الجامعة السورية الخاصة
SYRIAN PRIVATE UNIVERSITY

## السنة الثالثة

# كيمياء العقاقير

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200

# Hydrocarbons and Derivatives

TREASE AND EVANSE PHARMACOGNOSY

PROF. DR. ISAM AGHA

## Hydrocarbons and Derivatives

Hydrocarbons contain carbon and hydrogen only and, from these, by addition of functional groups and by interaction, all other natural compounds can theoretically be derived.

# Monocarboxylic acids

| *Comon name* | *Systematic name* | *Structural formula* |
|---|---|---|
| Caprylic | *n*-Octanoic | $CH_3(CH_2)_6COOH$ |
| Capric | *n*-Decanoic | $CH_3(CH_2)_8COOH$ |
| Lauric | *n*-Dodecanoic | $CH_3(CH_2)_{10}COOH$ |
| Myristic | *n*-Tetradecanoic | $CH_3(CH_2)_{12}COOH$ |
| Palmitic | *n*-Hexadecanoic | $CH_3(CH_2)_{14}COOH$ |
| Stearic | *n*-Octadecanoic | $CH_3(CH_2)_{16}COOH$ |
| Arachidic | *n*-Eicosanoic | $CH_3(CH_2)_{18}COOH$ |

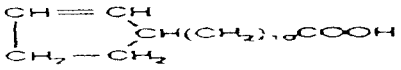
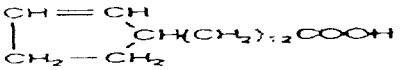
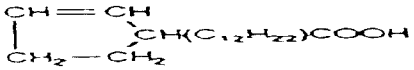
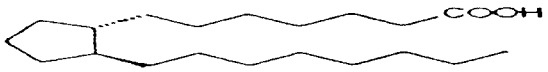
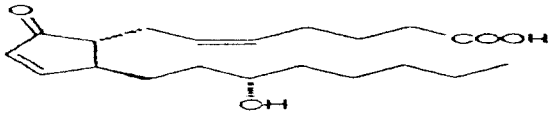


# Fatty acids

| *Common name* | *Number of unsaturated bonds* | *Structural formula* |
|---|---|---|
| Palmitoleic | 1 | $CH_3(CH_2)_5CH=CH(CH_2)_7COOH$ |
| Oleic | 1 | $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ |
| Petroselinic | 1 | $CH_3(CH_2)_{10}CH=CH(CH_2)_4COOH$ |
| Ricinoleic | 1 | $CH_3(CH_2)_5CH(OH)CH_2CH=CH-(CH_2)_7COOH$ |
| Erucic | 1 | $CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$ |
| Linolenic | 2 | $CH_3(CH_2)_4CH=CHCH_2CH=CH-(CH_2)_7COOH$ |
| α-Linoleic | 3 | $CH_3CH_2CH=CHCH_2CH=CHCH_2-CH=CH(CH_2)_7COOH$ |
| γ-Linolenic | 3 | $CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_4COOH$ |
| Arachidonic | 4 | $CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2-CH=CHCH_2CH=CH(CH_2)_3COOH$ |

# Cyclic unsaturated acids

**Table 18.4.** Cyclic unsaturated acids.

| *Common name* | *Structural formula* |
|---|---|
| Hydnocarpic |  |
| Chaulmoogric |  |
| Gorlic |  |
| Prostanoic |  |
| PGA2 |  |



# Formation of olefinic fatty acids

Acetate + malonate

↓

$CH_3(CH_2)_{14}COOH$ Palmitic

↓

$CH_3(CH_2)_{16}COOH$ Stearic

↓ − 2H

$CH_3(CH_2)_7CH{=}^{cis}CH(CH_2)_7COOH$ Oleic

↓ − 2H

$CH_3(CH_2)_4CH{=}^{cis}CH{-}CH_2{-}CH{=}^{cis}CH(CH_2)_7COOH$ Linoleic

↓ − 2H

$CH_3{-}CH_2{-}CH{=}^{cis}CH{-}CH_2{-}CH{=}^{cis}CH{-}CH_2{-}CH{=}^{cis}CH(CH_2)_7COOH$ Linolenic

**Fig. 18.1.** Sequence of formation of olefinic fatty acids in plants.

# Manufacturing of oleoyls

$$CH_3(CH_2)_{16}CO-S-ACP + O_2 + NADPH \longrightarrow$$

(stearoyl-*S*-ACP)

$$CH_3(CH_2)_7CH=CH(CH_2)_7-CO-S-ACP + H_2O + NADP$$

(oleoyl-*S*-ACP)





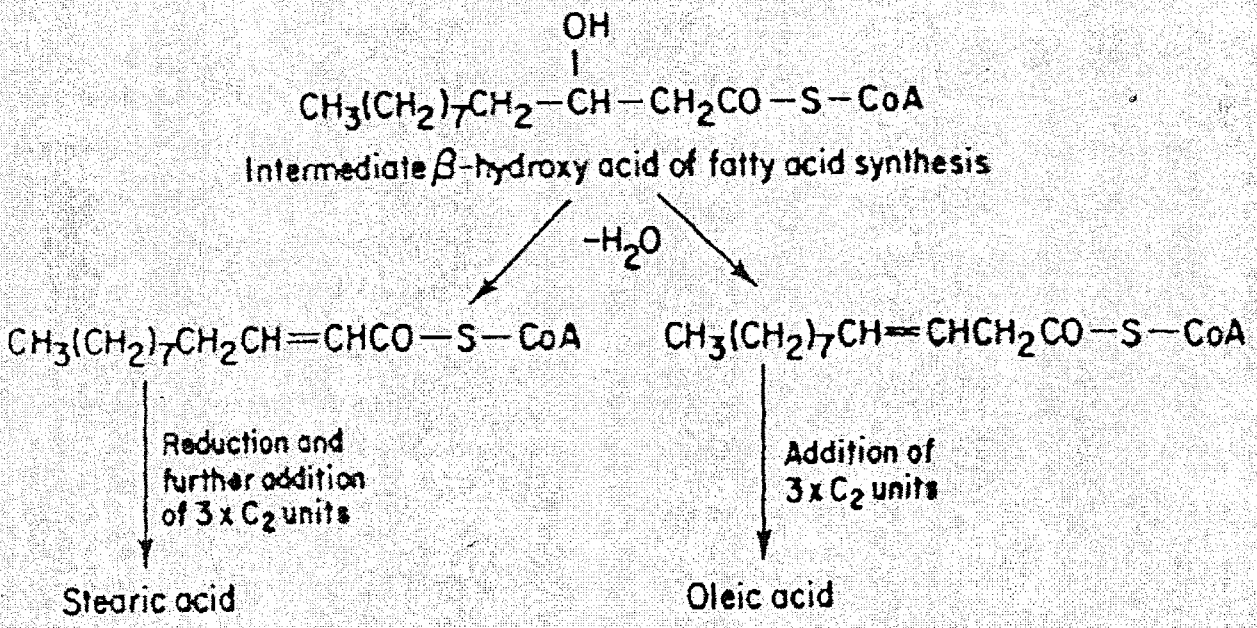



Fig. 18.2. Alternative pathways for synthesis of unsaturated fatty acids.

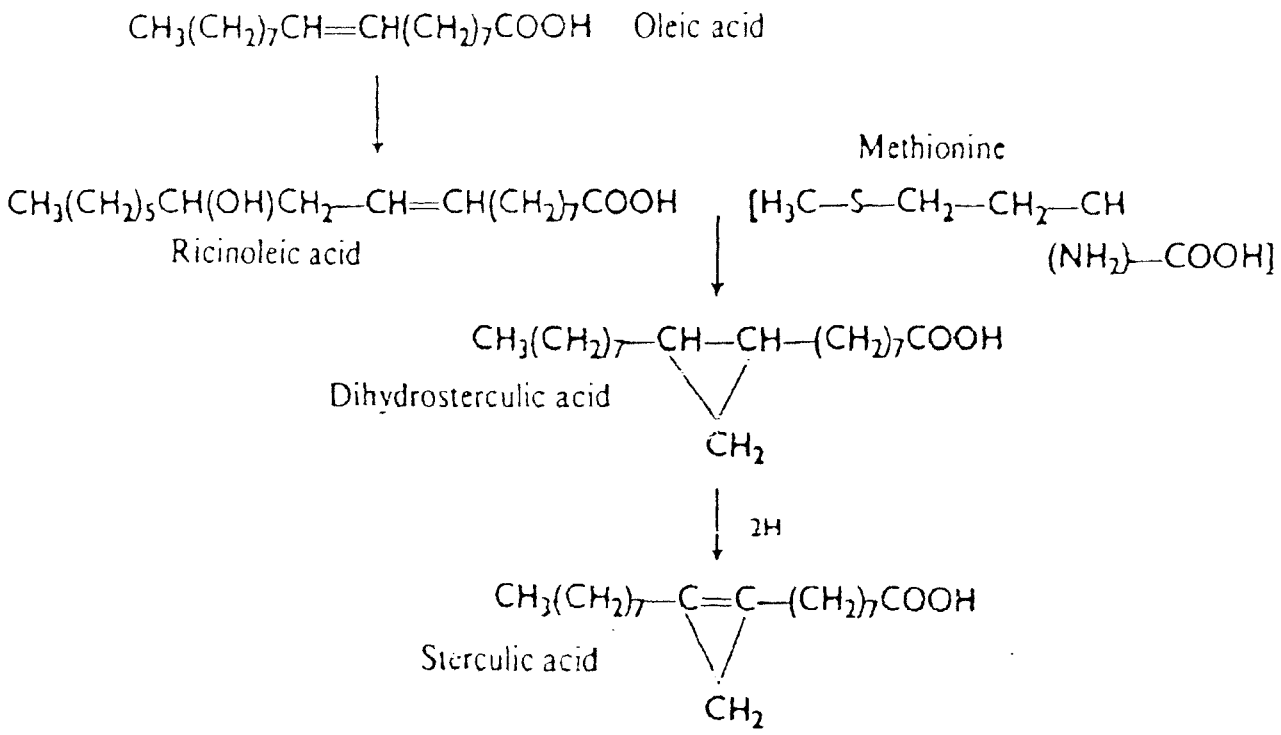



Fig. 18.3. Oleic acid as the precursor of ricinoleic and sterculic acids.

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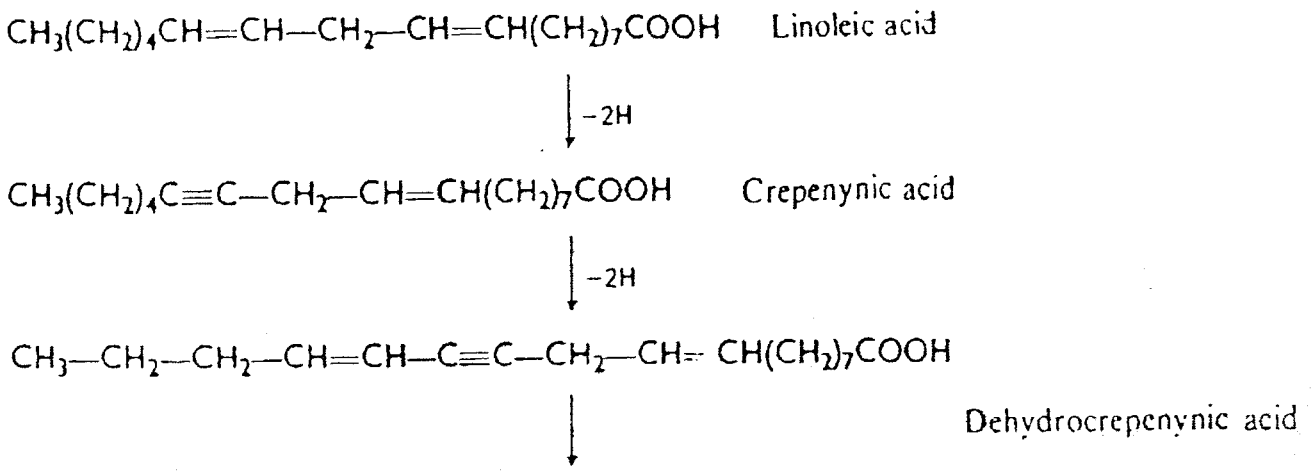


Range of acetylenes formed by further introduction of acetylenic bonds at the 'distal' part (furthermost from carboxyl group) of molecules and by chain shortening in 'proximal' part of molecule.

Fig. 18.4. Formation of acetylenic fatty acids.

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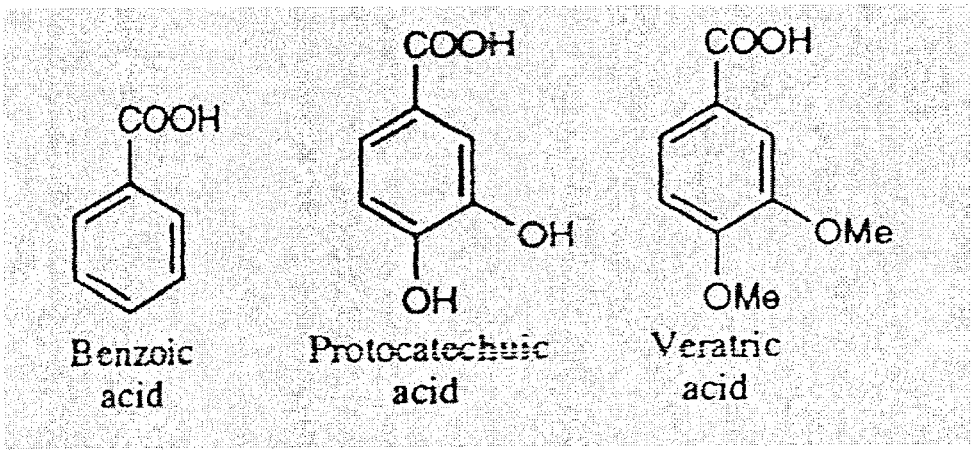
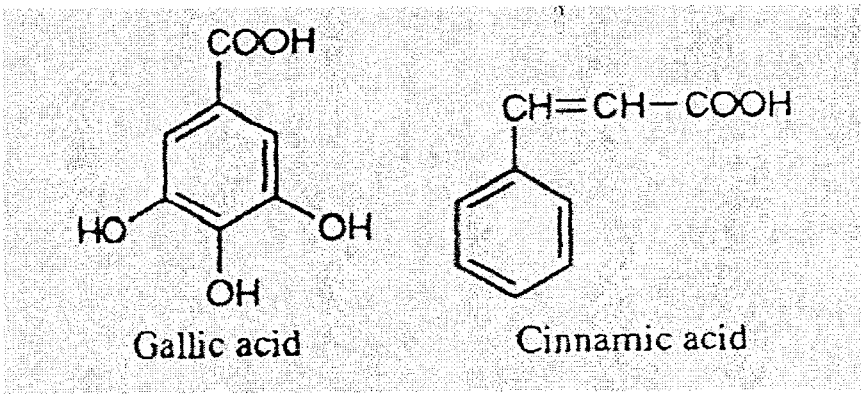
# Aromatic cyclic acids

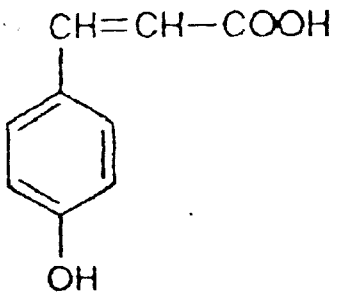




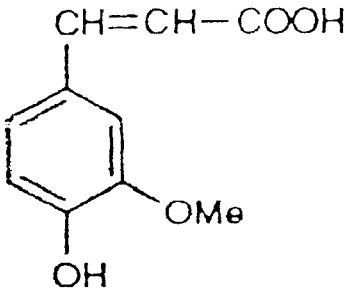

# Aromatic cyclic acids



# Aromatic cyclic acids



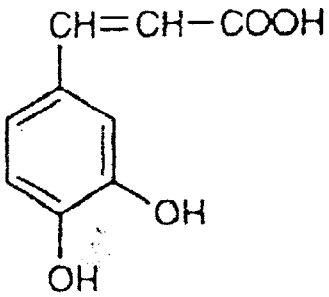

*p*-Coumaric acid



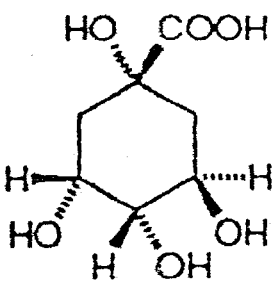

Ferulic acid



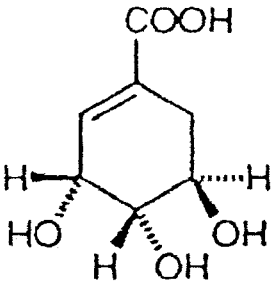
# Aromatic cyclic acids




Caffeic acid




Quinic acid




Shikimic acid

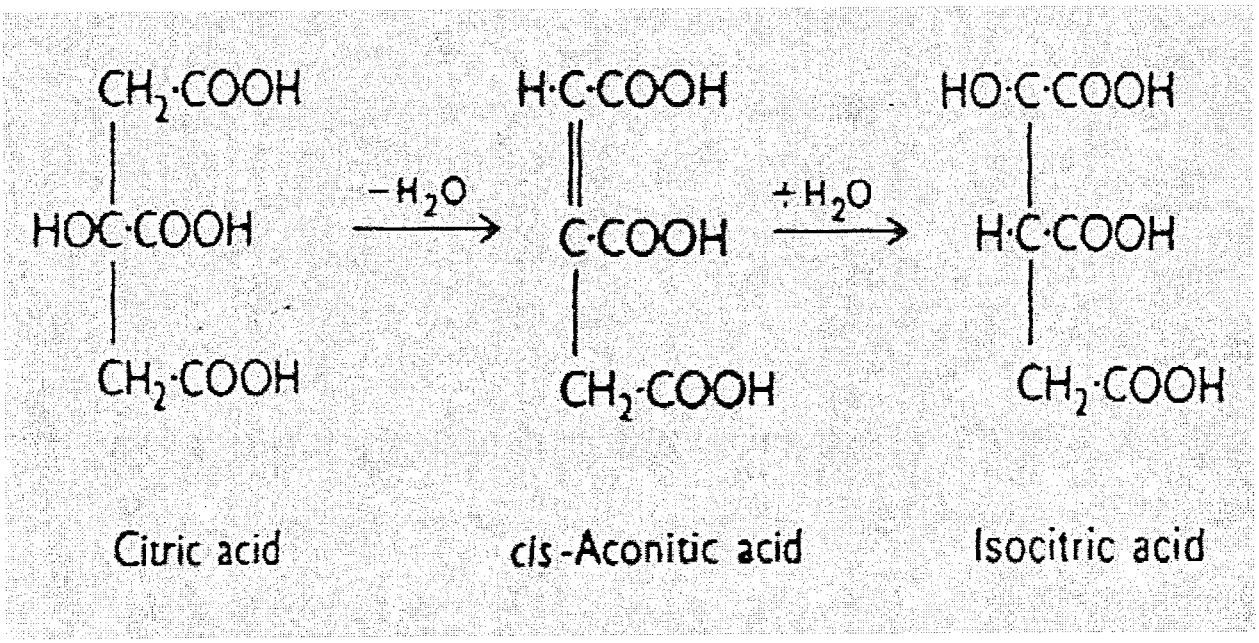
# Dib and Tri carboxylic acids

Oxalic acid, (COOH)2, forms the first of a series of dicarboxylic acids which includes malonic acid, CH2(COOH)2, and succinic acid, (CH2)2(COOH)2.

Malic acid contains an alcohol group and has the formula COO-CH2-CHOH-COOH. It is found in fruits such as apples and tamarinds.



# Formation of iso-citric acid



# Extraction of fats and fixed oils

Most commercial oils are derived from either seeds or fruits and nowadays are mostly extracted by the producing country and exported as the crude oil.

The initial treatment before extraction depends on the botanical structure (American cotton seeds require delinting and castor seeds and ground nuts require decorticating.



# Extraction of fats and fixed oils

- Removal of the oil may take the form of cold or hot expression, centrifuging or solvent extraction.
- The crude oil requires refining.
- Cold –drawn oils usually require nothing further than filtration; castor oil requires steaming to inactivate lipase; The addition of a determined amount of alkali may be required to remove free acid; and washing and decolorization may be performed.

# Quantitative tests of fats and fixed oils

- Acid value refers to the number of mg of potassium hydroxide required to neutralize the free acids in 1 g of the oil; high acid values arise in rancidified oils.
- Saponification value: the hydrolysis reaction of lipids can be used to determine the saponification value of the oil and is expressed as the number of mg of potassium hydroxide required to neutralize the total acids in 1 g of the substance.



# Quantitative tests of fats and fixed oils

Ester value is the difference between the saponification and acid value.

Iodine value gives a measure of the unsaturation of the oil.

Oils which partially resinify on exposure to air are known as semidrying or drying oils. Such oils (linseed oil) have high iodine values.

# Quantitative tests of fats and fixed oils

Acetyl value is the number of milligrams of potassium hydroxide required to neutralize the acetic acid freed by the hydrolysis of 1 g of the acetylated fat.

Certain physical constants of fixed oils and fats are significant: specific gravity, melting point, refractive index and sometimes optical rotation (castor oil).



# Quantitative tests of fats and fixed oils

The gas chromatographic separation and quantification of the acids produced by the hydrolysis of specific fixed oils is an official method for their identification and quality control;

TLC (Silica gel immersed in Paraffin, detection Starch sol.+Iodin sol.) is used in the detection of the degradation Products of Fats.

# Waxes

- An important practical difference between fats and waxes is that;

1-fats may be saponified by means of either aqueous or alcoholic alkali but waxes are only saponified by alcoholic alkali.

-Saponification of the wax ester cetyl palmitate may be represented as:

C15H31.COOC16H33+alcoholic KOH= C16H33OH Cetyl alcohol+C15H13.COOK Potassium palmitate.



# Waxes

2- While fats consist almost entirely of esters, waxes, in addition to esters of the cetyl palmitate type, often contain appreciable quantities of free acids, hydrocarbons, free alcohols and sterols.