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# RELATIONSHIP OF METHODS FOR RECOVERING ESSENTIAL OIL FROM FRESH CELERY ON THE CHEMICAL COMPOSITION AND FLAVOR

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## ABSTRACT

Simultaneous investigations on the chemical composition of celery essential oil, and practical methods for recovering the essential oil from fresh celery in good yield were conducted. Three methods for recovering celery essential oil were investigated. In the first, the essential oil was recovered from celery juice by a vacuum essence recovery technique in yields of 0.5-1.0 ppm. In the second, batches of celery puree were steam distilled and the vapors rectified in a packed distillation column. Yields up to 28 ppm of essential oil were obtained. In the third, the volatiles were stripped from celery puree in a Turba-film evaporator and then rectified in a packed distillation column of different design from the first. Yields up to 30 ppm of celery essential oil that approached the flavor and aroma of fresh celery were obtained. The essential oils were separated into functional groups and analyzed by gas-liquid chromatography. GLC analysis showed a definite difference in composition between the essential oils recovered by the three different methods. The organoleptic properties of the oils recovered by the different methods were quite different.

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## INTRODUCTION

Investigations on the chemical composition, and practical methods for recovering the essential oil from celery leaves and stalks were conducted to obtain information in support of celery processing studies. It was necessary to fortify the flavor of dehydrated products because a substantial portion of the volatile flavoring constituents were lost during dehydration.

Gold and Wilson (1, 2, 3) reported the results of chemical composition studies on the essential oil recovered from celery juice by a vacuum essence recovery technique. The essential oil was recovered in yields of 0.5-1.0ppm. Wilson (6, 7, 8, 9) reported on the chemical composition of celery essential oil recovered by batch and continuous atmospheric steam distillation of celery puree (5, 10). Yields of up to 30 ppm of essential oil were obtained.

The subject of this paper is the relationship of essential oil recovery methods to the chemical composition and flavor of the essential oil from celery leaves and stalks.

## EXPERIMENTAL

Three methods of recovering celery essential oil were used. In the first, about 5000 kg of celery that had been trimmed of leaves and blanched 4 min in flowing steam was used to obtain approximately 4130 kg of juice which was distilled in a modified continuous vacuum essence recovery unit (1). The juice was flash vaporized under vacuum and the vapors rectified in a distillation column, 2 in. x 4 ft, packed with ceramic Raschig rings. Fractions were collected

from the following portions of the distillation apparatus: 1) column bottoms, 2) chilled water trap, 3) ice trap, 4) salt-ice trap, 5) dry-ice-acetone trap, and 6) liquid nitrogen trap.

In the second, 120 kg batches of celery were steam distilled and the vapors were rectified in a distillation column, 12 ft x 4 in., that was packed with 5/8 in. stainless steel "Pall" rings. The upper 8 ft of the distillation column served as a fractionating section and the lower 4 ft comprised the stripping section. Distillation was completed in 1 hr (6, 10).

In the third, distillation equipment designed at this laboratory for recovering citrus essence was used (4, 6). Approximately 80 kg of celery puree was diluted with 160 kg of water and then 2% pectin was added to emulsify the slurry. The celery slurry was pumped into a Turba-film evaporator of 1 sq ft evaporation surface with the rotor operating at 1290 rpm. Steam at 43 psig was supplied to the jacket to provide 20% evaporation. The vapors were rectified in a glass distillation column which consisted of a glass tee with 30 in. x 3 in. packed columns above and below the tee. The columns were filled with ⅝ in. stainless steel "Pall" rings. The bottom half served as the stripping and reboiler section, and the upper half served as the fractionating column. A stainless steel reflux condenser of 22.5 sq ft was mounted on top of the fractionating column. Tap water was admitted to the cooling side of this condenser to remove most of the water vapor, but let through some of the water along with the volatile flavoring materials. The remaining vapors were condensed by a 4.5 sq ft condenser, cooled to 55°F with chilled water, into an oil trap where the oil and aqueous layers were separated. The aqueous layer was extracted with organic solvent and discarded.

The essential oil recovered from the vacuum essence unit was separated into functional groups for gas chromatographic analysis. The acids were removed with 5.0% aqueous sodium bicarbonate, the ketones and aldehydes with Girards T reagent, the alcohols were derivitized with p-phenylazobenzoyl chloride, the esters were saponified by a microsaponification technique; and the less acidic materials were extracted with 0.5% sodiu mhydroxide. Materials unaffected by these treatments were separated by column chromatography on silicic acid. Analytical separations were performed isothermally on a Perfkin-Elmer, Model 154D, GLC using 6 ft x 0.25 in. stainless steel columns packed with 0.25% Silicone 200 on glass microbeads, 10 ft x ⅛ in. stainless steel columns packed with 0.25% Silicone 200 on glass microbeads, and 200 ft x 0.125 in capillary columns coated with polypropylene glycol. The major components were were identified by comparing the infrared spectra and gas chromatographic retention times with authentic compounds. The minor components were identified by functional group analysis and by gas chromatographic retention times on two columns of different polarity (1, 2, 3). Infrared spectra were obtained on a Perkin-Elmer, Model 137, spectrophotometer.

The essential oils recovered by batch distillation and continuous distillation were separated into functional groups by column chromatography and each fraction was then analysed by temperature-programmed gas liquid chromatography (6, 7, 8, 9). Approximately 20 ml of each oil was placed on 30 cm x 2 cm neutral alumina columns (Fisher A-90, 80-200 mesh). The hydrocarbons were eluted with approximately 150 ml of n-hexane. The carbonyls were eluded in three 150 ml fractions with 1:1 v/v n-hexane-diethyl ether, and the alcohols were stripped with absolute ethanol.

The individual components were separated by temperature-programmed gas-liquid chromatography with an F & M, Model 700, dual column chromatograph that was equipped with an F & M, Model 240, temperature programmer, and a thermal conductivity detector heated to 325°C. The bridge current was 150 ma. The injection port temperature was 250°C. Stainless steel columns, 15 ft x 0.25 in., packed with 25% Silicone 200(2,500,000 cstks) or 30% Carbowax 20-M on 60-80 mesh Gas-Chrom P were used. Samples were temperature-programmed from 100 to 225° at 1°C/min. The helium flow rate was 60 to 80 ml/min, depending on which fraction was being analysed. Samples were collected by condensing in liquid nitrogen cooled glass capillary tubes (6, 7, 8, 9).

Infrared spectra were obtained on a Perkin-Elmer, Model 137, spectrophotometer, ultraviolet spectra were obtained on a Cary-14 recording spectrophotometer, mass spectra were determined on a Bendix Time-of-light, Model 3012, mass spectrometer, and nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60 instrument equipped with a time-averaging computer; carbon tetrachloride was

the solvent and tetramathylsilane was the internal standard. Identifications were made by comparing spectral data with that of commercially available compounds and by comparison of GLC retention times with known compounds.

## Results and Discussion

Table 1 shows the relationship of the different recovery methods to the hydrocarbons in the essential oils. Limonene and myrcene were the only two hydrocarbons found in the essential oil recovered in the vacuum essence unit. The hydrocarbons in the essential oils recovered by batch and continuous distillation were identical except for the presence of n-pentylbenzene and 5-pentyl-1,3-cyclohexadiene in the oil recovered by batch distillation. These two compounds probably arose from thermal decarbonylation during distillation. The lack of hydrocarbons in the essential oil recovered in the vacuum essence unit was attributed to the loss of volatiles during the blanching period to deactivate enzymes. Refinements in concentration procedures and improved analytical techniques were instrumental in identification of compounds in the essential oils recovered by batch and continuous atmospheric distillation.

Table 2 shows the relationship of the different recovery methods to the aldehydes, ketones, and epoxides isolated from the essential oils. Eleven aldehydes were isolated from the essention oil recovered from the vacuum essence unit, and none were isolated from the essential oils recovered by batch and continuous distillation. The reason for this difference is not apparent but may be due to increased water solubility of these compounds, which were isolated in small quantities from celery juice. Diacetyl and carvone were the only ketones common to the three recovery methods. Diacetyl was tentatively identified as a constituent in the vent gas from the distillation column during batch distillation. n-Butylphenyl ketone was isolated from the essential oil recovered by batch distillation and was not common to the essential oils from the other two recovery processes. The isomeric cis- and trans-limonene oxide were identified as constituents of the essential oils recovered by batch and continuous distillation, but not as a constituent of the essential oil from the vacuum essence unit.

Table 3 shows the relationship of the different recovery methods to the acids, esters and lactones that were isolated from the essential oils. Isobutyric, n-valeric, and pyruvic acids were isolated from the oil recovered in the vacuum essence unit, but were not found in the oils recovered by batch and continuous distillation. Acetic and tiglic acids were found in the oil recovered by batch distillation, and acetic, tiglic and angelic acids were found in the oil recovered by continuous distillation. The latter was not found in the oil recovered in the vacuum essence unit. The esters found in the essential oil from the vacuum essence unit were not isolated from the oils recovered by batch and continuous distillation, and with the excep-

Table 1. Hydrocarbons isolated from celery essential oil recovered by three different methods.

| Hydrocarbon | Recovery Method 1 | 2 | 3 |
|---|---|---|---|
| d-limonene | + | + | + |
| α-pinene | - | + | + |
| β-pinene | - | + | + |
| myrcene | + | + | + |
| γ-terpinene | - | + | + |
| cymene | - | + | + |
| n-pentylbenezene | - | + | - |
| n-pentylcyclohexadiene | - | + | - |
| elemene | - | + | + |
| caryophyllene | - | + | + |
| α-humulene | - | + | + |
| β-humulene | - | + | + |
| β-selinene | - | + | + |

Recovery method 1. vacuum essence
2. batch atmospheric steam distillation
3. continuous atmospheric steam distillation
+ signifies presence of compound
- signifies absence of compound

Table 2. Aldehydes, ketones and epoxides isolated from celery essential oil recovered by three different methods.

| | Recovery Method | | |
|---|---|---|---|
| Aldehydes | 1 | 2 | 3 |
| formaldehyde | + | - | - |
| acetaldehyde | + | - | - |
| propionaldehyde | + | - | - |
| hexanal | + | - | - |
| heptanal | + | - | - |
| octanal | + | - | - |
| undecanal | + | - | - |
| dodecanal | + | - | - |
| neral | + | - | - |
| citronellal | + | - | - |
| pentanal | +* | - | - |
| **Ketones** | | | |
| diacetyl | + | +* | - |
| t-dihydrocarvone | - | + | + |
| c-dihydrocarvone | - | + | + |
| carvone | + | + | + |
| α-ionone | - | + | + |
| n-butylphenyl ketone | - | + | - |
| **Epoxides** | | | |
| c-limonene oxide | - | + | + |
| t-limonene oxide | - | + | + |

* tentative identification
Recovery Method 1. vacuum essence
2. batch atmospheric steam distillation
3. continuous atmospheric steam distillation
+ signifies presence of compound
- signifies absence of compound

Table 3. Acids, esters, and lactones isolated from celery essential oil recovered by three different methods.

| | Recovery Method | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| **Acid** | | | |
| isobutyric | + | - | - |
| n-valeric | + | - | - |
| pyruvic | + | - | - |
| acetic | - | + | + |
| tiglic | - | + | + |
| angelic | - | - | + |
| **Esters** | | | |
| c-3-hexenyl-1-acetate | - | + | - |
| c-3-hexenyl-1-pyruvate | + | - | - |
| ethyl isovalerate | + | - | - |
| decyl acetate | + | - | - |
| linalyl acetate | + | - | - |
| terpinyl acetate | + | - | - |
| geranyl acetate | + | - | - |
| citronellyl acetate | + | - | - |
| neryl acetate | + | - | - |
| terpinyl propionate | + | - | - |
| geranyl butyrate | + | - | - |
| benzoyl benzoate | + | - | - |
| pinocarvyl acetate | - | + | + |
| t-carvyl acetate | +* | + | + |
| c-carvyl acetate | - | + | + |
| dihydrocarvyl acetate | - | - | + |
| c-p-1(7)8-menthadienyl-2-acetate | - | + | + |
| **Lactones** | | | |
| 3-isobutylidene-3a,4-dihydrophthalide | + | - | - |
| 3-isovalidene-3a,4-dihydro phthalide | + | - | - |
| 3-isobutylidenephthalide | + | - | - |
| 3-isovalidenephthalide | + | - | - |
| sedanonic anhydride | + | - | - |
| 3,n-butylhexahydrophthalide | - | + | + |
| 3,n-butylphthalide | - | + | + |
| sedanolide | - | + | + |

* distinction between cis and trans isomers was not made.

Recovery Methods 1. vacuum essence
2. batch atmospheric distillation
3. continuous atmospheric distillation

tion of carvyl acetate the esters found in the oils from batch and continuous distillation were not found in the essential oil from the vacuum essence unit.

The phthalides, which are cyclic esters or lactones, are the most important compounds in celery essential oil. These compounds are responsible for the typical flavor and aroma of celery and are detectable in tomato quice at 1 ppm (2, 5). The phthalides shown in Table 3 that were isolated from the essential oil from the vacuum essence unit are not the same phthalides that were isolated from the essential oils recovered by batch and continuous distillation. These compounds were isolated in small quantities from a large volume of starting material. It is conceivable that isobutylidene and isovalidenedihydrophthalide and the aromatic derivities were present in such small quantities that their presence were not detected in the essential oils recovered by batch and continuous distillation. Th compounds, 3-n-butylhexahydrophthalide, 3,n-butylphthalide, and sedanolide have been reported in the literature. These compounds were isolated from celery seed oil but they have not been isolated from the stem and leaf portion of the celery plant (9).

Table 4. Alcohols isolated from celery essential oil by three different recovery methods.

| | Recovery Method | | |
|---|---|---|---|
| Alcohol | 1 | 2 | 3 |
| propanol | +* | - | - |
| butanol | +* | - | - |
| isoamyl alcohol | + | - | - |
| hexanol | + | + | + |
| c-3-hexene-1-ol | - | + | + |
| t-2-hexene-1-ol | - | + | + |
| heptanol | + | - | - |
| octanol | +* | - | - |
| nonanol | +* | - | - |
| decanol | +* | - | - |
| undecanol | +* | - | - |
| dodecanol | +* | - | - |
| t-2,8-p-menthadiene-1-ol | - | + | + |
| c-2,8-p-menthadiene-1-ol | - | + | + |
| α-terpineol | - | + | + |
| dihydrocarveol | - | + | + |
| t-1(7)8-p-menthadiene-2-ol | - | + | + |
| t-carveol | - | + | + |
| c-carveol | - | + | + |
| c-1(7)8-p-menthadiene-2-ol | - | + | + |
| 8(9)-p-menthene-1,2-diol | - | + | + |
| isomer-8(9)-p-menthene-1,2-diol | - | - | + |
| guaiacol | + | - | - |

* tentative identifications

Recovery Methods 1. vacuum essence
2. batch atmospheric distillation
3. continuous atmospheric distillation

Table 4 shows the relationship of the three different recovery methods to the alcohols in the celery essential oils. The only alcohol common to the three different oils was hexanol. Isoamyl, hexanol, and heptanol were the only three alcohols in the essential oil from the vacuum essence unit that were positively identified. The alcohols, c-3-hexene-1-ol and t-2-hexene-1-ol, that were isolated from the essential oils recovered by batch and continuous distillation were not found in the essential oil recovered in the vacuum essence unit. However, this is not too surprising since these alcohols are generally found as constituents of leaves and the leafy material was removed prior to processing in the vacuum essence unit. The alcohols that were tentatively identified in the essential oil from the vacuum essence unit could be in the oils recovered by batch and continuous distillation. Several alcohols were not identified because enough material was not available for isolation. The terpene alcohols isolated from the essential oils recovered by batch and continuous distillation were not found in the essential oil recovered from the vacuum essence unit. Guaiacol, a phenol, was not detected in the essential oils

recovered by batch and continuous distillation.

The difference in chemical composition between the essential oil recovered by the vacuum technique and that recovered by batch and continuous steam distillation was attributed mainly to the method of preparation of the celery prior to distillation. The celery used in the vacuum technique was blanched in flowing steam and then pressed to remove the juice. Blanching resulted in the loss of some steam volatile flavoring materials. Pressing gave a juice containing most of the water soluble compounds, but oil globules remained in the celery pulp and press clothes. The celery used in the batch and continuous methods was pureed prior to distillation and the essential oil components were easily removed with steam.

The organoleptic properties of the three essential oils were quite different. The oil recovered by batch distillation possessed an aroma characteristic of cooked celery. The aroma of the oil recovered by continuous distillation resembled that of fresh celery. The difference in these two essential oils was attributed to the method of distillation. The continuous distillation procedure subjects the celery puree to heat for a short period in contrast to the 1 hr heating time required for the batch distillation. The improved design of the distillation column undoubtedly increased the recovery of the more volatile materials. Gas chromatographic analysis of the carbonyls indicated an increase in materials with chromatographic retention times of less than 45 min in the oil recovered by continuous distillation (8). The aroma of the essential oil recovered in the vacuum essence unit could not be examined neat. Therefore, glass stirring rods were placed in ether extracts of the different fractions, the solvent evaporated, and then the stirring rod was examined for aroma. The majority of the compounds were in the column bottom fraction which possessed a strong celery aroma. The other fractions possessed fruity terpene odors typical of the more volatile compounds.

Each of the major constituents in the essential oils were smelled as they emerged from the gas chromatograph. Only three compounds had a celery aroma. 3,n-Butylphthalide, and sedanolide possessed the strongest celery aroma. 3-n-Butylhexahydrophthalide had a celery-like aroma but it was not as strong as the other. Examination of the aroma of the effluent from the neutral alumina column indicated that the hydrocarbons contribute very little to the flavor of celery, and the alcohols and carbonyls in combination give celery a pleasant aroma.

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