Extraction of Volatile Compounds of Angelica (*Angelica archangelica* L.) Root by Liquid Carbon Dioxide[†]

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The volatile components of angelica roots were isolated by liquid carbon dioxide extraction. Operation conditions of 4.7 MPa/25 °C, 5.4 MPa/25 °C, and 6.9 MPa/45 °C were used. The effect of adding various quantities of water and a mixture of ethanol and water (1:1 v/v) to the extraction system on the relative amounts of the components was investigated. The extracts were analyzed by gas chromatography/mass spectrometry. Water as cosolvent increased the total yield of extract. In general, the cosolvents increased the percentage of monoterpene hydrocarbons and, to a smaller extent, the abundance of the oxygenated monoterpenes. Evidently the sorption of the cosolvent into the plant material enhanced the diffusion of the components from the matrix. The sensory properties of the extracts isolated at 5.4 MPa with or without cosolvent were determined by deviation-from-reference descriptive analysis. The liquid CO_2 extract was considered green and terpenic in odor. Addition of water did not alter the profiling given. The liquid CO_2 extract modified with ethanol/water solution was characterized as terpenic and beetlike, with a more fresh or cooling effect than the other extracts.

Keywords: *Liquid carbon dioxide; extraction; volatiles; odor; sensory; angelica*

INTRODUCTION

One of the fields in which extraction with dense gases on both analytical and industrial scales has had most success is the isolation of aroma components from herbs and spices (Moyler, 1988). Extraction at high density, i.e., with a high solvent power of CO_2, decreases selectivity and increases extractability of undesired coextracted lipophilic substances, e.g., fatty acids and their esters, cuticular waxes, and pigments. The isolates obtained exhibit viscous consistency and poor solubility to aqueous solutions. At low solvent densities the selectivity of CO_2 is high and the most soluble components can be collected separately from other carbon dioxide soluble components (Schultz et al., 1974; Sims, 1982; Stahl and Gerard, 1985), and fragrance products of high quality can be obtained (Moyler and Heath, 1988; Moyler, 1990; Nykänen et al., 1990). Fractionation of the total aroma extract has been suggested (Brogle, 1982; Stahl and Gerard, 1983; Bundschuh et al., 1988; Temelli et al., 1988; Reverchon and Senatore, 1992, 1994; Kerrola et al., 1994). The nonpolar character limits the solvency of the more polar oxygen-containing aroma components. They remain bound to the polar sites of the matrix rather than enter the nonpolar liquid phase (Bartle et al., 1990; Pawliszyn, 1993). In the liquid state carbon dioxide possesses less favorable diffusion and viscosity properties than in the supercritical state.

Effects of various cosolvents or enhancers, e.g., methanol, ethanol, 2-propanol, $CHCl_3$, CH_2Cl_2, DMSO, acetone, water, and THF, have been tested to increase the yield of polar substances primarily in studies on analytical scale extraction (Stahl and Gerard, 1985; Vidal and Richard, 1987; Sugiyama et al., 1990; Gopalakrishnan and Narayanan, 1991; Raghuram Rao et al., 1992;

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

attribute	composition
green	comminuted spider plant leaves
terpene-like	5 µL of α-pinene (turpentine, 99%)
fresh	the cooling effect of one eucalyptus flavored cough drop in 5 mL of distilled water
celery	2.5 g of grated fresh root celery (celeriac)

Hawthorne et al., 1993). Knowledge obtained by using modifiers in supercritical fluid chromatography (SFC) indicates that the polar modifiers exhibit a dual function in improving the solvating power of carbon dioxide and sorption to the active polar binding sites on the packed column stationary phase (Schoenmakers and Uunk, 1989).

Increasing the polarity by adding water to the samples has been found to enhance extractability of more polar, oxygen-containing volatiles by supercritical carbon dioxide extraction (Stahl and Gerard, 1985; Gopalakrishnan et al., 1990) and liquid CO_2 extraction (Kallio and Kerrola, 1992) of aroma components. Only ca. 0.1 mol % of water dissolves into liquid CO_2 at ca. 6.6 MPa pressure and 21–26 °C temperature (Francis, 1954) and less than 0.4 mol % into supercritical CO_2 at 80 atm and 50 °C (Page et al., 1992). Blilie and Greibrokk (1985) suggest the main effect of the small molecular weight straight-chain alcohol modifiers up to hexanol is to compete with the analytes of the active sites on the surface of the stationary phase in SFC.

The aim of the study was to investigate the effects of water and a mixture of ethanol and water as cosolvents on extractability of volatile compounds by liquid CO_2 from angelica root. Extracts with high resemblance to the native aroma of angelica containing only minor amounts of less volatile coextracted substances were desired. Sensory evaluation was used to assess effects induced on the odor characters of the extracts.

MATERIALS AND METHODS

Materials. A strain of *Angelica archangelica* subsp. *archangelica* L. var. archangelica native to Finnish Lapland was

Table 2. Relative Compositions of Liquid Carbon Dioxide Extracts of Angelica Roots Isolated at 4.7 MPa

I_K	compound	LCO₂	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
						distilled water added								EtOH/water solution added					
								Monoterpene Hydrocarbons											
947	α-thujene	tr[a]		tr		tr		0.1	0.1	tr		0.1	0.1	0.1	0.1	tr		0.3	0.1
1010	α-pinene	7.3	1.1	11.6	1.2	6.9	0.8	7.3	0.5	7.3	1.9	9.6	0.5	8.1	0.9	12.4	2.2	11.6	0.5
1043	camphene	0.6	0.1	tr		0.5	0.2	0.2	0.1	tr		0.4	0.3	0.2	0.1	0.8	0.3	0.3	0.1
1093	β-pinene	0.6	0.1	0.8	0.1	0.7	0.1	0.5	0.1	0.5	0.1	0.7	0.1	0.5	0.2	0.8	0.1	0.8	0.2
1111	sabinene	5.0	4.2	4.9	0.4	11.4	1.2	0.5	0.1	1.8	1.9	5.7	0.6	1.5	0.2	6.3	1.0	5.4	1.7
1145	3-carene	1.3	0.1	6.5	1.3	1.3	0.1	6.0	0.4	4.3	1.4	5.4	1.5	3.9	0.8	6.7	2.4	2.8	1.5
1166	α-phellandrene	2.1	1.0	1.7	0.5	0.8	0.1	2.8	0.2	4.9	2.6	5.3	3.7	6.0	0.7	2.1	2.6	4.3	0.1
1176	β-myrcene	0.9	0.1	1.1	0.3	1.1	0.1	1.0	0.1	2.0	0.8	2.2	1.5	2.5	0.2	0.9	1.0	1.9	0.1
1202	d-limonene	2.2	0.2	2.1	0.2	2.4	0.2	3.7	0.2	2.7	0.6	4.7	0.4	4.2	0.4	4.8	0.3	3.5	0.1
1210	β-phellandrene	25.9	9.1	27.5	1.7	14.3	1.0	29.4	2.0	31.2	2.0	30.7	4.0	27.9	2.5	9.2	2.2	26.7	0.8
1246	γ-terpinene	0.6	0.2	0.2	0.1	0.3	0.1	0.3	0.1	0.4	0.1	0.2	0.1	0.2	0.1	0.5	0.3	0.7	0.1
1259	trans-ocimene	tr		tr		0.4	0.1	0.4	0.1	1.0	0.1	tr		0.1	0.1	tr		1.3	0.1
1268	cymene	2.2	0.6	1.8	0.2	2.8	0.2	2.5	0.2	3.5	1.4	3.0	1.2	3.2	0.3	3.9	1.7	1.5	0.1
1276	α-terpinolene	tr		0.3	0.1	tr		0.3	0.1	tr		0.4	0.1	0.3	0.1	0.3	0.1	0.3	0.1
		48.7		58.4		42.8		55.0		59.5		68.2		58.6		48.6		61.2	
								Oxygenated Monoterpenes											
1568	bornyl acetate	1.4	0.3	1.6	0.1	1.7	0.1	0.8	0.1	2.0	0.2	0.5	0.2	0.4	0.1	0.5	0.2	0.4	0.1
1618	chrysanthenyl acetate	tr						1.0	0.4	0.9	0.3	0.3	0.2	0.3	0.1	0.7	0.3	tr	
1634	chrysanthenyl acetate	3.1	0.8	3.6	0.2	3.7	0.4	3.0	0.3	4.7	0.5	2.3	0.6	3.5	0.5	3.9	0.4	2.8	0.2
1646	4,4,6-trimethyl-2-cyclohexen-1-one	0.5	0.1	0.4	0.1	1.4	0.2	0.2	0.1	0.8	0.2	0.3	0.1	0.4	0.1	0.4	0.1	0.4	0.1
1687	phellandral	0.5	0.3					0.2	0.1			0.1	0.1	0.2	0.1	0.2	0.1	tr	
1723	cis-thujenol	0.2	0.1	0.2	0.1	0.4	0.1	0.5	0.1	0.3	0.1	0.3	0.1	0.4	0.1	0.5	0.1	0.5	0.1
1816	cuminyl alcohol	0.3	0.1	1.0	0.2	0.3	0.1	1.5	0.4	0.3	0.1	1.0	0.2	1.5	0.2	0.9	0.2	0.6	0.1
1853	p-cymen-8-ol	0.2	0.1	tr		0.2	0.1	1.3	0.2	0.3	0.1	0.6	0.3	0.8	0.1	1.2	0.3	1.2	0.2
		6.2		6.7		7.6		8.6		9.3		5.4		7.5		8.2		5.9	
								Sesquiterpene Hydrocarbons											
1456	α-cubebene	0.4	0.1	0.2	0.1	0.4	0.1	tr		0.3		0.1	0.1	0.2	0.1	0.4	0.1	tr	
1471	α-copaene	1.0	0.1	0.5	0.1	0.9	0.1	0.6	0.1	0.7	0.1	0.5	0.2	0.9	0.1	0.7	0.2	tr	
1530	MW = 204	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.1	0.1			0.1	0.1				
1550	MW = 204	0.3	0.1	0.2	0.1	0.3	0.1	0.2	0.1	tr	0.1	0.4	0.3	0.3	0.1	0.7	0.1	0.6	0.1
1579	δ-elemene	1.0	0.4	0.3	0.1	0.5	0.1	tr		0.4	0.1	0.2	0.1	1.4	0.2	1.1	0.2	1.1	0.1
1586	β-cedrene	0.6	0.2	0.3	0.1	0.4	0.1	0.3	0.1	0.3	0.1	0.1	0.1	0.3	0.1	0.3	0.1	0.3	0.1
1611	β-elemene	0.3	0.1	0.9	0.2	0.7	0.1	0.3	0.1	0.1	0.1	0.3	0.1	0.4	0.1	0.3	0.1	0.3	0.1
1629	MW = 204	0.5	0.1					0.8	0.1			0.4	0.1	0.1	0.1	0.2	0.1	1.0	0.2
1642	α-caryophyllene			0.5	0.1	0.4	0.2	0.3	0.3			0.2	0.1	tr		0.3	0.1	0.3	0.1
1658	γ-caryophyllene	2.7	0.3	3.2	0.4	2.1	0.3	2.7	0.1	4.4	0.8	2.1	2.0	1.6	0.2	3.7	1.3	1.6	0.1
1666	β-selinene	1.9	0.2	0.2	0.1	2.8	0.2	0.3	0.1	0.2	0.1	0.2	0.1	0.3	0.1	tr		0.4	0.1
1674	(Z)-β-farnesene	1.3	1.2	0.8	0.1	0.5	0.1	0.2	0.1	1.2	0.2	1.6	0.5	2.5	0.3	1.6	0.9	2.4	0.2
1691	germacrene D	0.8	0.4	0.5	0.1	0.9	0.1	1.2	0.2	0.6	0.1	0.2	0.1	0.3	0.1	0.3	0.1	tr	
1702	γ-muurolene	tr						0.4	0.1			0.1	0.1	0.2	0.1	0.2	0.1	tr	
1706	bicyclogermacrene	1.0	0.3	1.0	0.1	0.5	0.1	0.5	0.1	1.0	0.1	0.5	0.1	0.7	0.1	0.9	0.6	1.4	0.1
1711	β-bisabolene	0.3	0.1	0.2	0.1	0.7	0.1	0.6	0.1	0.3	0.1	0.4	0.1	0.5	0.2	0.7	0.5	1.1	0.1
1735	γ-cadinene	0.2	0.1									0.3	0.2	0.3	0.1	0.3	0.1	tr	
1748	thujopsene			0.2	0.1	0.2	0.1			0.3	0.1	0.2	0.1	0.2	0.1				
1757	MW = 204	0.5	0.2	0.2	0.1	0.7	0.1			0.3	0.1	0.1	0.1	0.1	0.1	0.2	0.1	tr	
1787	(+)-cuparene	0.3	0.1									0.1	0.1	tr					
1840	MW = 204			0.4	0.1	0.3	0.1					0.1	0.1	0.1	0.1	0.3	0.1	tr	
2005	MW = 204	0.7	0.1	0.2	0.1	0.3	0.1	0.8	0.3	0.2	0.1	0.4	0.4	0.3	0.1	0.7	0.1	0.4	0.1
		14.0		10.1		12.7		9.7		10.4		8.9		10.9		12.8		10.9	
								Oxygenated Sesquiterpenes											
2023	α-copaen-11-ol	0.3	0.1	tr		tr						0.1	0.1	tr		0.2	0.1	tr	
2082	α-copaen-8-ol	0.4	0.1	0.3	0.1	0.7	0.1									0.2	0.1		
2101	elemol	1.0	0.2	0.7	0.1	1.3	0.1	0.5	0.1	0.7	0.3	1.0	0.5	1.4	0.3	0.6	0.2	0.7	0.1
2120	MW = 220	0.2	0.1	0.2	0.1	0.4	0.1	0.8	0.1	0.7	0.4	0.5	0.5	0.5	0.1	1.0	0.3	0.6	0.1
2132	spathulenol	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.4	0.3	0.3	0.1	0.9	0.2	1.1	0.1
2151	MW = 220	0.4	0.1	0.1	0.1	0.4	0.1	0.3	0.1	0.2	0.1	0.2	0.1	0.3	0.1	0.2	0.1		
2200	rosifoliol	0.9	0.1	0.5	0.1	0.9	0.1	0.9	0.1	0.6	0.2	0.8	0.3	1.0	0.2	1.0	0.2	0.6	0.1
2216	dihydroeudesmol	1.2	0.7	0.3	0.1	0.8	0.1	1.6	0.2	0.3	0.1	0.4	0.2	0.6	0.2	0.9	0.4	1.3	0.2
2279	β-eudesmol	1.5	0.4	0.4	0.1	1.5	0.4	0.5	0.2	0.6	0.3	0.5	0.3	0.4	0.1	0.6	0.2	0.4	0.1
2333	MW = 220	0.5	0.1	tr		0.7	0.3	0.3	0.1	0.2	0.1	0.2	0.2	0.2	0.1	0.3	0.2	tr	
2360	cedrol	0.5	0.3	0.1	0.1	0.8	0.2	0.6	0.2	0.3	0.2	0.4	0.2	0.4	0.2	0.5	0.2	0.4	0.1
		7.2		2.7		7.6		5.6		3.8		4.7		5.2		6.3		5.1	

Table 2 (Continued)

relative proportion, %

| I_K | compound | LCO$_2$ | | distilled water added | | | | | | | | EtOH/water solution added | | | | | | | |
			SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
							Miscellaneous												
900	unknown	0.1	0.1					0.2	0.1	tr		0.1	0.1	0.1	0.1	0.3	0.1	0.3	0.1
1062	hexanal	0.4	0.1	0.7	0.2	0.4	0.1	0.4	0.1	0.5	0.1	0.7	0.1	0.6	0.1	0.6	0.1	0.7	0.1
1086	unknown	tr						0.2	0.1	tr									
1169								0.3	0.1	tr		0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1
1183												0.1	0.1	tr		0.2	0.1	tr	
1273	unknown			0.4	0.1	tr		0.2	0.1	0.4	0.1	0.2	0.1	0.2	0.1	tr		tr	
1388	5-undecen-3-yne	0.2	0.1	tr		0.2	0.1	0.3	0.1	0.1	0.1	0.5	0.1	0.5	0.1	tr		0.4	0.1
1463		0.2	0.1	0.1	0.1	0.2	0.1	0.2	0.1	tr		0.1	0.1	0.2	0.1	0.9	0.1	tr	
1489		2.0	0.2	4.4	0.2	1.8	0.2	0.8	0.1	3.0	1.8	2.1	0.8	1.0	0.1	2.5	0.3	2.1	0.1
1649		1.4	0.2	0.8	0.1	2.8	0.2	0.2	0.1	0.8	0.2	0.4	0.1	0.4	0.1	0.4	0.1	0.6	0.1
1669		0.4	0.1									0.1	0.1	0.2	0.1	tr		tr	
1774	(E,E)-2,4-decadienal	0.7	0.2	0.2	0.1	0.5	0.2	0.3	0.1	0.2	0.1	0.4	0.2	0.4	0.1	0.5	0.1	0.3	0.1
1781		tr		0.4	0.1	0.5	0.1	tr		0.2	0.1					0.3	0.2	tr	
1794	unknown	0.9	0.1	0.4	0.1	0.2	0.1	0.6	0.3	1.1	0.2	0.8	0.5	0.6	0.1	0.8	0.1	0.7	0.1
1812	(E,E)-2,4-dodecadienal	0.2	0.1	0.1	0.1	0.9	0.1	0.3	0.1	tr									
1906	tetradecanal	0.3	0.1	0.4	0.1	0.3	0.1	0.4	0.1	0.2	0.1	0.4	0.3	0.3	0.1	0.8	0.2	0.3	0.1
1913		0.4	0.2	0.4	0.1	0.6	0.1	0.6	0.1	0.3	0.1	0.3	0.1	0.4	0.1	0.7	0.1	1.2	0.2
1925	unknown	0.6	0.2	0.2	0.1	tr		tr		0.6	0.1	0.2	0.1	0.4	0.1	0.2	0.1	tr	
1974	tridecanol			tr		0.7	0.1					tr		0.1	0.1	0.2	0.1		
2032	tetradecanol	2.6	0.5	2.6	0.3	2.8	0.2	2.1	0.2	1.7	1.2	1.3	0.6	1.3	0.3	1.8	0.2	1.5	0.1
2044	pentadecanal	0.8	0.9	0.8	0.1	2.0	0.2	0.7	0.1	1.3	0.4	0.8	0.1	1.3	0.2	0.6	0.3	0.3	0.1
2055	13-tridecanolide	0.4	0.1	0.5	0.1	tr		0.3	0.1	0.5	0.2	0.2	0.1	0.1	0.1	0.3	0.1	0.3	0.1
2067	12-methyl-13-tridecanolide	0.8	0.1	0.3	0.1	0.7	0.1					tr		0.1	0.1	0.2	0.1	tr	
2116		0.4	0.2	0.9	0.1	0.3	0.1	0.2	0.1	0.8	0.3	0.2	0.1	0.1	0.1	0.3	0.1	tr	
2174		0.3	0.1									0.2	0.1	0.3	0.1	0.2	0.1		
2184	1-tetradecanyl acetate	0.4	0.1	tr		0.3	0.1	0.2	0.1	0.5	0.3	0.4	0.1	0.3	0.2	0.4	0.2		
2220		1.2	0.7	0.4	0.1	tr		0.4	0.1	0.6	0.3	0.2	0.1	0.2	0.1	0.3	0.1	tr	
2242	15-pentadecanolide	6.6	0.9	4.9	0.8	6.8	0.9	5.2	1.1	3.5	1.9	2.8	1.8	3.4	1.0	5.1	0.8	4.2	0.3
2253		0.3	0.1							0.4	0.1	0.3	0.2	0.1	0.4	0.1	0.3	0.1	
2268		0.4	0.1	0.2	0.1	0.5	0.1	0.7	0.2	0.4	0.2	0.4	0.3	0.5	0.2	0.6	0.3	tr	
2307		0.4	0.1	0.2	0.1	0.5	0.1	0.4	0.2	0.2	0.2	0.3	0.2	0.3	0.1	0.5	0.1	tr	tr
2347												0.2	0.1	tr		0.3	0.1	tr	
2387	hexadecanol	0.6	0.2	0.1	0.1	0.4	0.1	0.3	0.1	tr		0.4	0.1	0.4	0.1	0.4	0.1	0.3	0.1
2407	MW = 250	0.4	0.1	0.4	0.1	0.3	0.1	0.7	0.2	0.3	0.2	0.7	0.2	0.7	0.2	0.7	0.1	0.6	0.1
2420	unknown	1.9	0.3	1.7	0.2	2.8	0.3	2.7	0.5	1.4	0.6	0.5	1.6	1.0	0.3	2.8	1.1	1.6	0.2
2453	heptadecanyl acetate	1.2	0.2	0.9	0.2	1.2	0.3	1.0	0.4	0.6	0.3	0.8	0.4	0.7	0.2	1.0	0.2	0.8	0.1
2460	unknown	tr		0.2	0.1	0.2	0.1	0.2	0.1	0.1	0.1	tr		0.1	0.1	0.1		tr	
2487	octadecanol	0.7	0.3	0.5	0.2	0.8	0.4	0.4	0.1	0.5	0.3	0.6	0.1	0.8	0.2	0.4	0.1	0.4	0.1
		26.9		22.9		29.0		21.0		19.9		16.8		17.7		25.1		17.2	
		103.0		100.8		99.7		99.8		102.9		104.0		99.8		101.0		100.3	

a tr, in trace amount, less than 0.1%.

collected from Juutuajoki in 1987. The seeds were sown to an open field of sandy mold soil in Meltosjärvi (66° 31' N, 24° 40' E) and cultivated from May 1988 to mid September 1990. Compost (3 kg/m^2) was applied on the field each year. Weed control was carried out by hand, and no pesticides were used. The flowering shoots of the plants were bent downward to prevent flowering, which decreases the weight of the roots and induces rotting of the root. The roots of the third-year plants were harvested by hand, and most of the soil was washed off. Root material was dried at about 20 °C for 1 week and stored in paper bags at ambient temperature protected from light until analyzed.

Carbon Dioxide Extraction. A J&W high-pressure Soxhlet extraction apparatus (Jennings, 1979) had been modified by constructing two windows opposite one another (Kallio and Kerrola, 1992). The extraction process could then be observed and overloading of the system with liquid carbon dioxide prevented. Angelica root material was ground to 0.2 mm diameter particles, and 4.00 g was weighed to a thimble (Schleicher & Schuell, 19 × 90 mm, Dassel, Germany). The thimble was covered with a cotton–wool plug to keep the material from migrating to the Soxhlet during the loading of the apparatus (850 cm^3). Distilled water or ethanol/water solution (1:1 v/v) was used as a polar cosolvent. An aliquot of the modifier (0, 1.0, 2.0, 3.0 or 4.0 g) was applied on the cotton–wool plug. The thimble was subsequently placed into the Soxhlet, which was transferred into the extractor. The lid of the high-pressure extractor was carefully closed, and liquid CO_2 (AGA, Espoo, Finland) was introduced via high-pressure tubing. The extraction was carried out for 3 h under selected pressure and temperature conditions (4.7 MPa/25 °C, 5.4 MPa/25 °C, and 6.9 MPa/45 °C). The assembly was immersed up to 5 cm into a water bath at predetermined temperature. At the end of the operation, the apparatus was chilled to 0 °C and carbon dioxide very slowly discharged to avoid the loss of the most volatile compounds. For gas chromatographic analysis the extract was dissolved to 2 mL of the mixture of n-pentane and diethyl ether (1:2 v/v). The ether solution was transferred to a Teflon-sealed screw-cap vial, dried with sodium sulfate, and stored at −20 °C. A 5-fold dilution of the solution was made prior to gas gromatographic and mass spectrometric analyses. Triplicate extractions at each pressure and for all aliquots of the modifiers were made. The mean values were calculated on the basis of three replicate gas chromatographic determinations of the extracts obtained.

Gas Chromatographic and Gas Chromatography/Mass Spectrometric Analyses. The gas chromatographic analyses were carried out on a Varian 3300 capillary 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 NB-351 liquid phase [nitroterephthalate

Table 3.   Relative Compositions of Liquid Carbon Dioxide Extracts of Angelica Roots Isolated at 5.4 MPa

I_K	compound	LCO₂	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
				distilled water added								EtOH/water solution added							
								relative proportion, %											

Monoterpene Hydrocarbons

I_K	compound	LCO₂	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
947	α-thujene	tr[a]		tr		0.3	0.1	0.1	0.1	tr		tr		0.1	0.1	0.1	0.1	0.2	0.1
1010	α-pinene	12.2	3.1	8.5	0.6	2.4	0.5	7.6	0.8	9.0	1.0	8.3	0.7	8.9	0.5	12.1	0.8	11.2	0.6
1043	camphene	tr		tr		tr		0.2	0.1	tr		0.2	0.1	0.2	0.1	0.2	0.1	0.3	0.1
1093	β-pinene	0.9	0.3	1.0	0.1	0.2	0.1	0.5	0.1	0.6	0.1	0.6	0.2	0.6	0.1	0.9	0.1	1.0	0.1
1111	sabinene	7.4	4.3	18.3	2.3	0.8	0.2	0.8	0.3	3.2	3.9	3.8	2.3	0.6	0.1	8.8	0.5	12.0	1.3
1145	3-carene	1.7	0.3	3.3	0.3	0.9	0.2	5.7	0.6	3.8	0.4	4.2	0.4	4.7	0.2	2.8	0.2	4.0	0.9
1166	α-phellandrene	1.5	1.3	2.4	0.2	0.9	0.2	2.8	0.3	5.7	1.3	7.0	0.2	6.9	0.3	1.6	0.1	1.4	0.1
1176	β-myrcene	1.2	0.2	3.6	0.3	0.4	0.1	1.5	0.4	2.6	0.4	2.8	0.1	2.6	0.1	2.5	0.2	3.4	0.7
1202	d-limonene	2.1	0.2	2.0	0.2	1.1	0.2	4.0	0.4	3.0	0.2	4.4	0.4	4.8	0.2	3.3	0.2	3.8	0.5
1210	β-phellandrene	24.4	7.8	25.0	2.2	9.3	1.6	22.1	4.1	29.4	1.0	31.0	0.8	30.0	1.2	24.4	1.3	27.7	1.1
1246	γ-terpinene	0.5	0.2	0.3	0.1	tr		0.3	0.1	0.4	0.1	0.3	0.2	0.5	0.1	0.7	0.1	0.4	0.2
1259	trans-ocimene	tr		0.3	0.1	tr		0.5	0.1	0.8	0.2	0.6	0.5	1.0	0.1	1.6	0.1	1.0	0.7
1268	cymene	1.5	0.7	1.3	0.1	1.7	0.3	3.5	0.7	3.5	1.1	2.7	0.9	4.0	0.2	1.4	0.1	1.2	0.1
1276	α-terpinolene	tr		tr		tr		0.2	0.1	0.4	0.1	0.4	0.1	0.3	0.1	0.2	0.1	0.3	0.1
		53.4		65.9		18.0		49.8		62.4		66.1		65.3		60.7		67.9	

Oxygenated Monoterpenes

I_K	compound	LCO₂	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
1568	bornyl acetate	1.6	0.5	1.8	0.1	2.1	0.1	0.3	0.1	0.4	0.3	0.4	0.1	0.3	0.1	0.5	0.1	0.3	0.1
1618	chrysanthenyl acetate	tr						0.2	0.1	0.8	0.1	0.1	0.1	0.2	0.1	0.5	0.1	0.7	0.2
1634	chrysanthenyl acetate	2.4	0.4	2.5	0.2	5.1	0.2	4.7	1.3	3.6	0.9	2.8	1.2	4.6	0.6	2.4	0.5	2.9	0.5
1646	4,4,6-trimethyl-2-cyclohexen-1-one	0.4	0.1	0.5	0.1	0.3	0.1	0.4	0.1	0.6	0.1	0.3	0.1	0.5	0.1	0.2	0.1	0.3	0.1
1687	phellandral	0.9	0.5					0.2	0.1			0.1	0.1	0.1	0.1	tr		tr	
1723	cis-thujenol	0.4	0.2	0.3	0.1	0.4	0.1	0.6	0.2	0.3	0.1	0.4	0.1	0.4	0.1	0.5	0.1	0.4	0.1
1816	cuminyl alcohol	0.3	0.1	0.2	0.1	0.5	0.1	1.6	0.3	0.5	0.1	0.1	0.1	1.1	0.1	0.6	0.1	0.6	0.1
1853	p-cymen-8-ol	tr		tr		0.4	0.1	1.0	0.4	0.3	0.1	0.4	0.1	0.5	0.2	1.5	0.3	0.7	0.3
		6.1		5.2		8.8		9.0		6.6		4.7		7.7		6.1		5.9	

Sesquiterpene Hydrocarbons

I_K	compound	LCO₂	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
1456	α-cubebene	tr		0.3	0.1							0.1	0.1	0.2	0.1	0.2	0.1	tr	
1471	α-copaene	0.3	0.1	0.6	0.1	0.4	0.1	0.5	0.1	0.4	0.3	0.4	0.1	0.2	0.1	0.6	0.1	0.3	0.1
1530	MW = 204											0.2	0.1	0.2	0.1	tr		tr	
1550	MW = 204	0.3	0.1	0.2	0.1	0.4	0.1	0.4	0.1	0.1	0.1	0.3	0.1	0.2	0.1	0.3	0.1	0.2	0.1
1579	δ-elemene	1.2	0.2	0.4	0.1	0.4	0.1	1.3	0.4			1.6	0.3	1.2	0.1	1.6	0.1	1.5	0.1
1586	β-cedrene	tr		0.2	0.1	0.6	0.5	0.3	0.1	0.3	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.2	0.1
1611	β-elemene	tr		0.4	0.2	1.9	0.1	0.4	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.4	0.1	0.4	0.1
1629	MW = 204	tr		tr		tr		0.8	0.1	0.1	0.1	0.5	0.1	0.4	0.1	tr		tr	
1642	α-caryophyllene	0.6	0.1	0.4	0.1	0.4	0.1	0.3	0.1	tr		tr		tr		0.2	0.1	0.2	0.1
1658	γ-caryophyllene	2.2	0.4	3.4	0.6	4.4	0.2	2.6	0.3	3.8	0.7	1.1	0.3	1.5	0.3	1.6	0.2	1.2	0.2
1666	β-selinene	2.4	0.8	0.5	0.1	4.6	0.2	0.3	0.1	0.2	0.1	0.3	0.1	0.2	0.1	0.2	0.1	tr	
1674	(Z)-β-farnesene	0.3	0.1	1.4	0.2	0.3	0.1	2.7	1.2	1.0	0.3	2.1	0.2	2.2	0.3	1.6	0.2	1.7	0.4
1691	germacrene D	1.1	0.5	0.4	0.1	0.7	0.2	0.3	0.1	0.7	0.2	0.2	0.1	0.1	0.1	0.2	0.1	0.6	0.2
1702	γ-muurolene	tr						0.2	0.1	tr		0.1	0.1	0.2	0.1	0.2	0.1	tr	
1706	bicyclogermacrene	0.7	0.2	0.3	0.1	1.1	0.1	0.4	0.1	0.7	0.2	0.5	0.1	0.4	0.1	0.4	0.1	0.5	0.1
1711	β-bisabolene	tr		0.2	0.1	1.2	0.1	0.7	0.1	0.3	0.1	0.6	0.1	0.6	0.1	0.4	0.1	0.3	0.1
1735	γ-cadinene			0.1	0.1							0.1	0.1	0.2	0.1				
1748	thujopsene			0.1	0.1	0.4	0.1	tr		tr		0.2	0.1	0.2	0.1	0.2	0.1	tr	
1757	MW = 204			0.1	0.1	1.3	0.1	tr		tr		0.1	0.1	0.1	0.1	0.1	0.1	tr	
1787	(+)-cuparene	tr		0.3	0.1	0.8	0.1												
1840	MW = 204	tr		0.2	0.1	0.5	0.1							0.1	0.1	0.2	0.1	tr	
2005	MW = 204	0.5	0.2	0.1	0.1	0.4	0.1	0.4	0.1	0.2	0.1			0.3	0.1	0.4	0.1	0.4	0.1
		9.6		9.8		19.8		11.6		8.1		8.8		8.9		8.9		7.5	

Oxygenated Sesquiterpenes

I_K	compound	LCO₂	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
2023	α-copaen-11-ol	0.3	0.1									0.1	0.1						
2082	α-copaen-8-ol	0.8	0.4	0.6	0.1	2.2	0.2					0.1	0.1	0.1	0.1	0.2	0.1		
2101	elemol	2.2	1.0	0.4	0.1	1.5	0.1	0.5	0.2	1.0	0.5	1.1	0.5	0.5	0.1	0.5	0.1	0.5	0.1
2120	MW = 220	tr		0.3	0.1	0.3	0.1	0.8	0.1	0.8	0.2	0.3	0.1	0.4	0.1	0.5	0.1	0.4	0.1
2132	spathulenol	tr		0.2	0.1	0.3	0.1	0.5	0.2	tr		0.2	0.1	0.4	0.1	0.3	0.1	0.2	0.1
2151	MW = 220	tr		0.2	0.1	1.3	0.1	0.2	0.1	tr		0.1	0.1	0.1	0.1	tr		0.2	0.1
2200	rosifoliol	0.9	0.4	0.5	0.2	1.9	0.2	1.2	0.3	0.9	0.3	0.8	0.1	1.0	0.2	0.6	0.1	0.4	0.2
2216	dihydroeudesmol	0.6	0.4	0.2	0.1	2.6	0.2	1.3	0.3	0.3	0.1	0.4	0.1	0.4	0.1	0.6	0.1	0.5	0.1
2279	β-eudesmol	1.5	0.5	0.6	0.2	3.1	0.4	0.9	0.2	1.1	0.2	0.5	0.1	0.5	0.1	0.8	0.1	0.4	0.3
2333	MW = 220	0.4	0.1	0.1	0.1	1.0	0.4	0.3	0.1	0.3	0.1	0.2	0.1	0.2	0.1	0.2	0.1	tr	
2360	cedrol	0.5	0.1	0.2	0.1	1.1	0.2	0.8	0.2	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	
		7.2		3.4		15.2		6.6		4.6		4.2		3.8		4.0		2.9	

Extraction of Angelica Root Volatile Compounds

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Table 3 (Continued)

				distilled water added								EtOH/water solution added							
		LCO$_2$																	
I_K	compound		SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
							Miscellaneous												
900	unknown							0.2	0.1	tr		0.1	0.1	0.1	0.1	0.2	0.1	0.3	0.2
1062	hexanal	0.7	0.2	0.7	0.1	0.5	0.1	0.5	0.1	0.7	0.1	0.7	0.1	0.6	0.1	0.8	0.1	0.8	0.1
1086	unknown											0.1	0.1	tr	0.2			0.1	0.2	0.1
1169								0.3	0.1	tr		0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1
1273	unknown			0.4	0.1	tr		0.2	0.1	tr		0.2	0.1	0.2	0.1	0.1	0.1	0.2	0.1
1388	5-undecen-3-yne	tr		0.2	0.1	tr		0.3	0.1	0.2	0.1	0.5	0.1	0.3	0.1	0.3	0.1	0.4	0.1
1463		tr		0.2	0.1	tr		0.2	0.1	tr		0.2	0.1	tr		0.3	0.1	0.6	0.2
1489		1.7	0.3	1.5	0.1	2.0	0.1	1.6	0.5	1.4	0.1	1.6	0.1	1.4	0.1	2.4	0.1	1.6	0.6
1649		0.9	0.2	0.2	0.1	tr		0.3	0.1	0.2	0.1	0.4	0.1	0.3	0.1	0.8	0.1	0.5	0.1
1669				0.1	0.1	tr		0.2	0.1	tr		0.1	0.1	0.2	0.1	tr		tr	
1774	(E,E)-2,4-decadienal	0.5	0.2	0.2	0.1	0.7	0.1	0.4	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.2
1781		tr		0.1	0.1	0.7	0.2	tr		0.3	0.1								
1794	unknown	0.5	0.1	0.4	0.1	1.8	0.1	0.6	0.1	0.9	0.3	0.4	0.1	0.4		0.1	0.6	0.1	0.6	0.1
1812	(E,E)-2,4-dodecadienal	0.4	0.1	0.3	0.1	1.1	0.1	0.3	0.1	tr						0.1	0.1	0.2	0.1
1906	tetradecanal	0.3	0.1	0.2	0.1	0.6	0.1	0.4	0.1	0.2	0.1	0.2	0.1	0.3	0.1	0.2	0.1	0.2	0.1
1913		0.2	0.1	0.5	0.1	0.6	0.1	0.5	0.1	0.2	0.1	0.2	0.1	0.3	0.1	0.7	0.1	0.6	0.1
1925	unknown	0.5	0.2	0.1	0.1	0.4	0.1	0.2	0.1	0.5	0.2	0.2	0.1	0.2	0.1	0.2	0.1	tr	
1974	tridecanol	0.4	0.1	0.1	0.1	0.5	0.1					0.1	0.1	0.1	0.1				
2032	tetradecanol	2.4	0.3	1.5	0.3	3.1	0.3	2.0	0.3	1.5	0.4	1.0	0.1	1.0	0.1	1.3	0.1	1.2	0.1
2044	pentadecanal	0.6	0.3	1.4	0.3	1.9	0.2	0.7	0.1	1.3	0.4	0.7	0.2	0.5	0.1	0.7	0.1	0.8	0.2
2055	13-tridecanolide	0.4	0.1	0.6	0.1	0.7	0.1	0.2	0.1	0.5	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.1
2067	12-methyl-13-tridecanolide	0.9	0.1									0.1	0.1	0.1	0.1	0.2	0.1	tr	
2116		0.6	0.1	0.6	0.1	0.6	0.1	tr		0.5	0.1	0.2	0.1	0.2	0.1	tr		tr	
2174		0.3	0.1					0.3	0.1	tr		0.2	0.1	tr					
2184	1-tetradecanayl acetate	0.4	0.1	0.1	0.1	0.3	0.1	0.2	0.1	0.5	0.2	0.4	0.1	0.3	0.1	0.3	0.1	0.4	0.1
2220		0.9	0.4	0.5	0.1	1.9	0.2	1.2	0.3	0.9	0.3	0.8	0.1	1.0	0.2	0.6	0.1	0.4	0.2
2242	15-pentadecanolide	6.2	1.3	3.2	0.5	9.8	0.8	5.4	0.5	3.3	0.7	3.1	0.2	2.8	1.1	5.0	0.4	4.2	0.9
2253												0.1	0.1	0.2	0.1	0.3	0.1	0.2	0.1
2268		0.4	0.1	0.4	0.1	1.6	0.1	1.1	0.2	0.5	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.4	0.1
2307		0.6	0.3	0.3	0.1	0.6	0.1	0.4	0.1	tr		0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1
2347												0.1	0.1	0.1	0.1	0.2	0.1	tr	
2387	hexadecanol	0.6	0.2	0.2	0.1	1.1	0.1	0.5	0.1	0.4	0.1	0.4	0.1	0.3	0.1	0.4	0.1	0.8	0.4
2407	MW = 250	0.3	0.1	0.2	0.1	0.8	0.1	0.8	0.2	0.4	0.1	0.6	0.1	0.6	0.2	0.4	0.1	0.5	0.1
2420	unknown	2.9	0.7	0.5	0.1	3.0	0.4	2.5	0.4	1.2	0.3	0.6	0.2	0.9	0.2	1.5	0.2	1.1	0.4
2453	heptadecanyl acetate	1.1	0.3	0.4	0.1	2.1	0.2	1.0	0.3	0.5	0.1	0.6	0.2	0.6	0.2	1.0	0.1	0.8	0.2
2460	unknown	0.3	0.1	0.1	0.1	0.5	0.1	0.2	0.1	0.1	0.1								
2487	octadecanol	0.6	0.2	0.6	0.2	2.3	0.2	0.6	0.2	0.8	0.3	0.7	0.1	0.6	0.2	0.9	0.1	0.5	0.2
		25.9		15.7		39.1		23.2		17.5		15.6		14.7		21.0		18.6	
		102.2		99.9		101.0		100.3		99.2		99.4		100.6		100.7		102.7	

a tr, in trace amount, less than 0.1%.

modified poly(ethylene glycol) polymer, corresponds to OV-351] were applied 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) 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 chromatograph with the same capillary column and temperature program as in the gas chromatographic analysis was used in GC/MS analysis. Quantitative analysis was based on comparison with mass spectral libraries (Stenhagen et al., 1974; TNO, 1979; Ramaswami et al., 1988) and Kovats indices (I_K) [e.g., Holm et al. (1988) and Davies (1990)]. Pure reference compounds were used in the identifications of the monoterpene compounds.

Sensory Evaluations. *Samples.* The samples evaluated were carbon dioxide extracts of angelica root isolated at 5.4 MPa and 25 °C with 2.0 g of distilled water or 2.0 g of a mixture of ethanol and water or without any modifier. The extracts were isolated on the previous day and stored at −20 °C protected from light. Approximately 50 g of the extracts was applied on a disk of Whatman No. 1 filter paper and placed into 35 mL glass bottles wrapped in aluminum foil. The sample was covered with cotton–wool to avoid visual identification, and the bottle was capped with a lid. All samples

were coded with three-digit random numbers and served in randomized order to each assesor in every session. The samples for each assessor were prepared simultaneously about 1 h prior to the sessions to allow the headspace to develop in the bottle. Powdered angelica root was used as the reference and prepared the same way as the samples. 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$_2$ injection. A 0.5 g sample of freshly prepared angelica root flour was weight into the glass bottles and covered as described above.

Assessors. Originally 20 assessor candidates were chosen from the staff and graduate students of our department. All had experience in sensory evaluation methods and had previously participated in descriptive sensory analyses. 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 and between 25 and 52 years of age.

Procedure. Deviation-from-reference descriptive analysis (Pangborn, 1984) was used to determine both the character of the odor and the magnitude of the differences in the intensities of these characters among the angelica extracts. A set of triangle tests was conducted as described by Amerine et al. (1965) prior to profiling of the samples to establish whether sensorially detectable differences in odor exist. The liquid carbon dioxide extracts obtained with or without cosolvent were tested against each other. Differentiation of the odd sample was requested in a forced-choice design using all six

Table 4. Relative Compositions of Liquid Carbon Dioxide Extracts of Angelica Roots Isolated at 6.9 MPa

relative proportion, %

I_K	compound	LCO$_2$	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
				distilled water added								EtOH/water solution added							
Monoterpene Hydrocarbons																			
947	α-thujene	tr^a		0.1	0.1	tr		0.1	0.1	tr		tr		0.1	0.1	0.1	0.1	0.1	0.1
1010	α-pinene	11.8	1.9	8.3	1.1	1.4	0.2	8.2	1.8	7.4	0.9	7.6	1.5	6.4	0.5	9.9	0.5	9.1	1.0
1043	camphene	tr		0.2	0.1	tr		0.2	0.1	tr		0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1
1093	β-pinene	0.9	0.1	0.8	0.1	tr		0.6	0.3	0.6	0.1	0.8	0.1	0.7	0.1	0.7	0.1	0.7	0.1
1111	sabinene	9.1	1.2	13.0	2.9	0.5	0.1	1.1	0.4	6.6	0.7	10.5	0.5	13.3	1.0	5.2	0.2	5.0	0.4
1145	3-carene	1.7	0.2	3.5	0.4	0.6	0.1	4.7	0.7	3.6	0.4	3.5	0.5	3.4	0.2	4.2	0.2	4.1	0.3
1166	α-phellandrene	0.5	0.1	1.7	0.7	0.5	0.1	2.2	0.4	3.5	0.4	1.3	0.2	1.8	0.1	2.5	0.1	2.4	0.2
1176	β-myrcene	1.2	0.1	3.3	0.4	0.3	0.1	2.4	1.3	2.4	0.3	3.2	0.5	2.8	0.2	2.5	0.1	2.4	0.2
1202	d-limonene	1.7	0.2	3.5	0.3	0.8	0.1	3.9	0.6	2.5	0.2	3.3	0.5	3.1	0.3	4.0	0.2	3.8	0.2
1210	β-phellandrene	16.7	2.4	25.0	2.6	6.4	0.6	17.8	0.9	25.6	2.6	23.7	1.0	22.6	1.0	25.3	1.1	24.4	1.4
1246	γ-terpinene	0.2	0.1	0.2	0.1	tr		0.3	0.1	0.3	0.1	0.2	0.1	0.3	0.1	0.3	0.1	0.3	0.1
1259	trans-ocimene	tr		0.4	0.1	tr		0.4	0.2	0.5	0.1	0.1	0.1	0.2	0.1	0.5	0.1	0.5	0.1
1268	cymene	0.8	0.2	0.9	0.3	1.2	0.2	2.5	1.3	1.8	0.2	0.9	0.1	0.8	0.1	2.3	0.1	2.2	0.1
1276	α-terpinolene	tr		0.3	0.1	tr		0.2	0.1	0.4	0.1	0.3	0.1	0.4	0.1	0.3	0.1	0.3	0.1
		44.5		61.3		11.6		44.7		55.0		55.8		56.2		58.1		56.0	
Oxygenated Monoterpenes																			
1568	bornyl acetate	1.8	0.2	0.2	0.1	2.2	0.1	0.3	0.1	2.3	0.3	0.3	0.1	0.3	0.1	0.4	0.1	0.4	0.1
1618	chrysanthenyl acetate	tr		0.2	0.1	tr		0.2	0.1	1.1	0.1	0.6	0.1	0.6	0.1	1.0	0.1	1.0	0.1
1634	chrysanthenyl acetate	2.3	0.3	4.2	1.0	5.7	0.2	5.7	0.5	2.8	0.2	3.1	0.1	1.9	0.2	2.8	0.2	3.3	0.3
1646	4,4,6-trimethyl-2-cyclohexen-1-one	0.3	0.1	0.6	0.2	0.4	0.1	0.5	0.1	0.4	0.1	0.4	0.1	0.3	0.1	0.4	0.1	0.4	0.1
1687	phellandral	1.4	0.1	0.2	0.1	tr		0.2	0.1	tr		0.2	0.1	0.2	0.1	tr		tr	
1723	cis-thujenol	0.2	0.1	0.5	0.1	0.8	0.6	0.6	0.1	0.4	0.1	0.5	0.1	0.4	0.1	0.5	0.1	0.6	0.1
1816	cuminyl alcohol	0.4	0.1	0.6	0.1	0.4	0.1	1.5	0.6	1.3	0.2	0.9	0.1	0.8	0.1	1.1	0.1	1.2	0.1
1853	p-cymen-8-ol	tr		0.7	0.2	1.7	0.4	1.2	0.2	0.3	0.1	0.9	0.1	0.8	0.1	1.0	0.1	1.2	0.3
		6.5		7.2		11.3		10.1		8.7		7.0		5.5		7.1		7.9	
Sesquiterpene Hydrocarbons																			
1456	α-cubebene	tr		0.2	0.1							0.2	0.1	0.2	0.1	tr		0.1	0.1
1471	α-copaene	0.2	0.1	0.8	0.2	0.4	0.1	0.4	0.1	0.1	0.1	0.8	0.1	0.6	0.1	0.2	0.1	0.2	0.1
1530	MW = 204			0.1	0.1									0.2	0.1				
1550	MW = 204	0.3	0.1	0.4	0.1	0.4	0.1	0.5	0.1	0.2	0.1	0.3	0.1	0.3	0.1	0.4	0.1	0.4	0.1
1579	δ-elemene	1.3	0.1	1.9	0.2	0.4	0.1	1.8	0.4	tr		1.7	0.2	1.7	0.1	1.8	0.1	2.0	0.2
1586	β-cedrene	tr		0.2	0.1	0.7	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.4	0.1
1611	β-elemene	tr		0.4	0.1	1.9	0.1	0.5	0.1	0.6	0.1	0.4	0.1	0.3	0.1	0.3	0.1	0.4	0.1
1629	MW = 204	tr		0.6	0.2	tr		0.8	0.1	0.1	0.1	tr		tr		tr		0.1	0.1
1642	α-caryophyllene	0.5	0.1	0.1	0.1	0.4	0.1	0.2	0.1	0.6	0.1	0.1	0.1	0.2	0.1	tr		tr	
1658	γ-caryophyllene	2.0	0.5	1.3	0.2	4.7	0.2	2.3	0.6	3.8	0.4	1.4	0.2	0.9	0.1	1.6	0.1	1.9	0.2
1666	β-selinene	3.5	0.4	0.4	0.1	4.5	0.3	0.4	0.1	0.4	0.1	0.3	0.1	0.3	0.1	0.4	0.1	0.4	0.1
1674	(Z)-β-farnesene	0.3	0.1	2.8	0.4	0.5	0.3	3.7	0.3	0.8	0.1	2.8	0.5	2.8	0.7	2.7	0.2	3.2	0.3
1691	germacrene D	1.7	0.1	0.4	0.2	1.0	0.3	0.3	0.1	1.3	0.2	0.7	0.2	0.3	0.1	0.2	0.1	0.2	0.1
1702	γ-muurolene	tr		0.4	0.4	tr		0.2	0.1	tr		0.1	0.1	0.1	0.1	0.2	0.1	tr	
1706	bicyclogermacrene	0.6	0.1	0.8	0.2	1.2	0.1	0.5	0.2	0.7	0.1	0.7	0.2	0.7	0.2	0.4	0.1	0.5	0.2
1711	β-bisabolene	tr		0.8	0.2	0.8	0.4	1.0	0.2	0.5	0.1	0.5	0.2	0.6	0.1	0.7	0.1	0.7	0.2
1735	γ-cadinene	0.3	0.1	0.2	0.1							0.2	0.1	0.4	0.1	0.1	0.1	0.2	0.1
1748	thujopsene	0.6	0.2	0.1	0.1	0.6	0.1	tr		tr		0.4	0.1	0.3	0.1	0.2	0.1	0.1	0.1
1757	MW = 204	0.4	0.1	0.2	0.1	1.4	0.3	0.2	0.1			0.2	0.1	0.2	0.1	0.3	0.1	0.3	0.1
1787	(+)-cuparene	tr		0.1	0.1	0.8	0.1												
1840	MW = 204			0.1														0.1	0.1
2005	MW = 204	0.2	0.1	0.2	0.1	0.5	0.1	0.4	0.1	0.3	0.1	0.4	0.1	0.2	0.1	0.3	0.1	0.3	0.1
		11.9		12.8		20.2		13.3		9.6		11.6		10.8		10.3		11.6	
Oxygenated Sesquiterpenes																			
2023	α-copaen-11-ol	0.4	0.1	0.1	0.1							0.1	0.1	0.1	0.1				
2082	α-copaen-8-ol	1.1	0.1	tr		2.3	0.1					0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1
2101	elemol	3.6	0.3	1.9	0.3	1.7	0.2	1.3	0.7	2.0	0.5	1.0	0.6	1.3	0.2	0.9	0.1	1.0	0.3
2120	MW = 220	0.2	0.1	0.5	0.1	0.4	0.1	0.8	0.3	0.6	0.1	0.5	0.1	0.3	0.1	0.6	0.1	0.7	0.2
2132	spathulenol	0.3	0.1	0.7	0.2	0.3	0.1	0.7	0.1	0.1	0.1	0.3	0.2	0.4	0.1	0.6	0.1	0.7	0.2
2151	MW = 220	0.2	0.1	0.2	0.1	1.5	0.1	0.2	0.1	tr		0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1
2200	rosifoliol	0.6	0.1	0.3	0.1	1.8	0.1	1.1	0.6	0.7	0.2	0.6	0.1	0.5	0.1	0.8	0.1	0.7	0.1
2216	dihydroeudesmol	1.3	0.5	0.4	0.1	2.6	0.3	1.0	0.4	0.4	0.1	0.6	0.1	0.6	0.1	0.4	0.1	0.5	0.1
2279	β-eudesmol	1.5	0.4	0.8	0.2	4.0	0.3	1.1	0.1	0.9	0.3	0.6	0.2	0.6	0.1	0.5	0.1	0.5	0.2
2333	MW = 220	0.5	0.2	0.1	0.1	1.5	0.1	0.3	0.2	1.2	0.2	0.2	0.1			0.2	0.1	0.2	0.1
2360	cedrol	0.5	0.2	0.3	0.1	1.5	0.3	0.7	0.4	0.4	0.1	0.5	0.2	0.4	0.1	0.4	0.1	0.4	0.1
		10.2		5.4		17.5		7.2		6.4		4.6		4.6		4.7		5.1	

Extraction of Angelica Root Volatile Compounds

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Table 4 (Continued)

| | | relative proportion, % | | | | | | | | | | | | | | | | | |
| | | LCO$_2$ | | distilled water added | | | | | | | | EtOH/water solution added | | | | | | | |
I_K	compound		SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD	1 g	SD	2 g	SD	3 g	SD	4 g	SD
						Miscellaneous													
900	unknown	tr		0.1	0.1	tr		0.2	0.1	tr		0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1
964		tr										tr		0.2	0.1	0.2	0.1	0.2	0.1
1062	hexanal	0.7	0.1	0.7	0.1	tr		0.5	0.1	0.6	0.1	0.6	0.1	0.6	0.1	0.8	0.1	0.8	0.4
1086	unknown																		
1169				0.2	0.1	tr		0.2	0.1	tr		0.2	0.1	0.2	0.1	0.3	0.1	0.2	0.1
1183																			
1273	unknown			0.2	0.1	tr		0.2	0.1	0.3	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1
1388	5-undecen-3-yne	tr		0.4	0.1	tr		0.3	0.1	0.4	0.1	0.5	0.2	0.6	0.1	0.3	0.1	0.3	0.1
1463		tr		0.2	0.1	tr		0.1	0.1	tr		0.5	0.2	0.7	0.1	0.3	0.1	0.4	0.1
1489		1.5	0.1	1.3	0.4	2.0	0.1	1.7	0.4	1.6	0.1	1.5	0.4	1.6	0.2	2.6	0.1	2.5	0.8
1649		0.7	0.2	0.6	0.2	tr		0.4	0.3	0.5	0.1	0.6	0.1	0.5	0.1	0.7	0.1	0.7	0.2
1669		0.3	0.1	0.2	0.1	tr		0.2	0.1	tr		0.2	0.1	0.2	0.1	0.1	0.1	0.2	0.1
1774	(E,E)-2,4-decadienal	0.7	0.1	0.3	0.1	0.8	0.2	0.4	0.1	0.4	0.2	0.3	0.1	0.3	0.1	0.4	0.1	0.4	0.1
1781		tr		tr		1.0	0.1	tr		0.4	0.1								
1794	unknown	0.4	0.1	0.2	0.1	1.8	0.2	0.9	0.3	0.7	0.1	0.9	0.2	0.8	0.2	0.7	0.1	0.7	0.2
1812	(E,E)-2,4-dodecadienal	0.6	0.1	0.2	0.1	tr		0.4	0.1	tr		0.2		0.1	0.1	0.2	0.1	0.2	0.1
1906	tetradecanal	0.4	0.1	0.2	0.1	0.7	0.1	0.5	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1
1913		0.3	0.1	0.2	0.1	0.6	0.1	0.4	0.1	0.2	0.1	0.4	0.1	0.4	0.1	0.5	0.1	0.4	0.2
1925	unknown	0.5	0.2	0.3	0.2	tr		0.2	0.1	0.4	0.1	0.3	0.1	0.2	0.1	tr		tr	
1974	tridecanol	0.5	0.1	tr		0.6	0.1					0.2	0.1	0.2	0.1				
2032	tetradecanol	2.6	0.2	1.8	0.4	3.4	0.1	2.0	0.2	2.7	0.5	1.4	0.3	1.4	0.2	1.4	0.1	1.4	0.5
2044	pentadecanal	0.9	0.2	0.7	0.9	2.0	0.1	0.8	0.1	0.4	0.1	1.2	0.2	1.1	0.2	0.4	0.1	0.4	0.2
2055	13-tridecanolide	0.4	0.1	0.2	0.1	0.7	0.1	0.2	0.1	0.3	0.1	0.1	0.1	0.2	0.1	0.2	0.1	0.2	0.1
2067	12-methyl-13-tridecanolide	1.1	0.1																
2116		0.2	0.1	tr		0.8	0.1	0.2	0.1	0.6	0.1	0.2	0.1	0.2	0.1	tr		0.1	0.1
2174		0.4	0.1									0.2	0.1	0.2	0.1				
2184	1-tetradecanyl acetate	0.5	0.1	0.4	0.2	tr		0.4	0.1	0.3	0.1	0.4	0.3	0.6	0.1	0.2	0.1	0.2	0.1
2220		tr		0.2	0.1	tr		0.4	0.2	1.1	0.3	0.3	0.1	0.2	0.1	tr		0.2	0.1
2242	15-pentadecanolide	7.7	1.4	3.5	1.0	9.9	0.2	5.0	0.8	5.1	1.2	4.2	0.4	3.7	0.3	4.5	0.3	3.9	1.3
2253		0.2	0.1	0.2	0.1	tr		0.3	0.1	tr		0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1
2268		0.6	0.1	0.4	0.1	1.7	0.1	1.0	0.4	tr		0.7	0.1	0.3	0.1	0.4	0.1	0.4	0.2
2307		0.5	0.2	0.2	0.1	0.7	0.1	0.3	0.2	0.4	0.2	0.3	0.1	0.2	0.1	0.2	0.1	0.2	0.1
2347		tr		0.1	0.1	tr		0.2	0.1	tr		0.2	0.1	tr		tr		0.1	0.1
2387	hexadecanol	0.6	0.3	0.3	0.1	1.0	0.3	0.5	0.1	tr		1.3	0.5	1.5	0.5	1.2	0.2	1.0	0.4
2407	MW = 250	0.4	0.2	0.2	0.1	1.0	0.1	0.5	0.2	0.5	0.1	0.8	0.1	0.8	0.2	0.7	0.1	0.6	0.2
2420	unknown	3.2	0.4	0.7	0.1	5.2	0.1	2.0	0.8	1.4	0.3	1.1	0.2	0.6	0.1	1.2	0.2	1.1	0.4
2453	heptadecanyl acetate	1.6	0.3	0.4	0.1	2.0	0.2	1.8	0.2	0.7	0.2	0.9	0.1	1.7	0.1	0.8	0.1	0.7	0.2
2460	unknown	0.2	0.1	tr		0.7	0.1	0.2	0.1	0.1	0.1	0.1							
2487	octadecanol	0.9	0.3	0.7	0.2	2.6	0.5	0.8	0.3	1.1	0.4	0.8	0.3	2.0	0.1	0.7	0.1	0.5	0.2
		28.8		15.1		39.1		23.5		20.2		21.1		22.0		19.8		18.8	
		101.9		101.9		99.7		98.9		99.9		100.1		99.1		100.0		99.5	

^{a} tr, in trace amount, less than 0.1%.

combinations of presentation equally. 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 the three selected liquid CO$_2$ extracts of angelica root. A total of 35 different terms were used, from which 4 were predominant (green, terpene-like, fresh, root celery). 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. 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" was indicated 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. Tukey's test was used to determine differences among the means at $p < 0.05$.

The evaluation of the samples was performed in individual assessment booths from 1 to 3 p.m. throughout the study. The sessions were held twice a week during 5 consecutive weeks from the end of May until the end of June 1993.

RESULTS AND DISCUSSION

The liquid CO$_2$ extractions were carried out under three different conditions with or without one of the two modifiers. Twenty-seven extracts were produced in three replicates, each of which was analyzed as triplicates. The relative proportions of components in these extracts and the standard deviations are presented in Tables 2–4. Essentially the same compounds were identified in all extracts, and the results were in agreement with the components previously identified in this strain (Kerrola et al., 1994).

Composition of Liquid Carbon Dioxide Extracts. All of the liquid CO$_2$ extracts obtained without cosolvent were bright yellow viscous liquids at room temperature. Extraction at 4.7 MPa yielded 0.6% of the angelica root material and at 5.4 MPa of pressure the yield was 0.5%. Rise in both pressure and temperature increased the yield to 0.7%. As comparison the essential oil content

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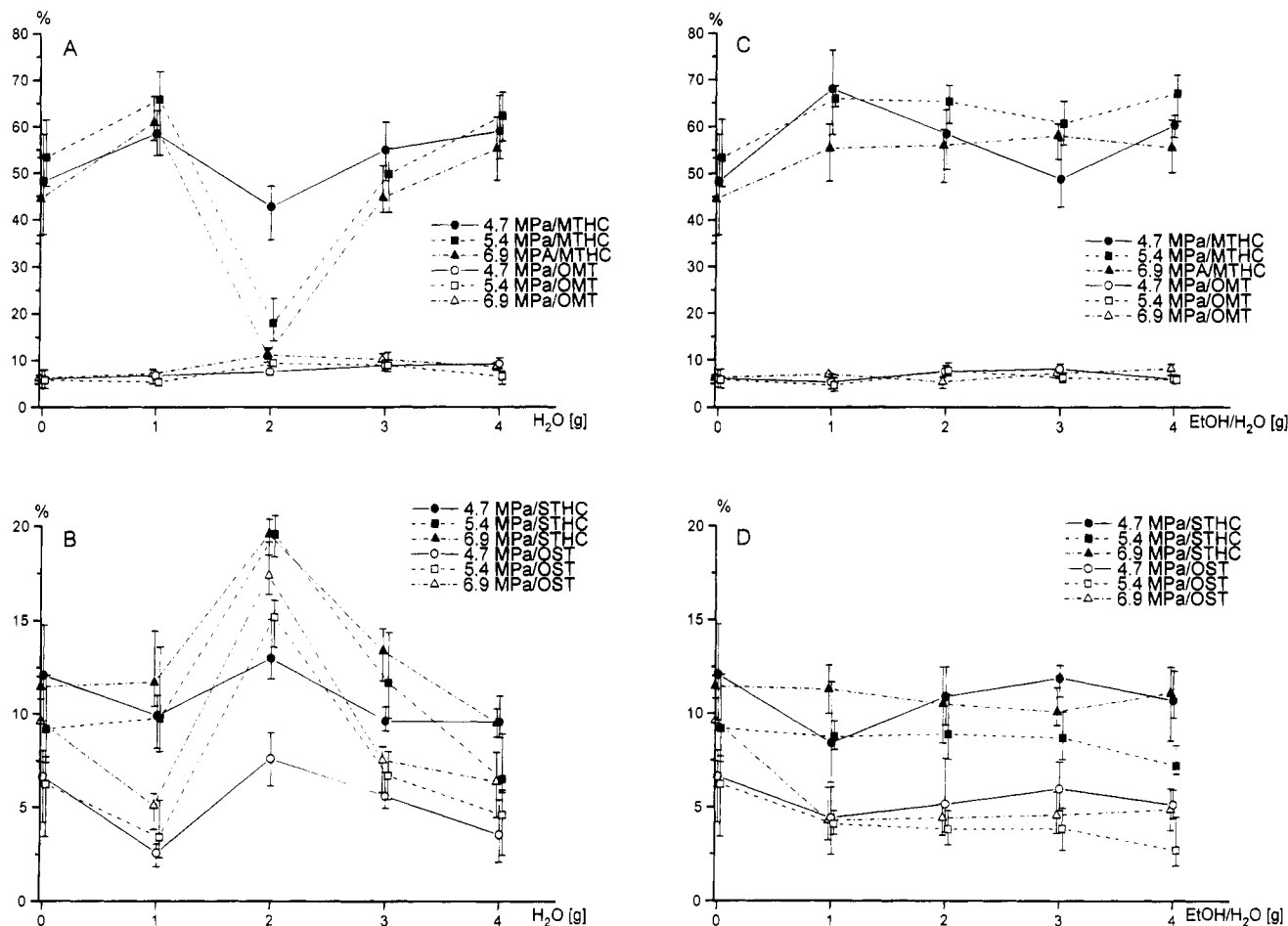
Figure 1. Means and variation of the relative proportions of terpene classes in LCO_2 extracts isolated with various amounts of cosolvent. Monoterpene hydrocarbons (MTHC) and oxygenated monoterpenes (OMT) were extracted with water (A) or ethanol/water (C) as cosolvent, and sesquiterpene hydrocarbons (STHC) and oxygenated sesquiterpenes (OST) were extracted with water (B) or ethanol/water (D) as cosolvent.

isolated by hydrodistillation from dried roots of different strains of angelica originating from various parts of the northern Fennoscandia ranged from 0.3 to 1.1% in 1981–1982 (Ojala et al., 1986).

Monoterpenes were the largest class of substances contributing more than 50% of the compounds included into the calculations (Figure 1A). At all pressures several peaks could be detected in the latter part of the chromatogram [shown in Kerrola et al. (1994)] representing, e.g., medium-chain fatty acids and their esters and other lipophilic components with minor effects on the odor of the angelica root extract. Only the components eluting prior to *n*-pentacosane were included in the comparisons made among the extracts obtained under various operation conditions. The relative proportion of the monoterpene compounds was most abundant, approximately 60%, at 5.4 MPa. Increase in pressure to 6.9 MPa and increase in temperature to 45 °C decreased the proportion of the monoterpene moiety to 50% level. At 4.7 MPa and 25 °C the monoterpene compounds comprised about 55% of the components. *β*-Phellandrene, α-pinene, and sabinene were the major monoterpene hydrocarbons in all extracts, comprising from 38 to 44% of the analytes (Tables 2–4). The percentage of camphene, α-phellandrene, *β*-phelland-rene, and cymene decreased, whereas the proportion of sabine increased, with raised pressure and temperature. Only a minor variation in the proportion of oxygenated monoterpenes was found among the liquid CO_2 extracts. Chrysanthenyl acetate was the most abundant com-

pound. The two components identified as chrysanthenyl acetate could not be differentiated on the basis of their mass spectra. It has been suggested by Nykänen et al. (1991) that they represent different isomers of the same compound. Elevated pressure had a decreasing effect on the proportion of chrysanthenyl acetate but an increasing effect on the proportions of bornyl acetate and phellandral. Increase in pressure decreased the relative abundance of sequiterpene hydrocarbon but had little effect on the oxygenated sesquiterpenes at 25 °C (Figure 1B). Raising both pressure and temperature resulted in an increase in the proportion of oxygen-containing sesquiterpene moiety. The relative abundances of *β*-se-linene, germacrene D, α-copaen-8-ol, and elemol increased with raised pressure, whereas several others e.g., α-copaene, *β*-cedrene, *γ*-caryophyllene, and (*Z*)-*β*-farnesene, decreased in relative abundance. Among the compounds included in the miscellaneous compounds, 13-tridecanolide and 15-pentadecanolide exhibit significant importance for the odor of angelica root (Guenther, 1953). At 6.9 MPa and 45 °C 15-pentadecanolide and 12-methyl-13-tridecanolide showed an increase in abundance, but the proportion of 13-pentadecanolide remained constant.

Effect of Water Addition. Highest yields of the yellow viscous liquid were obtained at 25 °C and 4.7 MPa with 2.0 g addition (0.8%) of water and at 5.4 MPa with 4.0 g (0.9%). At higher temperature (45 °C) and at 6.9 MPa a yield of 1.0% was isolated with 1.0 g of water addition. Regardless of pressure and temperature

used, the yields recovered increased when an aliquot of water was added to the system. After the extraction had been completed and carbon dioxide released, the water cosolvent formed a separate phase, but some residual amount could have remained trapped within the lipophilic phase. The increase in volume was considered a positive factor. The cosolvent was suggested to act as the primary solvent, thus enhancing the diffusivity within the matrix.

Most pronounced was the effect of a 2.0 g aliquot of distilled water on the monoterpene hydrocarbon moiety (Figure 1A). Addition of water decreased the proportion at all extraction conditions in comparison to liquid CO_2 extracts without a modifier and by more than 35 percent units at 5.4 MPa; 1.0 and 4.0 g additions of water increased the proportion of monoterpene hydrocarbons at each pressure. A major increase in the relative abundance of sabinene was found at 4.7 MPa with 2.0 g addition and at 5.4 MPa as well as at 6.9 MPa with 1.0 g addition. Increasing the amount of water beyond this level had an adverse effect on sabinene content. The extracts obtained at 6.9 MPa with 2.0 g of water addition contained the smallest amounts of monoterpene hydrocarbon compounds, resulting mainly from the decrease in the relative amount of β-phellandrene. At 4.7 MPa the relative abundance of the oxygenated hydrocarbon moiety increased with increasing amount of water added. At 5.4 and 6.9 MPa pressures the amount of 2.0 g resulted in highest proportions of oxygenated monoterpenes to be recovered. The largest amount of water added was found to have a decreasing effect on the abundance of oxygen-containing monoterpene proportion and on the relative percentages of individual substances within the moiety. Difference between the smallest and largest proportion of oxygenated monoterpenes found in the extracts varied significantly, ranging from 5.2 (at 5.4 MPa and 1.0 g of water added) to 11.3% (6.9 MPa and 2.0 g of water added). The compounds most affected by the use of an enhancer were chrysanthenyl acetate, cuminyl alcohol, and *p*-cymen-8-ol. The highest proportions of sesquiterpene hydrocarbons and oxygenated sesquiterpenes were extracted at each pressure with 2.0 g of water as cosolvent. Increasing the pressure and adding the same aliquot of water increased the relative amount of oxygenated sesquiterpenes extracted. Other oxygen-containing compounds, 13-tridecanolide and 15-pentadecanolide, were most effectively extracted at 5.4 MPa with addition of 2.0 g of water.

Effect of a Mixture of Ethanol and Water. The extracts obtained with liquid carbon dioxide modified with an aliquot of ethanol/water solution (1:1 v/v) were bright yellow, low-viscosity liquids. They consisted of one phase only; i.e., cosolvent could not be removed. Some of it had condensed on the walls of the extractor and was reatined in the sample, and therefore yields could not be measured. As with the water as the cosolvent, the extracted sample was detected to have increased in volume due to sorption of some of the modifier. The extract obtained was water soluble, unlike the liquid CO_2 extracts without a cosolvent or the water-modified liquid CO_2 extracts. The relative composition of these extracts differed from the composition found in the liquid CO_2 extracts obtained with or without water as modifier.

The proportion of the monoterpene hydrocarbons was higher in the liquid CO_2 extracts obtained with the mixture of ethanol and water as cosolvent in comparison

to the liquid CO_2 extracts without a modifier at each pressure (Figure 1C). The mixture of ethanol and water appeared to increase the proportion of monoterpene hydrocarbons when compared with water alone used as modifier. At 4.7 MPa addition of 3.0 g of the ethanol and water solution did not increase the relative abundance of monoterpene hydrocarbons as much as the addition of a 3.0 g aliquot of water. As discovered with water also the mixture of ethanol and water yielded the highest relative proportion of monoterpene hydrocarbons at 5.4 MPa and 25 °C. The effect of the cosolvent added on extractability of a compound varied considerably. β-Phellandrene was the most prominent compound in all extracts obtained with the mixture of ethanol and water as modfier, but the relative abundance varied from 9.2 to 30.7% depending on extraction conditions. Any amount of ethanol and water solution did not have as significant an enhancing effect on extractability of oxygenated monoterpenes as a 2.0 g addition of water at 5.4 and 6.9 MPa. The proportions of cuminyl alcohol and *p*-cymen-8-ol showed an increase and the relative amount of bornyl acetate a decrease due to addition of a mixture of ethanol and water as cosolvent.

The relative proportion of both sesquiterpene hydrocarbons and oxygenated sesquiterpenes decreased when the polarity of the solvent was increased by the mixture of ethanol and water (Figure 1D) in comparison to liquid CO_2 extracts obtained without a modifier. The decrease in sesquiterpene hydrocarbons was about 3 percent units at 4.7 MPa. In the oxygen-containing sesquiterpenes the decrease was most evident at higher pressures (more than 5 percent units), reaching a minimum level at 5.4 MPa with a 4.0 g addition of the cosolvent. The percentage of β-selinene, germacrene D, α-copaen-8-ol, and eudesmol showed a major decrease and, (Z)-β-farnesene and β-bisabolene showed an increase. The relative abundances of the lactone substances extracted decreased compared to either liquid CO_2 extracts or liquid CO_2 extracts with water as cosolvent.

The standard deviations of several compounds were found to be large and resulted in marked variation of the relative abundances. Visual adjustment of the introducing of CO_2 enabled us to prevent overloading but to only estimate the amount of liquid CO_2. When the pressure in the extractor was slowly and carefully released, some loss of volatiles were observed. The cosolvent was added on the top of the sample, and uneven distribution into the sample was suggested.

Sensory Evaluations. Three angelica root extract samples were selected on the basis of expected differences in odor. The extracts isolated at 5.4 MPa showed largest variation in volatile composition and coextracted substances affected by the amount of cosolvent. The same amounts of cosolvents were used in extractions of both modified samples for sensory analysis.

In the selection of attributes to describe the odor profile of the liquid carbon dioxide extracts, the liquid CO_2 extract modified with the mixture of ethanol and water was characterized as terpenic and beetlike, with a more fresh or cooling effect than the other extracts. The liquid CO_2 extract without a modifier was considered mostly green and terpenic in the odor profiling. Adding water did not alter the profiling given by the assessors, and the terms were essentially the same. The four most predominant terms (green, terpene, fresh, root celery) were selected for the evaluations by the panel in round-table discussions.
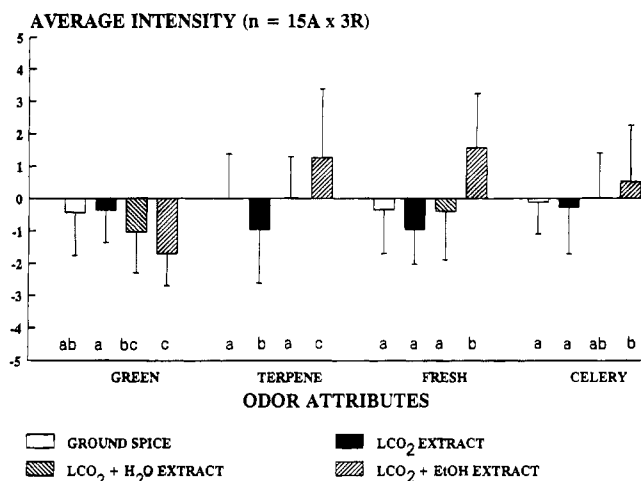
Figure 2. Means and standard deviations for odor attributes of angelica root. The samples were liquid carbon dioxide extracts of angelica root isolated at 5.4 MPa and 25 °C with 2.0 g of distilled water or 2.0 g of ethanol/water (1:1 v/v) solution or without any cosolvent. Values show degree of deviation from reference: values less than 0 indicate weaker intensity compared with reference (freshly powdered angelica root), 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 in analysis of variance.

The means of the intensities detected for the odor attributes in liquid carbon dioxide extracts isolated at 5.4 MPa with or without a modifier are presented in Figure 2. 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. Some minor differences between the ground angelica root and the liquid carbon dioxide extract and between the distilled water modified liquid CO_2 extract were detected. The water-modified extract was evaluated as less green than the liquid CO_2 extract without a modifier. The liquid CO_2 extract without a modifier was perceived as less terpenic than the ground spice and, in fact, the least terpenic of the samples. The result was an unexpected one. The low percentage of monoterpene hydrocarbons in the water-modified liquid CO_2 extract was expected to result in a decrease in terpene-like character in the odor. However, the water-modified liquid CO_2 extract was perceived as more terpenic than the liquid CO_2 extract obtained without a modifier. In agreement with our expectations, the extract obtained with the mixture of ethanol and water as cosolvent differed distinctly from the other samples. The extract was assessed as most terpenic and most fresh of the extracts. Intensities of the green and root celery attributes did not differentiate the modifier-containing extracts from one another. The ethanol odor clearly present in this sample caused some difficulties because it hindered the assessment of the green attribute. Ethanol was also considered to enhance the cooling effect in the nostrils. It is possible that some of the differences detected in the green and fresh attributes are produced by ethanol and not the compounds isolated from angelica root material.

To control the performance of the panel, the reference sample was presented to the assessors as one of the samples to be evaluated. Some deviation between the reference and the blind control was detected at the green and fresh attributes as were negligible deviations at the terpene or celery attributes, reflecting a satisfactory level of assessment reliability. When the sources for

Table 5. *F* Values from Analysis of Variance for the Attributes

source	df	green	terpene	fresh	celery
assessor	14	2.43***[a]	3.38***	2.15*	2.90***
sample	3	12.85***	19.24***	27.53***	3.94*
replication	2	0.09	0.91	0.13	2.33
assessor × sample	42	2.88***	2.09**	1.55*	2.33***

[a] *, **, ***, significant at $p < 0.05$, 0.01, and 0.001, respectively.

the differences were studied, both the assessors and assessor × sample interactions were revealed as significant sources of variation (Table 5). The differences detected among the samples in assessment of the celery attribute originate to greater extent from the assessors and assessor × sample interactions than from the samples. The other interactions were not significant as sources of variation.

The differences in the sensory profiles of the extracts were smaller than expected on the basis of chemical data collected. Neither the low relative amounts of monoterpene hydrocarbons nor the small proportions of α-pinene and β-pinene were directly detected as low intensity of terpenic character. To assess the importance of the differences, which were detected in volatile composition among various samples by chromatographic and mass spectrometric analyses, for the odor of the samples, sensory evaluation should always be used.

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