

1: Steroid - Wikipedia

Also, referred to as terpenoids or prenyl lipids, isoprenoids are any of a class of organic compounds composed of two or more units of hydrocarbons, with each unit consisting of five carbon atoms arranged in a specific pattern. These compounds are derived from five-carbon isoprene units and are.

General Information[edit] Isoprene, the basic building block of isoprenoids. Also, referred to as terpenoids or prenyl lipids, isoprenoids are any of a class of organic compounds composed of two or more units of hydrocarbons, with each unit consisting of five carbon atoms arranged in a specific pattern. These compounds are derived from five-carbon isoprene units and are biosynthesized from a common intermediate known as mevalonic acid, which is itself synthesized from acetyl-CoA. These lipids are considered to be the largest group of natural products, playing a wide variety of roles in physiological processes of plants and animals, and having a number of commercial uses. In living organisms, these compounds range in function from pigmentation and fragrances to vitamins and precursors of sex hormones. Uses in industrial settings range from flavorings, solvents and raw materials for chemicals. These compounds are more commonly associated with being the main ingredients of perfumes and incense. But these are just a few of the many commercial uses for isoprenoids, which to this day are still expanding. Isoprenoid Isolation and Identification[edit] Isolation of isoprenoids from their natural sources is achieved through numerous procedures. Substances that are volatile and plentiful, such as turpentine, are best obtained by distillation of oleoresins. Rosin acids and fatty acids, which occur together in tall oil, are separated by fractional distillation at reduced pressure. Other compounds that are more on the rare side are best isolated by chromatography. A very laborious process known as enfleurage is employed for the isolation of heat-sensitive perfume ingredients. This process involves carefully placing the petals containing the oily isoprenoids in thin layers of purified fat to dissolve the oils. The oils are then recovered from the fat by washing the solution with alcohol. Physical properties of an isoprenoid compound are the main factor that must be looked at to identify the best purification technique that will yield the best results. A heat-sensitive compound will not be efficiently and successfully purified with techniques such as distillation or sublimation, which require heat. Similar compounds in one source are best isolated and purified by treatment into a mixture of new substances that can be more readily separated. After separation, the original products can be attained by reconvertng them. Generally, solid compounds can be purified by recrystallization and volatile compounds solid or liquid are best purified by distillation. Similar and nonvolatile substances might require chromatography to best achieve separation. The determination of the elemental composition of isoprenoids is not a difficult task due to their simple hydrocarbon makeup and the availability of simple and reliable procedures for quantitative analysis of carbon and hydrogens. The presence of the other element in these compounds, oxygen, does not interfere with the analysis of the carbon and hydrogen makeup in a significant way, but does make it a more laborious task. A particularly difficult compound that was difficult to determine throughout the history of isoprenoid studies was camphor, which had a total of more than 30 different structures presented before the correct one was found. Structures are more commonly identified by using nuclear magnetic resonance NMR. This technique uses the help of a magnetic field to generate a response of the compound to this energy. This data is then collected and interpreted computer analysis gives the best results to this day. High-resolution mass spectrometry enables the exact chemical formula of a compound to be determined, while X-ray crystallography permits the detailed spatial location of each atom to be determined from a diffraction pattern of the crystallized form of the structure. Structural Features and Some Isoprenoid Compounds[edit] The five-carbon unit that constitutes the basic building block of isoprenoids is a hydrocarbon called isoprene. This compound is a branched-chain unsaturated hydrocarbon, meaning it has one or more double bonds between carbon atoms. Isoprenoids can have one or more functional chemical groups attached to their carbon backbone, such as hydroxyls and carbonyls, which make up the diversity of isoprenoids. The dashed line indicates the bonding location. The dashed line indicates the bonding locations. Monoterpenes C₁₀H₁₆ [edit] The first isoprenoids that were studied initially in the history of these lipids were the monoterpenes, the molecules of which contain 10 carbon

atoms. These compounds are isolated from their natural sources by distillation of the plant matter with steam. Fractional distillation at reduced pressures work best at purifying these compounds. Some widely known monoterpene derivatives include the oxygenated acyclic monoterpene derivative citronellol and its corresponding aldehyde citronellal, which occur in oil of citronella. Others include the compound citral, which is found in lemongrass oil and geraniol, most commonly found in Turkish geranium oil. Some common monoterpene derivatives. The process used to convert citronellal is widely used commercially to supplement the natural sources of menthol, since this process produces a mixture of stereoisomeric menthols by catalytic hydrogenation. Citral is used in the production of rose-scented perfumes. The reduction of citral with sodium amalgam yields a compound called geraniol, which is responsible for the scent. Sesquiterpenes $C_{15}H_{24}$ [edit] Sesquiterpenes are of lower volatility than monoterpenes and thus, can be isolated from their natural sources by extraction. Purification of these compounds involves either vacuum fractional distillation or chromatography. The oxygenated sesquiterpenes are the most commonly encountered ones. Sesquiterpenes may be acyclic or contain rings. A longer chain length and more double bonds contributes to a wide variety of cyclization structures. For example, there are two arrangements of isoprene units found in bicyclic sesquiterpenes: Forms of bicyclic sesquiterpenes. Diterpenes $C_{20}H_{32}$ [edit] Diterpenes are known to be antimicrobial and antiinflammatory. They derive from geranylgeranyl pyrophosphate. One well known diterpene is phythol, an oxygenated acyclic diterpene that is the building block of the chlorophyll molecule. This compound is obtained on treatment with an alkali solution. Phythol is similar to vitamin A in terms of arrangement of their isoprene units head-to-tail arrangement. Another common diterpene is the commercially utilized tricyclic abietic acid. This compound is a carboxylic acid that constitutes the major portion of rosin. Rosin is the residue left after the isolation of turpentine and is the nonvolatile portion of the oleoresin of members of the pine family. It is used in the production of varnish and coating materials, among many other products. The versatility of this compound was discovered due to it being one of the cheapest organic acids available. Triterpenes $C_{30}H_{48}$ [edit] An example of a triterpene is the acyclic hydrocarbon squalene pictured above. This constitutes more than half of the liver oil of certain species of sharks and is otherwise, widely distributed in nature. Among shark liver oil, is it found in other fish liver oils, vegetable oils, fungi, and in human earwax. Squalene is a metabolic intermediate in the biosynthesis of cholesterol. The most common types of triterpenes found in nature are those having five carbon rings. Its skeletal structure shares many similarities with that of squalene and cholesterol.

2: Terpenes, terpenoids

Lipids. The lipids are a large and diverse group of naturally occurring organic compounds that are related by their solubility in nonpolar organic solvents (e.g. ether, chloroform, acetone & benzene) and general insolubility in water.

Classification of Lipids Simple Lipids Triglycerides, neutral fats: Found in adipose tissue, butterfat, lard, suet, fish oils, olive oil, corn oil, etc. Esters of three molecules of fatty acids plus one molecule of glycerol; the fatty acid may all be different. Composed of esters of fatty acids with alcohol other than glycerol; of industrial and medicinal importance. Compound Lipids Phospholipids phosphatides: Found chiefly in animal tissues. Substituted fats, consisting of phosphatidic acid; composed of glycerol, fatty acids, and phosphoric acid bound in ester linkage to a nitrogenous base. Found in brain, egg yolk, and organ meats. Phosphatidyl choline or serine; phosphatide linked to choline; a lipotropic agent; important in fat metabolism and transport; used as emulsifying agent in the food industry. Occurs predominantly in nervous tissue. Phosphatidyl ethanolamine; phosphatide linkage to serine or ethanolamine; plays a role in blood clotting. Found in brain, heart, and muscle. Phosphatidyl ethanolamine or choline; phosphatide containing an aliphatic aldehyde. Found in brain, heart, kidneys, and plant tissues together with phytic acid. Phosphatidyl inositol; phosphatide linked to inositol; rapid synthesis and degradation in brain; evidence for role in cell transport processes. Found in nervous tissue, brain, and red blood cells. Sphingosine-containing phosphatide; yields fatty acids, choline, sphingosine, phosphoric acid, and no glycerol; source of phosphoric acid in body tissue. Yields on hydrolysis of fatty acids, sphingosine, galactose or glucose, but not fatty acids; includes kerafin and phrenosin. Sulfur-containing glycolipid; sulfate present in ester linkage to galactose. Complexes of protein and lipids having solubility properties of lipids. Terpenoids and Steroids Terpenes: Found in essential oils, resin acids, rubber, plant pigments such as carotenoids and lycopenes, Vitamin A, and camphor. Large group of compounds made up of repeating isoprene units; Vitamin A of nutritional interest; fat soluble Vitamin E and K, which are also related chemically to terpenes. A constituent of bile acids and a precursor of Vitamin D. Converted to Vitamin D₂ on irradiation. Converted to D₃ on irradiation. Sex hormones Found in ovaries and testes. Derived lipids Fatty acids: Obtained from hydrolysis of fats; usually contains an even number of carbon atoms and are straight chain derivatives. Classification of fatty acids is based on the length of the carbon chain short, medium, or long; the number of double bonds unsaturated, mono-, or polyunsaturated; or essentiality in the diet essential or non-essential. A current designation is based on the position of the endmost double bond, counting from the methyl CH₃ carbon, called the omega end. The most important omega fatty acids are: Omega 6 " linolein and arachidonic acids and Omega 3 " linolenic, eicosapentaenoic, and docosahexaenoic acids. Sample nomenclature for fatty acids: Name " Carbon Length: Number of Double Bonds position of double bond.

3: What are terpenoid lipids? | Socratic

Compounds composed of isoprene subunits may be called isoprenoids or terpenoids, and come in a variety of sizes and structures, both cyclic and acyclic. Biosynthesis of terpenoids occurs by polymerization (process that combines several smaller molecules to form a larger one) of several C 5 isoprene subunits.

Abbott Australia New Zealand Food Authority, Canberra, Australia Evaluation Introduction Estimated daily per capita intake Absorption, metabolism, and elimination Application of the Procedure for the Safety Evaluation of Flavouring Agents Consideration of combined intakes from use as flavouring agents Conclusions Relevant background information Biological data Absorption and metabolism Toxicological studies Acute toxicity Short-term and long-term studies of toxicity and carcinogenicity Genotoxicity Other relevant studies References

1. The substances in this group are terpenoid ketones, secondary alcohols, and related esters containing a 2-menthyl carbon skeleton Table 1. The Committee previously evaluated carvone on several occasions. A conditional ADI of Owing to lack of data on - -carvone per se, the temporary ADI for - -carvone was not extended. Summary of the safety evaluation of carvone and structurally related substances used as flavouring agents Substance No. The estimated total daily per capita intake of carvone No. Seven of the substances in this group have been reported to occur naturally in foods, including fruits, spices, and berries. Quantitative data on the natural occurrence and consumption ratios have been reported for five of these substances Nos , , , , and , which indicate that they are consumed predominantly in traditional foods i. The group consists of three ketones Nos , , and , three secondary alcohols Nos , , and , and three esters Nos , , and Their structures are shown in Table 1. Terpenoid esters Each of the tthree esters would be expected to be hydrolysed to its corresponding alcohol and carboxylic acid by carboxylesterases, which predominate in hepatocytes. Esters of carveol Nos and and dihydrocarveol No. Terpenoid alcohols and ketones The terpenoid alcohols resulting from ester hydrolysis and their corresponding ketones are metabolized like other alicyclic terpenoid ketones and secondary alcohols. Five detoxification pathways have been identified: Most recent annual usage of carvone and structurally related substances as flavouring agents in Europe and the United States Substance No. According to the decision-tree structural class classification Cramer et al. Sufficient data were available on carvone to define the major pathways of metabolism. This compound contains all of the key structural elements and potential sites of metabolism of all other members in the group. Better data were available on the metabolism of isophorone 3,4,5-trimethyl-cyclohexenone , which is not a member of this group of flavouring agents but which shows close structural similarities to carvone and uses the same routes of metabolism reduction of the carbonyl group, conjugation of the resulting alcohol, and side-chain oxidation. For the three terpenoid esters in class I, the most likely route of metabolism is hydrolysis to carveol or dihydrocarveol. For the three terpenoid alcohols, carveol, dihydrocarveol, and para-menthanol, which are also in class I, the available data indicate that the most likely route of metabolism is conjugation with glucuronic acid, followed by excretion; however, other routes of metabolism such as side-chain oxidation followed by conjugation and excretion may also occur. For the three terpenoid ketones in class II, the available data indicate that the most likely route of metabolism is reduction of the ketone to the corresponding alcohol, followed by conjugation with glutathione and excretion. Other routes of metabolism may occur, such as side-chain oxidation followed by conjugation and direct conjugation of the ketone with glutathione. This substance therefore proceeds to step A4. Carvone is not endogenous in humans. Its safety evaluation therefore proceeds to step A5. Therefore, this substance would not be expected to be of safety concern. Table 1 summarizes the evaluations of the nine substances in this group. In using the procedure, the Committee noted that all of the available data on toxicity are consistent with the results of the safety evaluation. Evidence that this metabolic route is used for these esters comes from studies of related compounds, namely, the - -menthol esters, - -menthol ethylene glycol carbonate and - -menthol propylene glycol carbonate, which were completely hydrolysed after incubation with a rat liver homogenate Anon. Evidence for each of these pathway is given below: In rodents, but probably not in humans, the conjugate is excreted primarily into the bile, where it may be hydrolysed to yield the free alcohol Matthews, The alcohol may then enter enterohepatic circulation

and be excreted by the kidney Hamalainen, ; Tamura et al. The glucuronic acid conjugate of dihydrocarveol has been detected in the urine of rabbits Hamalainen, A racemic mixture of carvone was reported to undergo side-chain oxidation in rabbits. Urine collected over three days was separated into neutral, acidic, and phenolic fractions. Oxidation of the side-chain has been observed for other acyclic Nishizawa et al. Cytosolic glutathione S-transferase activity and acid-soluble sulfhydryl levels were measured in mouse liver, forestomach, lung, and small and large bowel mucosa. Carvone intake was associated with a decrease in glutathione content in the liver, lung, and large-bowel mucosa Zheng et al. Carvone rapidly conjugated with glutathione in the absence of glutathione S-transferase Portoghese et al. Details of the studies that were critical to the safety evaluation of carvone and related substances are given below. Acute toxicity of carvone and related substances tested by gavage Substance No. Short-term and long-term studies of the toxicity of carvone Species Sex No. Significant increases in serum cholesterol and triacylglycerol concentrations were reported in rats given carvone when compared with the controls. Significant decreases in food consumption and body weights were also reported in treated animals Imaizumi et al. Although the stereochemistry of the test material was unspecified, a survey of industrial producers of carvone who actively marketed carvone during the period of the study indicated that the material in commerce in the United States at that time was the - isomer Bauer, ; Flynn, ; Wrigley Co. Body weights and food intake were measured weekly and haematological examinations performed at 3, 6, 12, and 22 months. Although no effects were noted, only a very limited report of the results of this study was provided. The animals were necropsied 26 weeks after the initial dose of nitrosamine. Results of assays for the genotoxicity of carvone and related substances Substance No. Hydrogenation of unsaturated compounds in the animal body. Subacute and chronic toxicity. International Organization of the Flavor Industry European inquiry on volume of use. Unpublished report from the Research Institute for Fragrance Materials. Reduction and hydroxylation of camphor and related compounds. Qualitative and Quantitative Data, 7th Ed. Chemical basis for toxicity. Isolation and characterization of new metabolites. Its effects on microsomal enzymes in vivo. II Results from the testing of chemicals. A mechanism for setting priorities for safety evaluation. The influence of borneol, ionone and carvone on the urinary excretion of glucuronic acid and ascorbic acid. The biological reduction of l-menthone to d-neomenthol and of d-isomenthone to d-isomenthol in the rabbit. The conjugation of d-neomenthol with glucuronic acid.

4: Principles of Biochemistry/Biosynthesis of lipids - Wikibooks, open books for an open world

*Several of these substances belong to the triterpenoids and polysaccharides classes. Proteins, lipids, phenols, sterols, etc. are also present. In the present review, an extensive overview of the presence of antitumour, antimicrobial, antioxidant and antiacetylcholinesterase compounds in *G. lucidum* extracts will be given, along with an.*

By Thromboxane synthase into thromboxanes Prostaglandin E1 The three classes of prostanoids have distinctive rings in the center of the molecule. They differ in their structures. The PGH compounds parents to all the rest have a 5-carbon ring, bridged by two oxygens a peroxide. The derived prostaglandins contain a single, unsaturated 5-carbon ring. In prostacyclins, this ring is conjoined to another oxygen-containing ring. In thromboxanes the ring becomes a 6-member ring with one oxygen. Production of PGE2 in bacterial and viral infections appear to be stimulated by certain cytokines, e. The catalytic mechanism involves the insertion of an oxygen moiety at a specific position in the arachidonic acid backbone. The lipoxygenase pathway is active in leukocytes, including mast cells, eosinophils, neutrophils, monocytes, and basophils. When such cells are activated, arachidonic acid is liberated from cell membrane phospholipids by phospholipase A2, and donated by the 5-lipoxygenase-activating protein FLAP to 5-lipoxygenase. In cells that express LTC4 synthase, such as mast cells and eosinophils, LTA4 is conjugated with the tripeptide glutathione to form the first of the cysteinyl-leukotrienes, LTC4. The cysteinyl-leukotrienes act at their cell-surface receptors CysLT1 and CysLT2 on target cells to contract bronchial and vascular smooth muscle, to increase permeability of small blood vessels, to enhance secretion of mucus in the airway and gut, and to recruit leukocytes to sites of inflammation. The enzyme contains two active sites: The reaction proceeds through H atom abstraction from arachidonic acid by a tyrosine radical generated by the peroxidase active site. Two O2 molecules then react with the arachidonic acid radical, yielding PGG2. At present, three COX isoenzymes are known: Although both enzymes act basically in the same fashion, selective inhibition can make a difference in terms of side-effects. COX-1 is considered a constitutive enzyme, being found in most mammalian cells. COX-2, on the other hand, is undetectable in most normal tissues. It is an inducible enzyme, becoming abundant in activated macrophages and other cells at sites of inflammation. More recently, it has been shown to be upregulated in various carcinomas and to have a central role in tumorigenesis. However drug testing can be wildly inconsistent and, in some instances, has gone unenforced. Bile acid and its synthesis[edit] Bile acids are steroid acids found predominantly in the bile of mammals. Bile salts are bile acids compounded with a cation, usually sodium. In humans, the salts of taurocholic acid and glycocholic acid derivatives of cholic acid represent approximately eighty percent of all bile salts. The two major bile acids are cholic acid, and chenodeoxycholic acid. Bile acids, glycine and taurine conjugates, and 7-alpha-dehydroxylated derivatives deoxycholic acid and lithocholic acid are all found in human intestinal bile. An increase in bile flow is exhibited with an increased secretion of bile acids. The main function of bile acid is to facilitate the formation of micelles, which promotes processing of dietary fat. Bile acids are made in the liver by the cytochrome Pmediated oxidation of cholesterol. They are conjugated with taurine or the amino acid glycine, or with a sulfate or a glucuronide, and are then stored in the gallbladder, which concentrates the salts by removing the water. In humans, the rate limiting step is the addition of a hydroxyl group on position 7 of the steroid nucleus by the enzyme cholesterol 7 alpha-hydroxylase. Upon eating a meal, the contents of the gallbladder are secreted into the intestine , where bile acids serve the purpose of emulsifying dietary fats. Bile acids serve other functions, including eliminating cholesterol from the body, driving the flow of bile to eliminate catabolites from the liver, emulsifying lipids and fat soluble vitamins in the intestine to form micelles that can be transported via the lacteal system, and aiding in the reduction of the bacteria flora found in the small intestine and biliary tract. Bile acid refers to the protonated -COOH form. Bile salt refers to the deprotonated or ionized -COO- form. Conjugated bile acids are more efficient at emulsifying fats because at intestinal pH, they are more ionized than unconjugated bile acids. The body produces about mg of cholesterol per day and about half of that is used for bile acid synthesis. In total about grams of bile acids are secreted into the intestine daily. This allows a low rate of daily synthesis, but high secretion to the digestive system. Bile is also

used to break down fat globules into tiny droplets. Bile from slaughtered animals can be used in the preparation of soap. Lipids in membrane[edit] Space-filling models of sphingomyelin a and cholesterol b.

Phospholipids Phospholipids and glycolipids consist of two long, nonpolar hydrophobic hydrocarbon chains linked to a hydrophilic head group. The heads of phospholipids are phosphorylated and they consist of either: Glycerol and hence the name phosphoglycerides given to this group of lipids. Sphingosine with only one member - sphingomyelin. Glycolipids The heads of glycolipids contain a sphingosine with one or several sugar units attached to it. The hydrophobic chains belong either to: Fatty acids The fatty acids in phospho- and glycolipids usually contain an even number of carbon atoms, typically between 14 and The and carbon FAs are the most common ones. FAs may be saturated or unsaturated, with the configuration of the double bonds nearly always cis. Phosphoglycerides In phosphoglycerides, the hydroxyl groups at C-1 and C-2 of glycerol are esterified to the carboxyl groups of the FAs. The C-3 hydroxyl group is esterified to phosphoric acid. The resulting compound, called phosphatidate , is the simplest phosphoglycerate. Only small amounts of phosphatidate are present in membranes. However, it is a key intermediate in the biosynthesis of the other phosphoglycerides. Sphingosine Sphingosine is an amino alcohol that contains a long, unsaturated hydrocarbon chain. In sphingomyelin and glycolipids, the amino group of sphingosine is linked to FAs by an amide bond. In sphingomyelin the primary hydroxyl group of sphingosine is esterified to phosphoryl choline. In glycolipids, the sugar component is attached to this group. The simplest glycolipid is cerebroside , in which there is only one sugar residue, either Glc or Gal. More complex glycolipids, such as gangliosides , contain a branched chain of as many as seven sugar residues. Sphingosine is synthesized from palmitoyl CoA and serine in a condensation required to yield dehydrosphingosine Dehydrosphingosine is then reduced by NADPH to dihydrosphingosine sphinganine , and finally oxidized by FAD to sphingosine. There is no direct route of synthesis from sphinganine to sphingosine; it has to be acylated first to dihydroceramide , which is then dehydrogenated to ceramide. Sphingosine is formed via degradation of sphingolipid in the lysosome.

Cholesterol Cholesterol occurs naturally in eukaryote cell membranes where it is bio-synthesised from mevalonate via a squalene cyclisation of terpenoids. It associated preferentially with sphingolipids see diagram in cholesterol-rich lipid rafts areas of the membranes in eukaryotic cells. Top, an archaeal phospholipid: Middle, a bacterial or eukaryotic phospholipid: Archaeal membranes are made of molecules that differ strongly from those in other life forms, showing that archaea are related only distantly to bacteria and eukaryotes. These molecules possess both a polar part that dissolves in water the phosphate "head" , and a "greasy" non-polar part that does not the lipid tail. These dissimilar parts are connected by a glycerol moiety. In water, phospholipids cluster, with the heads facing the water and the tails facing away from it. The major structure in cell membranes is a double layer of these phospholipids, which is called a lipid bilayer [16]. These phospholipids are unusual in four ways: Bacteria and eukaryotes have membranes composed mainly of glycerol- ester lipids , whereas archaea have membranes composed of glycerol- ether lipids. In ester lipids this is an ester bond , whereas in ether lipids this is an ether bond. Ether bonds are chemically more resistant than ester bonds. This stability might help archaea to survive extreme temperatures and very acidic or alkaline environments. The stereochemistry of the glycerol moiety is the reverse of that found in other organisms. The glycerol moiety can occur in two forms that are mirror images of one another, called the right-handed and left-handed forms; in chemistry these are called enantiomers. Just as a right hand does not fit easily into a left-handed glove, a right-handed glycerol molecule generally cannot be used or made by enzymes adapted for the left-handed form. This suggests that archaea use entirely different enzymes for synthesizing phospholipids than do bacteria and eukaryotes. Archaeal lipids are based upon the isoprenoid sidechain and are long chains with multiple side-branches and sometimes even cyclopropane or cyclohexane rings. Although isoprenoids play an important role in the biochemistry of many organisms, only the archaea use them to make phospholipids. These branched chains may help prevent archaean membranes from leaking at high temperatures. In effect, the archaea fuse the tails of two independent phospholipid molecules into a single molecule with two polar heads; this fusion may make their membranes more rigid and better able to resist harsh environments. The basic molecular formulae of terpenes are multiples of that, $C_5H_8 n$ where n is the number of linked isoprene units. This is called the isoprene rule or the C5 rule. The isoprene units may be

linked together "head to tail" to form linear chains or they may be arranged to form rings. Isoprene itself does not undergo the building process, but rather activated forms, isopentenyl pyrophosphate IPP or also isopentenyl diphosphate and dimethylallyl pyrophosphate DMAPP or also dimethylallyl diphosphate, are the components in the biosynthetic pathway. An alternative, totally unrelated biosynthesis pathway of IPP is known in some bacterial groups and the plastids of plants, the so-called MEP 2-Methyl-D-erythritol phosphate pathway, which is initiated from C5-sugars. Dimethylallyl pyrophosphate Isopentenyl pyrophosphate As chains of isoprene units are built up, the resulting terpenes are classified sequentially by size as hemiterpenes, monoterpenes, sesquiterpenes, diterpenes, sesterterpenes, triterpenes, and tetraterpenes [23]. Mevalonate pathway and Statins[edit] The mevalonate pathway or HMG-CoA reductase pathway or mevalonate-dependent MAD route or isoprenoid pathway, is an important cellular metabolic pathway present in all higher eukaryotes and many bacteria. It is important for the production of dimethylallyl pyrophosphate DMAPP and isopentenyl pyrophosphate IPP, which serve as the basis for the biosynthesis of molecules used in processes as diverse as terpenoid synthesis, protein prenylation, cell membrane maintenance, hormones, protein anchoring, and N-glycosylation. It is also a part of steroid biosynthesis [24]. Several key enzymes can be activated through DNA transcriptional regulation on activation of SREBP sterol regulatory element-binding protein-1 and This intracellular sensor detects low cholesterol levels and stimulates endogenous production by the HMG-CoA reductase pathway, as well as increasing lipoprotein uptake by up-regulating the LDL-receptor.

5: Carvone and structurally related substances (WHO Food Additives Series 42)

TERPENOIDS INTRODUCTION Terpenoids (or isoprenoids), a subclass of the prenillipids (terpenes, prenylquinones, and sterols), represent the oldest group of small molecular products synthesized by plants and are probably the most widespread group of natural products.

History[edit] In , Henry Braconnot classified lipids graisses in two categories, suifs solid greases or tallow and huiles fluid oils. Theodore Gobley discovered phospholipids in mammalian brain and hen egg, called by him as " lecithins ". Thudichum discovered in human brain some phospholipids cephalin , glycolipids cerebroside and sphingolipids sphingomyelin. Hilditch divided lipids into "simple lipids", with greases and waxes true waxes, sterols, alcohols , and "complex lipids", with phospholipids and glycolipids. The fatty acid structure is one of the most fundamental categories of biological lipids, and is commonly used as a building-block of more structurally complex lipids. The carbon chain, typically between four and 24 carbons long, [21] may be saturated or unsaturated , and may be attached to functional groups containing oxygen , halogens , nitrogen , and sulfur. Cis-double bonds cause the fatty acid chain to bend, an effect that is compounded with more double bonds in the chain. Three double bonds in carbon linolenic acid , the most abundant fatty-acyl chains of plant thylakoid membranes, render these membranes highly fluid despite environmental low-temperatures, [22] and also makes linolenic acid give dominating sharp peaks in high resolution C NMR spectra of chloroplasts. This in turn plays an important role in the structure and function of cell membranes. Docosahexaenoic acid is also important in biological systems, particularly with respect to sight. Fatty esters include important biochemical intermediates such as wax esters , fatty acid thioester coenzyme A derivatives, fatty acid thioester ACP derivatives and fatty acid carnitines. The fatty amides include N-acyl ethanolamines , such as the cannabinoid neurotransmitter anandamide. Glycerolipids are composed of mono-, di-, and tri-substituted glycerols , [28] the best-known being the fatty acid triesters of glycerol, called triglycerides. The word "triacylglycerol" is sometimes used synonymously with "triglyceride". In these compounds, the three hydroxyl groups of glycerol are each esterified, typically by different fatty acids. Because they function as an energy store, these lipids comprise the bulk of storage fat in animal tissues. The hydrolysis of the ester bonds of triglycerides and the release of glycerol and fatty acids from adipose tissue are the initial steps in metabolizing fat. Examples of structures in this category are the digalactosyldiacylglycerols found in plant membranes [30] and seminolipid from mammalian sperm cells. In addition to serving as a primary component of cellular membranes and binding sites for intra- and intercellular proteins, some glycerophospholipids in eukaryotic cells, such as phosphatidylinositols and phosphatidic acids are either precursors of or, themselves, membrane-derived second messengers. The major sphingoid base of mammals is commonly referred to as sphingosine. Ceramides N-acyl-sphingoid bases are a major subclass of sphingoid base derivatives with an amide -linked fatty acid. The fatty acids are typically saturated or mono-unsaturated with chain lengths from 16 to 26 carbon atoms. Examples of these are the simple and complex glycosphingolipids such as cerebrosides and gangliosides. Sterol lipids[edit] Sterol lipids, such as cholesterol and its derivatives, are an important component of membrane lipids, [43] along with the glycerophospholipids and sphingomyelins. The steroids , all derived from the same fused four-ring core structure, have different biological roles as hormones and signaling molecules. The eighteen-carbon C18 steroids include the estrogen family whereas the C19 steroids comprise the androgens such as testosterone and androsterone. The C21 subclass includes the progestogens as well as the glucocorticoids and mineralocorticoids. Structures containing greater than 40 carbons are known as polyterpenes. Carotenoids are important simple isoprenoids that function as antioxidants and as precursors of vitamin A. Prokaryotes synthesize polyprenols called bactoprenols in which the terminal isoprenoid unit attached to oxygen remains unsaturated, whereas in animal polyprenols dolichols the terminal isoprenoid is reduced. Saccharolipids describe compounds in which fatty acids are linked directly to a sugar backbone, forming structures that are compatible with membrane bilayers. In the saccharolipids, a monosaccharide substitutes for the glycerol backbone present in glycerolipids and glycerophospholipids. The minimal lipopolysaccharide required for

growth in E. They comprise a large number of secondary metabolites and natural products from animal, plant, bacterial, fungal and marine sources, and have great structural diversity. Many commonly used anti-microbial, anti-parasitic, and anti-cancer agents are polyketides or polyketide derivatives, such as erythromycins, tetracyclines, avermectins, and antitumor epothilones. The glycerophospholipids are the main structural component of biological membranes, such as the cellular plasma membrane and the intracellular membranes of organelles; in animal cells, the plasma membrane physically separates the intracellular components from the extracellular environment. A biological membrane is a form of lamellar phase lipid bilayer. The formation of lipid bilayers is an energetically preferred process when the glycerophospholipids described above are in an aqueous environment. In an aqueous system, the polar heads of lipids align towards the polar, aqueous environment, while the hydrophobic tails minimize their contact with water and tend to cluster together, forming a vesicle; depending on the concentration of the lipid, this biophysical interaction may result in the formation of micelles, liposomes, or lipid bilayers. Other aggregations are also observed and form part of the polymorphism of amphiphile lipid behavior. Phase behavior is an area of study within biophysics and is the subject of current research. So in an aqueous environment, the water molecules form an ordered "clathrate" cage around the dissolved lipophilic molecule. They are a major source of energy because carbohydrates are fully reduced structures. In comparison to glycogen which would contribute only half of the energy per its pure mass, carbohydrate carbons are all bonded to hydrogens unlike in carbohydrates. Migratory birds that must fly long distances without eating use stored energy of triglycerides to fuel their flights. They accomplish this by being exposed to the extracellular face of the cell membrane after the inactivation of flippases which place them exclusively on the cytosolic side and the activation of scramblases, which scramble the orientation of the phospholipids. After this occurs, other cells recognize the phosphatidylserines and phagocytose the cells or cell fragments exposing them. Acyl-carnitines are involved in the transport and metabolism of fatty acids in and out of mitochondria, where they undergo beta oxidation. Polyprenol phosphate sugars and polyprenol diphosphate sugars function in extra-cytoplasmic glycosylation reactions, in extracellular polysaccharide biosynthesis for instance, peptidoglycan polymerization in bacteria, and in eukaryotic protein N-glycosylation. The process of lipid metabolism synthesizes and degrades the lipid stores and produces the structural and functional lipids characteristic of individual tissues. Biosynthesis [edit] In animals, when there is an oversupply of dietary carbohydrate, the excess carbohydrate is converted to triglycerides. This involves the synthesis of fatty acids from acetyl-CoA and the esterification of fatty acids in the production of triglycerides, a process called lipogenesis. The acyl chains in the fatty acids are extended by a cycle of reactions that add the acetyl group, reduce it to an alcohol, dehydrate it to an alkene group and then reduce it again to an alkane group. The enzymes of fatty acid biosynthesis are divided into two groups, in animals and fungi all these fatty acid synthase reactions are carried out by a single multifunctional protein, [88] while in plant plastids and bacteria separate enzymes perform each step in the pathway. The synthesis of unsaturated fatty acids involves a desaturation reaction, whereby a double bond is introduced into the fatty acyl chain. For example, in humans, the desaturation of stearic acid by stearoyl-CoA desaturase-1 produces oleic acid. In animals and archaea, the mevalonate pathway produces these compounds from acetyl-CoA, [93] while in plants and bacteria the non-mevalonate pathway uses pyruvate and glyceraldehyde 3-phosphate as substrates. Here, the isoprene units are joined together to make squalene and then folded up and formed into a set of rings to make lanosterol. For the most part, fatty acids are oxidized by a mechanism that is similar to, but not identical with, a reversal of the process of fatty acid synthesis. That is, two-carbon fragments are removed sequentially from the carboxyl end of the acid after steps of dehydrogenation, hydration, and oxidation to form a beta-keto acid, which is split by thiolysis. Hence the citric acid cycle can start at acetyl-CoA when fat is being broken down for energy if there is little or no glucose available. The energy yield of the complete oxidation of the fatty acid palmitate is ATP. Nutrition and health [edit] Most of the fat found in food is in the form of triglycerides, cholesterol, and phospholipids. Some dietary fat is necessary to facilitate absorption of fat-soluble vitamins A, D, E, and K and carotenoids. Most vegetable oils are rich in linoleic acid safflower, sunflower, and corn oils. Alpha-linolenic acid is found in the green leaves of plants, and in selected seeds, nuts, and legumes in particular flax, rapeseed, walnut, and soy. Fats that are good for you can be turned into

trans fats by overcooking. The Nutrition Source, a website maintained by the Department of Nutrition at the Harvard School of Public Health , summarizes the current evidence on the impact of dietary fat:

6: Neurosporaxanthin | C35H46O2 - PubChem

The reaction of ROS with biomolecules like lipids, proteins, and DNA may lead to increased risk of chronic diseases, such as cancer, CVD, atherosclerosis, age-related macular degeneration (AMD), or cataract.

Animal waxes
Bee wax This wax is an abdominal secretion of bees *Apis mellifera*, its colour being dependent of the flowers gathered by these insects. Bees used it to form the hive cells. Bee wax is easily saponifiable and emulsifiable because of its content in free fatty acids, diols and hydroxyacids. The ratio of triacontanylpalmitate or melissylpalmitate, C30 alcohol esterified by C16 fatty acid to cerotic acid C Ethyl esters are also present, the most abundant species being ethyl palmitate, ethyl tetracosanoate, and ethyl oleate Jimenez JJ et al. A chemometric method based on the use of high-temperature gas chromatography has been reported for the detection of bee wax adulteration with mineral paraffin Maia M et al. Bee wax is used since ancient times since its presence was detected in the wall pictures of the Lascaux cave and in Egyptian mummies. Ancient Egyptians used it also for its adhesive and coating properties, and in shipbuilding. In the Roman period, bee wax was used as a waterproofing agent and treatment for painted walls medium for the "Fayum portraits". In the Middle Ages, this wax was valuable and exchanged as a form of currency. In recent times, bee wax was used as a modeling material, as component of seals, coatings, polishes, and candles.
Chinese wax insect wax This wax is secreted by insects *Coccus ceriferus* and laid on tree branches insects are needed to produce 1g chinese wax. That insect is cultivated in China. Chemically, the esters are formed of chains with 46 up to 60 carbon atoms, the majority of alcohols and acids having 26 or 28 carbon atoms. The purified wax is used to make candles and polish.
Shellac wax This wax known also as lac wax is produced by a cochineal insect *Tachardia lacca* native of India. The esters are formed of chains of 28 up to 34 carbon atoms. This wax is used in varnish industry and may replace carnauba wax. The frontal organ, used as a sonar by the animal, contains about 3 tons spermaceti for a 15 meters animal. Fatty esters are formed essentially of cetyl palmitate C32 and cetyl myristate C Purified spermaceti has an aspect of a light mass of white crystals which can be powdered. It can be fused with bee wax and other fatty compounds oils, fatty acids. Spermaceti was used in medicine in England 15th century and later in cosmetics, pharmacy and also in candles but, after the recent international regulation concerning whale captures, it is no longer produced and sold. It is now replaced by synthetic spermaceti made of pure cetyl palmitate or mixtures based on jojoba.
Lanolin wool wax This material is secreted by sheep sebaceous glands and collected from crude wool by dilute alkali or detergent washing. Hydroxylated fatty acids mainly hydroxy palmitate are found either free or esterified. Fatty acid chains have from 14 up to 35 carbon atoms, many of them having branched chains iso or anteiso conformations. Two third of the diols belong to the iso series Fawaz F et al. As bee wax, lanolin is used since very ancient times in cosmetic and dermatology but is actually used in industry fabric, ink, lubricant.
Vegetal waxes
Carnauba wax This wax known as "queen of waxes" is secreted by leaves of a Brazilian palm tree *Copernicia prunifera cerifera*, about g for one tree in a year. This last phenolic acid compound antioxidant in free form may be hydroxylated or methoxylated. This wax is the hardest and highest melting of the natural waxes melting point: It is used also in the paper industry for paper coating the largest application in the USA.
Ouricouri wax It was first exported from Brazil in but has fallen in use in recent times. It was extracted from the ouricouri palm *Syagrus coronata*, *Cocos coronata* by scraping the wax from the leaf surface. Ouricouri resembles carnauba wax in its physical properties, thus, it was used as substitute in carbon paper inks, mould release lubricants and polishes.
Jojoba oil This product resulted from the pressure on governments to replace spermaceti. This wax is fluid melting point: The cultivation of jojoba is also experimented in Israel, Africa, Australia, and China. The fatty acids are Jojoba oil is very resistant to oxidation and is largely used in cosmetic applications soaps, shampoos, skin cream, anti-solar oils. Industries use sulfonated or hydrogenated oil as lubricant, polishes, candles and coatings. Future uses could be as foam control agent and low-calorie food additive.
Candelilla wax This wax is produced by small shrubs from Mexico, *Euphorbia cerifera* and *E.* The wax is extracted by boiling the plant to separate the wax and the plant material. The wax floats to the top of the water and is skimmed off and processed. It has been used mainly mixed with other waxes to harden

them without raising the melting point. This wax is used in cosmetics lip balms and lotion bars , pharmaceuticals and in food stuffs E , GRAS to improve stability and texture as a substitute to beeswax melting point: While its composition is highly variable, it contains hydrocarbons, esters, alcohol C₂₈ and triterpenoids.

Japan wax That product is not a true wax but is more like a vegetable tallow found in the kernel and outer skin of the berries of *Rhus* and *Toxicodendron* species, including those yielding Japanese lacquer. That wax is much used in Japan in cosmetics, ointments and to make candles but becomes rancid with age.

Rice bran oil Rice bran from the milling of rice, *Oryza sativa*, contains a wax mixed with triglycerides. That wax is much used as a constituent of chocolate enrobers, various fruit and vegetable coating and as a lipstick. It is used in making lubricants, lipsticks, deodorants, polishes, and adhesives.

Montan wax This wax is derived by solvent extraction of lignite or brown coal sub-bituminous coal. As it has been preserved in the coal it is really fossilized plant wax. Thus, it has many characteristics similar to those of vegetal waxes. The composition of Montan wax depends on the material from which it is extracted, but all contain varying amounts of wax, resin, and asphalt. Resins must be removed by extraction with solvents diethyl ether, acetone. The wax component of Montan is a mixture of long. Montan wax is hard and is one of the most resistant to oxidation. Carbon papers were the largest consumer of crude Montan wax. Additional applications are shoe polishes, electrical insulators, and lubricant in plastics and in paper industry.

Synthetic waxes and esters As natural waxes are versatile, they can suffer inherent variability in quality and availability, cosmetic product include more and more frequently synthetic waxes. They are made of ethylene glycol diesters or triesters of long-chain fatty acids CC While having the structure of waxes, esters of alcohols and fatty acids either with a straight or branched chain, but shorter than for waxes, are manufactured for cosmetic applications. Depending on the chain length and structural arrangement of the two starting materials, esters are tailored to provide different physical properties and types of emolience. Straight chain esters, such as cetyl palmitate and cetostearyl stearate, which are solid at room temperature, are used to increase the viscosity of emulsions. Liquid branched chain esters, such as isopropyl myristate or cetostearyl ethylhexanoate, provide products with good spreading properties. Furthermore, the choice of the ester influences both the solubility and spreadability of sunscreen agents and their ability to penetrate the skin.

7: Terpenoid - Wikipedia

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INTRODUCTION Terpenoids or isoprenoids, a subclass of the prenylipids terpenes, prenylquinones, and sterols, represent the oldest group of small molecular products synthesized by plants and are probably the most widespread group of natural products. Terpenoids can be described as modified terpenes, where methyl groups are moved or removed, or oxygen atoms added. Inversely, some authors use the term "terpenes" more broadly, to include the terpenoids. During the 19th century, chemical works on turpentine led to name "terpene" the hydrocarbons with the general formula $C_{10}H_{16}$ found in that complex plant product. These terpenes are frequently found in plant essential oils which contain the "Quinta essentia", the plant fragrance. They are universally present in small amounts in living organisms, where they play numerous vital roles in plant physiology as well as important functions in all cellular membranes. The various functions of terpene natural products in the natural world have been reviewed Gershenzon J et al. On the other hand, they are also accumulated in many cases, and it is shown that the extraordinary variety they then display can be due to ecological factors playing an evolutionary role Ourisson G, Pure Appl Chem, 62, More than 50, terpenoids have been isolated from both terrestrial and marine plants, and fungi. In contrast, only some compounds have been identified in prokaryotes. The first study of bacterial terpenes grew out of an investigation of the characteristic odor of freshly plowed soil reported in by the famous French chemist M. Berthelot Berthelot M, et al. They noted that a volatile substance apparently responsible for the typical earthy odor of soil could be extracted from soil by steam distillation but they could not assign a structure to the odor constituent. Some 75 years later M. Gerber studied the characteristic odor of cultures of Actinomycetales microorganisms, which are widely distributed in soil, and determined the structure of a C_{12} degraded sesquiterpene alcohol, the geosmin means earth odor, likely detected by Berthelot Gerber NN, et al. Later, numerous volatile terpenes have been detected in streptomycetes. The three most commonly detected are geosmin, 2-methylisoborneol and the tricyclic α,β -unsaturated ketone albaflavenone. The two terpene alcohols are the most frequently found secondary metabolites in actinomycetes, filamentous Cyanobacteria, and Myxobacteria, and also in a small number of fungi. Enzymatic studies have suggested that genes encoding terpene synthases are widely distributed in bacteria and that these genes represent a fertile source for discovery of new natural products Yamada Y et al. All terpenoids may be defined as a group of molecules whose structure is based on a various but definite number of isoprene units methylbuta-1,3-diene, named hemiterpene, with 5 carbon atoms. Terpenoids are extraordinarily diverse but they all originate through the condensation of the universal phosphorylated derivative of hemiterpene, isopentenyl diphosphate IPP and dimethylallyl diphosphate DMAPP giving geranyl pyrophosphate GPP. In higher plants, IPP is derived from the classic mevalonic acid pathway in the cytosol but from the methylerythritol phosphate pathway in plastids. It is generally accepted that the cytosolic pool of IPP serves as a precursor of sesquiterpenes, triterpenes, sterols and polyterpenes whereas the plastid pool of IPP provides the precursors of mono-, di- and tetraterpenes Bohlmann J et al. Some exceptions have been described showing that interactions between the two biosynthetic pathways may exist Dudareva N et al.

8: Ternatin | C₁₉H₁₈O₈ - PubChem

The main difference between terpenes and terpenoids is that terpenes are hydrocarbons (meaning the only elements present are carbon and hydrogen); whereas, terpenoids have been denatured by oxidation (drying and curing the flowers) or chemically modified.

9: Lipid - Wikipedia

relatively low-polar substances (lipids) found in oil-bodies of lipids is related to their application as biomarkers [5] of hydrocarbons and terpenoids. Bryophyte lipids can be considered.

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