

Analysis of Basil Oils by GC-MS Data Bank

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The genus *Ocimum basilicum* L. is extremely widespread through the world and its essential oils have acquired commercial significance. Native to Asia and the tropical regions, this labiate spread rapidly through Europe, particularly in Southern France, Italy, Hungary and Spain, the USA, south and north Africa, and Reunion Island. Table I recapitulates the research work devoted to these essential oils.

According to Lawrence (1978) several types of oils can be distinguished depending on their geographical origin. European essential oils from France, Italy, Bulgaria, Hungary and South Africa can be determined by their approximately equal linalool and methyl chavicol proportions. The so-called exotic essential oils that originate from Reunion Island, the Comoro Islands, Madagascar, Thailand and Vietnam are rich in methyl chavicol (80% to 90%). Tropical essential oils (India, Pakistan, Haiti, Guatemala) have a higher methyl cinnamate content than the others. Essential oils distilled in the USSR and north Africa (Egypt, Morocco) are rich in eugenol.

Finally, some oils coming from Nigeria are said

to have a high thymol content (19% to 32%) (Dro 1984). An oil of Vietnamese origin has recently been found containing 70% citral (Van Phiet Hoang 1980). But in these last two cases, it is alleged to be another variety *Ocimum gratissimum* L.

The present study was undertaken in order to achieve the following objectives:

- to test our data bank containing mass spectra and Kovats indices, to feed it with compounds as yet absent from the file and possibly find new constituents
- to demonstrate the usefulness of GC-MS analysis in combination with positive chemical ionization and mass chromatography (reconstructed mass chromatogram of selected ions)
- to carry out a gas chromatography analysis of these samples under standard conditions in order to detect qualitative and quantitative differences
- to propose, with the aid of our results and those of the literature, a rational classification scheme based on statistical methods. This latter study will be presented in another paper.

Experimental

Gas chromatography analyses were carried out on an Intersmat IGC 15 gas chromatograph equipped with a fused silica capillary column (50 m x 0.2 mm) wall-coated with 20M Carbowax.

A VG 70-70 F mass spectrometer equipped with a combined EI/CI source and a Perkin Elmer SIGMA 3 gas chromatograph was used for GC-MS analysis. Samples were injected on a fused silica column (50 m x 0.2 mm) coated with FFAP using 1:40 split ratio. Data acquisition and reprocessing were performed by a VG 2035 system.

In electron impact mode, the electron energy was set at 70 eV for a trap current of 200 μ A.

In positive chemical ionization mode ammonia was used as reagent gas at a housing pressure of 2×10^{-5} Torr, which corresponds to 0.2–0.3 Torr, inside the source. In both ionization modes the source temperature was 180°C and the interface line temperature was 250°C.

Results and Discussion

EI and Positive CI GC-MS Analysis of Basil Essential Oils

In a previous paper we had set out the general principles concerning the design and the operation of the SPECMA bank, as well as exemplified some applications to the identification of the main components of geranium essential oils (Vermin et al. 1983).

The fundamental identification criteria of a compound require knowledge of its molar mass and its mass spectrum. The investigator must use the combined techniques of electron impact mass spectrometry along with positive or negative chemical ionization, but few examples can be found in this field (Anonymous 1981; Bruins 1979, Hendriks and Bruins 1980).

The use of these techniques and that of selected ions mass fragmentometry yield interesting information as to the composition of essential oils of various origin, as shown by the following results that concern basil oils from Yugoslavia and Madagascar. The chromatograms reconstructed from the total ion current are reported in figure 1.

In Table II, the retention indices and mass spectral data (EI and (NH₃) positive CI) of the detectable constituents of these oils are given. In the first column, we indicate the peak number and in the second column is listed the scan number corresponding to each chromatography peak. The peaks are numbered consecutively in order of their retention times. The retention

times were found to be reproducible to 5 seconds (corresponding to 2 to 3 scans) over a long period of time.

A simple linear relationship was found to exist between the Kovats index for a particular compound and its scan number at peak maximum. For the polar column, the relationship was found to be

$$IK_p = (0.335 \times S + 896.5) + S \quad [I]$$

where IK_p is the Kovats Index and S is the scan number (Table II, column 4). Equation [I] was established on the basis of ten standard samples whose Kovats indices were measured on the same column using the classical Kovats method—comparison with linear alkanes (See Table III).

The scan numbers obtained in (NH₃) positive CI are indicated in brackets in Table II. The two sets of scan numbers have a simple linear relationship. The main fragments obtained in EI are listed in decreasing order of intensity in the fifth column (the first one is always the base peak).

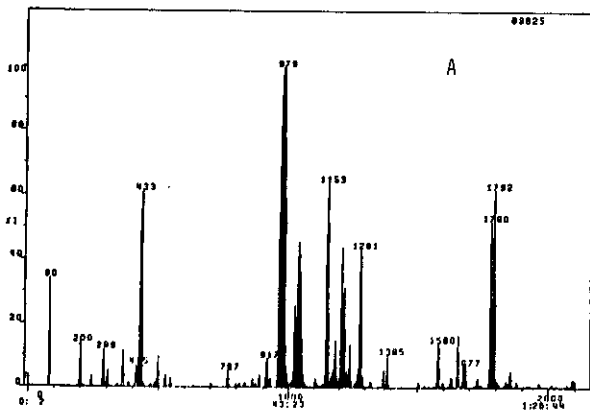
In (NH₃) positive CI the protonated molecular ion (M+H)⁺, the adduct ion (M+NH₃)⁺ and the base peak (100%) are listed in Table II, columns 6, 7 and 8, respectively. The protonated molecular ion is the base peak for all the monoterpenes, (except for γ -terpinene) and for the sesquiterpenes (except for the calamenene, sesquiterpinic epoxides and alcohols).

Terpinic ketones (fenchone, α -thujone, camphor), fenchyl and bornyl acetates, cis and trans-methyl cinnamates, most of the sesquiterpenes, methyl eugenol, anisaldehyde and eugenol all give a more or less important adduct ion corresponding to (M+NH₃)⁺. It is the base peak in the case of the ketones listed above.

Figure 2 shows the pathway formation of this ion in the case of oxygenated compounds.

The GC-MS analyses in positive CI with isobutane as reagent (i-C₄H₁₀) have also been carried out. They were not reproduced as they do not contribute anything more, if not less, than those carried out in PCI (NH₃). Indeed, the protonated molecular ion (M+H)⁺ is seldom the base peak, except for fenchone, camphor and methyl chavicol.

The SPECMA bank enabled this identification by the input of data such as the molar mass, the reduced spectrum which consists of the 2 to 25 most intense peaks and the Kovats index on the FFAP column. By way of examples, the searches for β -bourbonene, cis- α -bergamotene, methyl chavicol (estragol) and spathulenol are listed in figures 3, 4, 5 and 6.



SPECTRE PROPOSE :

M/E	I%
161.0	29
123.0	56
81.0	100
80.0	74

IKA = 930
IKP = 0

COMPOSES POSSIBLES :

Composé numéro : 438

BETA BOURBONENE FMO CEO
C15 H24 = 204 RN = 5208-59-3
IKA = 930 IKP = 1520
REF = 1: 1
Masse amort. = 40 ; m/e 28 et 32 absentes ; Fonction 17
81(100)
191(2) 161(30) 123(44) 105(12) 93(9) 91(10)
80(72) 79(22) 55(11) 41(20)
+++++ DI = 1126 +++++

Composé numéro : 437

ALPHA BOURBONENE FMO CEO
C15 H24 = 204 RN = 5208-58-2
IKA = 920 IKP = 1510
REF = 1: 1
Masse amort. = 40 ; m/e 28 et 32 absentes ; Fonction 17
81(100)
161(26) 123(40) 80(70) 79(29) 77(18) 44(20)
41(27) 40(24)
+++++ DI = 1935 +++++

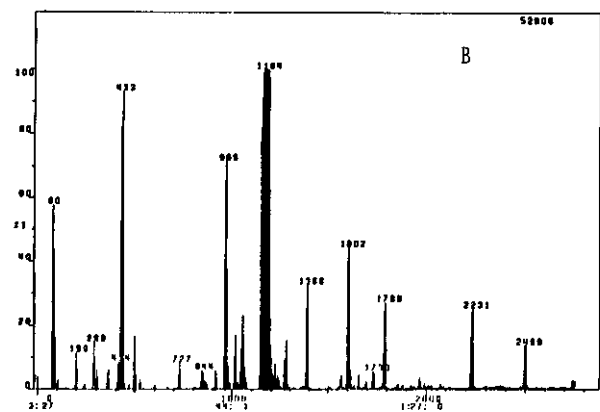


Figure 1. The total ion chromatograms (TIC) for basil essential oils: A (Yugoslavia), B (Madagascar)

Figure 3. Search for beta-bourbonene in basil (Yugoslavia)

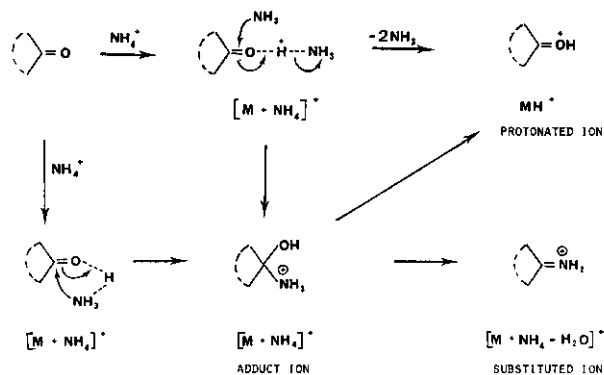


Figure 2.

For the two sesquiterpinic compounds, the computer points to two possible isomers. However, the Kovats indices and the fit parameter permit one to choose the correct isomer.

In all cases, the identification was confirmed by visual comparison of the unknown spectrum with the reference spectrum when the latter was available in the file. The mass spectra library (EPANBS) of the VG data systems connected to the mass spectrometer permits to find certain compounds. However, the amount of fits given by this library was quite limited, particularly 1,8-cineole, 1-octen-3-ol, fenchyl acetate, linalool, methyl salicylate and most sesquiterpinic compounds have not been identified.

Questions marks show when the identification was doubtful or if it could not be made by comparison with the reference spectrum.

Table I. Summary of Research Work on Basil Essential Oils of Different Origin

Origin	Main components ^{a)}						Authors
	1	2	3	4	5	6	
Reunion Island	4.6	-	87.8	-	traces	-	Lawrence, 1971
Thailand	?	0.5	88.2	0.1	-	0.3	Lawrence, 1972, 1980
Bulgaria	?	50-60	5	?	?	3	Georgiev & Genov, 1973
France	3.96	39.10	23.2	0.5	0.8	6.60	Zola & Garnero, 1973
France	2.45	40.72	23.79	0.34	?	5.90	Peter & Remy, 1978
Italy	5.15	43.80	31.8	0.16	0.49	3.40	Zola & Garnero, 1973
Morocco	12.6	41.90	2.6	traces	0.07	19.20	Zola & Garnero, 1973
Egypt	8.38	37.40	30.86	?	?	0.93	Karaway et al., 1974
Egypt (Delta)	6.0	45.55	26.56	0.25	-	5.90	Peter & Remy, 1978
Egypt (Fayoum)	13.0	48.09	3.04	-	-	9.45	Peter & Remy, 1978
Comoro Islands	5.8	1.16	85.76	0.05	-	0.74	Peter & Remy, 1978
Comoro Islands	2.0	0.7	87.8	-	1.6	0.5	Lawrence, 1980 ^{b)}
Reunion Island	2.3	-	85.6	-	1.5	0.75	Conan, 1977
India	-	10-28	68-87	-	-	-	Gulati et al., 1977
South Africa	6.12	54.37	2.38	0.34	-	12.19	Peter & Remy, 1978

^{a)} 1 = monoterpenes + *p*-cymene, 2 = linalool, 3 = methyl chavicol, 4 = *trans* methyl cinnamate, 5 = methyl eugenol, 6 = eugenol

^{b)} The following sesquiterpinic compounds have been identified in an essential oil from Comoro Islands : cyclosativene, α -cubebene, δ -elemene, β -cubebene, bicycloelemene, β -bourbonene, *cis*- α -bergamotene, isocaryophyllene, *trans*- α -bergamotene, β -elemene, α -gualene, α -humulene, γ -muurolene, α -amorphene, δ -gualene, α -farnesene, α -selinene, ϵ -bulgarene, β -selinene, δ -cadinene, calamenene, ledene, α -muurolene, 2-*epi*- α -cedrene, β -cedrene, γ -gurjunene, bibicyclgermacrene, D germacrene.

Table II. Electron Impact and Positive Chemical Ionization GC-MS Analysis with Ammonia of Basil Essential Oils from Madagascar (M) and Yugoslavia (Y)

Peaks N°	Scans (S) ^{a)}		I _K _P ^{b)}	EI ^{c)}	PCI ^{d)}		Base Peak	Identification ^{e)}	Origin
	EI	PCI (NH ₃)			M+H ⁺	M+NH ₄ ⁺			
3	200	(224)	1030	93, 92, 77, 91	137	154	134	α-Pinene	M, Y
4	240	(264)	1057	93, 121, 79	137	-	137	Camphene	M, Y
5	290	(316)	1085	93, 69	137	154	137	β-Pinene	M, Y
6	305	(332)	1100	93, 77, 91	137	-	137	Sabinene	M, Y
7	-	(368)	1112	-	137	-	137	δ-3-Carene	Y
8	362	(390)	1137	93, 41, 69	137	154	137	Myrcene	M, Y
9	-	(412)	1156	-	137	-	137	α-Terpinene	Y
10	415	(446)	1172	68, 93, 67	137	154	137	Limonène	M, Y
11	430	(455)	1182	43, 81, 71, 108	155	172	155	1,8-Cineole	M, Y
12	435	(463)	1185	93	137	154	137	β-Phellandrene	M, Y
13	470	(501)	1210	93, 79, 77	137	154	137	<i>cis</i> -β-Ocimene	M, Y
14	-	(521)	1222		137	-	94	γ-Terpinene	Y
15	497	(526)	1227	93, 79, 80, 77	137	traces	137	<i>trans</i> -β-Ocimene	M, Y
16	526	(552)	1246	119, 134, 91	(134)	-	119	<i>para</i> -Cymene	M, Y
17	-	(575)	1255	-	137	154	137	Terpinolene	Y
20	728	(754)	1380	81, 69	153	170	170	Fenchone	M
21	768	(791)	1410	81, 110, 68	153	170	170	α-Thujone	Y
24	811	-	1436	57, 43 ≡ 72		-		Oct-1-en-3-one	M, Y
25	-	(851)	1442	-	137	-	137	<i>cis</i> -Allo-ocimene	Y
26	830	(882)	1450	105, 161, 119	205	-	205	α-Cubébene	Y
27	845	(875)	1458	81, 43, 80	-	214	137	Fenchyl acetate	M
28	-	(898)	1475	-	137	-	137	<i>trans</i> -Allo-ocimene (mixture)	Y
28 ^a	860	-	1468	43, 56, 70, 83				Octyl acetate ?	M, Y
29	890	-	1488	161, 119, 105				α-Copaene	Y
30	916	(945)	1506	95, 81, 108	153	170	170	Camphor	M, Y
31	938	(960)	1520	81, 80, 123, 161	205	-	205	β-Bourbonene	Y
32	963	(985)	1537	71, 41, 93, 55	(154)	-	137	Linalool	M, Y
33	972	-	1543	161, 93, 105				β-Gurjunene	M

Table II (continued)

Peaks N°	Scans (S) a)		I _K ^{b)}	EI ^{c)}	PCI ^{d)}		Base Peak	Identification ^{e)}	Origin
	EI	PCI (NH ₃)			M+H ⁺	M+NH ₄ ⁺			
34	978	-	1543	56, 55, 41 ≡ 43				n-Octanol	M
35	991	-	1556	93, 71, 41, 43			137	Linalyl acetate (mixture)	Y
36	1008	(1024)	1567	93, 119, 41 ≡ 69	205		205	cis-α-Bergamotene	Y
37	1014	(1030)	1571	105, 119	205		205	β-Guaiene ?	Y
38	1015	(1040)	1571	81, 80	153	170	137	Fenchol	M
39	1018	(1050)	1573	161, 120, 105	205	-	205	β-Ylangene ? (mixture)	Y
40	1025	(1056)	1577	95, 43, 93, 136	-	214	137	Bornyl acetate	M, Y
41	1037	(1062)	1586	93, 119, 41 ≡ 69	205	-	205	trans-α-Bergamotene	Y
42	1043	(1078)	1590	81, 93	205	222	205	β-Elemene	M, Y
43	1050	(1076)	1595	71, 93, 111	(154)		137	Terpinen-4-ol	M, Y
	1054	-	-	93, 119				Bergamotene	M
44	1058	(1086)	1600		205	222	205	C ₁₅ H ₂₄	Y
45	1068	(1097)	1607	93, 69, 41, 133	205	222	205	β-Caryophyllene	M, Y
46	-	(1104)	1611	161, 105	205	-	205	C ₁₅ H ₂₄	M, Y
47	-	(1143)	1638		205	-	205	C ₁₅ H ₂₄	Y
48	-	(1149)	1641	-	205	-	205	C ₁₅ H ₂₄	Y
49	1149	(1178)	1660	148, 147	149	166	148	Méthyl chavicol	M, Y
50	1169	(1189)	1674	69, 41 ≡ 93	205	222	205	trans-β-Farnesene	Y
51	1183	(1200)	1687	59, 93, 81, 43	(154)		137	α-Terpineol	M, Y
					205	-	205	(mixture with C ₁₅ H ₂₄)	
52	1187	(1203)	1690	95	(154)	-	137	Borneol	Y
53	1203	(1225)	1696	93, 105, 79, 81 69, 41	205	222	205	C ₁₅ H ₂₄ Néral	Y M
54	1210	(1238)	1701	161, 105	205	traces	205	Germacrene D	M, Y
55	1217	(1250)	1706	107, 93, 108, 105	205	traces	205	Eremophyllene ?	M, Y
56	1221	(1253)	1708	93, 81, 105, 107	205	222	205	C ₁₅ H ₂₄	Y
57	1227	(1258)	1712	105, 121	205	222	205	C ₁₅ H ₂₄	M
	1230	(1263)	1713	93, 81, 105, 189	205	222	205	C ₁₅ H ₂₄ ?	Y
58	1236		1718	69, 41				Geranial	M
59	1240	(1274)	1721	121, 93	205	-	205	γ-Elemene	Y

Table II (continued)

Peaks N°	Scans (S) a)		IR _p b)	EI c)	PCI d)		Base Peak	Identification e)	Origin
	EI	PCI (NH ₃)			M+H ⁺	M+NH ₄ ⁺			
60	1270	(1295)	1741	69, 41, 43	-	(154)	137	Geranyl acetate	M, Y
61	1280	(1310)	1747	161, 105	205	222	205	γ-Cadinene	M, Y
62	1288	(1319)	1753	69, 93, 41 148, 147	205	222	205	β-Bisabolene (+ <i>cis</i> -anethole)	M, Y
63	1296	-	1758	120, 152				Methyl salicylate	M
64	1319	(1345)	1773	105, 161	205	222	205	α-Muurolene	Y
65	1324	-	1775	69, 41				Nerol	Y
66	1364	(1383)	1804	148, 147	149	-	149	<i>trans</i> -Anethole	M
67	1371	(1398)	1810	159	203		133	Calamenene	M, Y
68	1385		1817	69, 41				Geraniol	M, Y
69	-	(1523)	1894	-	203		203	C ₁₅ H ₂₂	M
70	1505		1897	82, 71, 43, 67				Hexenyl ester ?	Y
71	1527	(1539)	1912	131, 103, 162	163	180	180	<i>cis</i> -Methyl cinnamate	Y
72	1565		1937	41, 43, 79, 93	221	-	203	Caryophyllene oxide	M
73	1580	(1597)	1947	43, 81, 59, 189	205	traces	205	Humulene oxide ?	Y
74	1600	(1610)	1960	178, 163, 147	179	196	196	Methyl eugenol	M, Y
75	1612	(1623)	1968	135, 136, 77	137	154	137	Anisaldehyde	M
76	1630	(1645)	1980	69, 41, 93, 43			205	Nérolidol	M, Y
77	1635	-	1984	109, 43, 138					M
78	1655	(1674)	2000	161, 119, 179	205		205	C ₁₅ H ₂₄	M, Y
79	1665	-	2006	121, 77, 150, 91				<i>para</i> -Methoxyphenyl acetaldehyde ?	M
80	1677	(1685)	2010	131, 103, 162	163	180	180	<i>trans</i> -Methyl cinnamate	Y
81	1679	(1694)	2013	175, 190	191		191	?	M
82	1684	(1698)	2016	43, 69, 109			205	Ledol	Y
83	1694		2023	69, 68, 41, 93				?	M, Y
84	1730	(1740)	2045	43, 41, 205, 119	221		203	Spathulenol	M, Y
85	1762	-	2068	121, 164, 91, 77				<i>para</i> -Methoxyphenyl propan-2-one ?	M
86	1780	(1787)	2080	164, 149, 131	165	182	164	Eugenol	M, Y
87	1788	(1802)	2085	161, 204	(222)	-	205	T-Cadinol	M, Y
88	1840	(1849)	2120	69, 43, 109, 119	(222)	-	205	?	Y

Table II (continued)

Peaks N°	Scans (S) ^{a)}		IK _P ^{b)}	EI ^{c)}	M+H ⁺	PCI ^{d)}		Base Peak	Identification ^{e)}	Origin
	EI	PCI(NH ₃)				M+H ⁺	M+NH ₄ ⁺			
89	1853	(1863)	2130	59, 149	(222)		205	β-Eudesmol	Y	
90	1855	-	2130	121, 43, 59, 95				?	M	
91	1856	(1884)	2130	95, 121, 43	(222)		205	α-Cadinol	Y	
92	1880	-	2147	43, 81, 71				?	M	
93	1923	-	2175	164, 205 41, 43, 69, 68, 93				Acetyl eugenol + Farnesyl acetate	M	
94	1931	-	2180	43, 93, 208				?	M	
95	1938	-	2185	135, 41, 43, 93, 205				?		
96	1964	-	2203	134, 133, 107				Chavicol	M	
97	1971	-	2207	83, 41 (224)				?	M	
98	1996	-	2221	69, 41, 81				Farnésol	M	
99	2015	-	2236	133, 93, 41, 43				?	M	
100	2028	-	2245	162, 161, 109, 124				?	M	
101	2072	-	2274	41, 71, 81, 43				C ₁₅ H ₂₄ O	M	
102	2088	-	2285	55, 70, 41, 83				?		
103	2230	(2196)	2380	162, 161, 131				para-Methoxy cinnamaldehyde ?	M	
104	2301	-	2426	121, 164, 108				Anisy derivative	M	
106	2500	-	2560	121, 164, 108				para-Methoxy cinnamyl alcohol ?	M	

a) We indicate the scan numbers recorded with VG 70-70 at 70 eV in electron impact and in brackets are given the corresponding numbers in positive chemical ionization (the blank spaces mean that the corresponding spectra could not be acquired).

The analyses were carried out by means of a Sigma 3 Perkin Elmer system in conjunction with the mass spectrometer, on a FFAP quartz capillary column (50 m x 0.2 d.i.)

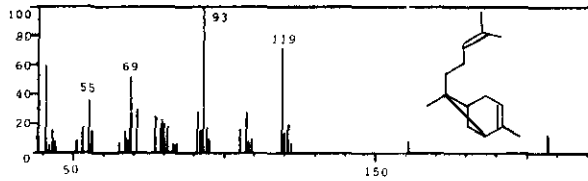
b) Kovats indices were computed from the electron impact scan numbers (S) with the aid of a formula based on ten reference compounds :

$$IK_P = (-0.335 \times S + 896.5) + S$$

c) We give the base peak and in decreasing order of intensity the main fragment(s)

d) In the case of ammonia positive chemical ionization we give the peak M+H⁺, M+NH₄⁺ and the base peak. When the ion in M+H⁺ is not visible, we indicate in brackets the molecular peak we observed.

e) This identification was carried out thanks to our SPECMA Bank (Essential oil option) by inputting for each compound : the molar mass, Kovats indice on polar column (FFAP) and the main peaks with their intensity (up to 25 peaks). Doubtful identifications resulting from the absence from the file of the reference spectrum or from too great a dissimilarity index are indicated by a ?.



SPECTRE PROPOSE :

M/E	I%
119.0	71
93.0	100
71.0	30
69.0	53
55.0	36
41.0	59

IKA = 1008
IKP = 0

COMPOSES POSSIBLES : 2

Composé numéro : 427

CIS ALPHA BERGAMOTENE FMO CEO
C15 H24 = 204 RN = 0-0-0

IKA = 1020 IKP = 1570

REF = 1: 2

Masse amort. = 40 ; m/e 28 et 32 absentes ; Fonction 17

93(100)	119(80)	107(22)	91(25)	79(20)	77(20)	69(50)
	55(30)	41(50)				

++++ DI = 1936 +++++

Composé numéro : 428

TRANS ALPHA BERGAMOTENE FMO CEO
C15 H24 = 204 RN = 0-0-0

IKA = 1040 IKP = 1590

REF = 1: 1

Masse amort. = 40 ; m/e 28 et 32 absentes ; Fonction 17

93(100)	119(85)	107(27)	105(20)	91(23)	79(23)	77(20)
	69(46)	55(30)	41(50)			

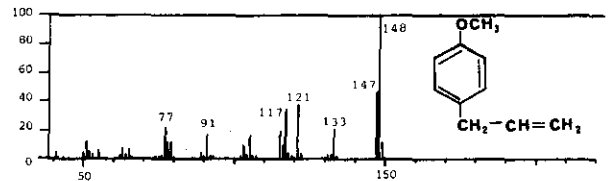
++++ DI = 2136 +++++

Figure 4. Search for cis- α -bergamotene in basil (Yugoslavia)

Scrutiny of the last column of Table II reveals marked qualitative differences in the composition of these two essential oils. The oil from Yugoslavia can be differentiated from the Malagasy oil by the occurrence of the following compounds (unidentified in Malagasy oil):

α and γ -terpinenes
terpinolene
3-octanone
 α -thujone
 α -cubebene
 α -copaene
 β -bourbonene
linalyl acetate
guaiane
cis and trans-methyl cinnamates

terpinen-4-ol
trans- β -farnesene
 α -terpineol
borneol
D germacrene
 γ -elemene
 α -muurolene
 β -eudesmol
 α -cadinol



SPECTRE PROPOSE :

M/E	I%
148.0	100
147.0	45
133.0	20
121.0	35
117.0	30
91.0	18
77.0	20

IKA = 0
IKP = 0

COMPOSES POSSIBLES : 1

Composé numéro : 143

ESTRAGOLE FM2411 CE184
C10 H12 O = 148 RN = 140-67-0

IKA = 1180 IKP = 1650

REF = 0: 756

Masse amort. = 20 ; m/e 28 et 32 absentes ; Fonction 17

148(100)	149(15)	147(54)	133(26)	121(38)	117(47)	105(16)
	91(18)	81(8)	79(8)	65(1)	59(2)	55(6)
	41(4)					

++++ DI = 1024 +++++

Figure 5. Search for estragole (methyl chavicol) in basil (Madagascar)

The oil from Madagascar can be distinguished from the previous one by the presence of fenchone, fenchyl acetate, n-octanol, methyl salicylate, trans-anethole, caryophyllene oxide, anisaldehyde and a certain number of para-methoxylated aromatic compounds such as para-methoxy cinnamaldehyde and the corresponding alcohol. The presence of an ester, conceivably cis-3-hexenyl acetate ($IK_p = 1300$) is also a characteristic of this oil. These differences involve different biogenetic processes in both cases.

These analyses have been extended to essential oils from Pakistan, the Comoro Islands, Vietnam, Egypt and Bulgaria. Except for the last two whose composition is to be compared with Yugoslavian oil, these oils exhibit a composition very

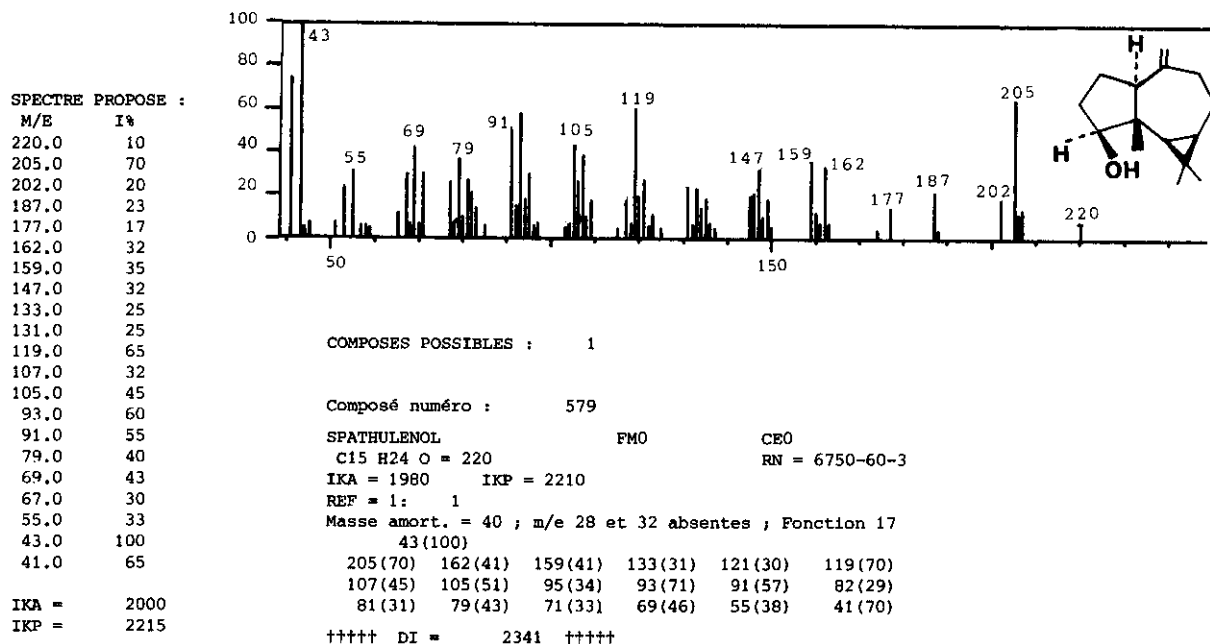


Figure 6. Search for spathulenol in basil (Madagascar)

close to that of Malagasy oil. However, one should note the presence of certain compounds that were not identified from the previous ones, such as that of menthol approximately (0.15% in Vietnamese oil), para-methyl anisole, benzyl acetate, benzyl benzoate and benzyl salicylate in the oils from the Comoro Islands.

The composition of these various oils reported in Tables IV and V is a clear indication of these differences.

GC-MS Reconstructed Specific Ion Chromatograms in NH₃ Positive CI Mode of Basil Essential Oils

The differences in composition between the oils of European origin and exotic oils are even more obvious in the analysis of different fractions by examining the reconstructed mass chromatograms for ions at m/z 137, 149, 153, 155, 170 and 205 which all correspond to the protonated ions (M+H)⁺ except for camphor which gives an adduct ion (M+NH₃)⁺ at m/z 170.

The ion current of m/z 137 enables the selective separation in these oils of monoterpenes, 1,8-cineole and certain monoterpinic alcohols.

1,8-Cineole is selected in Malagasy oil by ion m/z 155. Ion m/z 170 allows separation and dosage of fenchone, camphor and fenchol in the very same oil. Methyl chavicol and trans-

anethole can be positioned by ion m/z 149. Finally, ion m/z 205 provides an overall view of sesquiterpinic compounds. In that case, mass chromatography of selected ions is more effective and rapid than separation by silica gel chromatography, in the course of which isomerization can occur. The best known cases are those of D germacrene which is converted to γ -cadinene, δ -cadinene, γ -muurolene and α -muurolene (Yoshihara et al 1969), and of caryophyllene epoxide which isomerizes to sesquiterpinic alcohols (Garnero et al 1981).

By way of example, we compare in figure 7, the monoterpinic (+ 1,8-cineole) and sesquiterpinic fractions of basil oils from Yugoslavia and Madagascar. This brings out the greater complexity of the sesquiterpinic fraction of Yugoslavian oil, as shown in Table VI.

The presence of a certain number of these sesquiterpenes (α -copaene, β -elemene, β -caryophyllene, humulene, D germacrene, γ -cadinene) and sesquiterpinic alcohols (T-cadinol, α -cadinol, spathulenol) has also been reported in other essential oils such as vervain (*Verbena officinalis*) from Provence, France (Buil et al. 1981) and more recently clary sage (Maurer and Hauser 1983). A biogenetic process based on farnesyl pyrophosphate isomers (cis, trans-2,6 and trans, trans-2,6) has been proposed (Buil et al. 1981).

Table IV. Composition of Some Essential Basil Oils of Various Origin^{a)}

Compounds	Peaks N*	B	C	E	F	M	P	V	Y
Monoterpenes + <i>p</i> -cymene	(See Table 5)	1.0	2.78	3.35	1.1	1.08	2.21	1.7	3.75
1,8-Cineole	11	4.6	3.25	7.2	0.15	2.8	4.0	1.18	4.5
Fenchone	20	-	-	-	-	0.15	0.05	0.3	-
α -Thujone	21	0.2	-	0.11	-	-	-	-	0.4
Octen-1 ol-3	24	-	traces	0.05	-	0.01	0.04	traces	0.05
Fenchyl acetate	27	-	0.4	-	-	0.1	0.04	traces	0.05
Camphor	30	0.11	0.25	0.56	0.12	0.19	0.54	0.45	1.0
Linalool	32	62.7	0.96	58.2	79	2.12	8.6	0.62	56.0
Fenchol	38	-	0.25	-	-	0.2	0.15	traces	-
Bornyl acetate	40	2.2	0.45	1.1	-	0.03	0.05	0.20	2.5
Terpinen-4-ol + C ₁₅ H ₂₄	43	7.2	0.36	1.8	-	0.6	1.3	1.47	3.5
Menthol	47	-	-	-	-	-	-	0.15	-
Methyl chavicol	49	0.6	85.5	2.3	0.03	86	74.3	89	6.5
α -Terpineol + Borneol	51	2.5	0.2	1.2	-	0.30	0.45	0.3	1.8
	52								
Germacrene D + C ₁₅ H ₂₄	54	1.5	0.3	2.0	-	0.06	0.15	0.15	4.5
	55 et 56								
Geranyl acetate + γ -Cadinene	60	0.1	0.6	2.0	-	0.25	0.5	0.4	3.5
	61								
Nerol	65	0.25	traces	0.06	-	traces	traces	traces	0.06
Calamenene	67	-	-	0.22	-	0.18	-	-	0.025
Geraniol	68	2.24	0.5	0.45	-	0.6	0.3	0.08	0.45
?	70	-	-	0.45	-	-	-	-	1.3
Methyl eugenol	74	traces	1.35	0.05	-	1.0	2.0	0.55	0.05
<i>trans</i> -Methyl cinnamate	80	0.53	-	0.04	-	traces	traces	traces	0.4
Spathulenol	84	-	0.12	0.1	0.1	0.1	0.15	0.08	0.15
Eugenol	86	3.4	0.45	0.5	-	0.5	0.8	0.33	3
T. Cadinol	87	-	-	0.3	-	0.12	-	-	4
α -Cadinol	91	-	-	0.2	-	0.02	traces	-	0.4
Chavicol	96	-	0.05	0.02	-	0.06	0.06	0.06	0.06
<i>para</i> -Methoxy cinnamaldehyde	103	-	0.4	-	-	0.5	0.35	0.22	-
Benzyl benzoate	105	-	0.3	-	-	-	-	-	-
<i>para</i> -Methoxy cinnamyl alcohol	106	-	0.3	-	-	0.35	0.25	0.15	-
Benzyl salicylate	107	-	0.2	-	-	-	-	-	-
Total		89.1	99.3	90.26	80.5	97.42	96.68	97.44	99.4

a) B = Bulgaria, C = Comoro Islands, E = Egypt, F = France (this concerns an essential oil that was steam distilled in our laboratory and ether extracted, which accounts for the high linalool percentage), M = Madagascar, P = Pakistan, V = Vietnam, Y = Yugoslavia

b) The percentages were determined in gc on an Intersmat IGC 120 FL apparatus combined with an ICR 1B integrator. A quartz Carbowax 20 M (50 m x 0.2 mm) capillary column was used in programmed temperature from 70 to 210°C at the rate of 2°C/mn.

Table III. Reference Samples Used to Calculate Kovats Indices (IK_p) According to the Scan Numbers (S) of the Mass Spectrometer in Electron Impact

Samples	S	$\Delta(IK_p - S)^{a)}$	IK _p	
			measured ^{b)}	calculated ^{c)}
α -Pinene	200	829	1000	1029
<i>para</i> -Cymene	525	720	1229	1245
3-Octanol	718	655	1365	1373
Bornyl acetate	1024	553	1572	1577
Terpinen-4-ol	1045	546	1584	1591
<i>para</i> -Cymen-8-ol	1382	433	1793	1815
Geraniol	1386	431	1795	1817
Methyl eugenol	1597	361	1866	1958
Chavicol	1964	237	2347	2201

a) $\Delta(IK_p - S) = 896.5 - 0.335 \cdot S = f(S)$

- Determination coefficient : 0.9809

- Correlation coefficient : 0.9904

- Standard error : 0.1968

b) Measured on FFAP capillary column from the retention times of linear alkanes at n and n+1 carbon atoms according to the relation :

$$IK_p = \left[n + \left(\frac{t_{Rn} - t_{Rn-1}}{t_{Rn+1} - t_{Rn}} \right) \right] \cdot 100$$

c) Based on the relation : $IK_p = (896.5 - 0.335 \cdot S) + S$

Table V. Composition of the Terpinic Fraction of Basil Oils of Various Origin^{a)}

Terpenes	Composition %							
	B	C	E	F	M	P	V	Y
α -Pinene	13	7.2	13.1	13	12.1	13.1	6.5	15.7
Camphene	2	1.4	2.7	3	1.85	3.2	4	5.1
β -Pinene	30	9.9	22.4	2.5	22.2	19	7.6	14.7
Sabinene	13	34.2	10.15	-	9.3	8.6	4.7	7.2
Δ -3 Carene	-	-	-	-	-	-	-	1.0
Myrcene	10	3.2	17.3	11	6.5	7.2	11.2	12.8
α -Terpinene	-	-	1.2	-	-	-	-	1.6
Limonene	11	15.1	10.75	11	19.4	11.8	12.5	11.7
(Z)- β -Ocimene	2	2.2	1.2	10	2.8	1.4	2.5	1.3
(E)- β -Ocimene	12	20.1	13.7	27	19.4	28	47	18
(+ γ -terpinene) ^{b)}								
<i>para</i> -Cymene	5	4.9	5.4	3	4.6	5.9	2.2	6.1
α -Terpinolene	2	1.8	2.1	1	1.85	1.8	1.8	4.8

a) cf. Legend to Table 4

b) of which about 10% γ -terpinene in comparison with (E)- β -ocimene

Table VI. Analysis by Mass Fragmentometry and Positive Chemical Ionization (NH₄) of the Sesquiterpinic Fraction of Yugoslavian (Y) and Malagasy (M) Basil Essential Oils^a

Sesquiterpenes	Scans N°	Approximate Percentage ^{b)}	
		Y	M
α -Cubebene	830	0.6	-
α -Copaene	890	0.9	-
β -Bourbonene	938	1.9	-
β -Gurjunene	972	-	0.5
<i>Cis</i> - α -Bergamotene	1024	4	-
β -Guaiene ?	1030	0.6	-
β -Ylangene ?	1035	0.6	-
<i>Trans</i> - α -Bergamotene	1078	10	20
β -Elemene	1085	3.8	4
β -Caryophyllene	1090	traces	3
Germacrene isomer ? ?	1143	1.3	-
<i>Trans</i> - β -Farnesene	1208	0.6	-
γ -Muurolene	1213	0.5	9
α -Humulene	1223	0.7	5.5
C ₁₅ H ₂₄	1233	traces	1.5
Germacrene D	1238	10	-
α -Bulnesene	1250	5	5
C ₁₅ H ₂₄	1263	1.3	1.5
γ -Elemene	1274	5.7	-
γ -Cadinene	1310	11.5	20
β -Bisabolene	1320	0.6	-
α -Muurolene	1345	0.6	-
Calamenene		c	
Caryophyllene oxide	1565	-	2.5
Humulene oxide ?	1597	6	-
C ₁₅ H ₂₄ ?	1673	8	4
C ₁₅ H ₂₆ O ?	1698	3.8	-
Spathulenol	1740	0.4	1.5
T. Cadinol	1802	20	20
β -Eudesmol	1863	1.0	-
α -Cadinol	1884	0.6	-
Farnesol ^{d)}	1996	-	2

a) Each of these fractions respectively represents 20 and 6% of the Yugoslavian and Malagasy basil oils

b) These percentages were determined from the chromatogram reconstructed in positive chemical ionization (NH₄) with ion m/z 205. They are clearly indicative of the percentages observed in the corresponding oils.

c) Under these conditions, the calamenene content (M⁺ 202) cannot be determined. The latter can be obtained from chromatograms reconstructed in total ionization. Respectively, it represents 0.3% and 0.18% of the Yugoslavian and Malagasy oils.

d) Determined in electron impact.

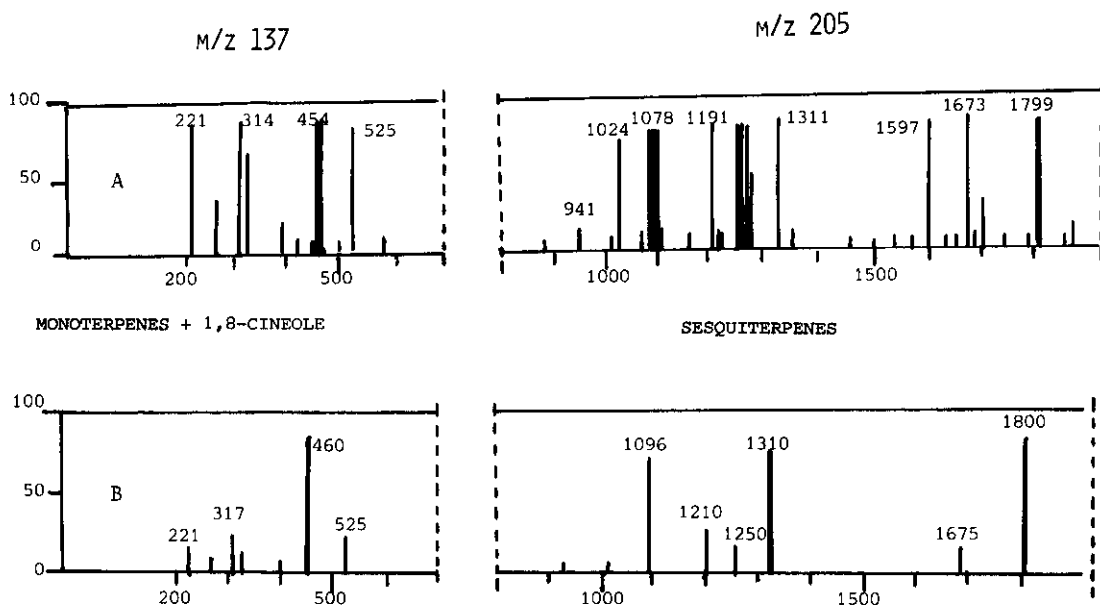


Figure 7. Comparison of the monoterpinic (+1,8-cineole) (m/z 137) and sesquiterpinic (m/z 205) fractions of Yugoslavian (A) and Malagasy (B) basil oils obtained by mass fragmentometry in positive chemical ionization

Conclusion

This study has allowed us to separate more than one hundred constituents in various basil essential oils and to identify ten new compounds. The usefulness of a library based not only on mass spectra but also on retention times has been demonstrated. Fundamental differences in the composition of these essential oils related to their origin have been observed. They appear not only as differences in the relative proportion of linalool, methyl chavicol, methyl cinnamate, methyl eugenol and eugenol but also in the presence or absence of a large number of other compounds notably the sesquiterpinic compounds. The results obtained by means of mass chromatography for selected ions in (NH₄) positive CI show that following the ions at m/z 137 and 205 is very effective in studying the monoterpinic and sesquiterpinic fractions.

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