Fruit from mango trees, such as the one above, will yield an oil that can be fractionated to produce an olein portion that is particularly useful for cosmetic applications because the valuable unsaponifiables tend to accumulate in that fraction.

Exotic butters as cosmetic lipids

The skin represents the barrier of the human body that shields it from a variety of strains such as heat, cold, and light, including ultraviolet (UV) and other types of harmful irradiation. Other stressing factors which the skin has to cope with are dehydration, noxious substances, insect bites, and infection by various microbes. To survive these strains, the skin performs a variety of specialized functions and reactions.

Natural lipids may be beneficial for the physical and biochemical properties of the skin. The physical benefits include occlusivity, which, in cosmetic and pharmaceutical practice, refers to the ability of a substance to create a film on the skin surface that interferes with the evaporation of water from the skin surface into the environment. Any increase of transepidermal water loss (TEWL) decreases the level of water retained in the epidermis. This is a significant problem in people with atopic eczema, chronic contact eczema, and other forms of dry skin (Figure 1). In the design of cosmetics for the repair of damaged skin and for skin protection, it is therefore important to assess the effect on TEWL. In this context it is important to notice that the term "moisturization" is often preferred, because "occlusion" may imply retention of dirt. In cosmetics, natural lipids are thus used as occlusive agents, but promoted as moisturizers.

The biochemical benefits of natural lipids include the regulation of epidermal growth, reduction of skin inflammation, and provision of a skin barrier function. The barrier properties of the skin and skin's ability to retard TEWL depend on the presence of epidermal lipids. The permeability barrier in

This article was prepared by Vijai K.S. Shukla, director of the International Food Science Centre, Postbox 44, Sønderskovvej 7, DK-8520 Lystrup, Denmark, and Knud Kragballe, professor, Department of Dermatology, Marselisborg Hospital, Department of Dermatology, P.P. Oerumsgade 11, DK-8000 Aarhus C., Denmark.

V.K.S. Shukla

K. Kragballe

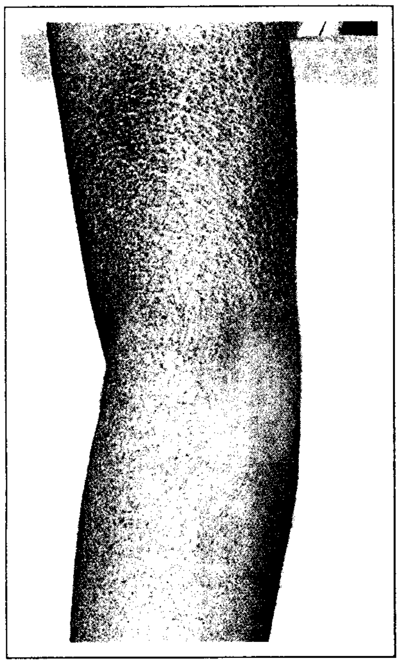

Figure 1. Dry, scaly skin on arm

Figure 2. Patient with atopic eczema on the legs

human skin is mediated by three lipid families—ceramides, free fatty acids, and cholesterol—present in an approximately equimolar ratio. The epidermal lipids are formed *de novo* by keratinocytes, although some lipids or their precursors are supplied from the circulatory system. Variations in the composition and proportion of these lipid families can lead to deterioration, normalization, or acceleration of barrier repair. One extensively documented benefit of the use of natural lipids is the presence of essential fatty acids (EFA). EFA deficiency impairs the skin's barrier properties and results in scaling and epidermal hyperplasia.

The specific effects of γ-linolenic acid on human skin health are well established. Linoleic acid and similar polyunsaturated fatty acids used in cosmetics may be beneficial for dry skin, aged skin, or skin that cannot retain water properly. Furthermore, these fatty acids are claimed to have therapeutic effects in atopic eczema (Figure 2), psoriasis, and acne.

The cosmetic industry, through intensive research, has developed products to cure skin disorders and to retain the skin's natural beauty. Long ago, natural fats were the dominant emollient material, but later these were replaced in many applications by mineral oils. However, because of the growing awareness in the 1980s and 1990s of the environment and an increasing interest in environmentally friendly products, natural renewable vegetable lipids are finding ever-increasing use in a wide range of cosmetic applications.

More systematic studies of a wide range of plant seeds and their oils have identified many interesting materials. Previously unknown oils with unusual properties and chemical structures have been discovered.

Most lipid-based products are nontoxic, nonhygroscopic, and normally are nonreactive with active ingredients. Some oils are rich in EFA while other contain natural antioxidants or sunscreens. Therefore, it is no surprise that such oils are receiving much more attention as safe, environmentally friendly ingredients for the cosmetic formulator.

Lipids play an important role in the formulation and performance of many cosmetic products. They may act as binders, lubricants, solubilizers, carriers, viscosity modifiers, spreading agents, emollients, and emulsifiers in a variety of applications including lipsticks, creams, lotions, makeup bases, moisturizers, bath oils, pressed powders, fragrances, and a variety of cleansers for hair, face and body.

Vegetable oils are primarily triglycerides (triacylglycerols) in which the predominant fatty acids are palmitic and stearic acids and their mono- and polyunsaturated forms, such as palmitoleic, oleic, linoleic, and linolenic acids. However, many other fatty acids also occur, usually in smaller quantities.

These fatty acids can be combined in endless variations resulting in a wide range of chemical and physical properties. Oils from the same plant species can show variations in the ratio of the same key fatty acids as a result of genetic differences and of weather influences.

Vegetable oils vs. synthetic chemicals

Several factors need to be considered when comparing possible replacement of petroleum-based chemicals, such as mineral oil fractions, with natural vegetable oils. These include economy, health aspects, functionality, and stability.

In general, vegetable oils are more expensive than the synthetic substances and are not as homogenous in content. Many types of vegetable oils have specific beneficial physiological effects as shown in numerous studies. Choosing the right type of oil can result in positive results for a given cosmetic application.

Edible plant-derived butter can, in general, be anticipated to be innocuous.

The major drawback in the use of vegetable oils instead of mineral oil fractions is the poorer oxidative stabil-

Table 1
Major fatty acids found in sebum (as % of total fatty acids)

Type	Saturated (%)	Monounsaturated (%)	Diunsaturated (%)
Straight-chain	41	40	3
Branched-chain	6	7	0

ity of vegetable oils, especially polyunsaturated oils, which poses an extra problem that until recently has been difficult to resolve.

However, progress is being made to ensure consistent quality and improved stability of unsaturated oils, which will allow wider use of vegetable oils as a basic cosmetic formulation ingredient. The importance of nontriacylglycerol constituents (unsaponifiables) in vegetable oils with regard to the stability of natural oils has been recognized in recent years (1). Many such constituents are potent natural antioxidants.

Physical effects of vegetable oils

Natural oils and fats are used for differing effects in a variety of cosmetic products. They remain on the skin, and their presence results in several important physical effects, including emolliency and occlusivity.

Emollients are defined as substances that impart softness, smoothness, and flexibility to skin and that have the ability to maintain these conditions for some time. Water alone can produce these effects, but the perceived benefits are lost rapidly as the water evaporates. The term "emolliency" in practice is rarely differentiated from the term "moisturization," although the latter implies that the water content of the skin is raised. It is well established that the application of a water–oil mixture in a simple emulsion causes a temporary increase in the skin's water content. Most of this water is lost within a few minutes, but the residual effect of the nonvolatile lipid produces emollient benefits. The lipid film on the skin surface may help to retard the evaporative loss of water when the emulsion dries on the skin.

With regard to occlusivity, any reduction of TEWL raises the level of water retained in various strata of the epidermis. The occlusive character of fats and oils therefore can be utilized to increase the water content of the skin. This increase alters the viscoelasticity of *stratum corneum* and makes the skin more supple. Occlusive substances impede the escape of water vapor; these materials, as a rule, also can act as water repellants, i.e., interfere with access of water.

Skin lipids

One of the rationales for the use of natural oils in cosmetics originally arose from the fact that these lipids are similar or even identical to those found normally in or on human skin. Solvent extraction of skin yields a blend of lipids from several sources, including the sebaceous gland. The major components of sebaceous lipids are about 12–15% squalene, 25% wax and sterol esters, 10% free fatty acids, and 45–60% triglycerides (2). The fatty acids found in sebum include odd- and even-numbered carbon chain acids not normally found in ingested lipids. They may be saturated or unsaturated and include some unusual substances such as sebaleic acid (18:2n-10). A general overview of the fatty acids found in human sebum is shown in Table 1.

Exotic butters

The term "butter" means a soft, waxy substance that forms a solid or semisolid at ambient temperatures.

The exotic butters are a group of natural fats with a high content of symmetrical monounsaturated triglycerides. The most important are cocoa, illipe, kokum, mango, sal, and shea butter. All of these butters contain 50–60% of saturated fatty acids, mainly stearic acid, and up to 47% of monounsaturated oleic acid. The plants that are sources of these butters are generally tropical jungle crops and are often fluctuate in their production volumes, dependent strictly upon the whims of nature.

The triglyceride composition of this group of fats results in the following physical properties: solid to semisolid fats at room temperature (20–30°C), and very sharp melting profiles at 35–45°C. These characteristics make these butters extremely attractive as cosmetic ingredients. The narrow melting range combined with the relatively high content of saturated fatty acids, which makes the fats mutually substitutable to a substantial degree, plus the high oxidation stability are some of the reasons why these fats are highly appreciated in skin-care products. Some chemical properties of these butters are shown in Table 2.

In cosmetics, exotic butters con-

Table 2
Major fatty acids (as % of total fatty acids) and unsaponifiable content (as % of total lipids)

Name	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	Unsaponifiables
Cocoa	27	33	35	0	0.5
Illipe	15	46	35	0	1.0
Kokum	2	58	39	0	0.5
Mango	6	44	45	0	0.8
Sal	6	42	41	0	0.9
Shea	4	43	47	6	6.0

tribute to viscosity and emulsion stability. They also have the ability to form durable structures in stick products. In addition, they contain many ingredients that are beneficial for hair and skin.

The tocopherol content of exotic butters is usually quite low.

It has been common practice to fractionate some of these butters, especially mango, sal and shea, by hydraulic pressure or by using solvents, into two components, e.g., a more solid part with a higher melting point containing a higher content of stearic acid (often called the stearin fraction), and a more liquid part with a lower melting point, containing more oleic acid (the olein fraction).

Whereas the stearin fractions are preferentially used for the confectionery industry, the olein fractions, because of their physical properties, are particularly useful for cosmetic applications because the unsaponifiable contents tend to accumulate in the olein fraction. Shea olein fractions are especially valued in the cosmetic industry. Because the oleins have been subjected to one extra processing, they are more expensive than the corresponding unfractionated butters.

Cocoa butter

Cocoa butter is obtained by pressing the crushed seeds of from the cacao tree, *Theobroma cacao*. Cocoa butter is a well-known and valued ingredient in chocolate. In cosmetics, it is valued for its melting point, which is close to body temperature. Cocoa butter is used extensively in the preparation of suppositories, skin-care products, bath oils, night creams, suntan preparations, and lip makeup. Due to its high price, it is gradually being replaced by cheaper alternatives among the exotic butters.

Illipe butter

Illipe butter is the fat obtained from the nuts of *Shorea stenoptera*. It is the exotic butter that comes closest to matching cocoa butter in triglyceride composition, but it has a lower iodine value and its melting temperature is 2 to 4°C higher. It has recently been introduced as a cosmetic raw material and is used in various skin-care preparations. Thus far it has not been possible to domesticate *S. stenoptera,* which grows as a wild crop in the jungles of Southeast Asia, especially in Malaysia, Sumatra, and Borneo. The plant flowers at irregular intervals, often only every six or seven years. This is a serious drawback to the commercialization of illipe butter.

Kokum butter

Kokum butter is obtained from the fruit kernels of *Garcinia indica,* which grows in the savanna areas of parts of the Indian subcontinent (3). It is mainly used as a cocoa butter improver due to its very high content of stearic-oleic-stearic triglycerides. It is the most stable and hardest exotic butter known, with a melting point of 38–40°C. It has a good white color, even as a crude butter. Kokum butter traditionally has been used as an astringent, for local application to ulceration and fissures of lips, hands, and soles. It has applications in skin and hair products, acne products, and skin tonics. The production of kokum butter is sparse, but it is highly appreciated in the international market, especially as a cocoa butter improver because it can be used straightaway without fractionation.

Mango butter

Mango butter is obtained from the deshelled fruit kernels of the mango tree, *Mangifera indica* (4,5). This butter has only recently been introduced into the cosmetic industry, but it is a promising ingredient for the future. The supply is constant and the butter usually is produced under conditions that meets the stringent requirements for cosmetic applications. Most of the produced mango butter is being used as a cocoa butter replacer in the confectionery industry. However, the emollient properties of this butter have attracted the attention of the cosmetics industry. Mango butter is a soft solid with a melting point of 31–36°C; it has a very slight sweet scent, a nice final touch for a natural product.

Mango butter can be incorporated into cosmetic product in high quantities. It produces stable emulsions due to its uniform triglyceride composition and high oxidative stability. Traditionally, in India, it has been used for soap making and as a an emollient in skin-care products.

Mango butter has good emolliency properties, making it a very suitable replacement for many synthetic emolliency enhancers. It has been shown to release drugs such as salicylic acid at a much higher rate than a standard paraffin-base emollient. It has a good softening effect and good spreadability on the skin. It prevents drying of the skin and the development of wrinkles. It reduces the degeneration of the skin cells and restores the flexibility of the skin.

Up to now mango butter has been used as an ingredient in skin care products, lotions, massage creams, hair products, makeup and sun care products. It has a protective effect against sunlight. Mango butter is suitable in emulsion products because of its turbidity at room temperature.

Sal butter

Sal butter is obtained from the kernels of the sal tree, *Shorea robusta* (5,6). Sal is a tree growing wild in the jungle forests of North, East, and Central India. The harvest and the quality of kernel vary considerably, but most of the time it is possible to get refined sal butter of high quality to meet the requirements for cosmetic applications. The butter is used locally for cooking and soap production, but a large part of the produced sal butter can be fractionated physically, the stearin fraction being used and export-

Table 3
Recommended amounts of shea butter in selected products (%)

Hair care	1–2
Baby care products	5–8
Hand cream	5–10
Lipcare products	5–10
Massage cream/lotion	5–8
Night cream	8–15
Skin cream	5–12
Soap	2–3
Sun care	6–20
Wintersport cream	2–15
Day cream	4–6
Different base formulations	10–15
Body lotions	2–5
Antiwrinkle products	5–7

ed as a cocoa butter replacer in the confectionery industry. Sal butter is solid at room temperature with a melting point of 34–38°C.

Sal butter is comparable to cocoa butter in physical properties and is used in some similar applications. Like mango butter, it combines good emolliency properties with superior oxidative stability, making it a suitable replacement for many synthetic emolliency enhancers. Sal butter has been reported to be used in skin and hair products, stick products, hair pomades, and dry-skin lotions.

Shea butter

Crude shea butter is a grey, tallow-like substance, which is extracted from the kernels of the fruit of the shea nut tree, *Butyrospermum parkii,* by hydraulic pressing or by using specially adjusted screw expellers (5,7,8). The greenish crude fat is usually more or less contaminated with the latex from the fruits, making it difficult to refine. Most quantities offered tend to be rather grey in color, but if proper care is taken in the selection of the nuts and if the raw material is adequately refined, an attractive white fat can be obtained which is very suitable for cosmetic applications. Shea butter can be refined, bleached, and deodorized to obtain a whitish product.

Shea butter is a nontoxic and nonirritating material derived from totally renewable natural resources and is easy to use within cosmetic formulations. Traditionally it has been used in Africa as a medical balm for rheumatism, muscle aches, burns, and light wounds.

Due to its unique fatty acid composition, shea butter is a soft fat, which readily melts at body temperature, making it a suitable emollient for many skin-care applications, such as baby-care products, massage creams, makeup, and similar products. Shea butter as an excellent ointment base releases medicaments faster than other well-known bases. Shea butter is absorbed quickly by the skin, acts as a refatting agent, and has good water-binding properties.

As its consistency at room temperature is somewhere between a liquid and a solid, it can be used in emulsions as a binding component between solid and liquid components. It is possible to incorporate substantial quantities of shea butter into both oil-in-water and water-in-oil emulsions. Shea butter exhibits two polymorphic forms at about 38°C, which makes it more predictable and stable in formulations than other fats with more polymorphic forms, such as cocoa butter. Stability tests by temperature cycling show a high degree of resistance to separation.

However, one unique characteristic of shea butter is its content of unsaponifiables (up to 8%) which imparts soothing properties and provides extra sun protection. Shea butter absorbs UV light at 275 nm and is therefore a useful complementary ingredient to UV screens in sunscreen products. With pure shea butter, a sun protection factor of 3 to 4 can be obtained.

The unsaponifiables consist of up to 75% terpenic alcohols and 5–10% phytosterols. Sterols and terpenic alcohols are found almost exclusively as cinnamic acid esters. This is unique to shea butter when compared to common oils, whose unsaponifiable components are found as free alcohols. Shea butter exhibits different behavior and properties when compared to other oils, such as avocado and soy, which contain high amounts of unsaponifiables. Avocado and soybean oils have high antielastic properties due to the sterols, the dominant unsaponifiables. It is the high content of cinnamic acid that gives shea butter its healing properties. Recommended amounts in specific products are listed in Table 3.

Due to shea butter's moderately high (up to 6%) content of linoleic acid, some cosmetic producers add 0.05–0.1% of an antioxidant, such as butylated hydroxytoluene (BHT). BHT is a more effective antioxidant in formulations than propyl gallate and butylated hydroxyanisole (BHA).

Health aspects

Shea butter has been studied in Europe in many clinical trials, giving excellent results for the treatment of cutaneous dryness, dermatitis, dermatoses, eczema, solar erythema, burns, and other skin irritation. While having a trophic effect, shea butter seems to induce the capillary circulation in the skin which in turn increases tissue reoxygenation and enhances the elimination of metabolic waste products.

The presence of esterified terpenic alcohols in shea butter favors its cutaneous compatibility. The unsaponifiables contain 5–10% phytosterols which are known to be active in cellular growth stimulation.

Shea butter is the number one selling exotic butter.

References

1. Shahidi, F., and V.K.S. Shukla, Nontriacylglycerol constituents of fats and oils, *INFORM 7*:1227–1232 (1996).
2. Rieger, M., Use of natural fats and oils in cosmetics, in *Bailey's Industrial Oil and Fat Products*, edited by Y.I. Hui, John Wiley & Sons Inc., New York, 1996, pp. 349–380.
3. Bringi, N.V., and D.T. Mehta, Garcinia indica choisy (Kokum), *Vateria indica* (Dhupa) and *Bassia butyracea* (Phulwara) seed fats, in *Non-traditional Oilseeds and Oils of India*, edited by N.V. Bringi, Oxford and IBH Publishing Co. Pvt Ltd. (Mohan Primlani), New Delhi, India, 1987, pp. 97–117.
4. Bhattacharyya, D.K., Mango (*Mangifera indica*) kernel fat, *Ibid.*, pp. 73–96.
5. Shukla, V.K.S., Confectionery fats, in *Edible Fats and Oils Processing: Basic Principles and Modern Practices*, edited by D.R. Erickson, American Oil Chemists' Society, Champaign, Illinois, 1989, pp. 228–232.
6. Bringi, N.V., Sal (*Shorea robusta*) seed fat, in *Non-traditional Oilseeds and Oils of India*, edited by N.V. Bringi, Oxford and IBH Publishing Co. Pvt Ltd. (Mohan Primlani), New Delhi, India, 1987, pp. 1–55.
7. Tran, T., Le beurre de karite proprietes biologiques et applications cosmetiques, *Parfums Cosmetiques Aromes 58*:65–66 (1984).
8. Peers, K.E., The non-glyceride saponifiables of shea butter, *J. Sci. Food Agric. 28*:1000–1009 (1977).

■