WELCOME TO DR. BILL'S ENVIRONMENTAL TOXICOLOGY
TERPENOIDS, ESSENTIAL OILS

http://www.geocities.com/RainForest/Andes/3804/terpenoids.html

Essential oils are a group of natural organic compounds that are predominantly composed of terpenes (hydrocarbons) and terpenoids (oxygen containing hydrocarbons). Essential oils also contain simple phenols, sulphur containing mustard oils, methyl anthranilate and coumarins.

ISOPRENE UNITS

Plants build terpenes and terpenoids from the basic building block 3-methyl-3-butenyl pyrophosphate. The 5-carbon unit of this molecule is the source of the "isoprene" unit that makes up all "isoprenoids". Combining two of these units give rise to geranyl pyrophosphate which then forms the skeleton of the MONOTERPENES (10 carbons).

Combining three of these units gives rise to farnesyl pyrophosphate which then forms the skeleton of the SESQUITERPENES (15 carbons).

Combining two geranyl pyrophosphates gives rise to geranylgeranyl pyrophosphates which then forms the skeleton of the DITERPENES (20 carbons).

Farnesyl and geranylgeranylpyrophosphates can dimerize to yield TRITERPENES (30 carbons) and TETRATERPENES (40 carbons).

MONOTERPENES (10 carbons)

There are about 400 known monoterpenes which occur widely among gymnosperms and angiosperms. Most are free but some are found as glycosides (combined with sugars).

Monoterpenes make up a major part of the volatile constituents (or essential oils) of plants. In nature, they are frequently involved in plant-animal and plant-plant interactions - such as pollination, seed and fruit dissemination, allomones, kairomones, and allelopathic agents. For example, the monoterpenoid, cantharidin, is produced by the blistering beetle (Cantharis vesicatoria) as an alarm substance.

Some examples of the monoterpenes and (-oids) are: pinene, geraniol, thymol, citral, citronellal, carvone, camphor, apiol, cinnamic acid, and safrol.

SECOIRIDOID MONOTERPENES - TYPES OF BITTER PRINCIPLES

The phrase bitter principles, which refers to the bitter-tasting monoterpenoid lactones known as iridoids are also components of volatile oils and have been used to stimulate gastric secretion in man.

Unlike the monoterpenes found in essential oils, secoiridoid monoterpenes occur in all parts of the plants in which they are found. They are not associated with specialized oil storage

structures. They often occur as glycosides (contain sugars) and are water soluble. They serve as precursors for indole and monoterpene alkaloids.

Examples of monoterpene bitter principles include: gentiopicrin, gentianin, procumbid, harpagid, oleuropein, aucubin.

Examples of sesquiterpene bitter principles include: cnicin, artabsin, absinthin.

Examples of diterpene bitter principles include: marrubiin, carnosol (picrosalvin).

Examples of triterpene bitter principles include: quassin and cucurbitacin.

SESQUITERPENES (15 carbons)

Sesquiterpenes make up the largest group of terpenoid compounds. There are about 1000 known compounds with the distribution being about the same as the monoterpenes. Thus, sesquiterpenes are common essential oil components. Abscisic acid, a plant growth compound, is also a sesquiterpene.

Farnesol, nerolidol are examples of sesquiterpenes found with monoterpenes in essential oils. They are both mite pheromone sex attractants (Regev - Rec. Adv. in Acarology - 1:147, 1979).

Sesquiterpenoids also occur in microorganisms, marine animals, and fighting insects. Some are very toxic, but some are antifungals, carminatives, and insecticides. With the addition of a lactone ring sesquiterpenoids become sesquiterpene lactones.

SESQUITERPENE LACTONES

Sesquiterpene lactones are restricted in distribution, occurring primarily in Apiaceae, Asteraceae, Lauraceae, and Hepaticae. These compounds possess potent biological activity and are responsibile for the bitter taste and toxic properties of many of the plants in which they occur. Often, these components cause contact dermatitis and some are lethal.

DITERPENES (20 carbons)

At least 650 diterpenes are found in a large number of plant families. They are chemically complex, difficult to isolate, purify and characterize. They are usually compoents of plant resins but are sometimes encountered as by-products from the isolation of essential oils (e.g., from turpentine production).

Diterpenes are found in gymnosperms but are also common in: Asteraceae, Erythroxylaceae, Euphorbiaceae, Fabaceae, Lamiaceae, and Verbenaceae.

Some diterpenes possess a configuration which can give rise to gibberellins.

TRITERPENES (30 carbons)

Triterpenes form a large group of lipid substances found in all plants. There are approximately 750 known triterpenes.

Triterpenes arise via dimerization of two farnesyl pyrophosphate units (15 carbons) to produce an intermediate compound called SQUALENE (30 carbons). Squalene can cyclize to form CHOLESTEROL and other steroid hormones.

Cholesterol occurs in all plants. Other important steroid compounds found in plants include: PHTOECDYSONES; PROGESTAGENS (pregnenolone and progesterone); and BETA SITOSTEROL.

Progestagens (21 carbon steroids) occur as animal hormones in addition to being found in plants. Progestagens and beta sitosterol give rise to a number of other types of steroids including the CARDENOLIDES.

CARDENOLIDES - CARDIAC GLYCOSIDES

Cardenolides have 23 carbon atoms and a lactone ring. They are formed by condensation of pregnenolone or progesterone with acetate. The sugar moieties of cardenolides are normal sugars or unbranched aldohexoses. About 50 cardenolides exist and are primarily found in: Apocynaceae, Asclepiadiaceae, Brassicaceae, Celastraceae, Euphorbiaceae, Liliaceae, Moraceae, Ranunculaceae, Scrophulariaceae, Sterculiaceae, and Tiliaceae.

Cardiac glycosides affect the dynamics and rhythm of dysfunctional heart muscle. Examples of important cardiac glycosides used in man include: digitoxin, digoxin, gitoxin, strophanthidin, hellebrin, scillaren.

Important sources of the digitalis glycosides (digoxin, digitoxin) include: Digitalis lanata (white foxglove) and Digitalis purpurea (red foxglove). Digitalis drugs are agents used for people in congestive heart failure. Cardenolides and bufenolides are triterpenoids which are highly poisonous and which come from 23- and 24-carbon steroids, with an isoprenoid substituent. Cardenolides occur combined with sugars, hence name glycosides; while bufenolides occur in either a free state or in glycosidic form.

CUCURBITACINS

CUCURBITACINS are classified as tetracyclic triterpenoids. First found in the seeds of particular Curcubita species (i.e., cucumber, pumpkin, summer squash) are generally bitter, but some are sweet, and some have cytotoxic, antitumor, and antileukemic activities.

Cucurbitacins are also derived from SQUALENE. They are found in: Begoniaceae, Brassicaceae, Cucurbitaceae, Primulaceae, Rosaceae, and Scrophulariaceae.

SAPOGENINS OR TRITERPENOID SAPONINS

Sapogenins are combined with sugars to form saponins. Generally, they include up to five sugar units and are always attached to the third carbon.

Cholesterol and beta-sitosterol are precursors to the formation of the sapogenins.

Sapogenins are plant glycosides which lather in water and are used in detergents, or as foaming agents or emulsifiers. They have antifungal, antimicrobial and some have antiinflammatory action. Glycyrrhizin, from licorice root, is an example of a saponin used for antiinflammatory purposes in place of cortisone. Aescin also has antiinflammatory action.

Steroidal saponins are similar to the sapogenins and are related to the cardiac glycosides. Therapeutically, steroidal saponins are mucosal irritants, expectorants, blood cell strengtheners, antiinflammatory and cholesterol-lowering agents.

TETRATERPENES (40 carbons)

Carotenoids, or 40-carbon tetraterpenoids, are lipid-soluble terpenes found in all forms of plants. Their value to animals comes from the splitting of the C40 molecule into the twenty-carbon isoprenoid alcohol known as vitamin A. Alpha tocopherol (vitamin E), while not a tetraterpene, is a higher terpenoid (29 carbons), that plays a role in reproduction in mammals and several invertebrate species: rotifer and cricket (Gilbert & Thompson - Science 159:734, 1968; Meikle & McFarlane - Can. J. Zool. 43:87, 1965)

Vitamin K, another higher isoprenoid vitamin, is required by mammals for prothrombin synthesis and blood clotting.