

# Characterization of Volatile Composition and Odor of Angelica (*Angelica archangelica* Subsp. *archangelica* L.) Root Extracts<sup>†</sup>

Kaisli Kerrola,<sup>\*‡</sup> Bertalan Galambosi,<sup>§</sup> and Heikki Kallio<sup>‡</sup>

Department of Biochemistry and Food Chemistry, University of Turku, FIN-20500 Turku, Finland, and The Agricultural Research Center, South Savo Research Station, FIN-60500 Mikkeli, Finland

The volatile components isolated from the root of two wild angelica strains (*Angelica archangelica* L. var. *Archangelica*) grown in the northern Finland were compared with the garden angelica (var. *Sativa*) grown in the north and in the south of Finland. More than 80 compounds were determined in the Soxhlet extracts by gas chromatography, and 67 were identified by gas chromatography-mass spectrometry. Large variability in the relative amounts of the compounds was found.  $\beta$ -Phellandrene was the main component in var. *Archangelica* and sabinene in var. *Sativa*. The relative proportion of both hydrocarbon monoterpenes and oxygenated monoterpenes was larger in var. *Sativa* cultivated in the north than in the south of Finland. Angelica strains were sensorially characterized as green, terpenic, fresh, celeriac, and sweet. Deviation-from-reference descriptive analysis was used to evaluate the intensity of these characteristics. Supercritical carbon dioxide extraction (12 MPa/50 °C) was used to isolate the aroma of the angelica root into three fractions with distinctly different compositions. Sensory analysis of the carbon dioxide fractions revealed a terpenic, fresh, and pomegranate-like character in the first fraction, and the same features but less pronounced were detected in the second fraction. The last fraction collected after exhaustive extraction was perceived as sweet and stale.

**Keywords:** *Volatiles; odor; sensory; angelica; supercritical fluid extraction*

## INTRODUCTION

Angelica strains native to northern Fennoscandia exhibit large morphological variety (Ojala, 1986). This phenomenon was explained by differences in local microclimatic conditions originating from the topography of this region (Kallio et al., 1978). Intense pressure of selection drives to differentiation of populations, which could be detected not only in the appearance of the plants but also in the chemical composition of volatile components (Ojala et al., 1986). Forsén (1979) studied the compositional differences in the root oil of angelica varieties *Archangelica* and *Sativa* originating from central Europe. The oil of var. *Archangelica* was evaluated to have higher quality than the root oil of var. *Sativa*, which is the commercially cultivated raw material for industrial fragrance production. Forsén attributed the difference in odor to the compositional differences of the volatiles, especially in the relative amounts of various monoterpene hydrocarbons. Yliaho (1981) did not find differences in the composition or amount of essential oil isolated from the root of angelica (var. *Archangelica*) cultivated in the north or in the south of Finland. No evidence of latitude effect was found on the amount of essential oil production or composition. Only a high relative proportion of limonene showed indicative correlation to the northern growing site.

Chialva et al. (1983) studied the odor of several herbs, including garden angelica, by combining the chemical analyses carried out by headspace chromatography with

the sensory quality of the herb evaluated by an expert panel. They presented the chromatograms of the herbs exhibiting the poorest and the highest qualities. However, they did not assess which compounds or abundance of a substance contributed to the poor or high quality. It can be assumed that a high number of different monoterpene compounds indicates high quality of the aroma in garden angelica.

The essential oil composition of angelica root has been investigated by Klouwen and ter Heide (1965b), Taskinen and Nykänen (1975), Forsén (1979), Héthelyi et al. (1985), and Srinivas (1986). Chalchat and Garry (1993) extracted angelica roots with pentane and obtained an oleoresin that contained coumarins as the main compounds. Kallio et al. (1987) isolated the volatile substances of angelica roots by liquid carbon dioxide extraction. More recently, Nykänen et al. (1991) compared the composition of various supercritical extracts of angelica root with steam distilled and subsequently liquid-liquid extracted angelica root oil. They reported high quality aroma in extracts collected at relatively low pressures. At high pressures and temperatures the amounts of coextracted nonvolatile substances increased, which decreased the sensory quality of the extracts.

Supercritical carbon dioxide extraction is a powerful tool in isolating lipophilic components from complex matrices. Depending on the operation parameters selected, supercritical extracts with considerable variation in composition can be obtained [e.g., Brogle (1982), Stahl and Quirin (1984), and McHugh and Krukoni (1986)]. Exhaustive extractions are seldom needed, if the aim is to produce aroma isolates. Moderate pressures and low temperatures have been found to be sufficient for isolating the most volatile components from aromatic plants [e.g., Schultz et al. (1974), Stahl and Gerard (1985), Kallio and Kerrola (1992), and Kerrola and Kallio (1993)]. Zosel (1978) was the first

\* Author to whom correspondence should be addressed (telefax 358-21-633 6860).

<sup>†</sup> The Academy of Finland and Aromtech Ltd. supported the research, which is gratefully acknowledged.

<sup>‡</sup> University of Turku.

<sup>§</sup> The Agricultural Research Center.

to demonstrate practical applications of fractionating complex mixtures by high-density gas. More recently, supercritical CO<sub>2</sub> fractionation has been used to obtain aroma isolates from wormwood (Stahl and Gerard, 1983) and apple peel waste (Bundschuh et al., 1988), to remove terpenes from orange essential oil (Temelli et al., 1988), to concentrate,  $\omega$ 3 fatty acids from fish oils [reviewed by Rizvi et al. (1988)], and to isolate volatile components from beef fat (Um et al., 1992).

In this study we characterized the volatile substances in the roots of angelica cultivated in Finland at two different latitudes. Our objective was to use supercritical carbon dioxide extraction to isolate an aroma fraction, which contains only the aroma components and no coextracted other substances, which might have a negative influence on the aroma.

## MATERIALS AND METHODS

**Materials.** A strain of *Angelica archangelica* subsp. *archangelica* L. var. *Archangelica* native to Finnish Lapland was collected from Juutuajoki in 1987. The plants were cultivated from seeds at Meltosjärvi, Finland (66°31'N, 24°40'E), from May 1988 to mid September 1990. Seeds of another strain growing wild near Peltajoki were collected in September 1983 and cultivated in Puumala, Finland (61°40'N, 28°15'E), from 1984 to 1987. Seedlings of the Peltajoki strain were transplanted to Kittilä, Finland (67°40'N, 24°50'E), on May 30, 1988, and the roots harvested on October 10, 1989. *Angelica archangelica* subsp. *archangelica* L. var. *Sativa* (Miller) Rikli, originating from Research Institute of Medicinal Plants, Budakalasz, Hungary, was cultivated at Puumala in 1984–1987. Seedlings were transplanted on May 10, 1987, and harvested on September 26, 1988. The same strain was cultivated at Kittilä in 1988–1989. Transplantation and harvest were the same time period as for the Peltajoki strain. The soil was coarse sand morena in Puumala, sand in Kittilä, and sandy mold in Meltosjärvi. In Puumala and Kittilä 400 kg of mixed fertilizer (NPK 7–5–15) per hectare was applied on the fields each year, with an additional nitrogen dressing (40 kg/ha) in the spring. In Meltosjärvi 3 kg/m<sup>3</sup> compost was applied each year. Weed control was carried out by hand, and no pesticides were used. The flowering shoots were bent downward to prevent flowering, which decreases the weight of the roots and induces rotting of the root. The material from Meltosjärvi and Kittilä was dried at about 20 °C for 1 week. The roots from Puumala were dried at about 30 °C for 5 days in a pilot-scale cabinet drier under continuous circulation of air. All of the material was stored in paper bags at ambient temperature protected from light until analyzed.

**Solvent Extraction.** Five grams of powdered angelica root was extracted for 6 h with 150 mL of the mixture of redistilled pentane/diethyl ether (1:2 v/v) using a modified Soxhlet technique (Huopalahti and Linko, 1983). The extract was concentrated at 45 °C, with a Widmer column, to approximately 2 mL. Purification of the concentrate was carried out at 8 °C using column chromatography with 5 g of silica gel (Merck, silica gel 60 extra pure, 70–230 mesh ASTM) as described by Scheffer et al. (1976, 1977) and Chamblee et al. (1991). The compounds were eluted with 30 mL of the solvent mixture used for extraction. The internal standard, *n*-tetradecane (purity >99%; Nu Chek Prep, Elysian, MN), was added to the effluent. The effluent was concentrated with a Widmer column as described above to a final volume of 2 mL. The samples were dried over anhydrous sodium sulfate and stored at –20 °C in Teflon-capped glass vials. A 20-fold dilution of the concentrate was made prior to gas chromatographic analyses. The relative amounts of compounds were calculated as the mean values from three gas chromatographic determinations of triplicate solvent extractions.

**Supercritical Fluid Extraction.** Angelica roots of var. *Sativa* cultivated at Puumala were sent to a supercritical extraction facility with commercial-scale equipment. The material was first ground in a cutting mill and then pulverized

in a pin mill under cooling by injection of liquid CO<sub>2</sub>. A batch extraction procedure was applied using 10-L autoclave-type extractors at 12 MPa and 50 °C. The operation conditions were selected on the basis of our instructions. The volatile substances of approximately 10 kg of plant material were fractionated into three extracts (referred to later as SFE1, SFE2, and SFE3). A total of 40 kg of CO<sub>2</sub> was used for the isolation of the first two fractions, and subsequently the extraction was continued with an additional 140 kg of CO<sub>2</sub> to obtain the third fraction. The extracts were collected at 6 MPa and 30 °C. After removal of coextracted water the extracts were transferred to brown glass bottles and stored at –20 °C until analyzed. A 20-fold dilution of the extracts in *n*-pentane/diethyl ether (1:2 v/v) was made, and internal standard was added prior to GC and GC–MS analyses.

**Gas Chromatography and Gas Chromatography–Mass Spectrometry Analyses.** The gas chromatography analyses were carried out on a Varian 3300 gas chromatograph (Varian Associates, Walnut Creek, CA) equipped with a flame ionization detector connected to a Shimadzu Chromatopac C-R3A integrator (Shimadzu Corp., Kyoto, Japan). Fused silica columns (HNU-Nordion, HNU Systems, Helsinki, Finland) (25 m × 0.32 mm i.d., film thickness 0.20 μm) coated with a NB-351 liquid phase (corresponds to OV-351) were used for the analyses. The oven temperature was programmed as follows: from 35 (isothermal for 5 min) to 150 °C at 2.5 °C/min and from 150 to 240 °C at 5 °C/min and isothermal period at 240 °C for 20 min. The temperature of the injector port and the detector was 240 °C. The split ratio was 1:20, and the flow rate of carrier gas (helium) was 1.6 mL/min. The 70-eV electron impact mass spectra were obtained on a VG Analytical 7070E instrument and VG-11-250 data system (VG, Wythenshawe, Manchester, U.K.). A Dani 3800 HR ch gas chromatograph with the same capillary column and temperature program as in the gas chromatography analysis was used in GC–MS. Qualitative analysis was based on comparison with mass spectral libraries (Stenhagen et al., 1974; TNO, 1979; Ramaswami et al., 1988) and Kovats indices (*I<sub>R</sub>*) [e.g., Holm et al. (1988) and Davies (1990)]. Authentic reference compounds were used in identifications of the monoterpene hydrocarbons only.

**Sensory Evaluations. Samples.** The samples evaluated were roots of two angelica strains (var. *Archangelica* from Meltosjärvi and var. *Sativa* from Puumala and Kittilä) as well as supercritical carbon dioxide extracts of angelica root (var. *Sativa* from Puumala). The samples for each assessor were prepared simultaneously about 1 h prior to the sessions to allow the headspace to develop in the bottle. The dried material was ground with a centrifugal mill (Model ZM 1, Retsch KG, Haan, Germany) equipped with a 0.5-mm sieve under liquid N<sub>2</sub> injection. Freshly prepared angelica root flour (0.5 g) was weighed into 35-mL glass bottles wrapped in aluminum foil. The sample was covered with cotton wool to avoid visual identification and capped with a lid. Twenty microliters of the SFE fractions was applied on a disk of Whatman No. 1 filter paper and covered as described above. All samples were coded with three-digit random numbers and served in randomized order to each assessor in every session. Angelica var. *Archangelica* from Meltosjärvi was chosen as the reference and prepared the same way as the samples.

**Assessors.** Originally 20 assessor candidates were chosen from the staff and graduate students of our department; 12 of them had previous experience in descriptive sensory methods, and another 4 had basic training in general sensory assessment. For the evaluations of the samples, 15 assessors (6 men, 9 women) were selected on the basis of their performance in pretrials. All were nonsmokers, between 25 and 52 years of age, and all had previously participated in descriptive sensory analyses.

**Procedure.** Deviation-from-reference descriptive analysis (Pangborn, 1984) was used to determine not only the characteristic features of the odor but also the magnitude of the differences in the angelica strains and the supercritical fractions. A set of triangle tests (Amerine et al., 1965) was conducted prior to profiling of the samples to establish whether sensorially detectable differences in odor existed. Differentia-

**Table 1. Odor Samples of the Attributes Evaluated in Sensory Analyses and Their Composition**

attribute	composition
green	comminuted spider plant leaves
terpene-like	5 $\mu$ L of $\alpha$ -pinene (turpentine, 99%)
fresh	cooling effect of one eucalyptus-flavored cough drop in 5 mL of distilled water
celery	2.5 g of grated fresh root celery (celeriac)
pomrance-like	0.2 g of orange peel powder in 5 mL of distilled water
sweet	2.0 g of honey in 10 mL of distilled water
stale	partly oxidized sunflower oil

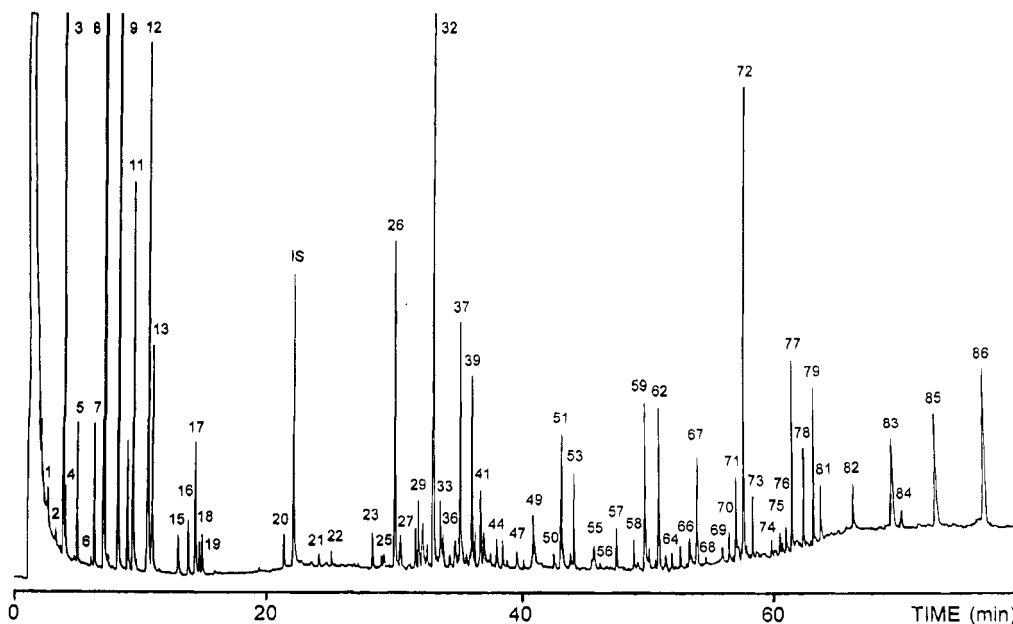
tion of the odd sample was requested in a forced-choice design. The root samples were tested against each other and the supercritical fractions against each other. On the basis of the discrimination tests it was concluded that there were statistically significant differences between the samples ( $p < 0.001$ ). In the selection of odor attributes the assessors were asked to describe the various sensory characteristics of freshly ground angelica root powder and the SFE fractions. From the 42 terms listed in the characterization of the different strains of angelica, 5 were selected (green, terpene-like, fresh, root celery, and sweet) according to the predominancy of the term in the round-table discussions. In the evaluation of the odor of the supercritical extracts 33 terms were used, of which 6 were predominant (green, terpene-like, fresh, pomrance-like, sweet, and stale). The 15 assessors were trained to connect the chosen term to the right attribute by presenting an odor sample for each attribute. The compositions of the odor samples and corresponding attributes are presented in Table 1. To ensure the similarity of definition for all assessors and all sessions, the odor samples were available throughout the study. The angelica root samples and the SFE fractions were evaluated in separate sessions to avoid fatigue of the olfactory system. For determination of the intensities of the odor characteristics, the angelica root or extract samples (including a "blind control", i.e., the same as reference) were compared with the reference sample and rated for deviation from the reference (R) using a nonnumerical, 100-mm graphic scale. The scale was anchored "less than R" and "more than R" at the end points, and "same as R" at the center of the scale. Assessor responses were converted to numerical values from 0.0 to 10.0 using 0.1-cm accuracy for the analysis of the results. Analysis of variance was applied to the results of three replicate sessions of both sample groups.

The evaluation of the samples was performed in individual assessment booths from 1 to 3 p.m. throughout the whole

study. The sessions were held twice a week during five consecutive weeks from the beginning of April through the middle of May 1993.

## RESULTS AND DISCUSSION

**Volatile Composition of Angelica Roots.** It was previously reported that the main proportion of angelica root oil consists of monoterpene hydrocarbons up to 88% (Forsén, 1979; Ojala et al., 1986). However, considerably smaller proportions of monoterpenes were detected in the Soxhlet extracts of var. *Archangelica* and *Sativa* in this study. The gas chromatogram of angelica root extract (var. *Sativa* from Kittilä) isolated with Soxhlet extraction using pentane/diethyl ether as solvent is shown in Figure 1. The relative amounts of volatile compounds of all four samples studied are presented in Table 2. The monoterpene hydrocarbons comprise from 24 to 46% of the total extracts. Nykänen et al. (1991) reported 28% monoterpenes in angelica root of commercial quality purchased from the international spice market. The most prominent feature within the hydrocarbon moiety was the dominance of  $\beta$ -phellandrene in the extracts obtained from var. *Archangelica*, comprising almost half of the total proportion. Klouwen and ter Heide (1965b) concluded the high amounts of phellandrenes in angelica root oil from var. *Sativa* are related to higher degree of maturity. Forsén (1979) reported higher relative proportions of phellandrenes in var. *Norvegica* (later included into var. *Archangelica*) than in var. *Sativa* of unknown origin cultivated at the same locations. In the same study, significant correlation between the stage of plant development and the abundance of 3-carene, not phellandrenes, was detected. The root oils steam distilled from 13 samples of angelica from Hungary, including the same strain of var. *Sativa* investigated in this study, contained  $\beta$ -pinene as the main component (Héthelyi et al., 1985). The most abundant monoterpene hydrocarbon detected in PE/DEE extracts of this strain cultivated at the two locations was sabinene, and only minor amounts of  $\beta$ -pinene were detected. In the studies by Forsén (1979) and Taskinen and Nykänen (1975)  $\alpha$ -pinene was the predominant monoterpene detected in var. *Sativa* root oils.



**Figure 1.** Gas chromatogram of the angelica root volatiles of var. *Sativa* cultivated in Kittilä. Numbering of the peaks corresponds to the compounds in Tables 2 and 4.

Table 2. Relative Proportions of Volatile Compounds in Angelica Roots of Various Origins

no.	$I_K$	compound	relative compositions (%)			
			var. Sativa		var. Archangelica	
			Puumala	Kittilä	Meltosjärvi	Kittilä
Monoterpene Hydrocarbons						
1	947	$\alpha$ -thujene	0.3	0.1	0.3	1.5
3	1010	$\alpha$ -pinene	4.8	9.9	9.1	2.2
4	1043	camphene	0.3	0.5	0.4	0.3
7	1093	$\beta$ -pinene	0.5	1.1	0.7	0.6
8	1111	sabinene	5.9	14.8	3.9	3.3
9	1145	3-carene	2.7	6.7	0.2	3.5
10	1166	$\alpha$ -phellandrene	0.4	1.0	0.4	0.2
11	1176	$\beta$ -myrcene	1.3	3.1	0.5	2.4
12	1202	<i>d</i> -limonene	1.9	4.6	1.5	3.4
13	1210	$\beta$ -phellandrene	4.0	2.1	12.3	15.4
15	1246	$\gamma$ -terpinene	0.7	0.4	tr <sup>c</sup>	1.9
16	1259	<i>trans</i> -ocimene	1.0	0.5	tr	0.2
17	1268	cymene	0.6	1.2	0.7	1.0
19	1276	$\alpha$ -terpinolene	0.2	0.3	0.2	0.5
			24.6	46.3	30.2	36.4
Oxygenated Monoterpenes						
26	1568	bornyl acetate	2.7	3.3	0.4	3.1
30	1618	chrysanthenyl acetate	0.2	0.6	1.8	0.4
32	1634	chrysanthenyl acetate	3.7	7.7	0.4	1.0
34	1646	4,4,6-trimethyl-2-cyclohexen-1-one	0.4	0.4	0.9	0.5
38	1687	phellandral	0.8	0.2	0.2	0.4
43	1723	<i>cis</i> -thujenol	0.5	0.2	0.9	0.3
51	1816	cuminyl alcohol	0.4	1.0	0.3	0.3
53	1853	<i>p</i> -cymen-8-ol	1.7	0.8	1.0	1.6
			10.4	14.2	5.9	7.6
Sesquiterpene Hydrocarbons						
21	1456	$\alpha$ -cubebene	0.2	0.1	0.5	0.7
22	1471	$\alpha$ -copaene	1.7	0.1	0.3	0.4
23	1530	MW = 204	tr	0.4	0.5	0.2
24	1544	$\beta$ -cubebene	tr	0.1	tr	0.6
25	1550	MW = 204	0.2	0.2	0.4	0.5
27	1579	$\delta$ -elemene	0.3	0.5	0.2	3.2
28	1586	$\beta$ -cedrene	0.2	0.3	tr	0.5
29	1611	$\beta$ -elemene	0.4	0.8	tr	0.3
31	1629	MW = 204	0.7	0.4	0.2	1.0
33	1642	$\alpha$ -caryophyllene	2.0	0.9	0.6	2.7
35	1658	$\gamma$ -caryophyllene	0.2	0.2	1.9	0.7
36	1666	$\beta$ -selinene	0.2	0.5	0.3	0.3
37	1674	( <i>Z</i> )- $\beta$ -farnesene	0.5	1.8	1.1	0.9
39	1691	germacrene D	4.0	2.2	0.2	1.3
40	1702	$\gamma$ -muurolene	0.8	0.2	0.2	0.8
41	1706	bicyclgermacrene	0.2	1.1	1.2	2.1
42	1711	$\beta$ -bisabolene	0.4	0.5	0.7	3.5
44	1735	$\gamma$ -cadinene	tr	0.5	0.2	3.2
45	1748	thujopsene	tr	0.4	tr	0.5
46	1757	MW = 204	0.3	0.2	tr	0.6
48	1787	(+)-cuparene	0.8	0.2	tr	0.5
52	1840	MW = 204	0.2	0.2	0.4	tr
58	2005	MW = 204	0.2	0.2	1.3	0.2
			13.5	12.0	10.2	24.7
Oxygenated Sesquiterpenes						
59	2023	$\alpha$ -copaen-11-ol	6.2	2.0	7.3	0.8
64	2082	$\alpha$ -copaen-8-ol	0.2	0.2	0.2	0.2
65	2101	elemol	1.0	0.3	1.9	2.2
66	2120	MW = 220	0.2	0.3	0.7	0.4
67	2132	spathulenol	0.4	1.4	2.6	1.0
68	2151	MW = 220	0.3	0.1	0.2	0.6
70	2200	rosifoliol	0.3	0.4	0.3	1.1
71	2216	dihydroeudesmol	1.0	1.0	2.3	2.3
73	2279	$\beta$ -eudesmol	0.3	0.3	0.3	1.1
74	2333	MW = 220	0.2	0.3	0.5	0.2
75	2360	cedrol	0.4	0.2	tr	0.4
			10.5	6.5	16.3	10.3
Coumarins						
83	3056	psoralen	0.3	0.8	1.3	0.8
86	3305	osthol	12.4	4.5	12.6	0.9
			12.7	5.3	13.9	1.7

Table 2 (Continued)

no.	$I_K$	compound	relative compositions (%)			
			var. Sativa		var. Archangelica	
			Puumala	Kittilä	Meltosjärvi	Kittilä
		Miscellaneous				
2	963	unknown	1.5	0.1	0.2	tr
5	1062	hexanal	0.5	0.9	0.4	0.6
6	1086	unknown	tr	tr	tr	0.2
14	1236	unknown				
18	1273	unknown	tr	0.3	tr	0.5
20	1388	5-undecen-3-yne	0.2	0.3	tr	0.1
47	1774	( <i>E,E</i> )-2,4-decadienal	0.5	0.3	0.2	0.2
49	1794	unknown	0.3	0.3	1.5	1.3
50	1812	( <i>E,E</i> )-2,4-dodecadienal	0.4	0.2	0.8	0.2
54	1860	unknown				
55	1906	tetradecanal	0.2	0.5	0.3	0.3
56	1925	unknown	0.5	tr	tr	0.5
57	1974	tridecanol	0.3	0.5	0.2	0.2
60	2032	tetradecanol	2.0	0.2	tr	0.2
61	2044	pentadecanal	0.2	0.2	tr	tr
62	2055	13-tridecanolide	2.7	2.1	2.2	2.0
63	2067	12-methyl-13-tridecanolide	1.3	0.2	0.3	0.2
69	2184	1-tetradecanyl acetate	0.3	0.5	0.2	2.0
72	2242	15-pentadecanolide	5.9	4.2	4.1	3.0
76	2387	hexadecanol	0.3	0.4	0.3	1.4
77	2407	MW = 250	0.6	0.8	0.4	1.1
78	2420	unknown	0.6	0.4	1.9	0.2
79	2453	heptadecanyl acetate	1.4	0.8	1.1	0.6
80	2460	unknown				
81	2487	octadecanol	0.8	0.8	0.7	2.0
82	2908	hexadecanoic acid	0.3	0.6	1.1	1.1
84	3067	octadecanoic acid	0.4	0.2	0.2	0.6
86	3216	( <i>Z,Z</i> )-9,12-octadecadienoic acid	6.1	1.1	6.7	0.3
			27.3	15.9	22.8	18.8
			99.0	100.2	99.3	99.5

<sup>a</sup> tr, in trace amount, less than 0.1%.

The morphology of the root structure differs between var. Archangelica and var. Sativa. The Archangelica strains have a strong, beetlike taproot with thin lateral roots connected to it (Forsén, 1979). The Sativa strains possess a short taproot with numerous lateral roots, resulting in a moplike structure (de Bruyn et al., 1954). Forsén reported statistically significant differences between the relative proportions of chemical components in taproot and lateral roots: the lateral roots contained on the average more  $\alpha$ -pinene, camphene, and cryptone and less 3-carene, myrcene, and tridecanolide than the taproot. The root material in this study had been dried and subsequently stored as whole roots. As an exception, the Puumala material had been chopped to homogeneous material to enhance water removal. During this procedure a large part of the small lateral roots was lost. The comminuted material was considered to resemble a commercially available raw material more closely than the whole roots. Representativeness of the whole root samples was enhanced by subsampling several roots at a time.

The relative proportion of oxygenated monoterpenes was higher in var. Sativa than in var. Archangelica. Main compounds were bornyl acetate and chrysanthenyl acetate. Two peaks, both presenting the features characteristic for chrysanthenyl acetate, were detected at Kovats indices of 1618 and 1634. There were only minor variations in their electron impact fragmentation patterns. On the basis of their mass spectra alone, the two compounds or a mixture of the compounds could not be differentiated. Nykänen et al. (1991) suggested the two chrysanthenyl acetate peaks represent different isomers.

The sesquiterpene hydrocarbons comprised 10–13.5% of the volatiles in Soxhlet extracts except in the var. Archangelica from Kittilä, for which the amount was as high as 24.7%. In steam-distilled oil the sesquiterpene moiety contributed only 8% of the total volatiles (Nykänen et al., 1991). Numerous sesquiterpene compounds were detected, generally in small quantities. Due to the lack of reference compounds only some could be identified on the basis of their MS spectra. The reliability of the identifications was further compromised by the possibility of several compounds eluting within the same peak.  $\alpha$ -Copaen-11-ol was the main sesquiterpene alcohol in the strain from Meltosjärvi and var. Sativa samples. The var. Archangelica strains contained larger amounts of elemol and dihydroeudesmol in comparison to var. Sativa.

Several aldehyde and alcohol derivatives of aliphatic short-chain hydrocarbons were detected, although their total amount contributed less than 5% of the extracts. The lactones of 13-hydroxytridecanoic acid and 15-hydroxypentadecanoic acid are typical substances found in angelica (Klouwen and ter Heide, 1965a). Their relative proportion in the samples was fairly stable, from 6 to 9%. The var. Sativa from Puumala exhibited the highest amount of these lactones. The musklike odor of angelica root oil is generally associated with 15-pentadecanolide. The lactone structure of the acid first isolated by Ciamician and Silber (1896) and the musk odor connected with it were detected by Kerschbaum (1927). Taskinen and Nykänen (1975) reported trace amounts of a compound tentatively identified as heptadecanolide in var. Sativa root oil, found also later by Nykänen et al. (1991). Another typical group of com-

pounds in angelica roots is the coumarins. In the recent study by Härmälä (1991) 15 different coumarins were identified in angelica subsp. *archangelica*. Psoralen and osthol were also found in the PE/DEE extracts.

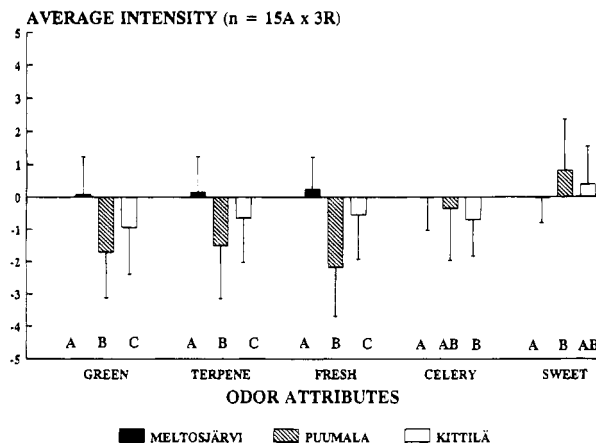
If the total area of the peaks included into the calculations represents the total amount of compounds in PE/DEE extracts, the amounts of volatile substances isolated from the different samples can be compared with one another. Using the internal standard, the amount of extracted compounds was estimated to present 0.6 and 1.1 g/kg of dry weight in var. *Sativa* cultivated in Puumala and in Kittilä, respectively. The var. *Archangelica* strains contained substantially smaller amounts of volatiles, e.g., 0.4 and 0.3 g/kg of dry root in Juutuajoki and Peltajoki strains, respectively. It can be concluded that the roots of var. *Sativa* of Hungarian origin and cultivated in Kittilä contained about 3 times more volatiles than did var. *Archangelica* originating from Juutuajoki and cultivated in Meltosjärvi.

**Odor of Angelica Roots.** On the basis of the significant variation detected in the relative amounts of volatile components in the angelica samples, differences in their odor profiles were anticipated. The assessors could discriminate the angelica strains in the triangle tests with great accuracy ( $p < 0.001$ ), thus ensuring the existence of sensorially detectable differences among the strains. Quantitative descriptive profiling was used in determining the characteristic features of the odor and quantitating the differences detected.

The essential oils of angelica root possess a strong aromatic odor. The aroma has been described as bitter and herby (Swaine, 1968) with terpenic character in oils from fresh roots or musklike odor in oils distilled from aged roots (Arctander, 1960). Generally the terpenic top note has been connected with  $\alpha$ -pinene and  $\alpha$ -phellandrene and the musklike bottom note with the high molecular weight oxygenated compounds, particularly lactones (Guenther, 1953). The assessors described the odor perceived from powdered angelica root samples with 42 terms. The samples from Meltosjärvi and Kittilä were predominantly characterized with terms such as green (grass, fresh leaves, pelargonium) and as turpentine-like (terpenic, pine needles) and as inducing a fresh and sharp or cooling effect in the nostrils. An earthy, root celery or beetlike character was given to the var. *Sativa* from Puumala. A sweet or honey-like tone was perceived from all samples.

The listed terms were divided into categories based on the similarity of the odor character evaluated by the panel in the round-table discussions. Attributes were selected to represent the odor character according to the predominancy of the term in the descriptions, and finally terms green, terpene-like, fresh, root celery, and sweet were agreed to by the panel. In this connection the absence of musk or any similar term should be noted.

The intensities of the attributes detected in Puumala and Kittilä samples (var. *Sativa*) were compared with the var. *Archangelica* from Meltosjärvi and are presented in Figure 2. The positive values represent intensities perceived as stronger in the samples than in the reference and intensities with negative values were assessed as weaker than in the reference sample. The intensities of an attribute designated with the same letter within an attribute did not differ significantly from one another by Tukey's test. The var. *Sativa* from Puumala in the south of Finland was evaluated as less



**Figure 2.** Means and standard deviations for odor attributes of angelica root. Var. *Sativa* cultivated in Puumala and Kittilä was compared with var. *Archangelica* from Meltosjärvi. Values show degree of deviation from reference: values less than 0 indicate weaker intensity compared with reference (freshly ground angelica root from Meltosjärvi), and values higher than 0 indicate stronger intensity than reference. Means designated with the same letter within an attribute did not differ at  $p < 0.05$  based on Tukey's test following analysis of variance.

**Table 3.** *F* Values from Analysis of Variance for the Attributes: Evaluation of Angelica Strains

source	df	green	terpene	fresh	celery	sweet
assessor	14	2.40 <sup>a</sup>	1.56	2.37 <sup>**</sup>	2.09 <sup>*</sup>	1.94 <sup>*</sup>
sample	2	26.66 <sup>***</sup>	21.92 <sup>***</sup>	45.47 <sup>***</sup>	3.79 <sup>*</sup>	6.88 <sup>**</sup>
replication	2	1.91	1.96	0.47	0.46	0.99
assessor × sample	28	2.05 <sup>*</sup>	2.51 <sup>***</sup>			1.64 <sup>*</sup>

<sup>a</sup> \*, \*\*, \*\*\*, significant at  $p < 0.05$ , 0.01, and 0.001, respectively.

green and less terpenic than the other samples. A fresh and cooling effect in the nose was perceived to be significantly weaker in this sample than in the others. Sweetness with celery/earth-like odor was characteristic for the aroma of the sample from Puumala. The var. *Sativa* cultivated in Kittilä in the north was assessed as distinctly more green, terpene-like, and fresh than the one from Puumala. It possessed the least root celery character and could not be distinguished from reference in sweetness. The reference sample was presented to the assessors also among the samples to be evaluated to control the performance of the panel.

The assessors were a significant source of variation revealed in analysis of variance (Table 3). Most notably, the differences in assessor perception affected the results of the fresh attribute. This could be attributed to difficulties in finding a suitable reference for the fresh character. The freshness was to be evaluated on the basis of the cooling effect in the nose rather than as the eucalyptus aroma inevitably perceived from the reference sample. The green attribute was detected by some assessors only with difficulty, because it was partly suppressed with the strong terpenic odor immediately emerging from the bottle when the lid was opened. The green effect also disappears rapidly from the headspace and could not be reassessed. The assessor × replication and sample × replication interactions were not significant in any of the attributes, but assessor × sample interaction did contribute to the variation detected in green, terpene, and sweet attributes. The interactions were listed only when significance ( $p < 0.05$ ) was detected. One reason for the interaction effect in the green and also in the terpene attributes was connected with the assessors who reported difficulties in detecting

Table 4. Volatile Composition of the Supercritical Carbon Dioxide Fractions

no.	<i>I</i> <sub>k</sub>	compound	relative composition (%)			no.	<i>I</i> <sub>k</sub>	compound	relative composition (%)			
			SFE1	SFE2	SFE3				SFE1	SFE2	SFE3	
Monoterpene Hydrocarbons												
1	947	α-thujene	tr <sup>a</sup>	0.1	0.2	11	1176	β-myrcene	6.7	4.0	0.7	
3	1010	α-pinene	20.9	13.3	3.7	12	1202	<i>d</i> -limonene	5.1	3.7	0.8	
4	1043	camphene	0.6	0.3	0.1	13	1210	β-phellandrene	7.2	6.3	1.2	
7	1093	β-pinene	1.5	1.1	0.3	15	1246	γ-terpinene	0.6	0.5	0.1	
8	1111	sabinene	24.6	15.8	3.8	16	1259	<i>trans</i> -ocimene	3.8	2.4	0.4	
9	1145	3-carene	9.1	6.5	1.7	17	1268	cymene	0.7	0.6	0.2	
10	1166	α-phellandrene	1.6	1.1	0.3	19	1276	α-terpinolene	0.6	0.5	0.1	
									82.9	55.1	13.8	
Oxygenated Monoterpenes												
26	1568	bornyl acetate	1.8	2.4	0.3	38	1687	phellandral				
30	1618	chrysanthenyl acetate	0.2	0.3	0.4	43	1723	<i>cis</i> -thujenol				
32	1634	chrysanthenyl acetate	1.6	2.8	1.4	51	1816	cuminyl alcohol	0.2	0.7	0.5	
34	1646	4,4,6-trimethyl-2-cyclohexen-1-one				53	1853	<i>p</i> -cymen-8-ol	tr	0.5	1.9	
									3.8	6.6	4.4	
Sesquiterpene Hydrocarbons												
21	1456	α-cubebene		0.4	0.4	37	1674	( <i>Z</i> )-β-farnesene	0.5	1.2	0.2	
22	1471	α-copaene	tr	2.2	0.3	39	1691	germacrene D	2.4	3.5	0.5	
23	1530	MW = 204		tr		40	1702	γ-muurolene	tr	tr	tr	
24	1544	β-cubebene		0.1	tr	41	1706	bicyclgermacrene	tr	tr	tr	
25	1550	MW = 204		tr		42	1711	β-bisabolene	0.3	0.8	0.2	
27	1579	δ-elemene	tr	0.3	tr	44	1735	γ-cadinene	tr	0.8	0.2	
28	1586	β-cedrene	0.2	0.2	tr	45	1748	thujopsene				
29	1611	β-elemene	3.1	4.0	0.5	46	1757	MW = 204				
31	1629	MW = 204		tr	tr	48	1787	(+)-cuparene	0.2	0.4	0.1	
33	1642	α-caryophyllene		tr	tr	52	1840	MW = 204				
35	1658	γ-caryophyllene		tr	tr	58	2005	MW = 204		0.4	0.1	
36	1666	β-selinene	tr	0.2	tr				6.6	14.3	2.4	
Oxygenated Sesquiterpenes												
59	2023	α-copaen-11-ol				70	2200	rosifoliol				
64	2082	α-copaen-8-ol		0.2	0.2	71	2216	dihydroeudesmol		0.4	0.5	
65	2101	elemol		0.6	0.4	73	2279	β-eudesmol		tr	0.1	
66	2120	MW = 220		0.1	tr	74	2333	MW = 220		0.3	0.5	
67	2132	spathulenol		tr	tr	75	2360	cedrol		0.2	0.2	
68	2151	MW = 220		0.1					0.0	1.8	2.0	
Coumarins												
83	3056	psoralen		0.8	2.7	86	3305	osthol		3.2	30.9	
									0.0	4.1	33.6	
Miscellaneous												
2	963	unknown				61	2044	pentadecanal				
5	1062	hexanal	1.5	0.3	0.3	62	2055	13-tridecanolide	0.6	2.4	0.8	
6	1086	unknown	0.1	1.0	0.3	63	2067	12-methyl-13-tridecanolide	0.2	1.1	0.6	
14	1236	unknown	1.4	0.9	0.2	69	2184	1-tetradecanyl acetate		0.2	0.2	
18	1273	unknown	0.4	0.3	tr	72	2242	15-pentadecanolide	0.9	4.9	2.4	
20	1388	5-undecen-3-yne	0.4	0.4	tr	76	2387	hexadecanol		0.2	0.3	
47	1774	( <i>E,E</i> )-2,4-decadienal				77	2407	MW = 250		0.4	0.4	
49	1794	unknown		0.2	0.5	13.2	78	2420	unknown		0.3	0.4
50	1812	( <i>E,E</i> )-2,4-dodecadienal				79	2453	heptadecanyl acetate	0.1	0.7	2.3	
54	1860	unknown		tr	0.3	80	2460	unknown		0.9	tr	
55	1906	tetradecanal				81	2487	octadecanol		0.4	1.4	
56	1925	unknown		0.5	0.1	82	2908	hexadecanoic acid		0.9	12.2	
57	1974	tridecanol		0.4	tr	84	3067	octadecanoic acid		1.5	4.6	
60	2032	tetradecanol		tr	tr	85	3216	( <i>Z,Z</i> )-9,12-octadecadienoic acid		1.1	3.5	
									4.3	17.8	42.9	
									98.3	100.3	99.5	

<sup>a</sup> tr, in trace amount, less than 0.1%.

the green attribute. Aroma components are highly volatile substances, and their relative proportions in the headspace of the ground root material varied as the same sample was evaluated several times during the session, which gave rise to some of the variation detected. The celery and sweet attributes were concluded to be typical rather than differentiating features in the samples. No significant difference between the var. *Sativa* cultivated in Puumala or Kittilä as to celery or sweet attributes was observed. The sample culti-

vated in Kittilä was perceived to be more green, more terpenic, and more fresh than the Puumala sample.

**Composition of Supercritical CO<sub>2</sub> Fractions.** In a study by Nykänen et al. (1991) supercritical carbon dioxide extracts were isolated from angelica to determine the suitability of various extraction conditions for the production of herb aroma additives. Significant differences were observed in the total yield and composition of the extract depending on the pressure used. High-quality aroma of extracts isolated at 40 °C and

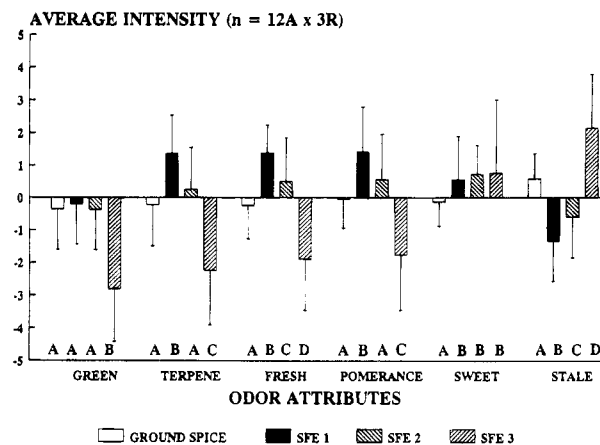
10.0–20.0 MPa was indicated, although no attempt to characterize these extracts with sensory methods was made. Instead of an exhaustive extraction of all material soluble in supercritical carbon dioxide under various pressures and temperatures, we aimed to isolate only the most essential components into one fraction and the remaining volatiles to another. The residue would be further extracted to remove all components that can be isolated at the selected conditions. Var. *Sativa* cultivated in Puumala was used as herb material, because we decided to determine whether herb material sensorially inferior to var. *Sativa* from Kittilä and var. *Archangelica* from Meltosjärvi could be utilized as raw material for a high-quality product.

The SFE1 fraction was a bright yellow liquid, which weighed 6.2 g and thus comprised 0.06% of the root material. The second fraction was also a liquid at room temperature and pale yellow in color. It comprised 0.43% of the dried root material. Exhaustive extraction yielded a waxy, semisolid fraction (SFE3), which was orange or dark yellow in color. SFE3 contained 1.65% of the raw material.

The relative proportions of volatiles in the fractions are presented in Table 4. Monoterpene hydrocarbons contributed 83 and 55% in SFE1 and SFE2 fractions, respectively, and only about 14% in the last fraction.  $\alpha$ -Pinene and sabinene were the most prominent compounds in all fractions. In previous studies (Hirvi et al., 1986; Kerrola and Kallio, 1993; Kerrola et al., 1994) the relative proportions of monoterpene hydrocarbons have been smaller in the total CO<sub>2</sub> extracts collected at moderate temperatures and pressures than in the respective PE/DEE Soxhlet extracts. By fractionation the monoterpenes could be concentrated and collected separately to produce an isolate. The contact time of the supercritical CO<sub>2</sub> and the ground angelica root material was short, and it could be argued that the SFE1 fraction represents only the headspace compounds.

Only a few oxygenated monoterpenes and sesquiterpenes were found in SFE1 fraction and in small amounts. All of these compounds were more abundant in the SFE2 fraction than in the SFE1 fraction. Bornyl and chrysanthemyl acetates were the significant oxygen-containing monoterpenes in these fractions. Only a trace amount of *p*-cymen-8-ol was detected in the first fraction, but in SFE3 it was the major oxygenated monoterpene. The SFE2 fraction contained mostly sesquiterpene compounds, all detected in the solvent extracts. Also, the amounts of lactones were highest in the second fraction. No coumarins could be detected in the SFE1 fraction, but their relative proportions increased as the extraction continued. As anticipated, the least volatile compounds dominate the third fraction. In addition to the coumarins, the medium-chain-length fatty acids were present in large amounts. The viscosity and waxy character are a result of the high proportion of these compounds.

**Odor of Supercritical CO<sub>2</sub> Fractions.** The aromas of the three carbon dioxide fractions were evaluated in separate sessions from the angelica root material. The panel consisted of almost the same assessors as in the above evaluations, and the evaluation procedure was the same. When the assessors were asked to describe the odor perceived, 33 terms were used. In addition to the terms, which predominated the angelica root samples, two new categories were found: pomegranate-like and stale. The root celery/beet-like odor was not evaluated



**Figure 3.** Means and standard deviations for odor attributes of the supercritical carbon dioxide fractions of angelica root isolated from var. *Sativa* cultivated in Puumala. Values show degree of deviation from reference: values less than 0 indicate weaker intensity compared with reference (freshly ground angelica root from Meltosjärvi), and values higher than 0 indicate stronger intensity than reference. Means designated with the same letter within an attribute did not differ at  $p < 0.05$  based on Tukey's test following analysis of variance.

as characteristic for the fractions and was omitted. No term associated with musk or musklike odor was suggested. The same reference as in the evaluations of the root samples was used.

The means of the intensities detected for the odor attributes in supercritical carbon dioxide fractions are presented in Figure 3. Significant differences ( $p < 0.05$ ) within an attribute were detected by Tukey's test following the analysis of variance between the means designated with different letters. From the bar lines representing standard deviations of the means in Figures 2 and 3, it was concluded that the quantitation of the differences in intensities of an attribute was more difficult among the SFE samples than among the root samples. This could be explained by the highly volatile character of the samples. The results of the blind control revealed more variation in reliability of assessment in evaluations of the SFE fractions than the root samples. Both the reference and the blind control contained root matrix, which retained odor compounds and released them in a more continuous manner. The more volatile substances were quite rapidly lost from the SFE samples, because the extracts were applied on a cellulose paper disk with limited retainability toward nonpolar aroma substances. It could be argued that the reappearing components exhibited competitive inhibition on perception of the other attributes in the reference and control samples in comparison to SFE samples.

The SFE1 fraction was perceived to be more terpenic, fresh, and pomegranate-like than the other fractions. The green and sweet attributes did not differentiate the SFE1 and SFE2 fractions from one another. The terpenic, fresh, and pomegranate-like characteristics were distinctly present but less pronounced in SFE2 than in the first fraction. Sweet and stale were the attributes with which the assessors characterized the SFE3 fraction. The absence of most typical features of angelica root aroma suggested poor flavoring properties. When the *F* values from analysis of variance in Table 5 were studied, the disagreement among the assessors became evident. The assessors and assessor  $\times$  sample interactions were significant sources of variation. Most of the variation was connected with the quantitation of the intensities of the various attributes in the SFE3 fraction.



**Table 5. F Values from Analysis of Variance for the Attributes: Evaluation of the Supercritical Fractions**

source	df	green	terpene	fresh	pomerance	sweet	stale
assessor	11	3.96*** <sup>a</sup>	1.59	2.31*	4.17***	5.16***	4.32***
sample	3	45.99***	67.62***	74.28***	67.66***	8.33***	92.62***
replication	2	2.03	1.74	1.65	0.73	0.51	3.36
assessor × sample	33	1.93**	2.72***	2.33**	3.89***	7.10***	3.37***
assessor × replication	22			2.19**			
sample × replication	6		2.90*				

<sup>a</sup> \*, \*\*, \*\*\*, significant at  $p < 0.05$ , 0.01, and 0.001, respectively.

This can be seen as larger standard deviations of the means for SFE3 than the other samples (Figure 3). The attributes pomerance-like and sweet were also confused by some assessors due to the floral and to some extent sweet note in orange peel used as reference for pomerance. Olfactory fatigue could also be one of the sources causing variation, although the assessors were advised to take sufficient pauses after each attribute.

The quality of these fractions was estimated in comparison to commercially available angelica aroma products. We asked the flavoring expert panel of a major producer of alcoholic beverages to preliminarily compare the aroma quality of these fractions with the angelica flavors they currently purchase. The panel consisted of four to five persons with extensive experience on aroma additives used in the alcoholic beverage industry. Evaluation of the supercritical fractions was carried out in the same fashion as for the commercial angelica aroma isolates, i.e., diluted into 10% ethanol solution. The flavoring experts expressed interest toward the SFE1 sample, which they characterized as high-quality, herbaceous angelica root aroma. The quality of the aroma was evaluated to be equal with the best commercially available products. The aroma of SFE2 was assessed by the expert panel as perfume-like and soapy, with some angelica odor characteristics with weak angelica root properties. The odor of the third fraction was described as uncharacteristic for angelica with resemblance to turnip and caraway in the odor.

## CONCLUSIONS

Distinct differences in the volatile composition of angelica root extracts of var. *Sativa* strain cultivated in the north and in the south of Finland were found. The composition of the volatiles in angelica var. *Sativa* and var. *Archangelica* exhibited different patterns as previously reported by Forsén (1979). An aroma fraction, which contained the most volatile components of the angelica root material, was isolated by supercritical fractionation. The odors of the var. *Sativa* strains differed from one another and from those of the var. *Archangelica* strain evaluated using deviation-from-reference descriptive analysis. The result indicative of benefit in collecting separate fractions of the total extract from angelica on the basis of the chemical data was verified by sensory analysis. The quality of the aroma fraction was preliminarily estimated by flavoring experts to resemble the commercially available angelica aroma isolates.

## ACKNOWLEDGMENT

We thank Anja Lapveteläinen, who guided and supported us through the sensory evaluations. We are grateful to the staff members and graduate students for their participation in the sensory evaluation panel. We appreciate the technical assistance of Kirsti Wiinamäki

in carrying out the mass spectrometric analyses. We thank Alko Ltd. for the angelica quality assessments.

## LITERATURE CITED

- Amerine, M. A.; Pangborn, R. M.; Roessler, E. B. *Principles of Sensory Evaluation of Food*; Academic Press: Orlando, FL, 1965.
- Arctander, S. *Perfume and Flavor Materials of Natural Origin*; Arctander: Elizabeth, NJ, 1960.
- Brogie, H. CO<sub>2</sub> in solvent extraction. *Chem. Ind.* **1982**, 385–389.
- Bundschuh, E.; Baumann, G.; Gierschner, K. *Dtsch. Lebensm. Rundsch.* **1988**, *84*, 205–210.
- Chalchat, J. C.; Garry, R. P. Pentane extracts of the roots of *Angelica archangelica* L. from France. *J. Essent. Oil Res.* **1993**, *5*, 447–449.
- Chamblee, T. S.; Clark, B. J.; Brewster, G. B.; Radford, T.; Iacobucci, G. A. Quantitative analysis of the volatile constituents of lemon peel oil. Effects of silica gel chromatography on the composition of its hydrocarbon and oxygenated fractions. *J. Agric. Food Chem.* **1991**, *39*, 162–169.
- Chialva, F.; Gabri, G.; Liddle, P. A. P.; Ulian, F. Direct headspace gas chromatographic analysis with glass capillary columns in quality control of aromatic herbs. *J. Chromatogr.* **1983**, *279*, 333–340.
- Ciamician, G.; Silber, P. *Ber. Dtsch. Chem. Ges.* **1896**, *28*, 1811–1816.
- Davies, N. W. Gas chromatographic retention indices of monoterpenes and sesquiterpenes on methyl silicone and Carbowax 20M phases. *J. Chromatogr.* **1990**, *503*, 1–24.
- de Bruyn, J. W.; Elzenga, G.; Keuls, M. Selection of living angelica roots for volatile oil content. *Euphytica* **1954**, *3*, 147–153.
- Forsén, K. Aroma constituents of *Angelica archangelica*. Variations in the composition of the essential root oil of strains of var. *norvegica* and var. *sativa*. *Rep. Kevo Subarctic Res. Stn.* **1979**, *15*, 1–7.
- Guenther, E. Oil of angelica. In *The Essential Oils*, 2nd ed.; van Nostrand: New York, 1953; Vol. IV, pp 553–563.
- Härmälä, P. Study on the isolation and chromatographic behavior of coumarins from angelica (*Angelica archangelica*) roots. Ph.D. Thesis, University of Helsinki, 1991.
- Héthelyi, I.; Tétényi, P.; Kálmán-Pál, Á.; Turiák, G.; Grezál, G. Mass-spectrometric examination of the oil components of *Angelica archangelica*. *Herba Hung.* **1985**, *24*, 141–163.
- Hirvi, T.; Salovaara, I.; Oksanen, H.; Honkanen, E. Volatile constituents of coriander fruit cultivated at different localities and isolated by different methods. In *Essential Oil Research*; Brunke, E.-J., Ed.; de Gruyter: Berlin, Germany, 1986; pp 111–116.
- Holm, Y.; Hiltunen, R.; Nykänen, I. Capillary gas chromatographic-mass spectrometric determinations of the flavour composition of dragonhead (*Dracocephalum moldavica* L.). *Flavour Fragrance J.* **1988**, *3*, 109–112.
- Huopalahti, R.; Linko, R. R. Composition and content of aroma compounds in dill (*Anethum graveolens* L.) at three different growth stages. *J. Agric. Food Chem.* **1983**, *31*, 331–333.
- Kallio, H.; Kerrola, K. Application of liquid carbon dioxide to the extraction of essential oil of coriander (*Coriandrum sativum* L.) fruits. *Z. Lebensm. Unters. Forsch.* **1992**, *195*, 545–549.

- Kallio, P.; Parviainen, R.; Yliaho, H. *Acta Lapponica Fennica* **1978**, *10*, 96–100.
- Kallio, H.; Huopalahti, R.; Nykänen, A.; Ojala, A. Extraction of angelica root with liquid carbon dioxide. In *Flavour Science and Technology*; Martens, M., Dalen, G. A., Russwurm, H., Eds.; Wiley: Brisbane, Australia, 1987; pp 111–114.
- Kerrola, K.; Kallio, H. Volatile compounds and odor characteristics of carbon dioxide extracts of coriander (*Coriandrum sativum* L.) fruits. *J. Agric. Food Chem.* **1993**, *41*, 785–790.
- Kerrola, K.; Galambosi, B.; Kallio, H. Volatile components and odor intensity of four phenotypes of hyssop (*Hyssopus officinalis* L.) *J. Agric. Food Chem.* **1994**, *42*, 776–781.
- Kerschbaum, M. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 902–909.
- Klouwen, M. H.; ter Heide, R. Quantitative determinations of pentadecanolide in the volatile oil of *Angelica archangelica* by gas chromatography. *Perfum. Essent. Oil Rec.* **1965a**, *56*, 156–158.
- Klouwen, M. H.; ter Heide, R. Studies on terpenes. II. The monoterpene hydrocarbon composition of the volatile oil of *Angelica archangelica* L. *Perfum. Essent. Oil Rec.* **1965b**, *56*, 224–228.
- McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction. Principles and Practice*; Butterworth: Stoneham, MA, 1986; pp 181–215.
- Nykänen, I.; Nykänen, L.; Alkio, M. Composition of angelica root oils obtained by supercritical CO<sub>2</sub> extraction and steam distillation. *J. Essent. Oil Res.* **1991**, *3*, 229–236.
- Ojala, A. Variation of *Angelica archangelica* subsp. *archangelica* (Apiaceae) in northern Fennoscandia. 4. Pattern of geographic variation. *Ann. Bot. Fennici* **1986**, *23*, 23–31.
- Ojala, A.; Huopalahti, R.; Nykänen, A.; Kallio, H. Variation of *Angelica archangelica* subsp. *archangelica* (Apiaceae) in northern Fennoscandia. 5. Inter-populational variation of essential oil composition and content. *Ann. Bot. Fennici* **1986**, *23*, 325–332.
- Pangborn, R. M. Sensory analysis as an analytical laboratory tool in food research. In *Modern Methods of Food Analysis*. Stewart, K. K., Whitaker, J. R., Eds.; AVI Publishing: Westport, CT, 1984; pp 265–291.
- Ramaswami, S. K.; Briscese, P.; Gargiullo, R. J.; von Geldern, T. Sesquiterpene hydrocarbons: from mass confusion to orderly line-up. In *Flavors and Fragrances: A World Perspective*; Proceedings of the 10th International Congress on Essential Oils, Fragrances and Flavors, Washington, DC, 1986; Lawrence, B. M., Mookherjee, B. D., Willis, B. J., Eds.; Elsevier: Amsterdam, 1988; pp 951–980.
- Rizvi, S. S. H.; Chao, R. R.; Liaw, Y. J. Concentration of omega-3 fatty acids from fish oil using supercritical carbon dioxide. In *Supercritical Fluid Extraction and Chromatography: Techniques and Applications*; Charpentier, B. A., Sevenants, M. R., Eds.; ACS Symposium Series 366; American Chemical Society: Washington, DC, 1988; pp 89–108.
- Scheffer, J. J. C.; Koedam, A.; Baerheim Svendsen, A. Occurrence and prevention of isomerization of some monoterpene hydrocarbons from essential oils during liquid–solid chromatography on silica gel. *Chromatographia* **1976**, *9*, 425–432.
- Scheffer, J. J. C.; Koedam, A.; Schüsler, M. Th. I. W.; Baerheim Svendsen, A. Improved gas chromatographic analysis of naturally occurring oxygen-containing monoterpenes following prefractionation by liquid–solid chromatography. *Chromatographia* **1977**, *10*, 669–677.
- Schultz, W. G.; Schultz, T. H.; Carlson, R. A.; Hudson, J. S. Pilot-plant extraction with liquid CO<sub>2</sub>. *Food Technol.* **1974**, *28*, 32–36, 88.
- Srinivas, S. R. *Atlas of Essential Oils*; Bronx, NY, 1986 (reviewed by Lawrence, B. M. *Progress in essential oils. Perfum. Flavor* **1989**, *14*, 41–42).
- Stahl, E.; Gerard, D. *Parfuem. Kosmet.* **1983**, *64*, 237–240.
- Stahl, E.; Gerard, D. Solubility behaviour and fractionation of essential oils in dense carbon dioxide. *Perfum. Flavor.* **1985**, *10*, 29–37.
- Stahl, E.; Quirin, K. W. Extraction of natural substances with dense gases. *Pharm. Res.* **1984**, 189–193.
- Stenhagen, E.; Abrahamsson, S. A.; McLafferty, F. W. *Registry of Mass Spectral Data*; Wiley: New York, 1974.
- Swaine, R. L. Natural and synthetic flavorings. In *CRC Handbook of Food Additives*; Furia, T. E., Ed.; The Chemical Rubber Co.: Cleveland, OH, 1968; pp 461–491.
- Taskinen, J.; Nykänen, L. Chemical composition of angelica root oil. *Acta Chem. Scand.* **1975**, *B29*, 757–764.
- Temelli, F.; Braddock, R. J.; Chen, C. S.; Nagy, S. Supercritical carbon dioxide extraction of terpenes from orange essential oil. In *Supercritical Fluid Extraction and Chromatography: Techniques and Applications*; Charpentier, B. A., Sevenants, M. R., Eds.; ACS Symposium Series 366; American Chemical Society: Washington, DC, 1988; pp 109–126.
- TNO. *Compilation of Mass Spectra of Volatile Compounds in Foods*; ten Noever de Brauw, M. C., Bouwman, J., Tas, A. C., La Vos, G. F., Eds.; Central Institute for Nutrition and Food Research–TNO: Zeist, The Netherlands, 1979.
- Um, K. W.; Bailey, M. E.; Clarke, A. D.; Chao, R. R. Concentration and identification of volatile compounds from heated beef fat using supercritical CO<sub>2</sub> extraction–gas liquid chromatography/mass spectrometry. *J. Agric. Food Chem.* **1992**, *40*, 1641–1646.
- Yliaho, H. *Luonnon Tutkija* **1981**, *85*, 144–146.
- Zosel, K. Separation with supercritical gases: Practical applications. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 702–709.

Received for review December 29, 1993. Revised manuscript received May 11, 1994. Accepted May 26, 1994.\*

\* Abstract published in *Advance ACS Abstracts*, July 15, 1994.