Phospholipids – the all-rounders

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What does an element like phosphorus that rather is associated with the match industry have to do with skin and cosmetics? As a matter of fact, most of the processes in which the substance is involved take place without becoming aware of them. It is not exaggerating to say that phosphorus and phospholipids are absolutely vital for life.

Phosphorus occurs in the phosphoric acid of the body fluids, in their salts such as the phosphates of the bone substance and the tooth enamel, and in phosphoric acid esters to which the nucleotides and phospholipids belong to. Phospholipids are compounds with lipid character which occur naturally everywhere where membranes or transport vehicles are needed for the metabolic processes:

- cell membranes of humans, animals and plants
- viral membranes as e.g. HI virus
- intracellular membranes such as mitochondria
- membranes of chylomicrons which transport dietary fats from the intestines into the lymph vessels and bloodstream
- transport lipoproteins of the blood circulation

Ether phospholipids such as the platelet activating factor (PAF) that among others, controls blood coagulation, blood pressure and lung function, similar to a hormone, and plasmalogens that are vital for muscles (heart) and brain, take a special position. Cardiolipin (CL) which is derived from phosphatidylglycerin (PG) is a component of the intracellular membranes of mitochondria. CL abnormalities lead to disorders of metabolic processes.

Lecithin

Lecithin is the main source for phospholipids which are also used as food supplements. Lecithin primarily is a waste-product of soya oil production where it occurs as a dark brown and oily sludge that is processed into crude lecithin which then is subjected to several additional refining processes before it is finally sold on the market in the form of light brown to yellowish granules. Lecithin contains several types of phospholipids:

- phosphatidylcholine (PC)
- phosphatidylethanolamine alias kephalin (PE)
- phosphatidylinositol (PI)
- phosphatidylserine (PS)
- phosphatidylglycerin (PG)
- phosphatidic acid (PA)

Lecithin is an appropriate and widely used anionic food emulsifier (E 322) due to its content of phosphatidylinositol, phosphatidylserine, phosphatidylglycerin and phosphatidic acid. This specific function of lecithin is used in the manufacturing of mayonnaise, bread improvers and chocolate. Conventional emulsions of cosmetic creams can also be stabilized by adding lecithin.
Initially, lecithin was not isolated from soya but from egg yolk which in Greek means “lekithos” and that is the reason for its name. Before the era of quats (quaternary ammonium salts) egg yolk additives were used in shampoos because of their conditioning properties: the hair will not become charged after washing. Mainly phosphatidylcholine (PC) is responsible for the antistatic properties of egg yolk. Soya lecithin contains up to about 30% of PC which currently is the most important phospholipid in skin care.

Phosphatidylcholine (from soya)

Concentration and isolation of PC from soya lecithin is a complex and elaborate process in which techniques like extractions and liquid chromatography are applied. In skin care vegetable PC from soya is preferred to PC gained from egg yolk.

- In contrast to PC gained from egg yolk which contains about 45% oleic acid, about 30% saturated acids (palmitic and stearic acid) and only about 18% linoleic acid, the PC from soya origin is dominated by a share of 65% of linoleic acid (essential ω-6 fatty acid).
- After enzymatic cleavage from PC, the linoleic acid can be integrated into the barrier active ceramide I of the stratum

corneum which will regenerate the disturbed skin barrier.[1]

- Another fraction of the linoleic acid will first be peroxidised by 15-lipoxygenase (15-LOX) into 13-hydroperoxy-9,11-octadecadienoic acid (13-HPODE) and then reduced to 13-hydroxy-9,11-octadecadienoic acid (13-HODE). 13-HODE has anti-inflammatory effects. [2]
- Besides linoleic acid, soya-based PC contains about 6% α-linolenic acid (essential ω-3-fatty acid), which in the skin is modified by 15-LOX via 13-hydroperoxy-9,11,15-octadecatrienoic acid (13-HPOTrE) into 13-hydroxy-9,11,15-octadecatrienoic acid (13-HOTrE). 13-hydroxy-9,11,15-octadecatrienoic acid (13-HOTrE) also has anti-inflammatory effects.[2]
- In the case of acne, linoleic acid of PC fluidizes the sebum but also has sebum-suppressive effects. Cornification disorders at the orifices of the sebaceous glands will return to normal. A clinical half-side test showed that 4 weeks of treatment with pure PC could reduce about 70 percent of the comedones and efflorescences of first and second degree acne vulgaris.[3] The cornification of scars also is reduced.
- Phosphatidylcholine proves beneficial in retarding liver injuries after poisonings due to e.g. alcohol or chlorinated solvents. Fat depositing also is impeded. In the case of a choline deficiency, isolated liver and also other cells are subjected to apoptosis. [4,5] A similar protective effect is assumed in skin cells in the case of exogenous noxa. Combinations of PC and caffeine are used against cellulite.[6]
- In the skin PC is poised with sphingomyelins from which ceramides are formed after the apoptosis of skin cells. That is the reason why frequently a modified skin condition can be observed after the topical application of PC.[7,8] The skin generally becomes finely pored. Thus, appropriate combinations will more or less unspectacularly and without any irritations achieve a well-recovered skin within 3-4 weeks.
- In how far the phosphorus uptake by the phospholipids plays a role in skin care still is unknown today.

Frequently the question is asked whether genetically manipulated soya influences the PC composition. So far the complex analytics has not yet proved evidence for the assumption. The fatty acid spectrum does not change though.

Liposomes and nanodispersions

In contrast to lecithin, pure PC will not form emulsions in aqueous environment – neither as oil in water (O/W) nor as water in oil (W/O) – but spontaneously create cellular bodies. They have first been discovered by Alec Douglas Bangham[9] and later on were called liposomes[10]. You'd almost think that PC had a memory because in equilibrium conditions, cell size and composition of the typical bi-membranes are identical with those of the plant cells from which they originate. Hence liposomes are no artificial bodies but a natural array of PC molecules in water. While emulsions already can be seen with a low resolution microscope, liposomes require high resolution electron microscopes.

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The interior of liposomes can integrate water-soluble (hydrophilic) substances. This way a carrier is formed for moisturizing factors, vitamins and extracts. However the illusion needs to be abandoned that liposomes may pass the skin barrier. Instead, they fuse with the skin barrier that also has a bilayer structure, and fluidize it for a short period of time so that the encapsulated active agents can penetrate easier.[11]
Liposomes are destroyed by emulsifiers in a concentration-dependent manner. Hence their formation from lecithin also is impeded by anionic-active phospholipids (see above). Cosmetic preparations with the PC typical membrane structure are considered to be emulsifier-free – a point of view that in physiological respect makes sense. Since who would like to claim that the cellular structures of all creatures consist of emulsions.
Also the initially described chylomicrons (diameter 180-500 nm) can be reconstructed with PC and then used in cosmetic preparations to transport lipid-soluble active agents. Biodegradable liquid nanodispersions are formed whose particles (100-200 nm) have a single membrane consisting of PC and a lipophilic interior. Their fusion with the skin barrier and the release of lipid-soluble vitamins, vegetable oils and other lipophilic substances occurs by analogy with liposomes.

Lamellar creams

Phosphatidylcholines such as dipalmitoyl phosphatidylcholine (DPPC) or hydrogenated PC (PC-H) with their saturated acids such as palmitic and stearic acid instead of unsaturated acids in their fatty acid composition also are physiological although they are produced semi-synthetically. They have the interesting property though that they form planar instead of cellular bilayers similar to the skin barrier[12]. They can be used to prepare lamellar creams that are particularly suited for skin protection purposes.[13,14] They stabilize the transepidermal water loss (TEWL) on a natural level and in contrast to conventional emulsifier containing preparations they excel by their minimal washout of skin care and natural protective substances of the skin.[15] Lamellar creams are the means of choice for problem skin as for instance atopic skin which reacts sensitively to emulsifiers. The creams are compatible with many physiological lipid and water-soluble active agents and can be individually adapted.[16]
The active agents are slowly and evenly released (depot effect). This partly is due to the fact that PC-H as well as PC binds to keratin containing skin structures – an effect that also explains the conditioning of hairs as described above.
Lecithin and PC more or less inactivate all the preservatives mentioned in the annex of the German Cosmetic Directive (KVO).[17] Hence lecithin and PC based preparations usually are produced without preservatives, a fact that still underlines their physiological significance.
An interesting protective effect of PC can also be observed in the case of sensitive stomach mucosa: non-steroidal anti-inflammatories and pain killers (NSAID) are better tolerated if taken in combination with lecithin or PC. And by the way: one of the main effects of anti-inflammatory corticoids consists of impeding the release of arachidonic acid by the phospholipase A_2 from the PC occurring in the body. Vegetable PC does not contain arachidonic acid. The choline of PC is considered as a substrate for acetylcholine which is an essential neurotransmitter for brain (memory) and nerves. In addition, it is an important methyl group carrier in the human metabolism.
Phosphatidylcholine has become established in dermatological cosmetics and corneotherapy.[18] Now, let's wait and see whether PI will gain in importance for the microcirculation, PS for facial masks and glycerophosphatidylcholine (GPC) as a moisturizer.

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