# Plants4Cosmetics :

## Perspectives for plant ingredients in cosmetics

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Report nr. 1603

Momentive EX1027
U.S. Patent No. 12,337,057

# Colophon


| | |
|---|---|
| Title | Plants4Cosmetics : perspectives for plant ingredients in cosmetics |
| Author(s) | Carmen G. Boeriu |
| Number | 1603 |
| ISBN-number | ISBN number |
| Date of publication | October 2015 |
| Confidentiality | no |
| OPD code | 15/186_15620279 |
| Approved by | Christiaan Bolck |



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## Samenvatting

In opdracht van Bio Base Westland en de TKI Tuinbouw Koepel PPS Plantenstoffen, heeft Wageningen UR – Food & Biobased Research een exploratieve desktop studie uitgevoerd gericht op de identificatie van veelbelovende routes voor de valorisatie van plantinhoudstoffen - waaronder ook reststromen uit de tuinbouw - voor de cosmetische industrie. Een uitgebreide analyse van de beschikbare informatie werd uitgevoerd om de mogelijkheden voor de Nederlandse tuinbouwsector te bepalen. Er is gekeken naar marktkansen in de cosmetische industrie met inbegrip van *natuurlijke* en *biologische* ingrediënten.

Cosmetische producten worden doorgaans ingedeeld in 5 categorieën met bijbehorende marktsegmenten. Dit zijn decoratieve cosmetica, parfums en parfumerie, haarverzorging, toiletartikelen en huidverzorging. Cosmetische producten zijn complexe mengsels van verschillende chemische verbindingen met verschillende fysisch-chemische en functionele eigenschappen. Ingrediënten worden geselecteerd op basis van functionaliteit teneinde de gewenste producten met de hoogste kwaliteit te verkrijgen. Ingrediënten zijn gemaakt van zowel synthetische als natuurlijke bronnen. De wereldwijde cosmetische industrie groeit gestaag met een groei van de omzet van meer dan 5% per jaar.

Een belangrijke factor voor groei is de vraag naar *natuurlijke, echt natuurlijke, plantaardige en biologische* producten. In de afgelopen jaren was de groei van de omzet voor natuurlijke cosmetica meer dan 10% per jaar. Deze toenemende vraag creëert nieuwe kansen voor innovatie en ontwikkeling van nieuwe producten om aan deze vraag van de consument te voldoen. Deze beweging van de cosmetische industrie in de richting van natuurlijke en biologische cosmetica ingrediënten is al geruime tijd aan de gang en leid al tot een toename van de productie en levering van natuurlijke en biologische cosmetica ingrediënten. Opvallend is overigens een groeiende neiging van cosmeticaondernemingen om natuurlijke cosmetica niet alleen toe te passen in luxe producten als parfum maar ook in massa producten als shampoo.

Als gekeken wordt naar mogelijk plantaardige bestanddelen met specifieke functionaliteiten waar de cosmetische industrie om vraagt kunnen de volgende productgroepen worden geïdentificeerd: essentiële oliën (geurstoffen, anti-microbiële), bioactieve fenolen (actieven, antimicrobiële middelen), kleurstoffen en pigmenten (actieven) en polysacchariden. Kijkend naar ingrediënten met de hoogste economische potentieel voor de tuinbouw dan lijken de essentiële oliën en bioactieve fenolen het meest veelbelovend. Deze inschatting volgt uit de markt analyse waarin naar voren komt dat er met name vraag is naar ingrediënten voor toepassingen in de huidverzorging, lichaamsverzorging en parfumerie segmenten. In deze selectie, is ook de nieuwe trends meegenomen van het gebruik van de werkzame bestanddelen van de traditionele eetbare en geneeskrachtige planten.

Op basis van deze bevindingen zijn vervolgens vier planten geselecteerd voor verdere studie. Één van de cases is de hyacint waarin gekeken wordt naar de selectieve extractie van een hoogwaardige etherische olie voor de geur en de parfum van de bloemen. Twee andere cases bekijken de winning van etherische oliën en flavonoïden uit de bovengrondse delen (bloemen,

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bladeren en stengels) van geranium en chrysant; beide cases zijn geschikt voor een bio-raffinage benadering, waaronder ook de isolatie van polysacchariden uit de wortels. De vierde case is meer verkennend van aard, gericht op het in kaart brengen van de waarde van mogelijk interessante ingrediënten aanwezig in orchideeën.

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## Abstract

In an assignment for Bio Base Westland, the "TKI Tuinbouw Koepel PPS Plantenstoffen" and Kenniscentrum Plantenstoffen, Wageningen UR – Food & Biobased Research has conducted an explorative desk-top study aiming to identify promising routes for the valorisation of plant components including green waste streams from horticulture for the production of value-added ingredients for the cosmetic industry. In order to identify the opportunities for new business opportunities, a comprehensive analysis of the available information was carried out to determine the perspectives for the Dutch horticulture sector.

The cosmetic products are classified in 5 categories and the corresponding market segments are: decorative cosmetics, fragrances and perfumery, hair care, toiletries and skin care. Cosmetic products are complex mixtures of many chemical compounds with different physic-chemical and functional properties selected based on functionality in order to obtain the desired products with the highest quality. The constituent compounds of cosmetics are made from synthetics and natural sources. The worldwide cosmetic industry is growing steadily with a growth of turnover of about more than 5% per year.

One important factor driving the market is the growing demand for *natural, true natural, herbal* and *organic* products creating also new chances for innovation and development of novel products to meet consumer preferences. In recent years the growth of turnover for natural cosmetics was more than 10% per year. These growth rates already initiated a move of the cosmetic industry towards natural and organic cosmetic ingredients, and subsequently an increase of the production and supply of natural and organic cosmetic ingredients. There is an emerging tendency of cosmetic companies to develop natural cosmetics not only for the luxury sector, but also for the mass sector.

Focussing on plant components with specific functionalities cosmetic industry shows increased demand for essential oils (fragrances, anti-microbials), bioactive phenolics (actives, antimicrobials), dyes and pigments (actives) and polysaccharides. Looking at ingredients with the highest economic potential for horticulture essential oils and bioactive phenolics seem to be most promising since the market analysis shows a continuous interest in ingredients particularly for applications in the skin-care, body-care and perfumery segments. In the selection, we have considered also the new trends for rediscovering the active principles of traditional edible & medical plants next to exotic plants.

Based on these findings, four cases have selected for further study. One case, related to hyacinth, refers to the selective extraction of a high value essential oil for fragrance and perfumery from flowers. Two other cases deal with the extraction of essential oils and flavonoids from the aerial parts (flowers, leaves and stems) from geranium and chrysanthemum; both cases are suited for a biorefinery approach, permitting as well the isolation of polysaccharides from the stems and roots (in case of chrysanthemum). The fourth case is more exploratory, aiming at the mapping of the value compounds in orchids, and the identification of valorisation routes.

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# 1 Introduction

## 1.1 Background

Horticulture is one important pillar of the Dutch economy, and it is an advanced, well- structured sector, that generates high quality products with very high productivity. The Dutch horticulture sector is the world market leader in flowers, plants, bulbs and reproductive material and the number three exporter in nutritional horticulture products [1].

Next to the main end-product streams, consisting of vegetables, decorative plants and fruits, a large amount of green plant waste (biomass) is collected at the production site and at the auction. Green biomass waste streams from horticulture (GBW) are usually discarded or used to obtain compost that is commonly recycled for soil improvement. However, GBW contains high amounts of protein, polysaccharides and lignin next to a broad range of minor components with exceptional properties like flavour, colour and bioactivity and therefore is a valuable source of both commodity and specialty chemicals. There are several options for the valorisation of GBW other than composting or utilisation for energy production:

(i) biorefining the biomass to separate the protein and lignin and utilise the carbohydrates for the production of chemicals, building blocks and polymers using chemical, biocatalytic or fermentative processes,

(ii) extraction of one or more high value plant components, such as vitamins and antibiotics, flavours and fragrances, antioxidants, dyes and pigments, oils, waxes, tannins, gums and specialty polymers for application in the cosmetic and pharmaceutical industry.

Integration of these two routes in a more complex biorefinery approach producing both low-volume, high-value specialty chemicals for cosmetics and pharma (route (ii)) and high-volume, lower value commodity chemicals (route (i)) in a biocascading process, is also possible, but the economic feasibility must be evaluated.

## 1.2 The aim of the study

In this assignment for Bio Base Westland, Koepel PPS Plantenstoffen and Kenniscentrum Plantenstoffen (KPS), WUR FBR has conducted an explorative desk-top study aiming to identify promising routes for the valorisation of plant ingredients including green waste streams from horticulture for the production of value-added ingredients for the cosmetic industry.

In mutual agreement with Bio Base Westland, KPS and the other partners in the Koepel PPS Plantenstoffen the following categories of plant ingredients have been selected for evaluation in this feasibility study:

- Polyphenols (other than anthocyanins); compounds of this class have important bioactive properties (e.g. antioxidant, antibacterial) and can be used as antiaging ingredients, antibacterial ingredients and UV-filtering ingredients in sun-protection creams, among other applications.

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- Essential oils, for application as fragrances in perfumes, creams, lotions, etc. They can also have bioactive properties, like antioxidant and antimicrobial.
- Dyes and pigments (e.g. indigo, carotenoids)
- Polysaccharides, with application as hydrogels, bioactive compounds and fillers/texturisers.

### 1.3 Overview

This study gives an overview of the market demand and market trends for cosmetic products and the selected classes of natural ingredients, respectively, a critical discussion of the opportunities and threats and regulation issues for natural cosmetic ingredients. Outcome of the market study was corroborated with available data on the amount and availability of decorative plants, the volume of green biomass waste stream from horticulture as well as with information on the pattern and level of selected active ingredients in the plants, to make a selection of the potential business cases.

The study is based on an analysis of the market demand and market trends in cosmetics and the natural cosmetic ingredients field, a thorough literature study on the composition and the levels of selected active ingredients in different plants, their functionality and application. Patent literature, databases and reports from Keniscentrum Plantenstoffen relevant to the topic of the project were also studied.

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# 2 Trends in cosmetic industry

## 2.1 Introduction

The cosmetic industry produces a wide range of personal care products that are used to enhance and embellish the appearance of individuals. There are many types of cosmetic products and they include fragrances, and perfumes, colour cosmetics, bathing shower gels, along with skin care, hair care, personal hygiene oral care, and personal hygiene products. The cosmetic products are classified in 5 categories and the corresponding market segments are: decorative cosmetics, fragrances and perfumery, hair care, toiletries and skin care. Cosmetic products are complex mixtures of many chemical compounds with different physic-chemical and functional properties selected based on functionality in order to obtain the desired products with the highest quality. The constituent compounds of cosmetics are made from synthetics and natural sources. If in the early years of the cosmetic industry most ingredients used were natural, of plant and animal origin and inorganic materials, with the development of synthetic chemistry a broad range of functional compounds became available and the focus shifted towrads synthetics. A large number of natural compounds were synthesized chemically or biochemically and were further utilized in cosmetics as "nature like" ingredients. In the past years, a strong demand for more natural cosmetics occurred, and the industry reacted positively resulting in a high emulation: new start-up producing "all natural" and natural cosmetics, leading cosmetic companies starting new research programs and launching new natural products on the market. There are many factors that impact on the cosmetic market as it will be discussed later.

## 2.2 Market trends

<u>European market</u>

Europe is a world leader in the cosmetics industry and a dominant cosmetics exporter. The sector is highly innovative and has a high positive economic and social impact in Europe, employing approximately 1700000 people of which 25000 scientists, working in research and development.

The data released by the Cosmetics Europe association [2] in the summer of 2015 indicate that in 2014 the European cosmetic industry had a slightly positive growth in sales (+ 0.5%) and showed signs of recovery as compared to a decrease of 1.4% in 2013. The European market retail size is about 72.5 billion euros [2], representing about 1/3 of the global market.

Germany is the main market in Europe (13.1 billion euros), followed closely by France and United Kingdom (Figure 1). While United Kingdom registered in 2014 a 5.3% growth, other countries showed a lower growth or were still in recession (Italy, -1.4%, Spain, -1.3) [2]. The main EU cosmetics producers are multinational companies such as L'Oréal (France), Unilever (The Netherlands/UK), Beiersdorf (Germany), LVMH (France), Chanel (France) and Henkel (Germany). They operate across a wide spectrum, being involved in sectors such as pharmaceuticals, chemicals, food and household products.

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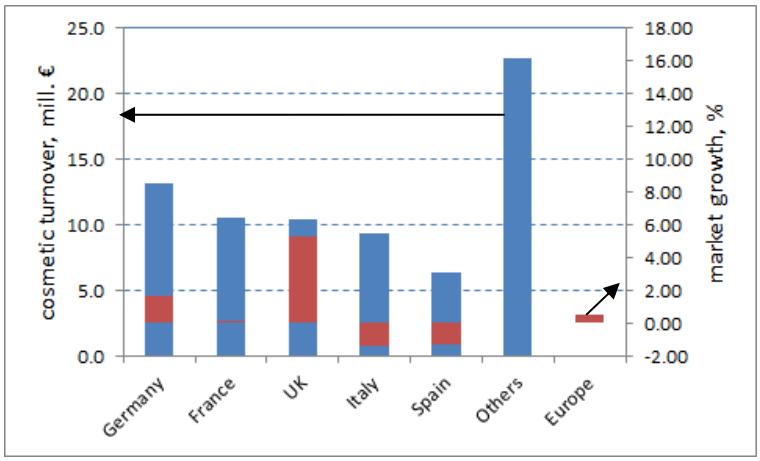


Figure 1. Cosmetic market retail size, per country, and performance in 2014. Data from [2, 3]

The market performance per product categories varied significantly. While the hair care products segment faced a decrease of -0.2%, all other product categories registered an increase in value, with colour cosmetics (+1.2%) and toiletries (+ 1.3%) showing the highest increase (table 1)[2].

Table 1 Market performance per product segment. Data from [2]

| **Product category** | **Market change (%)** | **Market share** |
|---|---|---|
| Decorative cosmetics | 0.1 | 13.4 |
| Fragrances & perfumery | 1.2 | 15.0 |
| Skin care | 0.1 | 25.4 |
| Hair care | -0.2 | 25.4 |
| Toiletries | 1.3 | 20.8 |

Skin care (25.4%) and toiletries (25.4%) are the most important product categories in Europe, followed by hair care (20.8%) and fragrances and perfumery (15.0%).

Global market

The global cosmetic market follows an ascending trend as well. It is estimated that the global cosmetic market will increase from 460 billion USD in 2014 by 675 billion USD by 2019 at a compound annual growth rate, CAGR[1], of 6.5% (Figure 2a) [4].

Asia Pacific region had a leading position with a market share of 35%, followed by Western Europe and North America. High increase of the cosmetic product market is expected to occur in emerging markets like Brazil, India, Pakistan, Morocco, Indonesia, Saudi Arabia, Vietnam and UAE and is associated with the increasing disposable income, the increase of the middle classes and urbanisation, the young population and the "sophistication of beauty habits" [5].

Predictions show that the skin & sun care segment will obtain the largest market share of the global cosmetics market in this period. One factor driving this growth is the rising consumption of skin & sun care products by both men and women. Another factor is the growing demand for

[1] *CAGR: Compound Annual Growth Rate and is the* mean annual growth rate *of an investment over a specified period of time longer than one year*

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natural, herbal and organic products creating also new chances for innovation and development of novel products to meet consumer preferences.

Figure 2. Estimated world Cosmetics Market size ($ billion) and %CAGR for 2014-2019, from [6]. Legend: E - estimated; p - projected

The leading players in the cosmetic products market include L'Oreal Group (France), Avon Products, Inc. (U.S.A), The *Estée Lauder* Companies, Inc. (U.S.A), and Oriflame Cosmetics (Luxembourg). Other big cosmetic companies are Procter and Gamble Corporation (USA), Unilever (UK), Revlon Inc. (USA), Kao Corporation (Japan) and Shiseido Inc. (Japan). Cosmetic companies continuously invest in R&D to introduce new products to meet the market demand. The number of small innovative cosmetic companies is increasing.

## 2.3 Natural and organic cosmetics

Natural cosmetics

The use of natural ingredients (e.g. polysaccharides, dyes and pigments, fragrances, essential oils) in cosmetic products alongside synthetic ingredients never ceased, but the concept of "natural cosmetic" gained recognition in the last decades of the 20$^{th}$ century, with (a) the establishment of companies like L'Occitane de Provence (1976, France), Aveda (1978, USA, now own by Estée Lauder), Melvita (1983, France), Korres (1996, Greece) dedicated to producing cosmetics containing natural and organic ingredients and avoiding the use of synthetic chemicals and (b) the new marketing strategies promoted. The market for natural cosmetics increased from less than US $ 1 billion in 1990s to US $ 9.1 billion in 2011 as a response to the increasing interest of consumers in health and wellness. Manufacturers have invested in developing new products containing natural ingredients[2]. With the use of natural plant extracts as cosmetic ingredients, a new generation of products has been introduced in the market of which a category has been claimed to contain biologically active ingredients with medicinal or drug-like effects, which satisfy the needs of both beauty and health. The natural products were easily accepted by consumers,

[2] *Natural ingredients are compounds of botanical, animal and mineral origin that are processed only by physical, microbiological or biocatalytic methods.*

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and the market volume increased with a high average of 9% a year between 2003 and 2008 [7]. The growing trend of natural cosmetics is continuing. The global natural cosmetic market in 2014 was evaluated by Kline at about 30 billion USD, which is about 7.2% of the global cosmetics market in 2014 (see 2.1.2), with a growth of 10.6% in 2013. Natural cosmetic markets in Europe and the United States, increased with 6.5% and 7.7%, respectively, in 2013. It is estimated that the trend is maintaining. Skincare products is the larger segment, with a market share of about 40% of the total.

In 2013, Kline Group [8] classified natural products and brands into "truly natural" and "natural inspired" and further segmented the markets into (1) skin care products, (2) hair-care products, (3) make-up, (4) fragrances, (5) oral care products other toiletries. Following, it developed a rating system, e.g. Kline's ratings system, which evaluates the naturalness of brands on a scale of 1 to 10, with 10 being completely natural. Based on this rating system, market analysis for 2014 showed that about 75% of the global natural personal care market is taken by products containing a high ratio of synthetic ingredients vs. natural ingredients. However, the truly natural status is becoming more important with consumers, manufacturers, and retailers [9]. Weleda (Switzerald), Jason (USA), Yves Rocher (France) and Korres (Greece) are truly natural brands in US and Europe. In US, a large number of small companies share 75% of the market, the rest being taken by Johnson & Johnson, Shiseido, Estée Lauder, The Clorox Company and L'Occitane. Yves Rocher and Oriflame, followed by L'Oreal, L'Occitane and Weleda are leading the natural cosmetic market in Europe [9]. Several companies in Europe and US are revising their strategy shifting toward truly natural branding, as for example Avalon Organics (USA), JĀSÖN (USA), Annemarie Borlind (UK), and Melvita (France) [9].

Organic cosmetics

Organic cosmetics contain in their composition ingredients that are obtained from raw sources cultivated/grown under organic pharming, or in the wild, with respect for the environment and in a sustainable manner. Organic cosmetics are attracting more and more attention and recognition. An ascending trend has been observed for the organic cosmetics market as well. Market analysts estimate that the global demand for organic personal care products will reach 13.2 billion USD by 2018, growing at a CAGR of 9.6% from 2012 to 2018 [10]. In 2011, North America and Europe were the largest consumers of natural and organic personal care products, accounting for 34% and 29%, respectively, of the total global consumption. Japan was the bigger consumer in the Asia Pacific region, with 42% of the market in the region, and is expected to obtain the faster growth.

## 2.4 Drivers and constraints

There are many factors contributing to the growth of the natural and organic cosmetic market, covering the whole chain from consumer to supplier and retail [11-15]. A detailed discussion of all these factors is beyond the scope of this study, and in the discussion below the marketing and retail aspects are not addressed.

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The major factor driving the natural and organic cosmetics market is the increasing demand of the consumers for products containing natural and organic ingredients in their formulation. Consumers are committed to more natural and green products, and this was clearly visible during the recession period, when the market for natural products was less affected than the total market for personal care products, and recorded a higher growth rate.

The increase in consumers demand for natural ingredients for cosmetics parallels the trend in food additives, and it is driven by the rising consumer awareness of health, concerns about environmental and sustainability issues, and it is influenced also by the personal perception that "natural" is better, healthier and safer than "synthetic". On the other hand, consumers became more aware and are better informed about possible risks of synthetic chemicals in cosmetics and on the values of natural and organic ingredients. Recent studies on consumer behaviour regarding green/natural cosmetics showed that health is the primary motivation [11, 16]. This resulted in a rising demand for active ingredients as well as to high expectations for genuine efficiency of personal care products. This is well illustrated by the constant growing of the skin-care segment from 2015 to 2021 (Figure 3a), where the anti-aging segment has the highest share (Figure 3b). In the same period, the anti-aging cream segment is expected to grow to 36.1 billion USD in 2021, as reported by Research and Markets [17].

A. B.

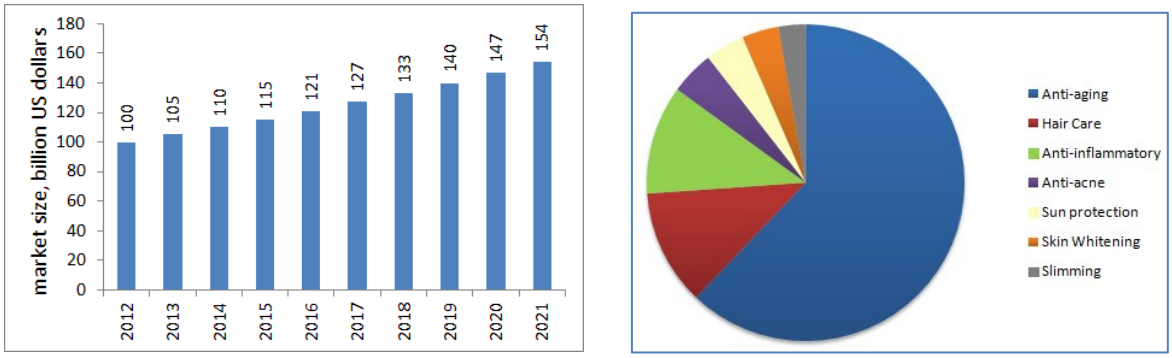


Figure 3. A) Market size for skin-care products for 2012-2021 (data from [18]). B) Active sales in Europe and USA in 2010, for the skin-care product, per functionality (figure from [14]).

In response to the consumer demands, cosmetic companies started to develop and to launch on the market new products containing natural ingredients, eventually bioactive; medical claims have been thoroughly investigated and supported by clinical trials. Known natural ingredients traditionally used in old cosmetics have been rediscovered. Ingredient suppliers have diversified their product portfolio and have developed new natural active ingredients from plants, animals or obtained by biotechnology routes (e.g. fermentation and biocatalysis). Plants traditionally used in small communities for their medical properties have been rediscovered for the extraction and utilisation of the active principles. Cosmetic industry and ingredient manufacturers have embraced the principles of the environmental conservation programs and sustainability. Strong collaborations have been started with raw material suppliers with the aim of ensuring ethical and

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sustainable supply. EcoDesign cosmetics have been launched using green and sustainable technologies and nature conservation [19]. For example, L'Oreal has produced a new anti-aging ingredient, Pro-Xylane, using as starting material the xylose side stream obtained from beech biorefinery. Guerlain has launched Orchidee Imperiale based on extract essence from orchid, a flower that is associated with long life, and they established an own platform, the Orchidarium, to analyse and discover the active/vital ingredients from orchids [19]. Ingredient suppliers have also invested in the discovery and development of new bioactive ingredients with properties superior to the synthetics used today. For example, Sabinsa's (NJ, USA) has developed a new antimicrobial composition containing blends of essential oils and phytoextracts with properties superior to that of parabens and DSM Nutritional Products (Parsippany, NJ, USA) is marketing a new line of natural ingredients for skin-care applications, that are based on the extract from the rare alpine plant *Epilobium fleischeri,* which is rich in flavonoids [15]. In addition, the cosmetic industry has benefitted from the developments in other scientific and technological fields, such as nanotechnology, which contributed to the development of performing cosmeceuticals. Nowadays, an important factor driving the growth of natural and organic cosmetics is the innovation along the chain, which results in new products with diversified and innovative formulations and added functionality, produced in a sustainable way, and meeting at the end the expectations of the consumers.

One main constraint is the lack of harmonization in guidelines of certifying agencies for certification of natural and organic products. Potential limitations of the supply of natural ingredients due to the increasing demand and high price of limiting components could also hamper the developments.

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# 3 Ingredients

## 3.1 Introduction

About 10000 chemical compounds are currently used in the cosmetic industry, the majority of which are synthetic chemicals. The content of natural ingredients is limited and varies significantly between the different important ingredient groups in cosmetics related to their application. A high share of natural ingredients is found in the groups of solvents, emollients, actives and humectants while the lowest natural content is in emulsifiers, fragrances and anti-microbials [20].

Currently, there is an increasing drive to diversify the range of natural plant extracts available for the industry and to enhance the utilisation of natural ingredients from plants by the cosmetic industry. The demand for natural ingredients is increasing through growth of the natural cosmetics market, as well as through the increasing use of natural ingredients in 'conventional' cosmetics.

There are several trends dominating the market of natural ingredients:

- innovation-driven search for new functional ingredients, due to safety concerns by certain groups of consumers that prefer natural above synthetic chemical ingredients
- reinventing older natural ingredients, particularly from the group of traditionally used ingredients/plants, while understanding the basis of their functionality
- the move to organic production of natural ingredients
- the use of natural ingredients collected from the wild, which are certified organics
- and increasing use of exotic ingredients, obtained preferentially from plants traditionally used in the country of origin.
- an increasing use of botanical ingredients with anti-oxidant properties in (sun) skin care products, such as green tea and sea buckthorn and the use of natural UV filters
- increased interest in plants with therapeutic properties, such as those with radical-scavenging properties

Specific trends and market value of the product groups a priori selected, namely essential oils (fragrances, anti-microbials), bioactive phenolics (actives, antimicrobials), dyes and pigments (actives) and polysaccharides are discussed further.

## 3.2 Essential oils

Essential oils are obtained as complex mixtures containing tens of volatile chemical compounds by extraction from different parts of plants (e.g. flowers, leaves, fruits, roots, woody parts) and include flower oils (e.g. rose, geranium and jasmine absolute), rosin oils (e.g. frakincense and opoponax), fruit oils (e.g. citrus oils), leaf oils (e.g. patchouli or cajeput oil), herb oils (e.g. peppermint oil) and bark/wood oils (e.g. sandalwood and cedar wood oils). They are obtained by water distillation, expression (e.g. cold-press), solvent extraction and enfleurage. The major producers of essential oils are Brazil, China, USA, Egypt, India, Mexico, Guatemala, Morocco and Indonesia. France, Italy, Spain, Portugal, Greece, Bulgaria, Hungary and Romania are producing essential oils in Europe. About 65% of world production of essential oils comes from

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developing countries. The major consumers are the USA (40%), Western Europe (30%) and Japan (7%). About 3000 types of raw materials and extracts are known, of which about 300 are of commercial importance. Some examples are rose, orange, eucalyptus, lavender, geranium, chamomile, peppermint, vetiver, bergamot, patchouli, jasmine, Ylang Ylang oils.
Essential oils are used as ingredients in cosmetics & toiletries, fine fragrances, soaps and detergents, household products and other products such as pesticides and aroma therapy. Application[3] of essential oils is due to their intrinsic properties and functionality:

- Co-preservatives: many essential oils have antibacterial activity and are added as supportive agents to synthetic preservatives.
- Fragrance: perfumery is the main use of essential oils in cosmetics although synthetic fragrances are more stable and have better longevity. Aroma chemicals such as α-amyl-cinnamaldehyde, p-anisaldehyde, benzyl acetate, benzyl benzoate, and coumarin are also used in cosmetics and toiletries.
- Hair care: as conditioning, anti-dandruff & permanent waving agents.
- Skin care: topical active ingredients for any skin care product since they can penetrate the skin and bind the membranes of skin cells, having sustained effects in the skin.

The global market for fragrance ingredients was valued at 12.3 billion US dollars in 2013 and is expected to reach 17.1 billion US dollars by 2019 at a CAGR of 5.6% from 2014 [21]. In 2013, the market was dominated by Europe, followed by North America; Latin America is estimated to be the fastest grower with Brazil leading the trend, due mainly to the supply of locally sourced raw materials for natural products.

Soaps & detergents are estimated to account for the largest share (e.g. 32%) of the total fragrance ingredients market; followed by the cosmetics & toiletries segment (27%) and fine fragrances (18%) (Figure 4). Skin and hair care products are driving the growth of the market. Despite the lower share of the market (< 6%), aromatherapy, which is using essential oils for their therapeutic effects, is an important niche market particularly for small essential oil producers. Strong growth (13%) of the demand for aromatherapy essential oils was reported in the US retail in 2013, representing about 30% of the total growth of organic sector [22].

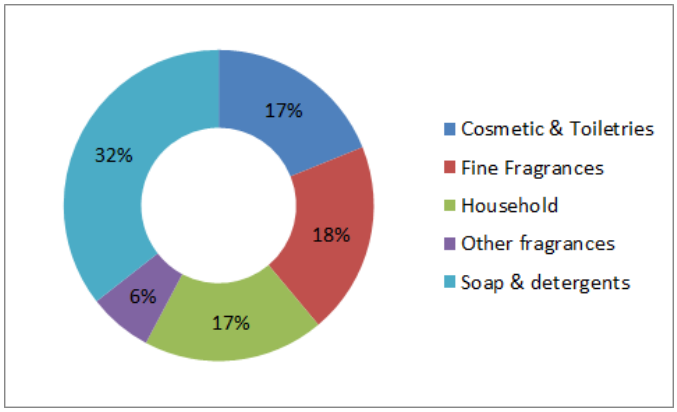

Figure 4. Market share of different segments using essential oils

As in the case of natural cosmetics in general, the main driver of the essential oils market growth is the change in the consumer preferences, together with the increase in demand for natural

[3] *Besides cosmetics, essential oils are used to give flavour to beverages and desserts, as solvent (e.g. citrus oil) and in pharmaceuticals.*

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fragrances, the fast growing demand from the developing nations, and technological advancements. However, high costs for R&D and compliance with quality and regulatory standards are limiting the growth of the market.
Some important trends were observed in the past years:

- Still increasing popularity for fruit oils (e.g. citrus; orange, bergamot, lemon, lime)
- Flower extracts (e.g. rose oil, jasmine oil, neroli) remain important;
- Essential oils from exotic plants are gaining popularity (e.g. orchid, used by French premium brands in exclusive products)
- Increasing interest of the cosmetic industry in many different, often very specific, essential oils, many of them of tropical origin.
- Many fragrance companies are establishing farming partnerships for ethical plant growth and supply of ingredients.

Givaudan SA (Switzerland) is the global leader of the fragrance market, followed by Firmenich International SA (Switzerland), International Flavors & Fragrances Inc. (U.S.), Symrise (Germany), Takasago (Japan), Wild Flavor (now part of ADM, US), Frutarom (Israel), Mane SA (Germany) and BASF SE (Germany), among others.

### 3.3 Bioactive cosmetic ingredients. Flavonoids and other phenolic compounds

Bioactive cosmetic ingredients are specific organic components found in plants that have bioactive properties and are believed to promote health benefits. They are known as phytonutrients and have attracted much interest from the food, feed, pharmaceutical and cosmetic industry due to their potential health benefits. Vegetables, legumes, nuts, grains, fruits, and teas, are rich sources of phytonutrients. Cosmetic products containing phytonutrients are known as cosmeceuticals. Based on their chemical structure and reactivity, phytonutrients are classified as:

Table 2. Phytonutrients and their functionality

| **Phytosterols** | **Bioactivity** | |
|---|---|---|
| Carotenoids (beta-carotene, lutein, lycopene, astaxanthin) | Soothing | Free radical scavenging |
| | Antioxidant | Moisturizing |
| Flavonoids | Anti-inflammatory | Hydration |
| Phenolic compounds | Antibacterial | Antimicrobial |
| Vitamin E | Antiaging | Lubricant |
| Others (betalains, alkaloids, monoterpenes, anthocyanins, and lignans) | Skin conditioning | UV-absorbers |

The global phytonutrients market, in terms of value, is expected to reach 4.63 billion USD in 2020, at a CAGR of 7.2% from 2015 to 2020, while the cosmeceuticals market is increasing from 37.9 US dollars in 2014 to 57.3 US dollars in 2019, at a CAGR of 8.62%. The market will grow in the next five years in almost all parts of the world, especially in European and North American

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countries. The growth of the market is determined by the health benefits and increasing end-use applications.
The high rate of adoption of phytonutrients by manufacturers drives the European market.
The phytonutrients industry has many players, (small, medium, and large); however the industry is dominated by a few. Raisio Plc. (Finland), FMC Corporation (U.S.), DSM N.V. (The Netherlands), Chr. Hansen A/S (Denmark) and BASF SE (Germany) collectively account for around ~35% of the total phytonutrients market. Pharmachem Laboratories, Inc. (U.S.), Archer Daniels Midland Co. (U.S.), Cargill Inc. (U.S.), Allied Biotech Corporation (U.S.), Arboris, LLC (U.S.), Dohler Group (Germany), Carotech Berhad (Malaysia), and D.D. Williamson & Co. (U.S.) also have a strong presence in the market.
The majority of cosmeceuticals has targeted skin care, with special emphasis on the subcategory of sun care and anti-aging products. The next biggest category is hair care at 15%, mainly focusing on sun protection and hair loss.
Key players present in the global natural antioxidants market include DuPont-Danisco, DSM, Ashland, Archer Daniels Midland, Tianjin Jianfeng Natural Products Co. Ltd (JF Naturals), Prinova, Indena S.P.A, AkzoNobel, Naturex and Ajinomoto OmniChem Natural Specialties.

Rapidly growing areas within the natural cosmeceutical category are:
- botanical ingredients with anti-oxidant properties in (sun) skin care products, such as green tea and sea buckthorn and the use of natural UV filters
- the need to substantiate the sun protection factors claims on products, so any natural ingredients used need to comply with the legal requirements
- expanding use of cosmeceuticals in other sectors, like firming/anti-cellulite products, skin whiteners, sun protection and hair care
- increase of use of traditional formulae/plants (e.g. Ayurveda), targeting ethnic populations
- increasing searching for plants with therapeutic properties.

### 3.4 Dyes and pigments

The market for colorants is specialised and extremely closed. Natural colorants used in cosmetics comprise inorganic pigments (e.g. azurite, iron oxide, titanium dioxide. etc.) and plant extracts, including food colorants (e.g. annatto, lycopene, curcumin, chlorophyll, anthocyanines, flavonoids, etc.), which can be applied without any regulation in cosmetics[4], and non-food dyes, like extracts from henna, madder[5], marigold and woad (indigo), that are mainly applied as hair dyes. From the 153 compounds included on the EU-positive list of dyes and pigments for cosmetic applications [23], approximately 8% are plant extracts, 20% are inorganic pigments and 72% are synthetic dyes and pigments. Natural colorants from plants belong to different chemical classes (e.g. carotenoids, polyphenols, alkaloids and quinones); due to their chemical reactivity,

[4] *Purity and constant quality are required*
[5] *Red dye from madder roots is industrially produced in the Netherlands by Rubia Natural Colours (rubia-nc.com) for cosmetics and other technical applications (textile, paper, etc.).*

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carotenoids and polyphenols have also antioxidant and antimicrobial properties, and have applications not only as dyes but as phytonutrients as well.
Global market for colour cosmetics is growing at a CAGR of 4% from 2014 to 2019, and is estimated to be about 47 billion US dollars by 2019 [24]. The global market for established natural colours is growing faster than the total colour market, but this trend is due to their use in foods, the percentage used in cosmetics being limited.
Consumer's desire to use natural, instead of chemical colorants is the driver of this market as well. This drives research to improve stability of natural plant-based colorants, which, due to their chemical structure, are instable to light, temperature and pH. Nanotechnology & encapsulation technology contributes significantly to increasing dyes stability and provide the solution to this problem. Although botanical dyes are more expensive than synthetic colorants (e.g. the cost of natural colours is two to ten time higher than of synthetic colorants [25]), the improvement in price-performance ratio has contributed to the increased use of natural colorants.
In general the market for existing natural colorants is increasing in the EU and creates opportunities for the new developments. However, limited opportunities exist for new colours that are not included on the EU-positive list, even though there is industry interest in stable natural colours.

### 3.5 Polysaccharides

Polysaccharides are much utilized in cosmetics for their ability to form hydrocolloids and the ability to function as film formers, gelling agents, thickener, conditioner and emulsifiers. A wide range of polysaccharides of botanical (starch, cellulose, pectin, guar gum), algal (e.g. alginate), animal (e.g. chitosan, hyaluronic acid) and microbial origin (e.g. hyaluronic acid, xanthan, dextran) are currently used for their physico-chemical and bioactive properties. Most used botanical polysaccharides are starch, guar gum and cellulose and their functional derivatives obtained by chemical modification.
There is a strong trend now to search for and utilize cosmetic active polysaccharides that have the ability to mobilize the water to the contacted skin, giving a hydrating benefit.
This creates the opportunity for the development of new polysaccharides with desired functionality / bioactivity for skin-hydrating cosmetics.

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# 4 New business for horticulture in relation to natural ingredients for cosmetics

## 4.1 Opportunities and threats.

Many of the specific sensory notes (e.g. fragrance and colour), functional attributes and bioactive properties of cosmetic products are/can be imparted by active ingredients from plants and plant extracts. The steady trend towards "natural" and "all- natural" cosmetics using plant ingredients in the formulation, the emerging tendency at cosmetic companies to develop natural cosmetics not only for the luxury sector, but also for the middle sector, the increasing demand for bioactive cosmetics products will lead potentially to an even higher demand of plant active ingredients. This opens new opportunities for the plant growers and the processing industry, can get enrolled into development of natural ingredients, both new compounds and established molecules. Table 3 summarizes the opportunities as well as the threats that we identified.

Table 3. Opportunities and threats for natural ingredients

| **Opportunities** |
|---|
| • Need for higher supply of natural ingredients to meet the industry request due to growth of the market<br>• Need for new functional ingredients with therapeutic properties<br>• Shift from "natural" to "organic" could bring new business to plant growers; certified organic becomes an opportunity<br>• New chances for innovation and technological development<br>• More opportunities for the plant growers to deliver directly raw materials to the industry<br>• Interest in exotic ingredients and functional ingredients bring opportunities for new sources and new ingredients |
| **Threats** |
| • Increasing competition and potential many new players (SMEs) on the market producing similar type of ingredients[6]; market saturation<br>• Long time line for product and technology development and market introduction<br>• High competition in the still niche market for natural- and organic- ingredients<br>• Competition from the biotech and synthetic ingredients<br>• Competition with generally lower priced, higher supply and more consistent chemical substituents, which take a higher share of the market<br>• Product certification (if needed): time consuming procedure and high associated costs |

The opportunities are major and address the whole value chain for natural ingredients, from crop selection and cultivation to processing and end application. Direct business with plant processors to deliver the plant material or by alliances with plant processors, cosmetic industry, marketers

[6] *In the last few years, new commercial plant extracts have been introduced in the market, like grape skin or grape seed extracts, anthocyanin colorants, biomass from grape cell suspension for application in skin care cosmetic products.*

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and R&D groups to develop either new/better, new and innovative ingredients and technologies and novel & performant cosmetics.
There are also threats, like the high competition that can occur if market diversifies and many competitors will start working in the same direction, as well as competition with the producers of synthetic ingredients, that have a lower price, higher stability and are available at higher amounts.

### 4.2 Potential topics for business development for horticulture

To identify options for valorisation of different streams from horticulture for the production of active ingredients for cosmetic products, we browsed the following steps:

a) Selection of the categories of ingredients that fit best the needs of the cosmetic industry.
To answer this question, we have analysed critically the market trends for cosmetics and the trends and opportunities for natural ingredients that were discussed in the previous chapters. This analysis showed the continuous interest of the cosmetic sector in natural ingredients and bioactive natural ingredients particularly for applications in the skin-care, body-care and perfumery segments. The same conclusion could be perceived from the description of the key innovations for cosmetic industry[7] in the 21st century presented by Cosmetics Europe [26].
In the selection, we have considered as well the new trends for rediscovering the active principles of traditional edible & medical plants next to exotic plants. On the pyramid of "trends in the natural ingredients market" (Annex 3), they belong to the "natural ingredients" – the most established class of natural cosmetic ingredients, "organic" and "exotic" classes.
The following categories have been selected to look primarily at: essential oils (fragrances, anti-microbials) and phenolic compounds (bioactives, antioxidant, antimicrobials) for application in perfumery, toiletries and skin-care products. From the phenolic group of compounds, we have focused on flavonoids, due to their exceptional bioactive properties, and biocompatibility. We did not search for phenolic acids with UV-absorbing properties, due to concerns regarding their efficiency and potential secondary harmful effects [27]. We have also addressed the group of active polysaccharides for skin hydration. Regarding natural colours, anthocyanins, the coloured constituents of petal of flowers, were *a priori* excluded due to current activities in this area at the client, while lycopene is found in much higher abundance in fruits and vegetables (e.g. watermelon, tomato, carrot).

b) Selection of plants based on composition and potential application,

Further, we have analysed the answers to the following questions and we have selected the cases with the most positive hits.

Below, the questions addressed:

[7] *The key innovation and milestones for the cosmetic industry for each market segment as presented by Cosmetics Europe – the Personal Care Association, on the webpage of the organization, are given in Appendix 2*

| Plant side | Product side / ingredient side |
|---|---|
| What is the available stream of the plant | Is the market segment growing? |
| Plant composition: Compound/ Content | Is the ingredient segment growing? |
| What is the bioactivity of the whole plant? | Does a market exist for the ingredient? |
| Can we find the desired activity? | What is the market price of the ingredient? |
| Is it easy to extract? | |

Some questions were difficult to be answered (particularly the market demand per compound), since there were no data available neither in accessible databases nor in the open literature and reports. Also, concentration of actives in plants is sometimes difficult to find, since databases contain composition data for plants that are already in use as ingredient producer and in most of the explorative research papers[8], the concentration of metabolites is given in relative units and don't allow the back calculation to weight/weight plant material.
Results of this analysis are summarised in Table 4.

### 4.3 Other aspects

In the process of defining possible routes for valorisation of plant materials for cosmetic ingredients, there are several aspects that must be answered a priori based on dedicated feasibility studies. The aspects listed below have also been considered in the analysis:

Commodity vs. specialty products

This aspect relates to the selection of the target product and market sector. Commodity products are traded at higher volume/lower value as for example mint oil (e.g. more 6500 tons per year with price ranging from 7 to 40 €/kg, depending on the plant source and country of origin), or citrus oil (> 100000 tons per year/2 to 4 €/kg), in the essential oil market. Optimising production process could minimise costs and enhance revenues.
Specialty compounds are usually low volume/high value products (e.g. Bulgarian rose oil, 5750 $/kg on the USA market in 2014[9]) with a quality that makes them unique (e.g. special aroma or bioactivity, exotic plant, grown in the wild, difficult to extract, etc.). New products require certification and marketing must demonstrate the uniqueness of the products.

Unique active component vs. whole extract

In the past years, it is more and more recognized that the active properties of plant extracts, which are usually complex mixtures of many components, are not due to the activity of one single component, but it is the results of the synergistic effects between the components in the mixture. This has been observed in the fragrance industry, but also in the use of bioactive

[8] *About 180 papers have been reviewed to find the necessary information; some are listed in the references. Dr. Duke's ethnobotanical and phytochemical database was also consulted.*
[9] *According to Georgiev, Y., personal communication at the 4th Polysaccharide EPNOE conference, 2015, Warsaw*

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extracts. Usually, when the active components are about 70 - 80% of the mixture, the whole oil is used. However, there are strict quality conditions for the use of mixtures in cosmetic products, demanding a constant quality, constant composition, and high purity, zero levels of pesticides and of toxins.
There are however situations when the end user requires the purified fraction for its application, as for example when complex aroma profiles are created by blending of various natural aroma chemicals.

Dedicated plants vs. valorisation of waste; Integrated processes
The extraction of active components for application in cosmetics is usually applied to dedicated cultivated plants grown under certified conditions and to wild plants collected in their natural areal. The use of biomass waste streams for this application faces some difficulties, given the great diversity in plant material with non-constant composition and the high variation in the chemical composition and level of active components. The use of biomass waste streams for extraction of cosmetic ingredients might require the selective collection of the waste. Also, a techno-economical evaluation of different processing strategies must be carried to identify the most suited solution to be adopted (a) dedicated extraction of the active component followed by composting of the residual biomass, or (b) and "integrated biorefinery" concept, including the extraction of target compound and the valorisation of other components in the residual biomass.

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Table 4. Major flower plants grown in NL and their bioactivity

| Plant | | Ingredient | | |
|---|---|---|---|---|
| Plant | Cultivated surface (ha)/green material[a] (ton), [28-30] | Constituents | (Bio)activity / price | Market segment / trends |
| Chrysanthemum* | 510 / 10000 | Volatiles: monoterpenes, limonene, pinene, farnesene, germacrene, etc. / flowers, leaves, stems<br>Flavonoids (acacetin, apigenin, luteolin, quercetin + glycosylated)* /(flowers, leaves, stems<br>Polysaccharides: pectins, water soluble oligosaccharides, fibres / stems, roots | Fragrances / 1-100 $/kg<br><br>Antioxidant, antimicrobial, antiviral, anti-inflammatory, anti-tumoral / > 100€/kg<br>Hydration, antioxidant / 10-20 €/kg | Perfumery, toiletries, hygiene / growing<br><br>Skin-care / increasing<br>Pharmaceutics<br>Skin care / increasing<br>Other technical applications |
| Rose[b] | 460 / 8700 | Tannins / leaves, roots<br>Essential oils | Anti-oxidant, antimicrobial<br>Antimicrobial | Skin care |
| Orchid* | 260 / 3700 | Glucomannans<br>Phytochemicals | Skin hydration / 10-100 $/kg<br>Skin protection, depigmentation | Skin care products/ increasing |
| Lily | 201 / 3400 | Flavonoids (quercetin, kaempferol, and their glucosides) / flowers [31]<br>Saponins (≈ 60 mg/g dw)/ bulb, stems, leaf, bud, flowers [30, 32]<br>Volatiles: terpenes, (e.g. β-myrcene, β-ocimene, linalool), 2-ethyl-1-hexanol | Antioxidant, antimicrobial, anti-inflammatory /> 100 €/kg<br>Surfactant, antitumor, antiviral, antidiabetic / 10-20 /kg<br>Fragrances / 10-50 $/kg | Skin-care (anti-ageing, hair-care) / growing<br>Pharmaceutical<br><br>Perfumery, toiletries |
| Fresia | 103 / 2000 | Volatiles: linalool, geraniol, terpineol, ionone / flowers | No market data about freesia essential oil (extract) found;<br>The volatiles named have antimicrobial properties, and could find application in perfumed hygiene products, soaps, shampoos, etc. | |

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| | | | | |
|---|---|---|---|---|
| Hyacinth* | 1200 | Volatiles: terpenoids, (e.g. p-ocimene, a-farnesene), benzyl acetate, indole, oct-1-en-3-ol, phenylacetaldehyde / flowers | Fragrances /≈ 5000 €/kg | Perfumery (high market segment) |
| Geranium/ pelargonium* | $310*10^6$ plants/year | Volatiles: α-pinene, myrcene, limonene, linalool, geranyl acetate, citronellol, geraniol / flowers, leaves, stems<br>Polyphenols and anthocyanins / roots<br>Polysaccharides | Fragrances / > 150€/kg<br><br>Antioxidant, anti-inflammatory | Perfumery, essential oils<br><br>Skin- care (anti-ageing) / growing |

*) details and references are given in subchapter 5; [a]) waste material in the green house and auction (from [30, 33]); [b]) Source of anthocyanins and carotenoids for natural colours, not considered in this study; [c]) tulips were not considered, since other studies have addressed it.

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# 5 Cases

Based on the study performed, four cases have been considered for further study. One case, related to hyacinth, refers to the selective extraction of a high value essential oil for fragrance and perfumery from flowers. Two cases deal with the extraction of essential oils and flavonoids from the aerial parts (flowers, leaves and stems) from geranium and chrysanthemum; both cases are suited for a biorefinery approach, permitting as well the isolation of polysaccharides from the stems and roots (in case of chrysanthemum). The fourth case is more exploratory, aiming at the mapping of the value compounds in orchids, and the identification of valorisation routes.

## 5.1 Geranium : extraction of essential oils and polyphenols

Value of the plant

Geranium plants, belonging to the genus *Pelargonium,* are decorative plants, much utilised for the production of essential oil. *Pelargonium spp*. leaves yield an essential oil after distillation. The world production of geranium oil is about 350-400 tones. The oil is produced in the Mediterranean region (Egypt, Algeria, France, Spain, Reunion) from *Pelargonium grave lens,* and *P. odoratissimum*, the rose geranium, *US (*Florida, Texas and California), Russia, India and China. Production in currently dominated by Egypt and China, that account together for more than 80% of the total world production.

Feasibility data geranium essential oil:

Reported production of oil varies between 60-70 kg/ha (Egypt) and 75-105 kg/ha (China).
Price vary between 150 USD/kg (Egypt) to 310 USD/kg (Madagascar, France) [22]
Existing high market for the oil

Properties of the oil:

- The main components of this oil include alpha-pinene, myrcene, limonene, menthone, linalool, geranyl acetate, citronellol, geraniol and geranyl butyrate [34, 35]. The oil has a rose-like odor, and it was produced historically to replace the more expensive rose oil.
- Geranium oil is nontoxic, nonirritant and generally non-sensitizing; many bioactive and therapeutic properties have been associated to the oil, including antidepressant, antiseptic and wound-healing

Applications of the oil:

- Perfumery oil - important floral component in blends, as an adulterant or a substitute to Otto of Roses (*Rosa damascena*);
- Essential oil (whole part of aerial plant: flowers, leaves, stems):
    - Aromatherapy: the 2nd oil used as volume in aromatherapy, after lavender oil.
    - Has strong antibacterial and antimicrobial properties: utilised as ingredient in skin-care products
    - Major component in the soap industry
    - Insect repellent
    - Health protection (anti-acne, reduce inflammation)

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Other value components of geranium:
Recent studies showed that geranium roots (*Geranium sanguineum*) contain high amount of polyphenols (gallotannin, catechins), and flavonoids (quercetin, apigenin, morin, myricetin), phenolic acids (caffeic, ellagic, quinic, chlorogenic) with very powerful antioxidant and antiviral properties. Polyphenols and flavonoids have been extracted with a high yield (14%) [36], and this offers good possibilities for the isolation of a rich phenolic extract for application in cosmetic products.

Plant availability
Geranium is not a major plant grown in the Netherlands; however, according to the CBS Statistics [28], about $310*10^6$ plants are sold at the auction.

Route for valorisation
Whole plant extraction, to extract both high value and commodity ingredients.

| Plant material | Extraction | Application |
|---|---|---|
| Whole aerial plant (flowers, leaves, stalks) | Essential oil | Perfumery, toiletries, skin care products<br>Aromatherapy |
| | Water soluble polysaccharides<br>Fibre | Skin hydration*<br><br>Adhesives |
| Aerial roots | Polyphenols<br>Flavonoids | Antioxidant, Antimicrobials<br>Skin care products, toiletries |

*) characterisation and application studies needed

## 5.2 Hyacinth: essential oil from flowers

The value of hyacinth
Hyacinth is an important ornamental plant, with flowers with intense and vital colours and a pleasant floral scent. The colour of the flowers is given by **anthocyanins**[10], and a number of coumaroyl- and malonyl- acylated delphinidin- and pelargonidin-glucosides [37, 38] have been identified in extracts of the red and blue hyacinth flowers of *Hyacinthus orientalis*. Recently, anthocyanins isolated from *H. orientalis* have been shown to have bioactive properties, like antioxidant, antimicrobial, anti-inflammatory. The **hyacinth flower scent** is given by a complex mixture of volatiles; more than 70 compounds have been identified by GC and GC-MS analysis in the headspace of the flowers, including terpenoids, like as (E)-p-ocimene and (E,E)-a-farnesene, and benzyl acetate as principal constituents and indole, oct-1-en-3-ol and phenylacetaldehyde as sensorily important substances [39].

[10] *Extraction of anthocyanins for isolation of the dyes is another potential route for valorisation the hyacinth materials; the anthocyanins have antioxidative and antimicrobial properties, and could find application in cosmetics, food. Anthocyanins are not addressed in this study.*

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The essential oil extracted from the flowers and leaves finds many applications in cosmetics and toiletries and in aroma therapy for its relaxing and calming effects. The hyacinth absolute was extracted from *H. orientalis* in a two-step solvent extraction process: production of concrete by extraction of fresh flowers with petroleum ether (yield ≈ 0.13-0.22%), and extraction of absolute from the waxy concrete (yield ≈ 10-14%) [40], which correspond to a total calculated yield of 0.013-0.038%. A comparable yield (0.014%) was reported in a feasibility study by [41] using solvent extraction of flowers. The hyacinth absolute is a red-brownish viscous liquid with a strong floral, green-fatty odour, with earthy and spicy notes. Benzene derivatives like benzyl alcohol, benzyl acetate, p-phenylethyl acetate, cinnamyl alcohol, 1,2,4-trimethoxybenzene and benzyl benzoate were found in higher amounts in commercial extracts and absolute; ocimenol, cinnamyl alcohol and ethyl-2-methoxybenzoate are major contributors to the hyacinth scent. Cinnamyl alcohol is usually used in the perfume industry to create a sweet, balsamic and hyacinth-like fragrance.
The genuine hyacinth absolute is scarce and sold at a high price (4600-5100 USD/kg); usually the hyacinth absolute is a reconstituted from synthetic and natural aromatic isolates.
Hyacinth absolute is used in top-class fragrances and perfumes (some examples: Hermes-Un jardin sur le Nil, Chanel No.19 and Balmain Vent Vert, Chamade pour homme, a Guerlain limited edition), to create a green accent in both feminine and masculine fragrances.
The **bulbs** of *H. orientalis* are rich in polyhydroxy alkaloids, which have strong enzyme *inhibitory* properties for bacterial and mammalian β-glucosidases [42]. The bulbs are also rich in glucomannan, a polysaccharide with potential application in cosmetics, and minerals.

Plant availability

Hyacinth is a major product of floriculture in the Netherlands[11]. Approximately 500 h of hyacinth are cultivated for the production of bulbs [41]. Flowers collected in the field could be used for the production of the hyacinth essential oil.

Potential route for valorisation

The classical methods used by now to extract the hyacinth oil, based on solvent extraction, had low yield; particularly, the yield of the second extraction step of the absolute was lower than in the case of other oils, like jasmine, for example, although the yield of the first extraction step was comparable.
I propose to explore, in a feasibility study, the $sCO_2$ extraction, which is very mild (condition absolute necessary for the hyacinth) and efficient, having also the advantage of no solvent waste. The utility and efficiency of $sCO_2$ for volatile extraction has been proven in many papers [34, 35].

### 5.3 Chrysanthemum : bioactive extracts and derived biomass streams

The value of the plant

Plants of the genus *Chrysanthemum,* belonging to the family of Asteraceae, have long been used in the traditional medicine due to their assigned biological effects. The genus *Chrysanthemum*

[11] *Traditionally, hyacinth absolute was extracted in Eastern Europe (Bulgaria), from flowers cultivated in the Netherlands.*

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contains approximately 200 species native to Europe and Asia, amongst which we mention *Chrysanthemum hortorum*, *Chrysanthemum morifolium*, *Chrysanthemum coronarium*, *Chrysanthemum indicum* and *Chrysanthemum cinerariifolium*. Antibacterial, antifungal, antioxidant, antiviral, insect repellent, insecticidal, anti-tumoral and anti-HIV1 effects have been reported for some *Chrysanthemum* species, and in the recent years several studies addressed the identification, quantification and characterisation of the active compounds in aqueous and alcoholic extracts from different parts of the plant (e.g. flowers, leaves, stems and roots)[43-48]. *C. cinerariifolium* and *C. coccineum* (now classified as *Tanacetum*) are widely used for the production of the potent natural insecticide containing pyrethrins extracted from the flowers/seeds of the plants, which is commercially applied. Pyrethrins are gradually replacing the synthetic organophosphate and organochloride pesticides. This valorisation route is outside the scope of this project and it will not be discussed further.

Many studies have showed the richness in bioactive compounds of chrysanthemums (Table 4). Flavonoids with antitumoral and antioxidant activity have been identified and isolated proving the biological activity as well as the possibility to fractionate the extracts and isolate pure compounds for pharmaceutical applications. The plant is also rich in volatile, aroma compounds that also have antioxidant and some antimicrobial properties.

The composition of the extracts very between the different varieties due to the intrinsic variation of the metabolites profile, and is influenced by the processing conditions.

The variability between members of the chrysanthemum genus is high and differences have been observed between the volatile profile that contain in different amounts terpene compounds such as alpha-pinene, eucalyptol, camphor, and borneol,, beta-caryophyllene and many others.

Table 4 Bioactive compounds of the Chrysanthemum plants

| Compounds | Species | Extraction / part of plant / yield | Bioactivity | Ref. |
|---|---|---|---|---|
| Acacetin, apigenin, luteolin, quercetin[12] | *C. morifolium* | Methanol / flowers /12% | Antimutagenic<br>Antioxidant | [43] |
| Acacetin, apigenin, luteolin, quercetin + glycosylated | *C. morifolium* Ramat | Methanol, flowers | Antimutagenic<br>Antioxidant | [45] |
| Acacetin, apigenin, luteolin, quercetin | *C. indicum Linnen* | Flowers, sCO2 | Anti-inflammatory | [46] |
| Essential oils | *C. indicum* | | Aroma, antimicrobial | |
| Essential oils | *C. trifurcatum* | Leaves, stems, roots | Aroma antimicrobial | [49] |

The plant contains as well constitutive components like pectins, fibres and inulin, in the roots.

[12] *All independent compounds were separated in good yield and characterised; antitumoral activity was showed for acacetin*

Availability of plant material

In Netherlands, chrysanthemum represents one of the major cultivated flowers in greenhouses, covering a surface of about 510 ha [30]. Highest production of chrysanthemums is localised in the counties Gelderland/Utrecht and Zuid-Holland greenhouse district [30]. A large amount of green waste material is produced both at the production sites and the flower auction sites, that was estimated at approximately 6800 tons/year [30]. Valorisation of the green waste materials consisting of the aerial parts (flowers and leaves) and the roots of the plants to produce ingredients for cosmetic application and bioactive compounds for pharma and medical application represents an opportunity for the sector.

Potential for valorisation

The potential for valorisation is high. Some prices[13] of chrysanthemum extracts and commercial products similar with those that could be extracted from chrysanthemum are listed.

| **Product** | **Market price** |
|---|---|
| Essential oil (*C. morifolium*) | 1-100 US Dollars/kg |
| Pure essential oil flower extract | 1600 - 1700 USD/kg |
| Chrysanthemum extract | 1 – 20 USD/kg |
| Medical grade | < 100 €/kg |
| Luteolin – natural extract | 200 – 400 €/kg |
| Quercetin | Price depends heavily on the plant source and quality; Ranges from 120-150 USD/kg up to 990 USD/kg |
| Acacetin (cosmetic grade) | 100 - 200 USD/kg. |

We propose a valorisation route to produce both the high value bioactive fractions/compounds for application in skin-care cosmetics, the essential oil as well as the commodity chemicals for technical applications (e.g. pectin, fibre) and in food (inulin).

| **Material** | **Selective fractionation** | **Application** |
|---|---|---|
| Whole aerial part | Essential oil | Fragrance, toiletries, |
| | Flavonoids (acacetin*, luteolin, quercetin) | Skin-care products (skin protection) |
| | Pectin | Skin care products (hydrating, skin protection)<br>binder |
| | Fibre | technical applications |
| Root | Inulin | food |

*) pure acacetin, with antitumor and anti-viral properties, can be isolated by fractionation from the phenolic mixture, for utilisation as a drug (pharmaceutical industry).

[13] *Prices are from AliBaba, if not specified*

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## 5.4 Orchid extracts

Value of the plant

Orchids have been traditionally used in the Chinese medicine due to their exceptional properties. Different parts of the plants have been used, the bulb, pseudobulb, the rhizome and the root. Medicinal orchids were reported to contain alkaloids. Recent work reported the isolation of anthocyanins, stilbenoids, tritepenoids and phytochemicals like orchinol, hircinol, cypripedin [50]. Polysaccharides from *Cyrtopodium cardiochilum* [51] contain a low molecular weight glucomannan polysaccharide with exceptional biologically active properties with immunomodulatory properties. A glucomannan with emulsion stabilising properties has been isolated and characterised form the roots of salep, an orchid growing wild in Turkey [52]. And a plant extract including orchid extracts has been shown to have skin-whitening properties when tested on Japanese female skin with melasma and lentigo senilis [53]. *Dendrobium* orchids, grown in the Netherlands, have also been shown to contain pharmacologically-active compounds (e.g. alkaloids, flavones, phenolic acids) and polysaccharides with immunomodulating properties [50]. It seems that there is a huge potential in identifying bioactive compounds in orchids for therapeutic applications in cosmetics related to skin disorders. This case is a proposal for an exploratory feasibility study to map the bioactive profile of selected orchids.

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## Appendix 1. Certification and regulation of natural and organic cosmetics.

In the past decade, the market for natural and organic personal care products has rapidly grown worldwide and several certification programs have been established by the cosmetic industry. Certification addresses the use of term "organic" that can be used only if the product has been certified by an authorized certification programs. The use of the term "natural" is not regulated. There are several certification programs for organic and natural cosmetics available in Australia (Australia Organic), Canada (Certech), Europe (EcoCert, BDIH, Soil Association), USA (NSF/ANSI305, USDA/NOP and OASIS) , and international and regional organisation such as Cosmos and NaTru, all with different criteria for certification.

For example, USDA has adopted the four organic levels of certification:

- 100% certified organic: products must contain 100% organic ingredients;
- organic: product must contain at least 95 percent organically produced ingredients (excluding water and salt);
- made with more than 70% organic ingredients: products contain at least 70 percent organic ingredients; up to three of the organic ingredients or "food" groups can be shown on the label
- made with less than 70% organic ingredients: products cannot use the term "organic" but specific ingredients are certified as organic may be identified.

The certification programs and the standards established in Europe are listed in Table 2.

Table 2. Certification programs for natural and organic cosmetics

| Certification program | Standards |
|---|---|
| EcoCert (France) | - standards for natural and organic cosmetics<br>- defines the practice of the respect of the environment throughout the production process<br>Natural cosmetic standard:<br>- at least 50% of the total plant ingredients must be certified organic<br>- at least 5% of the total ingredients must be certified organic<br>Natural and organic cosmetic standard:<br>- at least 95% of the total plant ingredients must be certified organic<br>- at least 10% of the total ingredients must be certified organic |
| BDIH (Germany) | guidelines for certified natural cosmetics<br>natural ingredients must be obtained from controlled biological cultivation or controlled biological wild collection |
| Soil Association (UK) | standards for organic beauty products are based on food standards |

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At EU level, the production, the use, the market access and the international trade of cosmetic products is regulated (EC regulation Nr. 1223/2009 and Cosmetic directive 76/768/EEC), aiming to ensure a high level of consumer safety. The annexes of the EC regulation list the ingredients that are prohibited for use in cosmetics (Annex 1, > 1300 compounds), the restricted ingredients (Annex 2 and 3) and the allowed colorants (Annex IV, 157 compounds), preservatives (Annex V, 57compounds) and UV filters (Annex VI, 28 compounds). All natural dyes and pigments are allowed for use in cosmetic, next to inorganic oxides and synthetic dyes. Purity criteria for dyes and pigments are regulated in Commission directive 95/45.

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## Appendix 2. Key innovations and milestones per market segment, as given in [26]

| Segment | Key innovation end 20th century | Milestones 21st century |
|---|---|---|
| Skin care | Alpha-hydroxyacids reverse photoaging damage, stimulates skin regeneration; vitamins, ceramides, fatty acids, fatty acids, retinoic acid and esters | **Organic and natural products** gain popularity<br>Stem cell research help address skin at molecular level, focusing on epidermal DNA protection |
| Sun care | Sunscreen potential levels are enhanced by use of UV filters and nano-absorbers | Sunscreen begin to contain a fixed ratio of UVB and UVA filters<br>Products with light and transparent textures |
| Hair care | Ammonia free tone colorants are introduced with tones similar to natural hair color | Particles containing emulsions improve the delivery of active ingredients and enable the use of **natural and organic substances as ingredients**<br>Innovative anti-aging technology to repair ageing hair structures |
| Body-care | Technology developed using corn starch microspheres to release fragrance in contact with sweat; body washes deliver moisture to dry skin | Cosmetic patches as delivery systems of **organic and natural products**<br>Antiperspirants with large inorganic polymers |
| Decorative cosmetics | Electrostatic sprays, photochromic pigments to create light reflecting makeup, silicon microfibers | **Natural**, mineral-based cosmetics; offer full but light coverage<br>Foundation contain **skin cleaning** benefits |
| Perfumery | Nobel-prize winning discovery that a big part of our genetic code is devoted to sense smell; Fragrances smell differently depending on a person genetic "body odour profile". | Major improvements in analytical methods allow better knowledge of **natural ingredients** |

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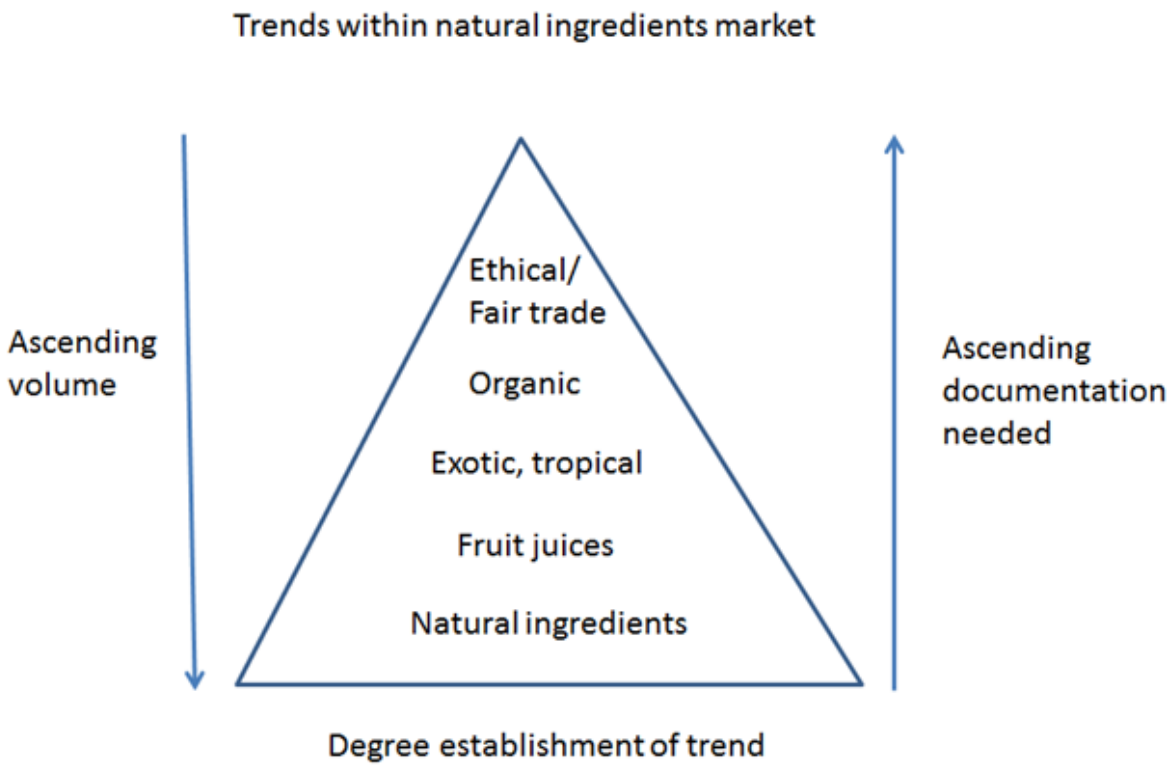
## Appendix 3. Trends within natural ingredients market

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