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The use of particular natural oils in formulations

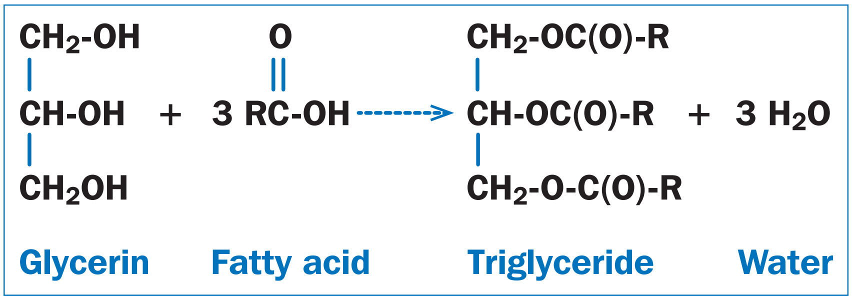

Figure 1: *The reaction.*[1]

ABSTRACT

Natural oils have become a common additive to personal care products. They fit the definition of natural, sustainable and can be renewable and even organic. While these classifications are sometimes unclear in meaning, the reason we formulate with a particular oil is often just as obscure. Is it marketing, or carbon distribution or aesthetics or perhaps a particular benefit rendered to the oil by a particular native material (antioxidants, UV absorbers)? This article will look at some of these properties.

The selection of a particular natural oil in a personal care application depends upon what the formulator wants to achieve with the particular formulation. The simplest choice is when the choice is simply a marketing choice. The product profile may say that the product should contain a particular oil like olive oil or argan oil. The aesthetics are dictated in large amount by two properties, carbon number and amount of unsaturation (measured by iodine value). Finally, there may be a particular reason to use an oil with an antioxidant or other active that is natural to the oil. While seaming simple, once the oil is chosen, the process by which the oil was prepared becomes the controlling factor. We will address each of these variables.

Definitions

The terms oils, fats, butters and waxes have been misused over the years. The historical definition of wax has previous been given. Butters, oils and fats are all triglycerides. Fats have a titer point of over 40.5˚C, oils have a titer point of below 40.5˚C. Butters have a titer below 40.5˚C but above 20˚C. Oils are liquid at room temperature and we now use this word to describe any compound that is a liquid and is insoluble in water.[2]

Because oils, fats, butters and waxes are complex mixtures of homologues of similar chemical structures, it is difficult to obtain a true melting point. The term titer is therefore used to define the re-solidification point of the melted oil, fat, butter or wax. The procedure is to heat the product to be tested until it is completely liquid, then to cool it slowly by stirring. This is done until the temperature stays constant for 30 seconds, or begins to rise. The titer point is the highest temperature indicated by this rise.[1]
As the lower molecular weight fractions melt, they act as solvents to dissolve the higher molecular weight products. This results in a very wide melting 'range' for these compounds. For this reason, titer point is generally determined on fats, oils, waxes and butters.

Triglycerides

Triglycerides are the tri-esters of glycerin with three equivalents of organic acid. Fatty acids are defined as those acids having alkyl or alkylene groups being C-5 and higher. The reaction is shown in Figure 1.

When the triglyceride is saponified to make a surfactant, such as soap, glycerin is liberated. When a wax is saponified, a fatty alcohol is liberated. Saponification is a general term to define the chemical reaction that breaks the ester linkage. This makes it possible to produce very different kinds of products using the two types of materials.

Glycerin, produced as a by-product of saponification is water soluble and fatty insoluble.

Table 1: Oil composition example.

Component	% Weight
C16	20
C18	20
C18:1†	20
C20	40
Total	100

†Note: C18:1 is our short to indicate the presence of 1 double bond or unsatuartion. So C18:1 would be oleic acid

Table 2: Carbon number calculation for oil example in Table 1.

	(a)	(b)	
Component	% Weight	Carbon atoms in component	Calculation (a)*(b)
C16	20	16	3.2
C18	20	18	3.6
C18:1	20	18	3.6
C20	40	20	8.0
Total	100		18.4

Therefore for the Carbon number = 18.4

The fatty alcohol produced as a by-product of the saponification of a wax is water insoluble and generally fatty-soluble. Triglycerides are commonly encountered as natural products. Plants use enzymatic systems to make triglycerides, effectively at ambient temperatures.

INCI nomenclature

INCI names require the genus and species of the plants or insects that produce a given wax, oil, butter or fat and all products which are derived from the various oils, fats, butters and waxes. This is due, in part, to the European Union's use of the Latin names for ingredient listings. This information is very helpful to the formulator in understanding the source of the fatty portion of the surfactant.

Classification

In order to simplify the information, we have divided the raw materials that we discuss into two groups: those derived from animal sources and those derived from plant sources. Within each of these groups one finds additional classes depending upon the carbon distribution of the raw material.

Carbon number

In addition to classifying products by their sources (animal or plant) and by their chemistry (triglyceride or ester), we have classified them within these groups by carbon number and unsaturation level. Carbon number is the value obtained by multiplying the percentage of a component in a product by the number of carbon atoms in the component, then adding up all the components.

For example, if an oil had the composition shown in Table 1, the carbon number calculation would be as seen in Table 2.

There are several types of oils that have very similar carbon numbers; consequently, we have classified them further by unsaturation. One can expect derivatives from oils having very similar carbon numbers and levels of unsaturation to have very similar, often identical functional properties. In this instance, the choice of which of the many oils to use depends upon the economics of the oil and the formulator's desire to name the oil for label and marketing purposes. As will become clear, there are many different fats, oils, waxes and butters, which when derivatised, result in compounds of strikingly similar carbon distributions, while having their source oil, wax, fat or butter being quite different. Thus, naming the material by the predominant species is not very enlightening to the formulator as to the source of the raw material.

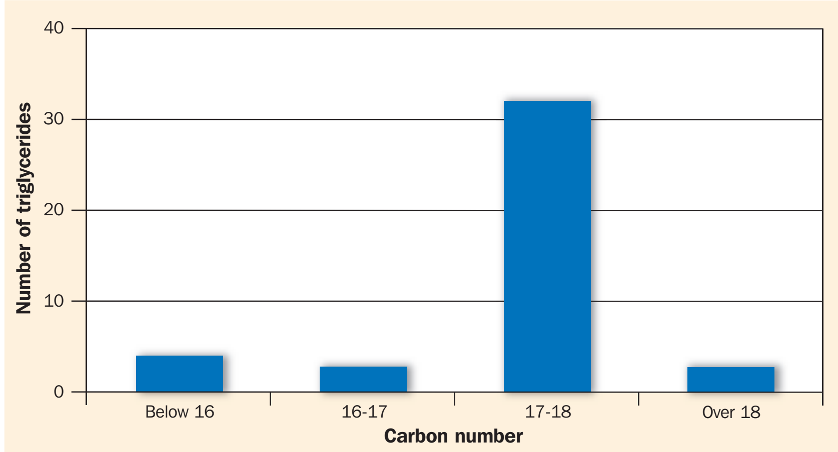

Figure 2: *Carbon number of common triglycerides.*

It is also quite interesting that nature has provided many triglycerides that have very similar carbon numbers. In fact, of 38 triglycerides presented here, 31 have carbon numbers between 17 and 18. This also explains why the other important variable, unsaturation, is critical in choosing an oil for a specific application (Figs. 2 & 3).

It is very interesting that there are only three triglycerides having a carbon number below 16. Since this is a key number for detergents, it becomes clear why coconut oil is so important to the surfactant industry. There has been a growing demand for products based upon oils having a carbon number over 18 (for example behenic derivatives). In order to get these products, one must choose a different class of oils. The selection of the oil is a major variable, which normally eludes the formulator, being made more commonly by the derivative manufacturer. Oil selection is assuredly one important factor in formulating cosmetic products.

Effect of carbon number

One major factor that affects the functionality of both the oil itself and any potential derivative is the number of carbon atoms in the chain. Other factors include the number and location of double bonds and the presence of additional functional groups.

Generally, as one evaluates the tactile properties of an oil on the skin, the lower the molecular weight is, the less oily the feel of the compound will be. Conversely, the higher the molecular weight is, the more greasy the feel will be. In surfactant preparation, detergent products and high-foaming products generally peak between a carbon number of 12 and 14. Conditioners and softeners have a carbon number of 16 to 18. Today there is a growing trend toward using materials with carbon numbers of 22 or more for conditioning. Since few oils offer these high carbon numbers, manufacturers often fractionate methyl esters to pure compounds or, alternatively, they hydrogenate unsaturated oils to make saturated compounds having high carbon numbers.

In general, double bonds lower the titer point of the triglyceride, resulting in a triglyceride that stays liquid at lower temperatures. Conjugated double bonds (i.e. those with only one carbon between two double bonds (-C=C-C=C-), are very effective in depressing titer point, but can present problems with rancidity, a process by which the double bond is oxidised and ultimately broken. This releases many different molecules, many of which have objectionable odors. Rancidity can be mitigated at times with the addition of antioxidants, prior to the start of the rancidity process.[3]

Finally, upon additional processing, many oils, fats, butters and waxes lose their identity as oils and become known by the fatty names of the predominant species present after treatment. These processes include preparation of methyl esters,

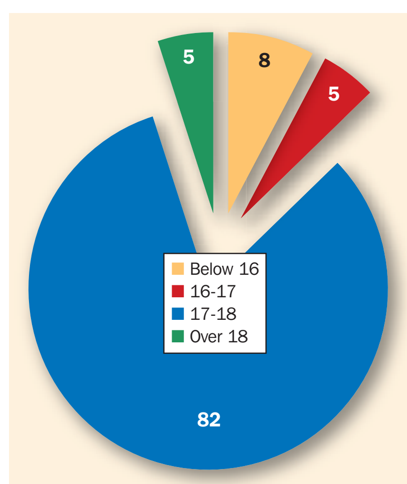

Figure 3: *Carbon number percentage shown in common triglycerides.*

Table 3: Carbon number and iodine value for common triglycerides.[2]			
Group 1: Animal derived triglycerides			
Section	**Triglyceride**	**Carbon number**	**Iodine value**
1.1	Milk Fat	15.5	39
Group 2: Plant derived triglycerides			
Section	**Triglyceride**	**Carbon number**	**Iodine value**
2.1	Coconut Oil	12.8	8
2.2	Palm Kernel Oil	13.3	19
2.3	Babassu Oil	13.4	15
2.4	Sunflower oil	16.0	130
2.5	Japan Wax	16.3	6
2.6	Palm Oil	17.1	50
2.7	Apricot Kernel Oil	17.1	102
2.8	Tallow	17.3	45
2.9	Coca Butter	17.5	37
2.10	Andiroba Oil	17.5	45
2.11	Mango Butter	17.5	46
2.12	Avacado Oil	17.6	84
2.13	Cottonseed Oil	17.6	108
2.14	Rice bran Oil	17.6	105
2.15	Shea Butter	17.6	60
2.16	Wheat Germ Oil	17.7	130
2.17	Illipe Butter	17.7	49
2.18	Corn Oil	17.8	123
2.19	Olive Oil	17.8	84
2.20	Poppyseed Oil	17.8	138
2.21	Grape seed Oil	17.8	135
2.22	Sesame Oil	17.8	110
2.23	Sweet Amond Oil	17.9	102
2.24	Hazelnut Oil	17.9	86
2.25	Soybean Oil	17.9	130
2.26	Safflower Oil	17.9	145
2.27	Hybrid Safflower Oil	17.9	140
2.28	Walnut Oil	17.9	150
2.29	Canola Oil	17.9	92
2.30	Peanut Oil	18.0	98
2.31	Tall Oil	18.0	130
2.32	Kokhum Butter	18.0	131
2.33	Cupuacu Butter	18.2	40
Group 3: Drying triglycerides, plant derived			
Section	**Triglyceride**	**Carbon number**	**Iodine value**
3.	Linseed Oil	17.9	190
3.2	Tung Oil	17.9	170
Group 4: Triglycerides having unusual components			
Section	**Triglyceride**	**Carbon number**	**Iodine value**
4.1	Borgae Oil	17.8	147
4.2	Evening Primrose	17.9	152
4.3	Veronia Oil	17.9	106
4.4	Ongokea Oil	18.0	190
4.7	Castor Oil	18.0	85
4.6	Meadowfoam Oil	20.5	95
4.7	Rapeseed Oil	20.6	100

fractionation of the methyl ester and preparation of a fatty alcohol. For example, if olive oil is completely hydrogenated under high pressure, both reduction of the double bond and hydrogenolysis occur, leaving mostly stearyl alcohol, the predominant material in the mixture. In order to preserve the double bond, special catalysts are used.

Effect of unsaturation[4]

Iodine value is a measure of the unsaturation present in particular chemical. The higher the iodine value, the more double bonds there are in the molecule. The preferred method is known as the Wijs procedure.[2] This method measures the absorption of iodine monochloride by the material being analysed and is very useful for non-conjugated double bonds. A rule of thumb for iodine values of less than 10, is that the percentage of mono-unsaturation roughly equals the iodine value. Therefore a wax with an iodine value of five can be predicted to have about 5% unsaturated species present.

It is important to note that other components in the composition that can react with iodine monochloride can falsely increase the indicated amount of unsaturation. Generally, as the iodine value increases, the liquidity of the oil increases and the titer point decreases. Some oils have high iodine values but are surprisingly resistant to rancidity. Meadowfoam seed oil is one such product. The stability is due to the presence of natural antioxidants in the oil and the and the fact that the double bonds are not conjugated. Some oil processors add antioxidants to their oils. BHT and BHA are some such antioxidants commonly added to oil (Table 3).

BHA is declining in usage due to its inclusion in California's Proposition 65 list. Antioxidants can only prevent oxidation, they cannot take a product that has started to oxidise and reverse the reaction. Surprisingly, too much antioxidant can accelerate oxidation, which is known as pro-oxidation.

The selection of oils from different classes will result in the most difference in physical and aesthetic properties (see Table 4).

Butters

The most common natural butters are:

- **Cocoa Butter** (*Theobroma cao*) – Cocoa butter is obtained from the cocoa bean (*Theobroma cacoa* L.).
- **Mango Butter** (*Mangifera indica*) – Mango butter is obtained from *M. indica*.
- **Shea Butter** (*Butyrospermum parkii*) – Shea Butter is a obtained from *Shorea stenoptera* L.

- **Illipe Butter** (*Bassia latifola*) – Illipe butter is obtained from *B. latifola*.
- **Kokum Butter** (*Garcinia indica*) – Kokum butteris obtained from *G. indica*.
- **Cupuacu Butter** (*Theobroma Grandiflorum*) – Cupuacu butter is obtained from *T. grandiflorum*.
- **Sal Butter** (*Shorea robusta*) – Sal butter is obtained from *S. robusta*.

A number of patents have been issued covering the reaction of cold pressed shea butter to make a variety of other cosmetic ingredients.[5-8] These patents use cold pressed butters in order to maintain the Mild Processed Shea Butter (MSB) has "significantly high concentrations of unsaponifiables, which posses highly desired antioxidant, ultra-violet radiation protection, and free-radical scavenging properties. MPSB of the present invention typically contains from about 5% to about 15% by weight of unsaponifiables. In contrast, other butters commonly used in personal care products have less than 2% unsaponifiables. For example, cocoa butter (from T*heobroma cacao*) averages 0.4% unsaponifiables and Illipe butter (from *Shorea stenoptera*) averages 1.1%".[8]

There are a number of manmade butters that are the result of partial hydrogenation of a triglyceride. While many times partial hydrogenation results in an acceptable feel, the materials have trans fats present which have been banned in foods by the FDA.

Additional compounds present

Many natural oils have present a variety of desirable compounds. These include a variety of antioxidants, polyphenols, falvonoids, tocopherols, antimicrobials and the like.

Additionally, there are a number of natural oils that have properties that are folklore properties. These materials are interesting and are becoming increasingly so. The issue is that just because a seed from a specific species has a specific material of interest in it, it does not mean that the oil sold commercially will have the same species at the same concentration in it. There needs to be certification and analysis to go with these species. Processing can vary the product purity.

Processing[9]

Oil extracted from the pressing of seeds contains many ingredients, some desirable and others undesirable. Crude oil is processed to separate the components. We generally take for granted the process that allows for the transformation of a plant seed into clear, low odour oil suitable for cosmetic use. The plant chosen for use, as well as the processing used,

Table 4: Classes of a selection of oils.

No.	Name	Source	CAS Number	Predominant species
CLASS 1: Animal-derived products rich in carbon chain lengths below C-18				
1.	Milk Fat	Cows milk	8029-34-3	C16 triglyceride
CLASS 2: Animal-derived products rich in C-18 unsaturated carbon chain lengths				
2.	Tallow	Animal fat	61789-13-7	C18:1 triglyceride
3.	Japan Wax	*Rhus succedanes*	8001-13-6	C16 wax
CLASS 3: Animal-derived products rich in carbon chain lengths greater than C-18				
4.	Beeswax	*Cera alba*	8006-40-4	C26 wax
5.	Shellac Wax	*Shellac cera*	97766-50-2	C30 wax
CLASS 4: Plant-derived products rich in carbon chain lengths below C-18				
6.	Coconut Oil	*Cocous nucifera*	8001-31-8	C12 triglyceride
7.	Babassu Oil	*Orbignya olefera*	91078-92-1	C12 triglyceride
8.	Palm Kernel Oil	*Elaeis guineenis*	8023-79-8	C12 triglyceride
CLASS 5: Plant-derived products rich in C-18 unsaturated chain lengths				
9.	Soybean Oil	*Glycerin soja*	8001-22-7	C18:2 triglyceride
10.	Peanut Oil	*Arachis hypogaea*	8002-03-07	C18:1 triglyceride
11.	Corn Oil	*Zea mays*	8001-30-7	C18:1 triglyceride
12.	Sunflower Seed Oil	*Helanthus annus*	8001-21-6	C18:2 triglyceride
13.	Grape Seed Oil	*Vitis vinifera*	8024-22-4	C18:3 triglyceride
14.	Safflower Oil	*Carthamus tinctorius*	8001-23-9	C18:2 triglyceride
15.	Poppy Seed Oil	*Populus nigra*	8002-11-7	C18:2 triglyceride
16.	Sweet Almond Oil	*Prunnus amygdalus dulcis*	8007-69-0	C18:1 triglyceride
17.	Hazelnut Oil	*Corylus americana*	185630-72-2	C18:1 triglyceride
18.	Walnut Oil	*Juglans regia*	8024-00-2	C18:2 triglyceride
19.	Olive Oil	*Olea europasa*	8001-25-0	C18:1 triglyceride
20.	Avocado Oil	*Persea gratissima*	8024-32-6	C18:1 triglyceride
21.	Sesame Oil	*Sesamum indicum*	8008-74-0	C18:1 triglyceride
22.	Tall Oil	Tallol	8002-26-4	C18:1 fatty acid
23.	Cottonseed Oil	*Gossypium*	8001-29-4	C18:2 triglyceride
24.	Palm Oil	*Elaesis guineensis*	8002-75-3	C18:1 triglyceride
25.	Rice Bran Oil	*Oryza sativa*	68553-81-1	C18:1 triglyceride
26.	Canola Oil	Canola	8002-13-9	C18:1 triglyceride
27.	Apricot Kernel Oil	*Prunus armeniaca*	72869-69-3	C16 triglyceride
28.	Cocoa Butter	*Theobroma cao*	8002-31-1	C18 C18:1 triglyceride
29.	Shea Butter	*Butyrospermum parkii*	977026-99-5	C18 triglyceride
30.	Wheat Germ Oil	*Triticum vulgare*	8006-95-9	C18:2 triglyceride
31.	Illipe Butter	*Bassia latifola*	68424-60-2	C18 triglyceride
CLASS 6: Products rich in carbon chain lengths greater than C-18				
32.	Meadowfoam Seed Oil	*Limnanthes alba*	153065-40-8	C20:1 triglyceride
33.	Rapeseed Oil	*Brassica capmestris*	8002-13-9	C22:1 triglyceride
CLASS 7: Products having unusual carbon chain lengths or composition				
35.	Borage Seed Oil	*Borago officinalis*	8401201608	C18:3 (n=6) triglyceride
36.	Linseed Oil	*Linum usitatissimum*	8001-26-1	C18:3 (cong) triglyceride
37.	Castor Oil	*Ricinus communis*	8001-79-4	C18:1 OH triglyceride
38.	Veronia Oil	*Veronia galamensis*	169360-96-7	C18 epoxy triglyceride
39.	Tung Oil	*Aleurites fordii*	8001-20-5	C13:3 (cong) triglyceride
40.	Jojoba Oil	*Buxus chinensis*	61789-91-1	C20 ester
41.	Candelilla Wax	*Euphorbia cera*	8006-44-8	C31 hydrocarbon
42.	Ongokea Oil	*Ongokea gore*		C18:3 acetylenic triglyceride

determines the properties of the oil. One must carefully consider if the desired ingredient, tocopherol, antioxidant or whatever else that is present in the starting oil is removed during subsequent processing and therefore does not provide a benefit in the finished product. Simply put just because the material is in the oil as expressed, does not mean it is present in the final refined oil added to the cosmetic.

The oils covered in this article are referred to as 'vegetable oils'. This differentiates them from 'essential oils', which are often aromatic oils obtained by steam extraction from a variety of plant parts, including flowers, leaves, peels and some seeds. The essential oils are not triglycerides like the vegetable oils, but usually 'isoprenoids'; that is, they come from a different chemical pathway in plants. Plants store vegetable oils (triglycerides) as energy sources for seeds when they germinate.

Steam works well to extract essential oils like coriander oil, but not for triglyceride oils. Triglyceride and wax ester oils can be squeezed out of seeds using a turning screw that presses the mashed up seed against a metal barrel with slits in the side. The oil and some fine particles squeeze out the narrow slits. The tool used for this operation is called an oil expeller, or seed oil press. The oil from the seed oil press can be filtered and called 'virgin' oil, especially if it is not heated up to obtain more oil. The oil from the seed oil press can also be called crude oil. The cold pressing process preserves most of the oil soluble actives in the resulting oil.

Almost every other process practiced on the oil removes some component. Odour and tocopherols are removed from soybean oil by steam distillation.

Olive oil has been consumed for thousands of years.

The resulting distillate is used to deodorise the oil, but also leads to a major source of tocopherol that ends up in natural vitamin E. This means the soybean oil that is treated by steam distillation is almost devoid of tocopherol.

Alternatively, oil is dissolved in solvent, extracted, and followed by evaporating of the solvent leaving the extracted oil. In this type of operation seeds are often flaked to increase surface area. The seeds are processed into thin flakes before pressing or solvent extraction. The flaking improves oil yield by breaking open the small oil pockets in the seeds. Sometimes the seeds are heated before flaking so that the proteins in the seed will not break down the oil or other parts of the seed. The pre-heating is also called preconditioning. The oil comes out more easily if it is hot, but too much heat damages the oil quality.

Sometimes the seeds are crushed and formed into pieces called 'collets' that have lots of holes or openings. This step also is done before solvent extraction to make the oil easier to flow out. Solvent extracted oil with some solvent still in it is called the 'miscella'.

Crude oil usually can be good enough for chemical uses. A well-filtered 'virgin' oil can be kept cold to remove any solid waxes that might crystallise out in a process called 'winterisation'. Many cosmetics applications, which retain the actives from the oil, are cold-pressed, virgin oil.

Refining is done by filtering the oil through clay or silica (like fine sand), which can remove colour. In an operation called 'degumming', alkali in water is added to the oil; some ingredients, especially fatty acids and one called 'phospholipids', go into the water and settle out or are filtered out. Finally, steam can be passed through the oil to remove odour in an operation called deodorisation. This step also breaks down oxygen attached to the oil, which might lower oil quality.

Hopefully, after all of this refining, the oil is light in colour, has no odour, no oxygen breakdown products and no solid wax. The amount of oil you have left after refining is often related to the amount of crude oil you started with, or to the amount of oil in the seed by the 'yield' of oil from each step in the process.

The oils that are commonly used in cosmetic products are complex mixtures of different triglycerides, but also contain various other useful components. For example, wheat germ oil can be processed to obtain highly desirable tocopherols. Solvent extraction or steam distillation would remove much of this material. The winterising of oils, that is, cooling and

Steam works well to extract essential oils like coriander oil.

filtration of solids from the liquid, results in a loss of the higher molecular weight fractions. Many times it is exactly these fractions that provide the unique skin feel or conditioning to the product. It should be clear that the different processes used in the oil preparation may be critical to its functionality.

Olive oil[10]

Olive oil has been consumed for thousands of years. It makes a good example of how oils are processed and the various olive oils that are commercial.

All production begins by transforming the olive fruit into olive paste by crushing or pressing. This paste is then malaxed (slowly churned or mixed) to allow the microscopic oil droplets to agglomerate. The oil is then separated from the watery matter and fruit pulp with the use of a press (traditional method) or centrifugation (modern method).

After extraction the remnant solid substance, called pomace, still contains a small quantity of oil. The grades of oil extracted from the olive fruit can be classified as:

- **Virgin** means the oil was produced by the use of mechanical means only, with no chemical treatment. The term virgin oil with reference to production method includes all grades of virgin olive oil, including extra virgin, virgin, ordinary virgin and lampante virgin olive oil products, depending on quality (see next section).
- **Lampante virgin oil** is olive oil extracted by virgin (mechanical) methods but not suitable for human consumption without further refining; lampante is Italian for 'glaring', referring to the earlier use of such oil for burning in lamps. Lampante virgin oil can be used for industrial purposes, or refined (see below) to make it edible.
- **Refined olive oil** is the olive oil obtained from any grade of virgin olive oil by refining methods that do not lead to alterations in the initial glyceride structure. The refining process removes colour, odour and flavour from the olive oil, and leaves behind a very pure form of olive oil that is tasteless, colorless and odorless and extremely low in free fatty acids. Olive oils sold as the grades extra-virgin olive oil and virgin olive oil therefore cannot contain any refined oil.
- **Crude olive pomace oil** is the oil obtained by treating olive pomace (the leftover paste after the pressing of olives for virgin olive oils) with solvents or other physical treatments, to the exclusion of oils obtained by re-esterification processes and of any mixture with oils of other kinds. It is then further refined into refined olive pomace oil and once re-blended with virgin olive oils for taste, is then known as olive pomace oil. PC

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