

Chemistry of the Sun, Vitamin D and Sunscreen

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Everyone has heard of the benefits and downfalls of sun exposure. In this note, we will take a closer look at the science of sunlight, sun exposure and sunscreen so that you can let the sun shine in without getting burned!

Introduction

The sun (or Sol), is at the center of our solar system, and all the planets, asteroids, and other objects are constantly rotating around it, due to its massive gravitational influence. The sun represents 99.86% of the mass of the entire solar system and its size is difficult to comprehend. Its diameter is over 100 times greater, and its mass is more than 300,000 times greater than the Earth's! If that isn't mind boggling enough, consider that our sun is actually a small to average sized star compared to some of the largest stars in the universe which can be upwards of 2,000 times larger than the sun (the size difference between an ant and a blue whale!).

The sun is composed of approximately 75% hydrogen and 25% helium. The huge mass of the sun has caused it to contract to its current size, and the enormous pressures at the center has made the sun's core around 160 times more dense than water. This results in very high pressure which leads to temperatures in the core of roughly 16 million degrees Kelvin. It's this combination of heat and pressure that fuels the nuclear reactions that produce the sunlight that we need to survive.

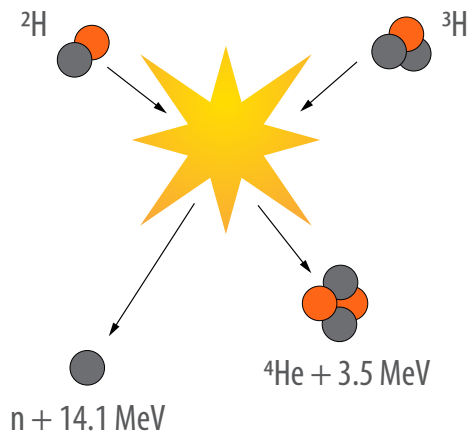


Figure 1. Fusion of deuterium and tritium to produce helium, a neutron, and massive amounts of energy
Source: https://en.wikipedia.org/wiki/Nuclear_fusion

The important solar reactions include pairs of hydrogen atoms moving at high velocity then fuse to form helium atoms (Figure 1). This reaction generates a huge amount of energy that escapes from the sun as sunlight. In this reaction, different isotopes of hydrogen (deuterium and tritium) collide and fuse to form molecules of helium, along with enormous amounts of energy. The sun fuses almost 40 billion tons of hydrogen into helium every minute.

The energy is released in the form of high-energy gamma rays, but these lose energy during their long trip through the sun and become sunlight by the time it reaches the Earth. These reactions occur in the sun's core and take tens of thousands of years for light to make its way through the layers of the sun and escape into the universe and provide sunlight (Figure 2).

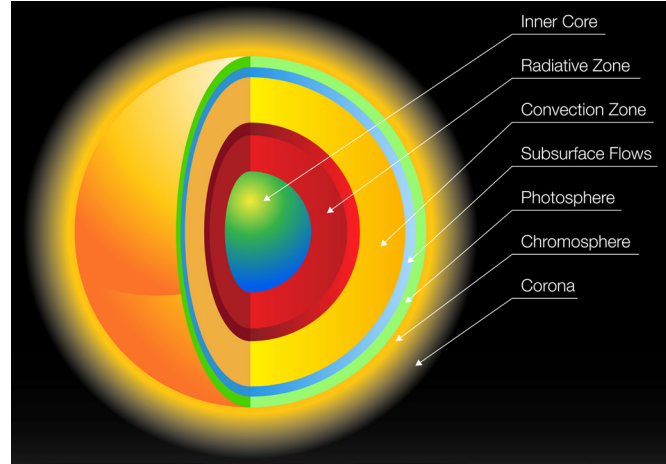


Figure 2. Layers of the sun

The sunlight that reaches us is just a small part of the electromagnetic (EM) spectrum. Its intensity is measured using a pyranometer, or a sunshine recorder. The Earth is over 92 million miles from the sun and receives approximately 1300-1450 watts per square meter (Wm^2) of solar radiation. The brightness of sunlight that reaches the Earth's surface is further filtered by the atmosphere. Damage to the atmosphere allows a higher percentage of higher frequency radiation to penetrate to the Earth's surface which can damage living species, including genetic mutations.

Electromagnetic Radiation and Light

The sun emits light across a wide spectrum of electromagnetic energy. But, the majority of light to reach Earth is in the range of 100 nm to 1 mm. This energy encompasses the ultraviolet ranges, visible light and the infrared spectrum (Figure 3).

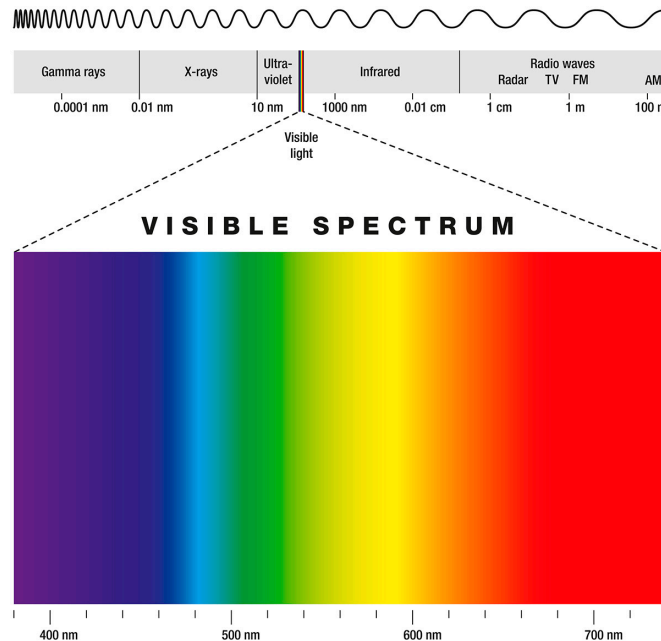


Figure 3. Electromagnetic spectrum

Most animals, including human beings, can only perceive light within the range of 400-700 nanometers which also gives us the perception of colors when they are absorbed by objects and reflect back as the opposite color (Table 1).

Table 1. Wavelengths of color

Wavelength (nm)	Color Absorbed	Color Observed
400-435	Violet	Yellow-Green
435-480	Blue	Yellow
480-490	Green-Blue	Orange
490-500	Blue-Green	Red
500-560	Green	Purple
560-580	Yellow-Green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-Blue
605-700	Red	Blue-Green

Wavelengths that are longer than the visible range of humans are infrared (IR) and microwave, which are even longer wavelengths. IR radiation is divided into Infrared-A (700-1400 nm), Infrared-B (1400 to 3000 nm) and Infrared-C (3000 nm to 1 mm). IR radiation is used in a wide variety of applications including scientific and industrial equipment, law enforcement, and medical devices. One of the common uses for IR is in the application of contactless thermometers during the COVID-19 pandemic.

Beyond IR is microwave radiation, which has wavelengths of 1 mm to 1 m. Microwaves are familiar to all of us for the use in ovens, but they are also commonly used in various communication applications, such as broadband and Bluetooth networking and satellite television.

Wavelengths shorter than visible light include ultraviolet (UV 10-400 nm), x-rays (0.01 nm-10 nm), and finally gamma radiation (0.0001-0.01 nm). As the wavelength gets smaller, the potential effects on humans increase. X-rays and gamma rays, of all wavelength, are dangerous to humans; whereas, higher wavelengths of UV are less dangerous, as long as you don't look directly at them.

Ultraviolet radiation is further divided into three categories of decreasing wavelength: Ultraviolet-A (UVA) from 315-400 nm, Ultraviolet-B (UVB) from 280-315 nm, and Ultraviolet-C (UVC) from 100-280 nm. UVA was frequently used in artificial tanning before it was discovered to cause formation of free radicals and reactive oxygen. UVB is absorbed, to a large extent (along with UVC), by the Earth's atmosphere. UVB and UVC are responsible for converting oxygen in the atmosphere into ozone. UVB is a double-edged sword, it is needed for the production of ozone and the production of Vitamin D in the body, but it is also the leading cause for sunburn and DNA damage leading to cancer. UVB is very photoreactive and can cause unwanted DNA changes in the photoreactive cells of the epidermis, such as melanocytes and basal cells. UVA has the longest wavelength and penetrates beyond the skin's hypodermis into the deeper dermis and can also change the DNA of skin cells, but not to the same degree as UVB radiation (Figure 4).

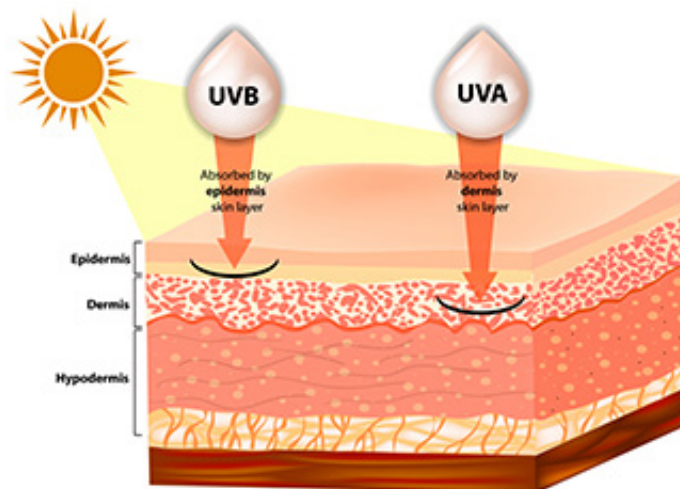


Figure 4. Skin depth penetration of UVA and UVB radiation

Vitamin D Structure and Function

Vitamin D is a group of key essential nutrients that the body requires for the absorption of several minerals including calcium, magnesium and phosphates. Humans get much of their required Vitamin D from their diet, but a significant amount is produced by the body, through the action of sunlight. All forms of Vitamin D are secosteroids (meaning cut-out from steroids), and they are all biosynthesized by light-induced breakdown of a steroid.

Of the 5 well-known forms of Vitamin D, the most important are ergocalciferol (Vitamin D2) and cholecalciferol (Vitamin D3). Vitamin D2 is produced by plants, while humans can make their own Vitamin D3. The steroid precursor used by plants to make Vitamin D2 is ergosterol, and the mammalian precursor of Vitamin D3 is 7-Dehydrocholesterol (Figure 5). Both vitamins are synthesized in a multi-step process that begins with the action of light on the corresponding steroid.

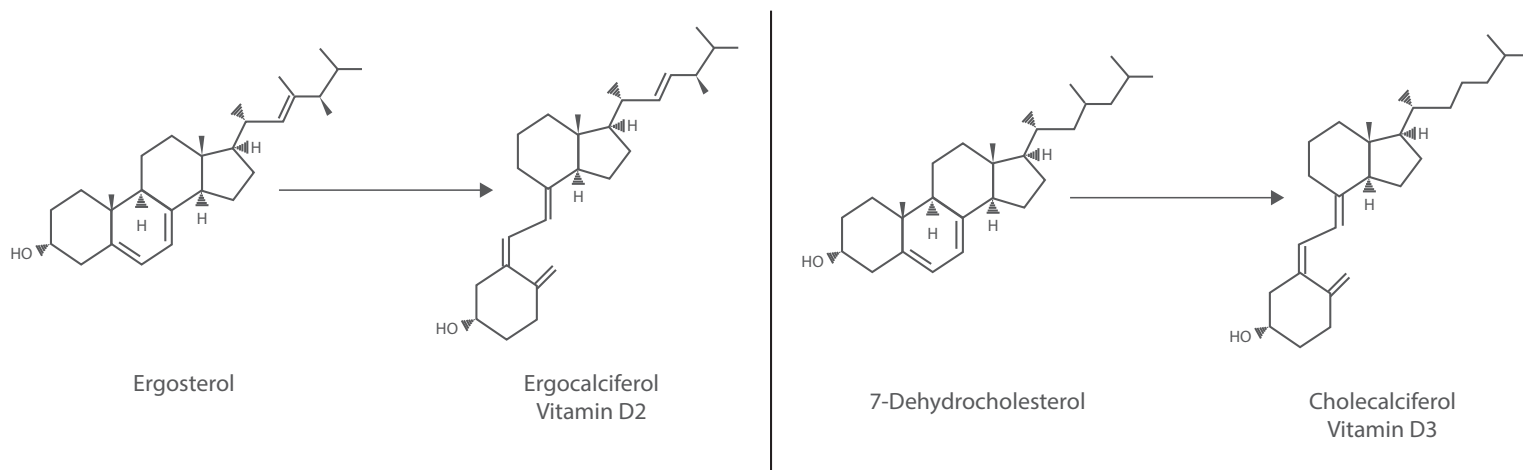


Figure 5. Important Vitamin D forms for human

Vitamin D2

Vitamin D2 is produced in plants, chiefly mushrooms and algae. Ergosterol resides in the cell membrane of these organisms. This steroid serves many of the same purposes as cholesterol in mammalian cells. In fact, the enzymes that synthesize this essential ergosterol have been targeted successfully as anti-fungicides.

Vitamin D3

Vitamin D3 is synthesized by both plants and animals in a similar process as Vitamin D2. In this case, the steroid precursor, 7-dehydrocholesterol, is stored in the skin, and the absorption of sunlight through the skin starts the biochemical pathway.

Table 2. CAS numbers for the various forms of Vitamin D and their precursors

Form	Chemical Composition	CAS #
Vitamin D1	Mixture of Ergocalciferol with Lumisterol, 1:1	520-91-2
Vitamin D2	Ergocalciferol	50-14-6
Vitamin D3	Cholecalciferol	67-97-0
Vitamin D4	22-Dihydroergocalciferol	511-28-4
Vitamin D5	Sitocalciferol	71761-06-3
Precursor	Ergosterol	57-87-4
Precursor	7-Dehydrocholesterol	434-16-2
Precursor	7-Dehydrositosterol	521-04-0
Precursor	Cholesterol	57-88-5

Vitamin D Production and the Skin

Human skin has many different layers grouped under two main sections called the epidermis and the dermis. The inner layer, called the dermis, is comprised of connective tissues. The outer layer, called the epidermis, has five layers or strata starting at the outermost later exposed to the environment (stratum corneum) to the innermost layer atop the dermis (stratum basale) (Figure 6).

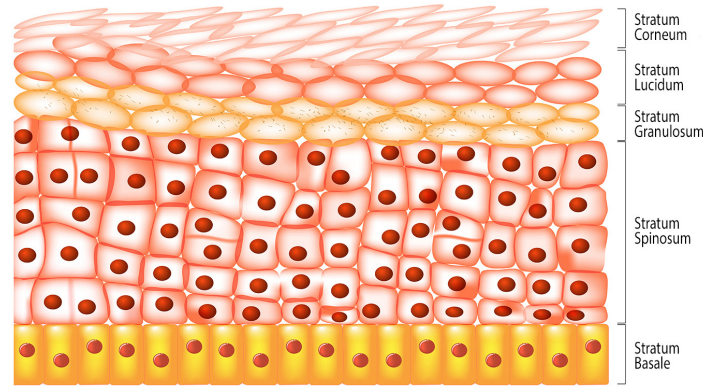


Figure 6. Stratum of the epidermis

The precursor, 7-dehydrocholesterol (7-DHC), is located in the lower layers of the epidermis (stratum spinosum and basale). Ultraviolet light penetrates the skin and breaks the bonds that connects the A and C ring of the steroid ring. The resulting adduct is further photolyzed by the UV radiation (primarily UVB) at 290-315 nm to cause isomerization to form cholecalciferol (Vitamin D3) (Figure 7). The amount of Vitamin D3 created depends on the amount of melanin present in the skin and the amount of exposure to UVB radiation.

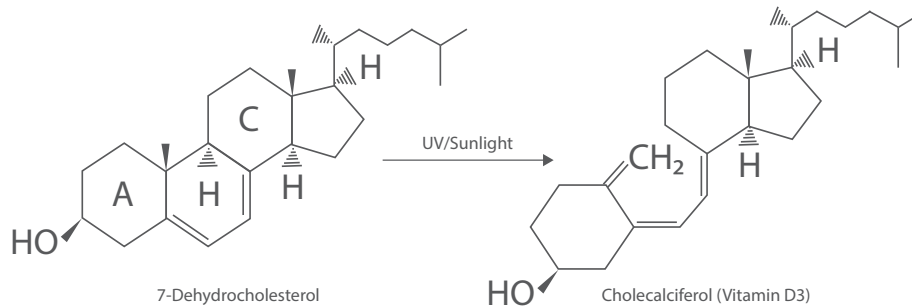


Figure 7. First steps in biosynthesis of Vitamin D production and use

These forms of Vitamin D2 and D3 are not biologically active at this stage. They must be activated in the liver and kidneys by two hydroxylation steps. Vitamin D2 and D3 are hydroxylated to 25-hydroxyergocalciferol and calcifediol in the liver, respectively. Calcifediol is later hydroxylated further in the kidneys to create calcitriol. Calcitriol is a hormone that circulates in the blood and regulates concentrations of minerals such as calcium.

Theoretically, Vitamin D can be synthesized by humans in sufficient amounts when exposed to enough sunlight. Despite that fact, there is a chronic Vitamin D deficiency in many populations due to age, skin color, vitamin absorption problems, or lack of sun exposure. This problem is further complicated by the type of radiation needed for the synthesis of Vitamin D, UVB. UVB radiation is of most concern for skin irritation, sunburn and skin cancer since it can alter DNA. Common practices are to apply sunscreen to filter out a large portion of the UVB radiation from entering the body which can lessen or prolong adequate Vitamin D production.

Sunblock and Sunscreens

Sunblock are formulations of chemicals and bases to prevent the passage of various ultraviolet radiations into the body through the skin. Usually sunblock contains a compound like titanium dioxide or zinc oxide which creates a physical barrier on the skin that prevents rays from entering the skin. Sunscreens are composed of chemicals that can have some ability to interact or disperse the radiation as it penetrates the skin. The U.S. Food and Drug Administration regulates sunblock and sunscreens as drugs. The FDA has approved more than a dozen active compounds to block radiation. Most of these compounds are approved to block UVB radiation, and fewer are approved to block UVA. The FDA also regulates the labeling of sunscreen requiring information such as the sun protection factor or SPF. SPF gives an estimated time of sun protection relative to the time it would take to typically burn. The effectiveness of sunscreen can be mitigated by not using enough, or not reapplying after sweating or activities in the water.

The SPF numbers on sunscreen are sometimes misleading. The protection factor for sunscreen is not linear and the amount of protection does not increase linearly with a corresponding increase in factor. SPF 2 means that it filters half of the radiation (which radiation depends on the compound) or about 50%, while SPF 15 products filter 1/15 of the radiation, or about 93%. Jumping to SPF 30 only increases the filtration from 93% to 97% (Figure 8).

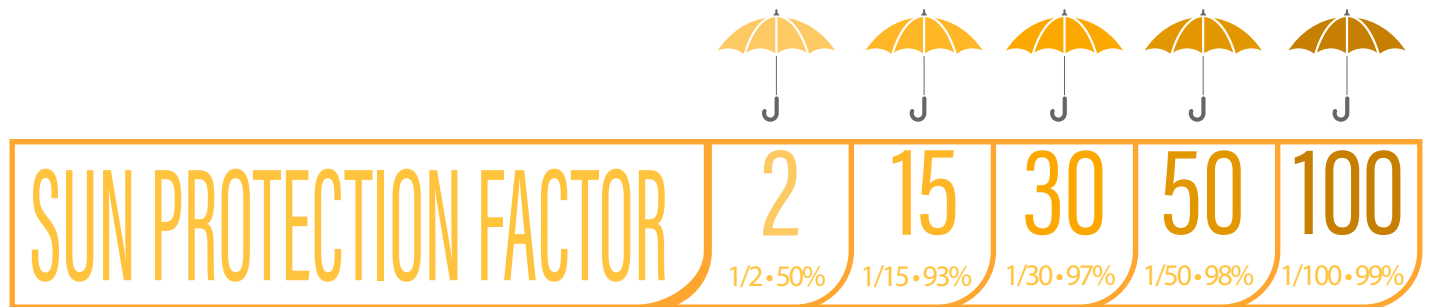


Figure 8. SPF factors and skin protection

The chemicals in sunscreens can vary widely with brand or type. The following list of active chemical compounds found in sunscreen formulas are approved by FDA legislation and the EU (Table 3).

Table 3. Accepted sunscreen compounds according to the FDA (US) and the EU

US	UVA	UVB	Additional Compounds for EU	UVA	UVB
p-Aminobenzoic acid (PABA)		X	4-Methylbenzylidene camphor		X
Avobenzene	X		Bisotrizole	X	X
Cinoxate	X	X	Bemotrizinol	X	X
Dioxybenzone	X	X	Drometrizole trisilozane	X	X
Homosalate		X	Bisdisulizole disodium	X	
Methyl anthranilate	X		Diethylamino hydroxybenzoyl hexyl benzoate	X	
Octocrylene	X	X	Octyl triazone		X
Octyl methoxycinnamate		X	Iscotrizinol		X
Octyl salicylate		X	Polysilicone-15		X
Oxybenzone	X	X	Isoamyl p-methoxycinnamate		X
Padimate O		X			
Phenylbenzimidazole sulfonic acid		X			
Sulisobenzene	X	X			
Titanium dioxide		X			
Trolamine salicylate		X			
Zinc oxide	X	X			
Ecamsule	X				

Sunscreens can contain other ingredients to provide fragrance, moisture or other benefits. Many of these additional compounds can possibly cause irritations or allergic reactions. The European Union has designated a list of several thousand compounds prohibited or restricted for use in cosmetics. In particular, the EU has issued lists of perfumes and fragrance compounds which are known or suspected allergens. List A contains perfume and fragrance chemicals that are the most frequently reported allergens. List B contains perfume and fragrance chemicals which have a possibility of causing allergic reactions (Table 4).

Table 4. *Perfume and fragrance chemicals known or believed to be allergens*

List A	CAS #	List B	CAS #
Amyl cinnamal	122-40-7	Anisyl alcohol	105-13-5
Amylcinnamyl alcohol	101-85-9	Benzyl benzoate	120-51-4
Benzyl alcohol	100-51-6	Benzyl cinnamate	103-41-3
Benzyl salicylate	118-58-1	Citronellol	106-22-9
Cinnamyl alcohol	104-54-1	Farnesol	4602-84-0
Cinnamal	104-55-2	Hexyl cinnamaldehyde	101-86-0
Citral	5392-40-5	Lilial	80-54-6
Coumarin	91-64-5	d-Limonene	5989-27-5
Eugenol	97-53-0	Linalool	78-70-6
Geraniol	106-24-1	Methyl heptine carbonate	111-12-6
Hydroxycitronellal	107-75-5	3-Methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	127-51-5
Hydroxymethyl pentyl-cyclohexene carboxaldehyde	31906-04-4	Oak moss extract	90028-68-55
Isoeugenol	97-54-1	Treemoss extract	90028-67-4

Final Thoughts

The benefit of sunlight to animals and people is well documented from aiding in mood to creating Vitamin D in the skin. The past decades have seen increases in solar radiation from damage to the atmosphere. Exposure to UV radiation can have both harmful and beneficial effects. The balance becomes allowing beneficial exposure without increasing risk of overexposure, sunburn or skin cancer. To this end, the recommendations of health officials are short exposures in increments less than about fifteen minutes and to apply and reapply sunscreen regularly. Popular advice is to be cognizant of your skin type and the time of day for your exposure since fair skinned individuals with less melanin, and those who are exposed at times of increased radiation (middle of the day) are prone to more exposure. Those individuals who are allergic to many types of chemicals or products should be aware of potential allergens in sunscreens from fragrances and other cosmetic additions.

Spex CertiPrep is your source for all of your Vitamin D, sunscreen compounds and allergen standards. Contact us to inquire about standards for any of the compounds mentioned in this paper.

Appendix

We now make custom vitamin standards. See our list of possibilities below. If what you need is not on our list, contact us to discuss your specific needs and we will determine if we can make it for you.

Vitamin Group	Compound	CAS #
Vitamin A	Retinol	68-26-8
Vitamin A	beta-carotene	7235-40-7
Vitamin B1	Thiamine	70-16-6
Vitamin B2	Riboflavin	83-88-5
Vitamin B3	Niacin	59-67-6
Vitamin B3	Nicotinamide	98-92-0
Vitamin B7	Biotin	58-85-5
Vitamin B7 (France)	Inositol	87-89-8
Vitamin B8 (US)	Inositol	87-89-8
Vitamin B9	Folic acid	59-30-3
Vitamin B12	Cyanocobalamin	68-19-9
Vitamin C	Ascorbic acid	50-81-7
Vitamin D2	Ergocalciferol (D2)	50-14-6
Vitamin D3	Cholecalciferol (D3)	67-97-0
Vitamin E	alpha-Tocopherol	59-02-9
Vitamin E	beta-Tocopherol	490-23-3
Vitamin E	delta-Tocopherol	119-13-1
Vitamin E	gamma-Tocopherol	54-28-4
Vitamin K1	Phytomenadione	84-80-0
Vitamin K3	Menadione	58-27-5