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A Review on Vetiver grass and its Essential Oil

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ABSTRACT

Vetivergrass (*Chrysopogon zizanioides,* L. Roberty*)* is a perennial graminaceous plant, which grows wild, half wild or cultivated in many tropical and subtropical areas. This rather interesting plant belongs to a Family of Poaceae. From the historical background Vetiver is native to India where it's mainly recognized under the name Khus-khus or Khas-khas. Followed with India, Indonesia (Java), China, Brasil , Japan and Haiti are the main producers of vetiver oil, a highly appreciated essential oil in perfumery and medicinal use. It is often said that the benefits from vetiver are being known since ancient times, much before the world became familiar with rose scents. Weather it is because of its termicidal, insecticidal, antimicrobial, antioxidant activity, land protectioning purpose as well as its sedative effect, or simply because of the pleasant aroma, this unique plant and its essential oil are beeing recognized as very interesting experimental materials among scientists. The chemical composition of vetiver oil is considered to be one of the most complex.

ZUSAMMENFASSUNG

Vetiverkraut (*Chrysopogon zizanioides,* L. Roberty) ist eine mehrjährige Pflanze. Diese kann wild, halbwild oder kultiviert in vielen tropischen oder subtropischen Zonen wachsen. Diese sehr interesante Pflanze gehört zu der Familie Poaceae. Von historische Seite gesehen, ist Vetiverkraut heimisch in Indien und ist oft Khus-khus oder Khas-khas gennant. Indien, Indonesien (Java), China, Brasilien, Japan und Haiti sind die grösste Hersteller von Vetiver Öl, eines sehr wertvolles ätherisches Öl welches im Parfumgeschäft wie auch in medizinischen Gebieten sehr geschätzt wird. Es wird oft gesagt dass die Vorteile von Vetiver noch von der Zeit der Antike bekannt sind, noch früher als die Welt die rose Duft kennengelernt hat. Vetiverkraut hat viele positive insektizide, antimikrobielle, antioxidative und beruhigende Wirkungen auf Menschen und Tiere. Es ist auch wichtig zu betonnen dass es oft als Bodenschutzmittel eingesetzt wird. Vetiver Duft wird als sehr angenehm beschrieben und deswegen ist es sehr begehrt in der Parfumindustrie. Die chemische Komposition von Vetiver Öl ist eine der meist komplexen, deshalb wundered es nicht dass es immer wieder eine sehr interessantes Thema für Wissenschaftler ist.

CONTENTS

1. INTRODUCTION

Vetivergrass (*Chrysopogon zizanioides L. Roberty*) is a perennial graminaceous plant, which grows wild, half wild or cultivated in many tropical and subtropical areas. *Chrysopogon zizanioides* is also known as vetiver (grass), khus or khus-khus and belongs to the family of Poaceae (Graminae).

It is well known that Vetiver grows in almost any type of soil, but a fairy well drained and rich loam is considered to have the best qualityes to grow Vetiver. The best climatic conditions for Vetiver have areas with warm summers and enough rain seasons.

There are distinct geographical differences in quality and perfumery note of essential oil obtained from different geographic regions of the world. Depending upon the country of occurrence, cultivation practices, climatic conditions, and genetic origin, there occurs tremendous diversity with respect to yield and quality of essential oil, ranging from a woody, earthy and as many describe it balsamic note to a sweet, roseate note (Lavania, 2003). A brief account of physicochemical characteristics of vetiver oil from different geographical regions of the world is given in Lavania (2003), and the chemical profile provided by Lemberg and Halley (1978).

In a broad sense, the essential oil of vetiver having high specific gravity, negative optical rotation, high vetiverol concentration and higher ester value is considered superior from perfumery view point. Reunion oil with roseate note is highly regarded in perfumery industry, but the vetiver oil (khus oil) obtained from the roots occurring in wild state in north Indian plains, commonly known as ‘khus’ is considered to be the best for its balsamic woody note.

Major components of vetiver oil are *α-vetivone*, *β-vetivone* and *khusimol.* The chemical composition of Vetiver oil obtained by steam distillation of the dried roots from Chrysopogon zizanioides of various geographic origins has been studied since 1901 (Smadja, 1994). The vetiver oil is extremely complex (Chia, 2000). It consists mainly of bicyclic and tricyclic sesquiterpenoids (hydrocarbons, alcohols, ketones, aldehydes, acids) (Cazaussus et al., 1988; de Guzman and Oyen, 1999; Vietmeyer

and Ruskin, 1993), but monoterpenoids (Nikiforov, 1992) and phenols (Garnero, 1971; Shibamoto and Nishimura, 1982) have also been detected.

In the typical vetiver oils (Haiti, Reunion, Java, Brazil and South India) sesquiterpene oils with valencane, eremophilane, eudesmane, epieudesmane, vetispirane, zizaane (or tricyclovetivane), prezizaane, guaiane and cyclocopacaphane skeletons were found (Anonymous, 1976; Garnero, 1971; Weyerstahl, 2000a; Weyerstahl, 2000b). However, the major representatives of the vetiver oil, (+)-α-vetivone, (-)-ß-vetivone and khusimol (Figure 19), can be considered as the "fingerprint" of oil (de Guzman and Oyen, 1999; Demole, 1995) even though they do not possess the typical odor characteristics associated with vetiver.

This review reports also about many positive aspects of vetiver essential oil, among which sedative, antibacterial and many other useful effects on humans play the main role.
Demographic varieties are described to understand how vetiver oil can give different odor, when grown in different parts of the world. Because of its complex chemical composition it is very expensive and well appreciated component in perfume industry.

Synthetic attempts were made to find structurally similar structures with vetiver character that could easily be synthesized. Until now, reconstitution of the pleasant vetiver aroma with synthetic compounds has yet not been achieved.

2. VETIVER GRASS

2.1. Taxonomy

Genus: Chrysopogon
Family: Poaceae alt. Gramineae
Nomen Number: 80369
Place of publification: J. K. Small, Fl. S. E. US. 67.1903.
Name verified on: 9-October-2007 by Systematic Botany Laboratory. Last updated: 9-October-2007

Synonyms:

- *Phalaris zizanioides* (H. Linn, 1771)
- *Andropogon muricatus* (Retzius, 1783)
- Andropogon zizanioides (L. Urban 1903, de Guzman and Oyen, 1999)
- *Anatherum zizanioides* (L. Hitchock & Chase, 1917)
- *Vetiveria zizanioides* (L. Nash, 1999)

2.2. Description of a plant

The generic name Vetiveria comes from the Tamil word "*vétiver*" meaning "root that is dug up". The specific name zizanioides was first given by the Swedish taxonomist Carolus Linnaeus in 1771, meaning "by the riverside" (Vietmeyer and Ruskin, 1993).

A wide range of conditions is suitable for Vetiver grass, for example different temperatures (- 15^0C to > 55^0C), soil pH (< 3 to > 10), and annual rainfall (< 300 mm to > 5000 mm). Diseases like pest do not hurt its quality and growth. Resistance towards salinity and prolonged waterlogged conditions is also of great meaning (Grimshaw, 2008).

Vetiver grows in any type of soil but a rich and well drained loam is considered to be the best. The loamy soils, which are loose in texture, are ideal for root growth and harvesting as well. Vetiver plant also grows on a variety of problematic soils like

waterlogged, or sandy soils and areas with high water table and flood prone. A luxuriant growth of healthier root is obtained from plants growing under warm and damp conditions on rich, temporary inundated, marshy land.

Vetiver grass is perennial, grows tall up to two meters and has a specific scent. Leafs can be described as keeled, glabrous with scarbid margins and about 80 cm long. Four to six milimeters long and paired spikelets are mostly grey-green and purplish. The plant shows typical complex underground root system for Poaceae family plants which blends with the soil and assures plants adaptability (Cunningham, 1994).

Figure 1. Vetiver grass in nature
(www.chaipat.or.th)

2.2.1. Clump

Vetiver grass grows through tillering and appears in a clump. It may grow densely tufted in a big cluster or scattering over the nearby spaces. The base of the clump is dense which makes it obviously distinctive from other types of grass. Normally, vetiver grass has a short culm with unclear pedicels and joints. The clump diameter is about 30 cm and the height is 50-150 cm. The growth is specified by the technique of tillering, which makes clump grow bigger and bigger while producing new shoots on the sides. Joints and pedicels are not clearly visible because of the shortness of the clump (Cunningham, 1994).

Figure 2. Vetiver clump
(www.chaipat.or.th)

2.2.2. Leaf

Vetiver leaves are sprouted from the bottom of the clump in narrow, long and coarse leaves. The base and the middle of the blade have few spines whereas the apex has numerous spines. All spines are pointing diagonally towards the apex. The leaves are erect and rather stiff with 80 cm of length and 8 mm of width (Maffei, 2002).

Figure 3. Vetiver leaf
(www.chaipat.or.th)

2.2.3. Inflorescence

Vetiver inflorescence is erect and it appears in the form of a panicle which is round and long about 100-150 cm high above the ground. However, it can be as high as 200 cm. The inflorescence or the panicle alone is about 20-40 cm, high and can spread out at a maximum width of 10-15 cm.

The inflorescence of *Chrysopogon zizanioides* is mostly purple, the colour which is an common attribute of this species. The spikelet appears in pairs with similar features and size, except for the base of the stalk which has three spikelets. Each pair of spikelets consists of both sessile and pedicelled spikelets. The sessile spikelet is at the middle, whereas the pedicelled one is at the tip. Each spikelet is similar in appearance to a spindle. The edge is parallel and oval. The cuneate apex is 1.5-2.5 mm wide and 2.5-3.5 mm long. The surface of the back of the spikelet is rough and consists of minute spines, the lower part of the spikelet is smooth (Maffei, 2002).

Figure 4. Vetiver inflorescence
(www.chaipat.or.th)

2.2.4. Roots

Vetiver roots are the most useful and very important part. The deep and thick root system, which spreads vertically, can efficiently endure harsh conditions and the root system expands sideway up to only 50 cm. Vetiver hedgerows maintain soil moisture and soil surface and at the same time, are suitable for cultivating along with economic crops. It is important to mention that the root system of vetiver grass does not expand horizontally like mostly other grass roots, instead it penetrates vertically into the soil.

The precious vetiver essential oil is produced by individual cells, called secretory idioblasts, in the roots in large quantities. These idioblasts also retrain the oil within the cell which occurs within the cortical layer and close to the endodermis (Bertea and Camusso, 2002).

Figure 5. Vetiver roots
(www.chaipat.or.th)

2.3. Impact of vetiver grass

2.3.1. Agriculture impact

Since Vetiver grass has a deep thick root system it is cultivated:

a) to preserve moisture in orchards
b) to filter silts around pond edges

The so called Vetiver System (VS) is a simple, low-cost technology that employs vetiver grass for soil and water conservation, bioengineering, environmental protection, disaster mitigation and phytoremediation of deteriorated or contaminated land and water (Chomchalow, 2006).

For various purposes in many countries around the world Vetivera system has been used extensively. The following showcases are cited to exemplify its role in strengthening rural communities:

a) Handicraft Making in Venezuela, (Luque, 2004),
b) Railway Rehabilitation in Madagascar, (Charanasri, 2006),
c) Poverty Eradication in Indonesia, (Booth and Adinata, 2006),
d) Community Strengthening through People Participation in Thailand, (Tansamrit and Salinla-umpai, 2006),
e) Riverbank and Dike Protection in Vietnam (Dung, 2006),
f) Watershed Management of the Dabie Mountains in China (Liyu Xu, 2006),
g) Toogoolawah Vetiver Wetland System in Australia (Anon, 2004b),
h) Mudslide disaster Mitigation in Thailand (Anon, 2004b),
i) Environmental Protection of Open-Cut Bauxite Mine in Venezuela (Luque et al., 2006),
j) Reduction of Watershed Sediment in Guam (Adams et al., 1998).

2.3.2. Medicinal impact

The plant of vetiver is often used in the Eastern world medicine. Some people claim that paste made of the roots has an almost “magic effect “, when applied to burns, swellings or any type of bruises. A stimulant drink is made from fresh rhizomes in India, and in Madya Pradesh (India) the plants are used as an anthelmintic (de Guzman and Oyen, 1999; Sreenath et al., 1994). Research was based on ethnobotanical interviews conducted from 1996 –2000 in Trinidad and Tobago with thirty male and female respondents which shows that plant *Chrysopogon zizanioides* was used for kidney problems and for gall stones as well as for cooling (Lans, 2006).

In the paper of Kumar and his coworkers has reported about how dessert dwellers who live in arid western Rajastan use plants as herbal coolant as their strategy to cope better with excessive heat, considering the continuous hot weather in eight months a year. The plants that were tested have been collected from the nearby fields and the informations about local names of the plants, parts used and preparatiopn of herbal drinks were gathered from village elders. The paper reported how also vetiver has a positiv effect when used as coolant. The roots are crushed in water to make a cooling drink. This juice can be applied on the body or simple taken as a herbal drink. The goal is to increase perspiration and evaporation, so that larger amount of water are not necessary to preserve hydratation (Suresh Kumar et al., 2006).

Throughout history women have tried to control or enhance their fertility using herbal juices, with various levels of societal support. Caribbean folk medicine has been influenced by European folk medicine, either through the early Spanish and French settlers or through the continuous immigration of Spanish-speaking peoples from Venezuela. Thirty respondents, ten of whom were male were interviewed from September 1996 to September 2000.
They were obtained by snowball sampling and found in thirteen different sites, twelve in Trinidad (Paramin, Talparo, Sangre Grande, Mayaro, Carapichaima, Kernahan, Newlands, Todd's Road, Arima, Guayaguayare, Santa Cruz, Port of Spain and Siparia) and one in Tobago (Mason Hall). Snowball sampling was used because

there was no other means of identifying respondents and to cover the entire islands. The validation of the remedies was conducted with a non-experimental method plant used for childbirth and infertility: *Chrysopogon zizanioides* (Lans, 2007).

2.4. Harvesting

In general, the crop is harvested after 15-18 months during the dry season from December to February to get a total developed root system for best quality oil. It is very important not to harvest earlier than 15 months because the immature roots yield oil of poor quality with a green earthy odor. When properly developed, the meaningfully thicker roots, yield an oil of better quality and its optical rotation and specific gravity are higher, the odor fuller, richer and more lasting. Oils derived from older roots are usually of darker colour than the oils distilled from the younger roots. If the roots stay in ground for over two years, the yield of oil decreases considerably as the root system tend to become woody and lose in essential oil content. The oil becomes very viscous with a dark colour but maintaines high quality.

Oil content of the root starts minimizing considerably after 20 months age. For harvesting, the moist areas are taken up first. The water logged areas become dry enough in February for digging up the roots. After February due to rising temperature, the soil become harder and makes digging very difficult. At this level the finer and thinner roots stay in the ground, which contains more oil resulting low yield per unit area (Engineers India Research Institute, 2007).

Characteristics to determine correct harvesting age

The roots that have the following characteristics have good oil composition. They should:

1. expose a hard surface when the skin is peeled off
2. be thick, hard, long and wiry and
3. give a very bitter taste when chewed.

2.4.1. Digging

When the stalk of vetiver grass attaines the hight of 15-20 cm it is being cut and the clumps usually stay uprooted. Cutting is certainly a more economic way of digging, because when dug out by spade or tractor almost 60% of the roots come away with the clump (Engineers India Research Institute, 2007).
Once the clumps are dug out, the earth adhering to the roots needs to be removed by beating the roots on a piece of timber, afterwards the roots are removed with a sharp knife.

When possible the soil should be dught again to collect all of the roots still remaining in the soil. One soaking may be done before harvesting to facilitate digging if available. Mechanical harvesting can also be very economic when a disc plough with single disc is connected on a tractor to uproot the roots from 35 cm depth. When done this way digging saves manpower and also gives about 15% higher root recovery than manual digging. The length of the roots can vary from 10-35 cm according to the condition of growth, soil, climate etc. of the locality. Considering the amount of the oil that the roots can produce, thicker roots have better biodiversity than very thin and almost white roots (Engineers India Research Institute, 2007).

2.4.2. Washing / Cleaning

Freshly harvested roots mainly contain large amounts of earth sticking to them, therefore the roots are immediately gently washed. Water used for washing should be clean and constantly running to remove the earth, but carefully so that the finer roots are not damaged or lost (Engineers India Research Institute, 2007).

2.4.3. Drying

After the roots are cleaned, they have to be spread on a dry ground and turned over in regular intervals until they are dry. During this process foreign matter if any is removed from the mass. The cleaned and dried roots are sent to the distillery or a special storage shed where they are left to mature. Drying is done in the conditions of

shade for 1-2 days, which improves the olfactory quality of the essential oil. Prolonged drying in the sun reduces the oil yield. Dry roots can be stored in shade for 60-70 days without loss of oil but quality improves appreciably (Engineers India Research Institute, 2007).

2.4.4. Yield of roots

The age, the soil, climatic conditions and also the strain are important factors governing the yield of roots. On an average, 30-45 kg/ha of dry root are obtained under good management. At 0.4% average recovery the oil yield of 12-20 kg oil/ha may be obtained (Engineers India Research Institute, 2007).

Vetiver grass has been yielded in many parts of the world for soil and water management. An interesting experiment was made to compare vetiver root essential oils from cleansed (bacteria- and fungus-free) vs. non-cleansed (normal) vetiver plants. Karnataka and Malaysia cultivars of vetiver were used to produce plants that are bacteria- and fungi-free. Tissue cultured (phytosanitary) vetiver was grown in unsterilized soil under the same conditions. 49 of the major oil components were submitted to statistical analysis and revealed numerous important diversities between tissue culture and natural plants for both genotypes. Even though oil yields differed, this may reflect the larger size of the initial plantlets obtained from natural source. Tissue cultured vs. natural plants yielded in sterilized soil resulted in the largest number of differences in compounds. Tissue cultured vs. natural plantlets grown in non-sterile soil showed the least number of differences of components. The claim that many of the compounds found in vetiver roots originate from endogenous fungi was not acknowledged (Adams et al., 2007).

3. VETIVER ESSENTIAL OIL

3.1. Essential oils

Essential oils are Komplex systems (mono-, sesqui- and some diterpenes) and a rich source of biologically active compounds. It has been shown that essential oils possess antibacterial, antiviral, antifungal, insecticidal and antioxidant aspects. There has been an increased interest in looking at antimicrobial properties of extracts from aromatic plants particularly essential oils (Milhau, 1997). It is reasonable to expect a variety of plant compounds in these oils with specific as well as general antimicrobial activity and antibiotic potential (Darokar, 1998). Essential oils are a mixture of fragrant, highly volatile substances isolated by a physical process from an odiferous plant of a single botanic species or variety (Encyclopaedia Britannica, 1986, Oyen and Dung, 1999). The essential oil is named after the aromatic plant from which it has been derived. They are often stored in specialized storage and secretory sites like glandular hairs, resin canals or oil ducts and schizogenous glands (Banthorpe, 1988; Charlwood and Charlwood, 1991). Essential oils may be found in any part of a plant and can be isolated from roots, wood, bark, leaves, flowers, fruit and seed for commercial purposes (Oyen and Dung, 1999).

Essential oils are secured by steam distillation. An estimated amount of 3000 essential oils are known, of which 300 are commercially of greath importance in the fragrance market (Van de Braak, 1999).

They are complex mixtures of sometimes hundreds of chemical compounds. Most of these compounds can be grouped into three major groups (Oyen and Dung, 1999):

1) terpenes and terpene derivatives,
2) benzene derivatives,
3) miscellaneous compounds.

Terpenes

Terpenes are a very large and diverse group of organic components, though some insects such as termites or swallowtail butterflies emit terpenes from their osmeteria, terpenes are mainly produced by plants. The odor of terpenes is often very strong and has a protective function.They are the major components of resin, and of turpentine produced from resin. The name "terpene" is derived from the word "turpentine". In addition to their roles as end-products in many organisms, terpenes are major biosynthetic constituents within nearly every living creature. When terpenes are modified chemically, such as by oxidation or rearrangement of the carbon skeleton, the resulting compounds are generally referred to as terpenoids. Some authors will use the term terpene to include all terpenoids. Terpenoids are also known as isoprenoids.

Terpenes basic groundwork is the hydrocarbon isoprene (*Isoprene rule*, Wallach, 1887):

$$CH_2=C(CH_3)-CH=CH_2$$

Terpene hydrocarbons therefore have molecular formulas:

$$(C_5H_8)_n$$

Terpenes and terpenoids are the major constituents of the essential oils of many plants and flowers. Synthetic variations and derivatives of natural terpenes and terpenoids also widely expand the variety of aromas used in perfumery and flavors used in additional food additives. Terpenes are released by trees more actively when the weather is warm. The clouds reflect sunlight, allowing the forest to regulate its temperature (David, 2008). The aroma and flavor of hops, desirable in many beers, comes from terpenes. Myrcene, β-pinene, β-caryophyllene, and α-humulene are found in the large quantities in hops (Tinseth, 1993).

Terpenes can be classified by the number of isoprene parts in the molecule; a prefix in the name gives the number of isoprene units needed to create the molecule.

Hemiterpenes consist of *a single isoprene* unit. Isoprene itself is considered the only hemiterpene, but has oxygen-containing derivatives such as:

a) prenol $C_5H_{10}O$

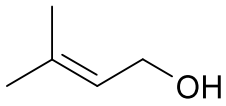


Figure 6. Chemical structure of prenol

Prenol is one of the most simple terpenes. The color of this compound is clear and it is not soluble in water but is miscible with most common known organic solvents. It has a very fresh fruity odor and sometimes it is used in perfumery. Prenol appears naturally in grapes, raspberry, blackberry, bilberry, cranberry, grapes, citrus fruits, passion fruit, tomato, white bread, hop oil, coffee, arctic bramble and currants (SIDS Initial Assessment Report, 2005).

b) isovaleric acid $C_5H_{10}O_2$

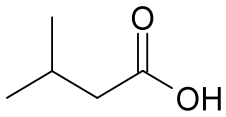


Figure 7. Chemical structure of isovaleric acid

Isovaleric acid is a natural fatty acid found in a wide spectrum of plants and essential oils. It is a colorless fluid that is sparingly soluble in water, but high soluble in most well known organic solvents.

Isovaleric acid has a strong pungent cheesy or sweaty smell, but its volatile esters have pleasing scents and are often used in perfumery, on the other hand an excess of isovaleric acid in wine is considered to be a defect (Katsutoshi, 2006).

The chemical structure of **Monoterpenes** consist of two isoprene compounds and are derived from the molecular formula $C_{10}H_{16}$.

a) myrcene $C_{10}H_{16}$

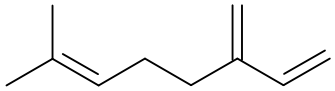


Figure 8. Chemical structure of myrcene

Myrcene is one of the most important monoterpenes and it can be found in essential oil of several plants including cannabis, bay, ylang-ylang, parsley, hops and wild thyme. It is produced semisynthetically from myrcia. Myrcene is one of the main components in the production of several fragrances.

b) geraniol $C_{10}H_{18}O$

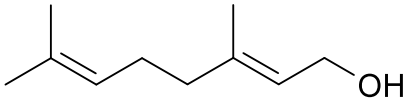


Figure 9. Chemical structure of geraniol

Geraniol is an acyclic, aliphatic monoterpenoid alcohol. It is the primary part of rose oil, palmarosa oil, and citronella oil (Java type). It also appears in small quantities in geranium, lemon, and many other essential oils. Geraniol appears as a clear to pale-yellow oil that is not soluble in water, but is soluble in most common organic solvents. It has a rose-like scent and is widely used in perfumes. It is used in flavors such as peach, raspberry, grapefruit, red apple, plum, lime, orange, lemon, watermelon, pineapple, and blueberry.

c) limonene $C_{10}H_{16}$

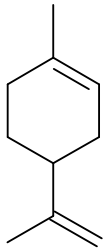


Figure 10. Chemical structure of limonene

Limonene is a colourless liquid hydrocarbon identified as a monocyclic monoterpene. The more common (+)-isomer possesses a strong smell of oranges (Fahlbusch et al., 2003). Because Limonene is not easily dissolved in ethanol its use in cosmetic products is avoided.

As the main odor constituent of citrus fruits (plant family Rutaceae), (+)-limonene is used in food manufacturing and some medicines, also as a flavoring to mask the bitter taste of alkaloids, and as a fragrant in perfumery.

d) α-terpineol $C_{10}H_{18}O$

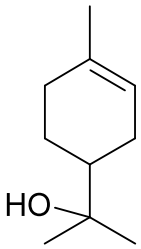


Figure 11. Chemical structure of α-terpineol

Terpineol has a pleasant odor similar to lilac and is a common element in perfumes.

e) camphor $C_{10}H_{16}o$

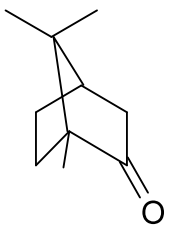


Figure 12. Chemical structure of camphor

Camphor is white or transparent solid with a dominant, aromatic odor (Mann, 1994). It has the semblence of wax. Camphor is extracted from the woods of Cinnamomum camphora, a tree located in North America and Southeastern Asia. It is also one of the major constituents of the essential oil of common sage (Salvia officinalis) and is commercialy used as a moth repellent and preservative in cosmetic and pharmaceutical products (Wichtel, 2002).

Sesquiterpenes consist of *three isoprene* units and are derived from the molecular formula $C_{15}H_{24}$. (The *sesqui*-prefix means one and a half.) Examples of sesquiterpenes are:

a) farnesol (acyclic sesquiterpene alcohol) $C_{15}H_{26}0$

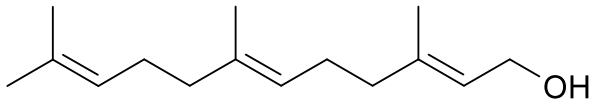


Figure 13. Chemical structure of farnesol

Farnesol is present in many essential oils such as neroli, citronella, cyclamen, lemon grass, rose, tuberose, musk and tolu-balsam. It is often used in perfumery to highlight the odors of sweet floral perfumes. It's method of action for enhancing perfume scent is as a co-solvent that regulates the vicissitude of the odorants.

b) α-vetivone $C_{15}H_{22}0$

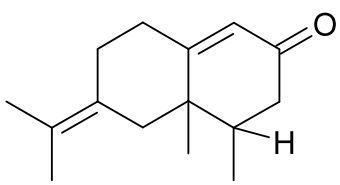


Figure 14. Chemical structure of α-vetivone

Diterpenes are composed of *four isoprene* units and have the molecular formula $C_{20}H_{32}$. They derive from geranylgeranyl pyrophosphate. Diterpenes also form the basis for biologically important compounds such as retinol, retinal, and phytol. They are known to have antimicrobial and antiinflammatory properties.

a) retinol $C_{20}H_{30}0$

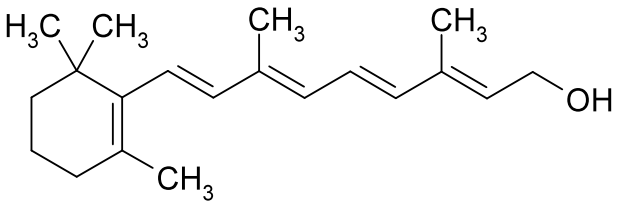


Figure 15. Chemical structure of retinol

Retinol is one of the forms of vitamin A, which can also be converted to other forms of vitamin A, retinal and retinoic acid. Vitamin A is essential for healthy vision and retinoic acid for skin health, teeth remineralization and bone growth.

b) phytol $C_{20}H_{40}0$

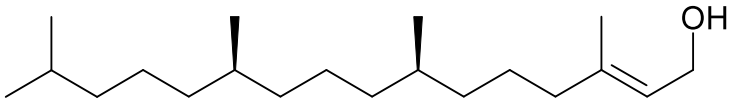


Figure 16. Chemical structure of phytol

Phytol is a diterpene alcohol which is used as a precursor for the production of synthetic forms of vitamin E and vitamin K. It is also a constituent of chlorophyll, which is then converted to phytanic acid and stored in fats.

3.2. Vetiver oil

Product identification:

- CAS RN 8016-96-4; 84238-29-9
- EINECS RN 282-490-8
- H.S. CODE 3301.26.0000

Major components:

- α- Vetivone
- β-Vetivone
- Khusimol
- Khusilol

Physical and chemical properties:

- Physical state: yellow to brown liquid
- Density: 0.985 -1.025
- Solubility in water: Insoluble (soluble in alcohol)
- Refractive index: 1.520-1.530
- Flash point: 130 ^{0}C

Stability and reactivity:

- Stability: Stable under normal conditions
- Incompatible: Strong oxidizing agents and reducing agents, strong bases
- Decomposition: Carbon monoxide, carbon dioxide
- NFPA ratings: Health:2, Flammability:0, Reactivity:0

Safety:

- Hazard notes: Irritating to eyes and skin
- Eye: Irritating to eyes
- Skin: Irritating to skin
- Ingestion: May be harmful
- Inhalation Irritating to respiratory system

Chrysopogon zizanoides is cultivated for its great capability among other grasses to produce an essential oil in the roots. As already mentioned before essential oil of vetiver is a vey complex mixture of sesquiterpene alcohols, hydrocarbons, aldehyds and ketons which are mainly used as a base for cosmetic and perfumery commodities. Once matured it has red to dark brown color and woody, almost musty scent, as many describe it. The oil has a strong odor, that is not attractive to everyone and needs to be well diluted to avoid the dominant character in a blend. Vetiver oil is produced in secretory cells localized in the first cortical layer outside the endodermis of mature roots (Viano, 1991). Vetiver oil is distilled from the roots of this monocotyledonous plant, unlike most essential oils isolated from aerial tissues of dicotyledonous plants. Because of this complexity, the oil is difficult to reproduce with synthetic aromatic chemical formulations (Alifano, 1978). Moreover, differences in the quality of the oil may depend on genetic, environmental and technological impacts (Champagnat, 2006).

The essential oils in aerial tissues are often found as a complex mixture of different terpene compounds, including monoterpenes and sesquiterpenes, arising from complex interactions between the action of the cytosolic (mevalonate) and plastidic (2-C-methylerythritol-4-phosphate) pathways, and the oils accumulate as extracellular exudates or in specialized glands (lactifiers) or oil bodies (associated with trichomes). Unfortunately not much is known about the biosynthesis, regulation and localization of terpenes synthesized in roots (Eisenreich, 2004).

3.2.1. Distillation - Production method of essential oil

The essential oil is derived from the roots by steam distillation. Freshly harvested roots on distillation give a higher yield of an oil than stored roots; the yield decreases progressively with the period of storage. The roots become moisten for about 19 hours in water before the distillation process to adduce the root material soft and thereby further facilitate the release of oil. Fresh roots when cut to lengths 2.5 cm – 5 cm increase recovery. As the most valuable quality constituents of the essential oil are found in the highe boiling fractions, the roots must be distilled for a prolonged period ranging from 20-24 hours. North Indian varieties yield 0.4 to 0.8% of oil.

During distillation two fractions are obtained, one is lighter and the other one heavier. At the beginning the highly volatile and lighter fraction is released first, and a cosiderable amount may escape before it is collected in liquid phase and is cooled off. This loss can be avoided when a piece of *markin* cloth is tied after cleaning of the roots at the delivery outlet in the swollen balloon shape in the receiver keeping it submerged in water. The lighter fraction that is likely to escape along with the steam/gas or running distillate water would be caught in the cloth. As the distillation goes on the heavier fraction will get deposited in the cloth and the lighter fraction will pass through it easily and get collected in the receiver. At the end of the distillation the cloth must be squeezed to get the oil. This piece of cloth is constantly used. Before thrown off, the cloth may be washed by diethyl ether to get back the adhering oil (Hand Book on medicinal and aromatic plants, 2005 Assam SFAC).

When done in this certain way, this practice helps to increase the recovery of the oil. Traditionally copper vessel with stainless steel condenser is considered to be good for vetiver since the oil shows reaction with free copper and turns blue in colour which fetches higher price in the perfumery market. The oil that is traditionally distilled, called “Ruh-Khus” done in Kannauj type “Deg Vopka” , fetches the highest price in the perfumery market, although recovery is relativly low (Hand Book on medicinal and aromatic plants, 2005 Assam SFAC).

3.2.2. Quality aspects of Vetiver oil

It is well known that distillation technique plays an important role in the quality of the oi. When the right steam pressure is acchieved and the post harvest treatment of the roots is well adjusted, the quality can be significantly increased as well as the yield itself. Besides distillation procedures the oil quality is governed by varietal selection, harvesting at proper age (15-18 months) and during dry season from December to February only. Roots left after oil extraction are used for making cartons and many handicrafts items like mats (for sitting), pen-stand etc. A simple syrup, called sharbat in India, can be prepared by using water encured during distillation, which was analyzed and is found to be tasty and also very good for health (Hand Book on medicinal and aromatic plants, 2005 Assam SFAC).

In the year of 2012, in Bangkok (Thailand) some experiments were implemented to evaluate lead tolerance and accumulation in vetiver grass. To examine the effect of lead on vetiver oil production, vetiver grass needed to be grown in hydroponics and elevated concentrations of lead decreased the lenght of roots and shoots of plants. No phytotoxicity was present in vetiver that was grown in highly contaminated soils.
The experiment showed that lead had an effect on vetiver oil production and constitution by stimulating oil yield and the number of its components. Lead concentrations in the shoots and roots of vetiver grown in hydroponics were up to 144 and 19530 mg kg(-1) and those grown in soil were 38 and 629 mg kg (-1).
The highest yields were found in plants which were grown in nutrient solution with 100 mg Pb 1(-1) for five weeks (1.29%) and seven weeks (1.22%). When lead was present in the yield medium, the number of total essays of vetiver oil also varied between 47-143 components. It is also important to mention that the dominant compound was khusimol (10.7-18.1%) followed by (e)-isovalencenol (10.3-15.6%).
This study leads to conclusion that lead could be of big importance in increasing the oil production of vetiver grass (Rotkittikhum, 2012).

3.2.3. Chemical composition of Vetiver oil

The chemical composition of Vetiver oil has been studied since 1901 (Smadja, 1994). The oil is extremely complex (Chia, 2000) and consists mainly of bicyclic and tricyclic sesquiterpenoids (hydrocarbons, alcohols, ketones, aldehydes, acids) (Cazaussus et al., 1988; de Guzman and Oyen, 1999; Vietmeyer and Ruskin, 1993), but monoterpenoids (Nikiforov, 1992) and phenols (Garnero, 1971; Shibamoto and Nishimura, 1982) have also been detected. Many of the vetiver oil components have been isolated, identified and even synthesized (Smadja, 1994; Weyerstahl, 1999; Weyerstahl, 2000a; Weyerstahl, 2000b; Weyerstahl, 2000c; Wolf, 1996).

In the typical Vetiver oils from Haiti, Réunion, Java, Brazil and South India scientists found sesquiterpene compounds with valencane, eremophilane, eudesmane, epieudesmane, vetispirane, zizaane, prezizaane, guaiane and cyclocopacaphane skeletons (Leupin, 2001).

The major representatives of the vetiver oil, (+)-α-vetivone, (-)-ß-vetivone and khusimol (Figure 14), are described as the ”fingerprint” of the oil, even though their contribution to the typical odor characteristics of vetiver oil is very low (Leupin, 2001).

Minor components such as zizanal and khusimone are much more important collaboraters which contribute to the typical odor notes of the oil (Sell, Maurer, 1980). Also some non-ketones, that are less prominent in the oil, seem to be of sensory importance to the specific odor as well (Maurer et al., 1972).

α - Vetivone

$C_{15}H_{22}0$

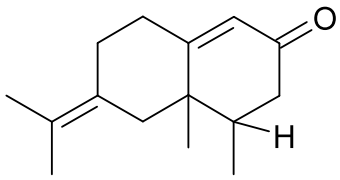


Figure 17. Chemical structure of α-vetivone

Also known as (AC1L3AGW, AC1Q6IMK, AR-1F7733) 4,4a-dimethyl-6-propan-2-ylidene-4,5,7,8-tetrahydro-3H-naphthalen-2-one.

Identifiers	
CAS number	15764-04-2
PubChem	442405
ChemSpider	390847

Table 1. Identifiers of α - vetivone

Chemical and physical properties	
Appereance	Colourless solid
Solubility in water	practically insoluble
Solubility in ethanol	Soluble
Solubility in diethyl ether	Soluble
Molecular Weight	218.33 [g/mol]
Molecular Formula	$C_{15}H_{22}O$
XLogP3-AA	3.1
H-Bond Donor	0
H-Bond Acceptor	1

Rotatable Bond Count	0
Tautomer Count	5
Exact Mass	218.17
Mono-Isotopic Mass	218.17
Topological Polar Surface Area	17.1
Heavy Atom Count	16
Formal Charge	0
Complexity	382
Isotope Atom Count	0
Defined Atom Stereocenter Count	0
Undefined Atom Stereocenter Count	2
Defined Bond Stereocenter Count	0
Undefined Bond Stereocenter Count	0
Covalently-Bonded Unit Count	1
Feature 3D Acceptor Count	1
Feature 3D Hydrophobe Count	1
Feature 3D Ring Count	2
Effective Rotor Count	1
Conformer Sampling RMSD	0.6
CID Conformer Count	8

Table 2. Chemical and physical properties of α- vetivone

On an odor rating scale α -Vetivone is dusty-woody, spicy, slightly fresh, green, sour, herbal (Haring, 1972). (4S,4aR)- (-)-α-vetivone - completely lacks the fruity character of (+)-α-vetivone (Ohloff, 1994). The odor threshold (in water) is 6.0-15.0 ppm (10.500 ppb average value).

β - Vetivone

$C_{15}H_{22}0$

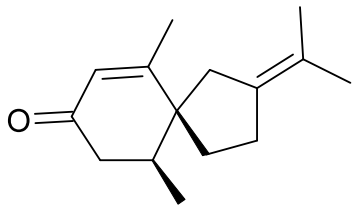


Figure 18. Chemical structure of β –vetivone

Also known as 2-isopropylidene-6,10-dimethylspiro[4.5]dec-6-en-8-one, (18444-79-6, AC1Q6IJD, UNII-V86K3R7R4P, AC1L3C78, AR-1E2969)

Identifiers	
CAS number	18444-79-6
PubChem	86738
ChemSpider	390848

Table 3. Identifiers of β - vetivone

Chemical and physical properties	
Appereance	Colourless solid
Solubility in water	practically insoluble
Solubility in ethanol	Soluble
Solubility in diethyl ether	Soluble
Molecular Weight	218.33 [g/mol]
Molecular Formula	$C_{15}H_{22}O$
XLogP3-AA	3.2
H-Bond Donor	0
H-Bond Acceptor	1
Rotatable Bond Count	0
Tautomer Count	5
Exact Mass	218.17
MonoIsotopic Mass	218.17
Topological Polar Surface Area	17.1
Heavy Atom Count	16
Formal Charge	0
Complexity	382
Isotope Atom Count	0
Defined Atom Stereocenter Count	0
Undefined Atom Stereocenter Count	2
Defined Bond Stereocenter Count	0
Undefined Bond Stereocenter Count	0
Covalently-Bonded Unit Count	1
Feature 3D Acceptor Count	1
Feature 3D Hydrophobe Count	1
Feature 3D Ring Count	2
Effective Rotor Count	1
Conformer Sampling RMSD	0.6
CID Conformer Count	8

Table 4. Chemical and physical properties of β – Vetivone

(5R,10R)-(-)- *β*-vetivone - quinoline-like, fruity (cassis, grapefruit) aroma with a woody by-note (the natural enantiomer) (Spreitzer et al., 1999).

Khusimol

$C_{15}H_{24}0$

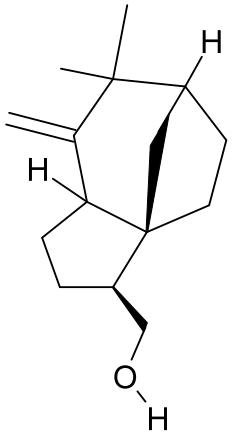


Figure 19. Chemical structure of khusimol

Also known as: [(3s,3ar,6r,8as)-7,7-dimethyl-8-methylideneoctahydro-1H-3a,6-methanoazulen-3-yl]methanol (19893-66-4, AC1Q77TW, AC1L503B, CHEMBL511334)

Identifiers	
CAS number	16223-63-5
PubChem	167519
ChemSpider	390848

Table 5. Identifiers of khusimol

Chemical and physical properties	
Appereance	Colourless solid
Solubility in water	practically insoluble
Solubility in ethanol	Soluble
Solubility in diethyl ether	Soluble
Molecular Weight	220.35[g/mol]
Molecular Formula	$C_{15}H_{24}O$
XLogP3-AA	3.7
H-Bond Donor	1
H-Bond Acceptor	1
Rotatable Bond Count	1
Exact Mass	220.18
MonoIsotopic Mass	220.18
Topological Polar Surface Area	20.2
Heavy Atom Count	16
Formal Charge	0

Complexity	330
Isotope Atom Count	0
Defined Atom Stereocenter Count	4
Undefined Atom Stereocenter Count	0
Defined Bond Stereocenter Count	0
Undefined Bond Stereocenter Count	0
Covalently-Bonded Unit Count	1
Feature 3D Acceptor Count	1
Feature 3D Donor Count	1
Feature 3D Hydrophobe Count	1
Feature 3D Ring Count	2
Effective Rotor Count	2.4
Conformer Sampling RMSD	0.6
CID Conformer Count	1

Table 6. Chemical and physical properties of khusimol

Khusilol

$C_{14}H_{18}0$

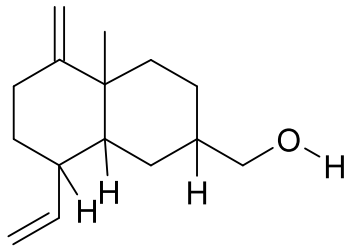


Figure 20. Chemical structure of khusilol

Also known as 2-Naphthalenemethanol, decahydro-5-methylene-8-vinyl (AC1LBEAK)

Identifiers	
CAS number	2221-68-3
PubChem	556427
ChemSpider	66741

Table 7. Identifiers of khusilol

Chemical and physical properties	
Appereance	Colourless solid
Solubility in water	practically insoluble
Solubility in ethanol	Soluble
Solubility in diethyl ether	Soluble
Molecular Weight	206.32 [g/mol]
Molecular Formula	$C_{14}H_{22}O$

XLogP3-AA	3.1
H-Bond Donor	1
H-Bond Acceptor	1
Rotatable Bond Count	2
Exact Mass	206.17
MonoIsotopic Mass	206.17
Topological Polar Surface Area	20.2
Heavy Atom Count	15
Formal Charge	0
Complexity	256
Isotope Atom Count	0
Defined Atom Stereocenter Count	0
Undefined Atom Stereocenter Count	4
Defined Bond Stereocenter Count	0
Undefined Bond Stereocenter Count	0
Covalently-Bonded Unit Count	1
Feature 3D Acceptor Count	1
Feature 3D Donor Count	1
Feature 3D Hydrophobe Count	1
Feature 3D Ring Count	2
Effective Rotor Count	3.4
Conformer Sampling RMSD	0.6
CID Conformer Count	84

Table 8. Chemical and physical properties of khusilol

The khus oil from Northern India differs markedly from the typical vétiver oil. It is characterized by the presence of antipodal cadinane and eudesmane sesquiterpenoids (e.g. khusol, khusinol, laevojunenol, epikhusinol and isokhusinoloxide) and contains a large amount of khusilal, a laevorotatory C14-terpenoid. The khus oil has laevorotatory characteristics, while the vétiver oil from all other sources is dextrorotatory (Andersen, 1970; Anonymous, 1976; de Guzman and Oyen, 1999; Garnero, 1971; Kalsi et al., 1985).

	Wild North Indian vétiver[1]	Cultivated South Indian vétiver[1]	Bourbon [2,3]	Java[2,3]	Haiti[4]
Relative density	0.990-1.032	0.992-1.015	0.986-1.015	0.980-1.022	0.986-0.998
Refraction index	1.512-1.523	1.516-1.530	1.521-1.530	1.521-1.530	1.521-1.526
Optical rotation	-50° to-130°	+10 to+25°	+14° to+32°	+17° to+46°	+22° to +38°
Miscibility in 80% ethanol (vol)			1:1-2	1 :22 insoluble 3	1 :2

Table 9. Physical properties of Vétiver oil

1: Data from Anonymous 1976.

2: Data from de Guzman and Oyen 1999.

3: Data from Masada 1976.

4: Data from Bauer et al., 1988.

The odor complexion of vetiver oil is still a big mistery to scientists, who still have not acchieved to prove which compounds and how many of them are responsible for the typical vetiver scent. Still, many of them agree that the unique scent does not depend on a single group of components but on a mix of skeletons and functional groups which contribute to the total sensory impression (Leupin, 2001).

Therefore and due to the problem to synthesize economically pure sesquiterpenoids, it has not been possible up to now to produce a synthetic vetiver odorant (Kraft et al., 2000; Spreitzer et al., 1999).

3.2.4. Demographic varieties

There are distinct geographical differences in quality and perfumery note of essential oil obtained from different geographic regions of the world. From a qualitative angle two distinct types of essential oil are obtained in India (Lavania, 2003):

1) North Indian type obtained from a profuse flowering, seed forming race of vetiver (khus) occurring in wild, and is called “khus oil”,
2) South Indian type called “vetiver oil / vetivert oil” obtained from non-flowering / late-flowering / non-seeding / low-seed forming types available in cultivation.

Vetiver was found in wild state at the Indian tropical subcontinent, meaning that it is original to India, but is not the biggest supplier. The Caribbean island Haiti is the major source for the supply of vetiver oil to the world market, followed by Java (Indonesia), China, Japan and India.

The “khus oil” from North India is distinctly superior on account of high ester value and higher concentration of heavier carbonyl fractions compared to the “vetiver oil” from any other sources. This type of oil also fetches higher market price. A rare C14 class of terpenoid ‘khusilol’ is unique to north Indian ‘khus oil” that imparts strong negative rotation to the oil and upgraded perfumery value (Lavania, 2003).

Depending upon the country of occurrence, cultivation practices, climatic conditions, and genetic origin, there occurs enormous diversity with respect to yield and quality of essential oil, ranging from an earthy, woody, balsamic note to a sweet and more roseate note (Lavania, 2003). A brief account of physicochemical characteristics of vetiver oil from different geographical regions of the world is given in Lavania (2003), and the chemical profile provided by Lemberg and Halley (1978).

In a bright sense, the essential oil of vetiver having high specific gravity, negative optical rotation, high vetiverol concentration and higher ester value is considered superior from perfumery view point. Reunion oil with roseate note is highly regarded in perfumery industry, but the vetiver oil (khus oil) obtained from the roots occurring in wild state in North Indian plains, commonly known as ‘khus’ is considered to be the best for its balsamic woody note. Lately, vetiver genotypes producing vetiver oil with roseate and saffron note have also been identified from north Indian plains (Lal et al., 1998).

Mallavarapu and his group (2012) analyzed the constituents of south Indian vetiver oils which were isolated from vetiver roots by GC-FID and GC-MS. Plants were collected from four locations in south India (Bangalore, Hyderabad, Kundapur and Mettupalayam). Eighty constituents, representing 94.5-97.8% of the oils, have been identified. The oils were rich in sesquiterpenes and oxygenated sesquiterpenes with cedrane, bisabolane, eudesmane, eremophilane, and zizaane skeletons. The main components of the four essential oils are (Mallavarapu et al., 2012):

- eudesma-4,6-diene (delta-selinene) + β-vetispirene (3.9-6.1%),
- β-vetivenene (0.9-9.4%),
- 13-nor-trans-eudesma-4(15),7-dien-11-one + amorph-4-en-10-ol (5.0-6.4%),
- trans-eudesma-4(15),7-dien-12-ol (vetiselinenol) + (E)-opposita-4(15),7(11)-dien-12-ol (3.7-5.9%),
- eremophila-1 (10),11-dien-2α-ol (nootkatol) + ziza-6(13)-en-12-ol (khusimol) (16.1-19.2%),
- eremophila-1(10),7(11)-dien-2α-ol (isonootkatol) + (E)-eremophila-1(10),7(11)-12-ol (isovalencenol) (5.6-6.9%).

The important compounds that impart the characteristic vetiver odor are (Mallavarapu et al., 2012):

khusimene

delta-selinene

β-vetivenene

cyclocopacamphan-12-ol (epimers A and B)

vetiselinenol

khusimol

isovalencenol

khusimone

α-vetivone

β-vetivone

zizanal

The chemical profiles of the oils are comparable to Haitian vetiver oil.

Vetiver Haitian essential oil aroma is described as sweet, earthy, rooty, balsam, woody, amber The parent plant is a a tall perennial grass which originates also in India as well as in Indonesia and Sri Lanka (Ceylon). Vetiver oil is steam-distilled from cleaned and washed rootlets which are dried, cut and chopped, then again, usually soaked in water before distillation. The distillation is conducted near the place of harvesting. Haitian Vetiver oil is the naturally occurring essential oil from the roots

of the Vetiver plant. No additives, solvents or chemicals are used at any point of the recovery process. Vetiver Haitian essential oil have brown to redish colour, strong aroma. By consistency, Vetiver Haitian essential oil is thick, viscous and sticky liquid. Intensely strong as a perfume note, Haitian Vetiver is very effective in aromatherpy.
One of the great perfume notes, Haitian Vetiver blends well with so many essential oils, but especially with Lime, Black Pepper, Vanilla, Ylang-Ylang, Orange, Patchouli, Palmarosa, Petitgrain, Rose Geranium and Rosewood. Haitian Vetiver is extremly rich and heady, without the “burnt” note that is so common in not so carefully distilled Vetivers (Leupin, 2001). The odor is sweet and very heavy woody earthy, reminiscent of roots and wet soil, with a rich backnote of precious wood notes. It is considered a safe oil and is non-toxic, non-irritant and non-sensitizing.

Compound	**Procent (%)**
Isovalencenol	18.45
Kushimol	12.43
4-Hydroxygermacra-1(19),5-diol	6.89
(E)-Eudesma-4(15),7-dien-12-ol	5.73
Eremoligenol	4.49
α-Vetivone	4.12
β-Vetivone	4.04
Vetiselinol	3.76
(Z)-Eudesm-11-ol	2.90
α-Amorphene	2.86
β-Vetivene	2.77
(E)-β-Farnesol	2.16
Khusinol	2.04
Helifolan-2-ol	1.43
Eudesma-4(15),7-dien-3-β-ol	1.19
Elemol	0.81
Zizanol	0.75
Zizanene	0.53
Epi-Marsupellol	0.35
Praezizaene	0.33
(Z)-Eudesma-6,11-dien	0.25
Vetivenic acis	0.25
β-Curcumene	0.18
β-Funebrebe	0.13
Cyclosativene	0.11
β-Elemene	0.02

Table 10. Compound procent of Haiti vetiver oil
(Leupin, 2001)

Many authors analyzed constituents of Haitian and Indian vetiver oil (Lawrence, 2006):

Anderson (1970a) analyzed samples of vetiver oil of Haitian, Reunion and North Indian origin and showed that the oil produced from roots grown in Northern India represented a chemicaly different race to that grown commercially in Haiti or Reunion.

Anderson (1970b) also showed that North Indian vetiver oil contained levojunenol [eudesm-4(15)-6-ol] and α-amorphene (old name zizanene).

Trivedi and his coworkers (1971) analyzed an oil of North Indian origin and found that it contained γ-cadinene, α-muurolol (old name δ-cadinol) and khusimol. The authors reported that γ-cadinene co-occurred with γ_2-cadinene, another constituent of the same oil.

The research group of Maurer (1972) characterized the presence of (1S,10R)-1,10-dimethylbicyclo[4.4.0]dec-6-en-3-one and (6S,10S)-6,10 dimethylbicvclo[4.4.0]dec-l-en-3-one in a vetiver oil of Reunion origin. Examination of the alcohol fraction of North Indian vetiver oil led Kalsi et al. (1972) to the characterization of epi-khusinol.

Another research by Kaiser and Naegeli (1972) identified 10-epi-y-eudesmol, bisabolol, acora-4,9-diene, acora-4,7-diene, α-cedrene, α-cedrenol, α-cedrenal, α-funebrene, α-funebrenol, α-funebrenal and α-funebrenic acid.

Hayama and his group (1973) extracted vetiver oil with a solution of 10% Na_2C0_3 with diethyl ether. After acidification and a series of washes, the authors structurally elucidated zizanoic acid and epi-zizanoic acid in the acid fraction.

Ganguly (1978ab) reported that in addition to zizaene and pre-zizaene another tricyclic tertiary alcohol that they named allo-khusiol was found in vetiver oil of North Indian origin.

Karkhanis (1978) analyzed a sample of North Indian vetiver oil and found that isovalencenol, vetiselinenol and isovetiselinenol were minor constituents of the oil.

Another study that was done by Karkhanis (1979) examined the minor alcohol fraction of North Indian vetiver oil. In this fraction they characterized α-cadinol, cadina-4a,10p-dio] and khusenediol (khusinodiol).

Back in the year of 1982 the scientists group together with Masada isolated and structurally elucidated khusimol, zizanol, isovalencenol, vetiselinenol and eremophila-10,1-dien-7-ol in vetiver oil. They also compared the percentage composition of three of the alcohols (khusimol, zizanol and isovalencenol) in oils from Reunion, Java, China and two from India.

Shibamoto and Nishimura (1982) isolated and identified 10 phenols and an acid in vetiver oil. The compounds characterized were (Lawrence, 2006):

- methoxyphenol (0.0048%)
- o-cresol (0.0076%)
- p-cresol (0.0062%)
- m-cresol (0.0045%)
- eugenol (0.0056%)
- 4-vinylguaiacol (0.154%)
- (z)-isoeugenol (0.0011%)
- (e)-isoeugenol (0.1.32%)
- vinylphenol (0.421%)
- vanillin (0.0014%)
- zizanoic acid (.3.250%)

Nishimura (1982) reported the same results on the phenols and acids of vetiver oil. Furthermore, they compared the relative amounts in various samples of vetiver oil of different geographic origin. The data from this study is summarized in Table 11.

	Origin of oil				
Compound	Tanegashima	Reunion	Haiti	Java	South India
khusimol	18.2	16.7	10.8	9.2	12.5
isovalencenol	6.3	8.7	8.0	4.1	6.8
zizanol	2.4	1.7	1.3	1.6	1.8
B-vetivone	2.8	4.6	2.7	5.6	2.7
A-vetivone	2.7	7.2	3.0	6.0	3.5
zizanoic acid	4.4	3.0	0.2	2.3	2.0

Table 11. Comparative chemical composition of the major oxygenated constituents of vetiver oil (Lawrence, 2006)

North Indian vetiver oil was found to contain nor-khusinol oxide (Kalsi, 1985a) and khusitoneol (Kalsi, 1985b) by the same scientific team.

Plavcan (1985) determined that the carbonyl containing compounds amounted to 17.67% of Indonesian vetiver oil. Column chromatographic separation of an aliquot of this fraction followed by preparative GC led to the isolation of 15 carbonyl compounds. Each compound was characterized by a combination of H-NMR, MS spectra and by comparison of spectral and GC retention time data with that of an authentic specimen wherever possible. The compounds identified were as follows (Lawrence, 2006):

- zizanal
  (0.90%.)
- epi-zizanal
  (0.79%)
- cadinenal
  (0.14%)
- dehydrocadinenal
  (0.22%)
- (e)-isovalencenal
  (0.43%)

- khusimone
  (1.10%)
- dimethyloctalone-1
  (0.31%)
- nor-isovalencenone
  (0.14%)
- zizanone
  (0.16%)
- epi-zizanone
  (0.13%)
- (z)-isovalencenal
  (0.23%)
- dimethyloctalone-11
  (1.26%)
- nor-eudesmadienone
  (0.68%)
- β-vetivone
  (3.49%)
- α-vetivone
  (4.48%)

Maheshwari (1985) compared the composition of two of the thirteen different strains of Indian vetiver. They did, however, show that the four major components ranged as follows (Lawrence, 2006):

- khusilol (0-33.61%)
- khusinol (trace-56.2%)
- khusimol (2.96-27.64%)
- khusol (5.79-9.03%)

Gopalakrishnan and Narayanan (1987) reported that on re-extraction of a

viscous very dark colored oleo-resin of vetiver with liquid CO_2, at 25°C and 100 bar, a less viscous golden yellow colored volatile concentrate was obtained in 84-85% yield that possessed only 5% nonvolatile compounds. Furthermore, the two authors noted that the volatile concentrate retained all of the aroma qualities of the original oleoresin.

Kalsi and Talwar (1987) isolated a new sesquiterpene diol from North Indian vetiver oil. Using IR 'H-NMR and derivatization, the authors were able to structurally elucidate the compound they named vetidiol.

Mookherjee and other scientists (1992) reported (in the analysis of a sample of Haitian vetiver oil. Starting with an acid/base extraction followed by a Girard P isolation of the carbonyl compounds, the authors found that the oil contained acids/bases (5%), carbonyl compounds (15%) and other neutral compounds (80%). In the carbonyl traction Mookherjee characterized 11 compounds. A list of these carbonyl compounds and their odor descriptions can be seen in Table 12.

Compound	Odor character
11,12,13-tri-nor-eremophil-1(10)-en-7-one	weak, green-woody, amber-like
11,12,13-tri-nor-eudesm-5-en-7-one	weak, woody, root-like
13,4-di-nor-eudesma-5,7,9-trien-11-one	styrax and leather-like
13-nor-eudesma-4,6-dien-11-one	sweet, woody, musky, ambrette-like
13-nor-eudesma-4(15),5-dien-11-one	strong, woody, amber-like, slightly musky weak, woody
spirovetiva-1 (10),11 -dien-2-one	weak, woody,
dehydro-β-vetivone (2-isomers)	(major) strong, rich, woody, peppery
α-vetivone	(minor) cedarwood-like
β-vetivone	very strong, woody with citrus nootkatone-like character
15-nor-eudesm-11-en-4-al	warm, woody, spicy
ziza-6(13)-en-4-one	phenolic, woody

Table 12. Carbonyl compounds in vetiver oil and their odor descriptions (Mookherjee, 1992)

Nikiforov used headspace GC/MS and GC/FTIR to characterize thirteen

sesquiterpenoid compounds and sixteen other constituents in a sample of vetiver oil from Reunion. Although the authors did not present any quantitative data nor any comparative data with the oil, they did characterize some new components octane, 2-acetyl-5-methylfuran, 2-butylfuran, 2-pentylfuran, furfural, 2-methyl-2-butenal, p-cymene, α-thujene, α-pinene, (β-pinene, camphene, myrcene, limonene, α-carene, 1,8-cineole, 1-phenethyl acetate, α-calacorene, β-vetivenene, selina-4(14),7(11)-diene, γ-cadinene, α-amorphene, zizaene, prezizaene, α-cedrene, allo-aromadendrene, α-vetivone, β-vetivone, khusimol and isovalerenol in the oil.

Hosse together with other coworkers analyzed an oil of vetiver using a range of analytical techniques. The components characterized in this oil were (Lawrence, 2006):

- prezizaene (2.95%)
- khusimene (2.97%)
- α-amorphene (5.01%)
- khusimone (1.99%)
- γ-muurolene (1.53%)
- y_2-cadinene (1.58%)
- δ-cadinene (4.48%)
- (e)-nerolidol (1.06%)
- β-vetivenene (2.56%)
- T-cadinol (1.79%)
- α-cadinol (3,45%)
- khusinol (5.23%)
- khusimol (7.55%)
- zizanoic acid (5.26%)
- β-vetivone (1.60%)
- α-vetivone (2.22%)

It has been proved that alcoholic perfumes rich in vetiveryl acetate can develope an unpleasant note during aging. GC/MS analysis of an alcoholic perfume rich in vetiveryl acetate having an off-odor revealed this phenomen by

finding that the culprit compound(s) occurred at levels below 1 ppm. Careful static headspace analysis revealed that the off-odor was caused by a butene isomer and 1,1-diethoxy-ethane (Lawrence, 2006). It was believed that the peroxidic material, which was derived from hydrocarbon auto-oxidation, was able to oxidize a small portion of ethanol to bring acetaldehyde that was converted into 1,1-diethoxyethane by acetylization with ethanol excessing.

Further the hydrocarbon fraction that was isolated from Reunion vetiver oil by silica gel column chromatography with m-chloroperbenzoic acid in methylene chloride at 0°C was treated and this reaction composition revealed that the main epoxides were (Lawrence, 2006):

- zizaene-6(13)-epoxide
- zizanene di-epoxide (2 isomers)
- valencene di-epoxide (2 isomers).

Reduction of the oxidized hydrocarbon mixture showed that zizanene di-epoxide was not reduced by lithium aluminium hydride or lithium triethyl-borohydride. But, the two epimeric zizaene epoxides and valencene di-epoxide were reduced to the adequate alcohols. It is the belief of the scientists that these oxidation and reduction products could be trace components in over aged vetiver oil (Lawrence, 2006).

The main components found in vetiver oil which was delivered from plants in Burundi, treated with various fertilizers (Lawrence, 2006):

- α-muurolene (0.5-1.2%)
- valencene (0.8-2.8%)
- β-vetivenene (1.4-5.8%)
- α-cadinol (2.3-4.8%)
- vetiselinenol (2.9-5.8%)

- isocedranol (2.1-4.0%)
- β-bisabolol (2.0-3.1%)
- khusimol (19.4-29.5%)
- isokhusimol (4.0-9.2%)
- β-vetivone (4.3-9.8%)
- nootkatone (3.5-9.2%)
- α-vetivone (0.5-2.1%)

Another oil that has been produced from vetiver roots, which grows in Kanpur (India) was examined using GC/MS as their only method of analysis, the authors reported that the oil possessed the following compositions (Lawrence, 2006):

- 8-methylheptadecane (0.7%)
- 2,6,10-triphenyldodecane (0.6%)
- α-longipinene (4.9%)
- isolongifolene (0.8%)
- longifolene (0.4%)
- 4,5-dehydro-isolongifolene (0.5%)
- α-amorphene (1.5%)
- aromaddendrene (1.2%)
- β-bisabolene (1.5%)
- isocaryophyllene (1.6%)
- β-caryophyllene (0.8%)
- clovene (2.2%)
- curcumene (2.0%)
- δ-guaiene (1.0%)
- dehydro-aromadendrane (0.5%)
- farnesene (1.3%)
- γ-cedrene (3.2%)
- β-guaiene (1.0%)
- α-humulene (0.9%)
- β-himalene (1.5%)

- longifolene (1.9%)
- azulene (0.9%)
- p-cymene (0.6%)
- α-muurolol (1.8%)
- β-eudesmol (0.9%)
- epi-globulol (4.0%)
- isokhusimol (2.0%)
- khusimol (9.1%)
- spathulenol (6.0%)
- khusinol (4.3%)
- viridiflorol (2.5%)
- α-cyperone (0.7%)
- 1-cyclopentenone (0.8%)
- khusinone (11.1%)
- khusimone (2.1%)
- vanillin (1.0%)
- khusinol acetate (6.1%)
- eugenol (1.1%)
- isoeugenol (0.5%)

Six common commercial representatives of vetiver oil were taken from two different countries, four from Haiti and two from India. The oils from Haiti and India were analyzed using GC-FID and GC/MS (Champagnat et al., 2006) The comparative results of these analyses can be found in Table 13.

	Compound	**Haiti**	**India**
1.	α-cubebene	-	-
2.	cyclosativene	0.2	-
3.	α-ylangene	0.3	0.3
4.	α-copaene	-	-
5.	acoradiene	0.2	0.2
6.	a-funebrene	0.1	0.1
7.	7s-2-nor-zizaene	0.2	0.2
8.	(3-cubebene	0.1	0.1
9.	cyperene	-	-
10.	B-funebrene	0.3	0.2

11.	cascarilladiene	0.1	
12.	β-caryophyllene	-	0.3
13.	β-cedrene	0.3	0.2
14.	β-copaene	0.2	-
15.	B-gurjunene	0.3	0.3
16.	α-guaiene	0.2	0.3
17.	guaia-6,9-diene	0.1	0.1
18.	acora-3,9-diene	0.1	0.1
19.	isoeugenol*	-	-
20.	preziza-7(15)-ene	0.8	0.6
21.	ziza-6(13)-ene	1.3	1.1
22.	selina-4(15),7-diene	0.5	0.5
23.	dimethyl-6,7-bicyclo-[4.4.0]-dec-10-en-4-one	0.7	-
24.	selina-4,7(11)-diene	0.1	-
25.	B-acoradiene	0.2	-
26.	A-gurjunene	-	-
27.	amorpha-4,7(11)-diene	-	0.3
28.	Oc-amorphene	1.9	1.9
29.	A-vetispirene	-	1.2
30.	β-selinene	1.0	-
31.	B-vetispirene	2.8	4.5
32.	c/s-eudesma-6,11 -diene	0.9	-
33.	γ-amorphene	0.8	1.3
34.	eudesma-4,6-diene[b]	0.1	—
35.	eudesma-2,4,11-diene	-	—
36.	valencene	-	-
37.	Δ-amorphene	1.4	-
38.	γ-cadinene	0.3	-
39.	7p,10p-epoxy-4p-erimophila-1,11(12)-diene	0.1	0.1
40.	nootkatene	-	-
41.	isocalamenene	0.1	-
42.	spirovetiva-1 (10),7(11)-diene	0.8	1.5
43.	eremophylla-1(10),7(11)-diene	1.2	0.9
44.	Γ-vetivenene	1.0	0.9
45.	A-calacorene	0.7	0.8
46.	selina-4(15)7(11)-diene	-	-
47.	selina-3,7(11)-diene	0.1	-
48.	elemol	0.5	0.7
49.	B-vetivenene	2.6	5.3
50.	13-nor-eremophila-1(10),6-dien-11-one	-	-
51.	c/s-eudesm-6-en-11 -ol	1.9	1.4
52.	p-calacorene	0.1	-
53.	13-nor-eudesm-5-en-11 -one (epimer A)	0.2	-
54.	c/s-eudesma-6-en-12-al	1.0	1.0

55.	c/s-eudesma-6,11-dien-3β-ol	0.4	-
56.	12-nor-preziza-7(15)-en-2-one	0.7	-
57.	c/s-guai-6-en-10-ol	-	-
58.	15-nor-funbran-3-one	-	-
59.	6,12-epoxy-spiroax-4-ene	0.3	0.3
60.	13-nor-eudesm-5-en-11-one (epimer B) 0.2	0.3	0.3
61.	khusimone	0.9	0.8
62.	12-nor-ziza-6(13)-en-2α-ol	0.7	0.7
63.	salvial-4(14)-en-1 -one	-	1.8
64.	selin-6-en-4-ol	-	2.7
65.	nor-ziza-6(13)-en-2β-ol	-	1.3
66.	13-nor-eremophil-1(10)-en-11-one	0.2	-
67.	funebran-15-al	0.6	-
68.	1-epi-cubenol	1.1	-
69.	10-epi-γ-eudesmol	1.2	0.6
70.	eremophila-1 (10),6-dien-12-al	-	1.2
71.	cedren-15-al	-	0.9
72.	prezizaan-7β-ol	1.1	-
73.	β-eudesmol	2.2	1.5
74.	intermedeol	-	-
75.	α-cadinol	-	6.5
76.	cyclocopacamphan-12-ol (epimer A)	2.0	-
77.	cyclocopacamphan-12-ol (epimer B)	1.9	1.3
78.	β-bisabolol	0.7	-
79.	khusinol	2.8	-
80.	ziza-6(13)en-3-one	1.9	2.3
81.	2-epi-ziza-6(13)-en-3α-ol	2.1	2.7
82.	prezizaan-15-al		0.5
83.	2-epi-ziza-6(13)-en-12-al	0.9	0.6
84.	helifolan-2-ol	2.1	1.8
85.	ziza-6(13)-en-12-al	0.4	-
86.	ziza-6(13)-en-12-yl methyl ether	-	-
87.	eudesm-7(11)-en-4α-ol	1.0	1.2
88.	Ziza-6(13)-en-3β-ol	1.6	1.3
89.	eremophila-1 (10),4(15)-dien-2α-ol	-	-
90.	(E)-opposita-4(15),7(11)-dien-12-al	0 5	-
91.	13-nor-eudesma-4,6-dien-11-one	1.1	1.5
92.	ziza-5-en-12-ol	-	0.7
93.	2-epi-ziza-6(13)-en-3β-ol	-	-
94.	1,7-cyclogermacran-1 (10),4-dien-15-al	0.4	-
95.	trans-eudesma-4(15),7-dien-12-ol	3.1	3 7
96.	helifolan-2-one	-	-
97.	eremophila-1 (10),7(11)-dien-2β-ol	0.7	-
98.	(E)-opposita-4(15),7(11)-dien-12-ol	1.0	-

99.	khusimol	11.4	11.9
100.	preziza-7(15)-en-12-ol	0.6	0.3
101.	(E)-eremophila-1(10),7(11)-dien-12-ol	0.8	1.5
102.	isokhusenic acid	-	-
103.	vetiselinol	6.2	6.0
104.	nootkatone	0.8	0.7
105.	(Z)-isovalencenal	0.7	1.0
106.	β-vetivone	3.5	2.0
107.	khusenic acid	-	-
108.	(E)-isovalencenal	1.3	1.3
109.	(E)-eremophila-1(10),7(11)-dien-12-yl methyl ether	-	0.3
110.	α-vetivone	4.6	2.5
111.	ziza-6(13)-en-12-yl acetate	0.2	0.2
112,	(E)-eremophila-1(10),7(11)-dien-12-yl acetate	-	-
113.	prekhusenic acid	-	-

Table 13. Comparative percentage composition of vetiver oils (Champagnat et al., 2006)

3.2.5. Analytic Analysis

Since quantitation of constituents is hardly achievable with usual GC techniques, scientists say that vetiver oil is a real analytical challenge because such a complexity always respresents a struggle to the direct and rush quantitative analysis.

In their very interesting congress contribution Filippi and coworkers recently presented their work on the assessment and identification of vetiver oil constituents by means of two dimensional gas chromatography.

The correct understanding and interpretation of 1D- and 2-D-chromatographic data is a major step of an analytical identification of odor impact components in vetiver oil. Considering that vetiver essential oil consists of nearly 300 constituents one-dimensional GC is definetly not a correct procedure to identify all of the components, because done in this way the chromatogram would be a real mess, with no measurable, overlapping peaks. Only by using a two-dimensional GC signals could be assesed and well identified.
In this study GCxGC (with both FID and MS detection) was used as the main tool for the identification and quantitation of vetiver oil constituents (Filippi et al., 2012).

Alcohols

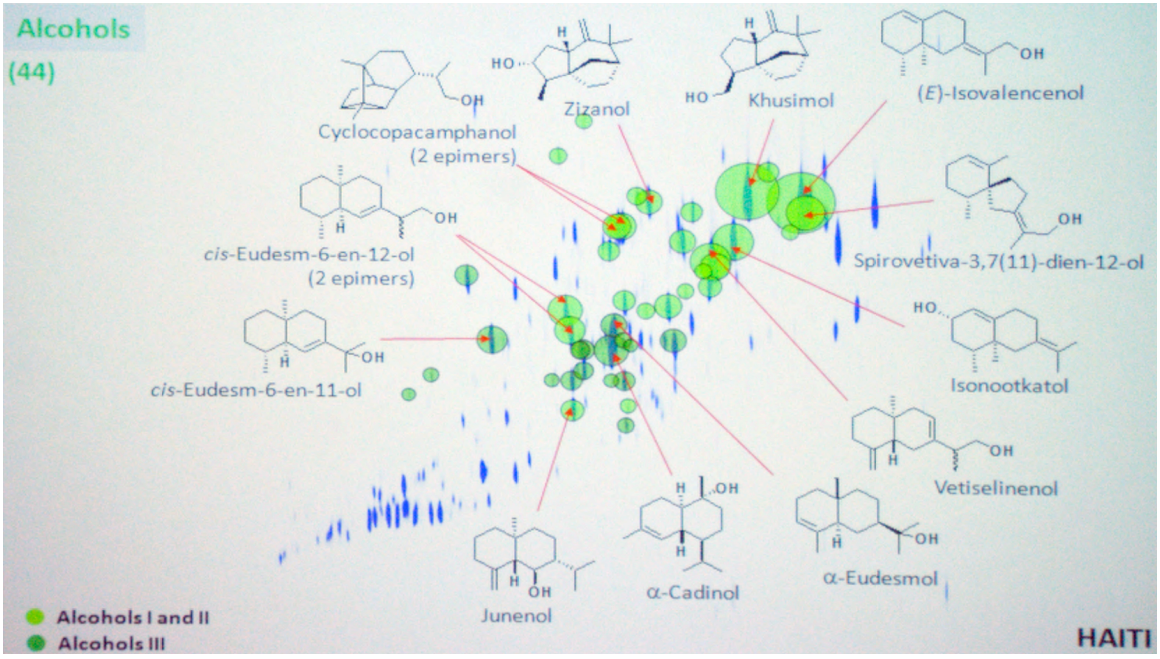


Figure 21. Qualitative and quantitative analysis of vetiver oils by comprehensive two – dimensional GC – Alcohols
(Filippi et al., 2012)

Hydrocarbons

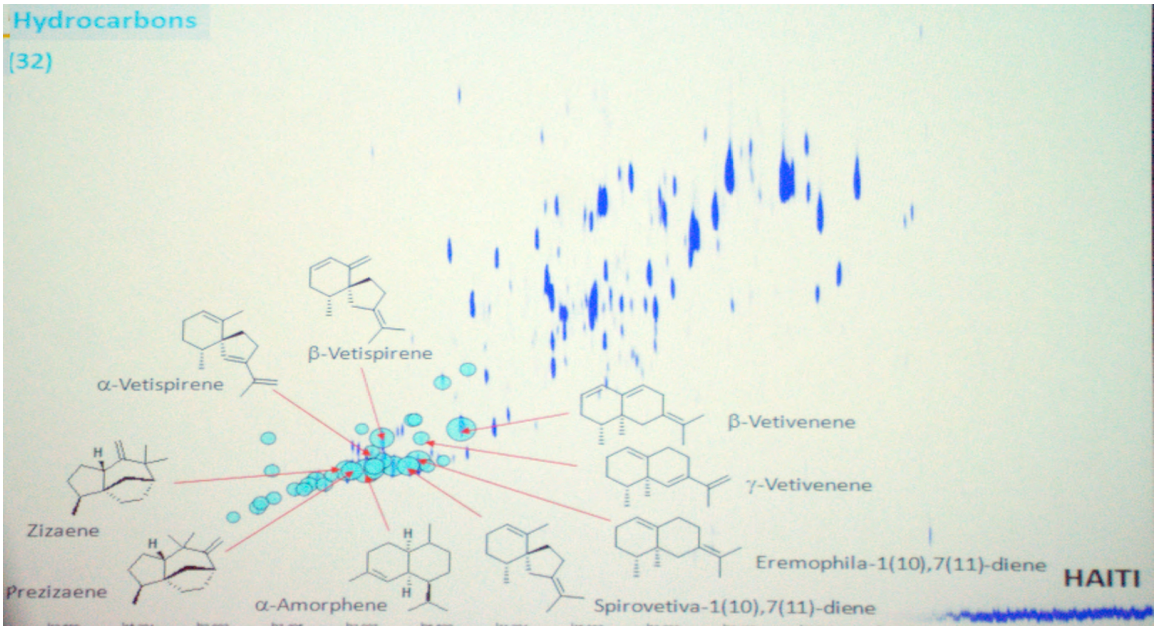


Figure 22. Qualitative and quantitative analysis of vetiver oils by comprehensive two – dimensional GC – Hydrocarbons
(Filippi et al., 2012)

Aldehydes and Ketones

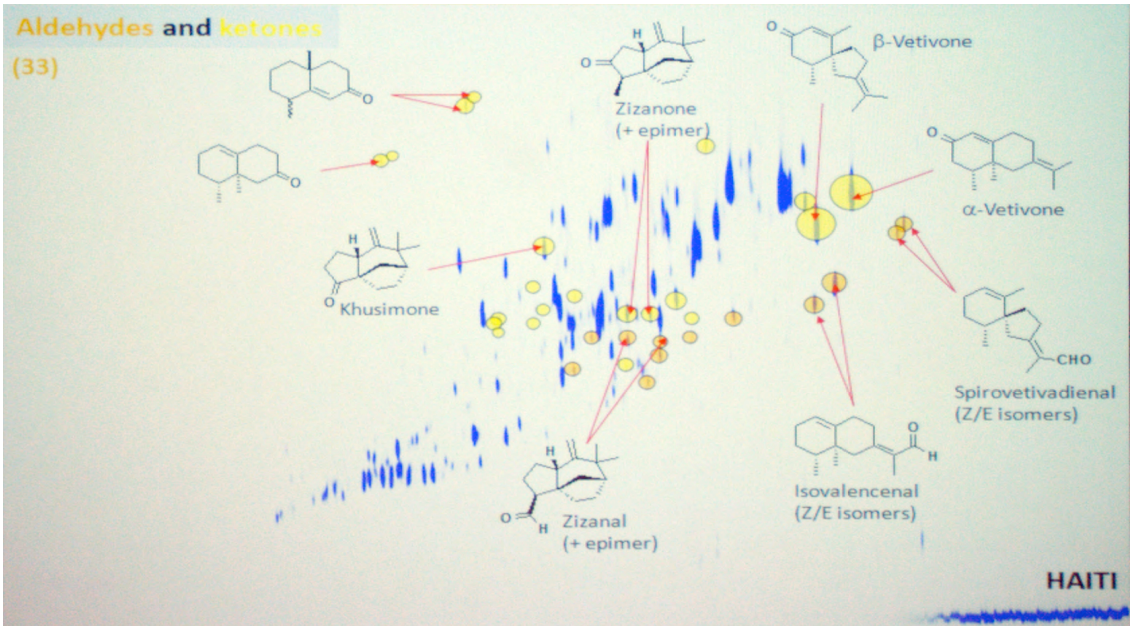


Figure 23. Qualitative and quantitative analysis of vetiver oils by comprehensive two – dimensional GC – Aldehydes and Ketones
(Filippi et al., 2012)

Determination of Response factors (RFs) (FID detection)

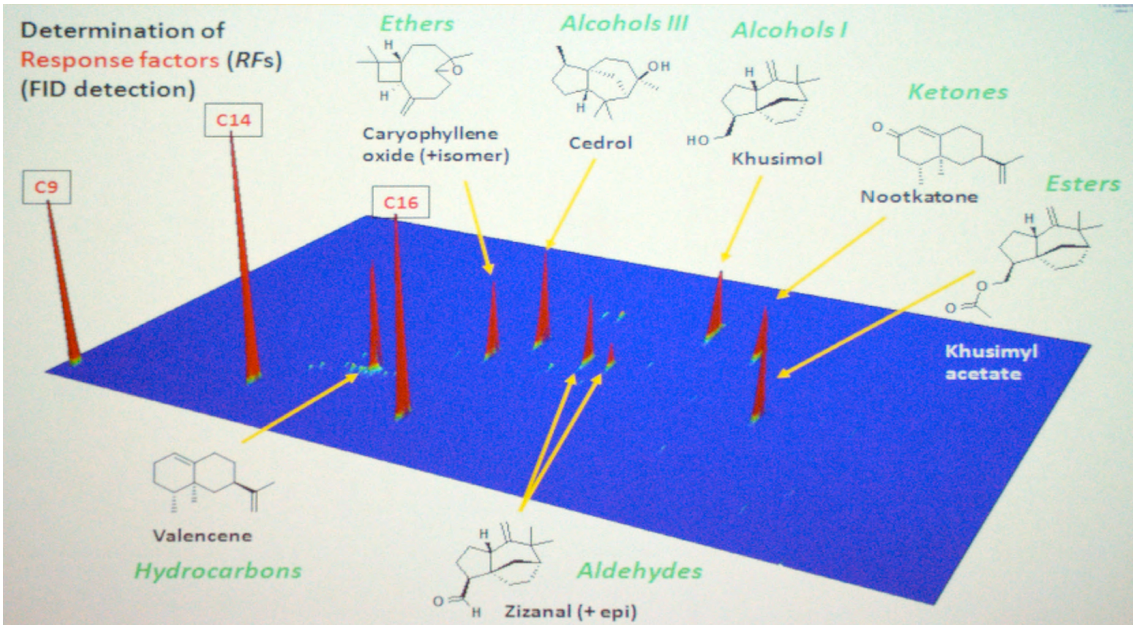


Figure 24. Qualitative and quantitative analysis of vetiver oils by comprehensive two – dimensional GC – Determination of Response factors (RFs) (FID detection)
Figure 25. (Filippi et al., 2012)

GCxGC 2D plot of vetiver oil from JAVA (FID detection)

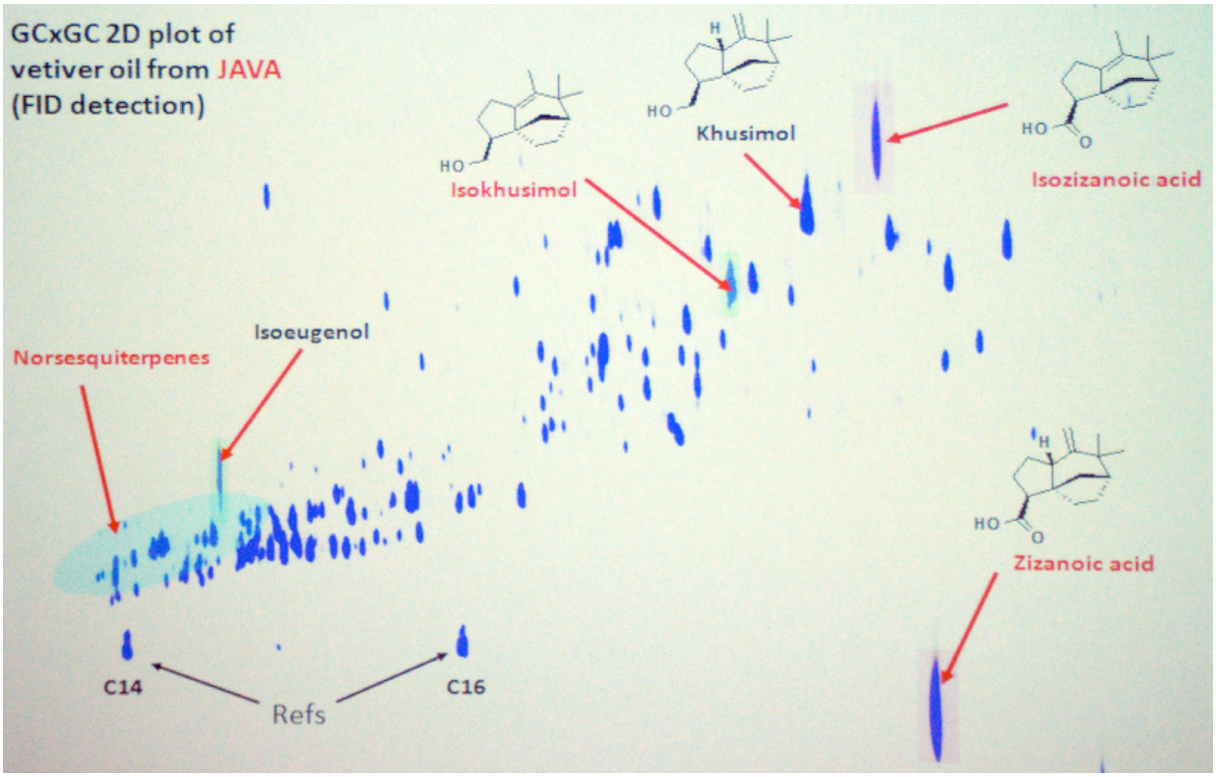


Figure 26. Qualitative and quantitative analysis of vetiver oils by comprehensive two – dimensional GC – GCxGC 2D plot of vetiver oil from JAVA (FID detection) (Filippi et al., 2012)

3.2.6. Demand and supply of vetiver oil

It did not took long for the World Market to realize what an incredible and unique scent Vetiver oil has, for which it is used in both flavor and fragrance industries. The fact that the demand for Vetiver oil is increasing rapidly day by day does not surprise because this oil cannot be substitued with reconstituted oil and cannot be produced synthetically. It is used as a base-note in flavor and perfume, among which the percent usage varies from 20-50% to 60-70%. Meaning, it has enough market potential and there is no doubt on its consumption.

The internal demand especially of Northern type oil always falls short of supply. The whole world production of vetiver oil is calculated to be around 300 tons per annum of which India conduces about 20-25 tons. In general, Haiti, Indonesia (Java) and Reunion produce most of the world's vetiver oil (Hussain et al.,1988).

Rajastan, Uttar Pradesh, Karnataka, Tamil, Nadu, Kerala and Andra Pradesh are the main states for cultivation in India, with an annual production of about 20 tons of oil. Unfortunatelly its demand for soap, perfume, attar and food flavor is much bigger than domestic production (Hassain et al., 1988; Kapoor, 1999).

North Indian origin oil is considered to be the best in the world market. The Indian consuming at present is about 100 tons and more than 80 % is provided by import. KS-1 (Bharaptur type) an improved selection released by CIMAP is recommended for commercial cultivation in Assam. Gulabi, Dharaini and Kesar are also some other improved varieties (Kapoor, 1999).

3.2.7. Vetiver oil in perfume industry

Since ancient times Vetiver has been appreciated in India for its perfumery value. Popular quotation says that it is a gift of India (Morris, 1983) to the world of perfumes, and its use in many different scents is known much before the world was introduced with so popular rose scents. Vetiver has very pleasant aroma and slow evaporation rate and can be used as a perfume in its own right; for which no synthetic substitute is yet availible. Those characteristics justify the fact that vetiver perfumes have high price on the market. Pure duly matured vetiver (khus) root oil, also known as „Ruh-Khus“ could be easily found in the perfumery shops in India (Lavania, 2003).

The khus oil distilled from wildly occurring vetiver (khus) roots by traditional slow fired copper vessel “*Bhapka*” distillation units, is air dried to remove traces of water as well as the lighter non-polar fractions that may be trapped in the oil during distillation. Subsequently, the oil is stored in aerated leather made containers called “*Kupp*i” and allowed to mature till the color of the oil turns dark green. Natural aeration available in the leather made containers facilitates evaporation of water if any, and the undesirable lighter fractions, as well as facilitates oxidation to add perfumery value to the oil through optimum esterification (Lavania, 2003).

Vetiver oil is very persistent and one of the finest fixatives known. Its complex chemical composition and oil odor, high solubility in alcohol that improves its

miscibility with other perfumery material, makes it a unique and worthy perfumery resource.

Vetiver oil is the basis of the Indian perfume ‘Majmua’ and is the major ingredient in some 36 % of all western perfumes (e.g. Caleche Hermes (1961), Paris, Chanel No. 5 (1921), Paris, Christian Dior Dioressence (1979), Paris, Guerlain Parure (1975), Paris, Yves Saint Laurent Opium (1977), Paris and 20 % of all men’s fragrances (Symris, 2006). A 15 – 30 % dilution of vetiver oil in alcohol is good enough to make true vetiver perfume, and its further dilutions have value as vetiver ‘eau de cologne’ and ‘eau de toilette.’ 'Vetiver pour Homme’ by Carven 1957, and ‘Vetivert’ by Guerlain 1961, are the two famous ‘eau de toilette’ for men prepared from vetiver oil (Groom, 1992).

In addition to its own perfumery value on account of vetiver hydrocarbons and carbonyl compounds, their alcohol derivatives, i.e. vetiverols lend unique position to vetiver oil for perfumery applications as a valuable resource. Because of clear-cut differences in boiling point of the various constituents of vetiver oil, its vetiverol fraction could be easily separated by fractional distillation of oil only under high vacuum. Also, vetiverol could be acetylated with acetic anhydride to produce vetiveryl acetate. Both vetiverols and acetates have softer odors and fixative qualities, and are used as blender with high-class perfumery products. They blend well with ionone, linalool, cinnamic alcohol, oakmoss, vanilla, sandalwood, patchouli and rose bases, and are frequently used in western type of fragrances having chypre, fougere, rose, violet and amber aldehyde base, as well as oriental fragrances and floral compounds (Lavania, 2003).

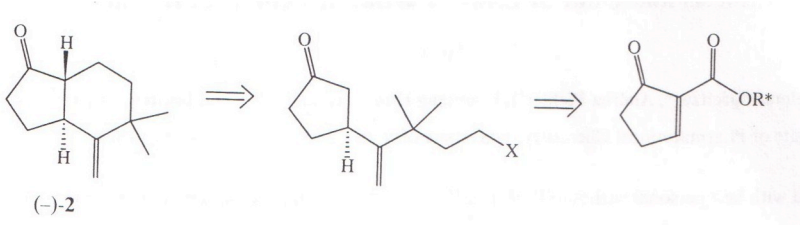
In its diluted form Vetiver oil is extensively used in after-shave lotions, air fresheners and bathing purposes, cosmetic as well as flavoring syrups, ice cream and other food preservation. Khus essence is used in cool drinks, and for reducing pungency of chewing tobacco preparations, providing sweet note to other masticatories and incense sticks.

3.2.8. Synthetic attempts

Attempts were made to find structurally similar structures with vetiver character, that could easily be synthesized. The olfactory characteristics of the main components α- and β-vetivone have been discussed controversially, but scientists definetly agreed that (-)-khusimone is one of the main odor-donating components. For economic reasons there were efforts to develope a short synthesis that starts from the also naturally occurring (+)-zizanoic acid, but until 1997 there were none structure/odor studies on (-)-khusimone (1) published (Spreitzer et al., 1997).

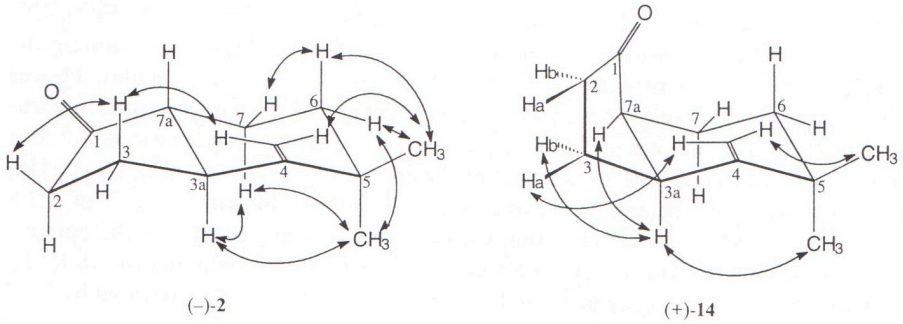
One of the main odor-donating compounds of vetiver oil is the theme of the following study on structure/odor mutual influences. The omittance of the ethano bridge of the tricyclic khusimone (1) directs to a bicyclic system. In this study by Spreitzer and his coworkers, the olfactory characteristics and the stereoselective approach to this degraded structure has been described. The momentous step of the hydrindane nucleus synthesis was based on a highly diastereoselective conjugate addition to a chiral oxo-cyclopentene-2-carboxylate.

The focus of interest in this report was put on the olfactory consequences of changing the tricyclic structure to the bicyclic structure (-)2 which had to be synthesized enantioselectively.



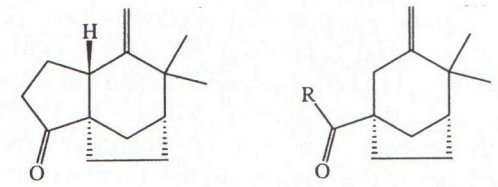
The odor impression of (-)2 was described as weak champhoraceus with a woody by-note, which proves that the degradation of the tricyclic khusimone (1) to the bicyclic

structure (-)-2 guides to the loss of the typical odor. The epimeric compound (+)-14 exibits an intense camphoraceous and fruity scent that resembles to strawberry and raspberry (Spreitzer et al.,1997).



(–)-2 (+)-14

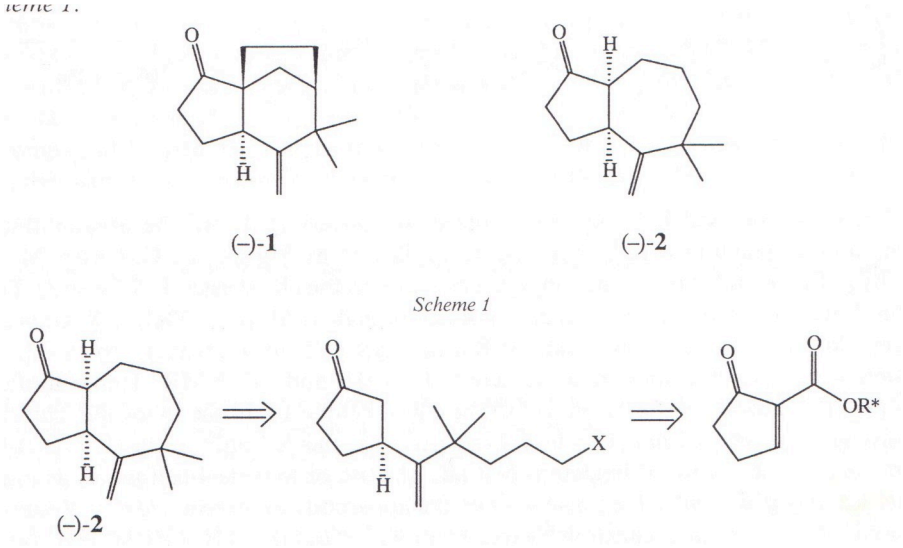
Further attempt was to open the ring of the carbonyl-functionalized bridge of the tricyclic khusimone which leads to bicyclic structures 2a/b. Considering the fact that optical antipodes in many cases exibit different odors, compounds 2 a/b needed to be synthetized enantioselectively.



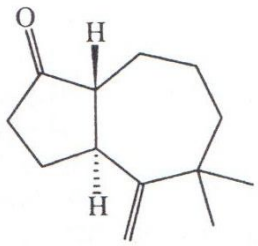
(–)-1 (–)-2a R = Me
(–)-2b R = Et

The odor note of (-)-2 a can be described as predominantly camphoraceous with a sweet-herbal by-note. The seco-khusimone (-)-2b incorporates a woody cedar-note but with no camphoraceous by-notes. Conclusion is that the typical odor descriptors of vetiver do not come from these partial structures either (Spreitzer et al., 1997).

Finally, the focus of interest was put on the olfactory consequences of omitting the methano bridge. This degradation of the tricyclic nor-sesquiterpene guides to structure (-)-2.



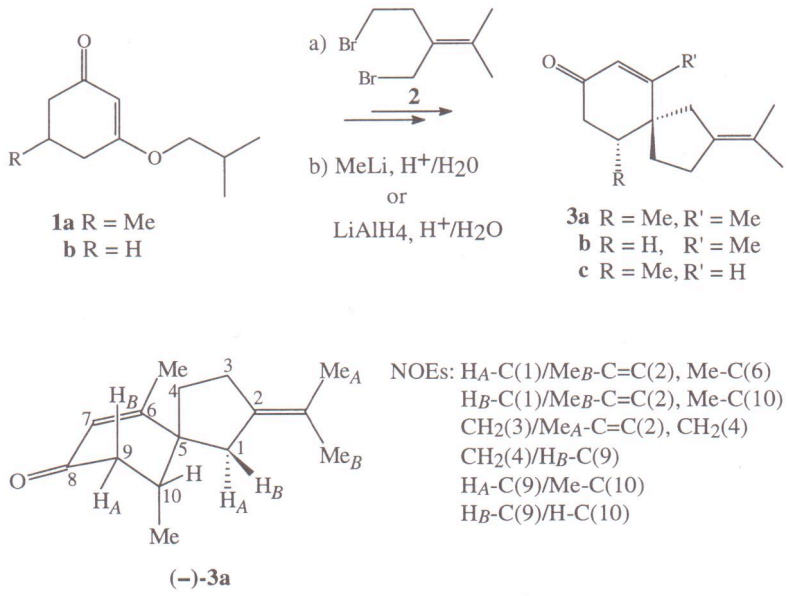
During the experiment structure (-)-16)-was synthetized and also did not match the tipycal and precious vetiver odor.



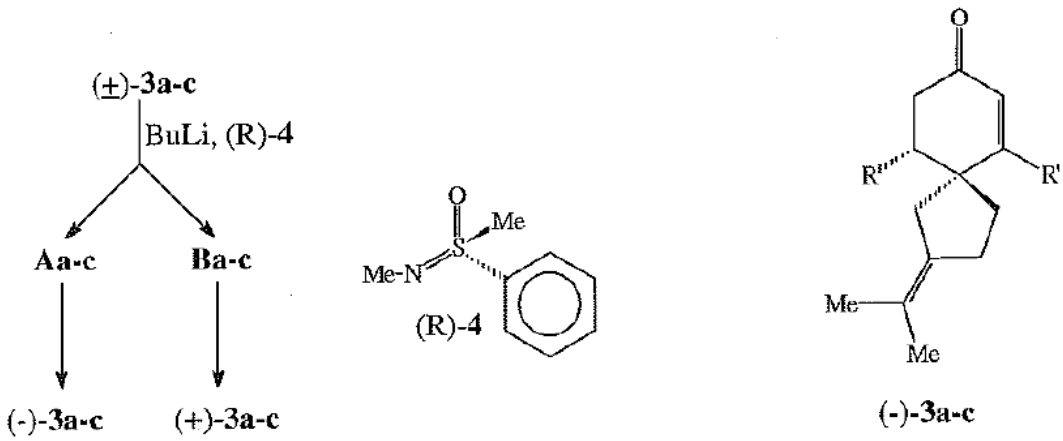
In general the odor was described as camphoraceous but pleasant, unfortunately also with a lack of the so wanted vetiver note (Spreitzer et al., 1997).

One of the major constituents of vetiver oil (-)-β –vetivone ((-)-3a) was also examined to find structure/odor relationship. In this study the influence of chirality on the odor properties was studied.

Furthermore the contributions of the methyl groups at the cyclohexenone ring to the scent are tested by synthesizing and rating the chiral demethyl derivatives 3b,c of 3a. Detailed 1H- and 13C-NMR-spectroscopic data were collected, and the absolute configurations were verified by CD operations.



This study proved once more that β-vetivone is often described wrongly as one of three odor-donators of vetiver oil. The odor impression given by demethyl derivatives (-)-3b and (+)-3b was described as intense cresolic. A sweet cumarine-like odor with a woody note was subjected to the enantiomer (-)-3c, while (+)-3c exhibits a woody smell with a quinoline-like by-note. To the scientists surprise, the odor of (-)-β-vetivone ((-)-3a) can be described as a quinoline like, fruity aroma, that resembles to cassis or grapefruit scent, but also has a woody by-note. (+)-3a has unpleasant medicinal note and there hasnt been detected any resemblance to the pleasant vetiver aroma (Spreitzer et al., 1998).

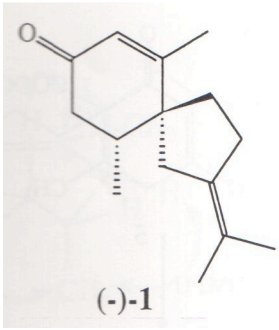


Resolution of β-Vetivone (**3a**) and Derivates **3b,c,** and Absolute Configuration of (-) -**3a-c** (Spreitzer et al., 1998)

The study by Maurer also stated that (-)- β - vetivone exhibits an odor with a lack of of

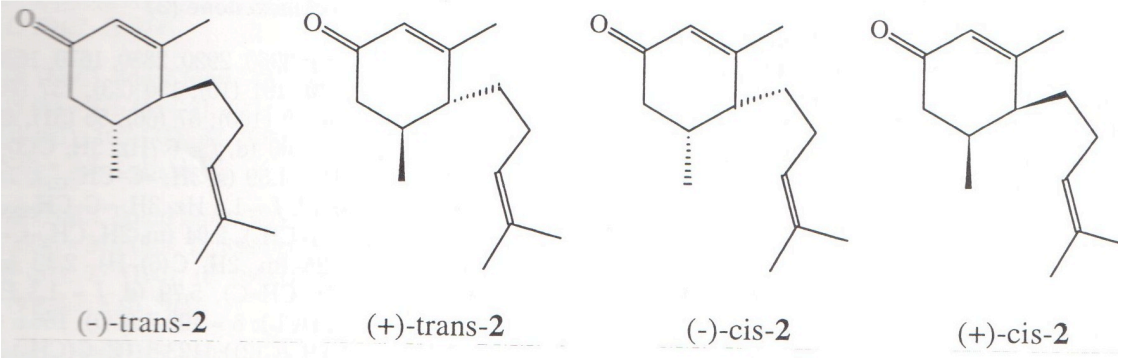
the typical odor characteristics associated with vetiver. When everything is summarized, it could be claimed that that configuration has a big influence on the character of the odor of β -vetivone (3a) and its demethyl analogue 3c, but none of the typical odor descriptors do not stem from these component nor from these partial structures (Spreitzer et al., 1998).

Although the results of the previous studies were not encouraging for the further search of compounds that mimic the vetiver odor, several stereoisomeric; monocyclic analogs of (-)-β-vetivone (1) were analysed to determine whether the olfactory properties of (-)-β-vetivone (1) could be reproduced from these structurally simpler; synthetically accessible compounds. The influences of diastereomeric and enantiomeric structural differences on the odor of the partial vetivone structure were tested. To separate the racemic mixtures a chiral phenyl sulfoximine was used. To determine the relative configurations detailed spectroscopic procedures 1H- and 13C-NMR were completed. Absolute configurations were determined by circular dichroismus (CD) methods (Spreitzer et al., 1999).



(-)-1

The lack of the bicyclic spiro structure and its olfactory consequences of analogs of (-)-β-vetivone were analysed. A result of the omitting of one methylene group (C1) from the cyclopentane ring is the cyclohexanene analog which can exist as four possible stereoisomers. (-)-trans –(2) represents the correct chiral partial structure of (-)-1, but the focus was also put in wining the olfactory properties of the other stereoisomers (+)-trans-(2), (-)-cis-(2) and (+)-cis-(2).



The odor sensation of (+)-trans-2 is described as not very intense fresh-woody, on the other hand, the optical antipode (-)-trans-2 exibits an intense and unpleasant phenolic scent. The isomers (+)-cis-2 and (-)-cis-2 are determined as nearly odorless. A single component or a mixture of these stereoisomers did not match the expected vetiver descriptors (Spreitzer et al., 1999).

In the second part of this examination, the olfactory consequences of omitting the C3-C4-ethylene group from the cyclopentane ring are studied.

These cyclohexenone analoga can exists as four possible stereoisomers, among which (-)-cis-(2) represents the correct chiral partial structure of (-)-1. Other three posssible stereoisomers are (+)-cis-2, (-)-trans-2 and (+)-(2).

The odor of (-)-cis-2 can be summarized as weak, fresh-woody and kind of reminiscent of vetiveryl acetate. Even though the odor is very pleasant the overal impression does not correspond the typical vetiver note and can be excluded as a possible additive for the reconstitution of the typical odor characteristics of vetiver. (+)-cis-2 gives an unpleasant, intense phenolic scent; the isomers (-)-trans-2 as well as (+)-trans-2 are very weak odorants. (-)-trans-2 was described as a weak cassis-like scent with a sulfur-like by-note and the aroma of the antipode (+)-trans-2 is balsamic with a woody by-note.
Unfortunately, once again the goal of this study to acchieve vetiver odor by faster and more economic procedures was not achieved (Spreitzer et al., 1999).

3.2.9. Effects on humans

Essential oil such as vetiver have been traditionally used by people for various purposes in different parts of the world (Table 14).

Common name	Botanical name (Family)	Properties
Vetiver oil	*Chrysopogon zizanioides* (Graminae)	Stimulant, refrigerant, flavouring agent, stomachic and fixative.

Table 14. Vetiver essential oil and its properties (Rastogi, 2002)

Vetiver oil owes several beauty benefits and emotional effects. Vetiver oil has antibacterial and antifungal properties (Chaumont and Bardey, 1989; Dikshitand Husain, 1984; Gangrade et al., 1991; Gangrade et al., 1990; Hammer et al., 1999; Maruzzella and Sicurella 1960). It balances the activity of the sebaceous oil glands, has deodorizing properties, and helps normalize oily skin and clear acne. It replenishes moisture in dry and dehydrated skin and has a rejuvenation effect on mature skin, as well as cuts / wounds / irritated and inflamed skin. When used regularly during pregnancy, vetiver oil reportedly prevents stretch marks.

Therapeutically, vetiver oil has a profoundly relaxing effect on the nervous system, and is helpful in overcoming depression, anxiety, stress, tension and nervousness (Wilson, 1995). Vetiver oil possesses sedative properties and has been traditionally used in aromatherapy for relieving stress, anxiety and nervous tension for a long time (Leupin, 2001). It is not scientifically proved, but in some parts of the world people use it to achieve positive effect in the treatment of insomnia. In India, vetiver oil is known as the oil of tranquility.

Vetiver oil also benefits the circulatory system, stimulating and warming, especially when used in combination with massage.

In baths or in massage, vetiver is beneficial in the treatment of the symptoms of disorders such as arthritis, rheumatism and a chin, stiff muscles. It is warming and

comforting and will help to relieve the tension that is often associated with chronic pain (Engineers India Research Institute, Delhi, 2003).

When locally applied in rheumatism, lumbago, headache, sprain, it is a relieving embrocation. Infusion of roots is a refreshing drink in fever, inflammation and irritability of the stomach.

Although some people use vetiver oil as aphrodisiac (Wilson, 1995) newest studies have not proved the aphrodisical effect on humans.
The study took place at the University of Vienna at the Department of Clinical Pharmacy and Diagnostics and tested attractivness rating and physiological parameters on men and women. This study verified the vitalizing effect of vetiver oil, by the physiological parameters such as cardiogramm, blinks per minute, blood pressure, skin temperature, pulse and breathing rate, however the aphrodisical effect could not be rated as positive (Meyer, 2010).

Another study which analysed salivatory cortisol effects on the emotional state of the participants as well as gender effects, also did not found any aphhrodisiac effect on people, but did prove that vetiver oil has significantly higher effect on women considering mood parameters tension, fatigue and depression (Denic, 2010).

3.2.10. Other effects

Vetiver oil has impact on animals. In the study of Zhu and his coworkers repellency and toxicity of eight essential oils were evaluated against the Formosan subterranean termite, Coptotermes formosanus. Among cassia leaf, clove bud, cedarwood, Eucalyptus globulus, Eucalyptus citriodora, lemongrass and geranium, vetiver oil showed the most effective repellent effect because of its long-lasting activity. The tunneling response of termites to vetiver oil also was examined and showed that the oil of vetiver diminished termite tunneling activity at concentrations as low as 5 micrograms/g sand. When vetiver oil concentration were higher than 25 micrograms/g sand, paper consumption and tunneling were not observed. This study concluded that vetiver oil is very promising termiticide with reduced environmental impact for the purpose to fight subterranean termites (Zhu et al., 2001).

In the course of a random screening of various plant extracts, khusimol, a non-peptide molecule that can be found and isolated in the root of Chrysopogon zizanioides, was detected to competitively inhibit the binding of vasopressin to rat liver V1a receptors (Ki= 50 microM). The 1H- and 13C-NMR spectra of this sesquiterpene alcohol were assigned distinctly (Rao et al., 2010).

The sedative effect of vetiver oil upon inhalation in rats was studied by observing the number of crossing and rearing motilities. The results showed that vetiver oil decreased rearing motility when compared to the control group (Sirinan et al., 2012).

Male Wistar rats with mean body weights of 124 g were divided into 3 groups (7 rats/group) and kept under conventional conditions at room temperature of 24^{o}C. The first group was used for testing with vetiver oil (5 % w/w) and the others with lavender oil (5 % w/w) and distilled water as a positive control and control group, respectively. The cage for inhalation (14 L) contained a perforated plastic, which was partitioned into two sections. One part contained soda lime (14 g) to absorb CO_2 and the other one contained calcium chloride (14 g) to remove humidity. After each group of animals was put into the cage, it was made airtight with a transparent plastic seal with 2 small openings. One was connected to a spirometer for O_2 admission (Sirinan et al., 2012).

The second was fitted with a folded 8x10 cm filter paper, which was used to add the volatile oil. The open-field test was modified from Brotto and Kovacs (Brotto et al., 2000, Kovacs, et al., 1999). After the animals inhaled the essential oils for 1 hour, they were rested for 30 minutes. Rats were placed individually in the center of a square measuring 10 x 10 cm each. The standard source of illumination was 60 W bulb from 80 cm. The activity was assessed during five minutes and recorded on a ceiling mounted video camera.
Videotapes were later scored and measured for the number of segments crossed by the animal (defined as at least three paws in a quadrant) and the number of rears (defined as the animal standing upright on its hind legs).

Group	No.	Number of Crossing		Number of Rearing	
		Mean	% Motility	Mean	% Motility
Vetiver oil	7	117.3	4.2	24.7	-20.1
Lavender oil	7	81.3	-27.8	27.6	-10.7
Control	7	112.6	-	-30.9	-

Table 15. Effect of vetiver oil administration on crossing and rearing behaviors in the open-field test in rats
(Buchbauer *et al.*, 1993)

The animal study explored the effect of vetiver oil on the motility of rats using inhalation procedure. The influence on motility is calculated to demonstrate sedative effect after aromatherapeutical application of the essential oils. In this study were used lavender oil, known to have potent sedative effect, as a positive control. (Buchbauer *et al.*, 1993). After the one-hour inhalation period, vetiver oil led to the most decrease in rearing motility compared to the control group and lavender oil but a small increase in crossing motility. These data showed that vetiver oil possesses sedation effect in agreement with traditional use. In order to understand the effect of every major component of vetiver oil, it may be necessary to study their activities individually on the animals further.

In the study of Tripathi (2006), an experimental approach is applied to vetiver oil to elicit toxic responses over an exposure period of 90 days. Since no data are available in this regard, it was thought worthwhile to carry out acute and subacute toxicity studies in male and female rats. Acute toxicity determination indicated that vetiver oil has LD50 values of 2985.38 mg/kg. The drug is practically non-toxic at oral doses. To carry out the subacute toxicity studies, the oil was administered to rats for 45 and 90 days, and the blood samples drawn from animals were subjected to full biochemical and hematological investigations. It was found that prolonged exposure of rats to vetiver oil exerted a mild hematotoxic effect and may alter lipid metabolism.
Glasshouse and field studies showed that Vetiver grass can produce high biomass (>100t/ tha(-1) year(-1)) and highly tolerate extreme climatic variation such as prolonged drought, flood, submergence and temperatures (-15 degrees - 55 degrees C), soils high in acidity and alkalinity (pH 3.3-9.5), high levels of Al (85% saturation percentage), Mn (578 mg kg(-1)), soil salinity (ECse 47.5 dS m(-1)), sodicity (ESP 48%), and a wide range of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Zn) (Danh et al., 2009).

Vetiver can accumulate heavy metals, particularly lead (shoot 0.4% and root 1%) and zinc (shoot and root 1%) (Danh et. al. 2009). The majority of heavy metals are accumulated in roots thus suitable for phytostabilization, and for phytoextraction with addition of chelating agents. Vetiver can also absorb and promote biodegradation of organic wastes (2,4,6-trinitroluene, phenol, ethidium bromide, benzo[a]pyrene, atrazine).

Although Vetiver is not as effective as some other species in heavy metal accumulation, very few plants in the literature have a wide range of tolerance to extremely adverse conditions of climate and growing medium (soil, sand, and railings) combined into one plant as vetiver. All these special characteristics make vetiver a choice plant for phytoremediation of heavy metals and organic wastes (Danh et al., 2009).

4. Discussion

The goal of the presenteor thesis was to collect and elaborate many scientific papers and studies about Vetiver plant and what is more important to describe many useful effects of it' s essential oil.

Although Vetiver plant has very important role in enviromental use, many scientists and generally other people would agree that this unique plant holds it' s value in it's much complex and esteemed essential oil. After a brief writing about the features of Vetiver plant, seeding, harvesting and it's impact on the whole agriculture, center of interest was put in describing demographic varietys, since it has shown that chemical profiles of the oil can vary due to different demographic position of the plant.

From qualitative aspect there are two distinct types of essential oil obtained in India: North Indian type (”khus oil ”) and South Indian type (vetivert oil). The ”khus oil” is considered to be more superior because of the fact that it has higher ester value and higher concentration of heavier carbonyl fractions compared to all other sources of vetiver oil. It is also important to mention that different geografic origins have also different odor notes from an earthy, woody to a sweet, roseate note and because of this characteristic are differently appreciated by the perfumers around the world.Haitian oil is also known as as one of the great perfume notes because it blends well with many other essential oils .

It is well known that essential oil of Vetiver is one of the most complex, with almost 300 components, among wich (-)-α-vetivone, (-)-β-vetivone and khusimol are considered as the “fingerprint“ of the oil. Although vetiver essentilal oil is becoming more and more popular in the western world it is still unclear which compounds are responsible for the typical scent, so the scientists are claiming that the typical scent is given by the combination of compounds. Since, the demand for vetiver oil is groving in the world market, many synthetic attempts have been made to find structurally similar structures with vetiver marks that could easily be synthetized. Unfortunatly it is still not proved that it is possible to produce a syntetic vetiver oil, which would be of great value due to it's also known positive effects on human health.

Through the experience while writing this paper, not many people in the western world have even heard and are not familiar with the benefits of this essential oil. While in the Eastern World, especiallly in India, it is well known and used as the oil of tranquility. Many scientific attempts report about its sedativ and relaxing effect on the nervous system and as a great help in overcoming depression, anxiety, tension and stress, when used in aromatherapy. When used in baths vetiver can help in the treatment of arthritis, rheumatism and a stiff muscles. Some poeple use it as aphrodisiac, although newest studies did not prove this effect but it is proven that it helps to increase women fertility. Also, because of its many other benefits such as antibacterial, antifungal, deodorizing properties, rejuvenating effects on skin and in general positive effects on the whole enviroment vetiver essential oil is definitely very interesting and a worthy compound for further analysis and synthetic attempts, because the world is yet to be introduced with many goods of this rather interesting and complex plant and its essential oil.

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5.2. List of Tables

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6. CURRICULUM VITAE

Lebenslauf ***CURRICULUM VITAE***

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