

# Progress in Essential Oils

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Table I. Comparative percentage composition

# **Rosemary Oil**

In 1996, Casabianca and Graff determined that, although linalool was a minor constituent of rosemary oil in French oil, It possessed the following enantiomeric distribution:

(3R)-(-)-linalool (23-34%) : (3S)-(+)-linalool (66-77%).

An oil of rosemary produced from plants cultivated in northeastern Spain was analyzed by Guillen et al. (1996) using GC and GC/MS. The compounds identified in this oil were:

tricyclene $(0.38\%)$ $\alpha$ -thujene $(0.08\%)$ $\alpha$ -pinene $(19.35\%)$ camphene $(9.93\%)$ sabinene $(2.93\%)$ $\beta$ -pinene $(1.26\%)$ myrcene $(9.50\%)$ $\alpha$ -terpinene $(1.75\%)$ p-cymene $(4.49\%)$ $\gamma$ -terpinene $(0.59\%)$ terpinolene $(0.64\%)$ 1,8-cineole $(12.89\%)$ linalool $(3.17\%)$ camphor $(19.60\%)$ pinocamphone $(0.10\%)$ borneol $(2.41\%)$ isopinocamphone $(0.25\%)$ terpinen-4-ol $(0.63\%)$	$\begin{array}{l} \alpha \text{-terpineol} \ (0.70\%) \\ \text{verbenone} \ (1.63\%) \\ \text{bornyl formate} \ (0.10\%) \\ \text{linalyl acetate} \ (1.25\%) \\ \text{neryl acetate} \ (0.12\%) \\ \text{neryl propionate} \ (0.04\%) \\ \alpha \text{-ylangene} \ (0.09\%) \\ \alpha \text{-copaene} \ (0.05\%) \\ \beta \text{-caryophyllene} \ (1.53\%) \\ \text{bergamotene}^{\circ} \ (0.01\%) \\ \text{aromadendrene} \ (0.03\%) \\ \alpha \text{-humulene} \ (0.55\%) \\ \text{farnesene}^{\circ} \ (0.10\%) \\ \gamma \text{-cadinene} \ (0.08\%) \\ \delta \text{-cadinene} \ (0.03\%) \\ \text{caryophyllene} \ oxide \ (0.24\%) \\ \alpha \text{-bisabolol} \ (0.05\%) \end{array}$
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° correct isomer not identified

In 1997, Boutekedjiret et al. compared the composition of Algerian rosemary oil produced either by steam distillation or water distillation. A summary of the results of this GC and GC/MS study are shown in Table I. Although the results reveal some large quantitative differences, the oil yield from the water distillation was 0.58% whereas that of steam distillation was 1.20%. These results should have been much closer; hence, the results of the analysis of the water-distilled oil must be considered to be inaccurate and no conclusions should be drawn from them.

Domokos et al. (1997) analyzed a Hungarian oil of rosemary that was produced from a selected clone that was found to be more frost resistant than commonly grown rosemary. It was found to contain the following components:

$\alpha\text{-pinene}\;(21.5\%)$
camphene (6.9%)
3-octanone (4.7%)
$\beta$ -pinene (6.9%)

γ-terpinene (1.7%) 1,8-cineole (17.5%) camphor (19.7%) borneol (4.4%)

Compound	Water distilled oil	Steam distilled oil
α-pinene	0.4	4.2
camphene	0.3	3.4
β-pinene	0.3	6.5
myrcene	t	2.9
p-cymene	t	1.1
1,8-cineole	31.9	51.6
γ-terpinene	t	0.6
terpinolene	t	0.3
sabinene hydrate*	0.4	0.9
camphor	19.7	14.1
linalool	3.9	1.3
borneol	12.1	4.2
terpinen-4-ol	4.0	0.9
α-terpineol	12.8	2.9
bornyl acetate	3.1	1.7
β-caryophyllene	3.0	1.8
α-humulene	t	t
ε-muurolene†	t	0.2
γ-cadinene	t	t
δ-cadinene	t	0.1
caryophyllene oxide	t	t

tentative identification t = <0.1%

verbenone (3.9%) bornyl acetate (2.0%)  $\beta$ -caryophyllene (0.9%)

Also in 1997, Mastelic and Kustrak analyzed an oil of rosemary produced from plants harvested from the Dalmatian coastal region of Croatia. The plant material was initially dried and after hydrodistillation to remove the oil, the bound glycosides were isolated from the water after purification by treatment with  $\beta$ -glucosidase. The released aglycones were extracted from the water with pentane. They found that the oil possessed the following composition:

Table II. Comparative composition (%) of the oils isolated from peltate and capitate trichomes of Rosmarinus officinalis				
Compound	Peltate oil	Capitate oil		
2-methyl-2-pentenal	36.84	-		
α-pinene	18.77	20.00		
camphene	7.82	3.52		
β-pinene	0.61	1.32		
myrcene	0.69	1.61		
limonene	0.61	0.29		
1,8-cineole	6.17	15.80		
linalool	4.00	16.00		
camphor	0.52	11.70		
borneol	3.04	8.00		
α-thujone	0.87	1.94		
α-terpineol	9.64	1.37		
bornyl acetate	9.50	12.80		
eucarvone	0.52	1.04		
α-humulene	0.43	4.80		

$\alpha\text{-pinene}\;(20.4\%)$
$\beta$ -pinene (4.6%)
sabinene (3.8%)
limonene (0.6%)
1,8-cineole (30.5%)
$\gamma$ -terpinene (2.7%)
p-cymene (1.5%)
terpinolene (1.3%)
allo-ocimene* $(0.4\%)$
$1\text{-octen-3-ol}\ (0.4\%)$

camphor (11.7%) pinocamphone (1.0%) linalool (2.2%) bornyl acetate (4.8%) terpinen-4-ol (1.7%)  $\beta$ -caryophyllene (2.2%)  $\alpha$ -terpineol (4.6%)  $\alpha$ -humulene (0.5%) borneol (3.9%)

°correct isomer not identified

The compounds that were isolated from the pentane extract containing the aglycones were as follows:

3-hexanol (0.4%)	2-phenethyl alcohol (8.7%)
2-methyl-2-butenol (2.1%)	phenol (0.9%)
(Z)-3-hexenol (22.1%)	eugenol (13.3%)
1-octen-3-ol (t)	4(4-hydroxy-3-methoxyphenyl)-2-
$\alpha$ -terpineol (t)	butanone (10.8%)
methyl salicylate $(1.1\%)$	borneol (1.1%)
benzyl alcohol (27.1%)	t = trace (<0.1%)

Also in 1997, Bini Maleci et al. separately isolated the oil from both the large peltate and small short capitate trichomes of *R. officinalis* using 20 mm i.d. micro needles. The oils isolated this way were transferred to a glass U-tube. Once enough oil had been isolated from each gland type, it was absorbed on a Chrompack Carbotrap and transferred via a purge and trap injector to a GC fitted with a mass selective detector. The results of this study are shown in Table II. It is interesting to note the differences between the oils isolated from the two gland types. Also, because the

Compound	Range	Mean
α-pinene	18.76-24.3	20.8
camphene	8.2-9.8	8.8
sabinene	1.1-1.4	1.3
β-pinene	2.9-4.5	3.1
myrcene	3.9-4.3	4.1
p-cymene	1.8-2.5	2.1
limonene + 1,8-cineole	25.2-26.9	26.0
linalool	0.8-1.5	1.1
camphor	16.9-21.2	18.9
borneol	2.8-3.7	3.1
terpinen-4-ol	0.7-0.9	0.8
α-terpineol	1.1-1.5	1.3
verbenone	1.4-1.9	1.6
bornyl acetate	0.7-1.2	0.9
β-caryophyllene	1.5-2.3	2.0
α-humulene	0.5-0.7	0.6

authors did not state how many glands were sampled or how many replications, the results are interesting but perhaps a little inconclusive. However, the authors did postulate that the reason 2-methyl-2-pentenal had not previously been found as an oil constituent was because it was too volatile and would, therefore, not be condensed during normal steam distillation.

An interesting, report appeared in 1997 in which a sample of Spanish rosemary oil was sent to nine different laboratories for comparative purposes. One of the objectives of this study was to determine the area percentage range found when the same oil was analyzed by nine different chemists using a similar non-polar capillary column which was temperature programmed under identical conditions. The results of this collaborative study can be seen in Table III. The fact that limonene and 1,8-cineole were not separated was because the non-polar column used is less satisfactory for separating these two compounds than a polar one.

As part of an anti-malarial screening study of essential oils, Milhau et al. (1997) found that rosemary oil contained the following components:

$\alpha$ -pinene (16.0%)	linalool $(0.6\%)$
camphene (7.3%) sabinene (0.9%)	α-thujone (0.3%) camphor (9.8%)
β-pinene (8.7%)	borneol (3.3%)
myrcene (3.3%)	terpinen-4-ol $(0.2\%)$
$\alpha$ -terpinene (0.3%)	$\alpha$ -terpineol (1.2%)
p-cymene (1.7%)	bornyl acetate (1.4%)
1,8-cineole (41.8%)	$\beta\text{-caryophyllene}\;(1.6\%)$
$\gamma$ -terpinene (0.5%)	$\delta\text{-cadinene}\;(0.2\%)$
terpinolene (0.4%)	

Compound	Spanish oil	Italian oil
ricyclene	0.1	t
e-thujene	0.1	-
-pinene	0.9	12.8
amphene	0.9	3.7
-pinene	1.8	3.5
abinene	0.1	-
-3-carene	-	0.8
nyrcene	0.5	0.6
monene	11.0	9.5
,8-cineole	24.0	23.5
Z)-β-ocimene	-	0.3
-terpinene	t	0.7
E)-β-ocimene	0.1	0.1
o-cymene	2.3	2.6
erpinolene	-	0.3
rans-sabinene hydrate	0.1	0.1
amphor	35.3	17.7
pinocamphone	0.1	0.1
nalool	t	1.1
nalyl acetate	0.5	0.2
oornyl acetate	0.2	1.1
-caryophyllene	0.1	2.8
erpinen-4-ol	0.5	2.5
nyrtenal	0.6	0.1
orneol	1.3	1.3
rerbenone	1.2	0.7
e-terpineol	3.8	7.8
arvone	0.7	0.1
geranyl acetate	0.8	0.2
nyrtenol	0.1	0.1
nymol	0.2	0.2
arvacrol	0.1	0.1
e-bisabolol	1.3	1.3

They found that rosemary oil possessed good antimalarial properties because at concentrations ranging from 150-270 µg/mL it inhibited two *Plasmodium falciparum* parasites that caused malaria. Although the authors did not recommend direct application of rosemary oil for the treatment of malaria, they noted that it could be used as an adjuvant treatment for malaria.

Ravid et al. (1997) used chiral GC analysis to determine the enantiomeric distribution of verbenone in rosemary oil. It was found to exist in the following distribution:

# $\begin{array}{l} (1{\rm R})\mbox{-}(+)\mbox{-verbenone} \ (95.9\mbox{-}100\%): \\ (1{\rm S})\mbox{-}(-)\mbox{-verbenone} \ (0\mbox{-}4.1\%) \end{array}$

Arnold et al. (1997) collected wild rosemary plants from Colle Renazo in Italy and in the vicinity of Madrid in Spain, isolated the oils by hydrodistillation and compared their compositions using both GC and GC/MS. The results of this study are shown in Table IV. As can be seen, the compositions are not typical of rosemary oil encountered in commerce even though they were produced from authentic plant material.

This same year, Satta et al. (1997) examined the composition of rosemary oil produced from plants harvested in different regions of Sardinia. Using GC/MS as their method of analysis, they also compared their lab-distilled oils with two commercial oils (probably of Spanish origin). The analytical results obtained from this study can be seen in Table V.

The composition of Sardinian rosemary oil was also the subject of another study by Tuberoso et al. (1998). The authors analyzed oils produced from plants harvested from eleven different locations in Sardinia. The oil compositions were found to range as follows:

0	
$\alpha$ -pinene (26.5-47.1%)	$\alpha$ -terpinene (0-0.7%)
camphene(2.9-8.1%)	p-cymene (0.4-2.7%)
$\beta$ -pinene (0.8-3.2%)	limonene $(2.0-5.6\%)$
myrcene (0.4-3.8%)	1,8-cineole (3.2-14.1%)
$\alpha$ -phellandrene (0-5.8%)	γ-terpinene (0-1.0%)
$\delta$ -3-carene (0-0.7%)	linalool (0.8-2.4%)

 $\begin{array}{l} {\rm camphor}\;(1.5{\rm -}9.2\%) \\ {\rm borneol}\;(2.5{\rm -}4.9\%) \\ {\rm terpinen-4{\rm -}ol}\;(0{\rm -}1.1\%) \\ {\rm \alpha}{\rm -terpineol}\;(0{\rm -}2.5\%) \end{array}$ 

verbenone (3.4-15.6%) geraniol (0-2.3%) bornyl acetate (3.3-23.0%) β-caryophyllene (0-2.6%)

Moroccan rosemary oil samples, which were produced in the laboratory by hydrodistillation, were analyzed by GC and GC/MS by El Amrani et al. (1998). The constituents identified in the oils were as follows:

anisole (0.01-0.09%) tricyclene (0.04-0.11%) α-thujene (0.10-0.40%)  $\alpha$ -pinene (2.20-9.20%)  $camphene~(1.30\mathchar`-2.60\%)$ sabinene (0.10-1.70%)  $\beta$ -pinene (2.10-7.80%) myrcene (1.00-3.10%)  $\alpha$ -phellandrene (0.09-0.12%)  $\delta$ -3-carene (0.11-1.10%) α-terpinene (0.30-1.10%) p-cymene (0.20-1.50%) limonene (2.00-6.70%) 1,8-cineole (41.20-63.30%) (E)-β-ocimene (0.01-0.07%) γ-terpinene (0.10-1.00%) cis-p-menth-2-en-1-ol (0.60-3.20%) fenchone (0.10-0.70%) terpinolene (t-0.04%)

Table V.	Composi	tion perce	entage co	ompositio	n of Sardi	nian rose	mary oil	
Compound	1	2	3	4	5	6	Α	В
α-pinene	34.7	37.3	32.1	34.9	31.4	35.0	8.7	9.0
camphene	6.6	8.1	5.6	5.9	2.9	7.4	3.2	3.1
β-pinene	1.9	1.2	1.8	3.2	1.4	2.1	5.1	5.0
myrcene	3.8	1.7	1.5	0.7	1.6	0.4	1.1	1.4
α-phellandrene	0.4	1.0	0.4	-	0.4	5.8	-	-
δ-3-carene	0.1	0.1	-	-	0.6	-	-	0.1
p-cymene	1.3	2.7	1.7	1.4	0.4	0.7	1.3	2.0
limonene	3.7	5.5	3.4	2.0	2.9	3.5	-	-
1,8-cineole	8.2	5.6	8.0	8.9	14.1	6.7	46.3	53.0
γ-terpinene	0.6	0.7	0.9	-	1.0	0.8	-	0.3
linalool	1.2	1.1	2.1	1.1	2.0	0.8	1.2	0.8
camphor	6.0	9.2	4.3	2.4	2.2	8.3	10.9	7.8
borneol	4.3	3.2	4.9	3.5	3.6	3.4	3.5	3.8
terpinen-4-ol	1.0	0.6	0.9	0.7	0.9	-	0.8	0.7
α-terpineol	1.6	0.9	1.4	1.4	2.5	-	2.4	1.4
verbenone	4.9	3.5	7.7	6.0	13.4	9.2	-	-
geraniol	0.5	0.4	1.6	0.9	2.3	0.5	-	-
bornyl acetate	11.2	6.1	9.9	10.6	3.3	7.5	2.5	2.6
β-caryophyllene	0.2	0.4	0.4	0.2	1.8	1.3	3.8	2.5

1-6 = different locations in Sardinia

A-B = commercial oils

α-p-dimethylstyrene (0.10-0.50%)α-pinene oxide (0.01-0.08%) linalool (0.80-2.70%) α-fenchol (0.09-0.40%) cis-sabinene hydrate (0.03-0.10%limonene oxide\* (0.10-1.10%) camphor (7.60-18.90%) β-terpineol\* (0.10-0.90%) citronellal (t-0.08%) isopinocamphone (t-0.06%) pinocarvone (t-0.04%) borneol (1.10-7.10%) nonanol (0.10-0.40%) terpinen-4-ol (1.00-3.80%) naphthalene (t-0.06%) α-terpineol (3.10-8.10%) myrtenal (0.08-0.20%) myrtenol (t-0.07%) linalyl propionate (t-0.01%) dodecane (t-0.02%) verbenone (0.10-1.10%) nerol (t-0.05%) α-fenchyl acetate (t-0.06%) cuminaldehyde (t-0.04%) carvone (t-0.05%) piperitone (t-0.03%) geraniol (0.01-0.05%) geranyl acetate (t-0.02%) bornyl acetate (0.10-0.80%) thymol (0.01-0.04%) carvacrol (t-0.01%) vanillin (t-0.03%) α-cubebene (0.03-0.10%) eugenol (0.02-0.10%)  $\alpha$ -ylangene (0.01-0.09%) α-copaene (t-0.01%) β-elemene (0.01-0.03%) methyl eugenol (t-0.06%) β-caryophyllene (0.20-4.20%) aromadendrene (t-0.01%) α-cadinene† (0.02-0.07%) geranyl acetate (t-0.01%)  $\alpha$ -humulene (0.01-0.03%) (Z)- $\beta$ -farnesene (0.03-0.10%) allo-aromadendrene (0.02-0.05%)γ-muurolene (0.01-0.03%) germacrene B† (t-0.01%) β-bisabolene (0.01-0.04%) γ-cadinene (0.02-0.06%)

γ-bisabolene\* (0.01-0.04%)  $\delta$ -cadinene (0.03-0.07%) calamenene\* (t-0.02%) ledol (0.10-1.70%) spathulenol (0.02-0.10%) caryophyllene oxide (0.90-1.50%) globulol (0.20-1.10%)  $\gamma$ -eudesmol (0.01-0.09%) T-cadinol (0.03-0.10%) β-eudesmol (0.10-1.10%)  $\alpha$ -eudesmol (t-0.08%) methyl jasmonate (t-0.09%) α-bisabolol (0.10-0.70%) pentadecanol (t-0.03%) octadecene\* (t-0.08%) octadecane (t-0.01%) farnesyl acetate\* (t-0.02%)

hexadecanol (t) cedrandiol\* (t) nonadecane (t) (E)-phytol (0.01-0.04%) eicosene\* (t) eicosane (t) phyllocladene (t-0.01%) abietatriene (t) octadecanol (t) heneicosane (t) totarol (t) tricosane (t) abietal\* (t) 1-nonadecanol (t) methyl octadecanoate (t) methyl eicosanoate (t) dioctyl phthalate‡ (t)

° correct isomer not identified

 $\dagger$  incorrect identification based on elution order

‡ artifact

t = trace (<0.01%)

These same authors, El-Amrani et al. (1998), compared the composition of Moroccan rosemary oil produced at three separate harvesting times. The results of this study can be seen in Table VI. As can be seen the oils changed quantitatively only very slightly with the May oils being slightly richer in 1,8-cineole, the November oils being slightly richer in verbenone and the May oils being slightly poorer in camphor.

A Chilean oil of rosemary was found by Montes et al. (1998) to contain the following constituents:

$\alpha$ -pinene (5.06%)	isomenthol <sup>†</sup> (0.13%)
camphene $(4.38\%)$	camphor (24.86%)
$\beta$ -pinene (4.19%)	isobornyl acetate† (3.48%)
limonene (2.11%)	dihydrocarvone† (1.64%)
myrcene (25.95%)	borneol $(2.06\%)$
1,8-cineole (13.93%)	isoborneol (0.19%)
$\gamma$ -terpinene (2.39%)	1,7-dimethyloctanol $\dagger$ (0.41%)
terpinolene (1.96%)	$\alpha$ -terpineol (1.63%)

† probably incorrect identification

It should be pointed out that this is an atypical rosemary oil with a very unusual myrcene content and low 1,8-cineole content.

Kedzia et al. (1998) studied the immunostimulating activity of eleven essential oils among which was rosemary oil. They reported that the oil examined had the following major components:

> p-cymene (10.3%) camphor (15.0%) linalool (4.9%)

camphene (3.3%)	
β-pinene (2.8%)	
limonene (9.1%)	
1,8-cineole (34.4%)	

Although the above composition is not typical for rosemary oils of commerce, they did find that 1,8-cineole had a distinct immunostimulant activity.

A sample of Algerian rosemary oil, which was analyzed by GC and GC/MS by Boutekedjiret et al. (1998), was found to contain the following components:

#### Table VI. Comparative composition (%) of Moroccan rosemary oil produced at three separate times

Iosemary on produced of fillee separate liftes					
Compound	May	September	November		
α-thujene	0.1-0.2	0.1-0.3	0.2-0.4		
α-pinene	5.8-6.1	6.1-6.3	5.9-7.0		
camphene	1.0-1.3	1.2-1.7	1.2-1.8		
β-pinene	2.6-3.2	2.9-3.1	2.7-3.7		
myrcene	0.8-1.1	0.9-1.3	1.0-1.7		
α-terpinene	0.3-0.4	0.4-0.6	0.4-0.5		
p-cymene	0.1-0.2	0.2-0.4	0.1-0.7		
limonene	1.7-2.1	2.3-2.7	2.1-2.4		
1,8-cineole	53.6-57.3	50.9-52.8	48.6-53.8		
γ-terpinene	0.4-0.8	0.8-1.1	0.7-0.9		
fenchone	0.1-0.4	0.2-0.4	0.3-0.5		
$\alpha$ -p-dimethylstyrene	0.3-0.5	0.1-0.3	0.1-0.3		
linalool	0.1-0.4	0.1-0.4	0.5-0.8		
α-fenchol	0.3-0.6	0.4-0.6	0.3-0.6		
camphor	9.7-13.4	12.7-15.3	12.7-16.4		
borneol	2.4-3.2	2.1-2.7	1.8-2.2		
terpinen-4-ol	1.2-1.6	1.3-1.7	1.1-1.7		
α-terpineol	3.1-4.3	4.2-5.2	4.1-5.0		
myrtenal	0.1-0.2	0.1-0.3	0.1-0.2		
myrtenol	0.1-0.2	0.1-0.3	0.2-0.4		
verbenone	0.1-0.4	0.1-0.4	0.5-0.7		
bornyl acetate	0.2-0.6	0.1-0.3	0.1-0.3		
β-caryophyllene	0.3-0.6	0.3-0.6	0.1-0.4		

#### Table VII. Comparative percentage composition of major components of rosemary oil grown in two different soil types

17000				
Compound	Aggius oil	Ottava oil		
α-pinene	35.80	28.95		
camphene	3.52	4.25		
β-pinene	5.36	4.03		
myrcene	0.23	0.52		
$\alpha$ -phellandrene	1.53	1.51		
limonene	3.00	2.34		
1,8-cineole	18.35	31.55		
γ-terpinene	1.09	1.16		
p-cymene	0.73	0.78		
camphor	1.83	2.24		
linalool	1.18	2.57		
bornyl acetate	3.15	3.17		
borneol	6.02	5.68		
verbenone	8.45	6.58		
geraniol	1.87	3.70		
β-caryophyllene	2.10	0.94		

$\alpha$ -pinene (5.2%)	α-hun
camphene (3.0%)	germa
$\beta$ -pinene (5.7%)	α-muu
myrcene (1.7%)	α-farn
p-cymene (2.2%)	piperi
1,8-cineole (52.4%)	eugen
$\gamma$ -terpinene (0.5%)	α-cop
trans-sabinene hydrate (0.3%)	methy
terpinolene (0.2%)	β-cary
linalool (1.1%)	methy
camphor (12.6%)	γ-muu
borneol (3.4%)	caryop
terpinene-4-ol (0.7%)	humul
α-terpineol (2.1%)	14-hyo
bornyl acetate $(1.1\%)$	(0.29
$\alpha$ -copaene (0.2%)	lyral (0
$\beta$ -caryophyllene (4.2%)	α-sant

nulene (0.4%) acrene D (0.3%) urolene (0.2%) nesene\* (0.1%) itenone (0.1%)nol (0.1%) aene (0.9%) yl eugenol (0.1%) yophyllene (1.1%) vl isoeugenol\* (0.1%) irolene (t) phyllene oxide (0.2%) lene oxide\* (0.1%) droxy-9-epi-β-caryophyllene %) 0.1%)talal (0.3%)

° correct isomer not identified

t = trace (<0.1%)

Moretti et al. (1998) examined the compositional change in two rosemary chemotypes (one rich in  $\alpha$ -pinene and the other rich in 1,8-cineole) after foliar treatment with a soluble iron salt with and without irrigation. They found that the absorption of iron did not produce a significant increase in oil content but an increase in the verbenone content from 6.26% to 7.40% was found. The authors postulated that the iron promoted the metabolic oxidation processes, which converted  $\alpha$ -pinene into verbenyl derivatives.

These same authors (Moretti et al. 1998) also found that Italian rosemary plants grown on granitic silt soil (Aggius, Northern Gallura) possessed a stronger aroma and had more luxuriant growth than plants grown on calcareous soil (Ottava, Sassari). The authors compared the composition of the major components of the oils as shown in Table VII.

Using oil produced from a commercial rosemary herb material available in the U.K., Tiziana Baratta et al. (1998) used GC/MS to determine that it possessed the following composition:

1	
tricyclene (0.2%)	linalool $(3.2\%)$
$\alpha$ -thujene (t)	chrysanthenone $(0.3\%)$
$\alpha$ -pinene (19.6%)	camphor (12.6%)
benzaldehyde (t)	borneol (10.0%)
camphene (3.8%)	terpinene-4-ol (1.0%)
sabinene (0.4%)	$\alpha$ -terpineol (12.3%)
$\beta$ -pinene (0.4%)	verbenone $(0.9\%)$
myrcene $(1.2\%)$	trans-carveol $(0.1%)$
$\alpha$ -phellandrene (0.3%)	nerol $(0.7\%)$
δ-3-carene (1.2%)	methyl thymol (2.8%)
$\alpha$ -terpinene (0.5%)	geraniol (0.3%)
p-cymene (1.5%)	thymol (0.2%)
1,8-cineole (13.0%)	carvacrol (0.2%)
limonene (3.5%)	bornyl acetate (0.9%)
(Z)- $\beta$ -ocimene (0.2%)	$\gamma$ -cadinene (0.4%)
(E)- $\beta$ -ocimene (t)	$\delta$ -cadinene (0.3%)
$\gamma$ -terpinene (0.3%)	calacorene* $(6.2\%)$
$\alpha$ -p-dimethylstyrene (0.2%)	caryophyllene oxide (0.1%)
terpinolene (1.0%)	humulene oxide* (0.1%)

\*correct isomer not identified

t = trace (<0.1%)

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In 1999, Reichling et al. used GC and GC/MS to analyze an oil of rosemary. They found that it contained the following constituents:

 $\alpha$ -thujene (0.33%) γ-terpinene (0.83%) α-pinene (9.17%) terpinolene (0.66%) camphene (3.31%) camphor (13.79%)  $\beta$ -pinene (2.29%) borneol (8.18%) myrcene (0.81%) terpinen-4-ol (0.22%)  $\alpha$ -phellandrene (0.48%)  $\alpha$ -terpineol (1.73%) δ-3-carene (1.14%) linalyl acetate (0.45%)  $\alpha$ -terpinene (1.27%) bornyl acetate (4.91%) p-cymene (2.44%)  $\beta$ -caryophyllene (1.64%) 1,8-cineole (42.24%)  $\alpha$ -humulene (0.16%)

Miguel et al. (1999) examined the effect of fertilizer and soil type on Portuguese rosemary grown in pots. The oils produced from these plants were analyzed by GC and GC/ MS and their compositions were found to be quite similar except for the camphor content. The range of constituents found was as follows:

$\alpha\text{-pinene}\;(10.0\text{-}13.5\%)$	linalool (1.3-2.3%)
camphene (2.5-2.6%)	camphor (7.2-13.2%)
sabinene (0.1-0.2%)	cis-sabinene hydrate (0.4%)
$\beta$ -pinene (2.0-3.2%)	eucarvone $(0.5-0.8\%)$
myrcene (21.0-26.9%)	$\delta$ -terpineol (0.4-1.3%)
$\alpha$ -phellandrene (0.4-0.6%)	borneol $(0.3-0.5\%)$
$\alpha$ -terpinene (0.6-0.7%)	terpinen-4-ol (1.0-1.5%)
p-cymene (0.6-0.8%)	$\alpha$ -terpineol (1.7-2.1%)
limonene $(5.7-6.4\%)$	verbenone $(10.4-14.6\%)$
1,8-cineole (7.4-8.1%)	linalyl acetate $(0.2\%)$
(Z)- $\beta$ -ocimene (0.9-2.7%)	bornyl acetate $(0.1-0.3\%)$
(E)- $\beta$ -ocimene (0.1-0.2%)	methyl eugenol (0.6-0.7%)
$\gamma$ -terpinene (1.5-2.7%)	$\beta$ -caryophyllene (0.7-2.0%)
trans-sabinene hydrate (0.1-0.2%)	caryophyllene oxide $(0.3\mathchar`-0.6\%)$
terpinolene (1.0-1.2%)	

Also in 1999, Ibanez et al. used a two-step supercritical fluid  $CO_2$  extraction of rosemary leaves at selected pressure and temperature conditions to produce oleoresin fractions with different antioxidant activities. Although the authors showed that the fractions contained a range of verbenone contents from 0.22-27.24%, the analysis will not be reviewed because it contained too many errors.

An oil of *R. officinalis* produced from plants grown in the experimental garden of the University of Fort Hare (S. Africa) was found by Mangena and Muyima (1999) to contain the following constituents:

$\alpha$ -pinene (18.18%)	camphor (30.12%)
camphene (6.08%)	bornyl acetate (3.17%)
$\beta$ -pinene (2.58%)	verbenone (4.12%)
1,8-cineole (31.12%)	

The changes in major component composition of Algerian rosemary oil produced from plants harvested at different times in the development cycle were studied by Bouterkedjiret et al. (1999). The results obtained can be seen in Table VIII. As can be seen, the highest 1,8-cineole content was found in oils produced from plants that had just commenced flowering. Dellacassa et al. (1999) used GC and GC/MS to compare the composition of rosemary oil produced from two cultivated populations growing in Uruguay, and oils produced from wild and cultivated plants grown in Brazil. A summary of the results of this comparison is presented in Table IX. As can be seen, the oils contained lower levels of 1,8-cineole than normally encountered with commercial rosemary oils. It is of particular interest to note the high level of myrcene in the oil produced from the wild population of rosemary from Rio Grande do Sul (Brazil).

Last year, Porte et al. (2000) analyzed a rosemary oil produced from plants grown in Brazil using GC and GC/MS. The composition of this oil was found to be as follows:

 $\begin{array}{l} \mbox{tricyclene} (0.1\%) \\ \mbox{$\alpha$-thujene} (0.2\%) \\ \mbox{$\alpha$-pinene} (11.5\%) \\ \mbox{$camphene} (4.3\%) \\ \mbox{thuja-2,4(10)-diene} (0.2\%) \\ \mbox{$sabinene} (0.1\%) \\ \mbox{$\beta$-pinene} (5.0\%) \\ \mbox{$myrcene} (12.4\%) \\ \mbox{$\alpha$-phellandrene} (0.2\%) \\ \mbox{$\alpha$-terpinene} (0.5\%) \end{array}$ 

p-cymene (1.0%)limonene (2.9%)l,8-cineole (22.1%)(Z)- $\beta$ -ocimene (t) (E)- $\beta$ -ocimene (t)  $\gamma$ -terpinene (1.4%)terpinolene (0.8%)linalool (1.1%)camphor (26.0%)iso(iso)pulegol (t) Table VIII. Major component percentage composition of rosemary oil produced from plants harvested at different stages of maturity

Compound	Full	Beginning	Full	After
	budding	of flowering	flowering	flowering
α-pinene	2.5	4.8	16.9	7.1
camphene	1.7	2.3	t	t
β-pinene	0.9	3.4	1.8	3.8
1,8-cineole	39.6	41.7	17.2	16.0
camphor	26.0	9.3	11.9	11.6
borneol	9.0	6.7	2.2	2.7
α-terpineol	4.2	4.5	9.3	12.8
bornyl acetate	2.3	1.3	1.7	2.9
β-caryophyllene	4.9	5.4	9.9	13.6

 $\begin{array}{l} \mbox{pinocamphone} \ (0.3\%) \\ \mbox{pinocarvone} \ (0.9\%) \\ \mbox{borneol} \ (0.2\%) \\ \mbox{isopinocamphone} \ (0.3\%) \\ \mbox{terpinen-4-ol} \ (0.8\%) \\ \mbox{$\alpha$-terpineol} \ (1.2\%) \\ \mbox{myrtenol} \ (0.1\%) \\ \mbox{verbenone} \ (2.4\%) \\ \mbox{citronellol} \ (t) \end{array}$ 

 $\begin{array}{l} pulegone (t) \\ (E)-tagetenone (t) \\ piperitone (t) \\ isopiperitenone (t) \\ bornyl acetate (0.3\%) \\ \alpha -ylangene (0.1\%) \\ methyl eugenol (t) \\ \beta -caryophyllene (1.4\%) \\ \alpha -humulene (0.2\%) \end{array}$ 

Table IX. Percentage composition of <i>Rosmarinus officinalis</i> oils from Uruguay and Brazil						
Uruguay Brazil						
Compound	Population 1	Population 2	Cultivated	Wild		
α-thujene	0.2	0.3	6.0	0.3		
α-pinene	46.2	37.8	32.2	12.4		
camphene	4.4	5.1	3.7	5.0		
thuja-2,4(10)-diene	0.4	0.4	0.3	0.3		
sabinene	0.1	0.2	0.5	0.1		
β-pinene	3.4	5.1	2.9	5.0		
myrcene	1.9	1.9	1.8	22.7		
α-phellandrene	0.3	0.3	0.3	0.3		
α-terpinene	0.8	0.6	0.6	0.9		
p-cymene	0.5	0.4	0.3	2.5		
limonene	5.0	6.6	6.3	3.9		
1,8-cineole	13.8	13.4	14.7	15.3		
(Z)-β-ocimene	t	t	t	2.6		
(E)-β-ocimene	t	t	t	0.2		
γ-terpinene	1.2	1.8	1.3	2.8		
cis-sabinene hydrate	0.3	0.3	0.4	0.2		
terpinolene	1.0	1.1	1.8	0.6		
linalool	1.6	1.2	2.3	0.4		
camphor	1.4	1.4	2.3	7.9		
pinocamphone	0.2	0.2	0.3	0.2		
borneol	1.5	1.6	3.2	0.3		
terpinen-4-ol	0.3	0.3	0.6	1.5		
α-terpineol	0.7	0.5	1.4	1.8		
verbenone	1.2	0.7	3.3	4.2		
neral	0.2	0.2	0.4	0.1		
geraniol	2.3	1.6	4.3	0.3		
geranial	0.2	0.2	0.4	0.1		
bornyl acetate	1.9	4.4	2.6	0.2		
geranyl acetate	0.3	0.4	0.4			
methyl eugenol	0.3	0.2	0.4	0.2		
β-caryophyllene	2.8	4.9	0.7	0.7		
α-humulene	0.4	0.7	0.1	0.3		
t = trace (<0.1%)						
γ-muurolene (0.1%)	β-bisabole	ne (0.1%)	trans-calamene	ne (t)		

valencene (t)  $\alpha$ -muurolene (t)

 $\gamma$ -cadinene (t)  $\delta$ -cadinene (0.1%)

Also in 2000, El-Am-

rani et al. examined the variability of rosemary oil produced in Morocco using GC and GC/MS. Plants were collected from Rabat, Elateuf (850 km east of Rabat) and Taforalt (480 km east of Rabat) and oils from the 10 samples of air-dried leaves and twigs taken from each area were produced by hydrodistillation. A summary of the composition of these oils, which were analyzed by both GC and GC/MS, can be seen in Table X.

The authors also performed a more detailed analysis of the oils and reported that they contained the following components:

anisole (t) tricyclene (t-0.2%)  $\alpha$ -thujene (0.1-0.4%)  $\alpha$ -pinene (2.2-9.2%) camphene (1.3-3.6%) sabinene(0.1-1.7%) $\beta$ -pinene (2.1-7.8%) myrcene (1.0-3.1%)  $\alpha$ -phellandrene (-1.3%) δ-3-carene (0.1-1.1%)  $\alpha$ -terpinene (0.1-1.1%) p-cymene (0.2-1.5%) limonene (2.0-6.7%) 1,8-cineole (41.2-63.3%) (E)- $\beta$ -ocimene (t) γ-terpinene (0.1-1.0%) fenchone (0.1-0.7%)terpinolene (t)  $\alpha$ -p-dimethylstyrene (0.1-0.5%) $\alpha$ -pinene oxide (t) linalool (0.8-2.7%)  $\alpha$ -fenchol (t-0.4%) sabinene hydrate\* (t) cis-limonene oxide (0.1 - 1.1%)camphor (7.6-18.9%) β-terpineol\* (0.1-0.9%) citronellal (t) pinocamphone (0-t) pinocarvone (t) borneol (1.1-7.1%) nonanol (0.1-0.4%) terpinen-4-ol (1.0-3.8%)  $\alpha$ -terpineol (3.1-8.1%) myrtenal (t-0.1%) myrtenol (t) linalyl propionate (t) dodecane (t) verbenone (0.1%)nerol (t)  $\alpha$ -fenchyl acetate (t) cuminaldehyde (t) carvone (t) piperitone (t) geraniol (t) bornyl acetate (0.1%)thymol (t) carvaerol (t)  $\alpha$ -cubebene (0.1-0.2%) nonadecanol (t)

eugenol (0.1-0.2%)  $\alpha$ -ylangene (t)  $\alpha$ -copaene (t) β-elemene (0.1-0.2%) methyl eugenol (t)  $\beta$ -caryophyllene (0.2-4.2%)aromadendrene (0.1-0.2%)geranyl acetone (0.1-0.2%) $\alpha$ -humulene (0.1-0.2%) β-farnesene\* (0.1-0.2%) allo-aromadendrene (-0.2%) $\gamma$ -muurolene (t)  $\beta$ -bisabolene (0.1-0.2%) γ-cadinene (0.1-0.3%)  $\gamma$ -bisabolene\* (t)  $\delta$ -cadinene (t-0.2%) calamenene\* (0.1-0.3%) ledol (0.2-0.5%) spathulenol (0.1-0.4%)caryophyllene oxide (0.5-1.0%)globulol (t)  $\gamma$ -eudesmol (t) T-cadinol (t) β-eudesmol (0.1-0.3%)  $\alpha$ -eudesmol (0.1-0.3%) methyl jasmonate (0.1-0.3%) $\alpha$ -bisabolol (0.3-0.5%) pentadecanol (0.1-0.2%) octadecene\* (t-0.1%) octadecane (t-0.2%) farnesyl acetate\* (0.1-0.3%)hexadecanol (0.1-0.4%) nonadecane (0.1-0.2%) (E)-phytol (t) eicosene\* (0.1-0.2%) eicosane (t) phyllocladene (0.1-0.2%) abietatriene (t) octadecanol (t) heinecosane (t) cis-totarol (t) tricosane (t)

\*correct isomer not identified

t = trace (<0.1%)

The main components of rosemary oil produced from plants collected from the wild in Greece were determined by GC/MS by Daferera et al. (2000) to be as follows:

Table X. Percentage c of rosemary oil produ loc	-	lants collected	
	Rabat	Elateuf	Taforalt
Constituents	oils	oils	oils
α-thujene	0.2-0.5	0.1-0.4	t-0.2
α-pinene	37.0-40.0	2.5-7.9	0.5-5.5
camphene	4.6-6.7	1.2-2.9	1.2-6.7
β-pinene	2.6-2.8	2.9-6.1	0.4-1.3
myrcene	0.3-0.6	1.0-3.1	0.6-0.9
α-terpinene	0.6-0.8	0.1-0.3	0.1-0.3
p-cymene	0.4-0.7	0.2-1.5	0.2-0.7
1,8-cineole	0.9-1.7	58.7-63.7	1.2-13.5
limonene	4.4-4.5	0.7-1.1	0.4-1.2
γ-terpinene	2.3-2.9	0.3-0.8	0.1-0.4
fenchone	0.1-0.4	0.1-0.7	0.2-0.5
$\alpha$ -p-dimethylstyrene	0.2-0.5	0.1-0.5	0.3-0.8
linalool	2.7-2.9	1.1-1.5	0.3-1.1
α-fenchol	0.2-0.3	0.2-0.4	0.3-0.5
limonene oxide*	0.1-0.4	0.1-1.1	0.4-0.7
camphor	4.6-7.6	5.3-12.3	41.7-53.8
β-terpineol*	0.5-0.8	0.4-0.9	0.5-0.8
borneol	1.6-3.0	2.6-6.7	3.7-6.3
terpinen-4-ol	0.9-1.3	0.8-2.1	1.0-3.1
α-terpineol	2.4-3.1	3.1-8.1	5.1-6.4
myrtenal	0.1-0.5	0.1-0.2	0.2-0.4
myrtenol	0.2-0.4	t-0.3	0.1-0.4
verbenone	4.8-5.5	0.2-0.6	0.1-0.3
bornyl acetate	0.3-0.5	0.1-0.8	0.1-0.4
$\beta$ -caryophyllene	1.1-2.5	0.2-1.6	1.2-2.3
ledol	-	0.1-1.7	0.1-0.3
spathulenol	-	t-0.1	0.2-0.5
caryophyllene oxide	0.1-0.5	0.9-1.5	0.1-0.4
$\beta$ -eudesmol	-	0.3-1.1	0.1-0.4
α-bisabolol	-	0.1-0.7	0.4-0.7
*correct isomer not iden t= trace (<0.1%)	tified		

 $\begin{array}{l} \alpha \text{-pinene} \ (2.7\%) \\ \text{ocimene}^{*} \ (0.7\%) \\ \text{p-cymene} \ (0.7\%) \\ 1,8\text{-cineole} \ (88.9\%) \end{array}$ 

 $\begin{array}{l} \text{camphor} \ (2.4\%) \\ \text{borneol} \ (1.5\%) \\ \alpha\text{-terpineol} \ (1.3\%) \end{array}$ 

Coleman and Lawrence (2000) examined the enantiomeric distribution of six components in the headspace of rosemary oils from eight different geographical sources using auto-SPME-chiral GC. Some of the oils examined were from commercial sources while others were from labdistilled oil either from plants collected in the wild or from cultivated garden plants. The enantiomeric distribution of the six component (-)-enantiomers [(the (+)-enantiomers

in the laboratory using water distillation. As a result, it can be seen that the enantiomeric distributions were affected by the mode of oil isolation.
 The enantiomeric distribution of these same six components in a number of commercial oils (Table XII) shows the wide range of distribution found in these oils indicating a combination of the effect of the method of isolation

the oil varied in composition as follows:

and adulteration on the amount of (-)-enantiomers found in these oils. Also in 2000, Ouahada and Benveniste examined the composition of commercially available rosemary oil produced in Tunisia. In addition to reporting that commercial production of rosemary oil in Tunisia has varied from 55-76 metric tonnes over the last five years, the also reported that

equal 100 minus the (-)-enantiomer)] in the authentic oils can be seen in Table XI. The Algerian oils were all produced by steam distillation, whereas the other oils were produced

I I I I I I I I I I I I I I I I I I I	
$\alpha$ -pinene (12.22-14.28%)	camphor (8.65-13.13%)
camphene (4.37-4.58%)	linalool (0.71-0.77%)
$\beta$ -pinene (4.83-9.21%)	bornyl acetate (0.95-1.22%)
myrcene (1.50-1.87%)	terpinen-4-ol (0.24-0.29%)
limonene (2.35-2.85%)	$\beta$ -caryophyllene (4.49-5.11%)
1,8-cineole (44.10-49.33%)	$\alpha$ -terpineol (1.24-1.40%)
$\gamma\text{-terpinene}\;(0.82\text{-}1.38\%)$	borneol (1.28-4.67%)
p-cymene (1.12-1.44%)	

Finally, Kodama and Kasahara (2000) examined the composition of rosemary oils produced in the laboratory from fourteen different plants cultivated in Japan. They categorized the oils into four groups based on their  $\alpha$ -pinene, camphene, 1,8-cineole, camphor, borneol and bornyl acetate contents. In addition, the authors performed a more detailed analysis of six of the fourteen oils and showed that their compositions ranged as follows:

tricyclene (0-0.46%)  $\alpha$ -pinene (3.42-16.65%)  $\alpha$ -fenchene (0-0.9%) camphene (1.86-9.12%)  $\beta$ -pinene (1.61-5.38%) sabinene (0.09-0.26%) δ-3-carene (0-2.48%) myrcene (1.00-5.99%)  $\alpha$ -phellandrene (0-1.09%)  $\alpha$ -terpinene (0-0.76%) pseudo-limonene (0-0.11%) limonene (3.55-5.00%) 1,8-cineole (8.08-22.74%)  $\beta$ -phellandrene (0-2.00%) ocimene\* (0-0.05%) γ-terpinene (0-1.66%) 3-octanone (0.10-2.10%)p-cymene (0.47-5.03%) terpinolene (0-1.42%)  $\alpha$ -pinene oxide (0-0.10%) 6-methyl-5-hepten-2-one (0-0.01%)(Z)-3-hexenol (0-0.03%) (Z)-3-hexenyl acetate (0-0.01%)

3-octanol (0-0.26%) fenchone (0.02-0.05%) amyl vinyl carbinyl acetate† (0-0.03%)2-methoxytoluene (0-0.05%) nonanal (0-0.1%) perillene (0-0.19%) α-thujone (0-0.17%) filifolone (0-0.22%) 6,7-epoxy-7-methyl-3-methylene-1-octene (0-0.06%)  $\alpha$ -p-dimethylstyrene (0-0.08%) linalool oxide\* (0-0.07%) limonene oxide\* (0-0.03%) 1-octen-3-ol (0.12-0.42%) acetic acid (0-0.05%) terpinolene oxide (0-0.07%) linalool oxide\* (0-0.06%)  $\alpha$ -cubebene (0-0.05%) (E)-2-hexenyl butyrate (0-0.07%) α-copaene (0-0.11%) α-ylangene (0-0.80%)  $\alpha$ -campholenic aldehyde (0-0.02%)

Table XI. Enantiomeric distribution of six components of authentic rosemary oils						
Origin	(-)-α-pinene	(-)-camphene	(-)-β-pinene	(-)-limonene	(-)-camphor	(-)-borneol
Algeria (5)	78.5-85.1	92.1-93.5	89.4-93.9	81.8-85.4	74.8-81.0	-
Australia (5)	17.5-54.8	14.0-65.9	72.9-85.1	39.1-54.0	10.8-34.6	47.7-93.8
Hungary (1)	8.7	53.5	91.2	30.2	49.0	78.4
Italy (4)	7.2-13.1	55.1-65.0	29.5-74.0	26.0-70.5	27.5-79.1	-
Slovakia (1)	70.5	41.0	92.4	53.2	48.4	58.0
Spain (2)	35.6-37.2	74.6-75.5	78.9-79.7	59.4-63.4	41.4-42.5	-

Table XII. Enantiomeric distribution of six components of commercial rosemary oils							
Origin	(-)-α-pinene	(-)-camphene	(-)-β-pinene	(-)-limonene	(-)-camphor	(-)-borneol	
Morocco (5)	36.8-43.9	56.4-65.8	72.2-74.1	2.1-57.8	17.1-32.6	48.1-69.3	
Tunisia (3)	41.7-52.1	48.7-66.2	74.7-82.1	2.8-56.3	17.1-34.6	44.1-79.1	
Spain (1)	16.4	54.0	90.8	20.8	47.9	-	
Australia (3)	16.0-50.2	52.3-61.7	56.5-79.4	37.2-52.2	25.6-73.3	53.7-86.3	

isomenthone (0-0.45%) decanal (0-0.02%) chrysanthenone (0.016-1.48%) camphor (10.24-26.06%) isopinocamphone (0-1.38%) terpinen-1-ol (0-0.45%) linalool (0.98-3.86%) trans-p-menth-2-en-1-ol (0.05-0.54%)pinocarvone (0.08-0.28%) isopulegol (0-0.17%) bornyl formate (0-0.19%) bornyl acetate (2.34-16.60%)  $\alpha$ -fenchyl alcohol (0-0.06%)  $\beta$ -caryophyllene (1.06-5.44%) terpinen-4-ol (0.69-1.37%) isoledene (0-0.11%) 2-undecanone (0-0.20%) citronellyl formate (0-0.06%) p-mentha-1,8-dien-4-yl acetate (0-0.03%) cis-p-menth-2-en-1-ol (0.03-0.15%)myrtenal (0-0.20%) pulegone (0-0.03%) menthyl formate (0-0.02%) pinocarveol\* (0-0.31%) aromadendrene (0-0.03%)  $\alpha$ -humulene (0.20-2.94%) methyl chavicol (0-0.05%)  $\delta$ -terpineol (0.12-0.45%) citral diethyl acetal† (0-0.17%) verbenol\* (0.26-0.70%) limonen-4-ol (0-0.08%) γ-muurolene (0-0.28%) myrtanyl acetate\* (0-0.40%)

 $\alpha$ -cadinene (0.35%) verbenone (0-3.50%)  $\alpha$ -terpineol (0-3.01%) borneol (3.36-10.22%)  $\delta$ -cadinene (0-0.22%) ledene (0-0.07%) piperitone (0-0.04%)  $\beta$ -bisabolene (0-0.30%) geranial (0-0.08%) carvone (0-0.18%) trans-piperitol (0-0.08%)  $\beta$ -sesquiphellandrene (0-0.11%) geranyl acetate (0-0.09%) 4-methylacetophenone (0-0.06%) γ-cadinene (0-0.03%) citronellol (0-0.23%) curcumene\* (0-0.04%) cuminaldehyde (0-0.04%) myrtenol (0.12-0.42%) calamenene\* (0-0.14%) isopiperitenone (0-0.26%) trans-carveol (0-0.20%) p-cymen-8-ol (0.02-0.35%) geraniol (0-0.60%) geranyl acetone (0-0.15%)  $\alpha$ -calacorene (0-0.12%) cis-carveol (0-0.03%) piperitenone (0-0.05%) (E)-jasmone (0-0.04%) isocaryophyllene oxide (0.12-7.39%) caryophyllene oxide (0-2.03%) perillyl alcohol (0-0.06%) methyl eugenol (0.07-0.51%) nerolidol\* (0-0.17%) humulenal\* (0-0.74%)

prenyl benzoate (0-0.06%) cuminyl alcohol (0-0.10%) geranyl tiglate (0-0.06%) methyl pentenyl benzoate° (0-0.09%) eugenol (0-0.03%) bisabolol° (0-0.10%) thymol (0-0.08%) correct isomer not identified doubtful identification

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# **Guarana Extract**

Over the past 10 years or so, a soft drink that hails from Brazil known as guarana has become a new item in Europe, Japan and North America (Bartsch and Faber 1996). This carbonated beverage probably qualifies as being the national soft drink of Brazil (Erickson et al. 1984). Guarana is a sapindaceous vine (*Paullinia cupana* Ducke) that is native to the Amazon River basin in Brazil. Although still found in the wild state, it is cultivated in the states of Amazonas, Mato Grosso, Bahia Acre, Para and even Mato Grosso do Sul.

The cultivated form of guarana is a low growing somewhat sprawling shrub, which often referred to as *P. cupana* Kunth. ex H.B.K. var *sorbis* (Mart.) Ducke. Fruit production commences after the third year and reaches a maximum after six years. The triloculate fruit, which are deep yellow to reddish orange when ripe, are borne on small groups of racemes. Several dozen fruit can be found on each raceme, although they differ in maturity because of a protracted flowering habit (Erickson et al. 1984). Each fruit bears 1-3 glossy black-brown seeds that, when mature, protrude from the fruit giving the appearance of an eye. This eye-like appearance of the seed has led to the mysticism surrounding its use by the aboriginal Sauterêr-Marué Indians of the Central Amazon region (Erickson et al. 1984).

Traditional processing of guarana is intriguing. The seeds are harvested and roasted to facilitate removal of the hard shell coat. Once this is done, the seeds are ground into a fine powder mixed with water and made into a paste. The paste, which has a dough-like consistency, is shaped into a roll or cylinder (known in Brazil as bastes) similar in size to a small salami and fire dried to harden. Prior to its use as a stimulant beverage, the roll is rasped into a powder using the ossified tongue of a fish (picrarucú —*Arapaima gigas* Cavier) (Erickson 1984, Walker et al. 2000). According to Bartsch and Faber (1996), guarana seed is rich in purine alkaloids, mainly caffeine, theophylline and theobromine. In fact, the seed contains approximately 3.2% caffeine.

For the large scale production of guarana products the seeds are first dried using a coffee bean dehydrator, after which the hard shells of the seed are removed and they are ground to a fine powder (Waller et al. 2000). The powder is either sold as such, made into a syrup (not less than 1% seed equivalent) or made into a tincture or concentrate by extraction with 60% aqueous ethanol.

In addition to the purine alkaloids, guarana extract, which now has a wider use in the flavor industry than just for soft drinks, contains a small amount of an essential oil. A steam distillate of chloroform soxhlet extract of guarana powder was subjected to analysis by Benoni et al. (1996). The oil, which was analyzed by TLC and GC/MS, was found to contain the following components:

1,4-dimethylbenzene	(E)-anethole
trimethylbenzene isomers	carvacrol
limonene	α-copaene
methyl chavicol	β-caryophyllene
4-dimethyl propylphenol	

<sup>4-dimethyl propylphenol</sup> Although the authors did not present any quantitative data, from the chromatogram presented, it was possible to determine that carvacrol was the major component with the other components being between 5-15% of the carvacrol level.

In 1998, Meurer-Grimes et al. reported that the purine alkaloid content of various guarana products were as follows: seeds: theobromine (0.012-0.016%), theophylline (trace-0.026%), and caffeine (2.953-3.741%)

- powder: theobromine (0.017-0.34%), theophylline (0.011-0.061%) and caffeine (3.498-6.593%)
- tincture/extract: theobromine (0.111-0.175%), theophylline (0.206-0.481%) and caffeine (9.821-11.026%)
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# Caboré Oil

An oil known as caboré is produced in Rio Grande do Sal (Brazil) from the wood chips of an unidentified tree. Using a combination of fractional distillation, flash chromatography GC, GC/MS and <sup>1</sup>H-NMR, Weyerstahl et al. (1988) performed a detailed analysis of this minor commercial oil. They found it contained the following components:

 undecane (0.1%)  $\alpha$ -cc

 dodecane (0.1%)  $\beta$ -ele

 safrole (0.3%) tetra

 tridecane (0.2%)  $\beta$ -ca

  $\delta$ -elemene (1.5%)  $\gamma$ -ele

  $\alpha$ -cubebene (2.4%) trans

 $\begin{aligned} & \alpha \text{-copaene} (22.9\%) \\ & \beta \text{-elemene} (4.4\%) \\ & \text{tetradecane} (0.4\%) \\ & \beta \text{-caryophyllene} (8.3\%) \\ & \gamma \text{-elemene} (5.2\%) \\ & trans - \alpha \text{-bergamotene} (0.9\%) \end{aligned}$ 

aromadendrene (0.3%)  $\alpha$ -amorphene (0.2%)  $\alpha$ -humulene (1.2%) allo-aromadendrene (2.3%) $\gamma$ -muurolene (2.7%) germacrene D (13.4%)  $\beta$ -selinene (0.7%) 4-epi-cubebol (0.9%) bicyclogermacrene +  $\alpha$ -selinene (3.0%)pentadecane (0.4%)  $\beta$ -bisabolene (3.5%)  $\gamma$ -cadinene (1.9%) trans-calamenene + cubebol (0.3%) $\delta$ -cadinene (7.8%)  $\alpha\text{-calacorene} + \gamma\text{-selinene} \; (1.7\%)$ selina-3,7(11)-diene (0.9%) 11-epi-6,12-epoxyspiroax-4-ene (t) (E)-nerolidol (t)  $\beta$ -calacorene (t)

germacrene B (8.3%) spathulenol (0.2%) caryophyllene oxide (0.3%) gleenol (t) 10-epi-junenol (t) salvial-4(14)-en-1-one<sup>a</sup> (t) 6,12-epoxyspiroax-4-ene (0.3%) hexadecane +  $\alpha$ -corocalene (0.4%)1,10-di-epi-cubenol (0.1%) junenol (t) 1-epi-cubenol (0.3%) T-muurolol + T-cadinol (0.7%) cubenol (t)  $\alpha$ -cadinol (0.4%)  $\beta$ -bisabolol (t) cadalene (0.3%) juniper camphor<sup>b</sup> (0.1%)heptadecane (0.3%) octadecane (0.2%) nonadecane (0.1%)

t = <0.01%

<sup>a</sup> also known as mint ketone

 $^{\rm b}$  also known as selina-7(11)-en-4 $\alpha\text{-ol}$ 

P. Weyerstahl, H. Marschall and D. Wolf, Constituents of commercial caboré oil. Flav.Fragr. J., 13, 85-86 (1998).

# **Cypress Oil**

In 1990, Kreis et al. used enantiomeric separation on a chiral capillary GC column to determine that the enantiomeric ratios of  $\alpha$ -pinene,  $\beta$ -pinene and limonene in cypress oil (*Cupressus sempervirens*) was found to be:

$$\label{eq:15.5S} \begin{split} &(18,\!58)\text{-}(\text{-})\text{-}\alpha\text{-}\text{pinene}\;(47\%):(18,\!58)\text{-}(\text{+})\text{-}\alpha\text{-}\text{pinene}\;(53\%)\\ &(18,\!58)\text{-}(\text{-})\text{-}\beta\text{-}\text{pinene}\;(73\%):(18,\,58)\text{-}(\text{+})\text{-}\beta\text{-}\text{pinene}\;(27\%) \end{split}$$

(4S)-(-)-limonene (2%) : (4R)-(+)-limonene (98%)

An oil of cypress produced in Croatia analyzed by Milos and Radonic (1996). Using GC/MS as their method of analysis, the oil was found to contain:

$\alpha$ -pinene (47.91%)	$\alpha$ -humulene (0.13%)
$\alpha$ -fenchene (0.11%)	α-terpineol (0.41%)
$\beta$ -pinene (1.03%)	$\alpha$ -terpinyl acetate (1.73%)
sabinene $(1.17\%)$	$\beta$ -cubebene† (0.65%)
$\delta$ -3-carene (19.81%)	epi-zonarene (0.15%)
limonene (4.16%)	$\delta$ -cadinene (0.30%)
$\gamma$ -terpinene (0.53%)	7-methoxybenzofuran (0.21%)
terpinolene (4.36%)	cedrol (6.84%)
$\alpha$ -p-dimethylstyrene (0.03%)	$\alpha$ -cedrene† (0.17%)
zingiberene† $(0.12\%)$	$\alpha$ -cadinol (0.37%)
bornyl acetate (0.37%)	4-hydroxy-3-methoxybenzene
methyl carvacrol (0.48%)	(0.69%)

† incorrect identification based on elution order

The following year, Chanegriha et al. (1997) used both GC and GC/MS to compare the compositions of four Algerian cypress oils produced from different *Cupressus* species. The oils produced from *C. sempervirens* in March and May were reported to contain the following constituents:

δ-3-carene (3.1-10.6%) myrcene (0.4-1.4%)  $\alpha$ -phellandrene (t) dodecane (0-t) limonene (2.2-4.5%) 1.8-cineole (t)  $\beta$ -phellandrene (0.2-0.4%)  $\gamma$ -terpinene (0-0.5%) (E)- $\beta$ -ocimene (0-t) terpinolene (0.9-2.7%)tridecane (0-t)  $\alpha$ -p-dimethylstyrene (0-t)  $\alpha\text{-cubebene}\left(t\right)$  $\alpha$ -copaene (t) camphor (t) linalool (t)p-isopropyl anisole (t)  $\alpha\text{-cedrene}\;(0\text{-}t)$  $\beta$ -cedrene (0-t) bornyl acetate (0.8-2.0%)

tricyclene (0-t)

undecane (0-t)

α-pinene (2.8-44.9%)

 $\alpha$ -fenchene (0-0.5%)

β-pinene (0.4-1.6%)

sabinene (t-0.6%)

isobornyl acetate (t) terpinen-4-ol (1.9%) umbellulone (t)  $\alpha$ -terpineol (t)  $\alpha$ -humulene (t)  $\alpha$ -muurolene (0-t) α-terpinyl acetate (5.5-12.0%) germacrene D (1.6-2.7%) cis-piperitol (t) δ-cadinene (0.5-1.2%) γ-cadinene (0-t) myrtenol (t) cuparene (0-t) cis-calamenene (t) p-cymen-8-ol (t) undecanol (0-t)  $\alpha$ -calacorene (0-t) dodecanol (0-t) caryophyllene oxide (t) cubenol (0-t) α-cadinol (0.3-0.8%) cedrol (t) cedrenol (t) sandaracopimaradiene (0.5-1.2%) manoyl oxide (1.5-6.7%) dehydroabietane (1.6-4.2%)

t = trace (<0.1%)

More recently, Lahlou et al. (2001) screened a number of oils to determine their effectiveness in controlling head lice (*Pediculus humanis capitatus*). Although a sample of cypress oil produced in Morocco was not shown to be a very effective controlling agent, the authors did report on its analysis. They found that their Moroccan oil contained:

$\alpha$ -thujene (1.7%)
$\alpha$ -pinene (16.3%)
$\beta$ -pinene (1.9%)
sabinene (24.4%)
myrcene (5.1%)
$\alpha$ -terpinene (4.8%)
p-cymene (1.0%)
limonene (2.9%)
1,8-cineole (1.1%)
γ-terpinene (8.0%)

terpinolene (2.9%) linalool (21.1%)terpinen-4-ol (0.4%)  $\alpha$ -terpineol (1.7%) thujanol\* (1.3%)myrtenol (1.0%) citronellol (1.9%) citronellal (1.8%) carvacrol (1.8%)

° correct isomer not identified

It should be pointed out that the above oil bears little resemblance to the cypress oil of commerce. It is either a new chemotype, an errant analysis or the plant material was misidentified.

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