

## Chemical Composition of Angelica Root Oil

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The volatile constituents of angelica root separated by extraction with ether-pentane and by extraction with alcohol-water were investigated by means of glass capillary and preparative gas chromatography, IR, UV, NMR and mass spectrometry. 16 monoterpene hydrocarbons, 13 sesquiterpene hydrocarbons, 12 monoterpene alcohols, 4 oxygenated sesquiterpenes, 11 esters, 3 lactones, 7 aliphatic carbonyl compounds and 4 aromatics were identified. Twenty additional compounds identified were present only in the alcoholic sample. These consisted of ethyl ethers of monoterpene alcohols, ethyl esters of long-chain fatty acids, and acetals. The relative proportion of many compounds was found to depend on the method used to isolate the essential oil.

*Angelica archangelica* L. is a herbaceous plant cultivated mostly in Middle Europe. Steam distillation of the roots yields 0.1–1 % of essential oil.<sup>1</sup> Dried angelica root and its derivatives (the essential oil, extracts, distillates) find extensive use in flavour formulations for alcoholic beverages, such as vermouths, bitters, benedictine and chartreuse-type liqueurs and liqueurs like gin.<sup>2</sup>

In the early investigations of angelica root oil, reviewed by Gildemeister and Hoffmann,<sup>1</sup>  $\alpha$ -pinene,  $\alpha$ -phellandrene, borneol, pentadecanolide, and 2-methyl butyric acid were found. Klouwen and ter Heide<sup>3</sup> confirmed the identity of pentadecanolide by its IR spectrum and developed a gas chromatographic method for its quantitative determination.

Gas chromatographic studies of the monoterpene hydrocarbons in angelica root oil have been carried out by Klouwen and ter Heide<sup>4</sup> and by Baerheim Svendsen and Karlsen.<sup>5</sup> The former report the following monoterpene hydro-

carbons, identified by retention times:  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, sabinene,  $\alpha$ -phellandrene,  $\beta$ -phellandrene, limonene, terpinolene, myrcene, *cis*-ocimene, *trans*-ocimene, and *p*-cymene. Baerheim Svendsen and Karlsen found camphene, fenchene,  $\alpha$ -terpinene, and  $\gamma$ -terpinene as minor constituents. Klouwen and ter Heide also reported the presence of borneol, carvacrol, bornyl acetate, carvotanacetone, carvone, pulegone, dihydrocarvone, and furfural.

The aims of this study were to obtain a more detailed knowledge of the volatile constituents of angelica root and to elucidate the actual aroma composition of an alcoholic angelica distillate used to flavour liquors. It is known that treating a herb with ethanol can affect the composition of the volatile oil.<sup>6</sup> Consequently two samples were studied, one isolated by extraction with ether-pentane followed by steam distillation and second prepared as an alcoholic distillate by Alko's flavour distillery.

### EXPERIMENTAL

*Apparatus.* Analytical gas chromatography was performed using glass capillary columns on a Hewlett-Packard 7620 A instrument equipped with FID and a glass inlet splitter. Of the two capillary columns (0.28 mm I.D.  $\times$  25 m) used one was coated with SP-1000 and the other with OV-101. Peak areas were measured with an Infotronics CRS-11 NSB/42 integrator. For preparative GLC the same instrument with TC detector and 4 mm I.D.  $\times$  3 m glass columns packed with 5 % LAC-2R-446 or 5 % OV-101 on 70/80 mesh Chromosorb G AW DMCS were used. 6 mm  $\times$  3 m stainless steel columns packed with 10 % FFAP or 15 % Apiezon L on 60/80 mesh Chromosorb W AW were used for some separations. Fractions were collected in 1 mm  $\times$  20 cm glass tubes cooled with dry ice.

IR spectra of pure samples were recorded as films between KBr pellets on a Perkin-Elmer

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521 spectrophotometer equipped with a beam condenser. UV spectra were measured in ethanol on an Opton PMQ II spectrophotometer. NMR spectra were determined on a Varian A-60 spectrometer in Department of Chemistry, Helsinki University of Technology, or Fourier transformation spectra on a JEOL JMM PFT 100 in Department of Organic Chemistry, University of Helsinki.  $\text{CCl}_4$  or  $\text{CDCl}_3$  was used as the solvent and TMS as an internal standard. The mass spectra were determined in Department of Medical Chemistry, University of Helsinki, on a Varian CH 7 combined GLC-MS instrument coupled with Spectro System 100 MS computer. A 2 mm I.D.  $\times$  2 m SE-30 glass column was used in the gas chromatograph.

**Materials and procedure.** Angelica root oil was isolated by extracting 600 g of the ground herb (purchased from G.H. Worlée & Co m.b.H, Germany) with ether-pentane (2:1) for two days in a Soxhlet-type extractor. After removing the solvent, the residue was distilled with steam to separate the volatiles. The distillate was extracted with pentane and, after drying over anhydrous  $\text{Na}_2\text{SO}_4$ , pentane was distilled off to leave 1.4 g of volatile oil.

The alcoholic angelica distillate was prepared in Alko's flavour distillery by percolating the herb with an ethanol-water mixture and distilling the percolate under reduced pressure. For analysis the essential oil was separated from the alcoholic solution by extracting with pentane as described previously.<sup>6</sup>

4 Litres of the alcoholic flavour distillate was distilled to 1.5 l under reduced pressure to concentrate the less volatile aroma fraction. Higher boiling compounds were extracted with pentane from the residue.

The steam distilled oil as well as the samples prepared from the alcoholic distillate were

fractionated by column chromatography on silica gel as described earlier<sup>6</sup> to obtain a hydrocarbon fraction and a fraction of oxygenated compounds. These were further fractionated by preparative GLC using the LAC-2R-446 column. Analysis of the subfractions with one or both of the capillary columns showed all of them to be mixtures of several compounds. Pure compounds for determination of spectra were obtained by rechromatographing these subfractions on the OV-101 column. A third preparative column was occasionally needed.

Some esters of monoterpene alcohols were hydrolysed using 10 % alcoholic KOH at room temperature to aid the identification.

Relative amounts of components were determined gas chromatographically from the peak areas without using response factors.

## RESULTS AND DISCUSSION

The gas chromatogram of angelica root oil obtained by extraction with ether-pentane followed by steam distillation (sample A) is shown in Fig. 1, and the chromatogram of the pentane extract from the alcoholic angelica root distillate (sample B) in Fig. 2. In Table 1 are presented the compounds identified with their percentage contribution and identification methods with references to literature spectra. The percentages calculated from peak areas are only approximate because of the use of the injection splitter and some incomplete separations.

GLC with capillary columns showed that the hydrocarbon fraction of both samples contained

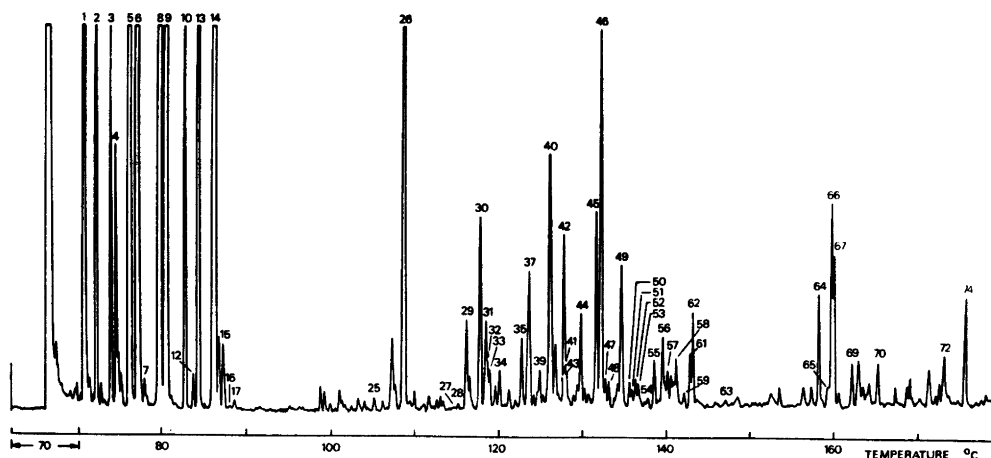


Fig. 1. Gas chromatogram of sample A on SP-1000 glass capillary column (0.28 mm I.D.  $\times$  25 m). Helium flow 0.7 ml/min. Temperature program: 4 min at 70 °C, 2 °C/min 70–215 °C.

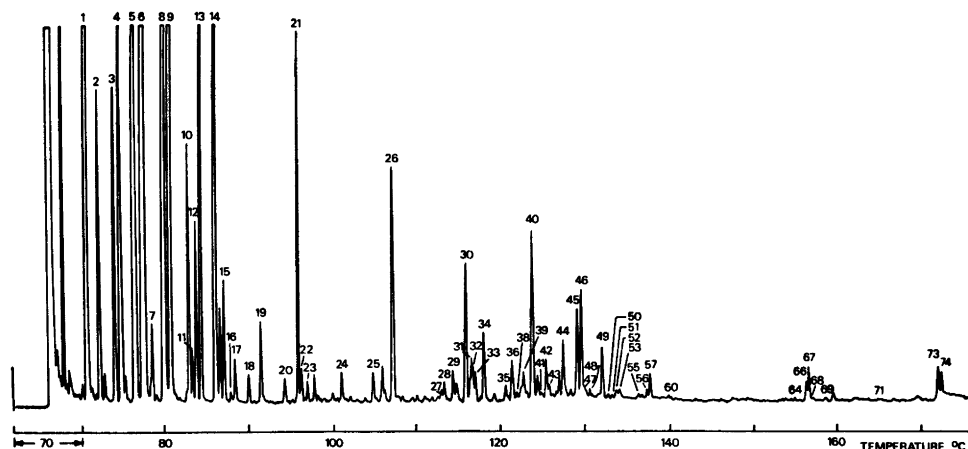


Fig. 2. Gas chromatogram of sample B on SP-1000 glass capillary column.

the same components in approximately the same relative proportions. The 16 monoterpene hydrocarbons identified, all of which had been found before, constituted about 82 % of sample A and 89 % of sample B. The main components were  $\alpha$ -pinene, 3-carene,  $\alpha$ -phellandrene,  $\beta$ -phellandrene, limonene, and *p*-cymene.

The sesquiterpene hydrocarbons formed about 7 % of sample A and about 4 % of sample B. For identification they were isolated from the high boiling fraction of the alcoholic distillate. The compounds identified were  $\alpha$ -copaene,  $\beta$ -copaene,  $\alpha$ -muurolene,  $\gamma$ -muurolene,  $\delta$ -cadinene, germacrene-D, caryophyllene,  $\alpha$ -humulene,  $\beta$ -farnesene,  $\beta$ -bisabolene,  $\beta$ -elemene, ar-curcumenene, and cuparene.

In the fractions containing the oxygenated compounds, which constituted about 11 % of sample A and about 7 % of sample B, striking differences were found between the two samples. In sample A terpene alcohols proved to be the principal constituents. From monoterpenes, *trans*-verbenol (the most abundant alcohol), *cis*-verbenol, *cis*- and *trans*-2-*p*-menthen-1-ol, *cis*- and *trans*-piperitol, *cis*- and *trans*-sabinene hydrate, linalool, terpinenol-4, and *trans*-carveol were identified.

Three additional alcohols were found, which, according to spectral evidence were derivatives of the phellandrenes. One of them (peak 46) had IR absorptions at 3390 and 1125  $\text{cm}^{-1}$ , corresponding to a tertiary OH group and at

3020, 820, 790, 770, and 730  $\text{cm}^{-1}$ , which were attributed to a trisubstituted and a *cis*-disubstituted double bond. The compound had a UV absorption maximum at 263 nm, showing conjugation of the double bonds. The mass spectrum gave a molecular weight of 152, clearly corresponding to the formula  $\text{C}_{10}\text{H}_{18}\text{O}$ , so that a ring besides the two double bonds should be present. The structure derived from 1,5-*p*-menthadiene giving 262 nm for the calculated  $\lambda_{\text{max}}$ ,<sup>7</sup> is compatible with these data. The base peak at *m/e* 59 suggests that the position of the hydroxyl is at C-8. Accordingly, this compound was tentatively identified as  $\alpha$ -phellandrene-8-ol. The mass spectrum of component 56 displayed the molecular peak at *m/e* 152 and base peak at *m/e* 92. The IR spectrum revealed the presence of secondary or primary OH (3360, 1035  $\text{cm}^{-1}$ ), *gem*-dimethyl (1382, 1365  $\text{cm}^{-1}$ ), terminal methylene (3070, 888  $\text{cm}^{-1}$ ) and a *cis*-disubstituted double bond (3020, 798, 760  $\text{cm}^{-1}$ ). The double absorption at 1635 and 1595  $\text{cm}^{-1}$  implied conjugation of the double bonds, which was confirmed by UV spectrum ( $\lambda_{\text{max}}$  232 nm). The most reasonable structure to fit these data seems to be 1(7),2-*p*-menthadiene with hydroxyl in the 5- or 6-position. The proposed structures give 232 nm for the calculated  $\lambda_{\text{max}}$ . The third alcohol (peak 59), which had a similar IR spectrum and almost identical mass spectrum to those of 56, is evidently the diastereomer of this compound.

Table 1. Compounds identified in angelica root oil obtained by extraction with ether-pentane followed by steam distillation (sample A) and in a pentane extract of alcoholic angelica root distillate (sample B).

GC peak	Compound	Percentage		Basis for identification
		Sample A	Sample B	
Hydrocarbons				
1	$\alpha$ -Pinene	24.0	25.4	GLC, MS <sup>a</sup> , IR <sup>a</sup>
1	$\alpha$ -Thujene	+	+	MS <sup>11</sup>
2	Camphene	1.30	1.15	GLC, MS <sup>a</sup>
3	$\beta$ -Pinene	1.25	1.22	GLC, MS <sup>a</sup>
4	Sabinene	0.76	3.17	GLC, MS <sup>a</sup>
5	3-Carene	10.1	10.8	GLC, MS <sup>a</sup> , IR <sup>a</sup>
6	$\alpha$ -Phellandrene	7.6	13.9	GLC, MS <sup>a</sup> , IR <sup>a</sup>
6	Myrcene			GLC, MS <sup>a</sup> , IR <sup>a</sup>
7	$\alpha$ -Terpinene	0.07	0.29	GLC, MS <sup>a</sup>
8	Limonene	13.2	12.5	GLC, MS <sup>a</sup> , IR <sup>a</sup>
9	$\beta$ -Phellandrene	10.0	10.7	IR <sup>12</sup> , MS <sup>13</sup>
10	<i>cis</i> -Ocimene	1.25	1.03	MS <sup>13</sup>
12	$\gamma$ -Terpinene	0.11	0.69	GLC, MS <sup>a</sup>
13	<i>trans</i> -Ocimene	2.68	2.38	MS <sup>13</sup> , IR <sup>12</sup>
14	<i>p</i> -Cymene	9.8	5.48	GLC, MS <sup>a</sup> , IR <sup>a</sup>
15	Terpinolene	0.16	0.46	GLC, MS <sup>a</sup>
26	$\alpha$ -Copaene	1.91	1.10	MS <sup>14</sup> , IR <sup>15</sup>
31	$\beta$ -Copaene	0.40	0.25	IR <sup>16</sup>
32	Caryophyllene			MS <sup>14</sup> , IR <sup>a</sup>
33	$\beta$ -Elemene	0.90	0.04	MS <sup>14</sup> , IR <sup>15</sup>
36	$\beta$ -Farnesene	0.15	0.21	MS, IR <sup>15</sup>
40	$\alpha$ -Humulene	0.5	0.4	MS <sup>14</sup> , IR <sup>15</sup>
43	$\gamma$ -Muurolene	0.04	0.03	IR <sup>17</sup>
44	Germacrene-D	0.26	0.30	IR <sup>18</sup>
45	$\beta$ -Bisabolene	0.72	0.42	IR <sup>15</sup>
46	$\alpha$ -Muurolene	1.2	0.5	IR <sup>17</sup>
49	$\delta$ -Cadinene	0.51	0.24	MS, IR <sup>15</sup>
52	ar-Curcumene	0.06	0.03	IR <sup>15</sup>
57	Cuparene	0.10	0.08	MS, IR <sup>15</sup>
Alcohols				
25	<i>trans</i> -Sabinene hydrate	0.01	0.14	MS, IR <sup>19</sup>
27	<i>cis</i> -Sabinene hydrate	+	0.03	MS, IR <sup>19</sup>
28	Linalool	0.01	0.05	MS <sup>a</sup> , IR <sup>a</sup>
29	<i>cis</i> -2- <i>p</i> -Menthen-1-ol	0.31	0.14	MS, IR <sup>10</sup>
34	Terpinenol-4	+	0.31	MS <sup>a</sup> , IR <sup>a</sup>
35	<i>trans</i> -2- <i>p</i> -Menthen-1-ol	0.24	0.09	MS, IR <sup>10</sup>
40	<i>cis</i> -Verbenol	0.1	0.05	MS, IR <sup>a</sup>
41	<i>trans</i> -Piperitol	+	+	MS <sup>20</sup>
42	<i>trans</i> -Verbenol	0.64	0.19	MS, IR <sup>a</sup>
46	$\alpha$ -Phellandrene-8-ol	0.4	0.1	MS, IR, UV
47	<i>cis</i> -Piperitol	0.05	+	MS <sup>20</sup> , IR <sup>10</sup>
58	<i>trans</i> -Carveol	0.11	+	MS, IR <sup>10</sup>
61	<i>m</i> -Cymene-8-ol	0.19	+	MS, IR
62	<i>p</i> -Cymene-8-ol	0.31	+	MS <sup>22</sup> , IR <sup>10</sup>
65	Cuminyl alcohol	0.02	+	MS, IR <sup>10</sup>
66	$\alpha$ -Copaene-11-ol	0.46	0.05	MS <sup>23</sup> , IR, NMR <sup>23</sup>
69	Elemol	0.18	+	MS, IR <sup>24</sup>
72	$\beta$ -Eudesmol	0.21	+	MS, IR <sup>25</sup>
Esters and lactones				
30	Bornyl acetate	0.73	0.69	MS <sup>26</sup> , IR
37	<i>trans</i> -Verbenyl acetate	0.46	0.02	MS, IR <sup>a</sup>

Table 1. Continued.

39	<i>trans</i> -Pinocarvyl acetate	0.17	0.18	MS, IR, H <sup>b</sup>
48	<i>cis</i> -Carvyl acetate	0.05	0.02	MS, <sup>26</sup> IR <sup>a</sup>
50	Bornyl isovalerate	0.07	0.01	MS, IR <sup>a</sup>
51	<i>trans</i> -Carvyl acetate	0.03	0.01	MS <sup>28</sup> , IR <sup>a</sup>
53	<i>trans</i> -Verbenyl 2-methyl-butylate	0.04	0.02	MS, IR, H
55	<i>trans</i> -Verbenyl isovalerate	0.17	0.02	MS, IR, H
17	Isoamyl isovalerate	0.02	0.02	GLC, MS <sup>27</sup>
	Heptyl isovalerate <sup>c</sup>	+	+	MS
	Octyl isovalerate <sup>c</sup>	+	+	MS <sup>a</sup> , IR <sup>a</sup>
38	Ethyl caprate		0.02	MS, IR <sup>a</sup>
60	Ethyl laurate		0.01	MS, IR <sup>a</sup>
67	Ethyl myristate		+	MS, IR
71	Ethyl pentadecanoate		+	MS, IR
73	Ethyl palmitate		0.19	GLC, MS <sup>a</sup> , IR <sup>a</sup>
67	Tridecanolide	0.45	0.13	MS, IR, NMR
74	Pentadecanolide	0.37	0.14	GLC, MS <sup>a</sup> , IR <sup>a</sup>
	Ethyl stearate <sup>c</sup>		+	GLC, MS, IR <sup>a</sup>
	Ethyl oleate <sup>c</sup>		+	GLC, MS, IR <sup>a</sup>
	Ethyl linoleate <sup>c</sup>		0.17	GLC, MS, IR <sup>a</sup>
	Ethyl linolenate <sup>c</sup>		+	GLC, MS, IR <sup>a</sup>
	Heptadecanolide <sup>c</sup>	+		MS
Ethers				
11	<i>trans</i> -4-Ethoxy-thujane		0.19	MS <sup>6</sup> , IR <sup>6</sup>
17	<i>cis</i> -4-Ethoxy-thujane		0.12	MS <sup>6</sup> , IR <sup>6</sup>
18	<i>cis</i> -4-Ethoxy-2-pinene		0.10	MS, IR
19	<i>cis</i> -1-Ethoxy-2- <i>p</i> -menthene		0.33	MS <sup>6</sup> , IR <sup>6</sup>
20	<i>trans</i> -3-Ethoxy-1- <i>p</i> -menthene		0.09	MS <sup>6</sup> , IR <sup>6</sup>
21	<i>trans</i> -4-Ethoxy-2-pinene		1.58	MS, IR, NMR
22	<i>trans</i> -1-Ethoxy-2- <i>p</i> -menthene		0.12	MS, IR
23	4-Ethoxy-1- <i>p</i> -menthene		0.06	MS <sup>6</sup> , IR <sup>6</sup>
24	<i>cis</i> -3-Ethoxy-1- <i>p</i> -menthene		0.15	MS <sup>6</sup> , IR <sup>6</sup>
Carbonyl compounds				
16	Octanal	0.01	0.03	GLC, MS <sup>28</sup>
	Nonanal <sup>c</sup>	+	+	MS <sup>28</sup>
63	Tetradecanal	0.02		MS <sup>28</sup> , IR
	Pentadecanal	+		MS
54	Cuminyl aldehyde	0.02	+	MS, IR <sup>29</sup>
	2-Nonanone <sup>c</sup>		+	MS
	2-Decanone <sup>c</sup>	+		MS
40	Cryptone	0.5	0.4	MS <sup>30</sup> , IR <sup>30</sup>
Others				
	1,1-Diethoxyhexane <sup>c</sup>		+	MS <sup>31</sup>
	1,1-Diethoxyoctane <sup>c</sup>		+	MS <sup>31</sup>
64	Humulene monoxide	0.41	0.01	MS, IR <sup>32</sup>

<sup>a</sup> Spectrum of an authentic sample. <sup>b</sup> Hydrolysis. <sup>c</sup> Retention time was not measured on the capillary column.

Several sesquiterpene alcohols, distributed from peak 66 to 72, were detected, although many of them remained unidentified. Peak 66 was composed of two sesquiterpene alcohols one of which was identified as  $\alpha$ -copaene-11-ol. Compounds represented by peaks 69 and 72 were identified as elemol and  $\beta$ -eudesmol, respectively.

Most of the above alcohols were also found in sample B, although generally in smaller relative proportions, whereas the presence of their ethyl ethers proved to be a characteristic feature of the alcoholic angelica distillate. The most abundant oxygen-containing compound (peak 21) in sample B was identified as the ethyl ether of *trans*-verbenol (*trans*-4-

ethoxy-2-pinene). Its IR spectrum had absorptions at 3020, 1647, 1380, 1365, 1080, 810, and 770  $\text{cm}^{-1}$  corresponding to a double bond, a *gem*-dimethyl group and an ether linkage. The NMR spectrum showed signals at  $\delta$  0.84 and 1.33 (each 3 H, singlets) due to two methyls at quaternary carbons, at  $\delta$  1.70 (3 H, doublet of doublets,  $J$  1.6 and 1.6 Hz) and 5.30 (1 H, multiplet) corresponding to a methyl on a trisubstituted double bond at  $\delta$  3.79 (1 H, multiplet) due to a methine proton adjacent to oxygen and at  $\delta$  1.13 (3 H, triplet,  $J$  7 Hz) and 3.43 (2 H, quartet,  $J$  7 Hz) from an ethoxy group.  $M^+$  at  $m/e$  180 corresponds to the formula  $C_{12}H_{20}O$ . Consequently, because only one double bond was found the compound should be bicyclic. These data are consistent with a structure such as 4-ethoxy-2-pinene. The choice between the possible stereoisomers was made by comparing the chemical shift of the C-9 methyl protons with that of *cis*-verbenol ( $\delta$  1.07) and *trans*-verbenol ( $\delta$  0.87).<sup>8</sup> A smaller component (peak 18) with similar IR and mass spectra to those of component 21 was concluded to be *cis*-4-ethoxy-2-pinene. In addition to these, the ethyl ethers of the sabinene hydrates, the piperitols, the 2-*p*-menthen-1-ols and terpinenol-4, which were previously identified from a sweet marjoram distillate,<sup>8</sup> were found. According to mass spectra some of the sesquiterpene alcohols were also present as ethyl ethers.

The ethyl esters of caproic, lauric, myristic, pentadecanoic, palmitic, stearic, oleic, linoleic, and linolenic acid formed another group of compounds found only in sample B. Both these esters and the ethyl ethers are evidently formed during the preparation of the alcoholic aroma distillate.

Esters of monoterpene alcohols were notable constituents in both samples, bornyl acetate being the most abundant oxygenated component in sample A. *trans*-Verbenyl acetate, *cis*- and *trans*-carvyl acetate and bornyl isovalerate were also found. Component 39 was identified as *trans*-pinocarvyl acetate. Its mass spectrum gave a molecular weight of 194. The IR spectrum showed absorptions at 1735 and 1240  $\text{cm}^{-1}$  typical for acetates and at 3070, 1655, and 885  $\text{cm}^{-1}$  corresponding to a terminal methylene. *trans*-Pinocarveol was obtained on hydrolysis. The components giving rise to

peaks 53 and 55 were identified as *trans*-verbenyl 2-methyl-butyrate and *trans*-verbenyl isovalerate respectively. The mass spectra of both displayed the molecular peak at  $m/e$  236 and prominent peaks at  $m/e$  57, 85, and 119. Both compounds had IR absorptions at 3030, 1650, 780, and at 1735 and about 1180  $\text{cm}^{-1}$  corresponding to a trisubstituted double bond and an ester function respectively. They gave *trans*-verbenol on hydrolysis. The identification of the acid parts was based on the comparison of absorptions in the 1300–1100  $\text{cm}^{-1}$  region of the IR spectra of the esters. Besides these terpene esters, isoamyl isovalerate, heptyl isovalerate, and octyl isovalerate were found in both samples.

The musk-like odour of angelica root oil is generally attributed to the lactone of 15-hydroxypentadecanoic acid. Besides pentadecanolide, three macrocyclic lactones were found in the samples studied. The mass spectrum of compound 67 showing  $M^+$  at  $m/e$  212, base peak at  $m/e$  55 and peaks for  $M-18$ ,  $M-36$  and  $M-60$  fragments at the high mass end, closely resembled that of pentadecanolide. The IR spectrum exhibited strong absorptions at 1733 ( $C=O$ ) and 1240  $\text{cm}^{-1}$  ( $C-O$ ). The NMR spectrum had signals at  $\delta$  4.14 (2 H, doublet of doublets,  $J$  4 and 5.5 Hz) due to methylene protons adjacent to oxygen, at  $\delta$  2.39 (2 H, doublet of doublets,  $J$  5 and 6 Hz) corresponding to methylene protons adjacent to a carbonyl group, and broad signals due to methylene protons at  $\delta$  1.3–1.8. The absence of signals corresponding to methyl protons revealed that the compound has a ring structure with no side chain. The obvious molecular formula,  $C_{13}H_{24}O_2$ , allows one ring in addition to a carbonyl double bond. Accordingly, compound 67 was identified as tridecanolide. A minor component, peak 68, had very similar IR spectrum to that of tridecanolide. The mass spectrum gave a molecular weight of 226. The fragmentation pattern showed marked similarity to that of the other lactones, but some anomalous peaks were also present, *e.g.*  $m/e$  153, 171. It remained unclear whether these were caused by impurities or some structural difference. A trace compound from sample A was identified as heptadecanolide. Its mass spectrum had molecular peak at  $m/e$  268 and the fragmentation pattern was analogous to that of pentadecanolide.

Carbonyl compounds constituted less than 1 % of both samples. Nevertheless, cryptone was one of the main components in the oxygen-containing fraction.<sup>5</sup> The other aliphatic carbonyl compounds identified were octanal, nonanal, tetradecanal, pentadecanal, 2-nonanone, and 2-decanone. 1,1-Diethoxy hexane and 1,1-diethoxy octane were detected in sample B, showing that the aldehydes are present partly as acetals in the alcoholic distillate.

Three aromatic compounds, cuminyl aldehyde, cuminyl alcohol and *p*-cymene-8-ol, were conclusively identified. The mass spectrum of compound 61 closely resembled that of *p*-cymene-8-ol, displaying  $M^+$  at *m/e* 150 and the base peak at *m/e* 43. The IR spectrum had absorptions at 3400 and 1165  $\text{cm}^{-1}$  corresponding to a tertiary OH, and at 1605 and 1487  $\text{cm}^{-1}$  for the aromatic nucleus. The out-of-plane bending absorptions at 773 and 703  $\text{cm}^{-1}$  suggested *meta*-substitution. Accordingly, compound 61 was tentatively identified as *m*-cymene-8-ol. The mass spectrum of peak 70 was almost identical with that published for carvacrol.<sup>9</sup> The IR spectrum showed absorptions corresponding to a phenolic OH (3380, 1250  $\text{cm}^{-1}$ ), a *gem*-dimethyl group (1380, 1360  $\text{cm}^{-1}$ ) and a 1,2,4-substituted aromatic ring (1615, 1585, 1500, 860, 810  $\text{cm}^{-1}$ ). The spectrum, however, differed from those published for carvacrol and thymol.<sup>10</sup> It seems likely that the compound is one of the other isomers with the same substituents in the 1, 2, and 4 positions. Besides the compounds discussed above, capillary gas chromatography revealed more than hundred minor components in the samples.

The results show that the method used to isolate the angelica root oil has a substantial effect on its chemical composition. Quantitative differences between the two samples were observed in the fractions of oxygenated compounds. Furthermore, the alcohol extraction was found to produce artefacts by esterification, etherification and acetal formation.

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