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Composition of the Essential Oil of Sweet Marjoram Obtained by Distillation with Steam and by Extraction and Distillation with Alcohol—Water Mixture

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The steam distilled oil of sweet marjoram (*Majorana hortensis* Moench) and an alcoholic distillate of this herb used for flavouring liqueurs were analysed by gas chromatography, infra-red spectrophotometry, nuclear magnetic resonance and mass spectrometry. 11 monoterpene hydrocarbons, 8 sesquiterpene hydrocarbons, 10 monoterpene alcohols, 5 esters of monoterpene alcohols and 4 other compounds were identified. Additionally, 6 ethyl ethers of monoterpene alcohols and 9 ethyl esters of long-chain fatty acids were found in the alcoholic distillate. Of the 53 components identified in the sweet marjoram aroma concentrates in the present study, 35 are reported for the first time.

Sweet marjoram is obtained from *Majorana hortensis* Moench (*Origanum majorana* L.), which has for centuries been cultivated in the Mediterranean countries and nowadays in the Northern Temperate Zone as well. The commercially available herb is prepared from the dried leaves and flowers. The content of volatile oil varies between 0.5 and 3.5 % depending on the origin of the herb and many other factors.[1]

The composition of sweet marjoram oil was first investigated at the turn of the century, when Biltz [2] found it to consist of 40 % monoterpene hydrocarbons, mostly terpinene. Somewhat later, Wallach [3,4] showed that sweet marjoram contains terpinenol-4 and α-terpineol. After that no further investigations into the aroma compounds of sweet marjoram were published until the sixties. Nicoletti and Baiocchi [5] found that the oil of sweet marjoram contains monoterpene hydrocarbons, terpinenol-4, α-terpineol, linalool, linalyl acetate and *cis*-sabinene hydrate, which had not previously been identified in natural oils. Lossner [6] found *trans*-sabinene hydrate as well, and identified 6 monoterpene hydrocarbons. In the same study, gas chromatographic analysis showed that the oils of sweet marjoram originating from seven different countries were all much the same. Lossner's analysis showed that the German oil contained 1 % α-pinene, 9 % myrcene, 8 % α-terpinene + limonene, 20 % γ-terpinene, 7 % terpinolene, 9 % linalool + *trans*-sabinene hydrate, 3 % linalyl acetate, 13 % *cis*-sabinene hydrate, 23 % terpinenol-4, and 5 % α-terpineol. Ikeda *et al.*[7] analysed the monoterpene hydrocarbons in the sweet marjoram oil by gas chromatography and, in addition to those above, identified α-thujene, camphene, β-pinene, sabinene, α-phellandrene, β-phellandrene, and ocimene by their retention times.

The volatile oil from sweet marjoram grown in India differs substantially in both physical characteristics and chemical composition from that of European and American origin.[1] The following compounds have been identified in the Indian oil: carvacrol,[8] eugenol,[8,9] chavicol,[8] methylchavicol,[8] linalool,[8,9] α-terpineol,[8,9] terpinenol-4,[9] geraniol,[9] and caryophyllene.[8]

The volatile oil is commonly separated by steam distillation; the oil of sweet marjoram produced by this method is used in the flavour industry, pharmacy *etc.* In the production of alcoholic beverages, however, it is considered that a finer quality aroma is obtained if the volatile components are separated by percolation and distillation with an alcohol-water mix-

ture. This work investigates both oil separated by steam distillation and the aroma concentrate used in the preparation of herbal liqueurs. The aims of the study were to identify the aroma compounds from sweet marjoram and to investigate the effect of the different methods of separation on the aroma concentrates.

EXPERIMENTAL

Apparatus. A Hewlett-Packard 7620 A gas chromatograph fitted with a TC detector was used for analysis. The temperature of the injection block and the detector was 240 °C. Four pairs of 6 mm × 3 m stainless steel columns were packed with: 10 % FFAP on 60/80 mesh Chromosorb W AW, 5 % SE-30 on 60/80 mesh Chromosorb G, 15 % Apiezon L on 60/80 mesh Chromosorb W AW, and 5 % LAC-2R-446 on 70/80 mesh Chromosorb G AW DMCS. Peak areas were measured by an Infotronics CRS-11 HSB/42 Integrator. For the preparative work the fractions eluting at the TCD exhaust were collected in 1 mm × 20 cm glass tubes cooled with dry ice.

The IR spectra were measured with samples between plates of KBr on a Perkin-Elmer 521 spectrophotometer equipped with a beam condenser. The mass spectra were measured on a Varian CH 7 combined GLC-MS connected with a Spectro System 100 MS computer. The ionisation energy used was 70 eV, and a 2 mm I.D. × 2 m glass column packed with FFAP or SE-30 was used in the GLC.

The NMR spectra were measured on a Varian A 60 model using carbon tetrachloride as solvent and tetramethylsilane as internal standard.

Materials and procedure. The alcoholic distillate of sweet marjoram used in the investigation was produced in Alko's flavour distillery from East-European plants. The herb is percolated for three weeks with a 55 % ethanol water mixture as the first stage in the preparation of the alcoholic distillate. The percolate is distilled under reduced pressure and a fraction with the desired aroma is collected. For the analysis, the aroma compounds were separated from the alcoholic distillate by extraction into pentane. 500 ml lots of the distillate were diluted with water to 50 % alcohol, saturated with NaCl and shaken in a separating funnel with pentane. The extract was dried over Na_2SO_4 and the pentane distilled off.

The volatile oil was separated from 200 g of sweet marjoram (from the same batch of herb as that used in the preparation of the alcoholic distillate) by 2 h steam distillation. The oil was extracted from the distillate with pentane, the exract dried over Na_2SO_4, and the pentane distilled off to leave 2.2 g oil.

The sweet marjoram oil obtained by steam distillation and the pentane extract from the alcoholic distillate were first fractionated by preparative GLC on a FFAP column, and the fractions collected were in most cases further separated on a second column so that pure compounds could be collected for determining the spectra. The combined GLC-MS analysis using an SE-30 column was made directly from fractions obtained with the FFAP column.

Before analysing the sesquiterpene hydrocarbons by GLC, the steam distilled oil and the pentane extract from the alcoholic distillate were each fractionated by column chromatography. 200 μl samples were added to a 1 cm × 15 cm silica gel column (Kieselgel, 0.2 – 0.5 mm, from Merck) and the hydrocarbons were eluted with 200 ml pentane.

The components were identified by comparing their GLC retention times and spectra with those of authentic samples or with published spectra or, when reference materials were unavailable, by interpreting the spectral data.

Ledene was synthesized by dehydrating ledol with 5 % H_2SO_4, as described by Kiryalov.[10]

RESULTS AND DISCUSSION

The gas chromatogram of the steam distilled sweet marjoram oil on FFAP column is presented in Fig. 1, and that of the pentane extract from the alcoholic distillate in Fig. 2. The compounds identified are shown in Table 1 with their percentage contribution as calculated from the peak areas and identification methods.

The monoterpene hydrocarbons constituted about 30 % of the oil separated by steam distillation and about 44 % of the aroma from the alcoholic distillate. The main components, γ-terpinene and α-terpinene, were separated from the steam distilled oil by preparative gas chromatography. A direct analysis of sweet marjoram oil by combined GLC-MS using a FFAP column identified α-pinene, β-pinene, sabinene, myrcene, α-phellandrene, β-phellandrene, limonene, and terpinolene by comparing retention times and mass spectra with those of authentic samples and α-thujene using a published mass spectrum.[11] Gas chromatographic analysis of the pentane extract of the alcoholic distillate showed that the same compounds were present and in approximately the same relative proportions.

The sesquiterpene hydrocarbons formed less than 3 % of the steam distilled oil and 7.5 % of the aroma fraction of the alcoholic distillate. The same two main components dominated in

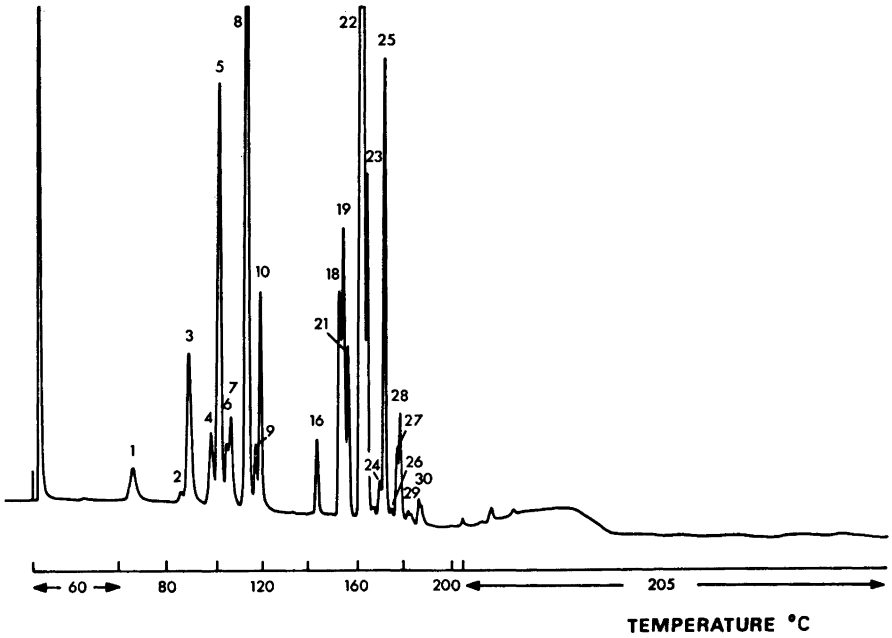


Fig. 1. Gas chromatogram of the oil of sweet marjoram separated by steam distillation. Column: 6 mm × 3 m FFAP.

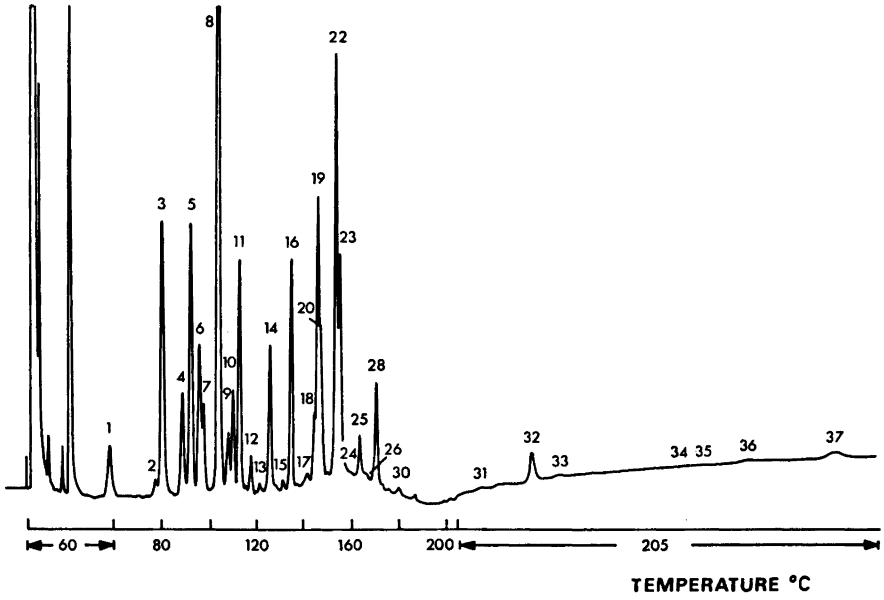


Fig. 2. Gas chromatogram of the pentane extract from the alcoholic distillate of sweet marjoram. Column: 6 mm × 3 m FFAP.

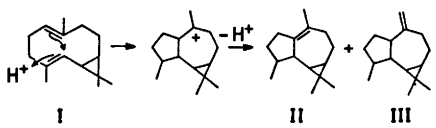
Table 1. Compounds identified in the steam distilled oil and the alcoholic distillate of sweet marjoram.

Peak No.	Compound	Steam distilled oil		Pentane extract of alcoholic distillate	
		Percentage	Evidence for identification	%	Evidence for identification
1	α-Thujene	1.0	MS[11]	1.9	GLC
	α-Pinene		GLC,MS[a]		GLC
2	β-Pinene	0.2	GLC, MS[a]	0.4	GLC
3	Sabinene	2.5	GLC, MS[a]	8.2	GLC
4	Myrcene	1.2	GLC, MS[a]	2.6	GLC
	α-Phellandrene		GLC, MS[a]		GLC
5	α-Terpinene	6.1	IR,[16] MS[11]	6.8	GLC
6	Limonene	0.6	GLC, MS[a]	3.8	GLC
7	β-Phellandrene	0.9	GLC, MS[a]	1.4	GLC
8	γ-Terpinene	14.0	IR,[16] MS[11]	21.3	GLC
	trans-4-Ethoxy-thujane				IR, MS, NMR
9	*p*-Cymene	0.7	GLC, MS[a]	1.1	GLC
10	Terpinolene	2.5	GLC, MS[a]	2.0	GLC
11	*cis*-4-Ethoxy-thujane			5.2	IR, MS, NMR
12	1-Ethoxy-2-*p*-menthene			0.7	IR, MS
13	*trans*-3-Ethoxy-1-*p*-menthene			0.2	IR, MS
14	4-Ethoxy-1-*p*-menthene			3.7	IR, MS, NMR
15	*cis*-3-Ethoxy-1-*p*-menthene			0.2	IR, MS
16	*trans*-Sabinene hydrate	1.0	IR[17] MS	5.1	IR
17	α-Copaene	+	IR[18]	+	IR
18	Linalool	3.3	GLC, MS,[a] IR[a]	0.7	GLC
19	*cis*-Sabinene hydrate	4.0	IR,[17] MS	7.5	IR
20	Linalyl acetate	0.1	GLC	3.4	GLC, IR[a]
21	*cis*-2-*p*-Menthen-1-ol	2.0	IR,[19] MS	0.2	GLC
22	Terpinenol-4	45.5	GLC, IR[a], MS[a]	10.3	GLC, IR
23	Caryophyllene	3.5	GLC, IR[a], MS[a]	6.1	GLC, IR
	trans-2-*p*-Menthen-1-ol		IR,[19] MS		
	4-Terpinenyl acetate				GLC, IR[a]
	Ethyl caprate				GLC, IR[a]
24	*trans*-Piperitol	0.3	IR,[19] MS		
	allo-Aromadendrene	+	MS[20]	+	MS
	β-Farnesene	+	MS	+	MS
	γ-Elemene	+	MS[20]	+	MS
25	α-Terpineol	6.7	GLC, IR[a], MS[a]	0.7	GLC, IR
	α-Terpinyl acetate			+	GLC, IR[a]
	α-Humulene	+	IR[18]	+	IR
26	Neryl acetate	+	GLC, MS	+	GLC, IR[a]
	Ledene	+	IR[a]	+	IR
27	*cis*-Piperitol	0.5	IR,[19] MS		
28	Bicyclogermacrene	1.2	IR, MS	2.7	IR, MS, NMR[12]
	Carvone		GLC, IR,[a] MS[a]		GLC
	Geranyl acetate		GLC		GLC, IR[a]
29	Geraniol	+	GLC, MS[a]		
30	*p*-Cymen-8-ol	0.5	IR[19]		
	Anethol		GLC, IR[a]	+	GLC, IR
	Ethyl laurate			+	GLC, MS
31	Ethyl myristate			+	GLC, IR[a]
32	Ethyl palmitate			1.2	GLC, IR[a], MS
33	Ethyl *trans*-hexadecenoate			+	IR, MS
34	Ethyl stearate			+	GLC, MS[a]
35	Ethyl oleate			+	GLC, IR[a], MS
36	Ethyl linoleate			+	GLC, IR[a], MS
37	Ethyl linolenate			+	GLC, IR[a], MS

[a] Spectrum of an authentic sample.

both samples. The larger of these was identified as caryophyllene. The other was tentatively identified as bicyclogermacrene. Its mass spectrum gave a molecular weight of 204. The IR spectrum had absorption bands at 3010, 1650, and 829 cm^{-1}, corresponding to a trisubstituted double bond. The NMR spectrum is identical with that reported by Nishimura *et al.*[12] for bicyclogermacrene in other respects, although it was not possible to resolve with certainty the cyclopropane ring multiplet from the background noise because of the small sample size available. The same minor components, ledene, α-humulene, α-copaene, β-farnesene, γ-elemene, and alloaromadendrene, were found in the hydrocarbon fractions from both samples. Ledene (II) was identified by comparing its IR spectrum with that of a sample synthesized by the dehydration of ledol.

Ledene (II) has not previously been reported to occur in natural oils. Its occurence, and that of alloaromadendrene (III), together with bicyclogermacrene (I) in the oil of sweet marjoram is in agreement with the suggestion by Nishimura [12] that bicyclogermacrene could be the biogenetic precursor of aromadendrane-type compounds. It is also possible, however, that ledene and alloaromadendrene have been formed from bicyclogermacrene during the isolation or analysis of the volatile oil.



Scheme 1.

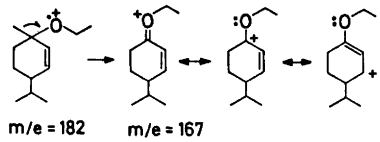
Monoterpene alcohols constituted about 65 % of the steam distilled oil and about 25 % of the aroma fraction from the alcoholic distillate. Ten alcohols were identified in the steam distilled oil: terpinenol-4, α-terpineol, linalool, geraniol, *cis*- and *trans*-sabinene hydrate, *cis*- and *trans*-piperitol, and *cis*- and *trans*-2-*p*-menthen-1-ol. Six of these alcohols, terpinenol-4, α-terpineol, linalool, *cis*- and *trans*-sabinene hydrate, and *cis*-2-*p*-menthen-1-ol were also found in the alcoholic distillate.

In the chromatogram of the pentane extract from the alcoholic distillate there was a group of peaks between the monoterpene hydrocarbons (peaks 1 – 10) and the monoterpene alcohols (starting at peak 16), all of which were absent from the chromatogram of the steam distilled oil. IR, NMR, and MS analysis showed that the peaks represented ethyl ethers of monoterpene alcohols, obviously formed during the preparation of the flavour distillate. These ethers made up about 15 % of the aroma fraction, comparable to the 25 % of the monoterpene alcohols.

The first of this group of components eluted from the FFAP column in peak 8 together with γ-terpinene, from which it could be separated using the SE-30 column. The mass spectrum revealed a molecular weight of 182 and fragments typical of monoterpenes at *m/e* 136, 121, 93. The IR spectrum exhibited the characteristic absorption of the C – H stretching of the cyclopropane ring at 3050 cm^{-1}, the typical double absorption of the *gem*-dimethyl group at 1382 and 1368 cm^{-1}, and the strong absorption band at 1070 cm^{-1} of the ether bond. The NMR spectrum contained two unsymmetrical doublet signals centered at δ 0.88 and 0.96 (each 3 H, $J = 6$ Hz) corresponding to the methyls of an isopropyl group, a 3 H singlet at δ 1.20 ($CH_3 - C - O -$), and a triplet centered at δ 1.10 (3 H, $J = 7$ Hz) and a quartet centered at δ 3.40 (2 H, $J = 7$ Hz) from an ethoxy group. The multiplet appearing at δ 0.1 – 0.5 is clearly caused by the methylene protons of the cyclopropane ring. An ether of ethanol and sabinene hydrate (4-ethoxy-thujane) would fit these data. The spectra from component 11 closely resemble those of the ether in peak 8, the main difference in NMR spectrum being that the signal from one of the methylene protons of the cyclopropane ring appears at lower field strength (δ 0.5 – 0.7) in the spectrum of component 11. It is reasonable that this proton would be less shielded if the ethoxy group were *cis* to the cyclopropane ring. Accordingly, the ether in peak 8 is tentatively identified as *trans*-4-ethoxy-thujane and peak 11 as the corresponding *cis* compound.

The absorption bands at 3020, 1635, and 730 cm^{-1} in the IR spectrum of compound 12 indicate the presence of a double bond, which is most probably *cis* disubstituted. The absorptions at 1380 and 1360 cm^{-1} reveal the typical double peak of the *gem*-dimethyl group. The molecular peak appears in the mass spectrum at *m/e* 182. A structure derived from 2-*p*-

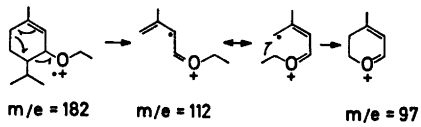
menthene is compatible with these data. The base peak in the mass spectrum is *m/e* 167 (M − 15). With the methyl and ethoxy groups on the same carbon, cleavage at the bond *β* to oxygen would result in a stable (M − 15) ion.



Scheme 2.

The (M − 45) peak too is larger (29 %) here than in the spectra of the other ethers found is sweet marjoram oil. The suggested structure favours this fragmentation as well, since cleavage of the ethoxy group would lead to the formation of a tertiary allylic carbonium ion.

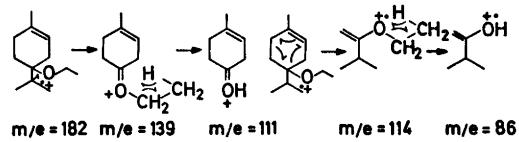
The IR spectrum of compound 13 displayed absorptions at 3010, 830, 1375, 1360 and 1080 cm^{-1}, corresponding to a trisubstituted double bond, a *gem*-dimethyl group, and a C − O bond. The mass spectrum showed the molecular ion peak at *m/e* 182 and the base peak at *m/e* 112. Considering only those ethyl ethers derived from the alcohols already identified in the aroma of sweet marjoram, the ethyl ether of piperitol has the most likely structure to accomodate these data. Cleavage of the ring at the bonds *β* to oxygen and the double bond would lead to the formation of the resonance stabilized *m/e* 112 ion. The base peak in the mass spectrum of piperitol is at *m/e* 84, which have been shown to occur by a corresponding mechanism.[13] Loss of a methyl group from the *m/e* 112 ion would produce a fragment of *m/e* 97, which is in fact the second most abundant ion (45 %) in the spectrum.



Scheme 3.

The IR and mass spectra of compound 15 closely resemble those of compound 13. According to the gas chromatographic behaviour of corresponding alcohols, peak 13 was tentatively identified as the ethyl ether of *trans*-piperitol (*trans*-3-ethoxy-1-*p*-menthene) and peak 15 as the *cis*-compound.

The mass spectrum of component 14 revealed that its molecular weight is also 182. Absorptions in the IR spectrum at 3010, 835, 790, 1385, 1365 and 1070 cm^{-1} were characteristic for a trisubstituted double bond, a *gem*-dimethyl group, and a C − O bond. The NMR spectrum of component 14 had a doublet centered at *δ* 0.87 (6 H, $J = 6.5$ Hz) corresponding to an isopropyl group, a signal at *δ* 1.64 caused by methyl adjacent to a double bond, a multiplet centered at *δ* 5.18 from a proton of the double bond, a triplet centered at *δ* 1.08 (3 H, $J = 7$ Hz) and a quartet centered at *δ* 3.28 (2 H, $J = 7$ Hz) corresponding to an ethoxy group. These data suggest a structure derived from 1-*p*-menthene. The (M − 15) peak in the mass spectrum is only 3 %, while the (M − 43) peak is 52 %. Attachment of the ethoxy group to C-4 would facilitate elimination of the isopropyl group. The *α*-cleavage and rearrangement of hydrogen after *β*-cleavage, which is usual for ethers,[14] would also rationalize the formation of the fragment *m/e* 111 (30 %) as well as the fragments *m/e* 114 (29 %) and 86 (64 %), when the ring cleaves at the bonds *β* to the double bond. The peaks *m/e* = 111 and 86 are also prominent in the mass spectrum of terpinenol-4. Accordingly, component 14 was identified as 4-ethoxy-1-*p*-menthene.



Scheme 4.

The following five monoterpene alcohol acetates were identified in the pentane extract from the alcoholic distillate of sweet marjoram by comparing their retention times and IR spectra with those of authentic samples: linalyl acetate, terpinenyl-4 acetate, *α*-terpinyl acetate, neryl acetate and geranyl acetate. Together these esters made up less than 5 % of the aroma fraction, with linalyl acetate making the largest contribution. The amount of esters found in the steam distilled oil was very low, although linalyl acetate, neryl acetate and geranyl acetate could be identified by GLC.

The only carbonyl compound found in sweet marjoram oil was carvone, which constituted

about a quarter of peak 28. The carvone from the alcoholic distillate formed only a small part of peak 28, but still lent its characteristic odour to this fraction.

The aromatic compounds *p*-cymen-8-ol, *p*-cymene and anethol were found as minor components in the steam distilled oil.

Nine long-chain fatty acid ethyl esters were found in the alcoholic distillate of sweet marjoram. Together they constituted less than 2 % of the aroma fraction of this distillate, and were completely absent from the steam distilled oil. Ethyl caprate, laurate, myristate, palmitate, oleate, linoleate, and linolenate were identified by comparing their retention times, IR and mass spectra with those of authentic samples. The IR spectrum of compound 33 is very similar to those of other unsaturated ethyl esters except that it exhibits the additional feature of the absorption band at 965 cm^{-1}, which is characteristic for a *trans*-disubstituted double bond. The molecular peak in the mass spectrum appears at $m/e = 282$ and the base peak at $m/e = 88$, the latter being characteristically formed in the fragmentation of ethyl esters as a consequence of the McLafferty rearrangement. This implies that components 33 is an ethyl *trans*-hexadecenoate isomer. The position of the double bond could not be settled by the available data.

Clearly the ethyl esters were formed by the action of the ethanol on the herb during the preparation of the alcoholic distillate, and their occurrence suggests the presence of the corresponding acids in sweet marjoram.

The results show that there are marked differences in the composition of the aroma between the sweet marjoram oil obtained by steam distillation and that produced by alcoholic distillation. With the exception of *cis*- and *trans*-sabinene hydrate, the proportion of monoterpene alcohols is clearly lower in the alcoholic distillate than in the steam distilled oil. Lossner [6] claims that *cis*-sabinene hydrate is especially important in the aroma of sweet marjoram. The proportion of mono and sesquiterpene hydrocarbons and esters of monoterpene alcohols is higher in the alcoholic distillate than in the steam distilled oil.

More interesting than these quantitative differences is the formation of new aroma compounds, such as ethyl ethers of monoterpene alcohols and ethyl esters of long-chain fatty acids, during the preparation of the alcoholic distillate. The newly-formed esters are present at quite a low concentration and have a relatively high odour threshold,[15] so that their contribution to the aroma of the alcoholic distillate is slight. The ethyl ethers of the monoterpene alcohols, however, made up about 15 % of the aroma fraction, and by smelling the aroma components as they eluted from the gas chromatograph it was found that many of these ethers had a relatively strong odour, which differed from that of the corresponding alcohols. It is probable, therefore, that the ethers contribute to the aroma of the alcoholic distillate from sweet marjoram.

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