PROCESSING OF FRESH, PARTIALLY DEWATERED HERBS WITH NEAR-CRITICAL FLUIDS

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The extraction of essential oils and oleoresins from dry herbs and spices using supercritical and liquid CO_2 is practised on an industrial scale. Extraction is only economically and technically feasible for herbs that have relatively high value essential oils that are not degraded by drying of the freshly harvested herb. The extraction of essential oils from fresh herbs is not regarded as feasible due to the very low initial concentration in the fresh herb, and the interference from water when the herb is crushed which prevents access for solvent extraction. Here, we present an extraction process for obtaining high quality essential oils and oleoresins from herbs that have been partially dewatered by a combination of chopping and passage through a screw press. The method has been applied to a range of herbs and spices, including onions, ginger root, celery (aerial parts), parsley, elder flower and oregano. Results are given in detail for celery, an example of a herb with internal secretary canals; and oregano, a herb with external glandular hairs. The processing trials examined the effects of herb storage time (before and after chopping), storage temperature, extent of dewatering, and pressure/temperature combination on extract yield and quality. High quality oleoresins were obtained from both herbs. Celery herb extracts had substantially higher concentrations of characteristic flavour components butyl phthalide, sedanolide and sedanenolide compared to commercially available celery oils. Oregano extracts had higher levels of characteristic aroma compounds *p*-cymene and carvacrol compared to steam distilled oil. Dewatered herb could be extracted up to three days without loss of yield or extract quality, providing the herb material was stored below 10 °C. The juices squeezed from the herbs were also extracted with supercritical CO_2. The yield of oleoresin was very small from the juice, as the majority of the essential oil and oleoresin remained with the herb.

INTRODUCTION

The extraction of essential oils and oleoresins from dry herbs and spices using supercritical and liquid CO_2 is practised on an industrial scale, and has been widely researched [1-3]. Extraction is only economically and technically feasible for herbs that have relatively high value essential oils that are not degraded by drying of the freshly harvested herb. The extraction of essential oils from fresh herbs is not regarded as feasible due to the very low initial concentration in the fresh herb, the interference from water when the herb is crushed to enable access for extraction, and the need to process immediately after harvesting to avoid degradation. However, the extraction of fresh herbs and flowers has been reported [4]. In this

work, we present an extraction process for obtaining high quality essential oils and oleoresins from herbs that have been partially dewatered by a combination of chopping and passage through a screw press. The method has been applied to a range of herbs and spices, including onions, ginger root, celery (aerial parts), parsley, elder flower, sage and oregano. Processing parameters, extraction yields and compositional data were determined in detail for fresh celery, an example of a herb with internal secretary canals; and fresh oregano, a herb with external glandular hairs. The extraction essential oils from dried celery leaf and stem [3] and oregano [5,6] has been reported previously.

EXPERIMENTAL

Celery stems, and leaf + stem were supplied by commercial growers in North Otago and Auckland (NZ) respectively. Oregano (high carvacrol type) was grown and harvested by Crop and Food Research, Redbank. CO_2 was supplied by BOC (NZ) Ltd. R134a (refrigerant grade) was supplied by Isceon. Celery was first chopped in a mincer, and then further chopped in an Urschel knife mill (Comitrol), prior to dewatering in a screw press (Vetter Mk 27). Juice and dewatered solids were collected in separate buckets and weighed to obtain a mass balance over the dewatering stage. Moisture contents of the feed, chopped herb and dewatered herb were determined by mass loss in a convection oven at 353 K. Oregano was chopped and dewatered in a similar manner, without the first stage chopping. The near-critical extraction of the dewatered herb was carried out in a 2 x 10 litre pilot scale extraction plant shown in figure 1.

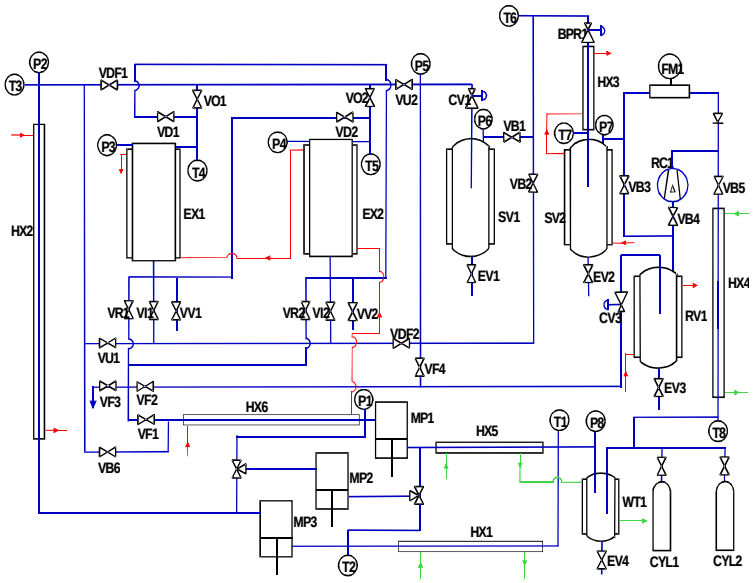

Figure 1: Schematic of pilot scale extraction apparatus

The dewatered herb was placed into either one of two pre-weighed extraction baskets, which were then placed in the 10 litre extraction vessels. Extraction was carried out either at supercritical conditions (300 bar, 313 K) using upflow of CO_2, with two stage separation of extract at 90 bar, 318 K and ~ 60 bar, 313 K; with liquid CO_2 at 70 bar and 293 K, with one separator at ~ 60 bar, 313 K; or with liquid R134a at 40 bar, 313 K, with one separator at ~ 5 bar, 313 K. Recycled carbon dioxide was cooled to 273 K before passing through a chilled water trap and sub-cooler heat exchanger. The water trap recovered most of the water that was co-extracted with the essential oils and oleoresins. Herbs were chopped and dewatered immediately upon receipt, and then extracted immediately, or after storage for 2-3 days. Extracts were analyzed by a quantitative NMR method adapted from previous work [7], and for comparison by GC for oregano.

RESULTS AND DISCUSSION

I - CELERY

The herb extraction process was developed over a three-year period for celery. In year one, the yields and composition of oleoresin from waste celery stems was determined as a function of gas type, plant part (leaf, stem, juice) and extraction conditions. Extraction of dried celery leaf was also carried out for comparison. The extracts were analyzed for the characteristic celery flavour components butyl phthalide, sedanolide and sedaneneolide. Limonene and apiole, present in the steam distillates of celery leaf and stem [8,9], were not found in the CO_2 extracts. The results are shown in table 1, where BP = butyl phthalide, SDE = sedanolide, and SDNE = sedaneneolide. The yield is reported on a fresh herb basis. There are compositional differences between stem and leaf extracts: stems had a higher ratio of SDE to SDNE. CO_2 and R134a were equally effective in the extraction of oleoresins. There was less water extracted when R134a was used than with CO_2. As expected, supercritical conditions resulted in the highest extraction of water, as the extraction was carried out at elevated temperatures. The first separator had high levels of water. The composition of juice oleoresin was similar to that from the stem. However, the yield was very low at 0.01 %. Thus, juice was not considered further. The moisture content of the herb (mainly stems) was very high, at around 90-92 % by mass. The yield of extract increased when the herb was dried. However, the extracts contained fatty acids and glycerides that were not found in the fresh herb extracts, and the aroma was distinctly different from the fresh herb.

Table 1: Composition Results for Celery extracts

Gas	Pressure, bar	Temp, K	Type	Separator	BP	SDE	SDNE	Yield, % by mass
CO_2	70	298	Stem, dewat	single	3	24	17	.024
CO_2	70	298	Stem, dewat	single	3	23	16	.018
CO_2	300	313	juice	second	2	22	5	.010
R134a	40	313	Whole leaf	single	4	56	19	.017
R134a	40	313	Leaf, dewat	single	4	52	17	.014
CO_2	70	298	Stem, dry	single	2	15	21	.133
CO_2	300	313	Stem, dry	first	1	7	10	
				second	4	25	22	.0882

In the second year of the project, the effect of storage time on extract quality and composition was determined using CO_2 as the extraction solvent. The celery used in these trials was predominantly fresh leaf. Composition and yield data are shown in table 2. Again, the yield is reported on a fresh herb basis. The trials demonstrated that chopped and dewatered celery leaf could be stored for at least three days in a refrigerator with minimal effect on extract yield and extract quality. The composition of the extracts with immediate (1 day) and two or three day storage were identical within experimental error. However, celery stored at room temperature for three days had become mouldy, and the extract was dominated by a musty smell. The extract obtained from this mouldy material had significantly lower levels of BP, SDE and SDNE. The extracts also had a much lower ratio of SDE to SDNE compared with the first year extracts, which suggests that the celery may have come from

different cultivars, or that leaf essential oil composition is different from stem. The yield of oil was slightly higher from fresh leaf material than from the previous work with stems.

Table 2: Composition results for storage trials

Pressure, bar	Temperature, K	Storage time	Separator	BP	SDE	SDNE	Yield, % by mass
300	313	1 day	second	2	12	36	0.12
		3 days, 277 K	second	4	21	58	0.14
70	298	1 day	single	2	27	67	0.04
		3 days, 277 K	single	2	26	53	0.05
70	298	1 day	single	1	26	43	ND
		3 days, 298 K	single	.05	4.5	2	ND

Notes: ND = not determined

In the third year of the project, the ability to scale up the process was established. Three trials using 50 kg each of fresh material were carried out. After chopping and dejuicing, the volume of the solids was reduced to around 20 litres from 50 kg of initial feed. This mass of feed occupied a volume of ~ 1.25 m^3. The volume of juice produced was around 30 litres. The overall yields after removal of water, on a fresh celery basis, were .042 % for the first separator, and .057 % for the second separator.

II - OREGANO

Oregano extraction was carried out over a two year period. In the first year, the effect of harvest time on extract composition and yield was determined, to see if the composition changed with time in the field. Whole leaf and stem; rubbed leaf and juice was used in the trials. In the second year of the project, a comparison between fresh and dried material was carried out on rubbed material only. The key components that were analyzed by quantitative ^{1}H NMR were *p*-cymene and carvacrol. Selected samples were also analyzed by GC to enable comparison with steam distilled plant material. GC analysis revealed a number of other essential oil components that were not quantified by NMR.

Table 3: Composition results for oregano storage trials

Pressure, bar	Temperature, K	Sample	Harvest date	Separator	p-cym	Carv.	Yield, % by mass
250	313	Whole	22/01/03	first	< 0.5	< 0.5	0.26
				second	5.5	38.5	0.49
250	313	rubbed	29/01/03	First	< 0.5	< 0.5	0.31
				second	3.4	27.1	0.47
250	313	rubbed	3/02/03	First	< 0.5	0.5	1.08
				second	9.3	26.7	0.51
250	313	rubbed	11/02/03	First	< 0.5	0.9	0.35
				second	7.0	25.9	0.34

The level of carvacrol was highest at the start of the harvest/processing period, and then dropped to a constant level. For consistent product, the material could be harvested and extracted over a three to four week period. The yield obtained from oregano was substantially

higher, at 0.7 – 1 % for fresh herb, as compared to celery, at < 0.3. However, the moisture level in oregano was lower, at around 70 %.

The extraction of dejucied oregano herb was compared with dried herb in the second year of the project. The oregano already had low moisture levels prior to dejuicing, at only 66.7 %.

Table 4: Extraction yield comparison between fresh and dry herb

Pressure, bar	Temp, K	Raw material	Moisture Content, %	S1 yield, %		S2 yield, %	
				As rec.	dry	As rec.	dry
300	313	Dejuiced	66.7	0.18	0.55	0.70	2.14
300	313	dry	8.98	3.01	3.31	3.58	3.94

The yield of first separator (S1) product was highly affected by the presence of moisture in the feed material - a very low yield was obtained from the dejuiced solids. A waxy extract was obtained from the dried material. The yield of second separator product (main flavour and fragrance fraction) was also higher for the dried material. However, the aroma was less intense, and the extract appeared to be diluted with non-volatile waxes that caused the extract to become semi-solid at room temperature. Leeke et al [6] noted that the apparent solubility of essential oils from oregano was dependent on the level of moisture in the herb. Water seems to affect the solubility of non-volatile components to the greatest extent. Similar extraction behaviour was observed with celery: non-volatile fatty acids and triglycerides were not present in the extracts from fresh, dejuiced solids; but were present in the extracts from dried material [3]. The aroma of the dried oregano extract seemed to be less intense than that of the fresh material: this may also be a result of dilution by unwanted non-volatile co-extractants.

III – OTHER HERBS AND SPICES

The extraction of flavours and fragrances from fresh onions, elder flowers, ginger root, parsley and Dalmatian sage was also carried out. Onions were representative of herbs/spices with very high moisture contents, whilst the other materials had moisture contents in the range 60 – 85 % by mass. The results of the experimental trials followed those for celery and oregano, and could be summarised as follows: the chopping and dewatering of the fresh herbs/spices resulted in very large increases in bulk density; the juices had very little extractable aroma; and the extracts obtained from the process were very similar to the fresh herbs/spice. The extract yield from onions was very low, at only 0.03-0.07 % by mass. However, these yields match those reported in the literature for supercritical CO_2, solvent and steam distillation yields [10-12]. Again, oleoresin yield from juice was very low, at less than 0.01 % by mass. The extraction of ginger oleoresin and essential oil was successfully achieved from fresh ginger. In this example, the relatively lowly volatile gingerols were extractable from the dejuiced ginger root. These gingerols were collected in the first separator as an oleoresin, in a similar manner to those obtained from dry ginger root in previous work [7]. A yellow essential oil was obtained in the second separator. Freshly harvested and dejuiced elder flowers were also processed successfully. A semi-solid essential oil that was identical to the fresh flowers was obtained as the main product.

CONCLUSIONS

A new process has been established for the extraction of fresh, partially dewatered herbs using supercritical fluids. The new process results in a large increase in the bulk density of the solids, and an improvement in the amount of water extracted relative to fresh, non-dejuiced solids. In addition, the process can be applied to dejuiced solids that have been stored up to three days, which means that the dejuicing process can be carried out at the point of harvest, and the solids transported to a remote extraction plant. The new process resulted in lower levels of non-volatile components, and better aroma quality relative to extracts obtained from dry herbs. The process has been applied to a wide range of common herbs, one spice and one flower. The process can also be carried out with other, lower pressure near-critical solvents, especially R134a (1,1,1,2 – tetrafluoroethane).

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