

Formation of Volatile Compounds from Oakmoss

By Mans H. Boelens

Boelens Aroma Chemical Information Service, Huizen, The Netherlands

It has been known¹⁻⁵ that oakmoss (*Evernia prunastri* (L.) Arch.) contains depsides, which are polyfunctional diaryl derivatives. The most important of these depsides are lecanoric acid, evermic acid, divaricatic acid, barbatic acid, atranorin, monochloroatranorin and thamnolic acid (see Figure 1).

It is generally accepted^{2,7,9} that these depsides are virtually nonvolatile and odorless. The depsides are converted into volatile monoaryl derivatives during treatment of oakmoss with water and solvents.^{1,2} The depsides can be hydrolyzed with water during a fermentation process, and with hot water or steam. Furthermore the depsides can undergo alcoholysis with ethanol, for example, under formation of polyfunctional monoaryl ethyl esters.

Various qualitative analyses of the odoriferous fraction of oakmoss have been published.²⁻⁶ So far only one investigation⁷ of the quantitative analysis of oakmoss oil has been found in the literature.

In the current investigation, the quantitative composition of the volatile components in oakmoss was studied. Also the formation of a few of the interesting monoaryl derivatives will be discussed.

New Chemical Aspects of Volatiles from Oakmoss

As previously mentioned, oakmoss contains various types of depsides, which are non-volatile, odorless, polyfunctional diaryl-derivatives. Schemes 1 and 2 show the volatiles that can be derived from the depsides barbatic acid and atranorin.

Scheme 1 - Volatile Compounds from Barbatic Acid:
On hydrolysis of barbatic acid (an odorless compound) one gets two odorless acids. Only after decarboxylation may one

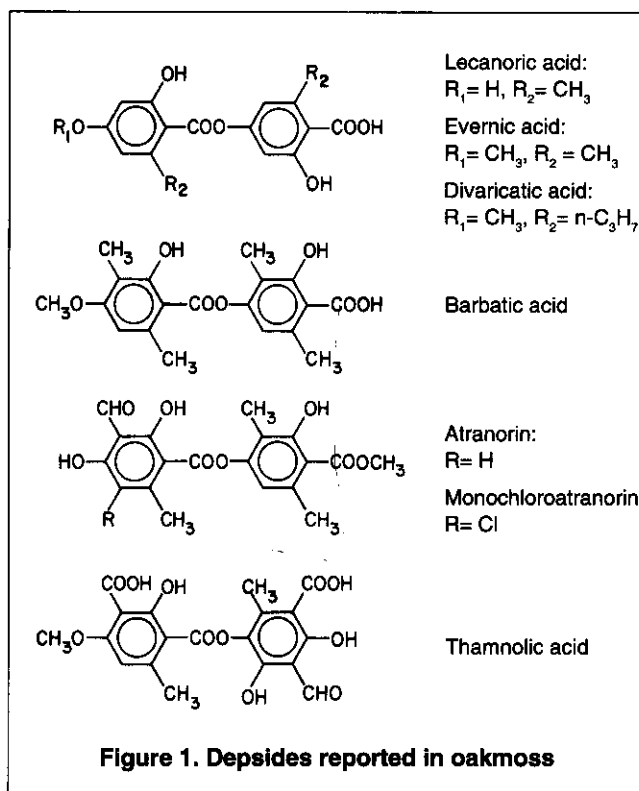


Figure 1. Depsides reported in oakmoss

obtain two volatile compounds, such as β -orcinol and its monomethyl ether. These products are present in the absolute up to 5%. It will be clear that for the hydrolysis and decarboxylation one has to force the conditions, by adding more water, lengthening reaction times, and raising temperatures.

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Because barbatric acid yields 50% β -orcinylic acid on hydrolysis, one could convert this acid into its methyl ester (the character-impact-compound of oakmoss); however, this requires transesterification with methanol.

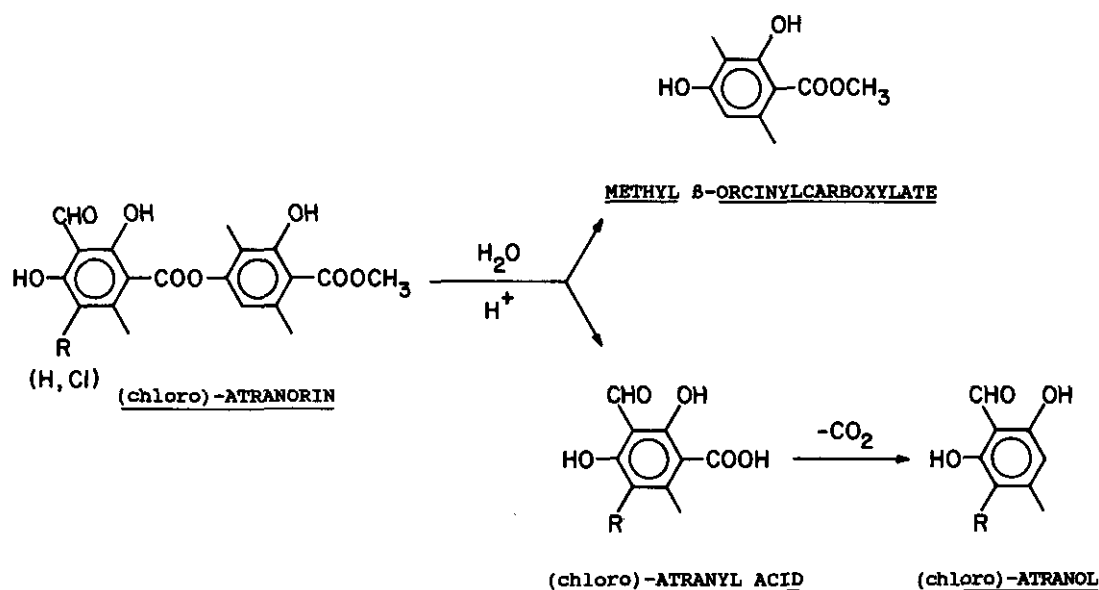
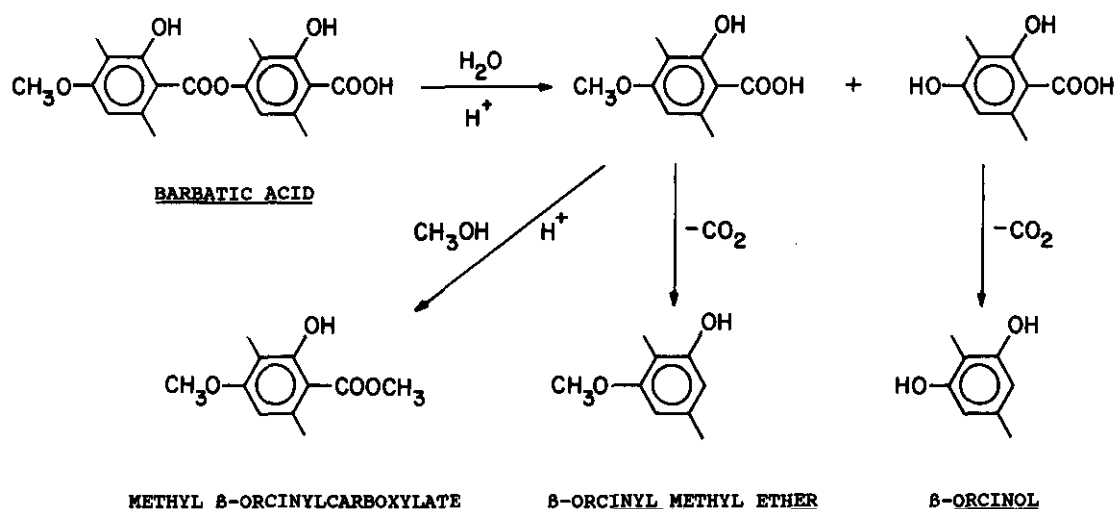
Scheme 2 - Volatile Compounds from Atranorin: Atranorin can be directly converted into methyl β -orcinylic carboxylate by hydrolysis. Atranyl acid, an odorless compound, is another product of hydrolysis. It can be decarboxylated into atranol. Atranol can occur in oakmoss absolute up to 15%.

From these two examples it can be readily understood that the formation of volatile compounds from oakmoss is more complicated than generally expected for an aromatic natural product. The ethanolysis of depsides or monoaryl

carboxylic acid derivatives during the extraction with ethanol or during the preparation of the absolute from the concrete has been mentioned in the literature. It was reported that the ethyl everminate was almost odorless.²

Experimental Conditions

In this study, 200 G of dried oakmoss lichen (moisture content 5%) was extracted c.q. reacted for 7 h with 1 L of solvent at the boiling point or for 7 h with 2 L of solvent in a Soxhlet apparatus. Solvents were evaporated in a rotavapor apparatus. Oakmoss absolutes were prepared by dissolving the concretes in 10 parts of boiling ethanol, cooling at 0°C for 24 h, filtering the precipitate and finally the solvent was removed by evaporation.



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Transesterifications were carried out with 200 g of oakmoss lichen in 500 mL methanol and 500 mL benzene, with 2 g of p-toluenesulfonic acid under reflux conditions also for 7 h.

The yields of the extractions and transesterification are shown in Table I.

Table I. Yields of extraction and transesterification

Solvent	Method	Yield (%)
hexane	extraction	2
dichloromethane	extraction	5
benzene	hydrolysis/extraction	7
acetone	hydrolysis/extraction	10
methanol	alcoholysis/extraction	15
benzene/methanol	transesterification	10

Table II. Chemical composition of volatiles from oakmoss absolutes

Chemical name	Benzene (%)	Benzene /MeOH (%)
N-methyl pyrrolidone	0.2	0.1
orcinol monomethylether (3-methoxy-5-methylphenol)	2.2	7.6
orcine (3-hydroxy-5-methylphenol)	4.8	23.8
β -orcinol monomethylether (3-methoxy-2,5-dimethylphenol)	0.1	0.1
β -orcinol (3-hydroxy-2,5-dimethylphenol)	0.3	1.3
chloro atranol (3-chloro-2,6-dihydroxy-4-methylbenzaldehyde)	13.2	6.6
atranol (2,6-dihydroxy-4-methylbenzaldehyde)	12.7	8.4
methyl everminate (methyl 2-hydroxy-4-methoxy-6-methylbenzoate)	1.2	3.5
methyl 2,4-dihydroxy-6-methylbenzoate	0.7	0.7
ethyl everminate (ethyl 2-hydroxy-4-methoxy-6-methylbenzoate)	6.2	3.5
methyl hematommate (methyl 3-formyl-2,4-dihydroxy-6-methylbenzoate)	0.6	1.1
methyl β -orcinolcarboxylate (methyl 2,4-dihydroxy-3,6-dimethylbenzoate)	52.0	33.4
ethyl 2,4-dihydroxy-6-methylbenzoate	0.3	0.4
ethyl hematommate (ethyl 3-formyl-2,4-dihydroxy-6-methylbenzoate)	0.2	-
ethyl 2,4-dihydroxy-6-propylbenzoate	0.2	0.3
ethyl β -orcinolcarboxylate (ethyl 2,4-dihydroxy-3,6-dimethylbenzoate)	0.3	0.1
dibutyl phthalate [impurity?]	4.0	4.6

The oils (absolutes) were analyzed on a Perkin Elmer 8,400 gas chromatograph (FID-detector) with a fused silica column (60 m length, 0.25 mm i.d.), coated with SPB-5, temp programmed from 50-240°C (2°C/min), carrier gas nitrogen with a flow rate of 1.2 mL/min, sample injection 0.2 μ L. GC/MS analyses of the oils were run on a Hewlett Packard mass spectrometer HP 5970 B, ion source 70 eV, coupled with a gas chromatograph HP 5890 A with fused silica capillary column (50 m length, 0.21 mm i.d.), coated with SE-54, temp programmed from 50 to 260°C (2°C/min), carrier gas helium with a flow rate of 0.4 mL/min, sample injection 0.2 μ L. The identities of the quantified constituents were checked by comparing their MS and retention times with those of authentic compounds. Percentages were calculated using methyl β -orcinyl carboxylate (veramos-IFF, evernyl-Roure) as internal standard. The constituents identified are shown in Table II.

Discussion

The so-called oakmoss concrete and absolute are widely used in perfumery in chypre-type perfumes. They contain various types of depsides, which are non-volatile polyfunctional di-aryl derivatives (see Figure 1).

It is generally accepted that the monoaryl derivatives reported as constituents of processed oakmoss extracts are considered to be degradation products of the depsides (see Figure 2). It will be clear from this discussion that if this degradation process were only hydrolysis, at least 50% of the depsides would be present in the extract as non-volatile monoaryl acids.

A recently published report describes the continuous extraction of oakmoss. It emphasizes the fact that hydrolysis was an integral part of the extraction process.^{8,9}

Benzene easily penetrates into plant cells and is difficult to remove from them. By pressing, one half of retained solvent can be released, while the other half can be removed by steam distillation.⁸

It seems likely that at higher temperatures (boiling point) the intimate contact of benzene and water in the cells promotes a phase transfer reaction in which depsides are hydrolyzed into monoaryl derivatives.

It has been reported that orcinol- or β -orcinol-carboxylic acid derivatives easily decarboxylate to orcinol- and β -orcinol derivatives.¹¹

From an olfactive standpoint the most important monoaryl derivative of oakmoss is methyl β -orcinyl carboxylate, which may be formed by hydrolysis of the depside atranorin and by esterification of the free acid (from barbatric acid hydrolysis or by transesterification).

During the investigation of oakmoss and its extraction the following observations were made:

- Neither freshly harvested (dry) nor heated

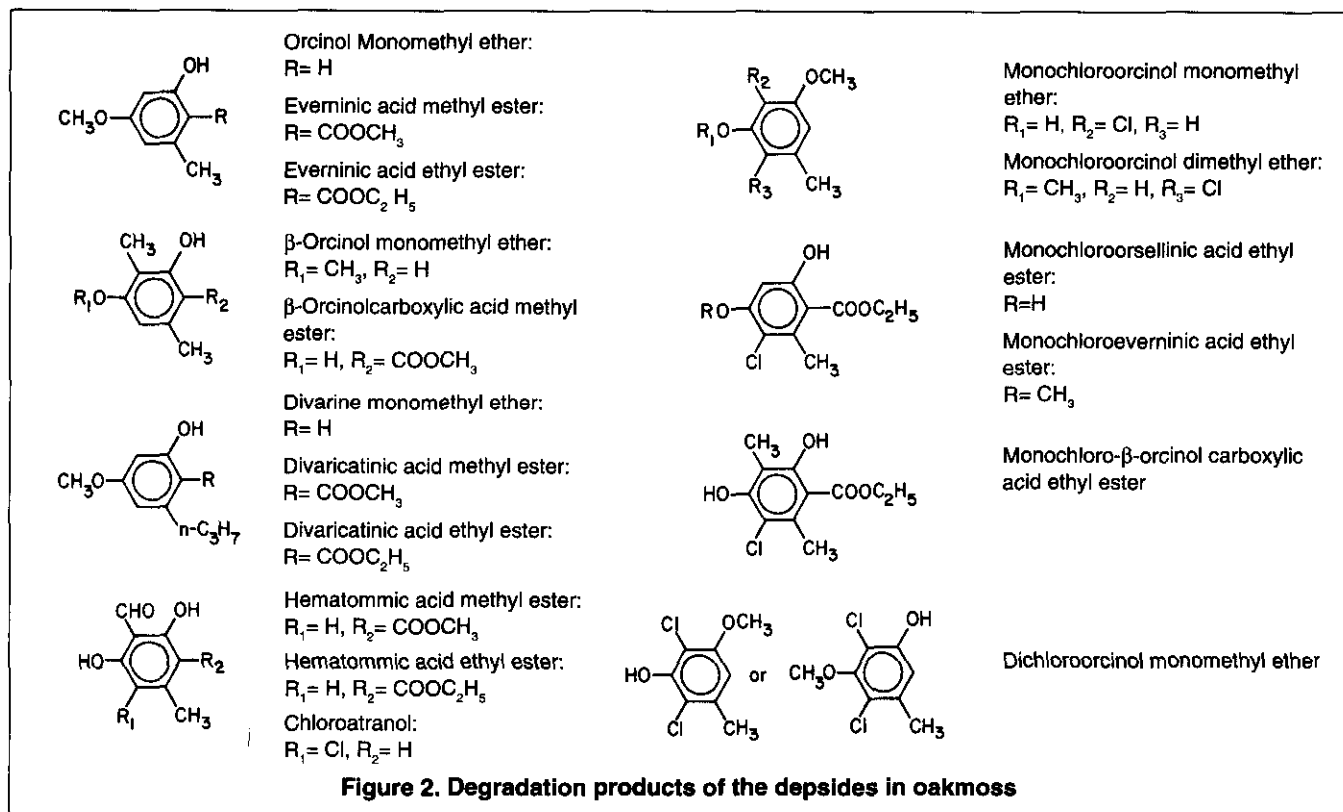


Figure 2. Degradation products of the depsides in oakmoss

(100°C) oakmoss (lichen) possesses the aroma of methyl β-orcinyl carboxylate, the character-impact component characteristic for oakmoss absolute;

- On burning (open flame), oakmoss strongly develops the familiar odor character;
- Dry oakmoss (5% moisture) can readily absorb 1-2 times its weight of solvent;
- The components of olfactive interest are formed during extraction of oakmoss lichen with certain solvents;
- The best quality oakmoss absolute is obtained by benzene (water/hydrolysis) extractions of the oakmoss (lichen);
- Although the yield of extract is high if the oakmoss (lichen) is extracted directly with alcohol, the product is semi-solid with a poor aroma;
- During the extraction, hydrolysis, decarboxylation, and (trans)esterification (alcoholysis) are all known to occur.

Conclusions

Freshly harvested oakmoss practically has no scent. The moss contains depsides, which are virtually odorless. The characteristic oakmoss fragrance is only developed after hydrolytic cleavage of the depsides. This hydrolysis can be performed in an enzymatic way or by treatment with hot water or steam. During this reaction a part of the potential odorants is lost in the form of free acids, which after esterification give the characteristic compounds.

The extraction of oakmoss was carried out with different

solvents. The yield of the concrete is strongly dependent on the polarity of the solvent. A good yield and quality of oakmoss absolute can be obtained after combined extraction and transesterification of the moss.

References

Address correspondence to Mans H Boelens, Boelens Aroma Chemical Information Service (BACIS), Groen van Prinstererlaan 21, 1272 GB Huizen, The Netherlands.

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