In the Kaleidoscope: Celery

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Apium graveolens L., related but not identical to the vegetable celery plant (belonging to any one of the several other varieties of the same species of which many cultivars exist) is a hepaxanthic, annual or bienneal herb, reaching approximately 30 to 60 cm high and grows wild or cultivated worldwide.[1-3] The plant has a grooved, fleshy and erect stalk, radical taproot,[4] coarsely toothed leaflets,[5] very small white flowers and schizocarpous fruits.[5]

Of the organs of the celery plant, the fruit which is termed as celery seed in trade parlance, is the most important. All parts of the plant contain essential oil but it is highest in the seed from where commercially available celery flavour is largely derived.

Celery seed is light brown, globular, two-seeded[7-9] and about 750,000 seeds weigh 1 lb.[3] In indigenous medicine celery is credited with therapeutic values[10] which recent pharmacological investigation seems to support.[11] From the dawn of history, with its "characteristic, agreeable odour, aromatic, warm and somewhat pungent taste"[2] and notably haylike and grassy note,[1] this spice is known as a celebrated food flavorant.

India and China are the principal sources of celery seed; France accounts for a small quantity.[1,2] India's annual production is of the order of 4,000 t. to 4,500 t.[12] In appearance, Indian and Chinese seeds are similar while the French variety, slightly darker.[1] Taste-wise, the most bitter is the Indian seed and the least, the French type.[1]

Celery seed contains essential oil in the elongated glands and a large proportion of fixed oil and protein in the endosperm.[9] Generally, 2.5 to 3.0% of essential oil is obtained by steam distillation of the seed,[6] French seed affording 1.90% to 2.45% and Indian seed 2.14% to 2.50%.[2] Apparently, no record is available on the performance of Chinese seed.

Some manufacturers distil the seed as such; others, prior to distillation, comminute the seed[2,13] or temper by addition of water. Superannuated seed yields less oil than the freshly harvested material; of inferior quality, this oil deviates physicochemically from the oil of normal seed.[2]

Problems of Distillation

For more than one reason, steam entrainment of oil from celery seed is combined with significant problems.[13] A time-consuming operation, it can lead to variable results.[14-16] Distillation of a batch of celery seed is stated to last 10 to 12 hours,[2] but this depends upon the size of the retort, quantity and composition of the charge, whether the seed is comminuted or not, wetted, and quantity and pressure of steam. Some of the high boiling odour and flavour principles are hardly distillable with steam[13] and phthalides, the prized ingredients in the aroma-flavour gamut are readily oxidized by air and easily tend to form polymers.[16]

Not less than 24 acids reside in celery seed and these include monoterpene acids: 1-p-menthen-9-acid and 1(7)-p-menthen-9-acid and perillic acid; benzoic, salicylic and phenylacetic acids.[17] The fatty oil amounts to 15% to 17% and comprises mainly of oleic, linolenic, palmitic, petroselinic and petroseladic acids and the lower fatty acids: isobutyric, valeric and heptenoic.[5,7,18-20]

Fatty acids, volatile in steam, may withhold part of the essential oil in solution and emulsion.[13] Total exhaustion of the seed is not pressed into in practice because the very small extra yield is not worth the

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trouble;[21,22] the fatty oil clutches the remnants of the volatiles. However, these untapped components plus other valuables are leached from the resulting marc if the latter is utilized in the manufacture of the oleoresin.

Complete celery seed oil need not necessarily obey the FCC,[23] EOA[24] and other specifications.[2,4] Fortunately, the distillation is flexible and can be engineered to deliver oil in accord with the specifications. Ultimately, it is the 'nose' that takes the momentous decision to "guillotine" or not the oil and this proud and sensitive "jury" "sees nothing" wrong in the deliberately and unethically shuffled oil as long as the sensory qualifications are enticing.

Properties of Celery Seed Oil

Celery seed oil is rich in monocyclic terpene hydrocarbons;[25,26] their concentration largely dictates the specific gravity, optical rotation, solubility and other properties of the oil. Too much of "low boilers" is undesirable and they are partially depleted by a "topping-off" process through rectification during steam distillation. Synchronised with this is the compelling necessity to stretch the distillation to the right endpoint in order to encompass the sesquiterpenes and oxygenated compounds which are valuable ingredients of the oil. Technical expertise to manipulate this intricate operation is needed to converge on an oil in harmony with the EOA and FCC parameters without compromising organoleptic excellence—and at the same time with a sharp eye on the economic viability of the process.

World's annual production of celery seed oil is ca. 25 t.; of this India's share is roughly 80%.[27]

Warmly spicy, sweet, rich, slightly fatty in odour, burning, powerful, long-lingering and highly diffusive—such are the phases of the sensory profile of the celery seed oil. Because celery is frequently used in soup, the odour of its oil is often classified as "soup-like".[28] Though normal, the sensory properties of the Indian oil are not quite as good as of the oil derived from French seeds;[29] its organoleptic profile has been meticulously recorded.[30]

Tremendous amount of research has been done to unravel the chemical composition of celery seed oil.[31-46] The available data have been collated by Guenther,[2] Lawrence[44,47,48] and elsewhere.[49]

Odour Characteristics

What are the components that impart celery-

like—aroma/flavour—quality which includes burning-numbering-bitter taste? Literature gives a confusing picture;[14] essentially two groups of compounds are involved in conferring the celery-like quality viz., hydrocarbons and phthalides.

Pioneering investigations[31] reported that β-selinene, sedanolide and sedanonic acid anhydride confer celery-like quality and this was a useful reference point in subsequent investigations.[2,32] Guenther[2] noted that the rectification of celery seed oil with live steam yielded 75% volatiles and 25% residue and in the latter was locked the odour and flavour principles viz., high boiling oxygenated constituents of the essence.

As pointed out earlier, celery oil is rich in terpene hydrocarbons with (+)-limonene as the major constituent;[25] however, the oil obtained by supercritical CO_2 extraction of the seeds disclosed only 9% of this p-menthadiene.[46] (+)-Limonene has a fruity and fragrant odour.[50,51] Whatever that may be, in general, the participation of the hydrocarbons in celery flavour is not appreciable, the exception being β-selinene. With its low threshold concentration[52,53] and typical aroma, this sesquiterpene is a generous contributor to celery quality.[2,53-55]

One must bear in mind the fact that β-selinene is not rated as celery-like as, for example, sedanolide; it appears to function synergistically supplementing celery-odour.[53] On the other hand, Salzer[56] asserts that the odour is determined primarily by β-selinene, the limonene acting only as a support. This explains why a level of 10% of this sesquiterpene is preferred though most commercial oils contain only 7.0 to 7.5%; as an odd case, a sample with 20% of β-selinene has been recorded.[39,2a]

Turning to phthalides which are cyclic esters or lactones, they have outstanding odour characteristics of celery.[14,26,31,35,38,39,41,43-45] For the purpose of discussion on the role of phthalides, we have drawn on the work on celery essence from other parts of the plant. The phthalides determine the afterodour or represent the basic gustatory body of the celery oil, as has been organoleptically determined following fractionation in a chromatographic column.[56] The phthalides associated with this property are listed in Table I.

To this list must be added neocnidilide and senkyunolide.[45a] Of these, (5) is rated as the most potent[52,53] in bestowing the most characteristic celery odour. Based on the odour threshold, this phthalide is ten times as strong as (*1*). Despite the fact that (*1*) has a celery-like aroma, it requires a much greater concentration to display its property.[52,53] β-Selinene is not as celery-like as (*1*) and (*5*). Here also these constituents might act synergistically to fresh celery odour.[53]

Table I. List of phthalides with Outstanding Odour Characteristics of Celery.

1. 3-n-Butyl Phthalide (*1*)
2. 3-n-Butyl-4,5-dihydrophthalide (Sedanenolide) (*2*)
3. 3-Isobutylidene-3a,4-dihydrophthalide (*3*)
4. 3-Isovalidene-3a,4-dihydrophthalide (*4*) and
5. 3-Butylidene-3a,4,5,6,-terahydrophthalide (Sedanolide) (*5*)

Whatever may be the earlier conclusions, we have to reassess the origin of celery odour due to phthalides in the light of the disclosure that "of the genuine compounds present in A. graveolens, neocnidilide, senkyunolide and E-butylidene phthalide are important contributors to the celery aroma of the plant. Lingustilide, butyl phthalide and Z-butylidene phthalide proved to be practically devoid of odour".[57]

While considering the aroma profile of celery, due attention has to be given to guaiacol which has a "definite celery note".[50] Another component is 1-p-menthen-9-acid with odour reminiscent of the top note of oak moss; perillic acid, on the other hand, smells weak.[17]

Similarity in the odour characteristics of celery

seed and lovage root oils stems from the phthalide constituents.[28] Celery seed oil has a far lighter and more penetrating sweetness in contrast to lovage root oil which has a profound sweet smell. This is attributed substantially to the qualitative, quantitative and constitutional differences of the phthalides in the oils.[28]

Nottingham group[58] have synthesized alkylidene phthalides of celery odour. 3-Propylidene phthalide, a flavourant with an odour characteristic of celery, is available commercially.[59]

Burning-numbing taste is associated with celery flavour.[60] Perhaps this originates from dihydrophthalides which in neat form possess intense burning-numbing sensation, (3) being more intense than (4).[61,62]

"One of the worst aspects of celery flavour is bitterness"; an infusion of the seed in water has this property.[63] The spice is "rich in water soluble saponins which are extremely bitter substances".[63] On the other hand, dihydrophthalides in the spice are mildly bitter.[61,62] Whether "colour-less non-flavanoid D-glucoside—which imparts even in traces the bitter sensation" is the author of this property is worth investigating.[64] The bitter principles seem to be soluble in methanol/ethanol which offers a route to debitter the extractives of the spice.

Celery Oleoresins

Technology is lacking for capturing oleoresin from the whole celery plant.[65] Currently, the oleoresin is manufactured exclusively from seed using hydrocarbons, preferably n-hexane, unless it is for pharmaceutical purpose, in which case, it is recovered through ethanol.[13] From Guenther,[2] one gathers that oleoresins of celery "are prepared by extracting celery seed with volatile solvents (particularly alcohol), filtering and freezing the solutions and driving off alcohol in vacuuo". At the desolventization stage, conditions must be such as to minimize the flight of low boilers. Whether the oleoresin ever fulfills the EOA[66] requirement viz., "the celery extractives are the sum of the non-volatile ether extract and the volatile oil content" is doubtful.

According to Lewis,[18] the hexane extracted celery oleoresin is partitioned by 90% alcohol into: (1) an oleoresin containing about 25% volatile oil and (2) a fatty oil containing about 3% volatile oil. One can use either of the two oleoresins for flavouring foods depending on "whether an oil rich in volatiles or a milder flavoured product is required".

Oleoresin celery is a dark grey or brownish green viscous liquid—"warm, fatty-spicy and rich, intensively sweet herbal, radiant and tenacious".[13]

Differences in organoleptic spectra exist between French and Indian oleoresins. Whereas the French type is "sweet, herbal and tenacious with only a slight citrus undertone", the Indian type is "more herbal with a slight lemon-like aroma and tenacious herbal undertones".[8]

Table II. Percentage of Volatile Oil in Commercial Oleoresins.

Oleoresin type	Volatile oil v/w
Oleoresin celery[65]	7%
Oleoresin celery standard[65]	9
Oleoresin[1]	10
Celery oleoresin[67]	10-15
Superesin® celery[65]	12
Standardized celery oleoresin[68]	12-14
Standardized celery oleoresin[68]	40-45

For appraisal of celery oleoresin, Salzer[56] regards essential and fatty oil contents as analytical criteria. The essential oil retrieved from distilling the extract is different from the one directly derived from distilling the fruit owing to loss of constituents during desolventization.[56]

Compared to hydrocarbon extractives, the oleoresin obtained with ethanol as menstruum contains less lower terpenes; hence it is stamped with superior flavour and solubility characteristics.[13]

Volatile oil level in typical commercial celery oleoresins are listed in Table II. EOA stipulates volatile oil between 10 to 12% v/w. An oleoresin exceptionally high in volatile oil, 40-45% v/w, is available.[68] By blending the volatile oil obtained by steam distillation of the spice and the solvent extractive of de-oiled residue, one can construct oleoresins with any desired voltile oil.[65,68] Celery flavour is also dispensed in forms other than oil and oleoresins.[1]

Excellent diffusive power and superb odor tenacity make the celery seed oleoresin a distinguished ingredient in perfumery compositions; splendid effects are achieved with very small amounts. An unwelcome feature of the oleoresin is its dark color; this, however, can be partially decolorized with activated carbon.

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