Nuts and nut-like fruits

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Apple, nut and almond kernel – don't worry, Father Christmas isn't knocking, but it's about an insight into kernel-like compositions that play a role in food and skin care.

ruits and seeds enclosed in a wood-like shell include nuts, but also legumes such as peanuts, stone fruits such as pistachios, the small fruit seeds of rose hips and pome fruits such as apples.

Not every nut is really a nut in the strict botanical sense. However, the subject of kernels is less about exact biological family trees than about the contents and commonalities of prominent representatives. Their compositions are decisive for the purposes for which they can be used in cosmetics.

The proportions of individual components, such as fatty acids, can vary, as they depend on the provenance (origin) of the respective oils resulting from the kernels, their batch, the time of analysis, the preparation (extraction and refining methods, conditions during pressing)¹ and, last but not least, the measuring laboratory. The literature sources² are often reticent with regard to this information, so that a certain range must be conceded to the data. In case of doubt, the manufacturer's certificate of analysis should be consulted.

Walnut – rich in serotonin

Even the first representative of the nuts, the walnut, stands out with a special feature. It is the high serotonin content of about 280 mg/kg, which surpasses all fruits and vegetables. Serotonin is a neurotransmitter whose deficiency is noticeable in depression and migraine, among other things. The fatty acid composition of the pressed fatty oil (INCI: Juglans Regia Seed Oil) is of interest for cosmetics and care

properties. Linoleic acid dominates with about 54 to 65 percent, along with α -linolenic acid (9 to 15 percent) and oleic acid (13 to 21 percent). The content of saturated fatty acids is six to eight percent palmitic acid and one to three percent stearic acid. Important: They are components of the skin barrier.

The fatty acids of the oils are present as triglycerides, i.e. as esters of glycerol. In the skin, the triglycerides are broken down by ester-splitting enzymes into the free fatty acids and glycerol. The latter is a component of the skin's Natural Moisturising Factor (NMF).

Extracts from the still green walnut shells contain juglone (5-hydroxy-1.4-naphthoquinone) and produce a brown complexion on the skin. Products of this kind have been associated with names such as Tyrolean nut oil for decades.

Peanut – oxidation stable

In general, nuts contain high levels of essential fatty acids, which explain, among other things, their liquid consistency up to low temperatures. An exception is the fatty oil of the peanut (INCI: Arachis Hypogaea Oil)³, which contains no omega-3 acid such as α -linolenic acid, less linoleic acid (omega-6⁴, 12 to 43 percent), but high proportions of oleic acid (35 to 69 percent) and saturated fatty acids (palmitic acid: 8 to 14 percent, stearic acid: 1 to 5 percent). It is therefore less susceptible to autoxidation (oxidation caused by atmospheric oxygen), which is noticeable by a rancid smell and taste. The solidification point is around freezing point. The cosmetic and pharmaceutical use of peanut oil has declined sharply in recent times. Instead, more other oxidation-stable mediumchain triglycerides are used, which come from palm oil production through refining or, for some time now, from coconut oil production.

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¹ Hans Lautenschläger, Ressourcen der Natur – Pflanzliche Öle im Rahmen der Hautpflege, Kosmetik International 2019 (4), 30-33.

² Sabine Krist: Lexikon der pflanzlichen Fette und Öle, Springer, 2013, ISBN 978-3-7091-1004-1;

Heike Käser: https://olionatura.de/oele-und-buttern;

Hans-Dieter Belitz, Werner Grosch, Peter Schieberle, Lehrbuch der Lebensmittelchemie, Springer, 2008, ISBN: 978-3-540-73201-3;

German Society for Fat Science e.V.: www.dgfett.de;

Wikipedia, keyword Pflanzenöle.

³ The peanut is a <u>closed</u> legume. This makes it a nut.

⁴ Omega-6 means that the first double bond, counting from the end of the molecule, is located at the 6th carbon atom. Analogously, other numbers apply.

Macadamia nut - nourishing

The macadamia nut is also rich in monounsaturated acids (about 80 percent) such as oleic acid (C_{18} -omega-9 fatty acid) and palmitoleic acid (C_{16} -omega-7 fatty acid). The proportions of essential fatty acids are marginal and those of saturated fatty acids relatively high at about 15 percent. Macadamia nut oil thus develops a good caring character, whereas the highly unsaturated oils like walnut oil are rather used in problem areas due to their substrate function for the skin's own 15lipoxygenase. The focus here is on an antiinflammatory effect, i.e. for example in perioral dermatitis, rosacea and sunburn.

Macadamia nut oil (INCI: Macadamia Ternifolia Seed Oil) caused a sensation at the end of the 1980s as the best skincare oil of the time. During this time, "edible" cosmetics also developed.

Brazil nut – high selenium content

The fatty acid spectrum of Brazil nut oil (INCI: Bertholletia Excelsa Seed Oil) is relatively balanced with up to 25 percent saturated acids, up to 45 percent oleic acid and 30 to 45 percent linoleic acid. However, another property of Brazil nuts stands out – it is the high selenium enrichment with about 2 mg/kg in the fruit flesh. Import restrictions exist for Brazil nuts after it was discovered that many suppliers were not able to control the often too high aflatoxin content. Aflatoxins are toxic metabolic products of moulds.

Cashew kernels – walnut-like

The nut-like cashew kernels belong botanically to the shell fruit. The fatty oil extracted from them (INCI: Anacardium Occidentale Seed Oil) has an oleic acid content of over 70 percent, about 12 percent saturated acids and only about 14 percent linoleic acid.

The high tryptophan content of 238 milligrams per 100 grams of the kernels is remarkable. In the human body, the amino acid is the precursor for serotonin (see walnut). Accordingly, similar effects are attributed to it.

Pecan, hazelnut, hemp

The pecan nut is a "real" nut and closely related to the walnut. However, the fatty acid spectrum of the oil (INCI: Carya Illinoensis Seed Oil) differs due to the high oleic acid content (57 percent). The values for linoleic acid (31 percent) and α -linolenic acid (approx. 1 percent) are correspondingly lower. The saturated fatty acids (10 percent) are similar to the walnut. An oil (INCI: Corylus Avellana Seed Oil) can also be pressed from the hazelnut. The oleic acid content is also high here at 66 to 83 percent, in addition to 8 to 25 percent linoleic acid and about 10 percent saturated acids.

Botanically genuine nuts are also supplied by hemp, which is hard to believe. The oil (INCI: Cannabis Sativa Seed Oil) of hemp nuts belongs to the drying oils and, in addition to oleic acid (about 15 percent), has high proportions of polyunsaturated, essential fatty acids, mainly linoleic acid (about 55 percent), α -linolenic acid (about 15 percent) and some percent γ -linolenic acid. Hemp oil does not contain any intoxicating tetrahydrocannabinol (THC), but considerable amounts (about 10 milligrams per kilogram) of its probable precursor cannabidiol (CBD), which is classified as skin-protective and antioxidant.⁵

Stone fruit

The **almonds**, which do not belong to the nuts but to the stone kernels of a stone fruit, produce oil (Prunus Amygdalus Dulcis Oil) that is listed in the pharmaceutical pharmacopoeias in the same way as peanut oil and contains between 64-82% oleic acid, 8-28% linoleic acid and 6-8% palmitic acid as well as 1-2% stearic acid. It is very suitable as a massage and body oil and can be found in almost every cosmetic sector where natural oils are used.

Botanically, the **coconut** is also a stone core in a drupe. Its oil, coconut oil (Cocos Nucifera Oil), contains a very high percentage of saturated fatty acids, but not only long-chain ones like palmitic acid (C_{16} , 7-10%) and stearic acid (C_{18} , 2-4%), but also a high percentage of medium-chain ones like C8: Caprylic, 5-10%; C₁₀: Capric, 5-8%; C₁₂: Lauric, 45-53%; C₁₄: Myristic acid, 17-21%. This also explains its melting point, which is 23-26°C, and the alternative name coconut fat. Of the unsaturated acids, oleic acid is represented by only 5-10% and linoleic acid by only 1-3%. By splitting the triglycerides and distilling the acids obtained, fractions are obtained which, in turn, esterified with glycerol, yield medium-chain triglycerides (INCI: caprylic/capric triglycerides) and are contained in many cosmetics as an inert (oxidation-stable) skin care oil. Lauric acid is processed into emulsifiers and surfactants by chemical conversion. Examples (INCI) are: Lauryl Alcohol, Sodium Lauryl Sulfate, Sodium Lauryl Ether Sulfate.

A similar spectrum of fatty acids and processing as coconut oil is offered by palm kernel oil alias palm kernel fat (Camellia Sinensis Seed Oil) from the kernels (stone

⁵ https://ec.europa.eu/growth/toolsdatabases/cosing

fruits) of **oil palms**, not to be confused with palm oil (INCI: Palm Oil), which is extracted from the fruit flesh. Palm kernel oil, palm oil and their processed products are declining in cosmetics because their progressive cultivation is increasingly interfering with nature.

Apricots (stone fruit) also have an oily stone kernel from which fatty oil (Prunus Armeniaca Kernel Oil) is extracted. In terms of skin care, it is described as rather light oil that is easily absorbed due to its high oleic acid content (65-70%). The linoleic acid content is about 23%, the saturated fatty acids 6.5%.

Unsaponifiables

In general, it can be stated that the long-chain saturated acids have a barrier caring effect, the essential acids of the omega-6 and omega-3 series have an anti-inflammatory effect and the triglycerides of the oleic acid are well absorbed. The ease of absorption has been exploited in particular in dermatological preparations by using free oleic acid as penetration enhancing additive for active pharmaceutical ingredients.

Other important components of the fatty oils are the plant sterols (phytosterols), to which cholesterol corresponds in the animal world. Together with saturated acids such as palmitic acid and the ceramides, cholesterol is one of the most important membrane components of the skin barrier and, if it is missing, can be replaced by phytosterols with their very similar structure in a functionally equivalent way. Phytosterols are part of the "unsaponifiables" of oils and fats, i.e. they remain unchanged during soap production, in the course of which the vegetable triglycerides are split ("saponification").

Outstanding in terms of phytosterol content is the shea nut, which, although originating from a tree, is classified as a berry. The shea butter (INCI: Butyrospermum Parkii Butter) obtained from its fruit contains up to 11% unsaponifiable matter and up to 50% triglycerides of saturated acids. The melting point (35-40°C) is therefore even higher than that of coconut oil in the skin temperature range. Shea butter is an ideal physiological skin care product and is increasingly used as a substitute for the nonbiodegradable mineral waxes, vaseline and paraffins. The advantage here is that shea butter with its strong skin lubrication only has a temporary occlusive effect, whereas paraffins & co. have a permanent occlusive effect and thus inhibit endogenous regeneration.

In this context, the oil of the **avocado** (Persea Gratissima Oil) should be mentioned comparatively, whose very good skin care effect also results from about 6% unsaponifiables and the high content of about 20% palmitic acid. In contrast to the oils described here, it is a pulp oil, like olive oil.

The hard-skinned berries also include the **argan fruit**, whose oil (Argania Spinosa Kernel Oil) has no special features, despite its high price. It has a relatively high proportion of saturated fatty acids, mainly palmitic acid, at about 20%, in addition to about 45% oleic acid and 34% linoleic acid. The phytosterol content is only between 1-2%.

The unsaponifiables of the fatty oils may also contain squalene. This is a pure unsaturated hydrocarbon that is also secreted by the sebaceous glands of the skin.

Accompanying substances in nuts and stone fruits

Nuts and nut-like fruits naturally contain many minerals in their fruit bodies, especially potassium, but also others such as magnesium, phosphorus, iron and trace elements. These substances, including the water-soluble vitamins such as thiamine (B_1) and niacin (B_3) , as well as proteins and carbohydrates, are only important for consumption because they do not pass into the cosmetically relevant fatty oils. Therefore, only the fat-soluble vitamins A and E are found in the oils. The amounts can vary greatly depending on how the oils are processed. Vitamin A or carotenoids in general are noticeable through a yellow colouration of the oils. Vitamin E (tocopherol) offers a certain protection as an antioxidant, especially to the sensitive polyunsaturated fatty acids or their triglycerides. However, this protection is limited when the oils are later used in skin care products, as the increasing proportion of unsaturated acids in the oils is to some extent a competitor as far as the reaction with radiation and oxygen radicals is concerned. The radical chain reactions that are possible as a result can lead to severe irritation, especially in the case of strong sun exposure.⁶ Therefore, the following applies to the processing and application of the oils:

- Use in moderate concentrations,
- together with other antioxidants if necessary.
- Simultaneous intensive care of the body's own NMF (Natural Moisturizing Factor), which effectively scavenges radicals with its amino acids.
- Use the care products in the evening and not during the day in the blazing sun.

⁶ Under these conditions, pure, highly unsaturated fatty oils can even self-ignite.

The more essential fatty acids they contain, the more suitable the oils are for skin care <u>after</u> sun erythema because, as mentioned at the beginning, they are a substrate for the 15-lipoxygenase. This enzyme oxidises the fatty acids in a controlled manner to form oxygenated metabolites that consistently have an anti-inflammatory effect.

Nutlets and their oils

Aggregate nut fruits are the small fruit bodies of the rosehip surrounded by shells. Their characteristic is that they contain highly unsaturated oil (Rosa Canina Seed Oil) with an omega-3 acid content of about 30% α-linolenic acid, almost 50% linoleic acid (omega-6) and 15% oleic acid (refined quality). This is nutritionally significant where the aim is to have the highest possible omega-3 content as a precursor for eicosapentaenoic acid (omega-3), which competes with arachidonic acid (omega-6). Eicosapentaenoic acid is a typical component of fish oil and the liver oils of haddock and cod. Both acids are metabolised in the liver to local hormone-like prostaglandins, thromboxanes and prostacyclins, among others.

The α-linolenic acid content of the oil of rosehip seeds is only surpassed by the oil of the hard-shelled seeds of the kiwi (INCI: Actinidia Chinensis Seed Oil) with 51%, which, however, is botanically classified as a berry. Linoleic acid only accounts for 17% and oleic acid for about 20%. Palmitic acid and stearic acid are present in about 10%. The composition is comparable to linseed oil (INCI: Linum Usitatissimum Seed Oil), which, however, by definition does not come from a nut. Both oils have a maximum anti-inflammatory potential and can even be used for minor burns, especially if they are still embedded in phosphatidylcholine-containing nanodispersions. The resulting aqueous lotions are absorbed very quickly and do not leave any unpleasantly oily skin surfaces. After touching a hot cooker top, for example, and immediately applying the dispersions, there are usually no burn blisters.

Strawberries are also included in the group of the nuts, also known as aggregate fruits, but they are not known to produce oil.

Oily and aqueous extracts

Nutritionally, nuts, seeds such as flax, sesame, wheat grain, bean (soy) or sunflower are more important in their entirety than the isolated oils, which are limited to fat-soluble components, especially with regard to the mentioned accompanying substances.

In skin care, the application of the whole fruit is practically impossible in the cases mentioned. A compromise is the simultaneous application of an oil and an aqueous-alcoholic extract. Examples are **grape seed oil** (INCI: Vitis Vinifera Seed Oil) and grape seed oil extract (INCI: Vitis Vinifera Seed Extract). Grape seeds, like nuts, have a wood-like shell. Botanically, grapes could be classified as berries, but they are panicles – so scientifically, it is a rather complicated matter.

The composition of refined grape seed oil is dominated by oleic acid (12-28%) and linoleic acid with 58-78%. Palmitic acid and stearic acid are 6-11% and 3-7% respectively. The aqueous-alcoholic extract of grape seeds or corresponding dry extracts are completely different. They consist largely of oligomeric proanthocyanidins (50%) with a flavone structure, which, like the majority of the extract, belong to the polyphenols (95%) and have a strong antioxidant effect. They are preferably used liposomal in anti-aging products. However, they are unsuitable as standard antioxidants for protecting products due to their sensitivity and high price.

Pome fruit

As indicated at the beginning, fatty oils are not only obtained by pressing the fruit bodies and subsequent refining, but also by extraction with organic solvents such as hexane. More and more frequently, supercritical carbon dioxide is used for this purpose, which escapes without residue after extraction. This is also the case when extracting the fatty oil from apple cores surrounded by a wood-like shell. During CO₂ extraction, the toxic amygdalin found in the seeds is largely retained. Amygdalin is a glycoside that is easily split into glucose, benzaldehyde with a bitter almond smell and prussic acid.

Apple seed oil (INCI: Pyrus Malus Seed Oil) contains oleic acid (38%), linoleic acid (51%) and about 10% saturated acids such as palmitic acid, stearic acid and arachidic acid (alias eicosanoic acid; $C_{20}H_{40}O_2$) as well as tocopherols.⁷ It is therefore well suited as skin care oil. Similar oils come from other pome fruits such as **quince**.

Alternatives

It does not always have to be the most expensive oil for cosmetic applications. If you look at the fatty acid spectrum, you will always find alternatives that have comparable properties and are easy on the wallet. The natural anti-

⁷ HL Tian, P Zhan, KX Li (2010), Analysis of components and study on antioxidant and antimicrobial activities of oil in apple seeds, International Journal of Food Sciences and Nutrition. 61 (4): 395-403.

oxidants contained are also often overrated in advertising. In contrast, components such as saturated fatty acids and sterols (unsaponifiables) that integrate into the skin barrier are important. Linoleic acid is a substrate for ceramide I. Linoleic acid and α -linolenic acid contents have an anti-inflammatory effect.

Dr Hans Lautenschläger