failed to retard color development. Treatment with tartaric acid to remove multivalent metal ions by chelating had no effect. When oil was heated (160°C), samples in air did not darken as rapidly as those heated in sealed tubes under nitrogen. Oil containing 100 ppm BHT antioxidant darkened faster during storage than controls without BHT, and a sample with BHT that was exposed to air darkened at an intermediate rate.

Vacuum distillation of a fresh oil sample (185°C and 8 mm Hg) produced 6% black viscous residue and a light yellow distillate which darkened during storage. Glc profiles of the original oil and of its distillate were virtually identical, suggesting that the unstable color-forming component polymerized or pyrolyzed during high-temperature glc analysis. This suggestion was supported by the formation of considerable black residue inside the glc injection port.

Organoleptic evaluation did not detect any significant odor change associated with oil darkening. A freshly recovered light yellow oil, heated in a sealed tube at 160°C for 1 1/2 hrs, yielded a black oil and a precipitate. The heated and unheated oils could not be distinguished at the 95% confidence level in a triangular odor test (80 ppm oil in water, 12 panelists). However, a few sensitive panelists could consistently detect a difference between samples.

Summary

Waste celery containing a large fraction of leaves yielded more oil of higher quality for celery flavoring than celery mixtures containing a high level of stalks. No significant seasonal variation in oil from the Utah 5270 variety was observed. Yields of individual components with celery-like aroma recovered from Utah 5270 and Flormart varieties were similar, since their lower concentrations in Flormart oil were offset by the 4-fold greater oil yield from this variety.

Sedanolide was identified as the most potent component of distilled celery oil, based on odor threshold concentration (1 ppm) and high celery-like preference rating. It was also the most prevalent phthalide in distilled celery oils. Low odor threshold (1 ppm) and relatively high concentration in distilled oils suggested that β-selinene was a major contributor to celery-like quality. Effects of the other known phthalides on odor were considered to be much less than sedanolide or β-selinene because of the high odor threshold of 3-n-butyl phthalide (10 ppm) and the relatively low celery-like preference rating of hexahydro-3-n-butyl phthalide. Although heat darkened the oil, odor quality was not significantly changed. The color-forming reaction is unknown.

Literature Cited

1. Boggs, M. M. and Hanson, H. L. 1949. Analysis of foods by sensory evaluation tests. Advances in Food Research II, Academic Press, Inc. 219-258.
2. Bryan, W. L., Wagner, C. J. Jr., Bissett, O. W., Lund, E. D., and Berry, R. E. 1973. Recovery of celery oil during disposal of packinghouse wastes. In press.
3. Dal Nogare, S. and Juvet, R. S. 1966. Gas-liquid chromatogarphy theory and practice. Interscience Publication, 220.
4. Johnson, A. E., Nursten, H. E., and Williams, A. A. 1971. Vegetable volatiles: A survey of components identified. Part II. Chem. and Ind. 212.
5. Scott, W. C., and Veldhuis, M. K. 1966. Rapid estimation of recoverable oil in citrus juices by bromate titration. J. Assoc. Offic. Anal. Chemists 49:628.
6. U.S.D.A. Agricultural Statistics, 1972. p. 205.
7. Wilson, C. W. III, Neubert, A. M., Veldhuis, M. K. and Miller, W. H. 1967. Recovery of volatile flavors from celery. Proc. Fla. State. Hort. Soc. 80:292.
8. Wilson, C. W. III. 1965. Separation of volatile flavors from celery. Proc. Fla. State Hort. Soc. 78:249.
9. ————. 1969. Terpene and sesquiterpene hydrocarbons in the essential oil from fresh celery. J. Food Sci. 34:521.
10. ————. 1970. Relative recovery and identification of carbonyl compounds from celery essential oil. J. Food Sci. 35:766.
11. Wolford, R. W., Alberding, G. E., and Attaway, J. A. 1962. Analysis of recovered natural orange essence by gas chromatography. J. Agr. Food Chem. 10:297.