



Health Properties of Olive oil minor constituents.

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A staple food

- A staple food for thousands of years for the inhabitants of the Mediterranean region, olive oil is now becoming popular among consumers all over the world.
- New consumers are looking to extract healthful benefits from the diet of the people living in the countries surrounding the Mediterranean Sea, since olive oil is a basic constituent of this diet.

Unique character

- Olive oil differs from other vegetable oils because it is used in its natural form and has unique flavor and other characteristics.
- In its production, technology and tradition, these two seemingly contradictory factors, interplay successfully.
- On the issue of health, the news about olive oil get better every day ,as more and more research suggests **beneficial properties described even by Hippocrates and other doctors of the ancient world.**
- In 2004 the **Food and Drug Administration (FDA)** announced the availability of a qualified **health claim** for monounsaturated fat from olive oil and **reduced risk of coronary heart disease.**

Epidemiological and other studies

- Several epidemiological studies suggest that olive oil significantly contributes to the well known effects of the **Mediterranean diet** in lowering the incidents of **degenerative pathologies, including coronary heart disease and cancer**.
- The protective effects could be ascribed to the fatty acid composition of the oil and also to **minor constituents**, as indicated by recent biochemical, pharmacological and other studies.

A functional food

- Virgin olive oil is a typical example of a **"natural" functional** food
- The health effects of olive oil are attributed to its **fatty acid** composition and the presence of **bioactive ingredients** such as:
- **Polar phenols**(hydroxytyrosol and its derivatives, the **ibuprofen-like** active compound **oleocanthal**, others).
- **Phenolic acids, lignans, flavonoids**
- **Triterpene acids and and triterpene alcohols**
- **a-tocopherol**
- **Squalene**, a chemopreventive compound

Antioxidants

- As we enter the 21st century research, which links food components with health, is increasing rapidly. **The focus on the beneficial effects of commonly available components of foods and plants has never been so strong.**
- The industry is now trying to develop technologies to improve **health functionality of food products, while a lot of information is now available for the presence of bioactive ingredients in traditional foods.**

Antioxidants (continued)

- An important field of research today is the control of “**redox**” status with the properties of natural food and food components.
- Natural antioxidants increase the resistance of food toward oxidative damage but they may also have a substantial impact on human health.
- Experimental and epidemiological studies have strongly indicated that dietary antioxidants **inhibit** or **modulate** oxygen related diseases such as **cardiovascular diseases, cancer, brain disfunction, immune system decline, eye diseases and others.**

Antioxidants (continued)

- Dietary antioxidants include **ascorbate, tocopherols, carotenoids and bioactive plant phenols**.
- The health benefits of fruits and vegetables are largely due to the antioxidant vitamins supported by the large number of phytochemicals, some with greater antioxidant properties.
- Sources of **tocopherols, carotenoids and ascorbic acid** are well known and there is a surplus of publications related to their role in health.
- **Plant phenols** have not been completely studied because of the **complexity of their chemical nature** and the **extended occurrence** in plant materials.

The antioxidant hypothesis

- Reactive oxygen and nitrogen species, **ROS/RNS** are essential to energy supply, detoxification, chemical signaling and immune function. They are continuously produced in the human body and they are controlled by **endogenous enzymes** (superoxide dismutase, glutathione peroxidase ,catalase).
- When there is an over-production of these species, an exposure to external oxidant substances or a failure in the defense mechanisms, a damage to valuable biomolecules(DNA,lipids,proteins) may occur (Aruoma ,1998) .

The antioxidant hypothesis (2)

- This damage has been associated with an increased risk of cardiovascular disease, cancer and other chronic diseases.
- The **antioxidant hypothesis** says that
“As antioxidants can prevent oxidative damage, increased intakes from the diet will also reduce the risks of chronic diseases.”
- This explains the huge volume of research work and the efforts of many researchers to link diets rich in natural antioxidants with degenerative disease

Effect of polyphenols

- The great focus on the subject resulted in data that not only support but also challenge the hypothesis. One of the main problems is the fact that intervention studies with humans have not shown a clear benefit that positively confirms the findings of epidemiological studies. Negative studies in the literature involve also vitamin antioxidants (vitamin E, vitamin C, carotenoids) given at high doses.

Effect of polyphenols

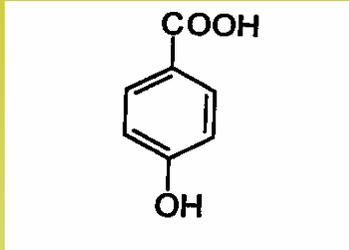
- However, in recent reviews in top nutritional journals it is underlined that the existing studies on humans demonstrate a **“convincing effect of polyphenols on some aspects of health”** (Kroon, 2005). It is also a fact that **bioavailability studies are accumulating** (Manach, 2004) ,while new **databases** are created for the various classes of polyphenols (Beecher,2003, USDA, 2003) and estimates of intakes in many countries are discussed more and more seriously.

OLIVE OIL

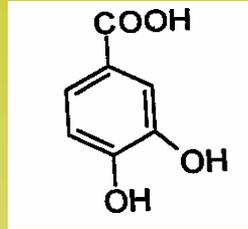
- Research related to olive oil polar phenolics indicates a **scavenging activity** of these compounds against superoxide anion and hydrogen peroxide and a capability to prevent the generation of reactive oxygen species.
- An *in vitro* **inhibitory effect** on **eicosanoids production** and on **platelet aggregation** have also indicated some mechanisms by which olive oil phenols help to protect against various **cardiovascular disorders**, while their capacity to **scavenge nitrogen reactive species** such as peroxynitrite suggests a protective effect against DNA damage.

Olive oil phenolics

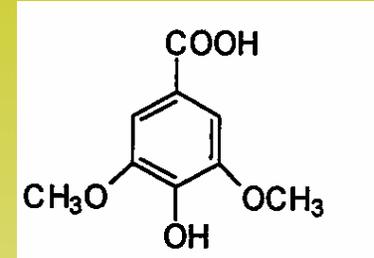
Phenolic Acids



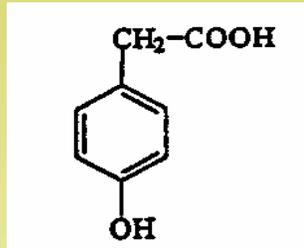
4-hydroxybenzoic acid



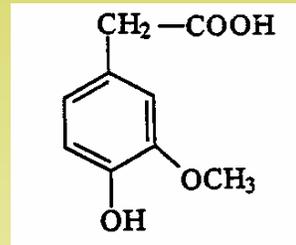
protocatechuic acid



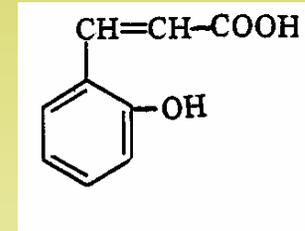
Syringic acid



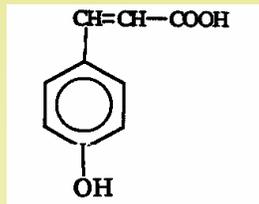
4-hydroxy-phenylacetic acid



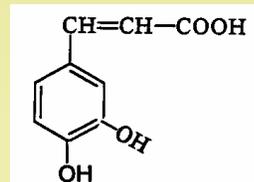
homovanillic acid



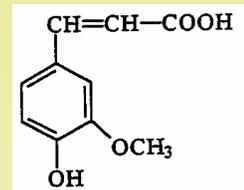
o-Coumaric acid



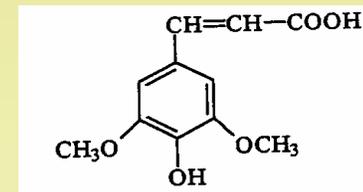
p-coumaric acid



caffeic acid

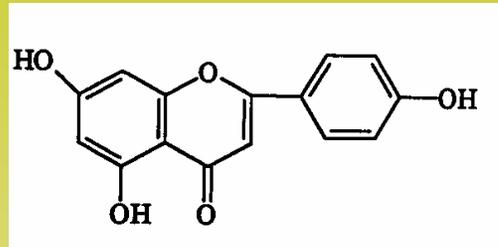


ferulic acid

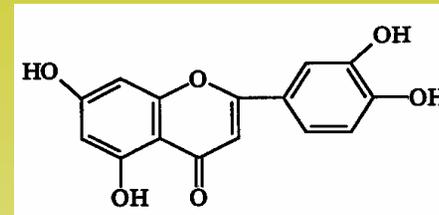


sinapic acid

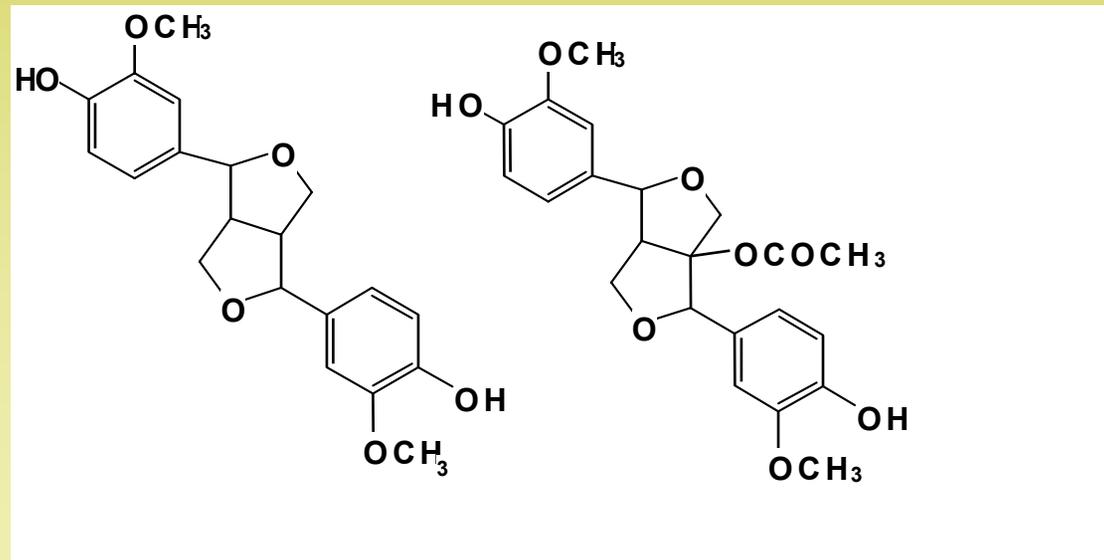
Flavonoids and Lignans



apigenin



luteolin

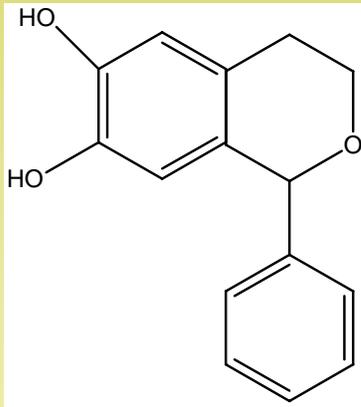


pinoresinol

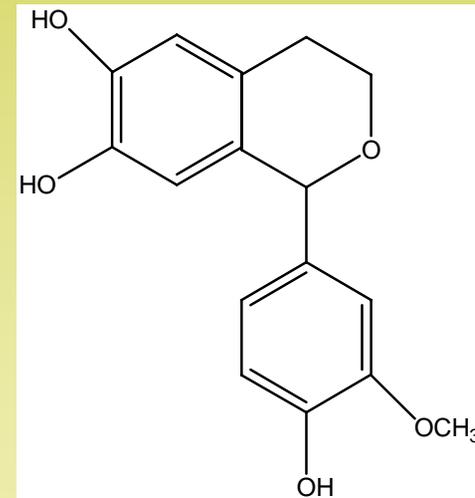
acetopinoresinol

Isochromans

- In a recent study Bianco, Coccioli, Guiso and Marra (2001) found a new class of phenols, **hydroxyl-isochromans**. Hydroxy-isochromans are now investigated (Togna et al, 2003) for their antioxidant power and their ability to **inhibit platelet aggregation**.



1-phenyl-6,7-dihydroxyisochroman

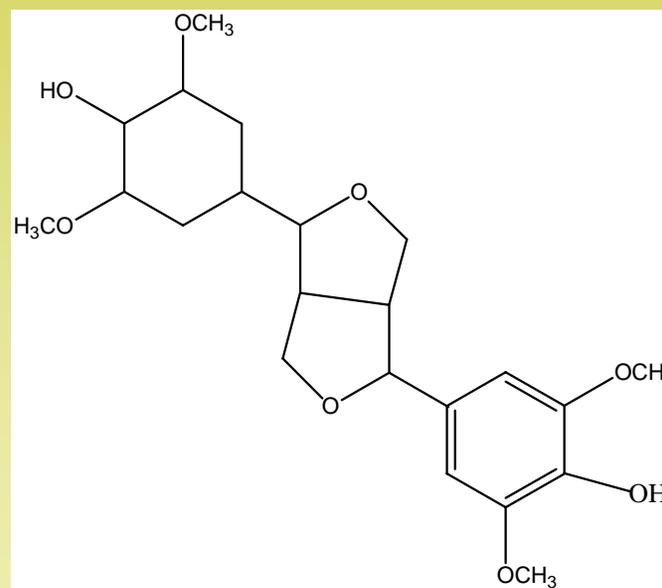


1-(3'-methoxy-4'-hydroxy)phenyl-6,7-dihydroxyisochroman

A new lignan

- More recently Christoforidou, 2005) applied hyphenated **LC-SPE-NMR**, to identify new phenols in the polar fraction of olive oil .The addition of a **postcolumn SPE system** in replacement of the loop system of the LC-NMR technique ,resulted in advanced sensitivity (significant increase of the signal to noise ratio).

The spectra recorded were **one dimensional (1D)** ^1H -NMR and **two dimensional (2D)** NMR. The presence of phenolics was confirmed from the respective LC-SPE-NMR spectra ,which were assigned on the basis of existing ^1H -NMR data bases and with total correlation spectroscopy (**TOCSY**). The most interesting findings of this study was the verification of the presence of the lignan **syringaresinol**,



syringaresinol

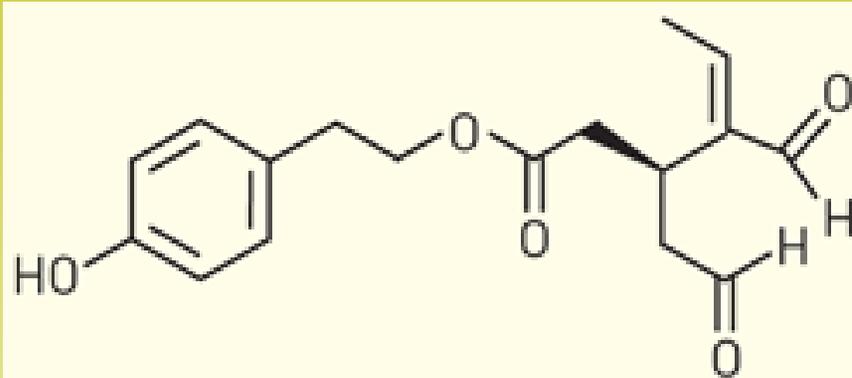
Polar Phenols levels

- The polyphenol content differs from oil to oil. Wide ranges have been reported (50-1000 mg/kg) but values are usually between 100 and 300 mg/kg.
- The cultivar, the system of extraction, and the conditions of processing and storage are critical factors for the content of polyphenols.

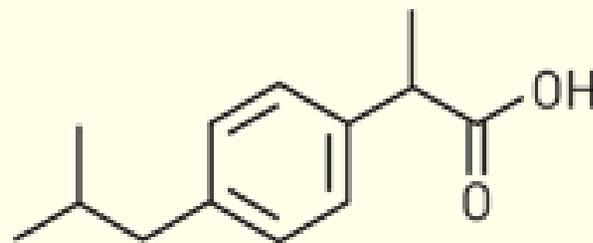
Oleocanthal

- **Phytochemistry: Ibuprofen-like activity in extra-virgin olive oil**
- Gary K. Beauchamp, et al. Nature, 2005, 437, 45-46.
- Newly pressed extra-virgin olive oil contains **oleocanthal** - a compound whose pungency induces a strong stinging sensation in the throat, similar to that caused by solutions of the non-steroidal anti-inflammatory drug ibuprofen. We show here that this similar perception seems to be an indicator of a shared pharmacological activity, with **oleocanthal** acting as a **natural anti-inflammatory** compound that has a potency and profile strikingly similar to that of **ibuprofen**
- **(inhibition of COX enzymes)**

Structural formulae of oleocanthal and ibuprofen



Oleocanthal



Ibuprofen

Synopsis of biological activities attributed to olive oil phenolics

- **In vitro** Antioxidant activity ,anti-inflammatory activity, antiatherogenic activity ,antimicrobial activity.
- **Animal studies.**Chemoprevention, antioxidant activity, anti-inflammatory effect, antithrombotic effect.
- **Human studies** .Reduction of oxidative stress, blood lipid modulation, absorption and metabolism. . Postprandial studies on the antioxidant effect in humans

Protection of LDL

- The oxidative modification of low density lipoproteins (LDL) is considered to be a hallmark for atherosclerosis and coronary heart disease development. In human studies, olive oil rich diets promote oleate-rich LDL which is more resistant to oxidative modifications than linoleate-rich LDL. The protection against oxidative lipid damage has been shown to be in a **dose-dependent manner with the phenolic content of the olive oil**. Also, olive oil consumption increase the **HDL cholesterol, which protects LDL from oxidation, in a dose-dependent manner with the phenolic content of the olive oil administered**.

Olive oil Phenols and Cancer

A large number of epidemiological studies have demonstrated a clear association between olive oil consumption and a reduced cancer risk, mainly attributed to **the combination of its high oleic acid content and its minor components like phenolic compounds.**

Olive oil constituents have been found to exert an inhibitory action by **interfering with basic cell functions** linked to the generation and/or progression of cancer.

In vitro and *in vivo* studies revealed that olive oil components can affect cancer cell growth **by cell cycle arrest and apoptosis, as well as angiogenesis, invasion and subsequently metastasis.**

The mechanism of action

The mechanism of action is complicated and not yet fully elucidated. According to existing experimental data the factors involved may be related to

Modification of gene response

Modulation of the oxidative inflammatory cascade

Induction of apoptosis

Cell differentiation and proliferation

Changes in the structure and function of cell membranes

Non Phenolic Compounds

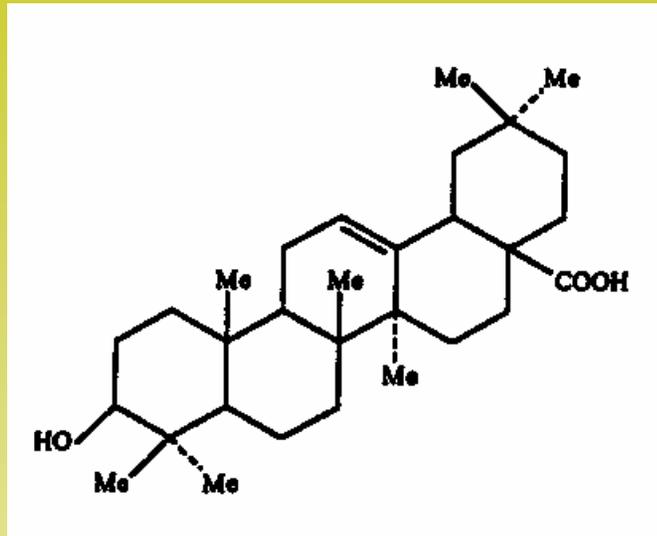
TRITERPENIC ACIDS AND TRITERPENE ALCOHOLS

- Triterpenic acids are compounds with important biological properties. They are widespread in plants. They are used in the pharmaceuticals industry for their antitumoral, anti-inflammatory and germicide activities. For the triterpenic acids present in **olive pomace oil**, the oil obtained from the milling residue by solvent extraction or specific centrifugation, there is a plethora of publications **suggesting a biological role**. They are claims that these acids may even become part of the fight against Human Immunodeficiency Virus (**HIV**), the cause of AIDS (Medical Research News, July 9, 1998).

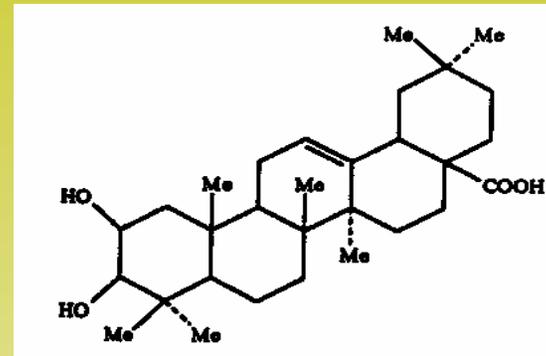
TRITERPENIC ACIDS AND TRITERPENE ALCOHOLS (continued)

- Maslinic acid significantly inhibited the enhanced production of nitric oxide (NO) induced by lipopolysaccharide (LPS) when it was measured by the nitrite production. Such properties suggest a possible biopharmaceutical use of hydroxyl-pentacyclic triterpenes present in olive pomace oil for the prevention of oxidative stress and pro-inflammatory cytokine generation.
- Rodriguez-Rodriguez et al (2006) conducted an *in vitro* study to analyze the vasorelaxation induced in isolated aorta from spontaneously hypertensive rats by the triterpenes present in olive pomace oil. The triterpenes examined (erythrodiol, uvaol, maslinic acid, oleanolic acid) induced concentration – dependent vasorelaxation, involving mostly endothelial nitric oxide (NO).

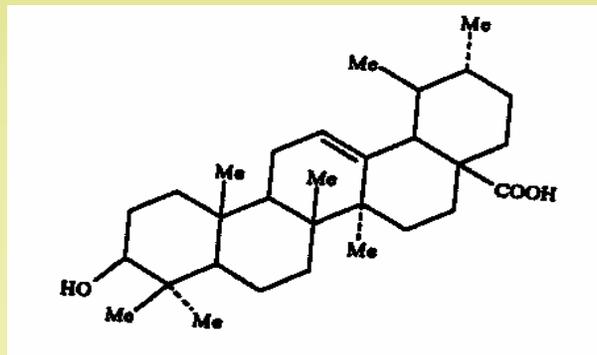
TRITERPENIC ACIDS



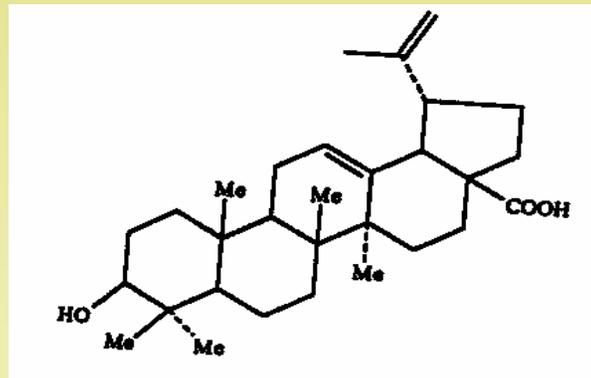
Oleanolic acid



Maslinic acid

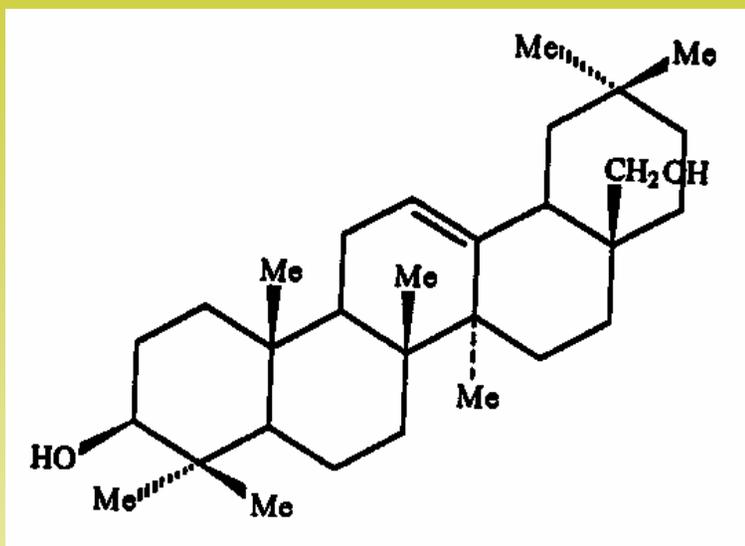


Ursolic acid

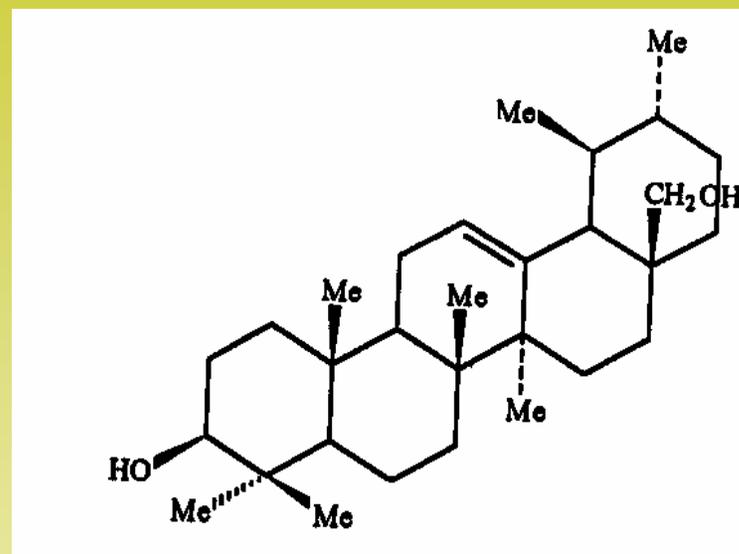


Betulinic acid

TRITERPENE ALCOHOLS

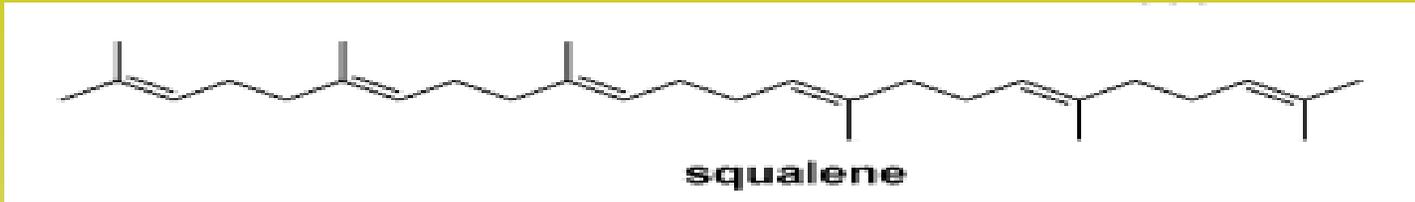


Erythrodiol



Uvaol

Squalene



- ***Squalene*(2,6,10,15,19,23,hexamethyl,2,6,10,14,18,22-tetreacosahexaene),is a highly unsaturated aliphatic hydrocarbon with important biological properties.**
- **It is a metabolic precursor of cholesterol and other sterols.**
- **As an oxygen carrier it has been extensively researched and found to play a key role in maintaining health {12,13}.**
- **Today there are claims that squalene can enhance the quality of life, if taken continuously, and that its consumption is beneficial for patients with heart disease, diabetes ,arthritis, hepatitis and other diseases.**

Squalene (Cont)

- **Squalene is found in large quantities in shark liver oil and occurs also in small amounts in olive oil (approximately 0.5%), wheat germ oil, bran oil and yeast**
- **The presence of squalene in olive oil probably makes a significant contribution to the health effects of the latter.**
- **A chemopreventive effect of squalene on colon cancer has been reported by Rao et al. (1998).**

CONCLUSION

- **To evaluate fully the role of phenols, pentacyclic terpenes and other biologically active compounds present in olive oil, the levels in the oil and the magnitude of the contribution of each active compound to the overall positive health effect has to be determined.**

BOOKS

Boskou ,D ., OLIVE OIL , Chemistry and Technology ,AOCS Press ,2006

**D. Boskou , I. Gerothanasis, P.kefalas,
NATURAL ANTIOXIDANT PHENOLS,
Sources,Structure –Activity Relationships, Currend Trends in
Analysis and Characteristion, Research Signpost
Trivandrum,Kerala,2006**

- **Boskou,D., OLIVE OIL:MINOR CONSTITUENTS AND HEALTH ,Under Preparation (CRC, Taylor and Francis). JUNE 2008**

TABLE OLIVES

- Table olives have a *different* qualitative and quantitative phenolic composition than the raw olive fruits from which they are prepared. The reason is the **diffusion** of phenols and other water soluble constituents from the olive fruit to the surrounding medium (**water, brine or lye**) and vice versa ,the **lye treatment** and **hydrolysis during fermentation**.
- When **Californian-type black olives** are prepared hydroxytyrosol and caffeic acid levels **decrease** markedly during the **darkening process**. Iron salts, used for colour fixation, catalyze the oxidation of hydroxytyrosol, which disappears.

Thank you for your attention



Harvest by beating the branches, Greek amphora, 6th cent. B.C.