South Valley University

Faculty of Education

Chemistry Department

Petroleum Industrial Chemistry

4th year students – Faculty of Education

Chemistry group

Second Term 2022/2023

Dr/ Ibrahim Abdul-Motaleb Mousa

CHEMISRY OF NATURAL PRODUCTS

4th Year Students Faculty of Education South Valley University

second term 2022/2023

Dr/ Ibrahim Abdul-Motaleb Mousa

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- **Structure elucidation of steroids**
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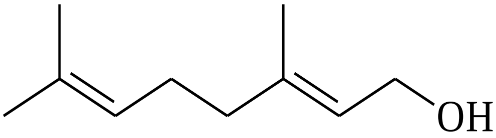
Introduction:

- Natural products are organic compounds produced by
- living organisms, such as human organs, plants,
- animal organs, sea organisms and micro-organisms,
- as a result of the metabolism. These compounds
- comprise, the so called, primary metabolites and
- secondary metabolites.

Classification of Natural Products:

- Classes of Natural Products
- Classification based on chemical structure



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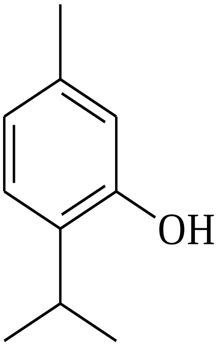
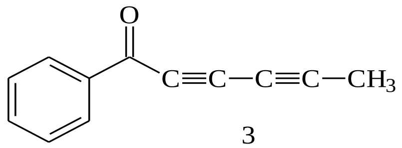


2

- ***Classification based on physiological activity***
- **as exemplified by hormones, antibiotics,..**
- ***Classification based on taxonomy***
- **xanthanolides from *Xanthium*, iridoids from *Iridomyrnex*, ergot alkaloids, alkaloid class of the ergot, iboga alkaloids, alkaloid of iboga, meinspermaceae alkaloids**



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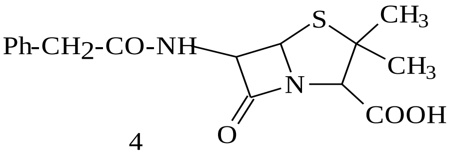
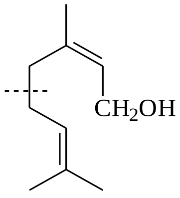


4

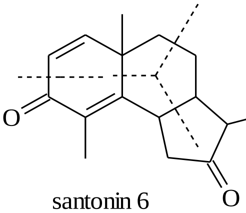
Classification based on biogenesis

Biogenesis : hypothesis

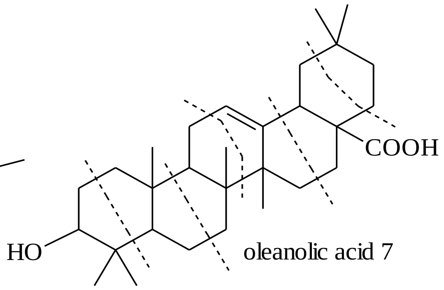
Biosynthesis : experimentally proven route



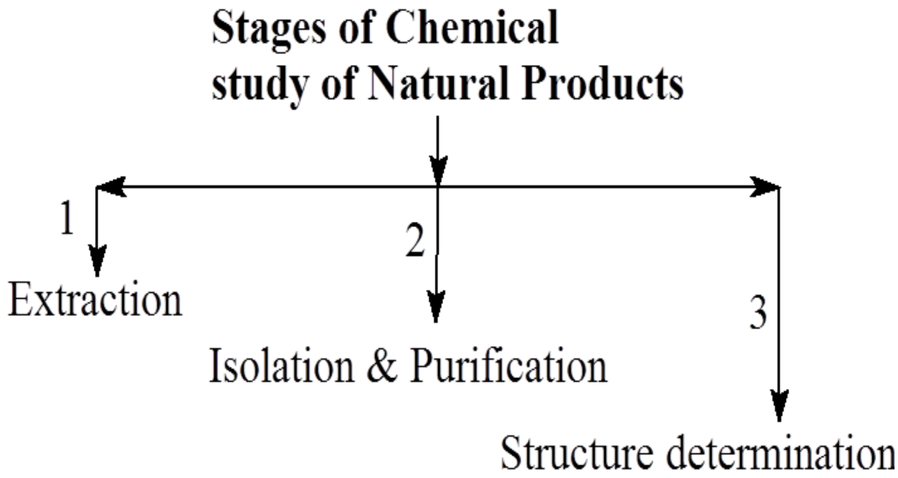
nerol 5



santonin 6

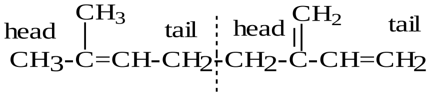


oleanolic acid 7



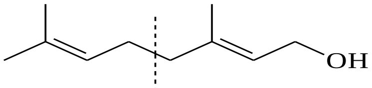
Terpenoids:

- **Terpenes are compounds, when heated in the absence of air (oxygen) give isoprene.**
- **Isoprene Rule, Wallach, 1887**
- **the skeleton structures of all naturally occurring terpenes can be built up of isoprene units**
- **Special Isoprene Rule, Ingold, 1925**
- **the isoprene units in natural terpenes were jointed "head-to-tail".**



$CH_3\text{-}\overset{\overset{CH_3}{|}}{C}\text{=}CH\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{CH_2}{||}}{C}\text{-}CH\text{=}CH_2$

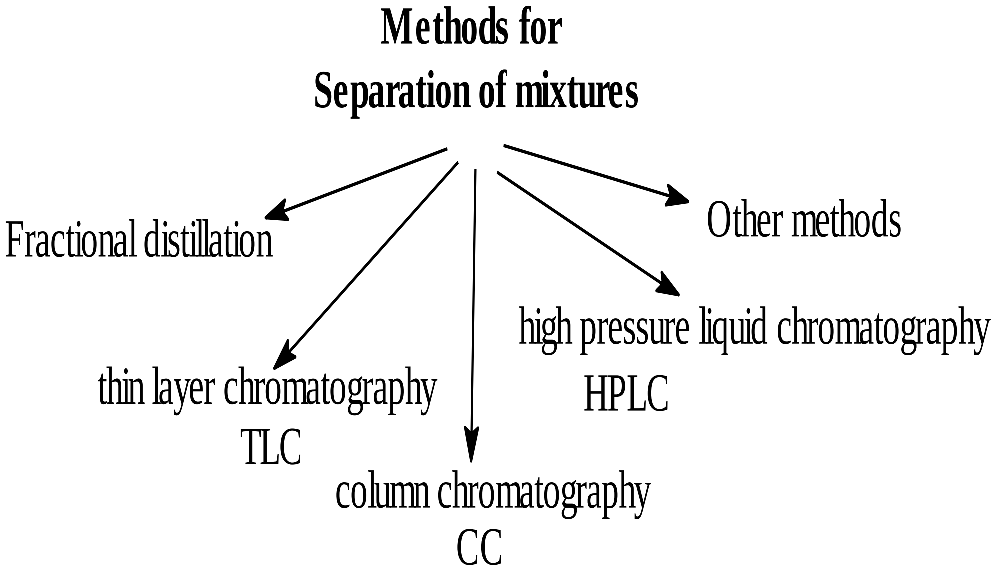
myrcene 8



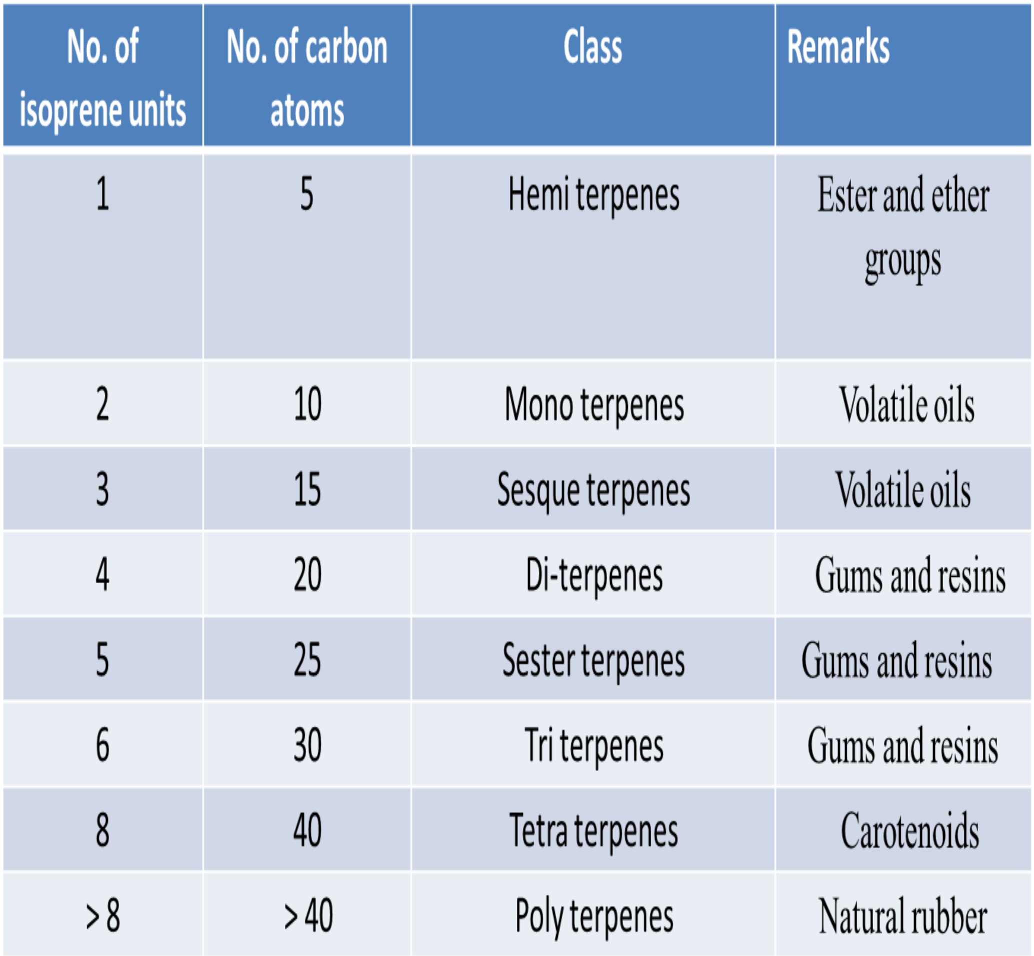
geraniol 9

Isolation of Mono- and Sesequeterpenes (essential oils)

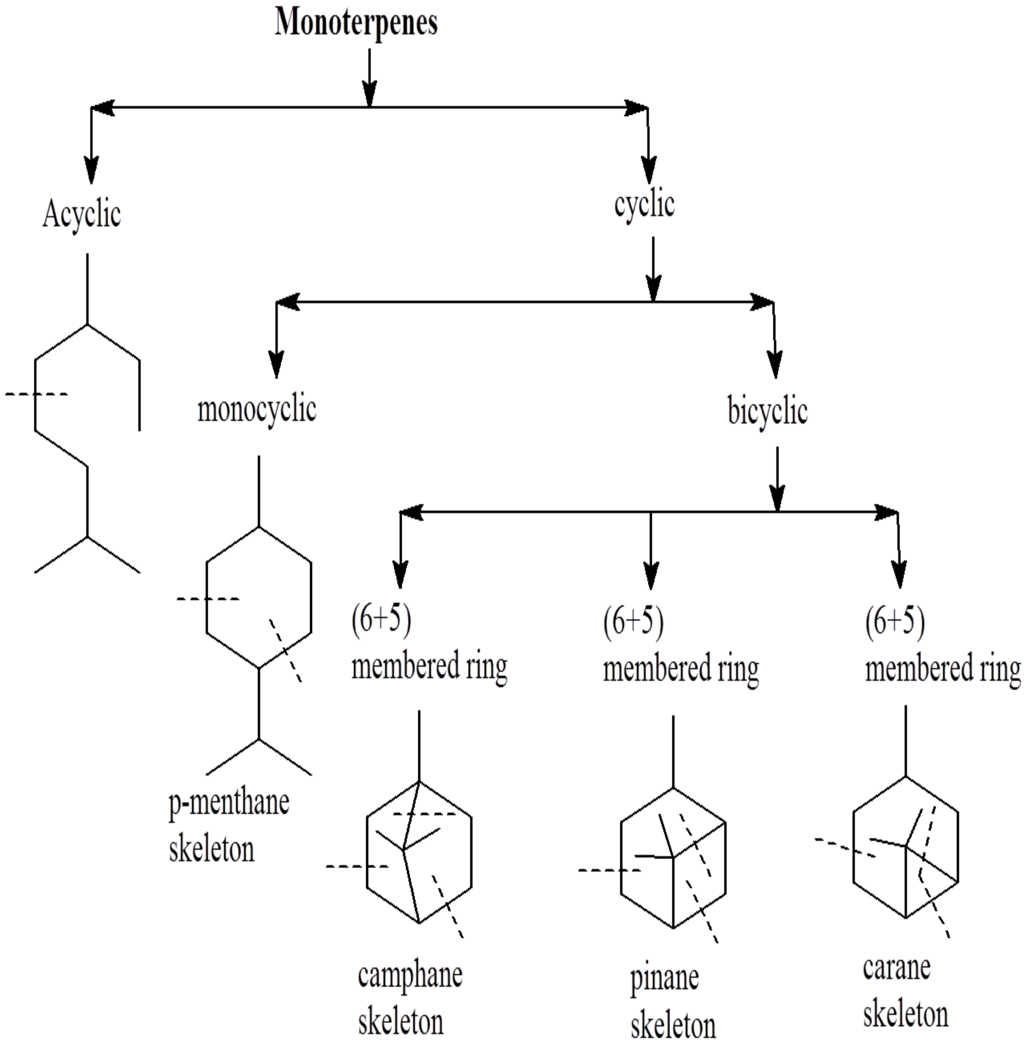
- **(i) Expression**
- · **(ii) Steam distillation**
- · **(iii) Extraction by means of volatile organic solvents**
- · **(iv) Adsorption on fats.**



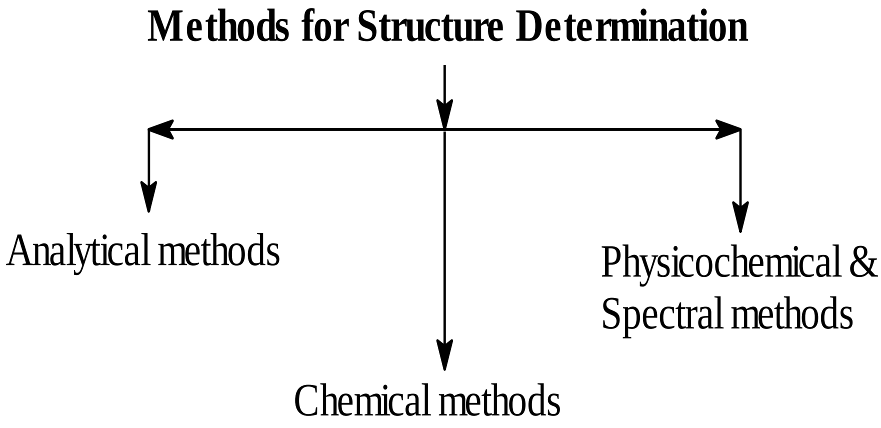
Classification of terpenes



No. of isoprene units	No. of carbon atoms	Class	Remarks
1	5	Hemi terpenes	Ester and ether groups
2	10	Mono terpenes	Volatile oils
3	15	Sesque terpenes	Volatile oils
4	20	Di-terpenes	Gums and resins
5	25	Sester terpenes	Gums and resins
6	30	Tri terpenes	Gums and resins
8	40	Tetra terpenes	Carotenoids
> 8	> 40	Poly terpenes	Natural rubber

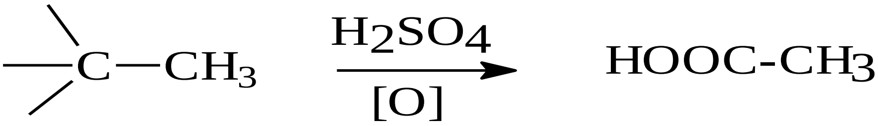

Monoterpenes
Acyclic
cyclic
monocyclic
bicyclic
(6+5) membered ring
(6+5) membered ring
(6+5) membered ring
p-menthane skeleton
camphane skeleton
pinane skeleton
carane skeleton

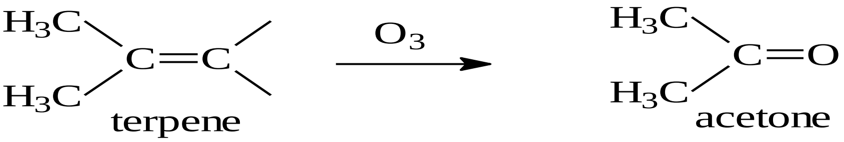
General methods for structure determination of terpenoids:



Analytical methods:

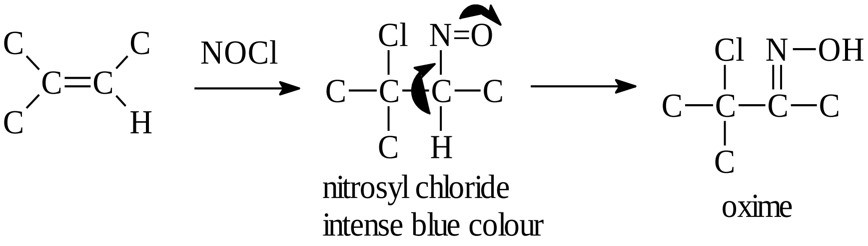
- **Analytical methods**
- **· Determination of % of C,H and O by combustion → empirical formula → molecular formula**
- **Degrees of unsaturation**
- **Estimation of groups**
- **· Active hydrogen**
- **Terpene + $LiA1H_4 \rightarrow H_2$ ----- estimated**





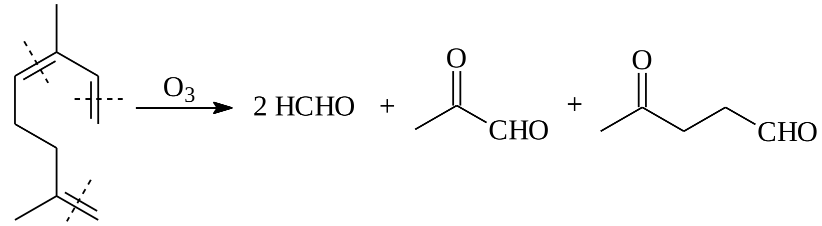
Chemical methods:

- **Functional groups**
- **Unsaturation**
- **· by bromination (Br_2)**
- **· by nitrosyl chloride NOCl**

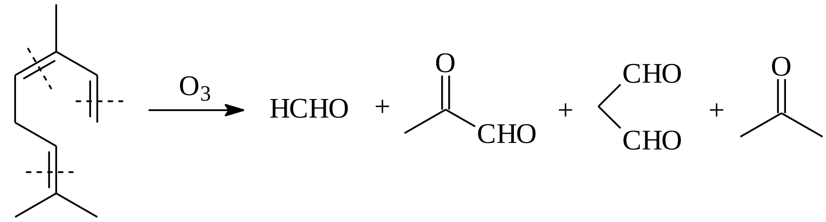


- **Ozonolysis is an example of oxidative degradation methods (O_3, $KMnO_4$, CrO_3 & OsO_4).**

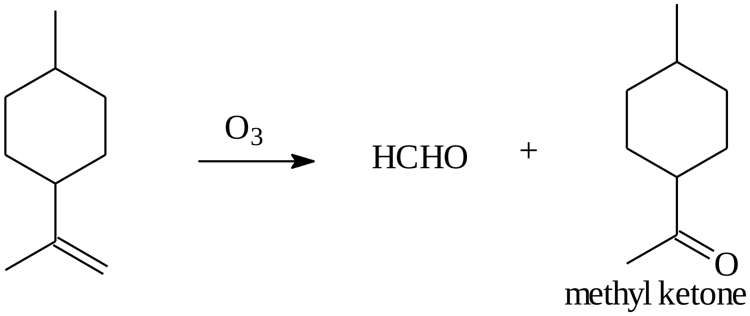
(i)



(ii)

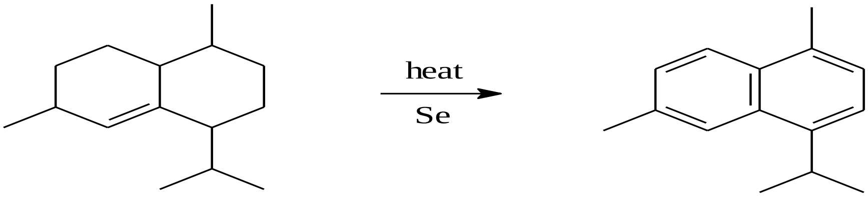


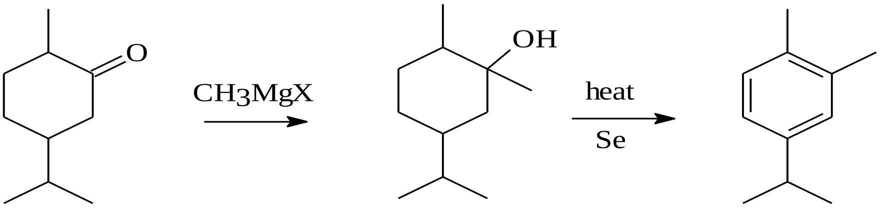
(iii)



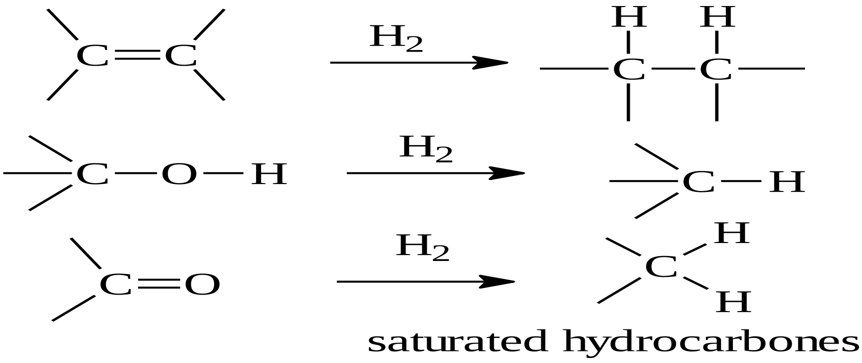
- **Conjugated and isolated double bonds are differentiated by Diel's Alder reaction.**

- **Dehydrogenation by heating the terpene with S or Se converts the terpene into aromatic derivative which is easily identified.**





- **Hydrogenation of the substance to the parent hydrocarbon leads to the cyclic nature of the terpene (acyclic, monocyclic, bicyclic, ... etc).**



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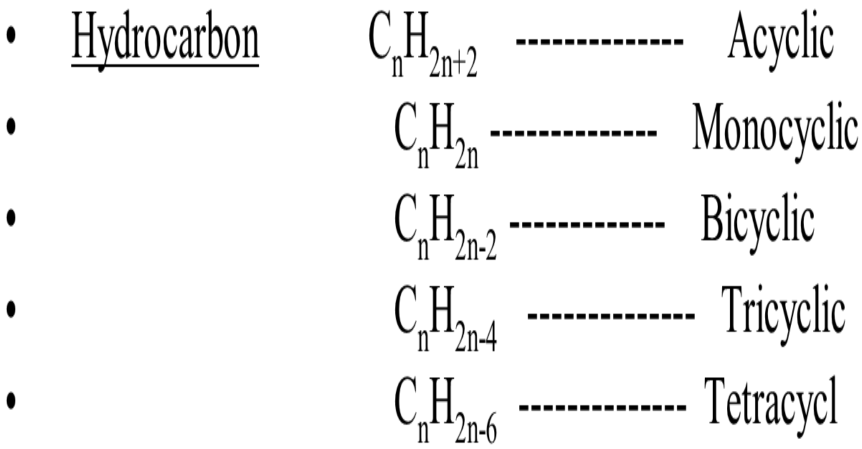
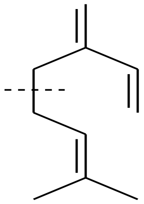


- **Hydrocarbon** C_nH_{2n+2} ------------- Acyclic
- C_nH_{2n} ------------- Monocyclic
- C_nH_{2n-2} ------------ Bicyclic
- C_nH_{2n-4} ------------- Tricyclic
- C_nH_{2n-6} ------------- Tetracycl

-

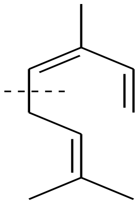
- **Physical and spectral methods:**
- **a) Molecular refraction (refractive index, refractometer).**
- **b) Optical rotation α_D (polarimeter)**
- **c) IR absorption**
- **d) NMR (^{1}H-NMR & ^{13}C-NMR)**
- **e) X-Ray analysis**
- **f) UV (ultraviolet absorption)**
- **· A final confirmation of the proposed structure is usually achieved by synthesizing the compound and comparing the spectral data with those of an authentic sample.**

- **Examples for different terpenes:**
- **Monoterpenes**
- **Acyclic**



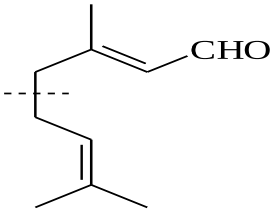
Myrcene

- occurs in verbena and bay oil



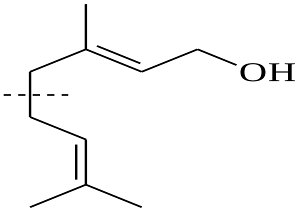
Ocimene

occurs in *Ocimum basilicum*



Citral

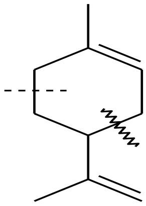
- occurs in lemon grass oil



Geraniol

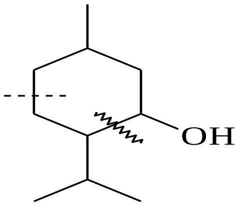
occurs in rose oil

- **Cyclic:**

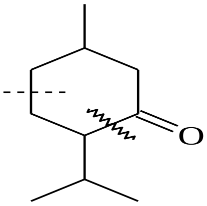


Limonene

occurs in lemon
and orange oils

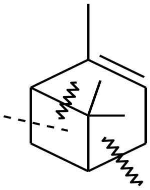


Menthol

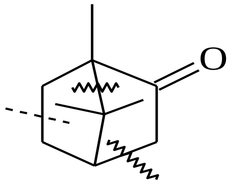


Menthone

both occur in pepermint oil

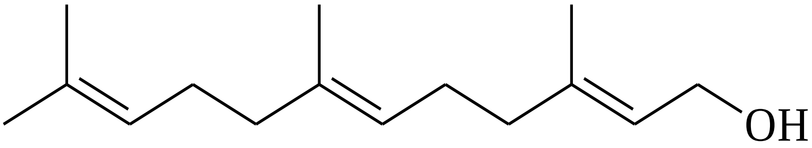


α-Pinene
occurs in turpentine oil

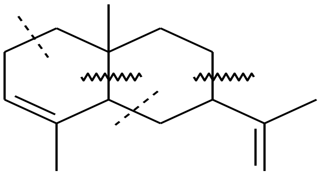


Camphor
occurs in camphor tree

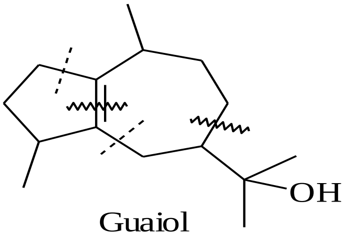
Sesquiterpenes:



Farnesol
occurs in oil of ambrette seeds

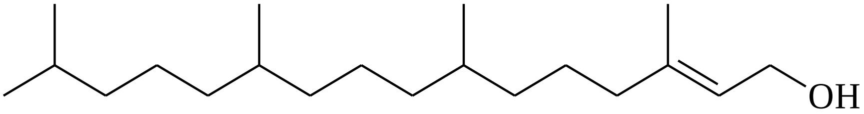


α-Selinene
occurs in celery oil

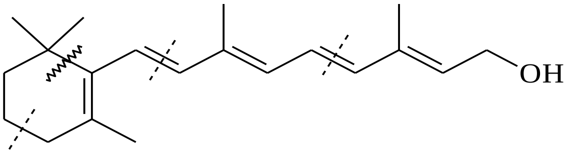


Guaiol
occurs in guaicum wood oil

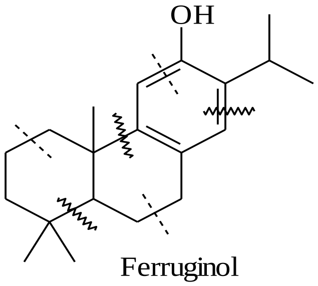
Diterpenes:



Phytol
is produced from hydrolysis of chlorophyll

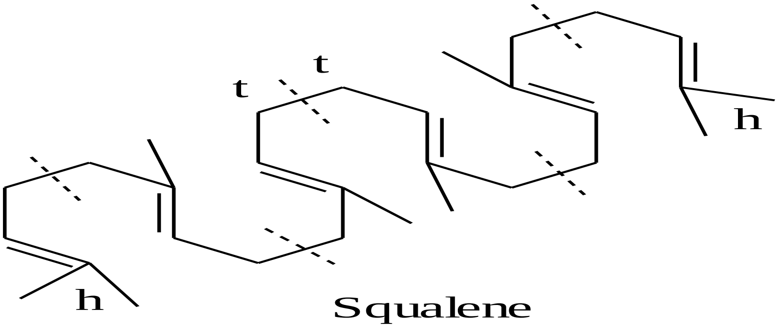


Vitamin A
occurs in carrot

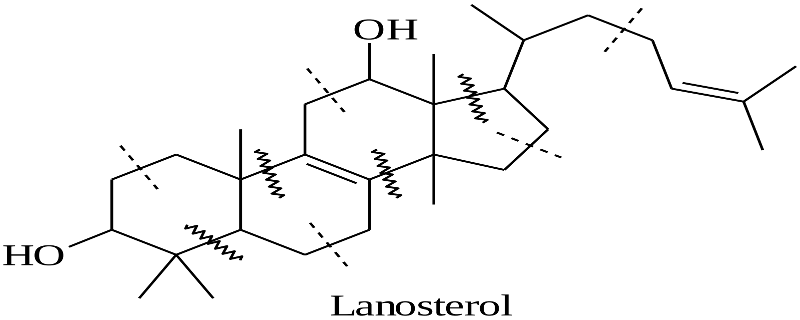


Ferruginol
occurs in *Podocarpus ferrugineus*

Triterpenes:

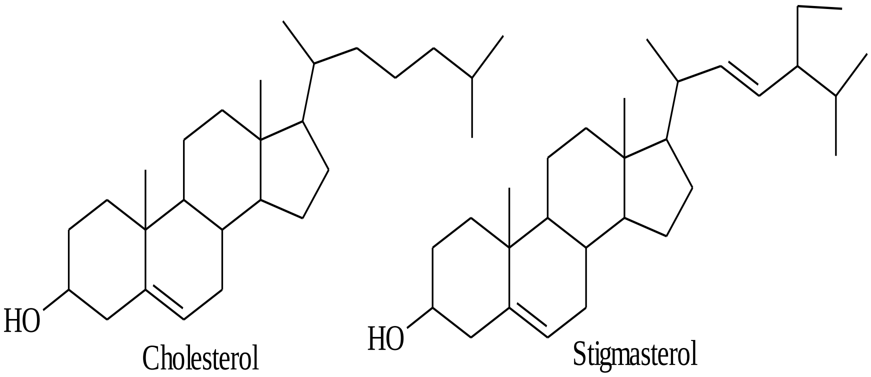


Squalene
occurs in olive oil



Lanosterol

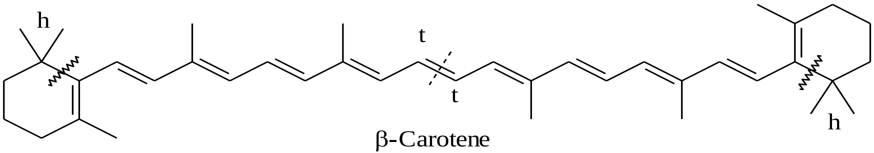
- **Sterols**



Cholesterol
the famous animal sterol

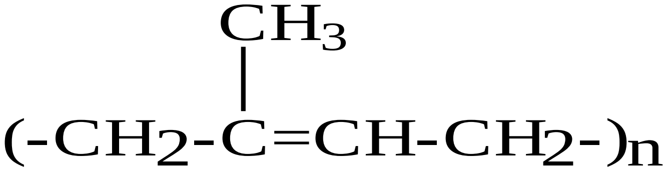
Stigmasterol
the famous plant sterol

Tetraterpenes:



β-Carotene
occurs in carrot, it is the precoursor of vitamin A

- **Polyterpenes**



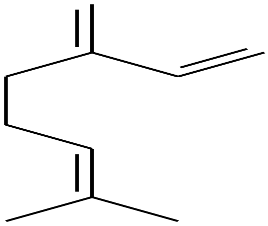
$$\begin{array}{c} \quad CH_3 \\ \quad | \\ (-CH_2-C=CH-CH_2-)_n \end{array}$$

Polyisoprene, natural rubber

Structure-elucidation and Synthesis of selected terpenoids

Acyclic monoterpenes

Myrcene ($C_{10}H_{16}$)



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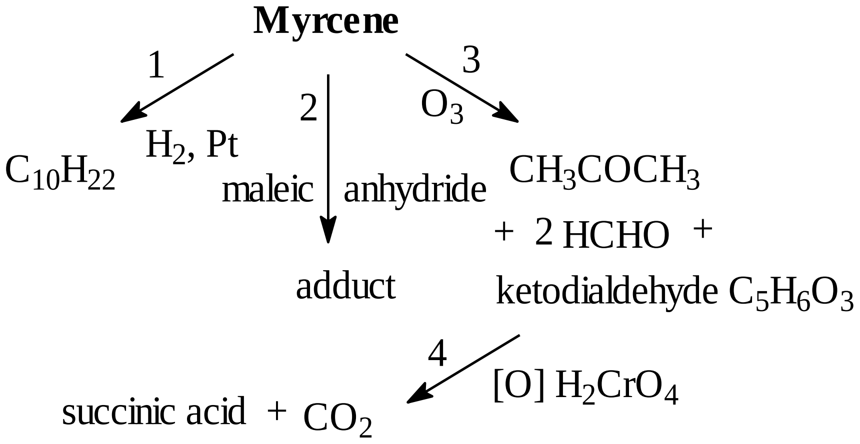

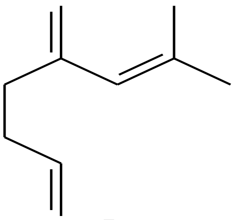

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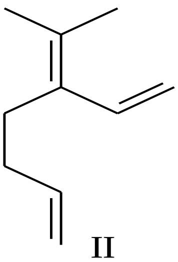

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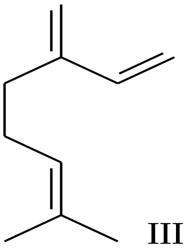
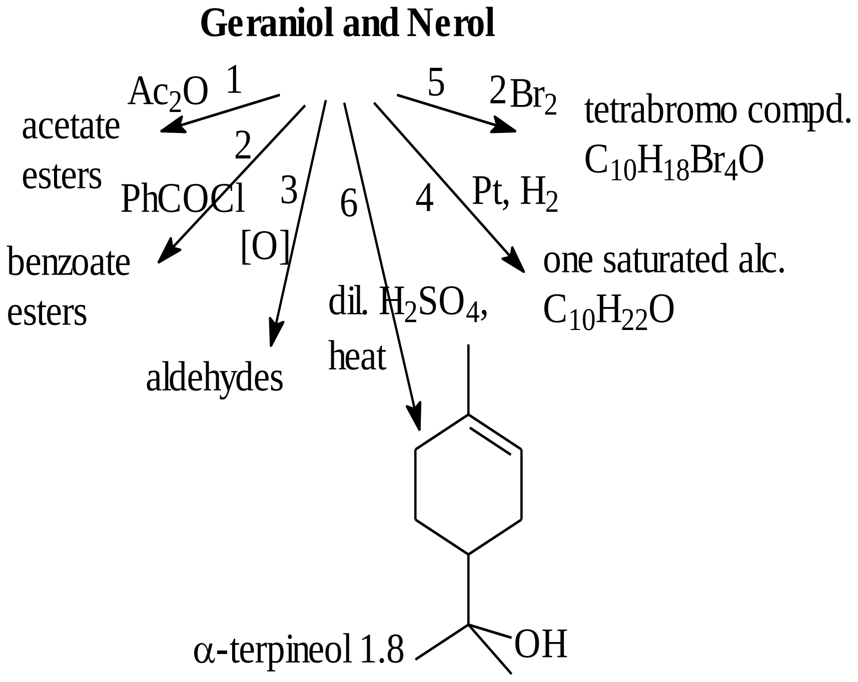


III

Geraniol and Nerol

$C_{10}H_{18}O$



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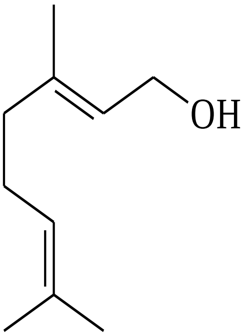

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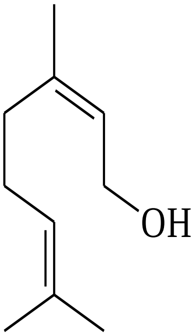

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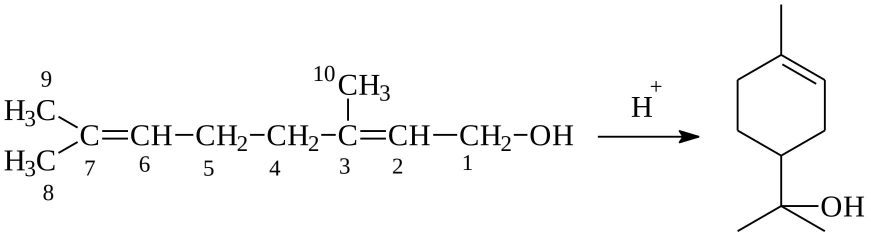
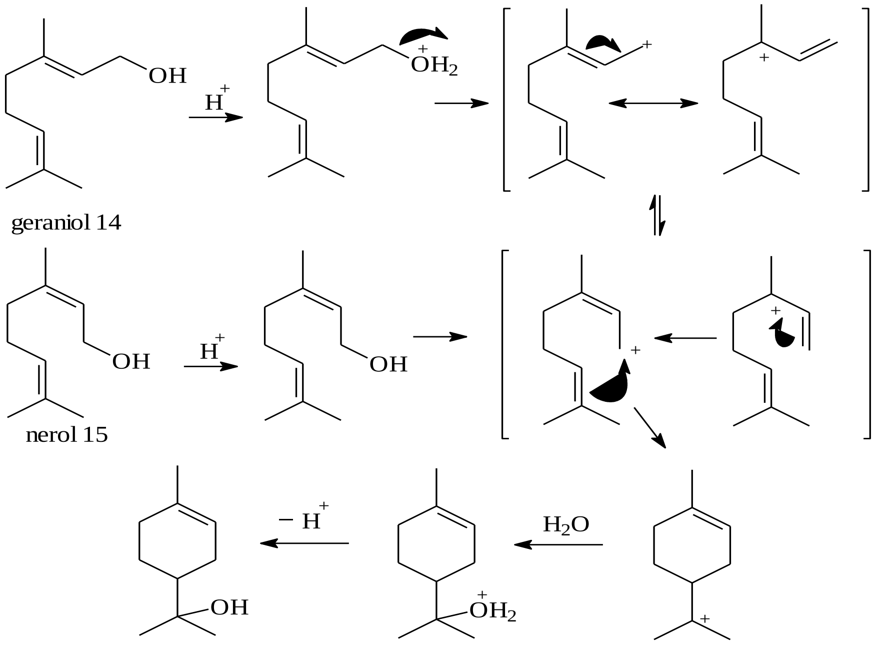


$$\overset{9}{H_3C}\diagdown\!\!\!\!\overset{}{} C{=}CH{-}CH_2{-}CH_2{-}\overset{^{10}CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}OH \xrightarrow{H^+}$$

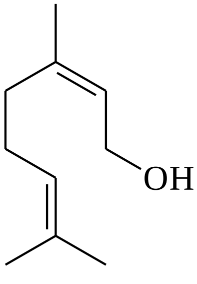
16



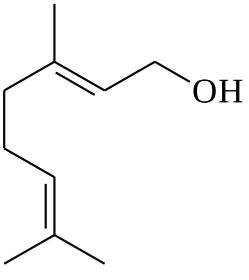
geraniol 14

nerol 15

α-terpineol 16



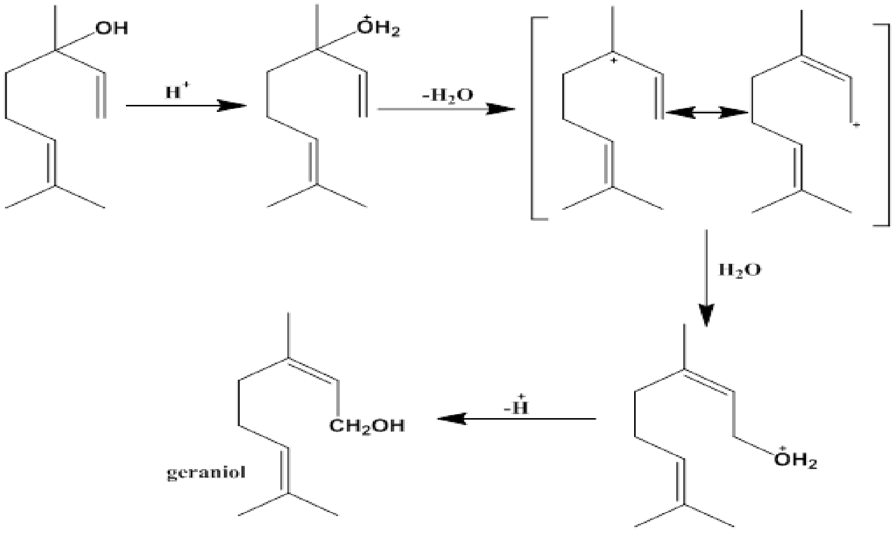
cis or Z



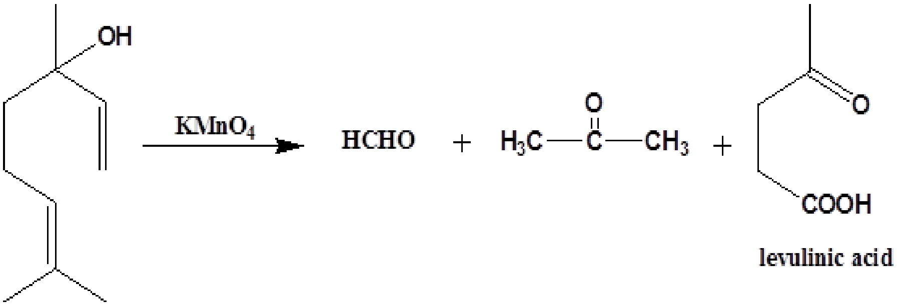
trans or E

Linalool (C$_{10}$H$_{18}$O)

1. **Elemental analysis shows that the molecular formula of linalool is $C_{10}H_{18}O$.**
2. **Catalytic hydrogenation of linalool give $C_{10}H_{22}O$,indicates the presence of two π–bonds.**
3. **Bromination of linalool give $C_{10}H_{18}Br_4O$, indicates the presence of two π–bonds.**
4. **Reaction of linalool with maleic anhydride give no adduct, this indicates the presence of isolated π-bonds.**
5. **Reaction of linalool with acetic anhydride give acetate, and with benzoyl chloride give benzoate, this indicates the presence of (OH) group.**
6. **Oxidation of linalool give no reaction, this indicates that (OH) is tertiary alcohol.**
7. **It is optically active. (-) form occurs in rose oil, and (+) form in orange oil.**
8. **Linalool reacts with acids and converted to geraniol.**

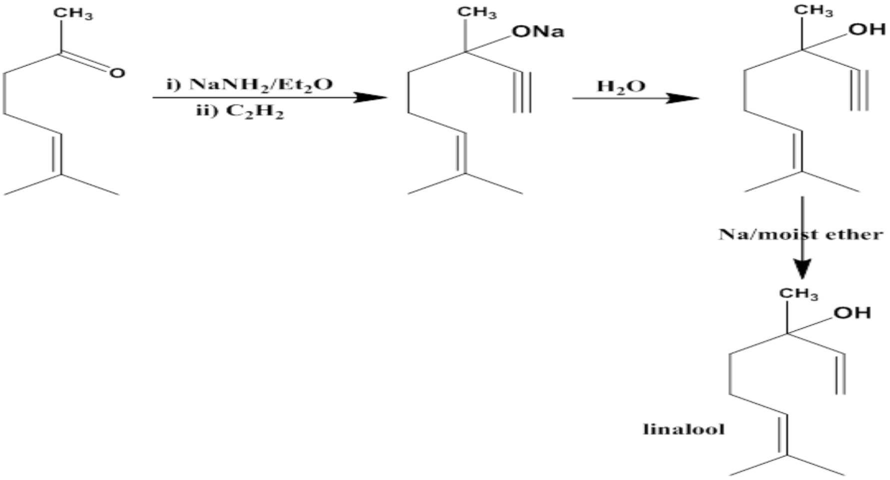


1. Ozonolysis:

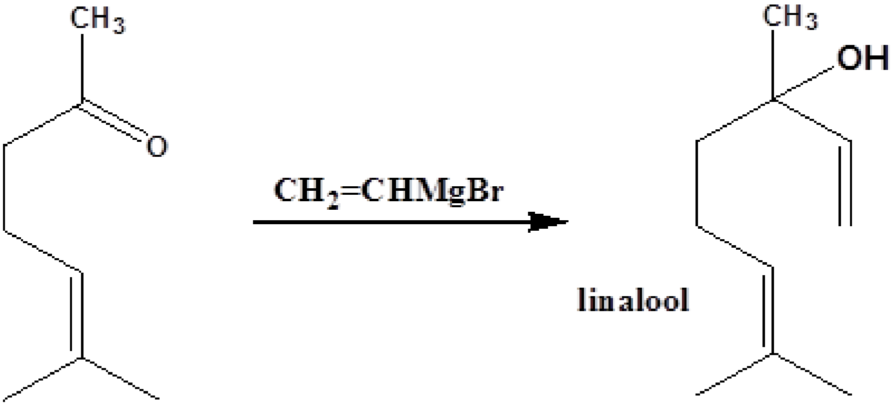


1. **Synthesis of linalool:**

a. **From methyl heptanone with acetylene followed by partial reduction of the triple bond to give linalool.**

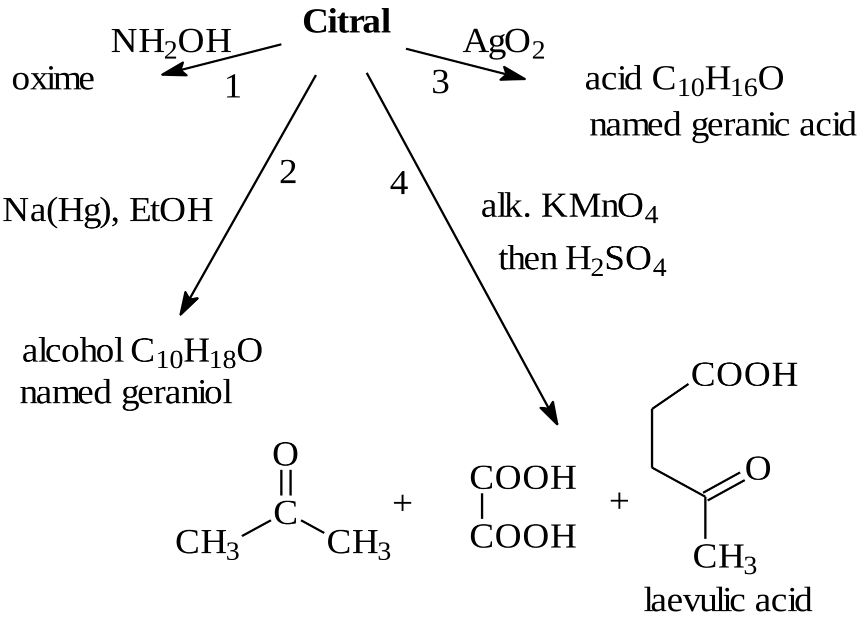


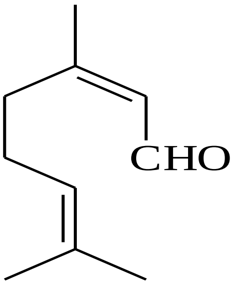
b- **Normant (1955): from methyl heptanone with vinyl magnesium bromide.**

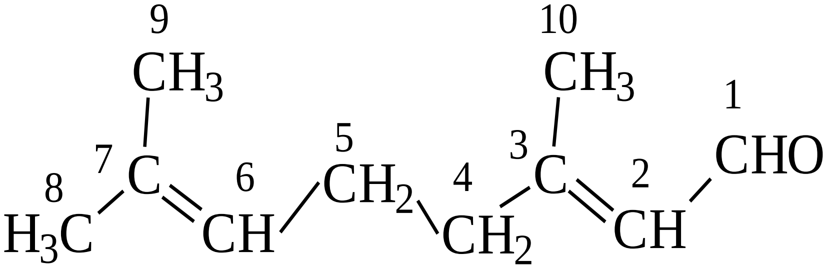


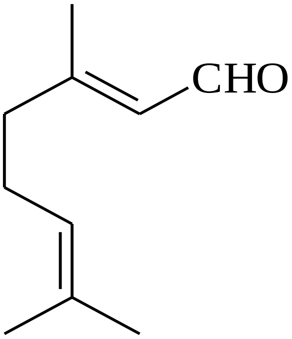
Citral

$C_{10}H_{16}O$

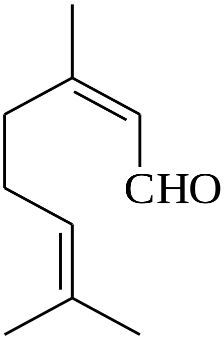








citral-a or geranial

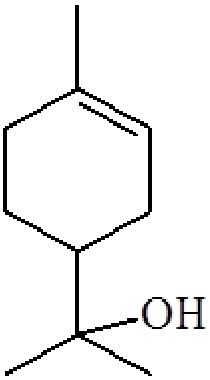


citral-b or neral

Monocyclic monoterpenes

α-Terpineol

$C_{10}H_{18}O$



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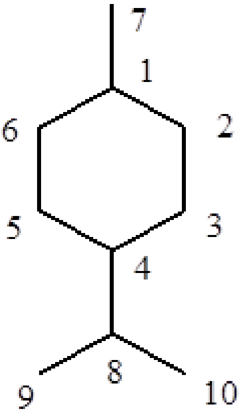
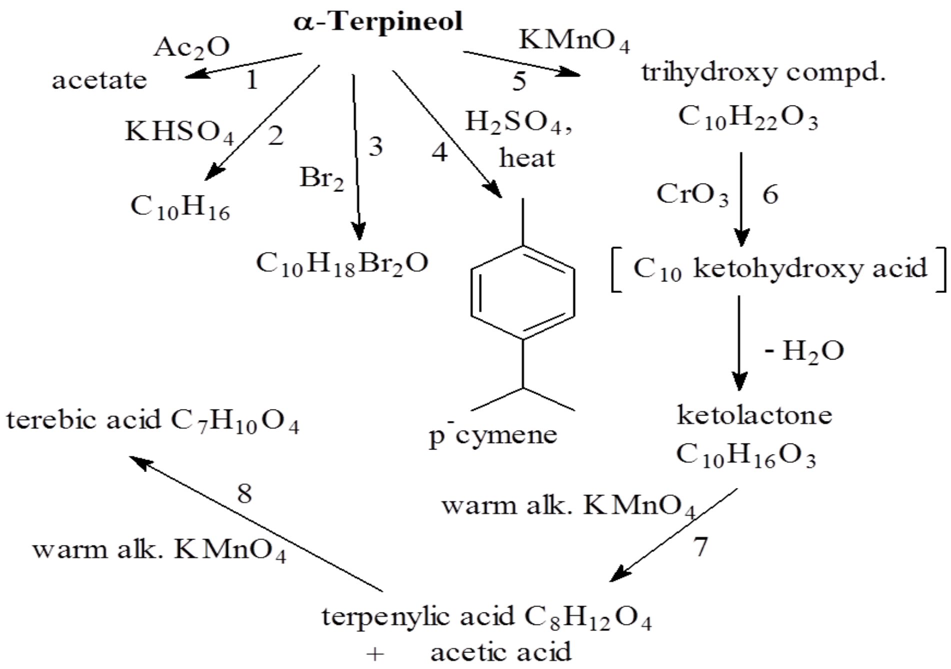
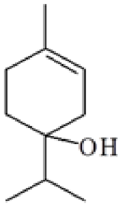
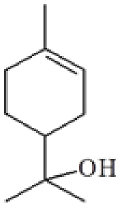


p-menthane or hexahydro- *p*-cymene

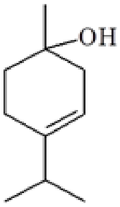



OH

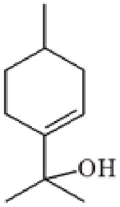
I


OH

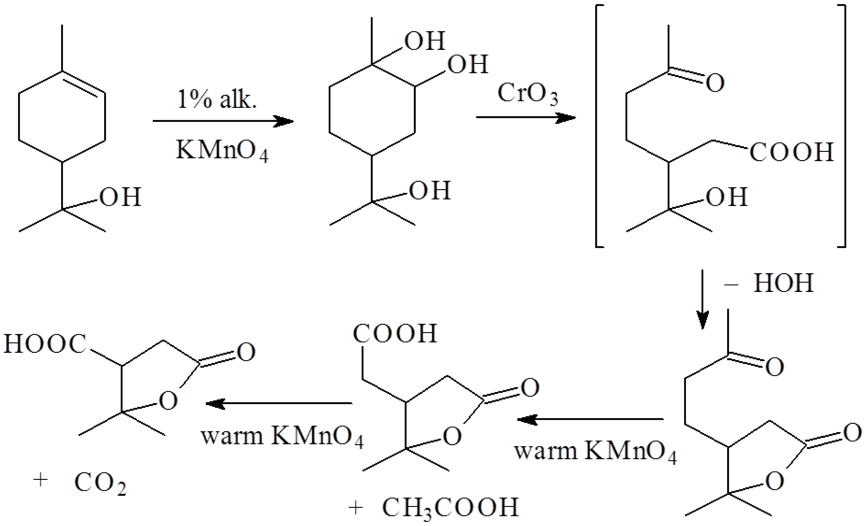
II


OH

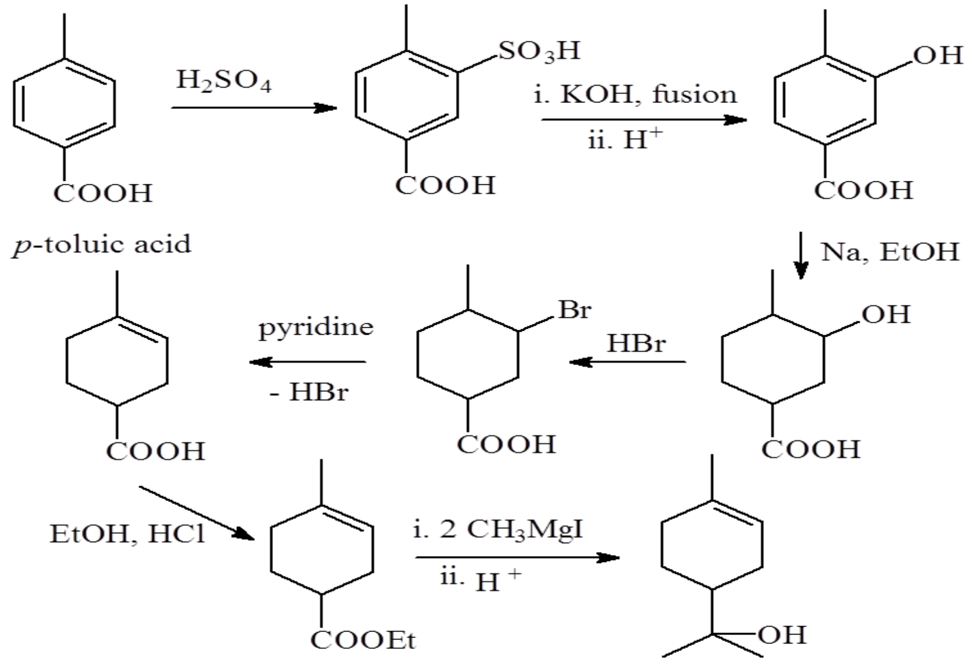
III

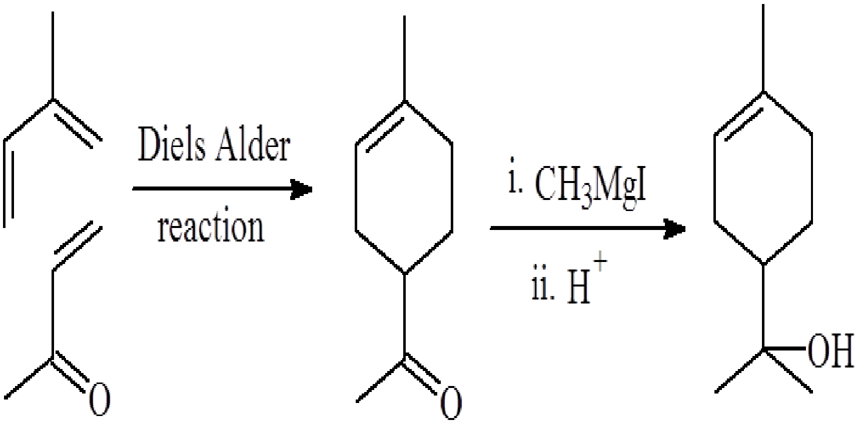

OH

IV


OH
1% alk.
$KMnO_4$
OH
OH
OH
CrO_3
O
COOH
OH
– HOH
O
O
O
warm $KMnO_4$
COOH
O
O
+ CH_3COOH
warm $KMnO_4$
HOOC
O
O
+ CO_2

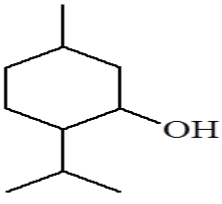
Synthesis of α-terpineol



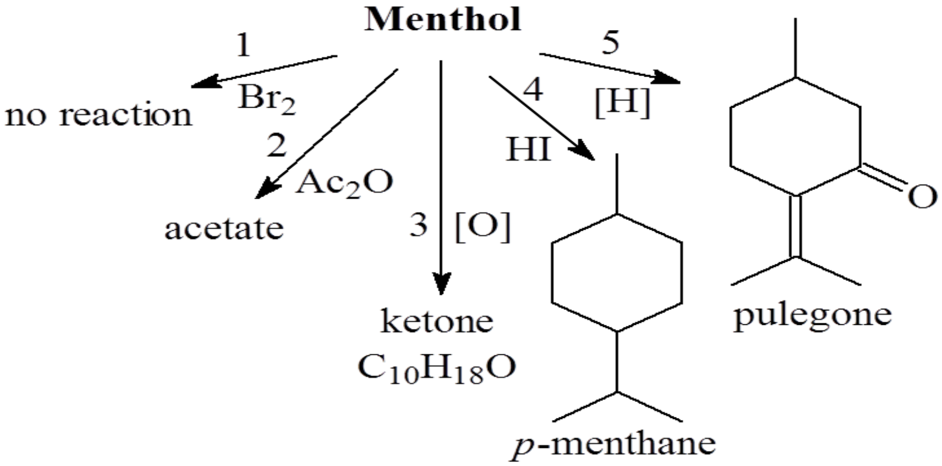


Carvone

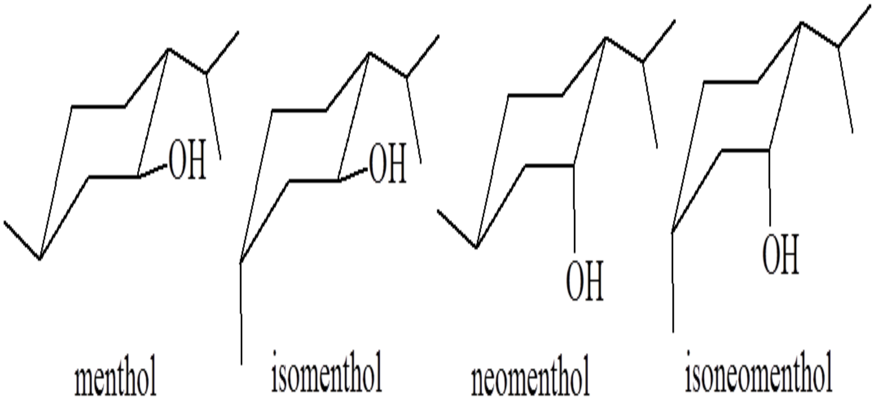
$C_{10}H_{14}O$



22



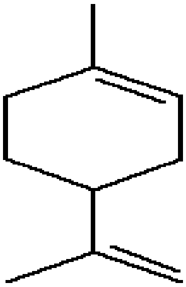
Stereochemistry of menthol



menthol isomenthol neomenthol isoneomenthol

Limonene

$C_{10}H_{16}$



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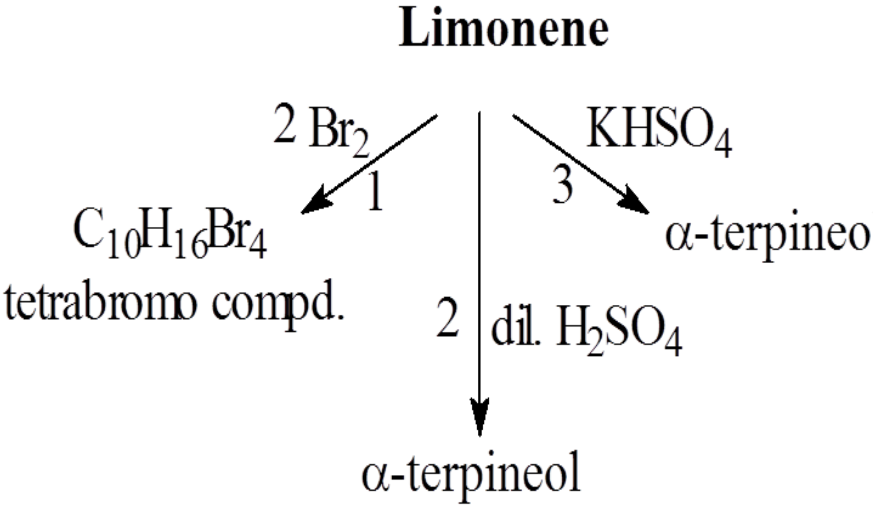
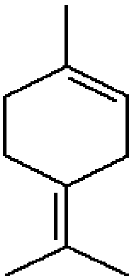
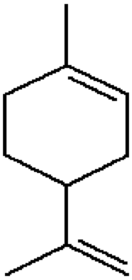




I



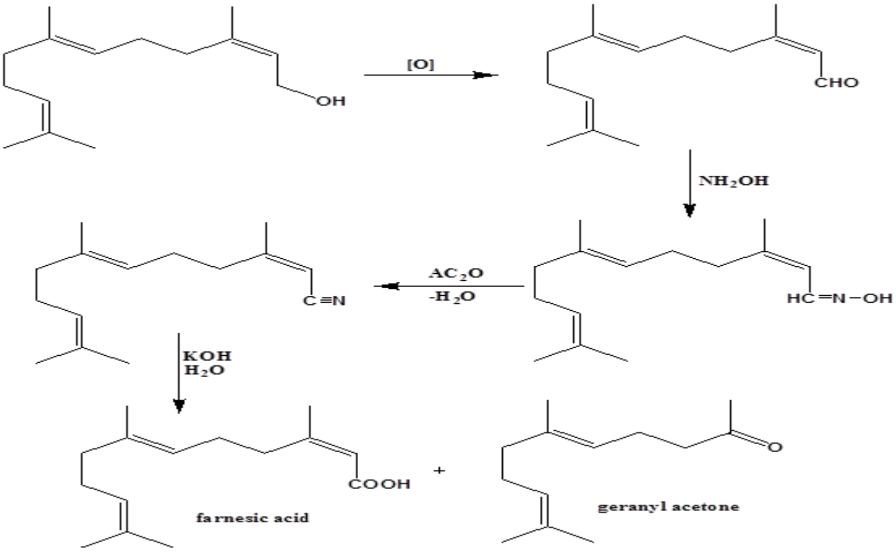
II

Sesqueterpenes and Diterpenes

Sesqueterpenes

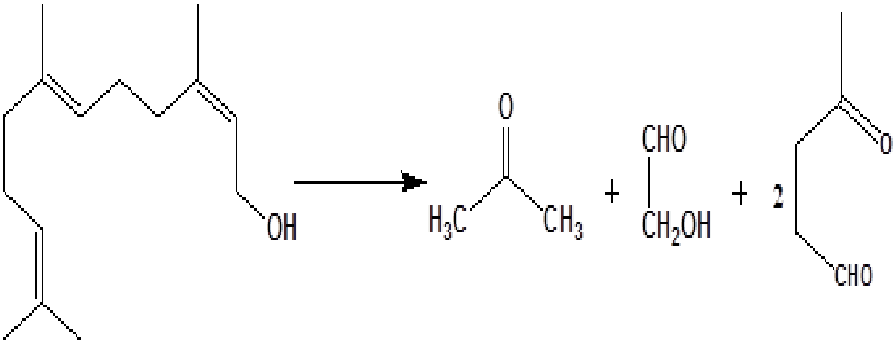
Farnesol $(C_{15}H_{26}O)$

- **Elemental analysis shows that the molecular formula of farnesol is $C_{15}H_{26}O$.**
- **Catalytic hydrogenation of farnesol give $C_{15}H_{32}O$, indicates the presence of three π–bonds.**
- **Bromination of farnesol give $C_{15}H_{26}Br_6O$, indicates the presence of three π–bonds.**
- **Reaction of farnesol with maleic anhydride give no adduct, this indicates the presence of isolated π-bonds.**
- **Reaction of farnesol with acetic anhydride gives acetate, and with benzoyl chloride gives benzoate, this indicates the presence of (OH) alcoholic group.**
- **Oxidation of farnesol give an aldehyde farnesal ($C_{15}H_{24}O$), this indicates that (OH) is primary alcohol.**



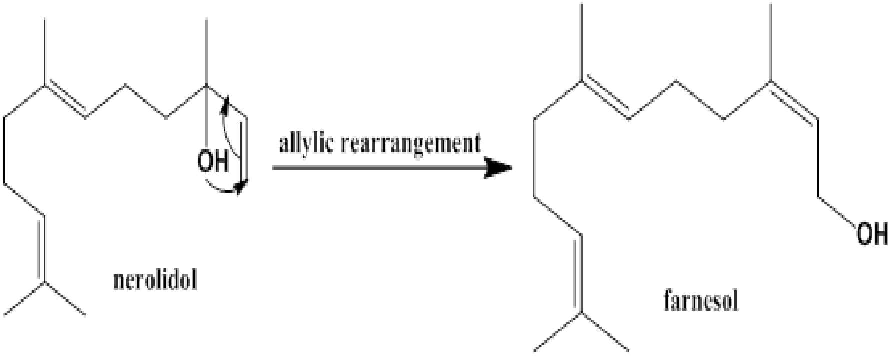
1. **Ozonolysis:**

- **Ozonolysis of farnesol give acetone & acryledehyde & two livunaldehyde.**

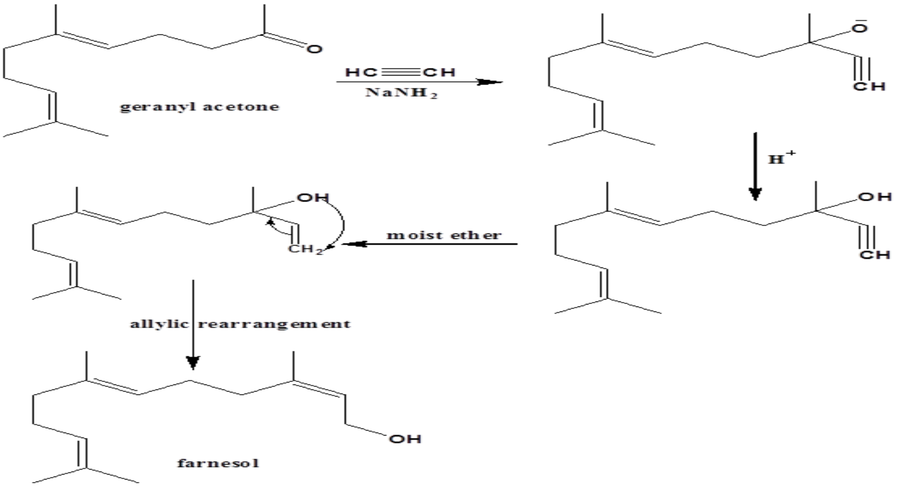


Synthesis of farnesol

- **From nerolidol:**



- **From geranyl acetone:**



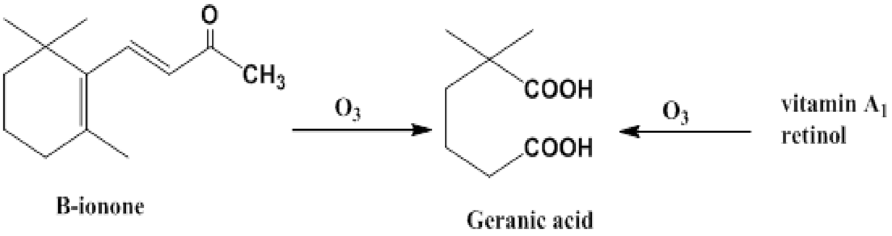
Diterpenes

Retinol (vitamin A_1) $C_{20}H_{30}O$

1. **Elemental analysis shows that the molecular formula of retinol is $C_{20}H_{30}O$.**
2. **Catalytic hydrogenation of retinol give $C_{20}H_{40}O$, indicates the presence of five π–bonds and it is monocyclic.**
3. **Bromination of retinol give $C_{20}H_{30}Br_{10}O$, indicates the presence of five π–bonds and it is monocyclic.**
4. **Reaction of retinol with maleic anhydride give adduct and consumed more than one molecule of maleic anhydride, this indicates the presence of multiple conjugated π-bonds.**
5. **U.V. absorption give λmax = 328, this indicates the presence of conjugated polyene.**
6. **Reaction of retinol with acetic anhydride gives acetate, and with benzoyl chloride gives benzoate, this indicates the presence of (OH) alcoholic group.**

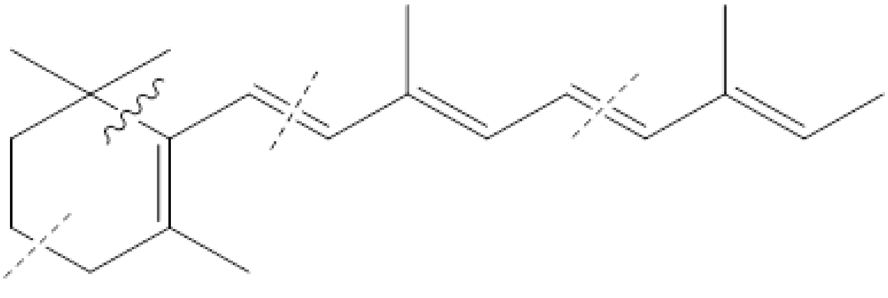
7. **Oxidation of retinol give an aldehyde retinal ($C_{20}H_{28}O$), this indicates that (OH) is primary alcohol.**

8. **Ozonolysis of retinol give geranic acid, also, ozonolysis of β-ionone give geranic acid, this indicates that retinol contains β-ionone.**

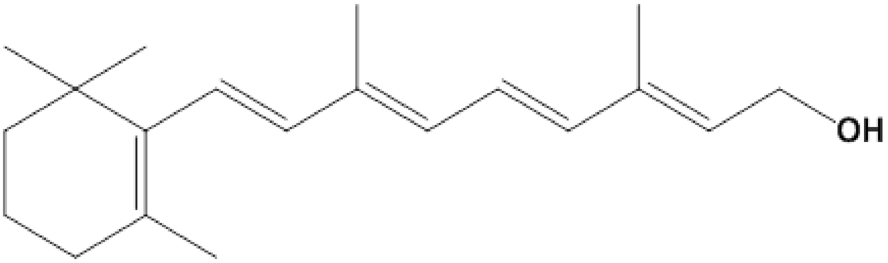


9- **Oxidation of retinol with $KMnO_4$ give acetic acid, this indicates that retinol contains some ($-C-CH_3$).**

10- **from the isoprene rule the hydrocarbon skeleton of retinol is:**

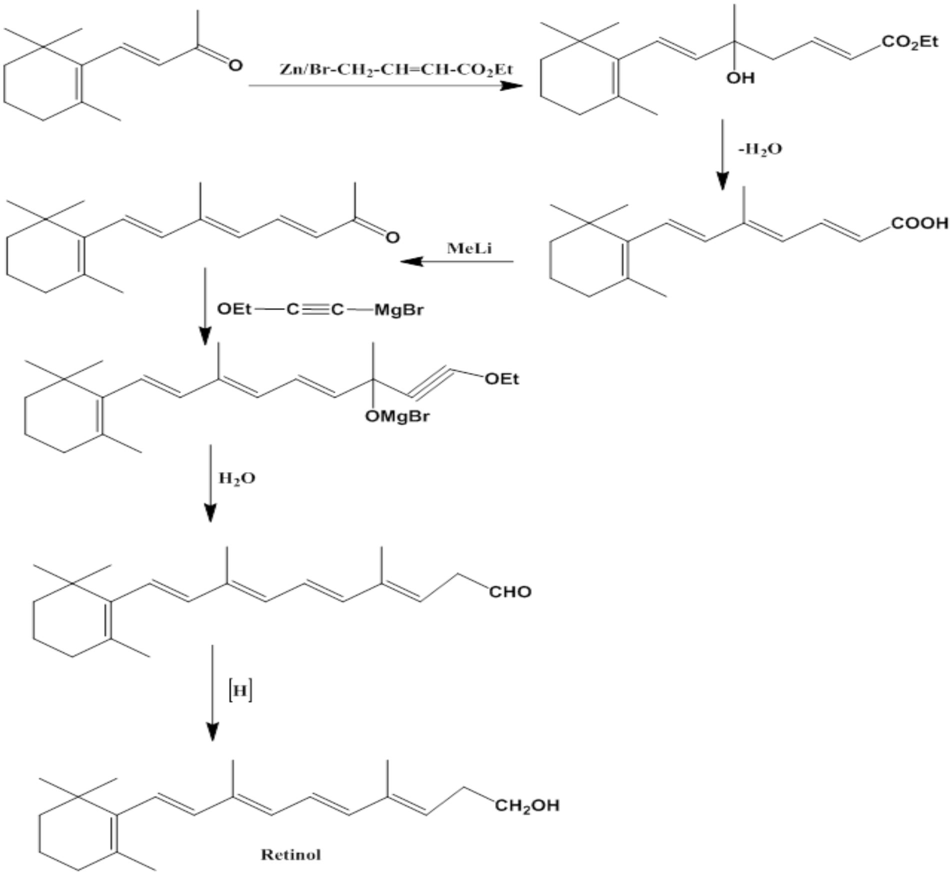


- **Structure of retinol is:**



- **The structure of retinol is half of β-carotene.**

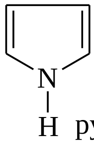
- **Synthesis of retinol:**



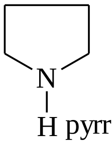
Alkaloids

- **Structure and classification of alkaloids**
- **(1) Phenylethyl amine alkaloids**
- **(2) Pyrrolidine alkaloids**
- **(3) Pyridine or piperidine alkaloids**
- **(4) Pyridine-pyrrolidine alkaloids**
- **(5) Tropane alkaloids**
- **(6) Quinoline alkaloids**
- **(7) Isoquinoline alkaloids**
- **(8) Phenanthrene alkaloids**
- **(9) Indole alkaloids**
- **(10) Tropolone alkaloids**

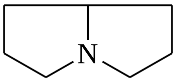
Basic nuclei of alkaloids



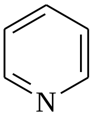
pyrrole



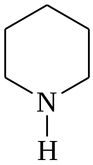
pyrrolidine



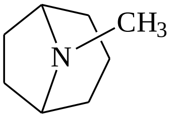
pyrrolizidine



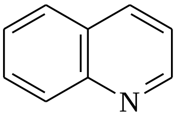
pyridine



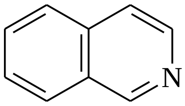
piperidine



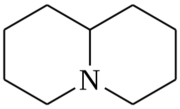
tropane
(piperidine-pyrrolidine)



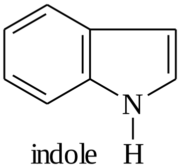
quinoline



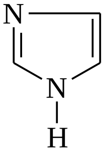
isoquinoline



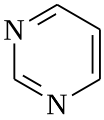
nor-hipinane



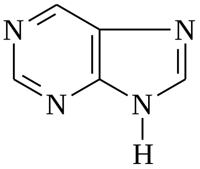
indole
(benzopyrrole)



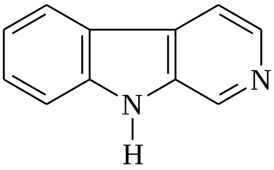
imidazole



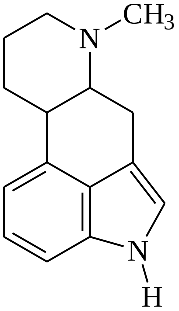
pyrimidine



purine

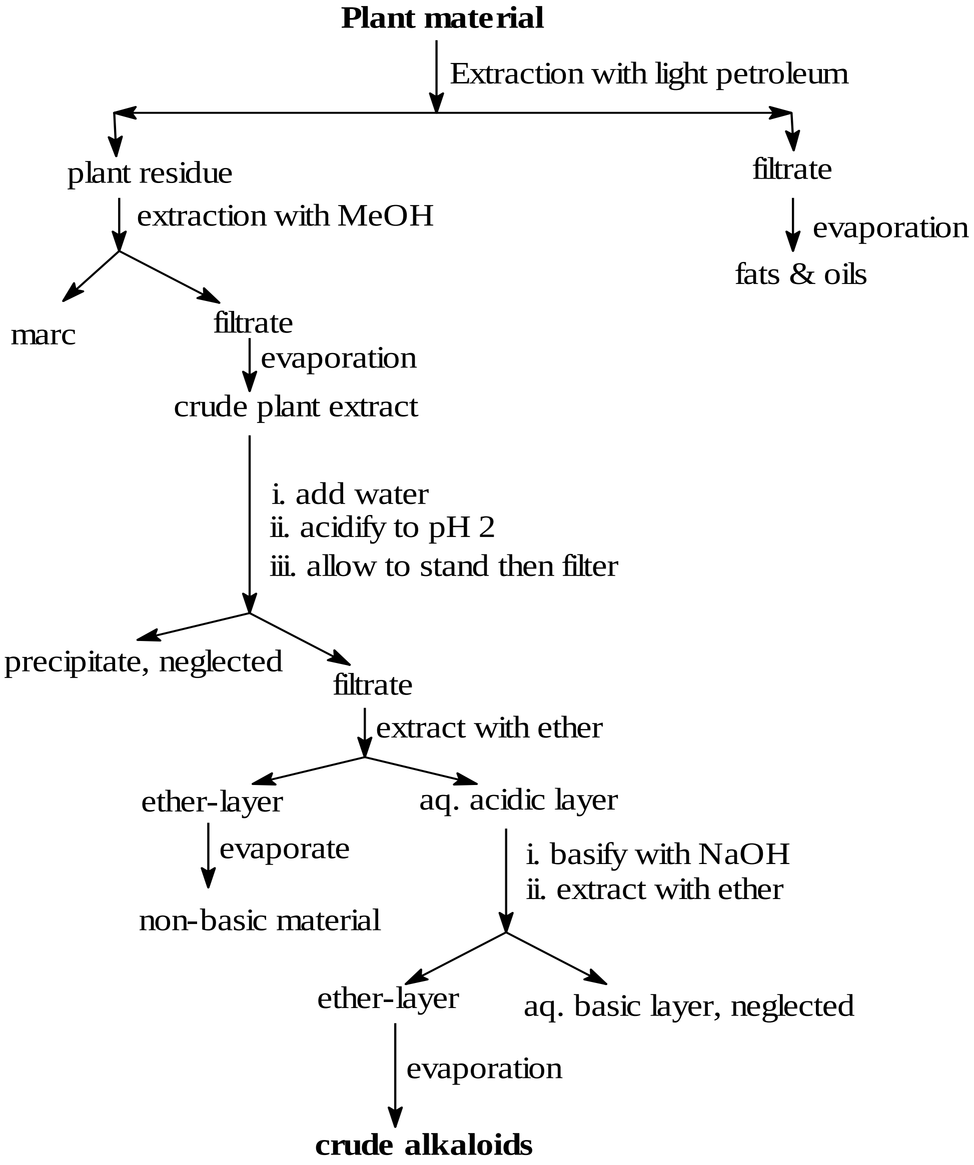


carboline



indole + hydroquinoline

Isolation of alkaloids



Structure-elucidation of alkaloids

- **1- The first step in determining the structure of a pure alkaloid consists in ascertaining its molecular formula and optical rotatory power.**
- **2- The presence of unsaturation in an alkaloid may ascertained by the addition of bromine or halogen acids or by hydroxylation with dilute alkaline permanganate.**
- **3- Frequently an alkaloid is cleaved into simple fragments by hydrolysis with water, acid or alkali and the fragments so obtained are examined separately since the structure of the fragment may easily be established than that of the whole molecule.**
- **4- The next step involves in ascertaining the functional nature of oxygen and nitrogen atoms either in the molecule itself or in its fragments obtained by hydrolysis as in step 2.**
- **5- Functional nature of oxygen: The oxygen atom may be present in the form of alcoholic or phenolic hydroxyl (-OH), methoxyl ($-OCH_3$),**

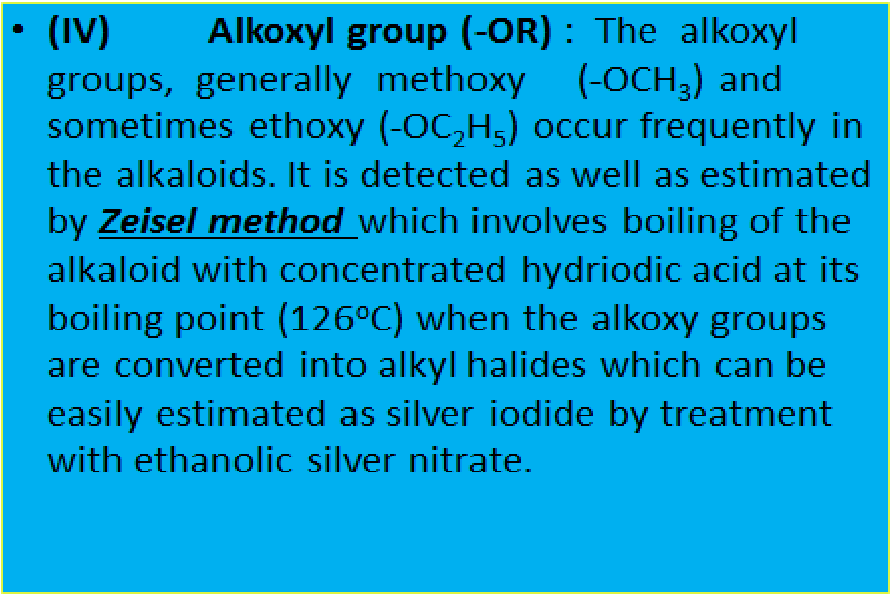
acetoxyl reOCOCH$_3$), benzoxyl (- COC$_6$H$_5$), carboxyl (-COOH) or carbonyl (C=O) group, various oxygen functional groups can be characterized according to the following characteristics

- **(i) Phenolic hydroxyl group (=C-OH) : The phenolic hydroxyl group is characterized by alkali solubility followed by reprecipitation by carbon dioxide, a colour reaction with ferric chloride, acylation to an ester and alkylation to an ether. The number of phenolic hydroxyl groups is estimated by acetylation.**

- **(i) Alcoholic hydroxyl group (-C-OH) : The alcoholic hydroxyl group is generally indicated by its acylation reaction along with the negative tests for phenolic group. It is further confirmed by characteristics like dehydration, oxidation, and absorption spectrum in the infrared. The three possible alcoholic groups are usually differentiated by their oxidation reactions.**

- **(iii) Carboxyl group (-COOH) : The carboxyl group is indicated by its solubility in weak bases, like**

$NaHCO_3$, NH_3, *etc.,* esterification with alcohols, and specific absorption in the infrared. The groups are generally estimated quantitatively either by acid-alkali titration or by silver salt method.



- **(IV) Alkoxyl group (-OR)** : The alkoxyl groups, generally methoxy ($-OCH_3$) and sometimes ethoxy ($-OC_2H_5$) occur frequently in the alkaloids. It is detected as well as estimated by ***<u>Zeisel method</u>*** which involves boiling of the alkaloid with concentrated hydriodic acid at its boiling point (126°C) when the alkoxy groups are converted into alkyl halides which can be easily estimated as silver iodide by treatment with ethanolic silver nitrate.

$$R-OCH_3 + HI \xrightarrow{126^{o}C} ROH + CH_3I \xrightarrow{AgNO_3} AgI\ (ppt.)$$

The number of moles of silver iodide is equivalent to the number of alkoxyl groups in the alkaloid.

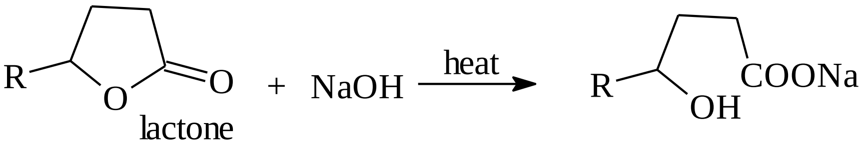
The related group, methylenedioxy ($-O-CH_2-O-$) is estimated on the basis that it librates formaldehyde

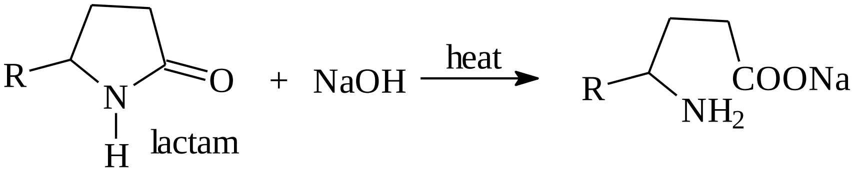
when treated with hydrochloric or sulphuric acid; thus the quantitative estimation of formaldehyde will give the number of methylenedioxy groups.

- **The number of moles of silver iodide is equivalent to the number of alkoxyl groups in the alkaloid.**
- **The related group, methylenedioxy (-O-CH_2-O-) is estimated on the basis that it librates formaldehyde when treated with hydrochloric or sulphuric acid; thus the quantitative estimation of formaldehyde will give the number of methylenedioxy groups.**
- **(vi) Ester groups (-OCOR) : Esters (such as -$OCOCH_3$, -$OCOC_6H_5$) and related groups like amide, lactone, and lactam are detected by their hydrolysis with water, dilute acids, alkali to hydroxyl and acidic compounds. The nature is established by knowing the nature of the acid.**

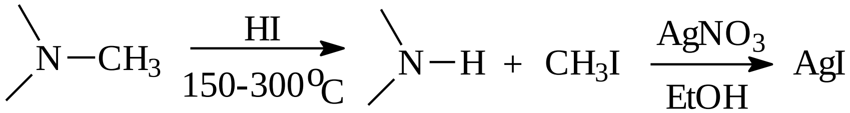
$$—CONH_2 + NaOH \xrightarrow{heat} —COONa + NH_3$$

$$—COOR + NaOH \xrightarrow{heat} —COONa + ROH$$

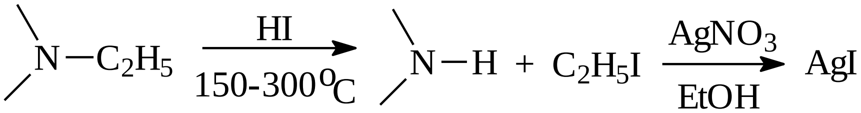




- **functional nature of nitrogen**
- **The N-alkyl groups are frequently estimated by Herzig Meyer method**

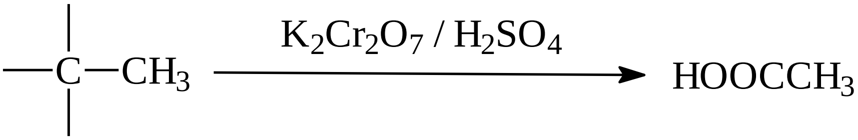


$$N{-}CH_3 \xrightarrow[150\text{-}300\,^{o}C]{HI} N{-}H + CH_3I \xrightarrow[EtOH]{AgNO_3} AgI$$



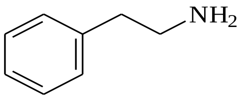
$$N{-}C_2H_5 \xrightarrow[150\text{-}300\,^{o}C]{HI} N{-}H + C_2H_5I \xrightarrow[EtOH]{AgNO_3} AgI$$

- **Estimation of C-methyl groups**

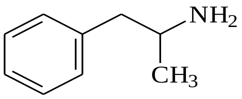


$$-\overset{|}{\underset{|}{C}}-CH_3 \xrightarrow{K_2Cr_2O_7\,/\,H_2SO_4} HOOCCH_3$$

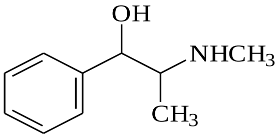
Phenylethyl amine Alkaloids



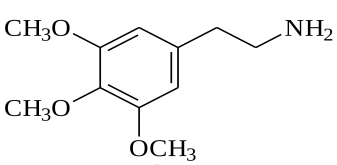
β-phenylethyl amine 47



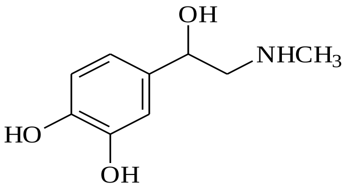
amphetamine 48



ephedrine 49

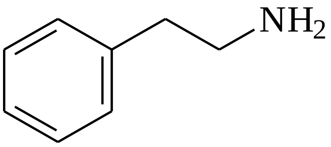


mescaline 50



adrenaline 51

β-Phenylethyl amine



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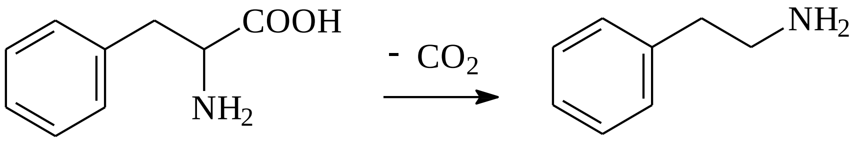
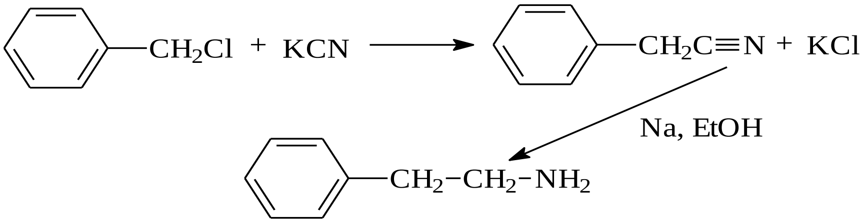
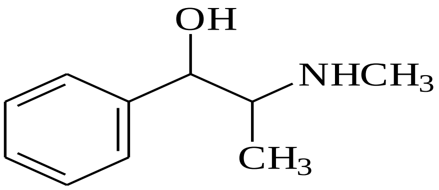


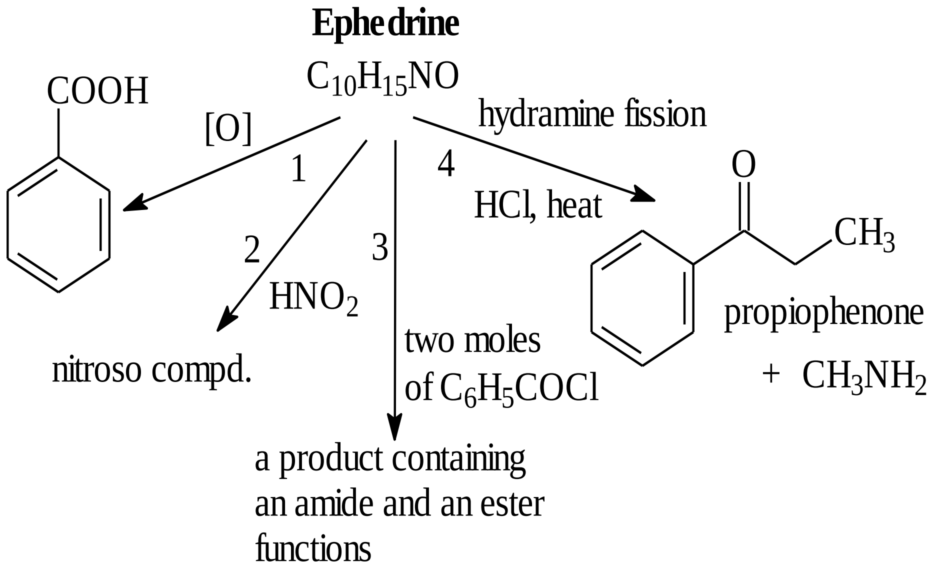
phenylalanine β-phenylethyl amine

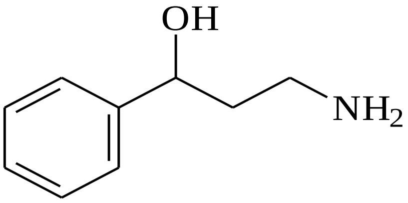


(-)- Ephedrine

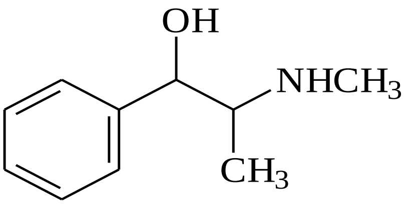


49

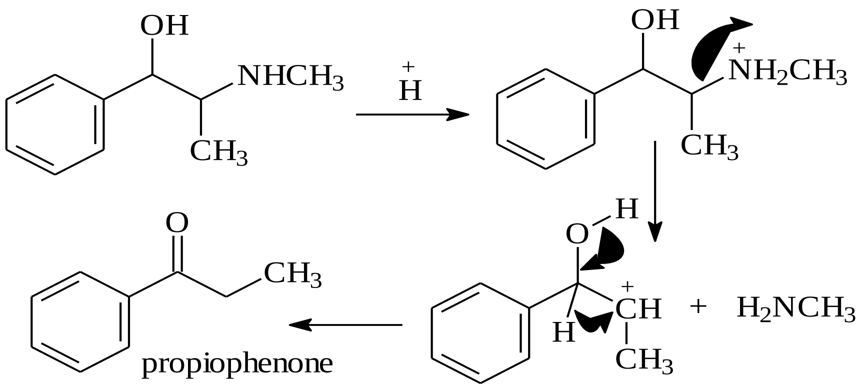


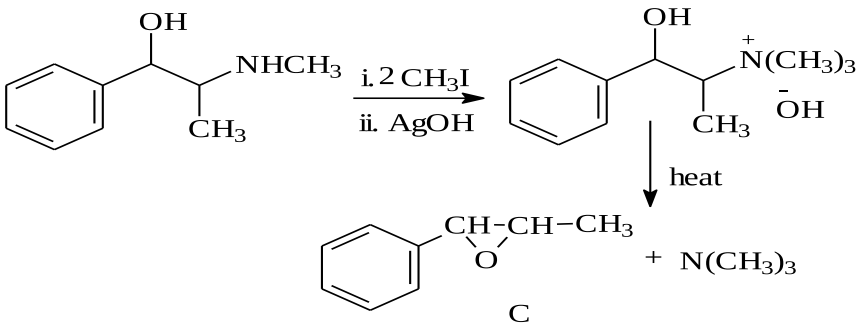


A



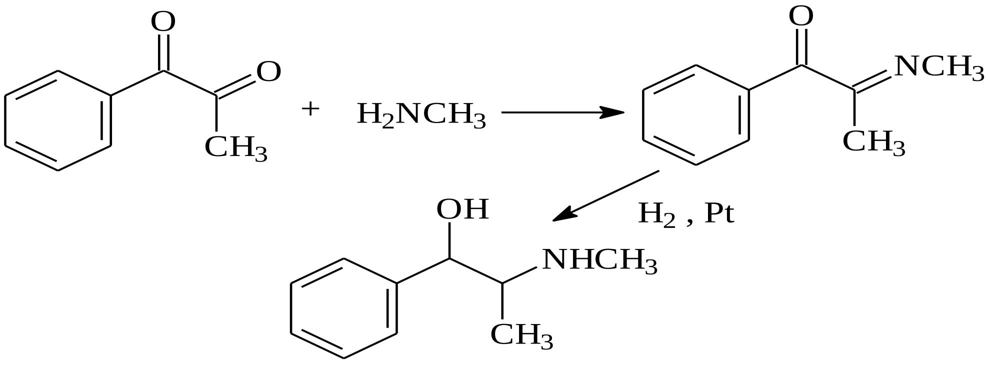
B





C

Synthesis of ephedrine

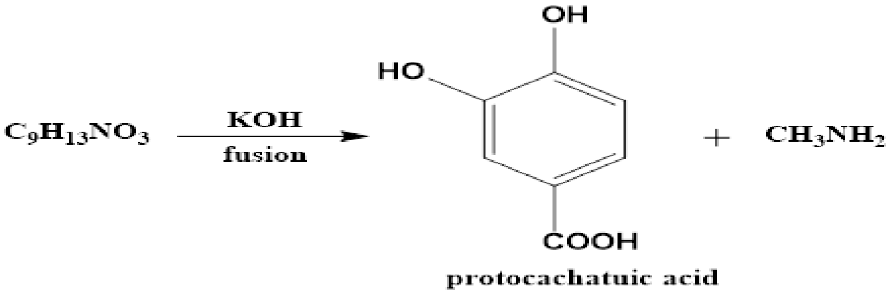


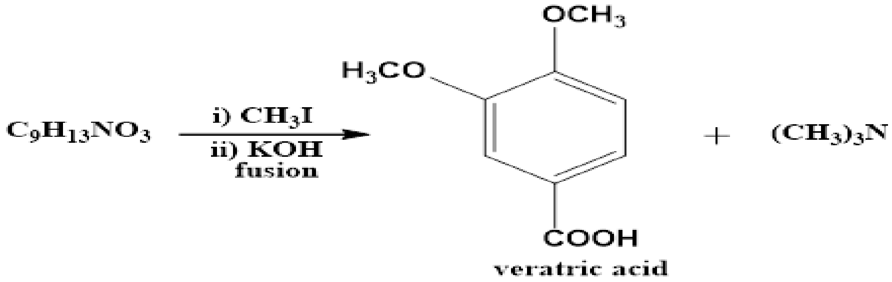
Adrenaline

$C_9H_{13}NO_3$

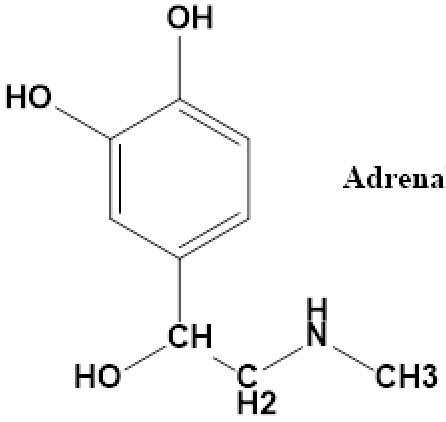
- **Adrenaline is colorless crystals.**
- **Reaction of adrenaline with three moles of benzoyl chloride give benzoate, this indicates the presence of three (OH) groups.**
- **Adrenaline is soluble in NaOH and reprecipitated by carbon dioxide, so adrenaline has phenolic character.**
- **Reaction of adrenaline with $FeCl_3$ give green color, so adrenaline is catechol having a side-chain, so adrenaline must contain two phenolic hydroxyl groups, and the third must be an alcoholic hydroxyl group and present in the side-chain.**
- **Oxidation of adrenaline give ketone, so the alcoholic hydroxyl group is secondary (CHOH).**
- **Boiling of adrenaline with aqueous KOH, methyl amine (CH_3NH_2) is involved, thus a methylamine group is present.**
- **Fusion of adrenaline with KOH, the product is protocatechuic acid and methylamine. On the other hand, methylation of adrenaline followed by fusion with KOH gives veratric acid and trimethylamine, so, the formation of**

trimethylamine indicates that the nitrogen atom must occur at the end of the side-chain.



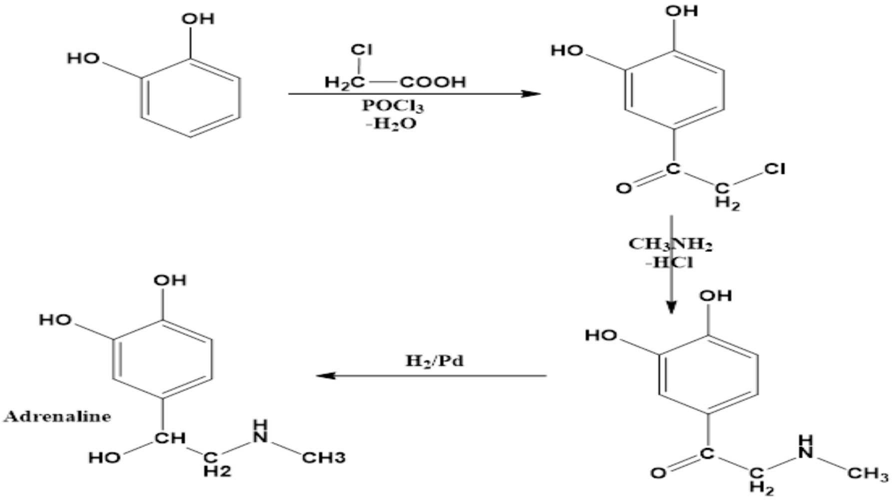


- **<u>Adrenaline is optically active, it contain at least one chiral center.</u>**
- **So, the structure of adrenaline is:**



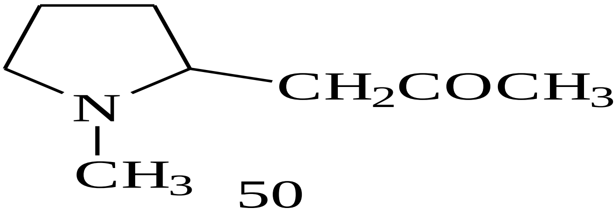
Adrenaline

- **Synthesis of adrenaline from catechol:**

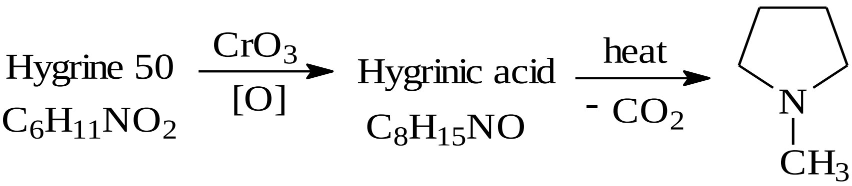


Pyrrolidine Alkaloids

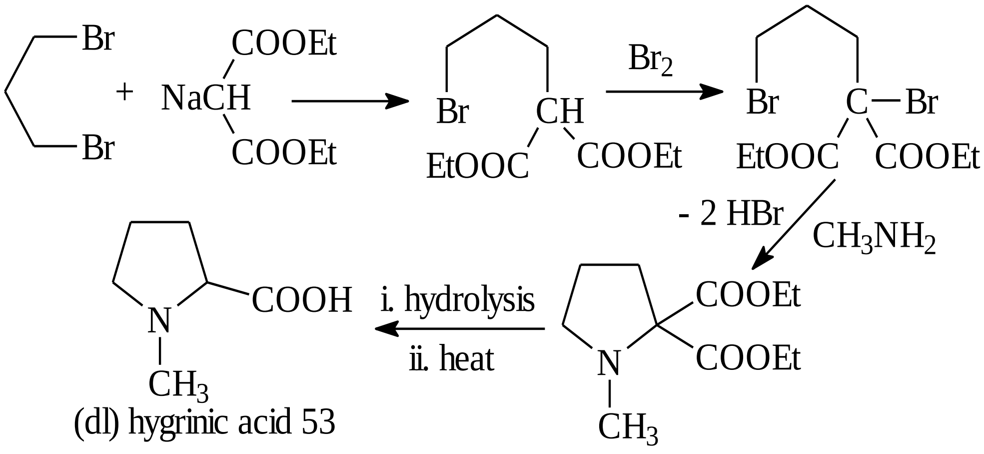
Hygrine



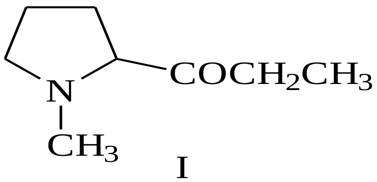
50



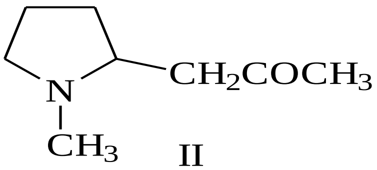
Synthesis of hygrinic acid



Based on the above results, hygrine 50 may be formulated either I or II.

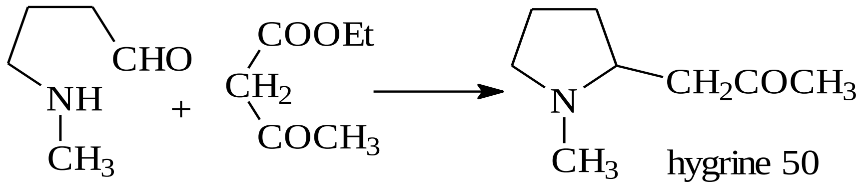


I



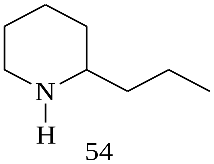
II

Synthesis of hygrine

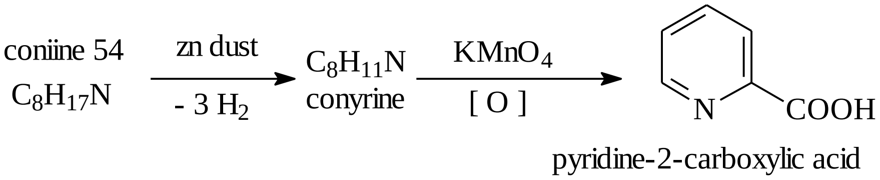


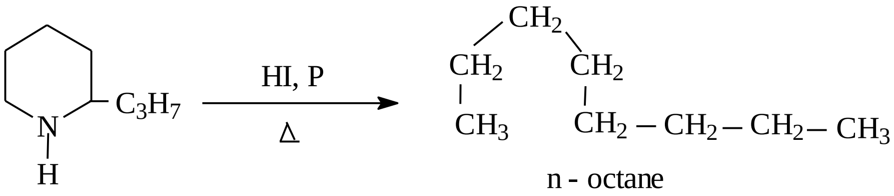
Pyridine or Piperidine alkaloids

Coniine

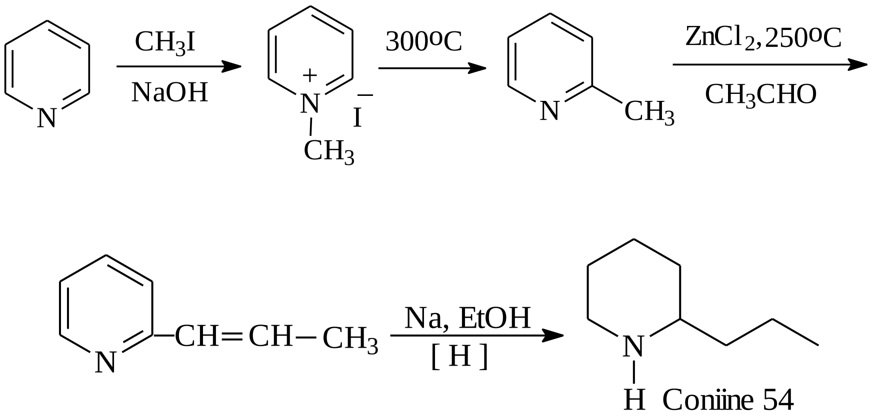


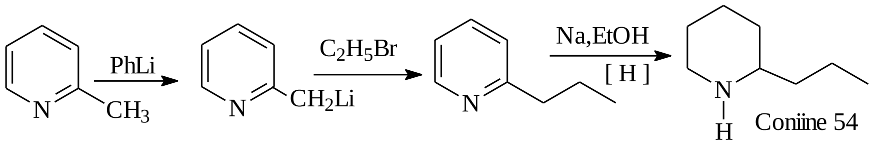
54





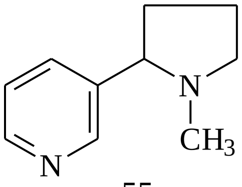
Synthesis of Coniine



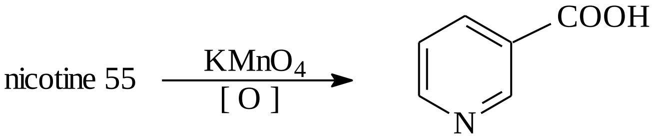


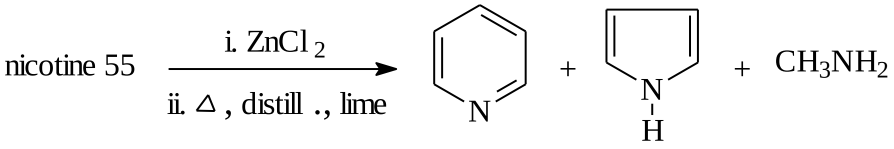
Pyridine, pyrrolidine alkaloids

Nicotine



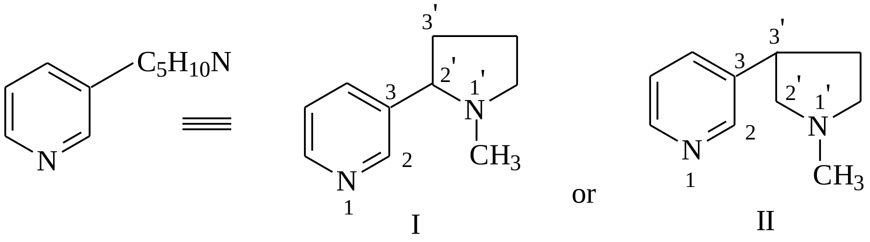
55



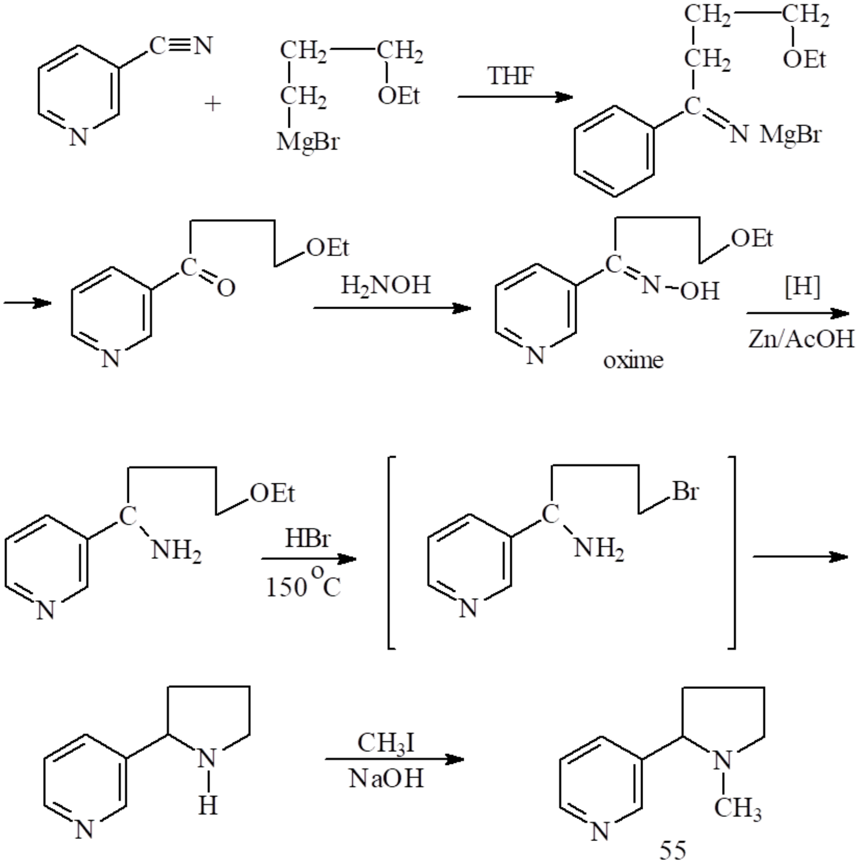


$$\underset{C_{10}H_{14}N_2}{\text{nicotine 55}} \xrightarrow{H_2\,/\,Pt} \underset{C_{10}H_{20}N_2}{\text{hexahydronicotine}}$$

$$\text{nicotine 55} \xrightarrow[\Delta]{HI} CH_3I$$


$C_5H_{10}N$
≡
3'
2'
1'
3
2
N
1
CH_3
or
3'
3
2'
1'
2
N
1
CH_3

I or II


C≡N
N
+
CH_2—CH_2
CH_2
MgBr
OEt
THF
C
N MgBr
C
O
OEt
H_2NOH
C
N-OH
oxime
[H]
Zn/AcOH
C
NH_2
OEt
HBr
150 °C
Br
N
H
CH_3I
NaOH
CH_3

55

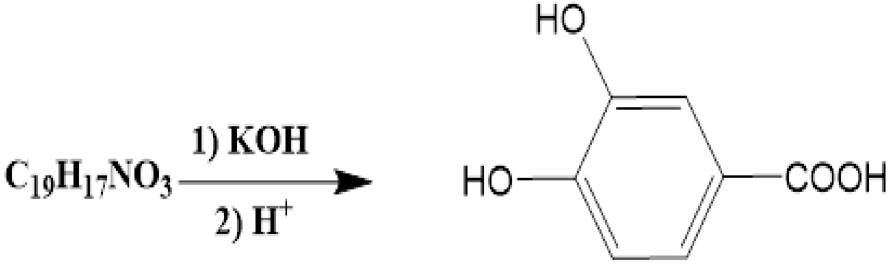
Quinoline Alkaloids

Cusparine

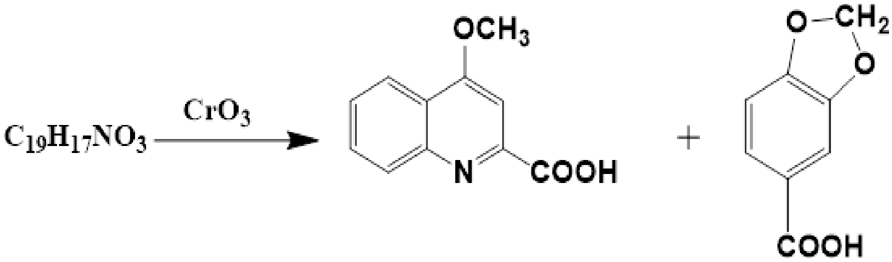
$C_{19}H_{17}NO_3$

1. **Cusparine has been to contain one methoxy group by Zeisel method.**

- **$C_{19}H_{17}NO_3$ + HI -------------- CH_3I ---- $AgNO_3$ --- AgI**
- **Fusion of cusparine with potassium hydroxide, protochtechuic acid was obtained.**

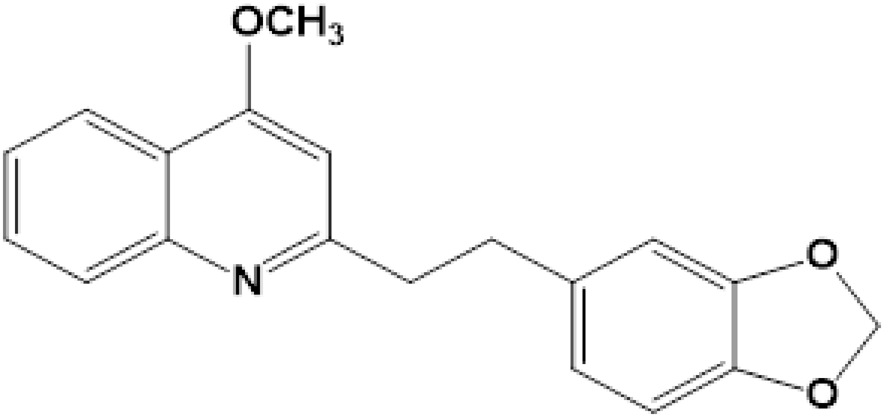


- **Oxidation of cusparine gives piperonylic acid and 4-methoxyquinoline-2-carboxylic acid.**

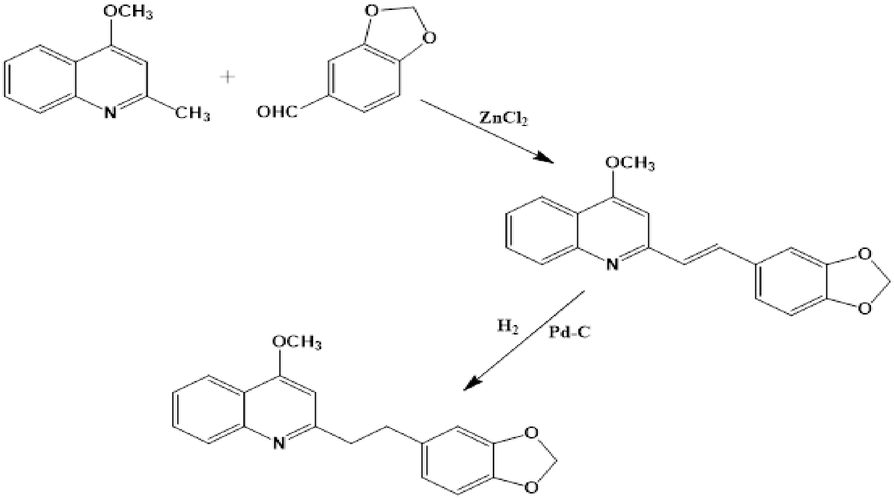


-

- **Consideration of this information led to the suggestion of the following structure of cusparine.**



- **The considered structure for cusparine has been confirmed also by synthesis of it, as follow:**



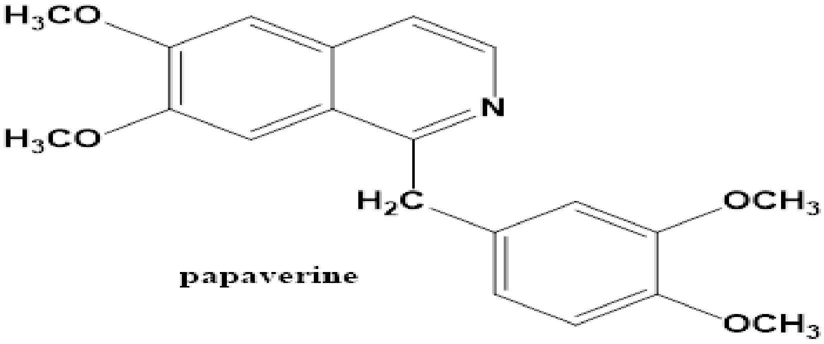
Isoquinoline alkaloids

Papaverine ($C_{20}H_{21}NO_4$)

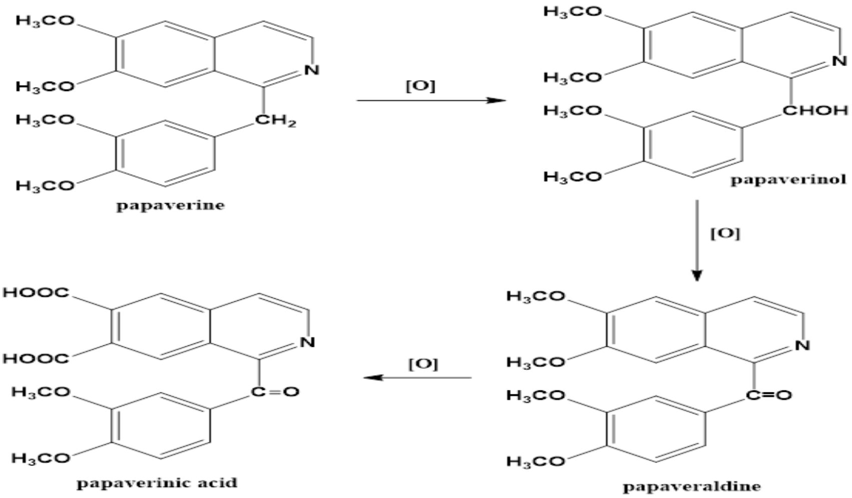
- **Papaverine is one of the optically inactive alkaloids.**
- **Papaverine reacts with one molecule of methyl iodide to form a quaternary iodide salt,**
- **$C_{20}H_{21}NO_4$ ------ CH_3I -------- quaternary iodide salt**
- **Thus, the nitrogen atom in papaverine is in the tertiary state.**
- **Application of Zeisel method on papaverine, afforded the presence of four methoxy groups, and the demethylated product is known as papaveroline ($C_{16}H_{13}NO_4$).**
-
- **$C_{20}H_{21}NO_4$ + 4HI ----------------- $4CH_3I$ + $C_{16}H_{13}NO_4$**
-

Papaveroline

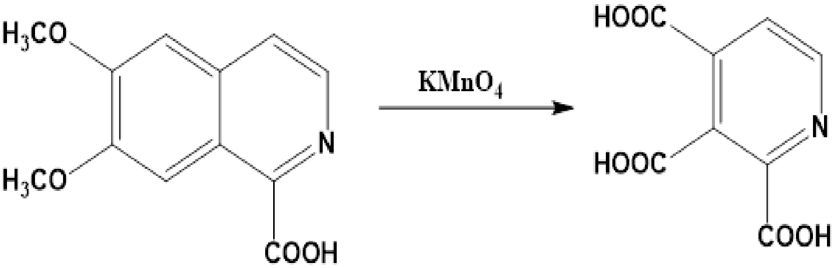
- **Oxidation of papaverine by using cold dilute permanganate, an alcohol papaverinol ($C_{20}H_{21}NO_5$) is obtained. Oxidation with hot permanganate give a ketone papaveraldine ($C_{20}H_{19}NO_5$) is obtained, thus this indicates that the structure of papaverine must be contain an methylene group ($-CH_2-$).**
- **($C_{19}H_{19}NO_4$)CH_2 ---[O]--- ($C_{19}H_{19}NO_4$)CHOH ---[O]-- ($C_{19}H_{19}NO_4$)CO**
- **Papaverine papaverinol papaveraldine**
- **Oxidation of papaverine by concentrated permanganate give:**
- **veratric acid.**
- **Metahemipinic acid.**
- **Pyridine-2,3,4-tricarboxylic acid.**
- **6,7-dimethoxyisoquinoline-1-carboxylic acid.**
- **Thus, the structure of papaverine is:**



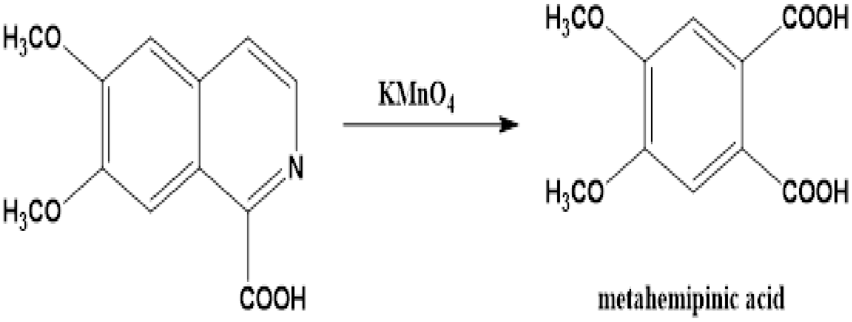
With this formula, we can formulate the oxidation of papaverine as follow:



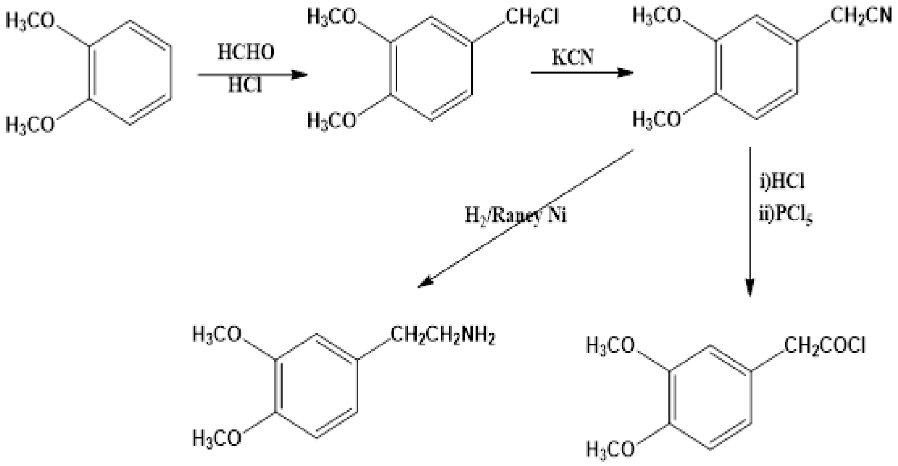
- Pyridine-2,3,4-tricarboxylic acid:

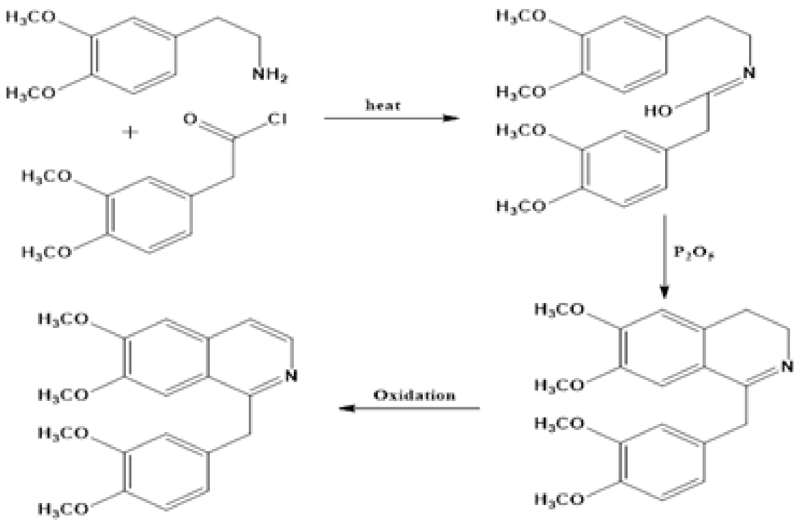


- Metahemipinic acid:



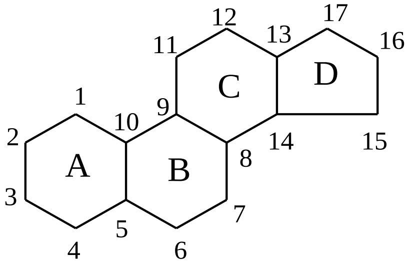
This structure for papaverine has been confirmed by synthesis as follow:



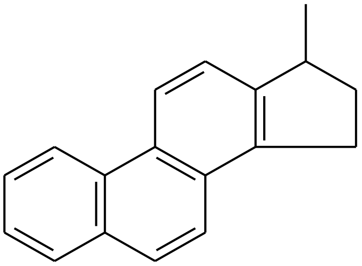


Steroids

- **Steroids (Gk., stereos = solid) are solid alcohols that are widely distributed in the animal and plant kingdoms. The basic skeleton consists of 17 carbon atoms arranged in the form of a perhydro-cyclopentenophenathrene 25. A steroid could be defined, in another way, as any compound which gives Diel's hydrocarbon 26 when distilled with selenium.**



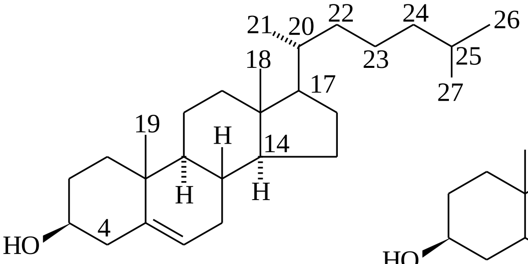
steroid nucleus 25



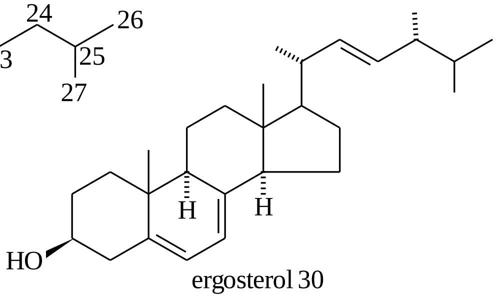
Diel's hydrocarbon 26

Classes of steroids

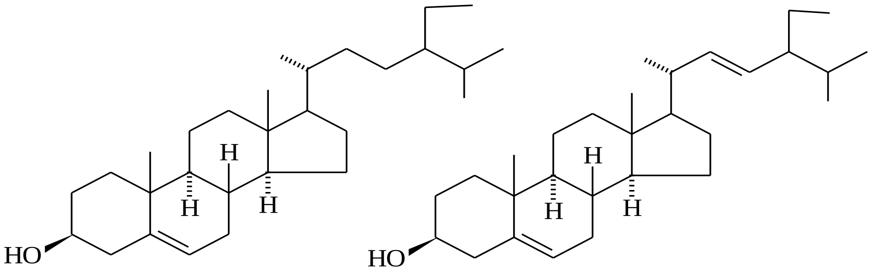
Sterols



cholesterol 29



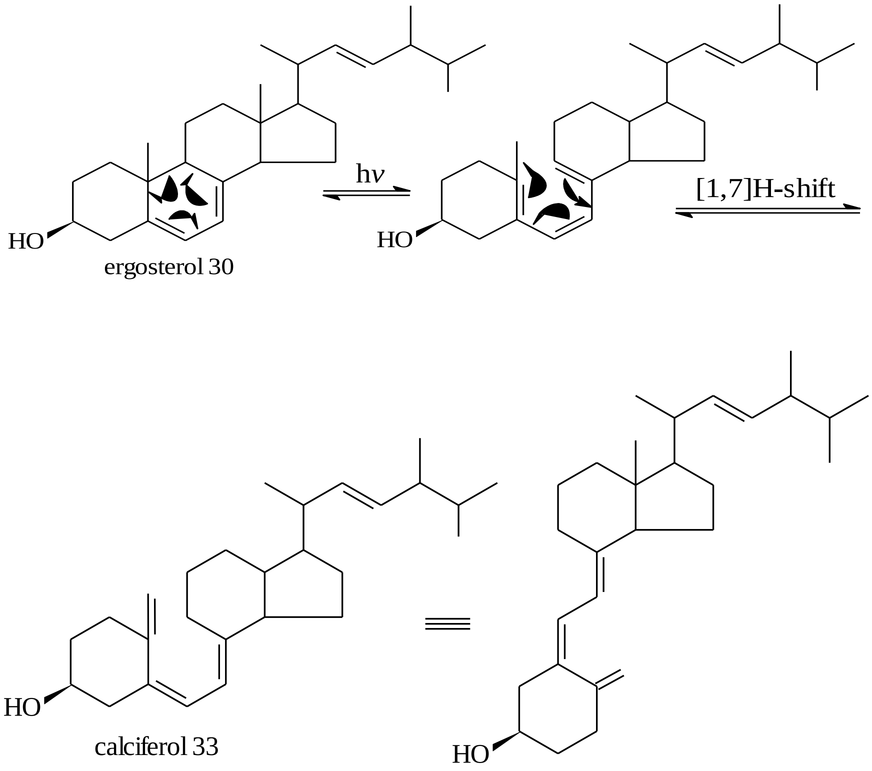
ergosterol 30



β-sitosterol 31 stigmasterol 32

Vitamine D group

- they are about seven compounds (Vitamin D1 - D7) with the ring B being opened. Vitamin D2 33 (or calciferol) is formed from ergosterol 30 by the sunlight irradiation

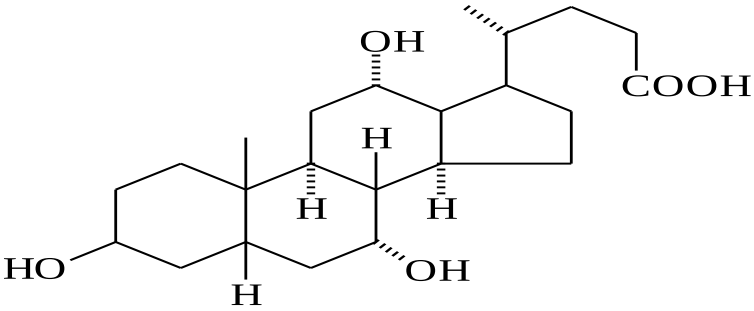


ergosterol 30

calciferol 33

Bile acids

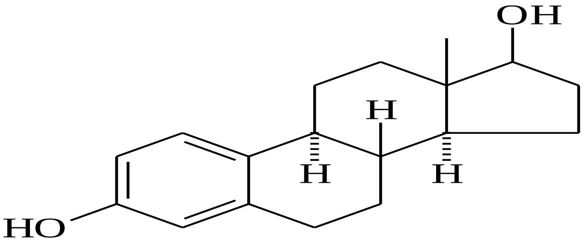
are isolated from the bile of various animals



cholic acid 34

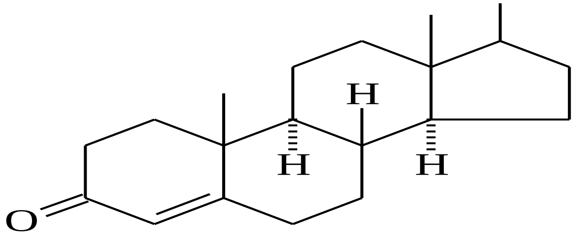
Sex hormones

- ***Estrogens* (female sex hormones)**



α-oestradiol 35

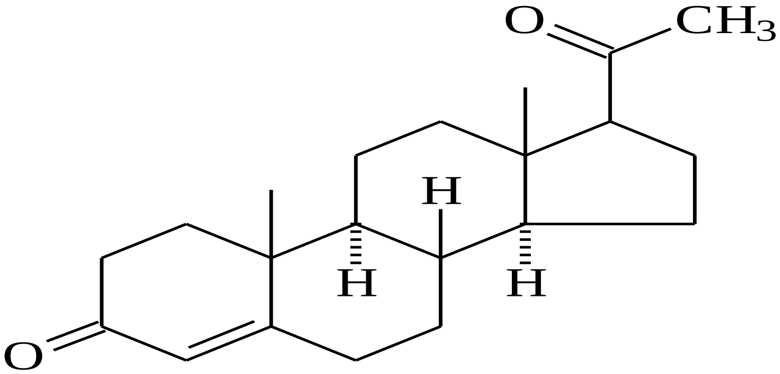
***Androgens* (male sex hormones**



testosterone 36

- ***Gestogens***

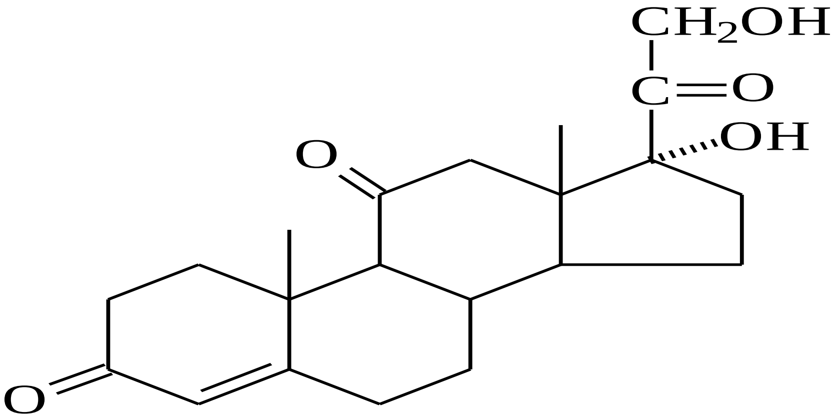
- **hormones which are responsible for the maintenance of pregnancy**



progestrone 37

- **Adrenocortical hormones**

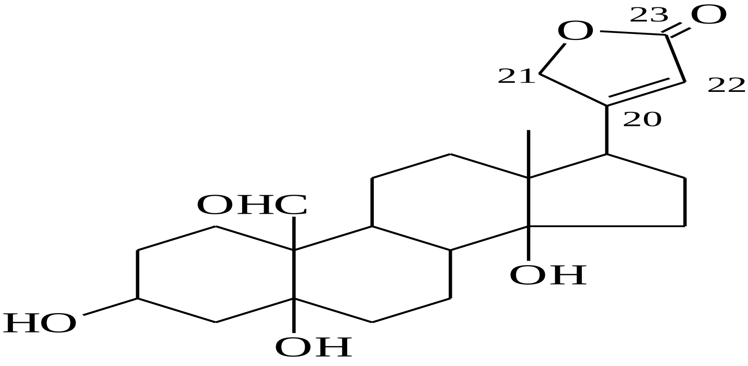
- **produced by the cortex of the adrenal glands**



cortisone 38

- **Cardenolides**

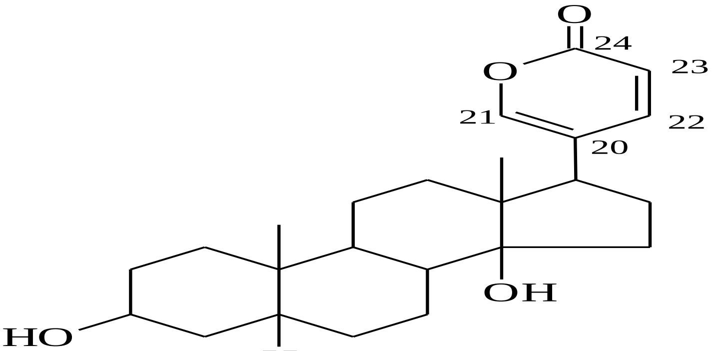
- **Cardiac glycosides have powerful cardiotonic activity and can be used for treatment of some heart diseases**



strophanthidin 39

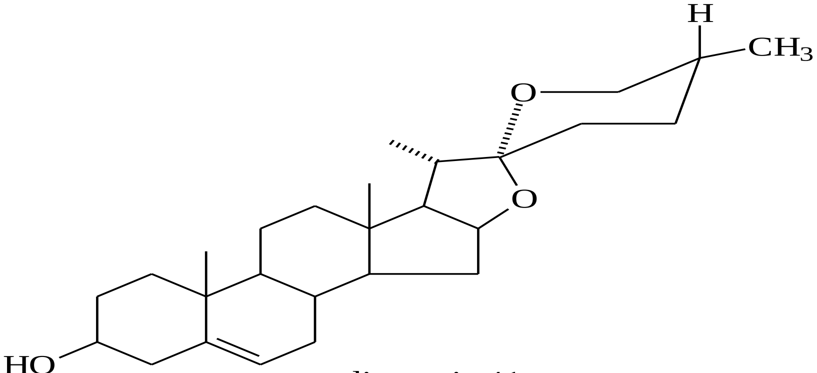
- **Bufadienolides**

- **present in the toad venoms secreted from the parotid glands and also some of these compounds were isolated from plants**



bufalin 40

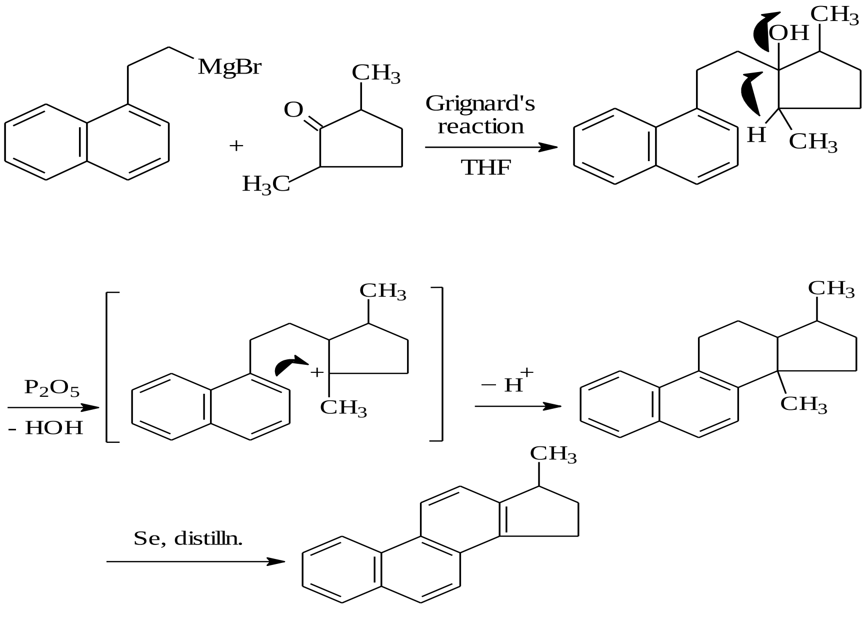
- **Sapogenins**
- **are the aglycones of saponins (named spirostane)**



diosgenin 41

Diel's hydrocarbon

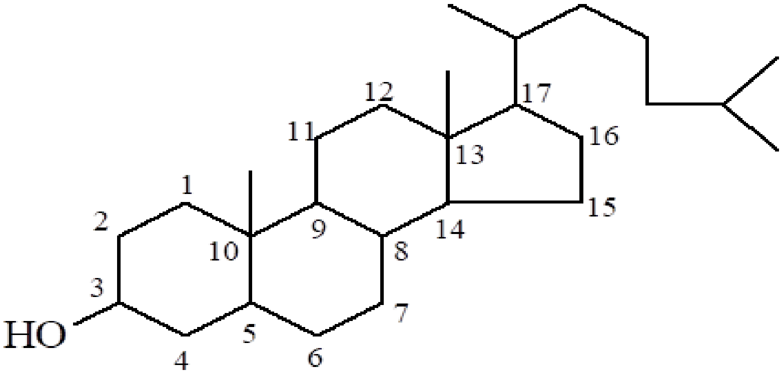
- **3’-methyl-1:2-cyclopentenophenanthrene**



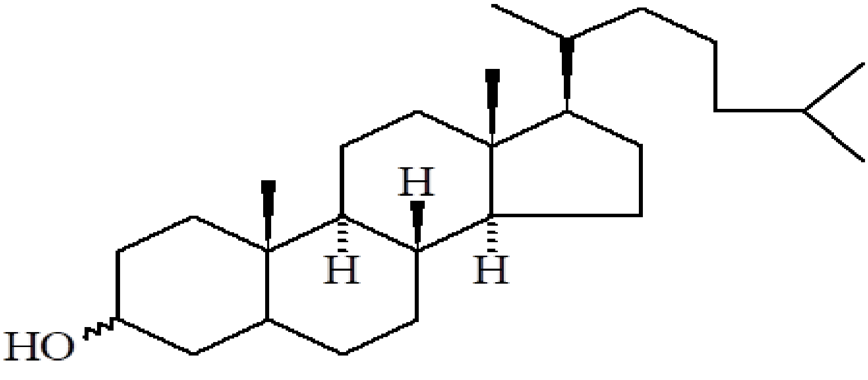
Diel's hydrocarbon 26

Stereochemistry of the steroid nucleus

- **there are eight dissimilar chiral centers in the nucleus (3,5,8,9,10,13,14 and 17). Thus there are 2^8 = 256 possible optical isomers**



- **In most naturally occuring sterols the configuration at C-8, C-9, C-10, C-13, C-14 and C-17 is definite, i.e. does not change from one molecule to the other**



Structure elucidation of some steroids by chemical methods

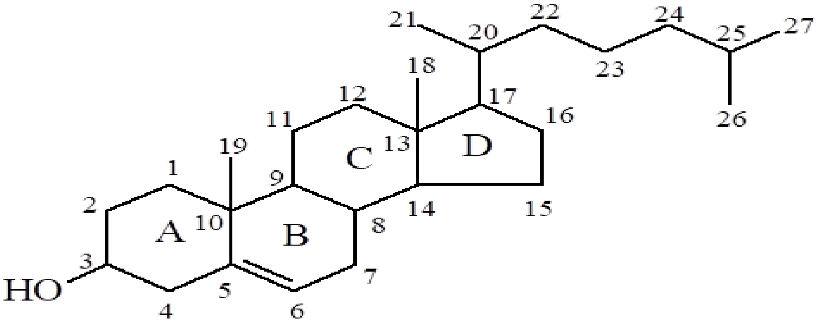
Cholesterol

characteristic features :-

i) The nucleus of cholesterol is tetracyclic composed of three six-membered rings (A, B and C) and one five-membered (D) ring.

ii) There is a secondary OH group at C-3, and a double bond at C-5 (between C-5 and C-6).

iii) There are two angular methyl groups at C-10 and C-13, and a saturated side-chain C_8H_{17} at C-17.



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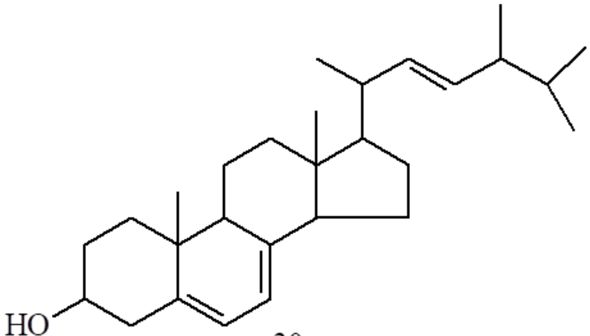
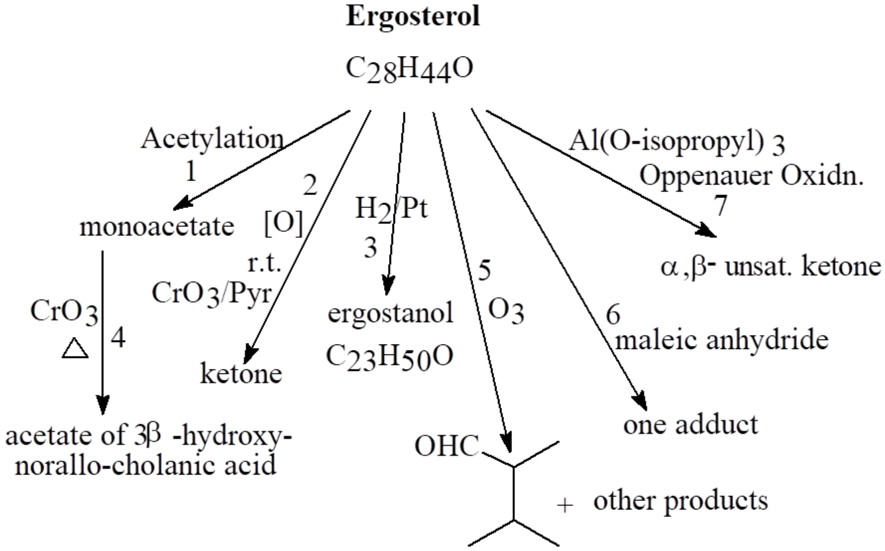
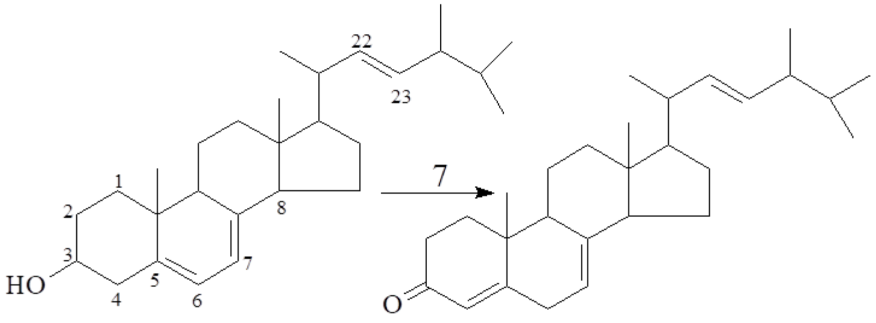
Ergosterol



30

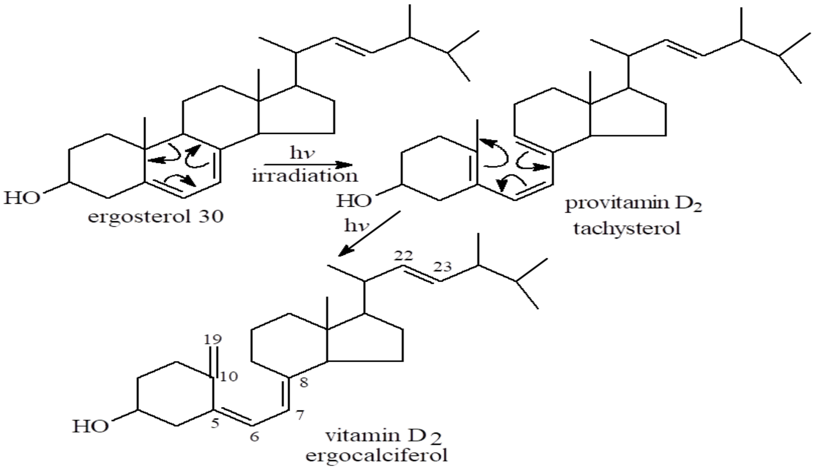




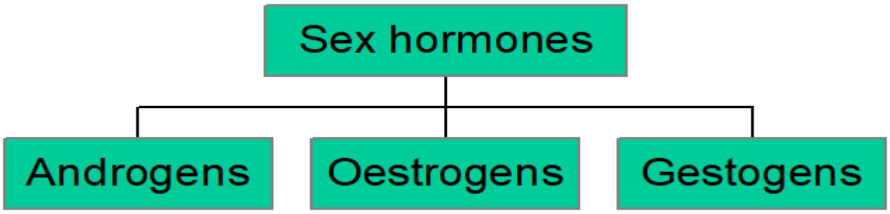
ergosterol 30

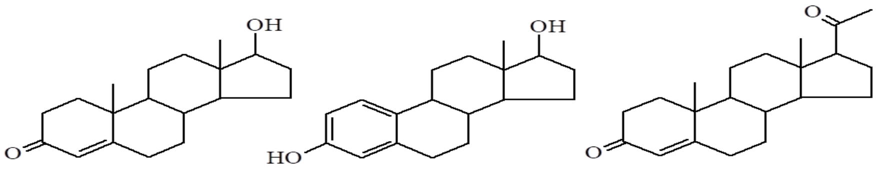
λ_{max} found 235 nm, calc. 239 nm

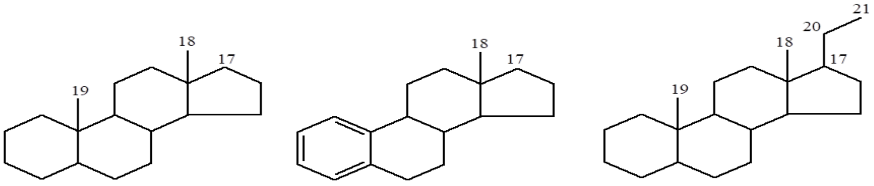
Formation of vitamin D_2 from ergosterol 30 by sunlight irradiation.



Sex hormones

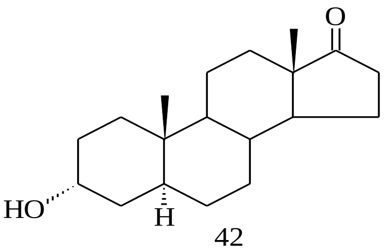






Androgens

Androsterone



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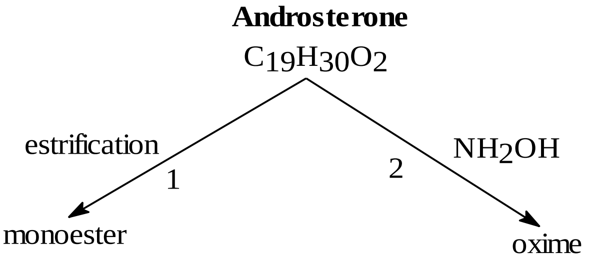
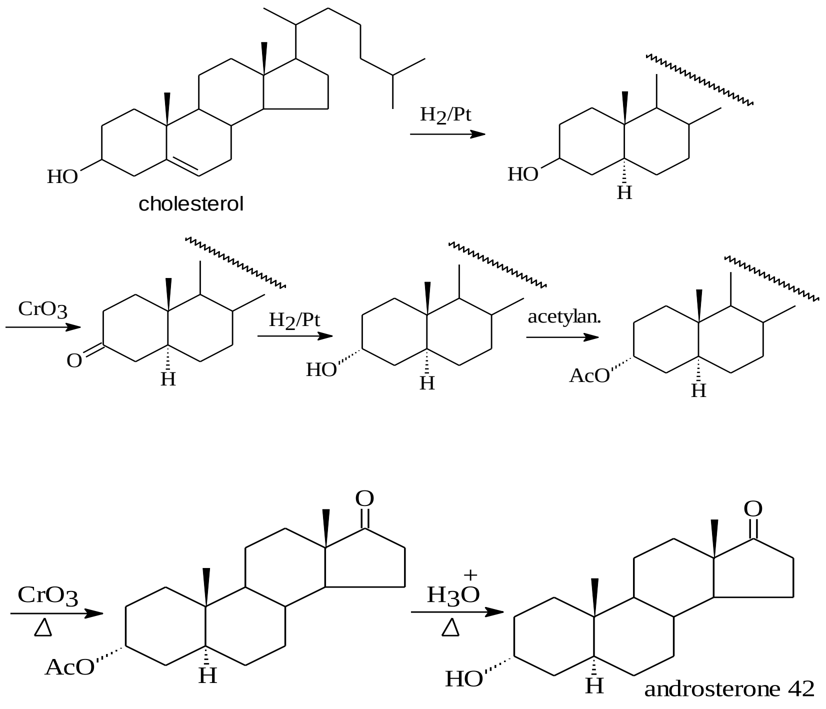
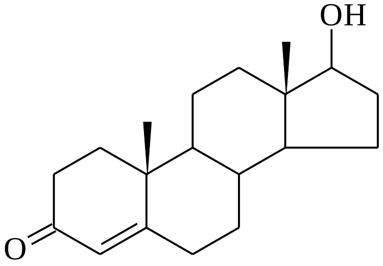




Testosterone

manufacture of testosterone



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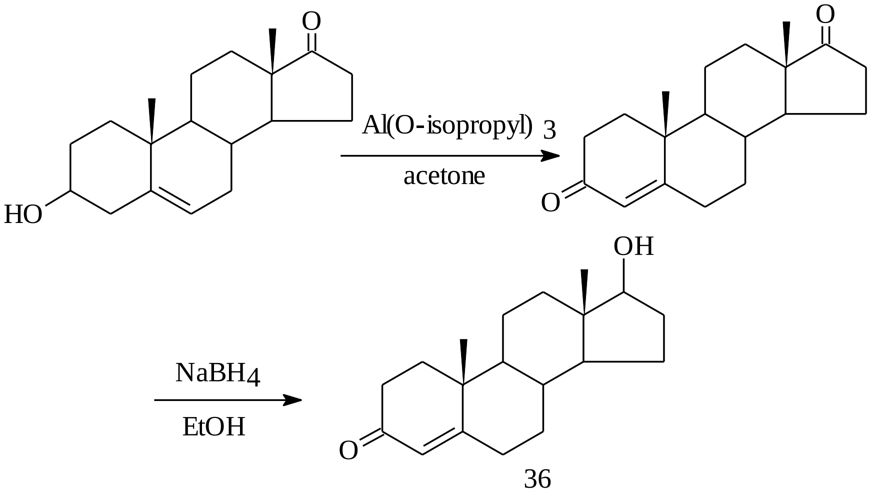

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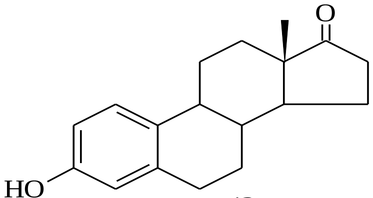
Oestrogens

Oestrone



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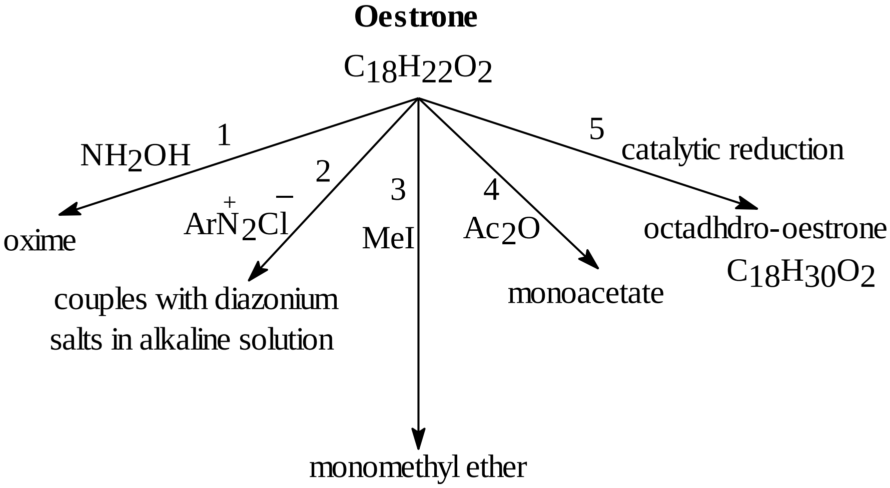
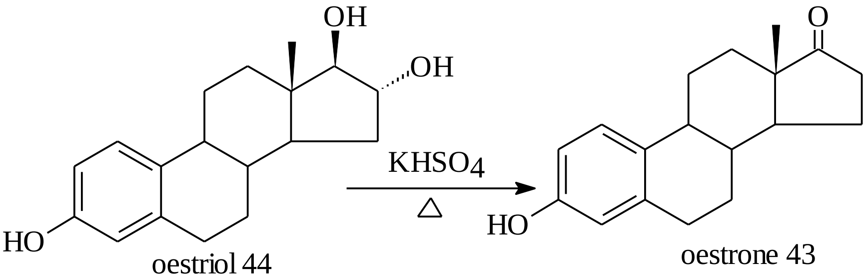
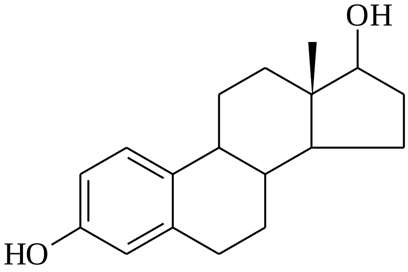




oestriol 44

oestrone 43

Oestradiol



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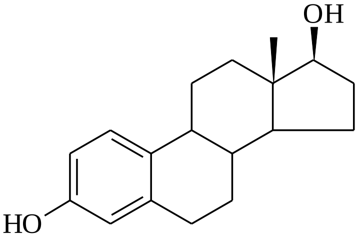
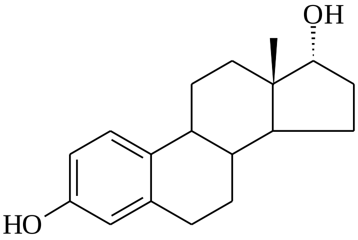


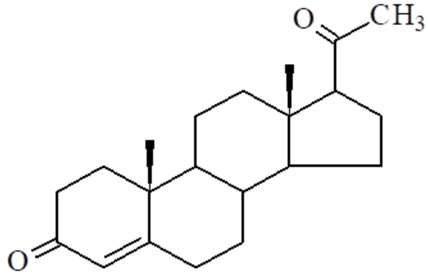


35a, α-oestradiol (oestraiol-17 β) **35b, β-oestradiol (oestradiol-17 α)**

m.p 178°C **m.p 222°C**

Gestogens

Progesterone



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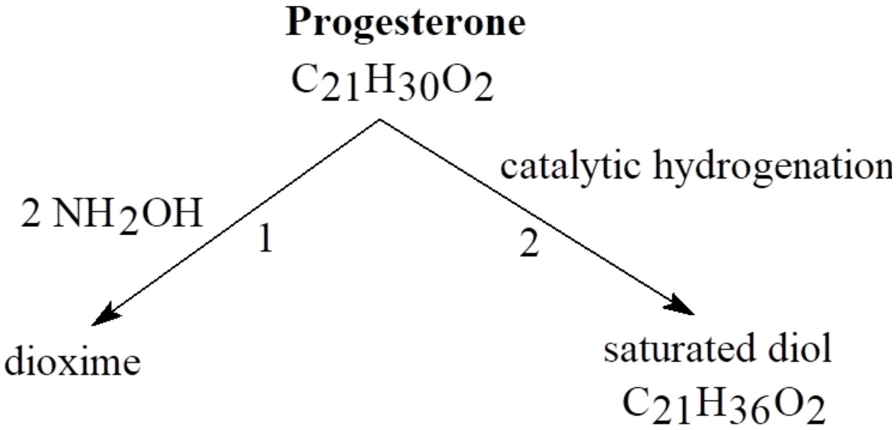
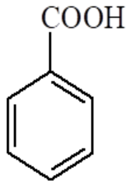


Shikimates

Benzoic acid and related compounds (C6-C1)



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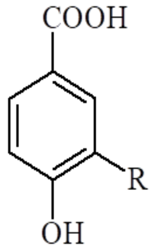
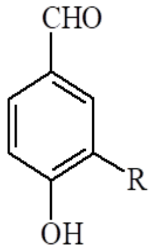
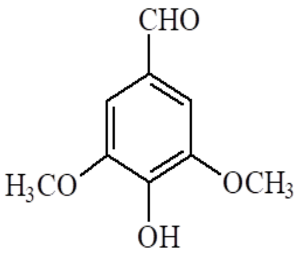


61; R = H
62; R = OH
63; R = OMe

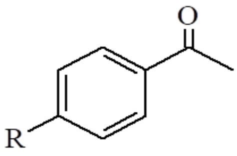


64; R = H
65; R = OMe

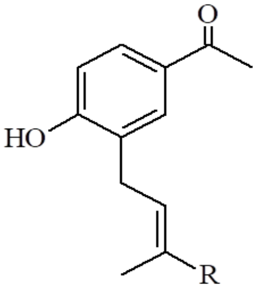


66

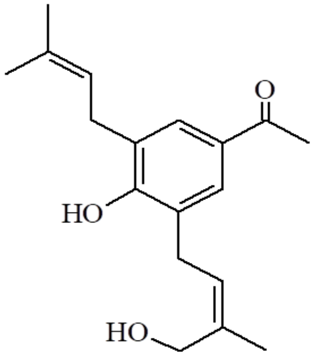
Acetophenones and related compounds (C6-C2)



67; R = OH
68; R = OMe



69; R = Me
70; R = CH_2OH



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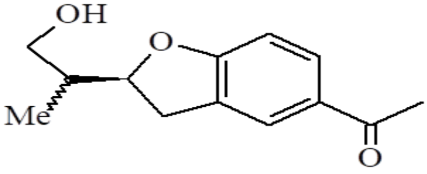
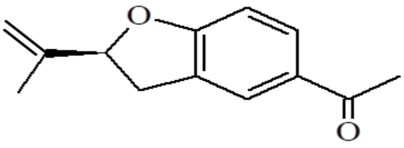


72; R = α-Me
73; R = β-Me



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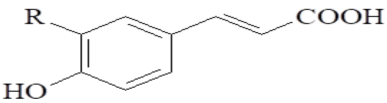
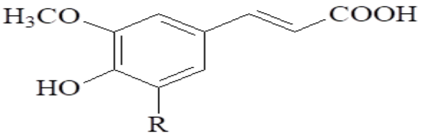
Phenylpropanoids (C6-C3)

Cinnamic acids

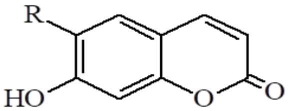


75; R = H
76; R = OH

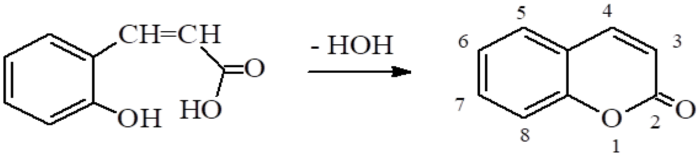


77; R = H
78; R = OMe

- **Coumarins**



81; R = H
82; R = OH
83; R = OMe



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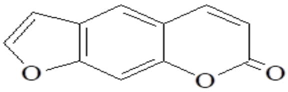
80



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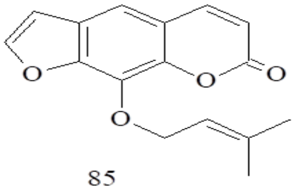

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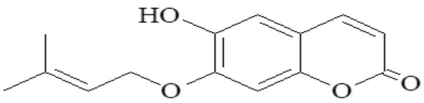

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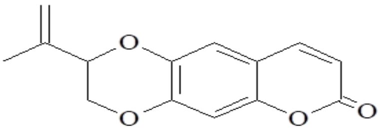

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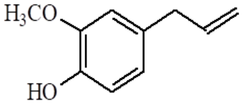
Phenyl propenes



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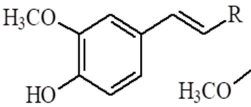
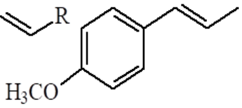


89; R = Me

92; R = CH_2OH

93; R = CHO



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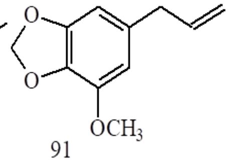

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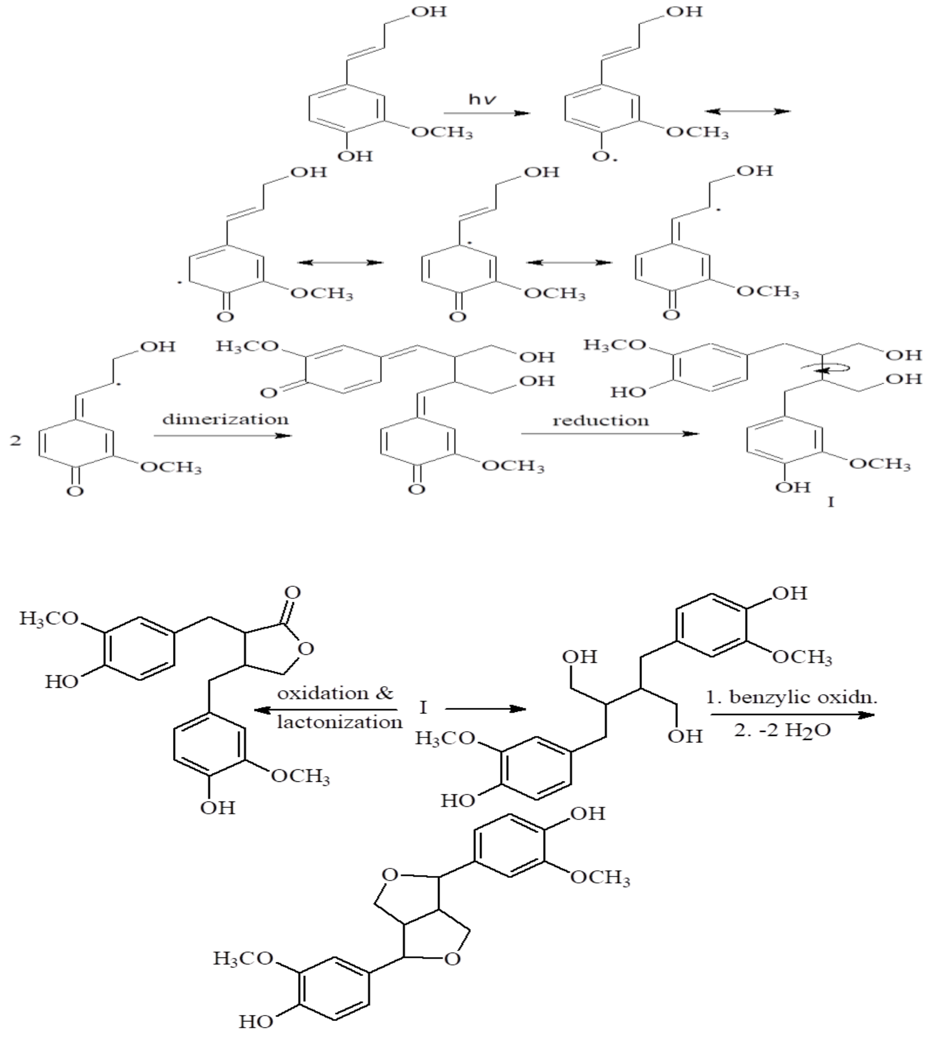
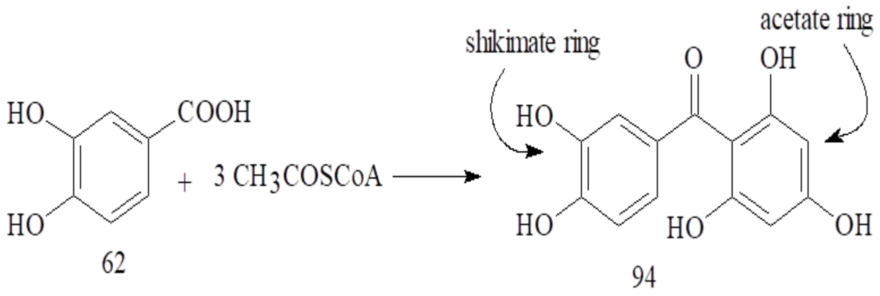
Lignans

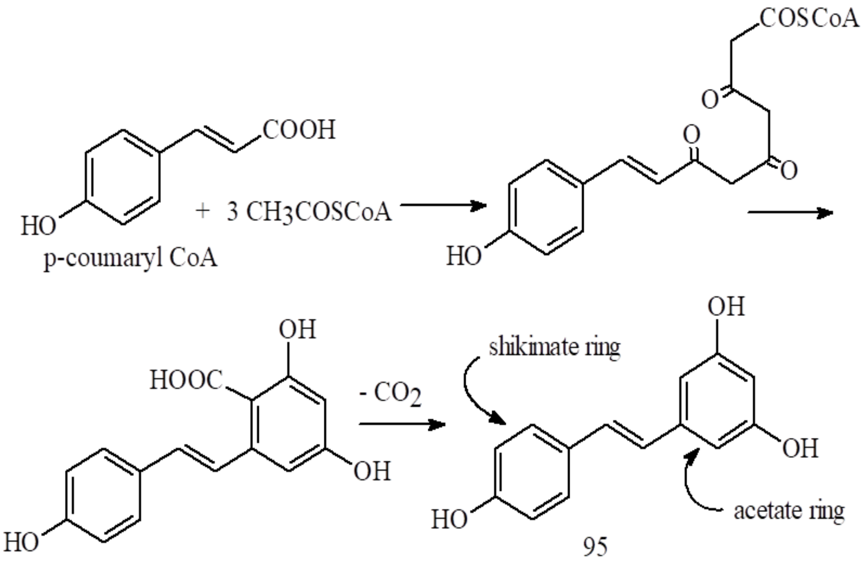


Compounds containing “shikimate” ring

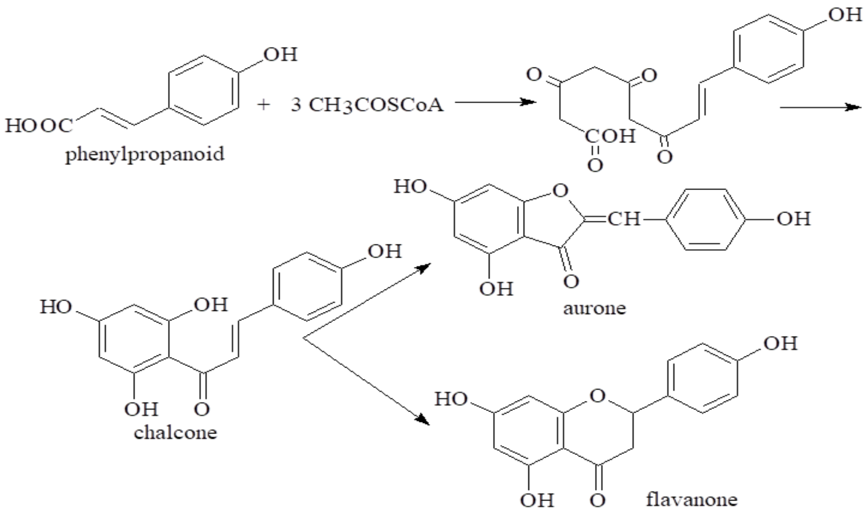
- **Benzophenones (C6-C1-C6)**

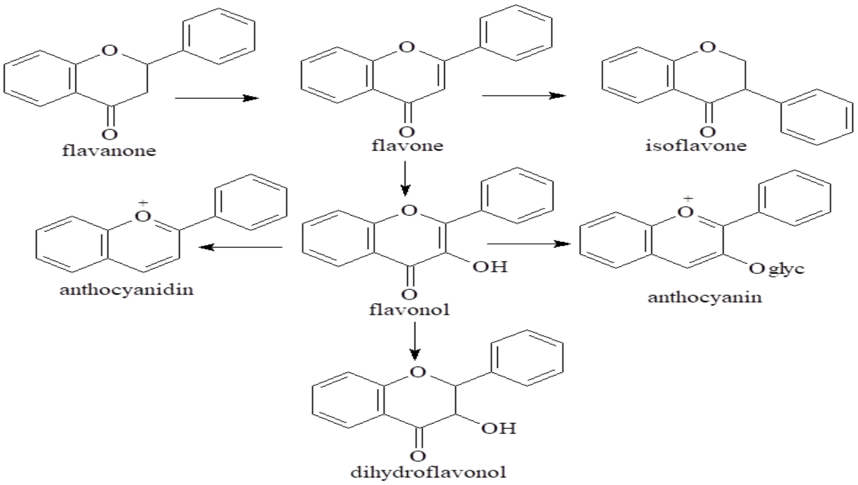


Stilbenes (C6-C2-C6)



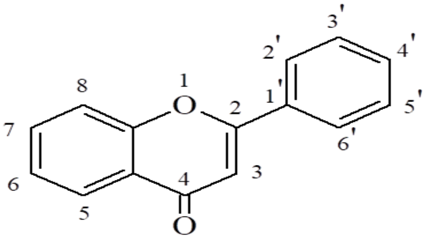
Flavonoids (C6-C3-C6)



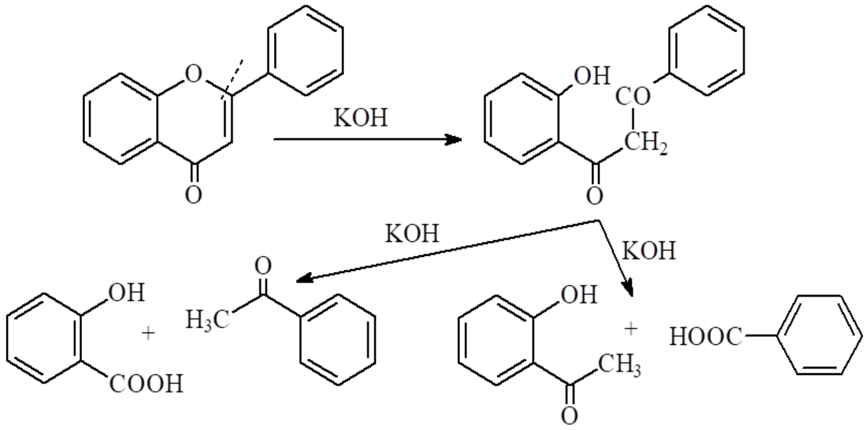


Structure-elucidation of some flavonoids

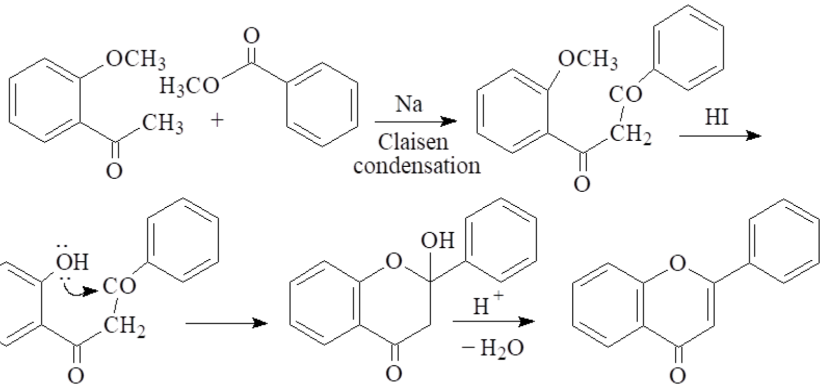
Flavone, 102, $C_{15}H_{10}O_2$



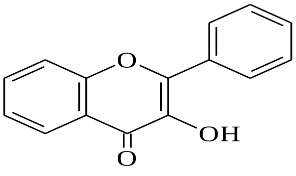
102



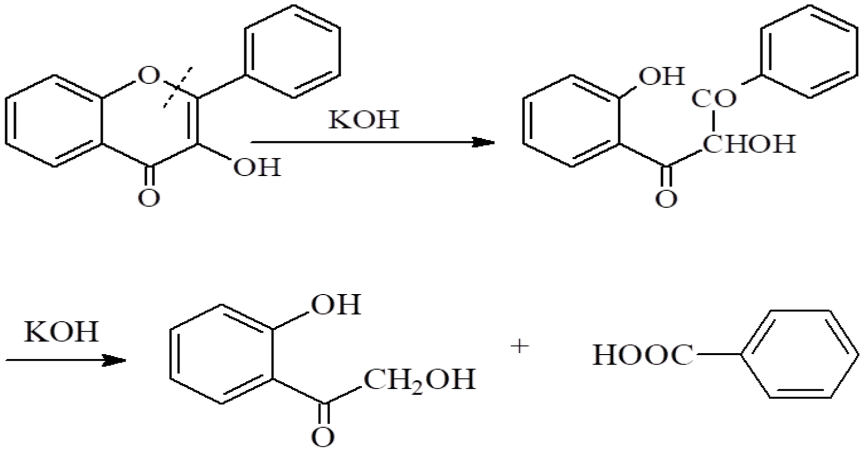
general method for synthesizing flavones



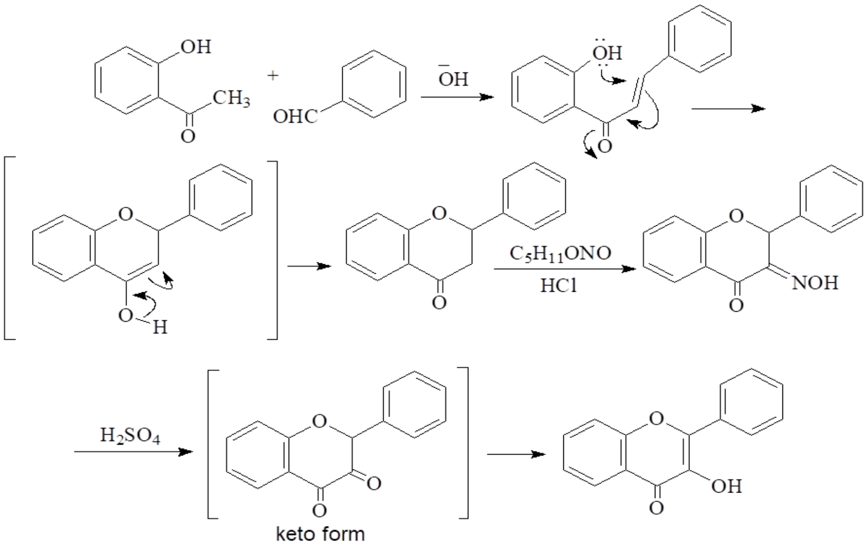
Flavonol (3-hydroxyflavone), 103,$C_{15}H_{10}O_3$



103



Kostanecki synthesis of flavonol



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- **4- Organic chemistry of natural products volume II, O. P. Agarwal, 2018.**
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Industrial Chemistry

4th year students Faculty of Education

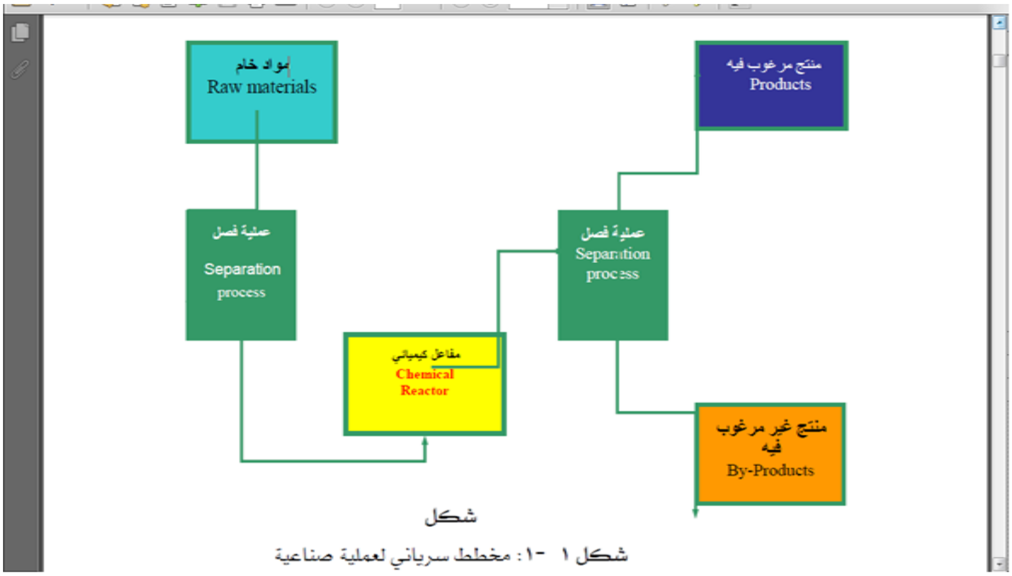
Chemistry group

Second term 2022/2023

Dr. Ibrahim Abdul-Motaleb Mousa

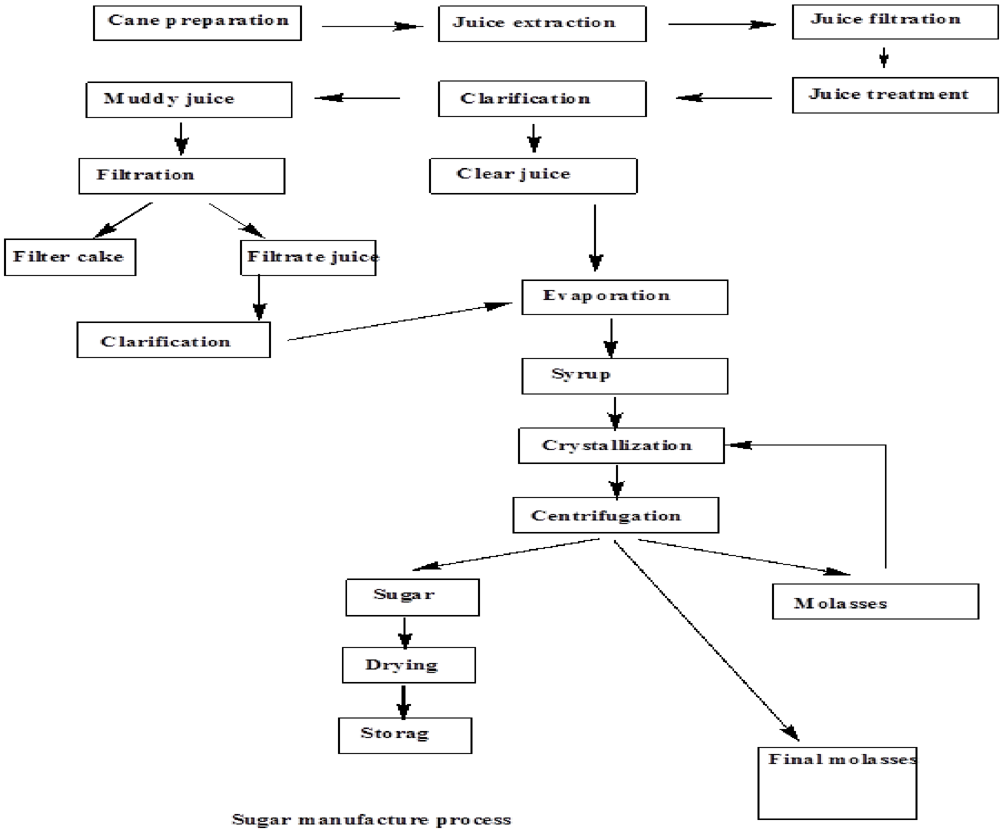
Contents

Sugar Cane Manufacture Process



شكل

شكل ١ -١: مخطط سرياني لعملية صناعية



Sugar manufacture process

Types

- **Cane:**

Harvested sugarcane from Venezuela ready for processing

Since the 6th century BC, cane sugar producers have crushed the harvested vegetable material from sugarcane in order to collect and filter the juice. They then treat the liquid (often with lime (calcium oxide)) to remove impurities and then neutralize it. Boiling the juice then allows the sediment to settle to the bottom for dredging out, while the scum rises to the surface for skimming off. In cooling, the liquid crystallizes, usually in the process of stirring, to produce sugar crystals. Centrifuges usually

remove the uncrystallized syrup. The producers can then either sell the sugar product for use as is, or process it further to produce lighter grades. The later processing may take place in another factory in another country.

Sugarcane is a major component of Brazilian agriculture; the country is a top producer of sugarcane products, such as crystallized sugar and ethanol (ethanol fuel). The sucrose found in sugarcane produces ethanol when fermented and distilled. Brazil has implemented ethanol as an alternative fuel on a national scale.

Beet

Beet sugar producers slice the washed beets, then extract the sugar with hot water in a "diffuser". An alkaline solution ("milk of lime" and carbon dioxide from the lime kiln) then serves to precipitate impurities (see carbonatation). After filtration[clarification needed], evaporation concentrates the juice to a content of about 70% solids, and controlled crystallisation extracts the sugar. A centrifuge removes the sugar crystals from the liquid, which gets recycled in the crystalliser stages. When economic constraints prevent the removal of more sugar, the manufacturer discards the remaining liquid, now known as molasses, or sells it on to producers of animal feed.

Sieving the resultant white sugar produces different grades for selling.

Cane versus beet

It is difficult to distinguish between fully refined sugar produced from beet and cane. One way is by isotope analysis of carbon. Cane uses C4 carbon fixation, and beet uses C3 carbon fixation, resulting in a different ratio of ^{13}C and ^{12}C isotopes in the sucrose. Tests are used to

detect fraudulent abuse of European Union subsidies or to aid in the detection of adulterated fruit juice.

Sugar cane tolerates hot climates better, but the production of sugar cane needs approximately four times as much water as the production of sugar beet, therefore some countries that traditionally produced cane sugar (such as Egypt) have built new beet sugar factories since about 2008. Some sugar factories process both sugar cane and sugar beets and extend their processing period in that way.

The production of sugar leaves residues that differ substantially depending on the raw materials used and on the place of production. While cane molasses is often used in food preparation, humans find molasses from sugar beets unpalatable, and it consequently ends up mostly as industrial fermentation feedstock (for example in alcohol distilleries), or as animal feed. Once dried, either type of molasses can serve as fuel for burning.

Pure beet sugar is difficult to find, so labelled, in the marketplace. Although some brands label their product clearly as "pure cane sugar", beet sugar is almost always

labeled simply as sugar or pure sugar. Interviews with the 5 major beet sugar-producing companies revealed that many store brands or "private label" sugar products are pure beet sugar. The lot code can be used to identify the company and the plant from which the sugar came, enabling beet sugar to be identified if the codes are known.

The constituents of the ripe cane

The constituents of the ripe cane vary widely in different countries but fall generally within the following limits:

- Water	**69-75%**
- Sucrose	**8-16%**
- Reducing sugars (glucose & fructose)	**0.5-2%**
- Organic matter other than sugar	**0.5-1%**
- Inorganic compounds	**0.2-0.6%**
- Nitrogenous bodies	**0.5-1%**
- Ash	**0.3-0.8%**
- Fiber	**10-16%**

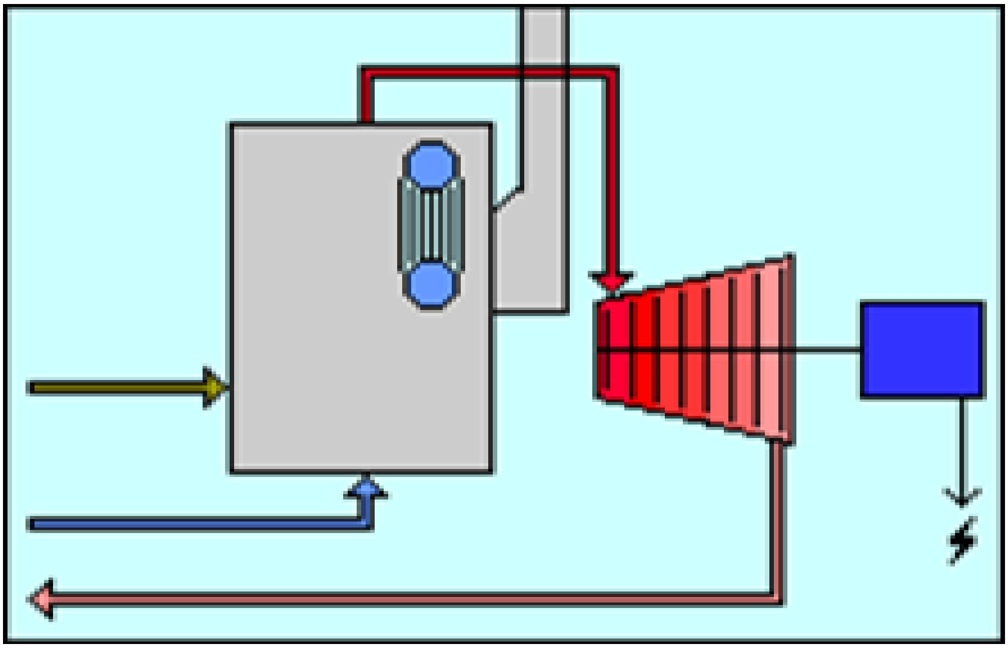
Storage

The final raw sugar forms a sticky brown mountain in the store and looks rather like the soft brown sugar found in domestic kitchens. It could be used like that but usually it gets dirty in storage and has a distinctive taste which most people don't want. That is why it is refined when it gets to the country where it will be used. Additionally, because one cannot get all the sugar out of the juice, there is a sweet by-product made: molasses. This is usually turned into a cattle food or is sent to a distillery where alcohol is made.

Power

So what happened to all that fibre from crushing the sugar cane? It is called "bagasse" in the industry. The factory needs electricity and steam to run, both of which are generated using this fiber.

The bagasse is burnt in large furnaces where a lot of heat is given out which can be used in turn to boil water and make high pressure steam. The steam is then used to drive a turbine in order to make electricity and create low pressure steam for the sugar making process. This is the same process that makes most of our electricity but there are several important differences.



Chemical treatment

1- Lime and milk of lime:

$CaCO_3$ -------1200c--------- $CaO + CO_2$

$CaO + H_2O$ ------------------- $Ca(OH)_2$

2- Phosphoric acid:

$H_3PO_4 + Ca(OH)_2$ ----------------- $Ca_3(PO_4)_2$

$Ca(OH)_2 + H_2SO_3$ ----------------- $CaSO_3 + H_2O$

H_2SO_3 (Sulphurous acid) has bleaching effect on color of the juice.

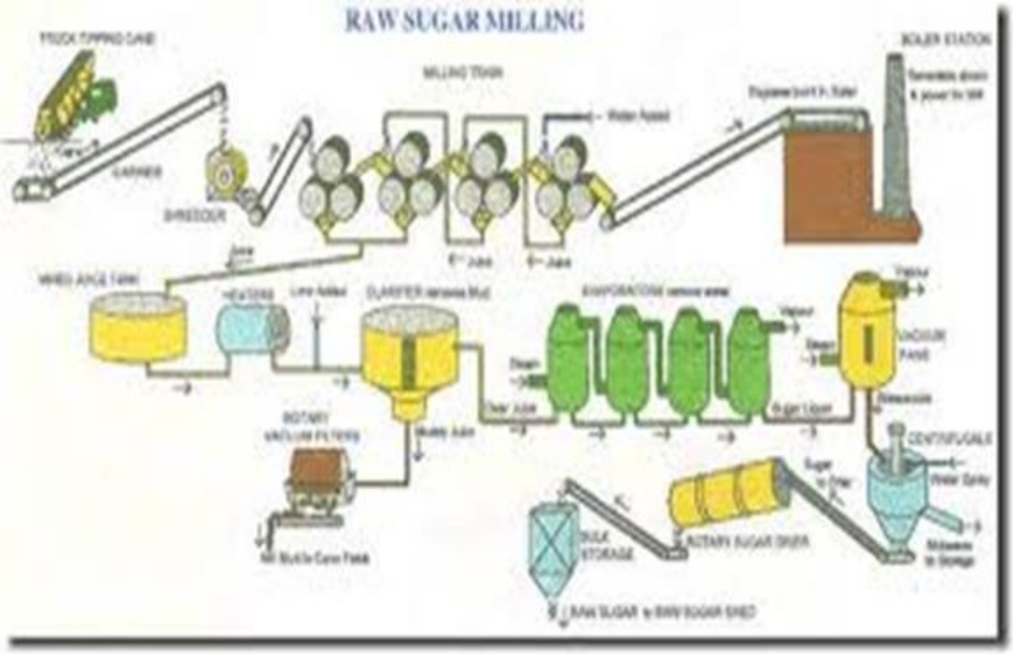
$CaSO_3$ (Calcium sulfite) adsorbed colloidal and coloring matters and some impurities.

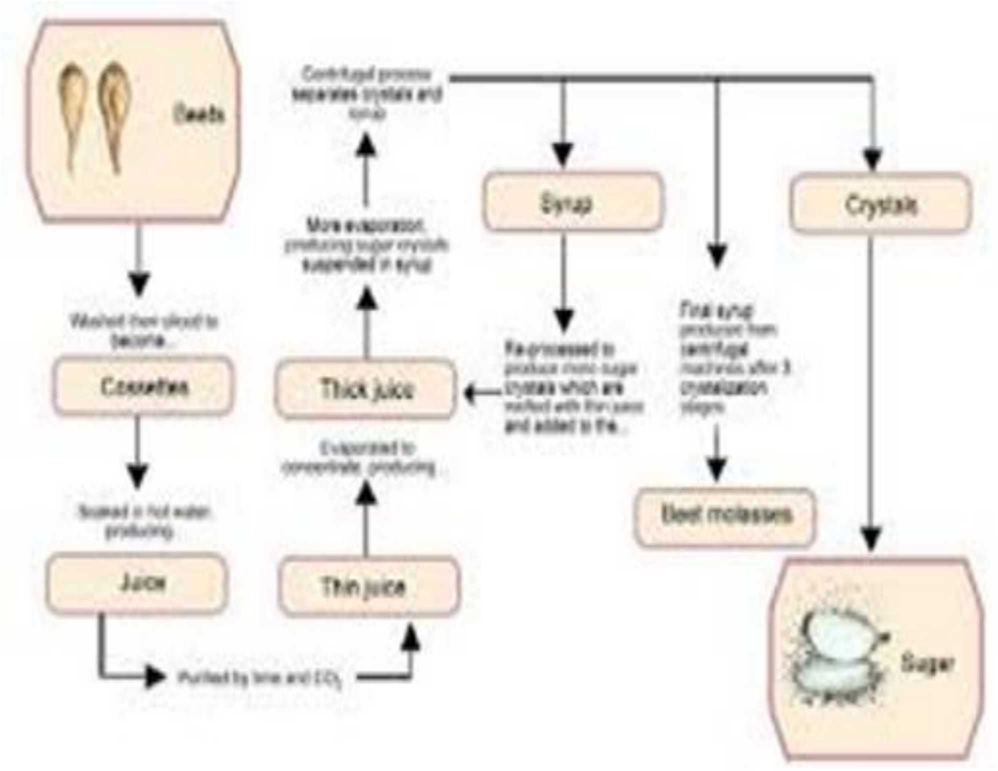
Safety factor

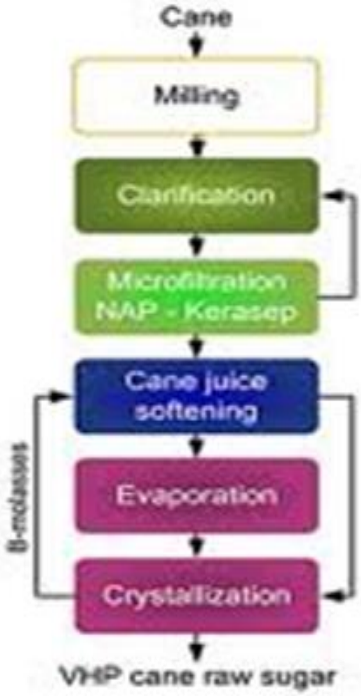
$$\text{Safety factor} = \frac{\text{Moisture \% in sugar}}{100 - \text{Polarization}}$$

0.2 in case of white sugar.

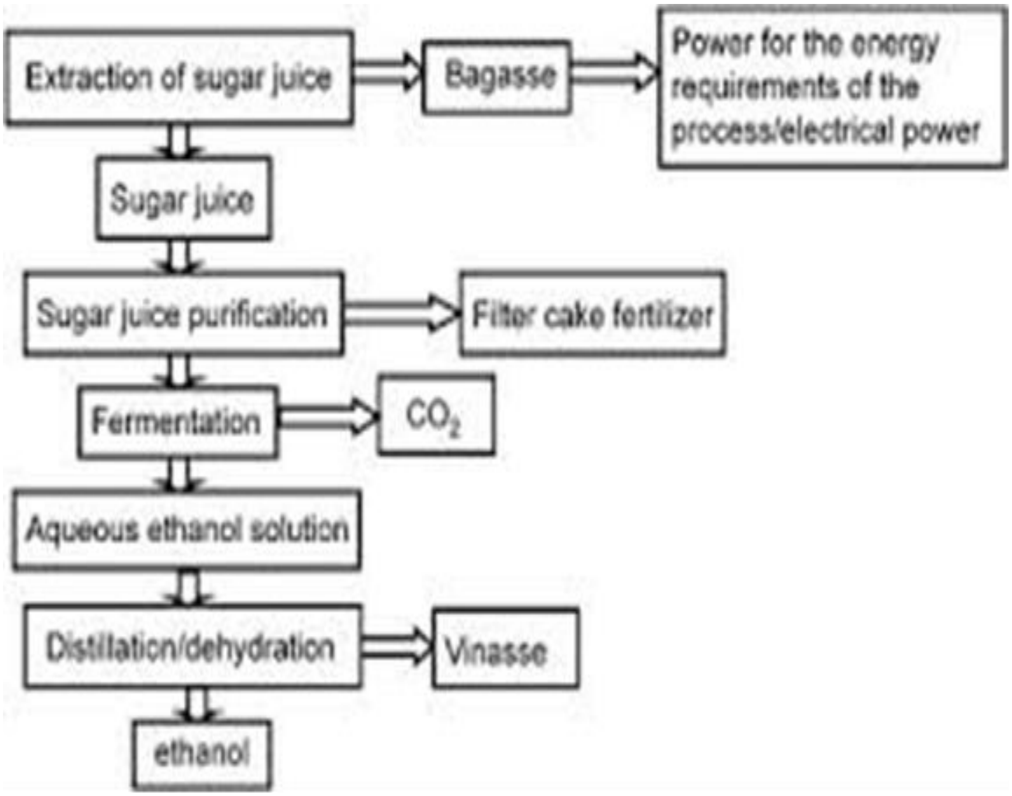
0.25 in case of raw sugar.


RAW SUGAR MILLING
TRUCK TIPPING CANE
CARRIER
SHREDDER
MILLING TRAIN
Water Added
Juice
Juice
Juice
Bagasse burnt in Boiler
BOILER STATION
Generates steam & power for Mill
MIXED JUICE TANK
HEATERS
Lime Added
CLARIFIER removes Mud
EVAPORATORS remove water
Steam
Vapour
Steam
Vapour
VACUUM PANS
Clear Juice
Sugar Liquor
Massecuite
ROTARY VACUUM FILTERS
Muddy Juice
Mill Mud to Cane Fields
CENTRIFUGALS
Water Spray
Sugar to Drier
Molasses to Storage
ROTARY SUGAR DRIER
BULK STORAGE
RAW SUGAR to RAW SUGAR SHED


Beets
Washed then sliced to become...
Cossettes
Soaked in hot water producing...
Juice
Purified by lime and CO2
Thin juice
Evaporated to concentrate, producing...
Thick juice
More evaporation, producing sugar crystals suspended in syrup
Centrifugal process separates crystals and syrup
Syrup
Crystals
Re-processed to produce more sugar crystals which are melted with thin juice and added to the...
Final syrup produced from centrifugal machines after 3 crystallization stages
Beet molasses
Sugar


Cane
Milling
Clarification
Microfiltration NAP - Kerasep
Cane juice softening
Evaporation
Crystallization
B-molasses
VHP cane raw sugar


Bagasse Pulpboard
Quality Tableware
Biodegradable & Compostable
Sugar Cane
Sugar Mills
A Natural Resource that is Annually Renewable


Extraction of sugar juice
Bagasse
Power for the energy requirements of the process/electrical power
Sugar juice
Sugar juice purification
Filter cake fertilizer
Fermentation
CO_2
Aqueous ethanol solution
Distillation/dehydration
Vinasse
ethanol

Ethanol Manufacture Process

Ethanol fuel

Ethanol fuel is ethanol (ethyl alcohol), the same type of alcohol found in alcoholic beverages. It is most often used as a motor fuel, mainly as a biofuel additive for gasoline. World ethanol production for transport fuel tripled between 2000 and 2007 from 17 billion to more than 52 billion liters. From 2007 to 2008, the share of ethanol in global gasoline type fuel use increased from 3.7% to 5.4%. In 2011 worldwide ethanol fuel production reached 22.36 billion U.S. liquid gallons (bg) (84.6 billion liters), with the United States as the top producer with 13.9 bg (52.6 billion liters), accounting for 62.2% of global production, followed by Brazil with 5.6 bg (21.1 billion liters). Ethanol fuel has a "gasoline gallon equivalency" (GGE) value of 1.5 US gallons (5.7 L), which means 1.5 gallons of ethanol produces the energy of one gallon of gasoline.

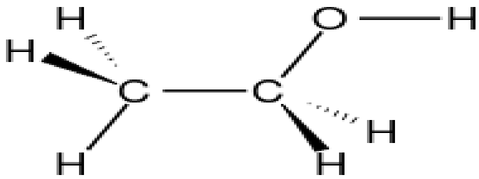
Ethanol fuel is widely used in Brazil and in the United States, and together both countries were responsible for 87.1% of the world's ethanol fuel production in 2011.

Most cars on the road today in the U.S. can run on blends of up to 10% ethanol, and ethanol represented 10% of the U.S. gasoline fuel supply derived from domestic sources in 2011. Since 1976 the Brazilian government has made it mandatory to blend ethanol with gasoline, and since 2007 the legal blend is around 25% ethanol and 75% gasoline (E25). By December 2011 Brazil had a fleet of 14.8 million flex-fuel automobiles and light trucks and 1.5 million flex-fuel motorcycles that regularly use neat ethanol fuel (known as E100).

Bioethanol is a form of quasi-renewable energy that can be produced from agricultural feedstocks. It can be made from very common crops such as sugar cane, potato, cassava and corn. There has been considerable debate about how useful bioethanol is in replacing gasoline. Concerns about its production and use relate to increased food prices due to the large amount of arable land required for crops, as well as the energy and pollution balance of the whole cycle of ethanol production, especially from corn. Recent developments with cellulosic ethanol production and commercialization may allay some of these concerns.

Cellulosic ethanol offers promise because cellulose fibers, a major and universal component in plant cells walls, can be used to produce ethanol. According to the International Energy Agency, cellulosic ethanol could allow ethanol fuels to play a much bigger role in the future than previously thought.

- **Chemistry**



Structure of ethanol molecule. All bonds are single bonds

During ethanol fermentation, glucose and other sugars in the corn (or sugarcane or other crops) are converted into ethanol and carbon dioxide.

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 + \text{heat}$$

Like any fermentation reaction, the fermentation is not 100% selective, and other side products such acetic acid, glycols and many other products are formed to a considerable extent and need to be removed during the purification of the ethanol. The fermentation takes place in aqueous solution and the resulting solution after fermentation has an ethanol content of around 15%. The ethanol is subsequently isolated and purified by a combination of adsorption and distillation techniques. The purification is very energy intensive.

During combustion ethanol reacts with oxygen to produce carbon dioxide, water, and heat:

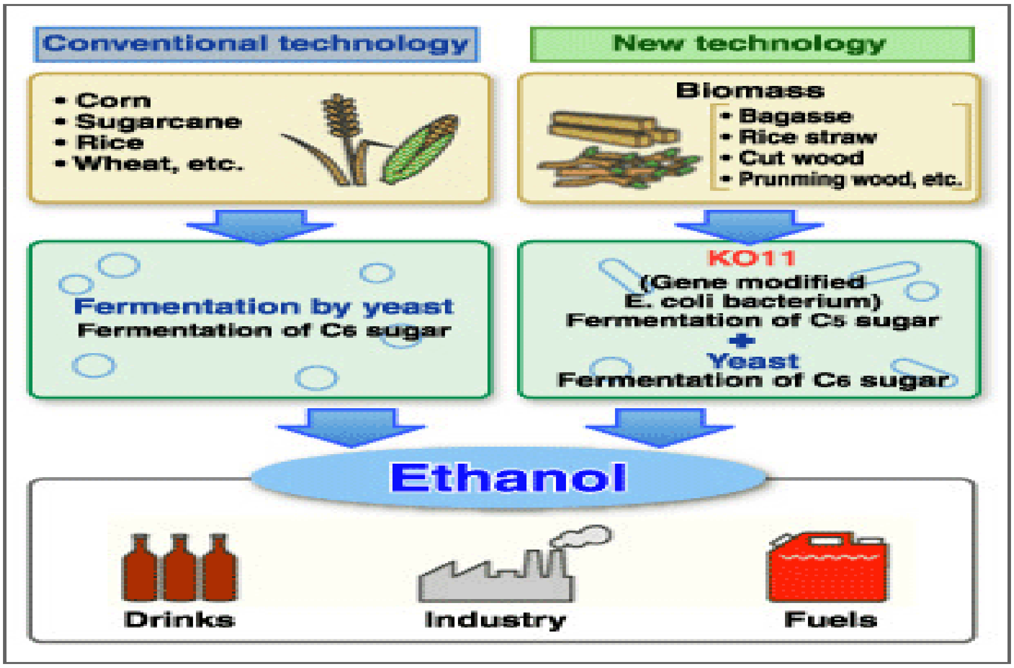
$$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O + \text{heat}$$

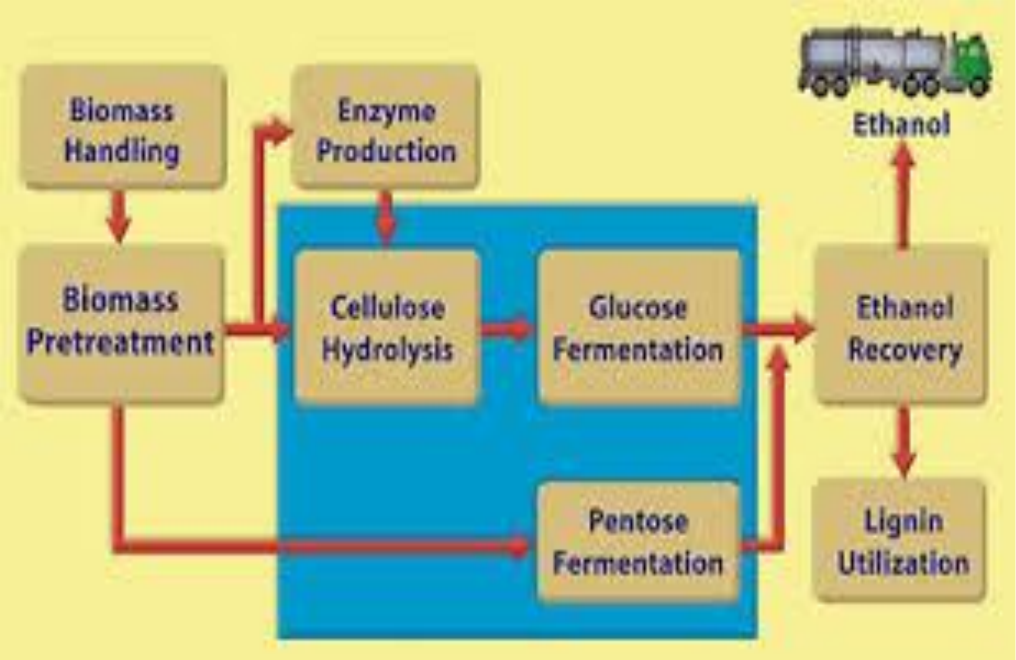
Starch and cellulose molecules are strings of glucose molecules. It is also possible to generate ethanol out of cellulosic materials. That, however, requires a pretreatment that splits the cellulose into glycose

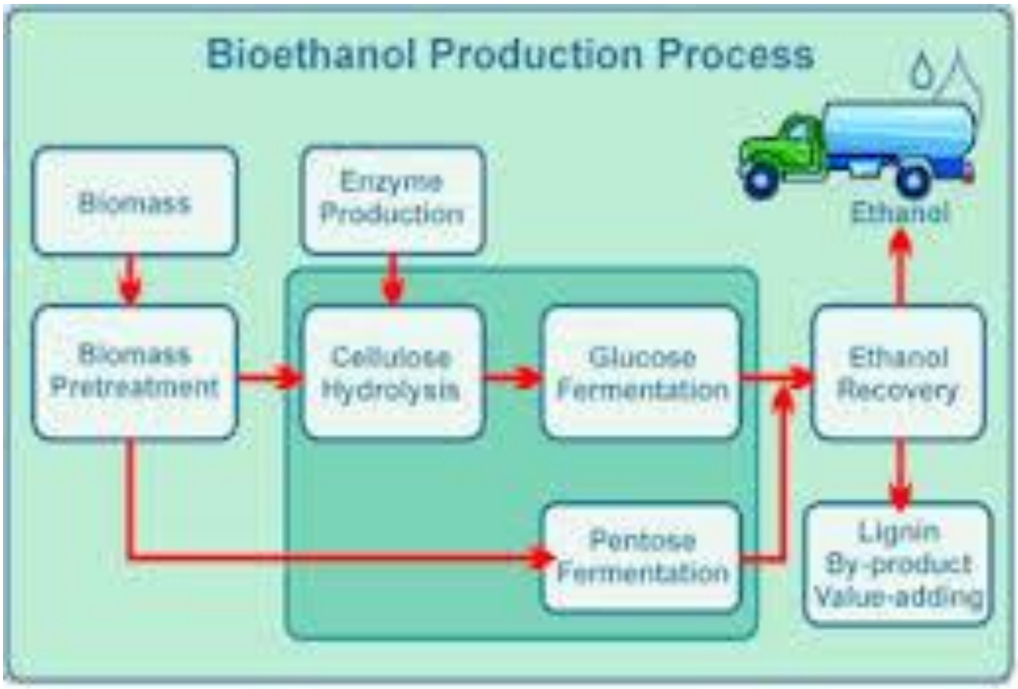
molecules and other sugars that subsequently can be fermented. The resulting product is called cellulosic ethanol, indicating its source.

Ethanol may also be produced industrially from ethene (ethylene), by hydrolysis of the double bond in the presence of catalysts and high temperature.

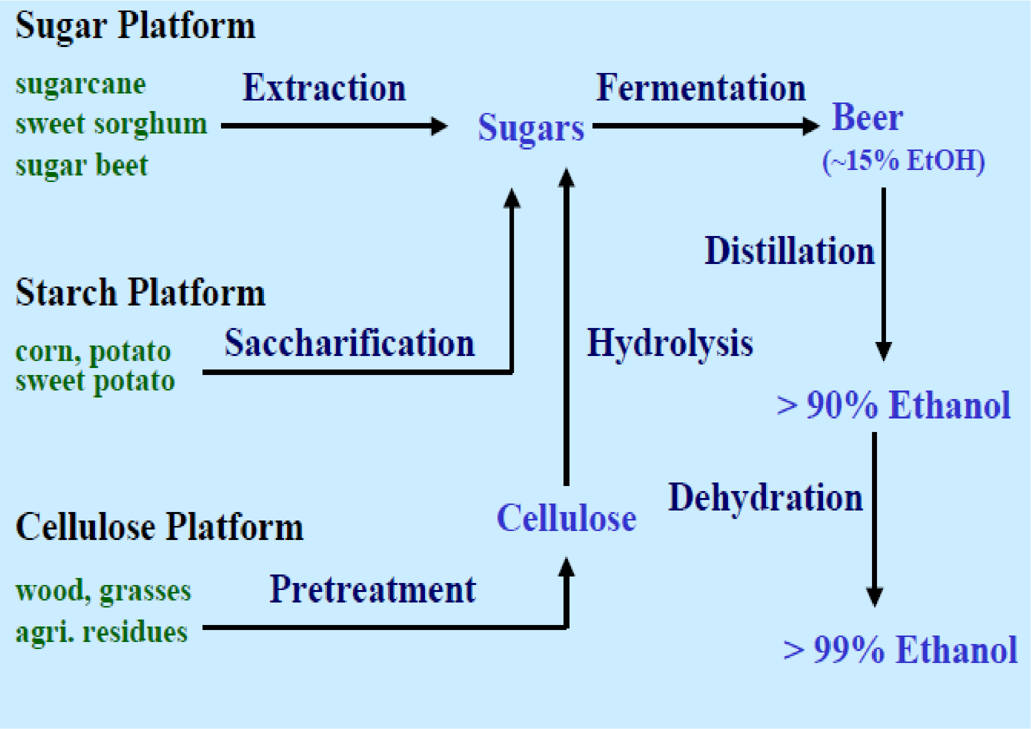
$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$




Biomass Handling
Enzyme Production
Ethanol
Biomass Pretreatment
Cellulose Hydrolysis
Glucose Fermentation
Ethanol Recovery
Pentose Fermentation
Lignin Utilization


Bioethanol Production Process
Biomass
Enzyme Production
Ethanol
Biomass Pretreatment
Cellulose Hydrolysis
Glucose Fermentation
Ethanol Recovery
Pentose Fermentation
Lignin By-product Value-adding

Bio-Ethanol Production Processes



Sugar Platform

sugarcane
sweet sorghum
sugar beet

Extraction

Sugars

Fermentation

Beer
(~15% EtOH)

Distillation

Starch Platform

corn, potato
sweet potato

Saccharification

Hydrolysis

> 90% Ethanol

Cellulose Platform

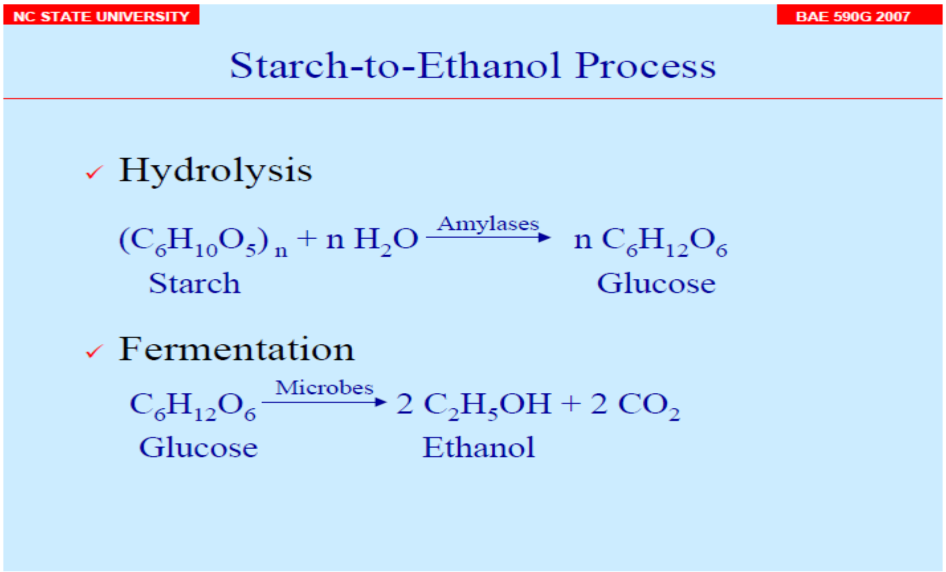
Cellulose

Dehydration

wood, grasses
agri. residues

Pretreatment

> 99% Ethanol



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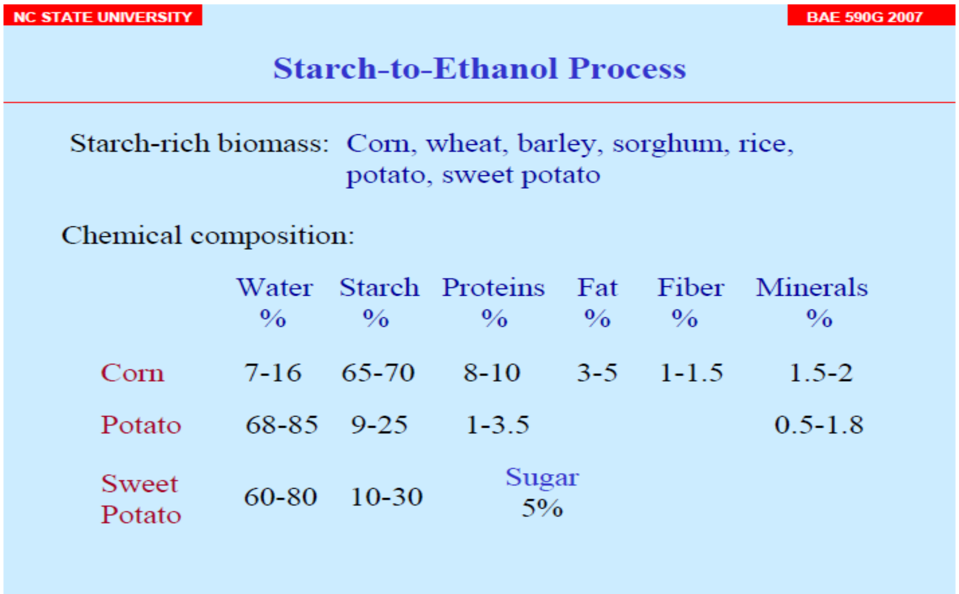
Starch-to-Ethanol Process

- ✓ Hydrolysis

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow{\text{Amylases}} \underset{\text{Glucose}}{n\,C_6H_{12}O_6}$$

- ✓ Fermentation

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Microbes}} \underset{\text{Ethanol}}{2\,C_2H_5OH} + 2\,CO_2$$



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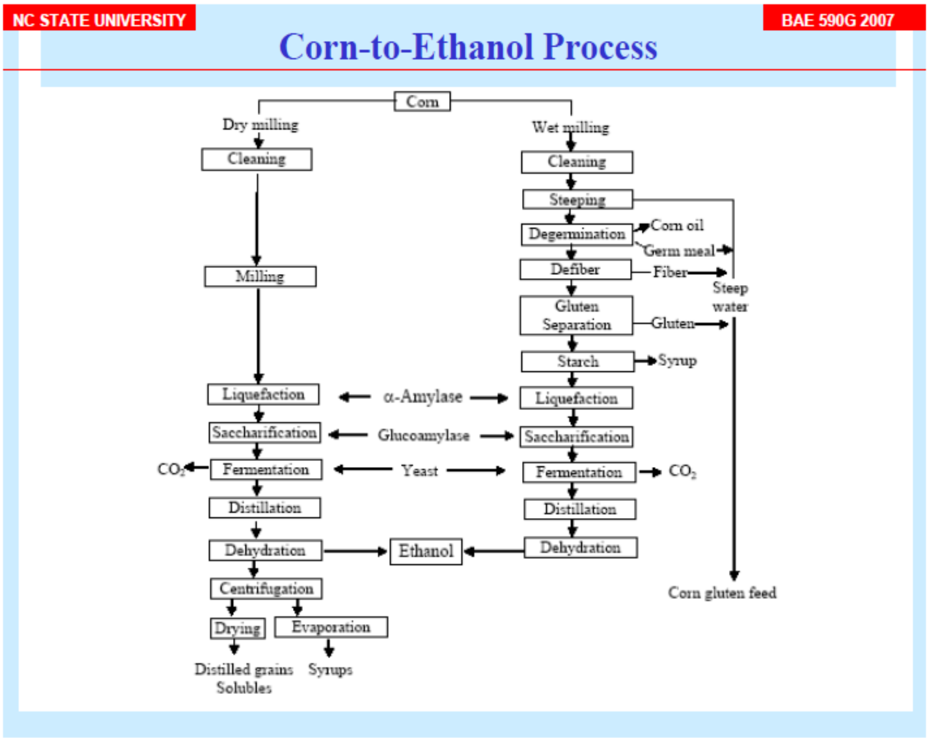
Starch-to-Ethanol Process

Starch-rich biomass: Corn, wheat, barley, sorghum, rice, potato, sweet potato

Chemical composition:

	Water %	Starch %	Proteins %	Fat %	Fiber %	Minerals %
Corn	7-16	65-70	8-10	3-5	1-1.5	1.5-2
Potato	68-85	9-25	1-3.5			0.5-1.8
Sweet Potato	60-80	10-30	Sugar 5%			



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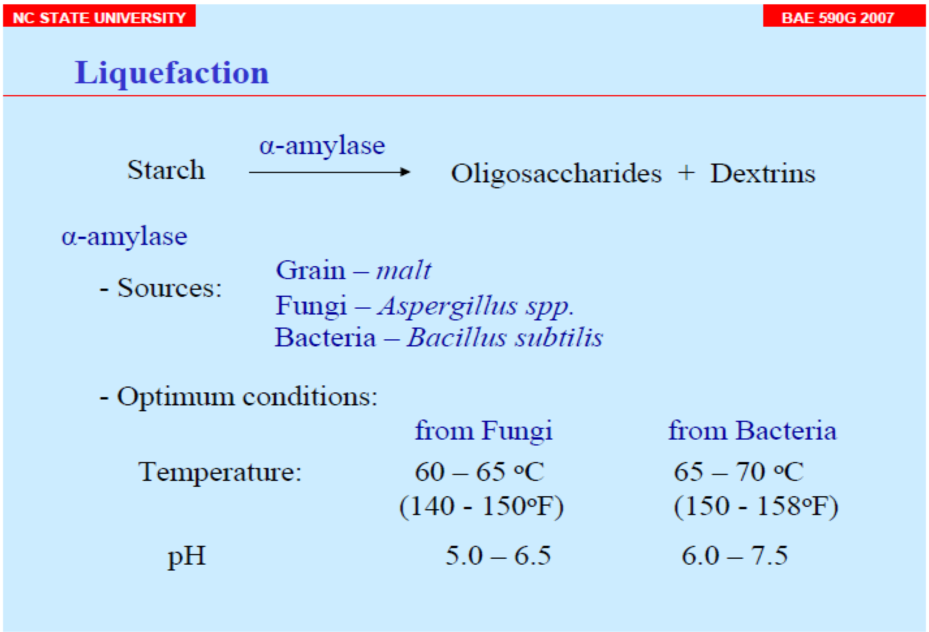
Corn-to-Ethanol Process



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Liquefaction

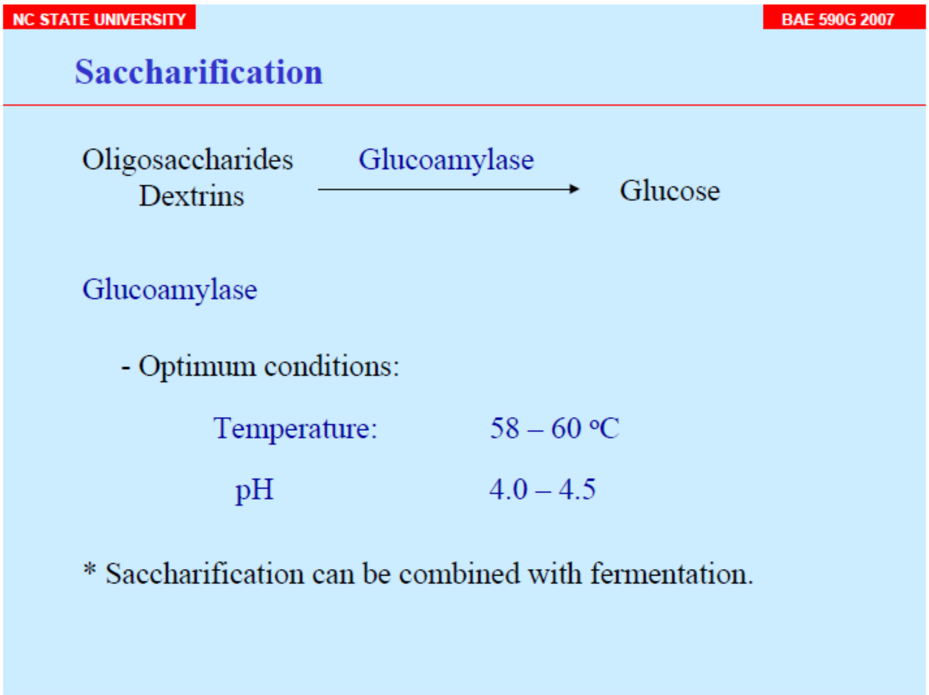
Starch $\xrightarrow{\alpha\text{-amylase}}$ Oligosaccharides + Dextrins

α-amylase

- Sources:
  - Grain – *malt*
  - Fungi – *Aspergillus spp.*
  - Bacteria – *Bacillus subtilis*

- Optimum conditions:

	from Fungi	from Bacteria
Temperature:	60 – 65 °C (140 - 150°F)	65 – 70 °C (150 - 158°F)
pH	5.0 – 6.5	6.0 – 7.5



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Saccharification

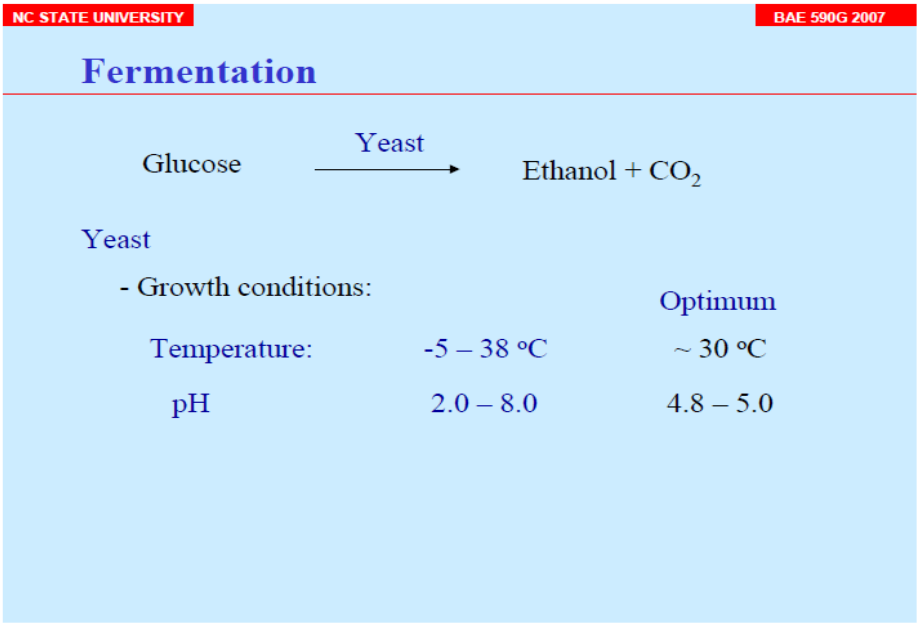
Oligosaccharides, Dextrins $\xrightarrow{\text{Glucoamylase}}$ Glucose

Glucoamylase

- Optimum conditions:

Temperature:	58 – 60 °C
pH	4.0 – 4.5

* Saccharification can be combined with fermentation.



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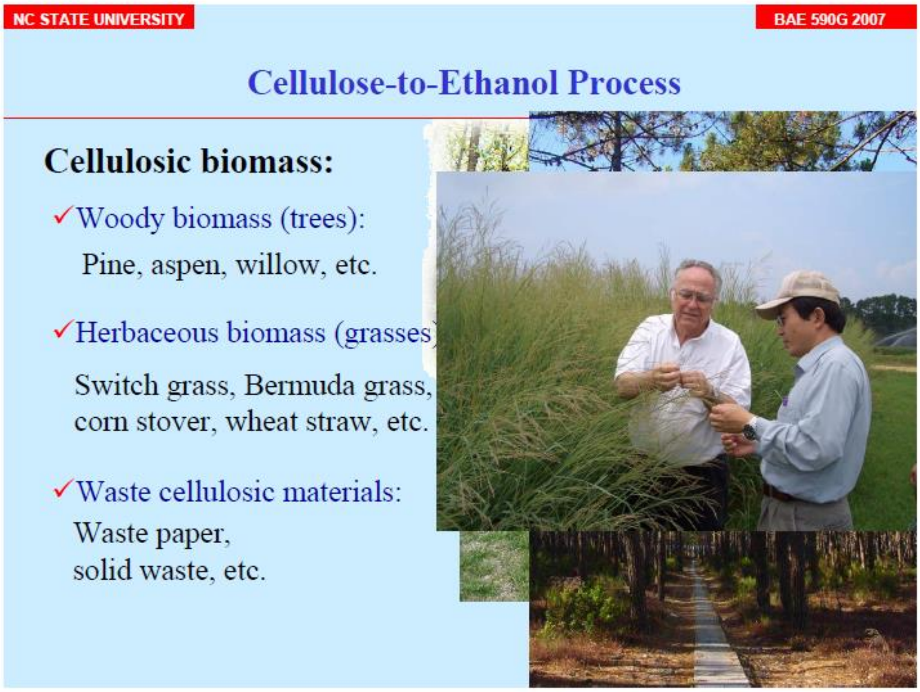
Fermentation

$$\text{Glucose} \xrightarrow{\text{Yeast}} \text{Ethanol} + CO_2$$

Yeast

- Growth conditions:

		Optimum
Temperature:	-5 – 38 °C	~ 30 °C
pH	2.0 – 8.0	4.8 – 5.0



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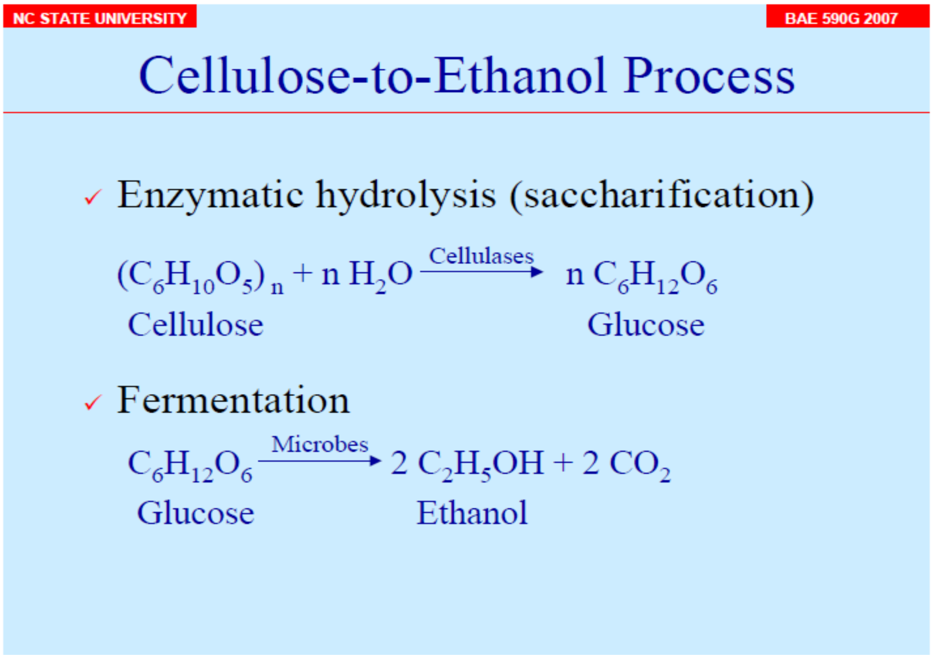
Cellulose-to-Ethanol Process

Cellulosic biomass:

✓ Woody biomass (trees):
Pine, aspen, willow, etc.

✓ Herbaceous biomass (grasses):
Switch grass, Bermuda grass, corn stover, wheat straw, etc.

✓ Waste cellulosic materials:
Waste paper,
solid waste, etc.



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Cellulose-to-Ethanol Process

- ✓ Enzymatic hydrolysis (saccharification)

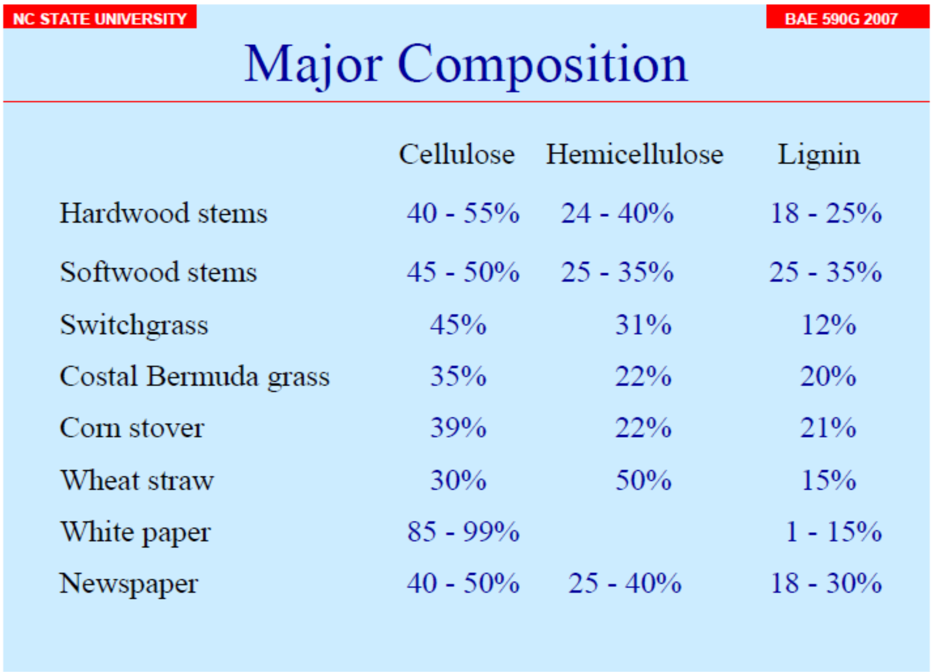
$$(C_6H_{10}O_5)_n + n\,H_2O \xrightarrow{\text{Cellulases}} n\,C_6H_{12}O_6$$

Cellulose Glucose

- ✓ Fermentation

$$C_6H_{12}O_6 \xrightarrow{\text{Microbes}} 2\,C_2H_5OH + 2\,CO_2$$

Glucose Ethanol



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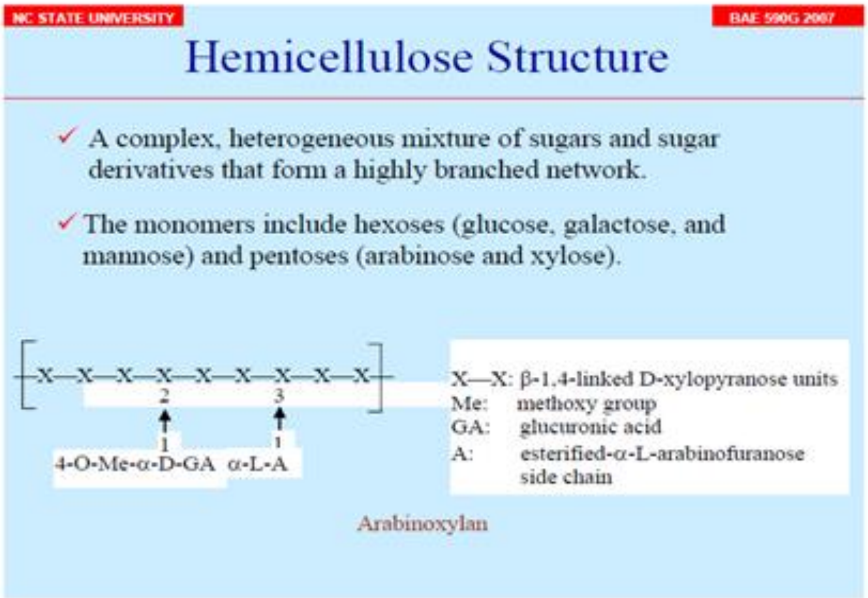
Major Composition

	Cellulose	Hemicellulose	Lignin
Hardwood stems	40 - 55%	24 - 40%	18 - 25%
Softwood stems	45 - 50%	25 - 35%	25 - 35%
Switchgrass	45%	31%	12%
Costal Bermuda grass	35%	22%	20%
Corn stover	39%	22%	21%
Wheat straw	30%	50%	15%
White paper	85 - 99%		1 - 15%
Newspaper	40 - 50%	25 - 40%	18 - 30%



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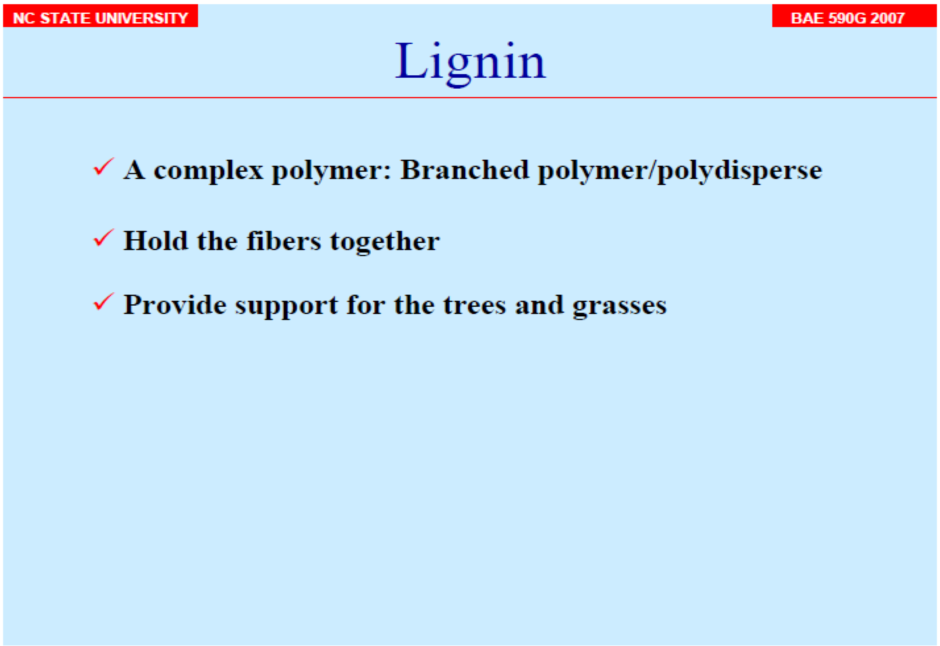
Hemicellulose Structure

- ✓ A complex, heterogeneous mixture of sugars and sugar derivatives that form a highly branched network.
- ✓ The monomers include hexoses (glucose, galactose, and mannose) and pentoses (arabinose and xylose).

X—X: β-1,4-linked D-xylopyranose units
Me: methoxy group
GA: glucuronic acid
A: esterified-α-L-arabinofuranose side chain

Arabinoxylan



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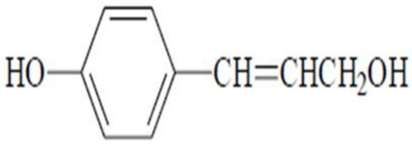
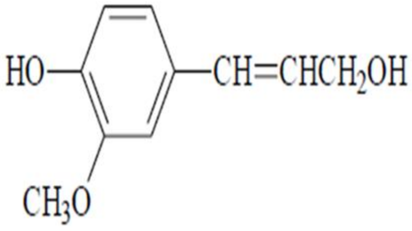
Lignin

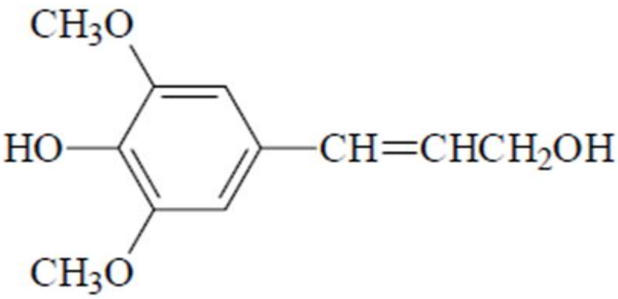
- ✓ **A complex polymer: Branched polymer/polydisperse**
- ✓ **Hold the fibers together**
- ✓ **Provide support for the trees and grasses**



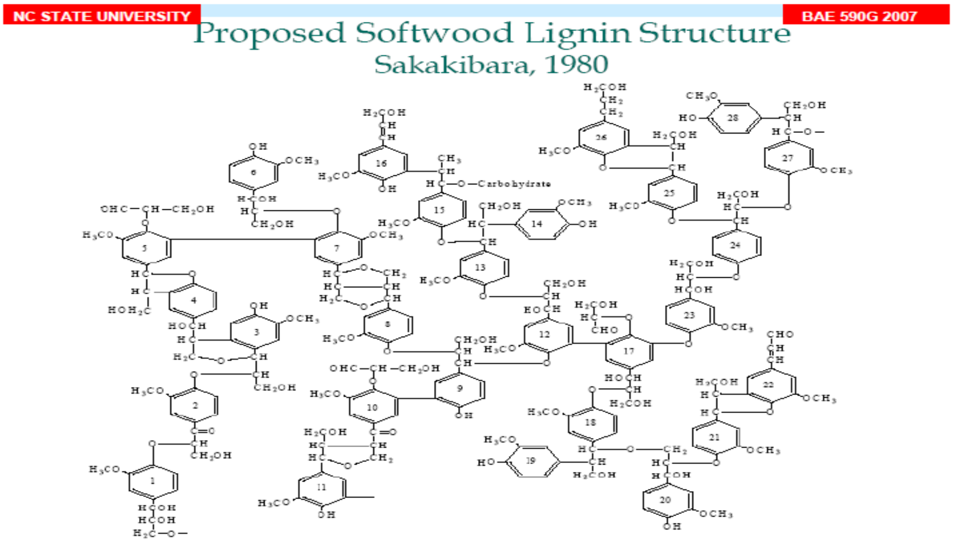
trans-*p*-coumarol



trans-coniferol

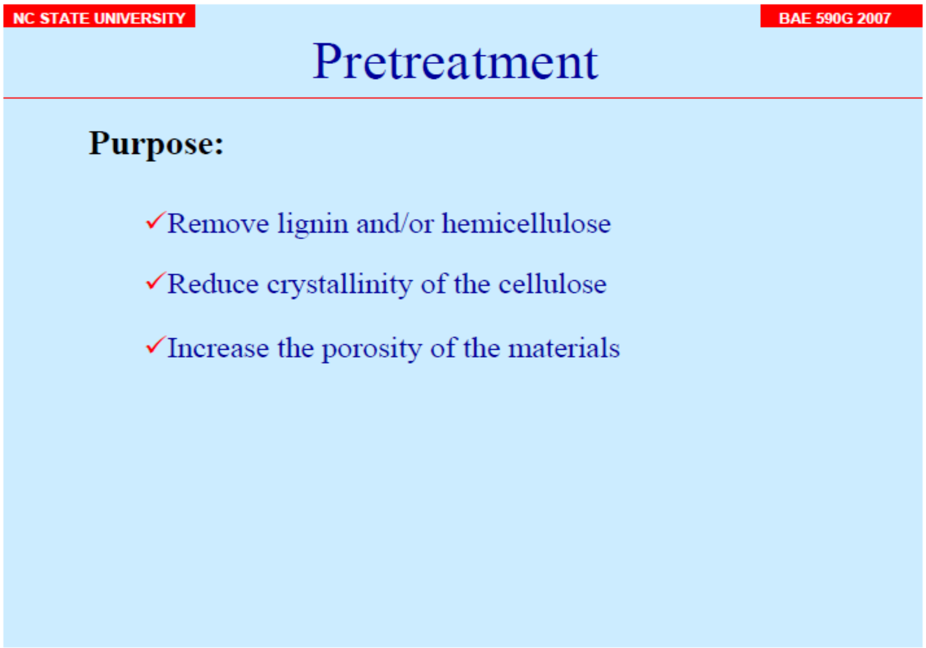


trans-sinapol



Proposed Softwood Lignin Structure

Sakakibara, 1980



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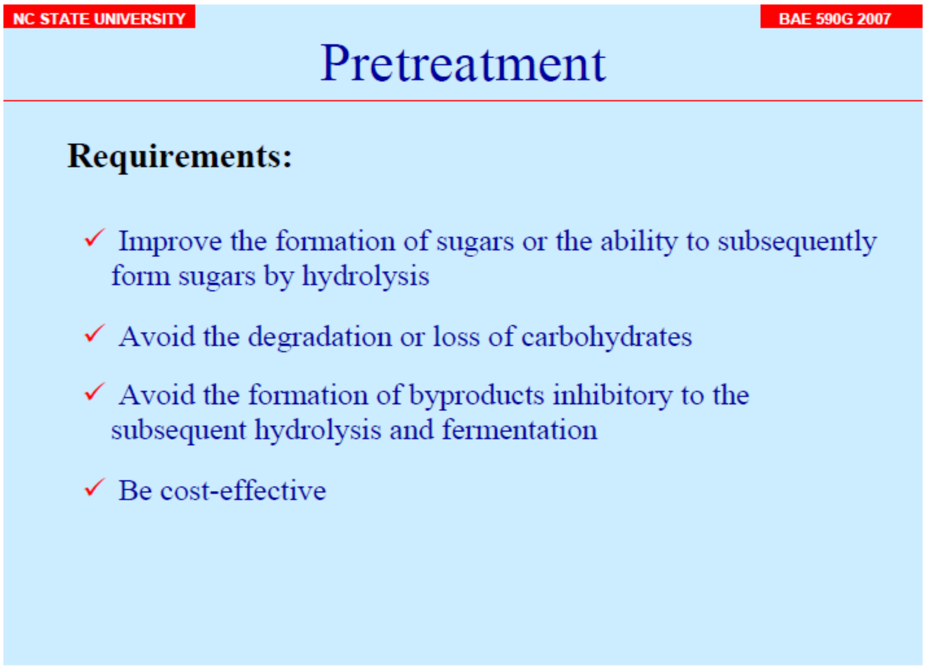
Pretreatment

Purpose:

- ✓Remove lignin and/or hemicellulose
- ✓Reduce crystallinity of the cellulose
- ✓Increase the porosity of the materials



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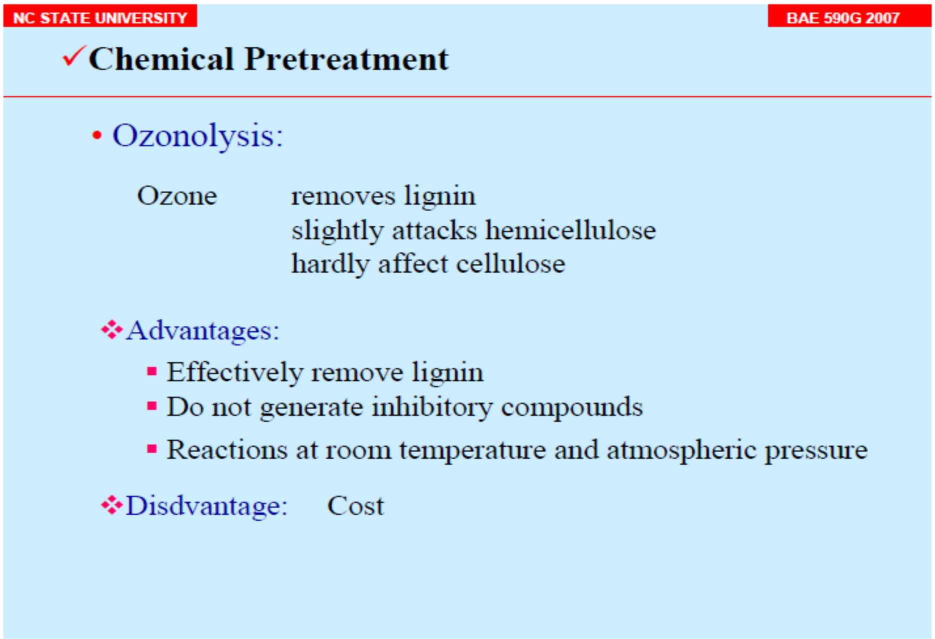
Pretreatment

Requirements:

- ✓ Improve the formation of sugars or the ability to subsequently form sugars by hydrolysis
- ✓ Avoid the degradation or loss of carbohydrates
- ✓ Avoid the formation of byproducts inhibitory to the subsequent hydrolysis and fermentation
- ✓ Be cost-effective



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✓Chemical Pretreatment

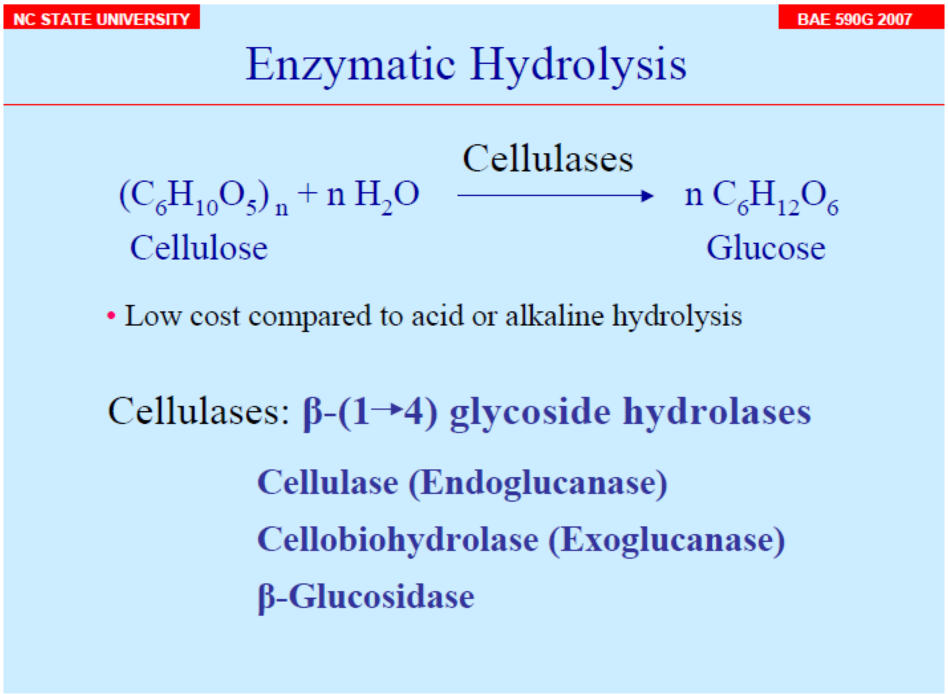
- Ozonolysis:

Ozone	removes lignin slightly attacks hemicellulose hardly affect cellulose

❖Advantages:

- Effectively remove lignin
- Do not generate inhibitory compounds
- Reactions at room temperature and atmospheric pressure

❖Disdvantage: Cost



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Enzymatic Hydrolysis

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow{\text{Cellulases}} \underset{\text{Glucose}}{n\,C_6H_{12}O_6}$$

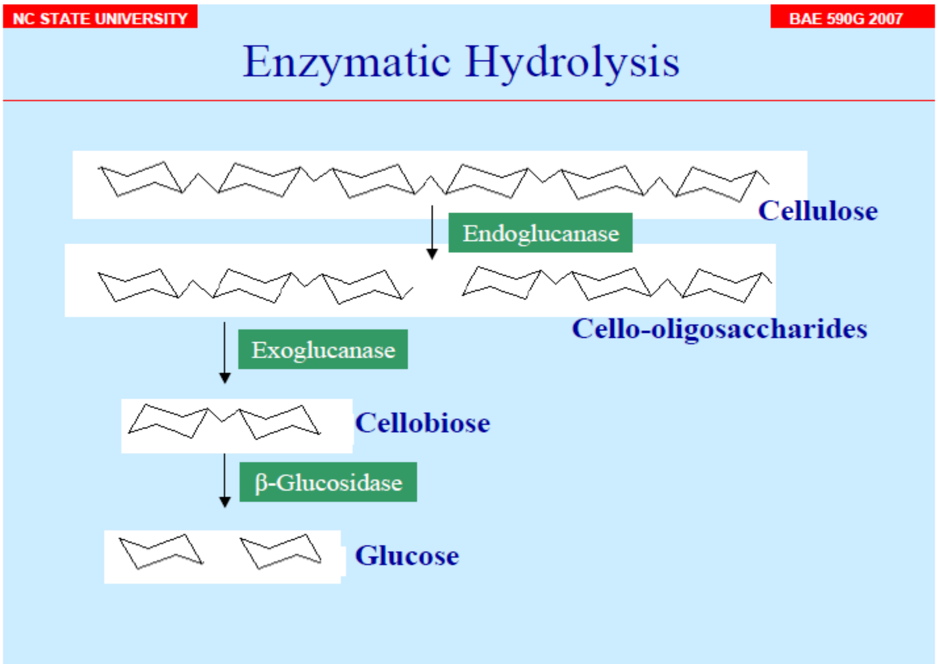
- Low cost compared to acid or alkaline hydrolysis

Cellulases: **β-(1→4) glycoside hydrolases**

Cellulase (Endoglucanase)

Cellobiohydrolase (Exoglucanase)

β-Glucosidase



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Enzymatic Hydrolysis

Cellulose

Endoglucanase

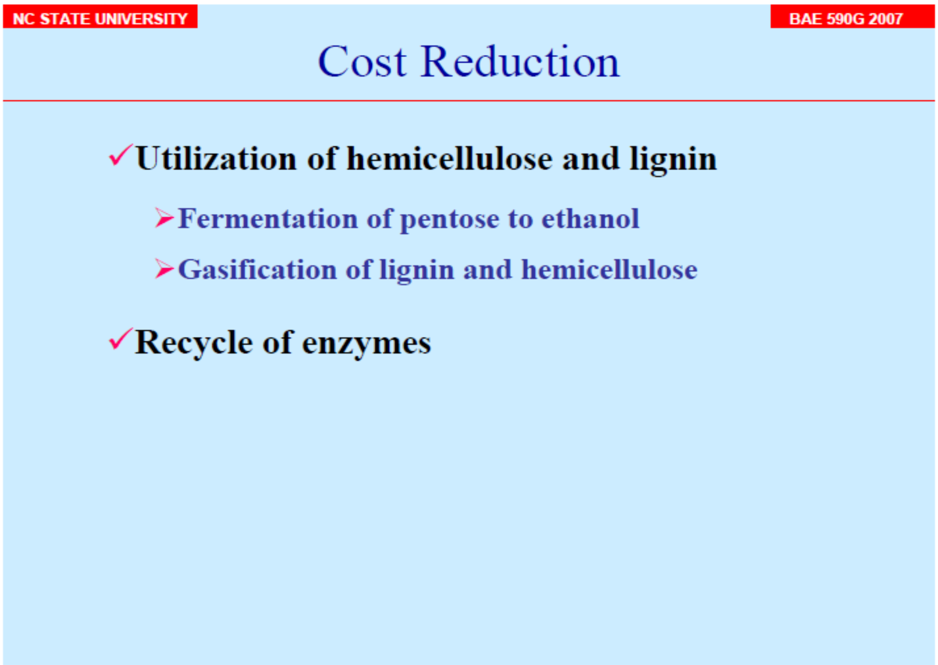
Cello-oligosaccharides

Exoglucanase

Cellobiose

β-Glucosidase

Glucose



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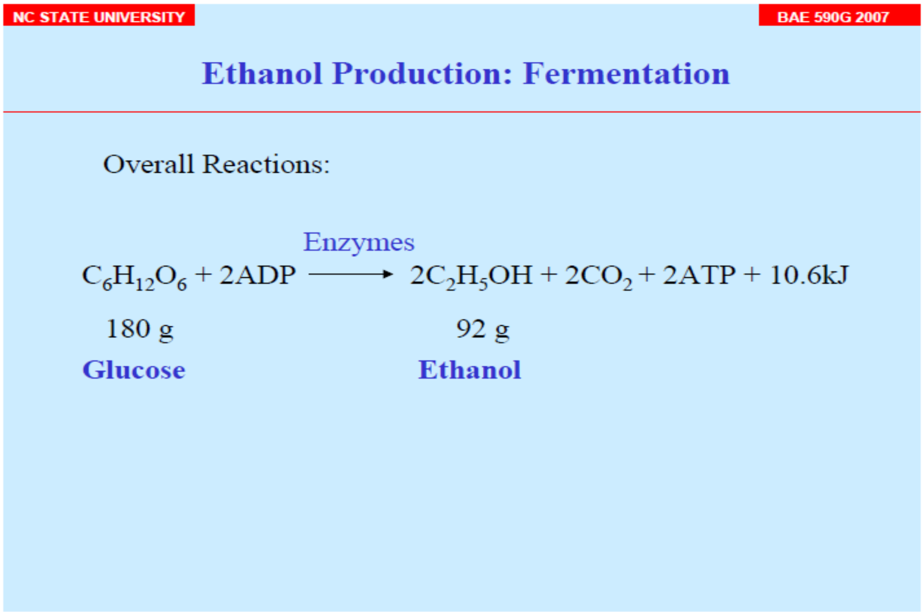
Cost Reduction

- ✓ **Utilization of hemicellulose and lignin**
  - ➢ **Fermentation of pentose to ethanol**
  - ➢ **Gasification of lignin and hemicellulose**
- ✓ **Recycle of enzymes**

Ethanol Production Fermentation



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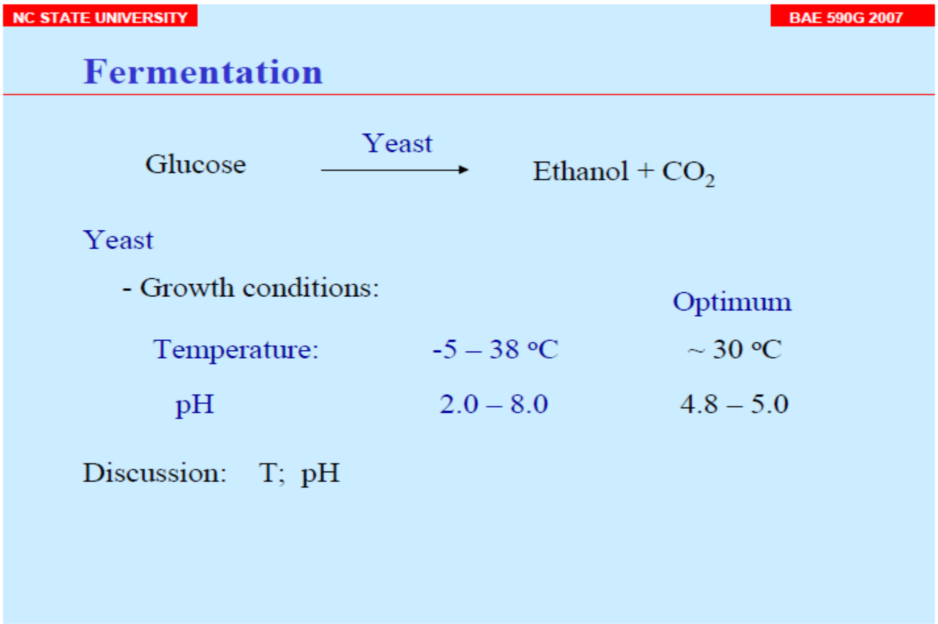
Ethanol Production: Fermentation

Overall Reactions:

$$C_6H_{12}O_6 + 2ADP \xrightarrow{\text{Enzymes}} 2C_2H_5OH + 2CO_2 + 2ATP + 10.6kJ$$

180 g **Glucose** 92 g **Ethanol**



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Fermentation

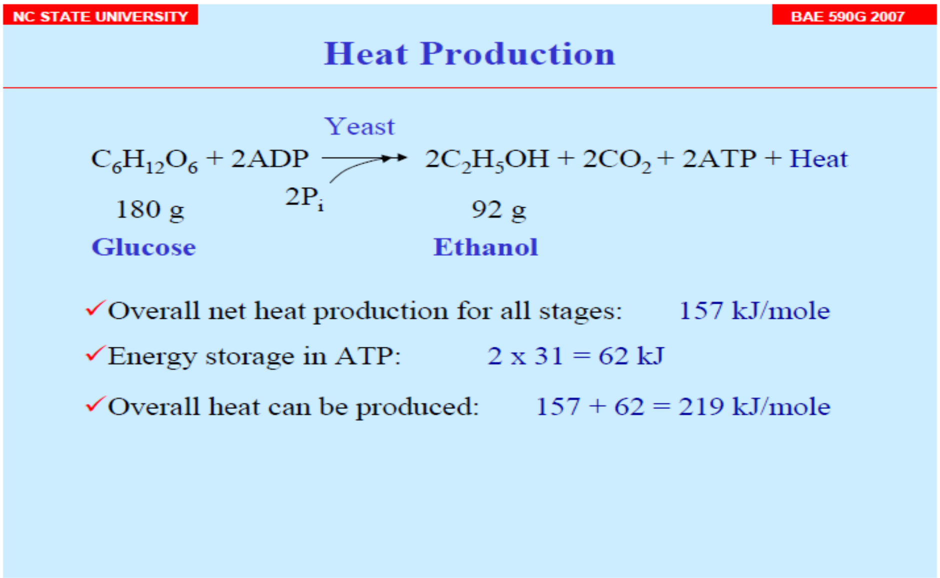
$$\text{Glucose} \xrightarrow{\text{Yeast}} \text{Ethanol} + CO_2$$

Yeast

- Growth conditions:

		Optimum
Temperature:	-5 – 38 °C	~ 30 °C
pH	2.0 – 8.0	4.8 – 5.0

Discussion: T; pH



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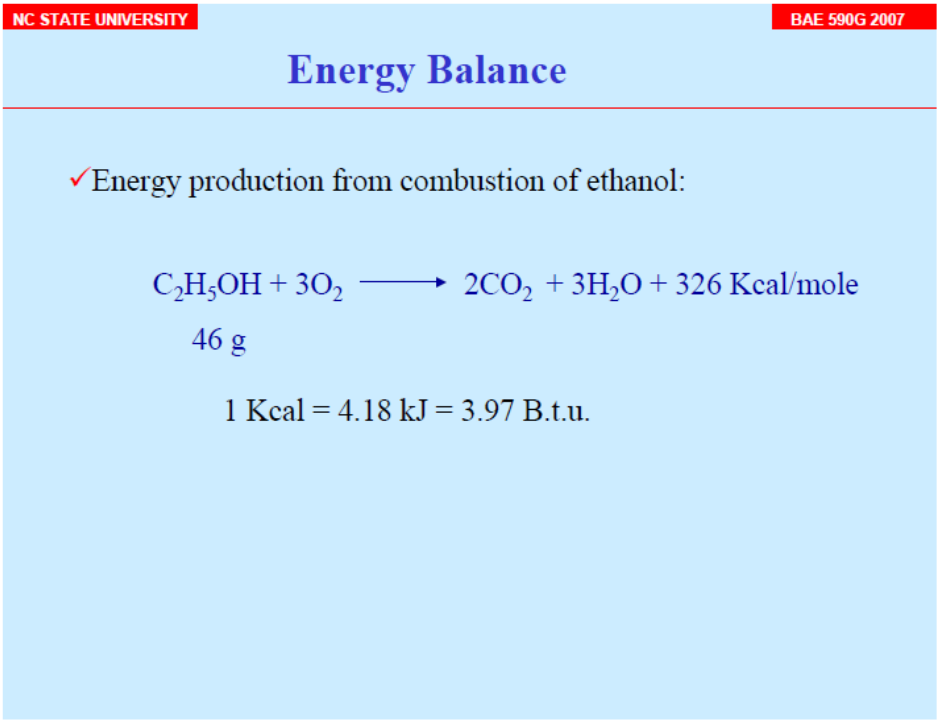
Heat Production

$$C_6H_{12}O_6 + 2ADP \xrightarrow[2P_i]{\text{Yeast}} 2C_2H_5OH + 2CO_2 + 2ATP + \text{Heat}$$

180 g 92 g

Glucose **Ethanol**

- ✓Overall net heat production for all stages: 157 kJ/mole
- ✓Energy storage in ATP: 2 x 31 = 62 kJ
- ✓Overall heat can be produced: 157 + 62 = 219 kJ/mole



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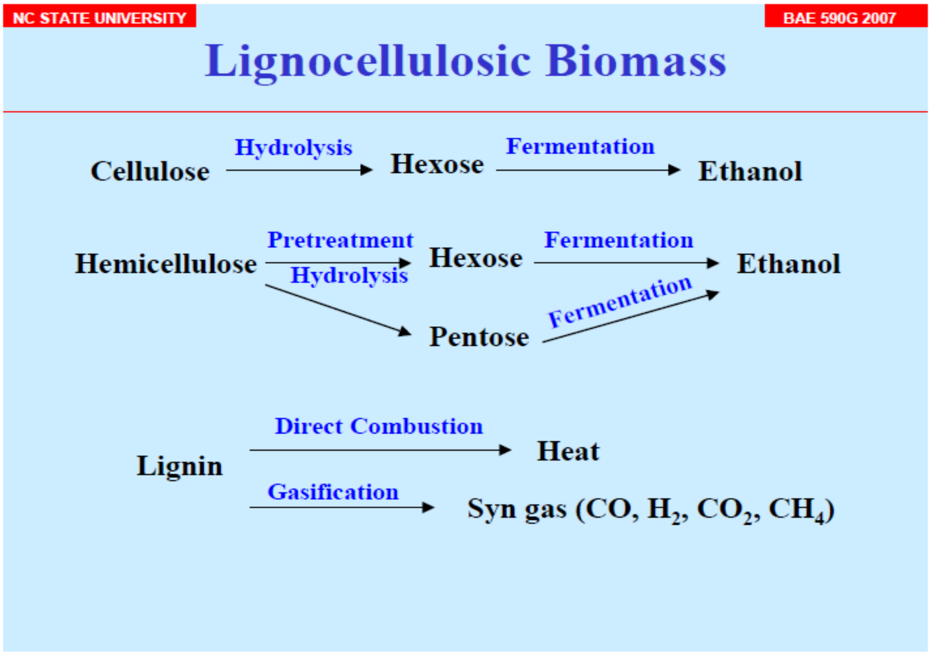
Energy Balance

- ✓Energy production from combustion of ethanol:

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O + 326\ \text{Kcal/mole}$$

46 g

1 Kcal = 4.18 kJ = 3.97 B.t.u.



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Lignocellulosic Biomass

$$\text{Cellulose} \xrightarrow{\text{Hydrolysis}} \text{Hexose} \xrightarrow{\text{Fermentation}} \text{Ethanol}$$

$$\text{Hemicellulose} \xrightarrow[\text{Hydrolysis}]{\text{Pretreatment}} \text{Hexose} \xrightarrow{\text{Fermentation}} \text{Ethanol}$$

$$\text{Hemicellulose} \longrightarrow \text{Pentose} \xrightarrow{\text{Fermentation}} \text{Ethanol}$$

$$\text{Lignin} \xrightarrow{\text{Direct Combustion}} \text{Heat}$$

$$\text{Lignin} \xrightarrow{\text{Gasification}} \text{Syn gas } (CO, H_2, CO_2, CH_4)$$

SOAP AND DETERGENT MANUFACTURE

Soaps and detergents are widely used in our society. Soaps are the product of the reaction between a fat and sodium hydroxide:

fat + 3NaOH → glycerine + 3 soap

Soap is produced industrially in four basic steps. This article lists different steps because in the industrial processes described each of these is done over several process steps, but in principle it could be done in the three steps outlined here.

Steps of soap manufacture:

Step 1 – Saponification:

A mixture of tallow (animal fat) and coconut oil is mixed with sodium hydroxide and heated. The soap produced is the salt of a long chain carboxylic acid.

Step 2 - Glycerine removal:

Glycerine is more valuable than soap, so most of it is removed. Some is left in the soap to help make it soft and smooth. Soap is not very soluble in salt water,

whereas glycerine is, so salt is added to the wet soap causing it to separate out into soap and glycerine in salt water.

Step 3 - Soap purification:

Any remaining sodium hydroxide is neutralized with a weak acid such as citric acid and two thirds of the remaining water removed.

Step 4 – Finishing:

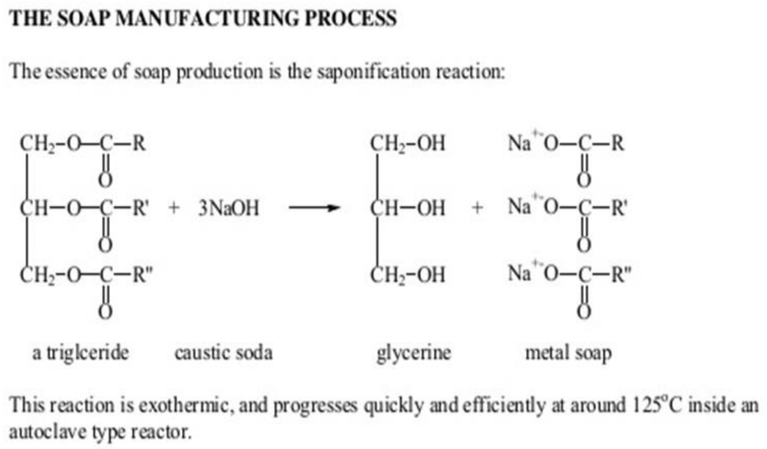
Additives such as preservatives, color and perfume are added and mixed in with the soap and it is shaped into bars for sale.

Detergents

Detergents are similar in structure and function to soap, and for most uses they are more efficient than soap and so are more commonly used. In addition to the actual ’detergent’ molecule, detergents usually incorporate a variety of other ingredients that act as water softeners, free-flowing agents etc.

THE SOAP MANUFACTURING PROCESS

The essence of soap production is the saponification reaction.

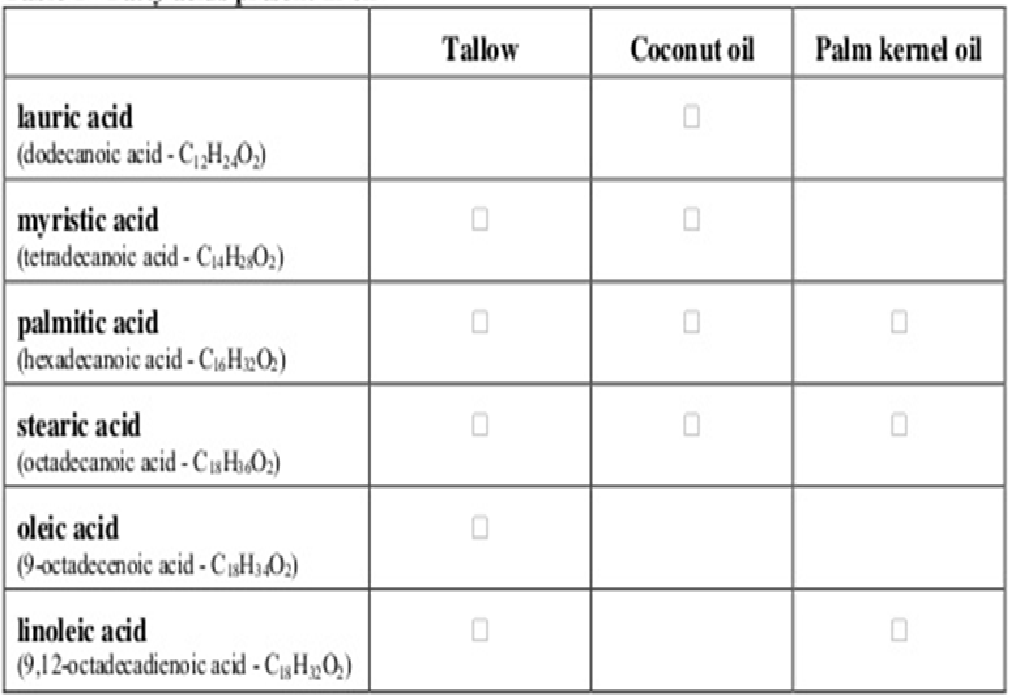


THE SOAP MANUFACTURING PROCESS

The essence of soap production is the saponification reaction:

This reaction is exothermic, and progresses quickly and efficiently at around 125°C inside an autoclave type reactor.

Table 1 - Fatty acids present in oil



	Tallow	Coconut oil	Palm kernel oil
lauric acid (dodecanoic acid - $C_{12}H_{24}O_2$)		☐	
myristic acid (tetradecanoic acid - $C_{14}H_{28}O_2$)	☐	☐	
palmitic acid (hexadecanoic acid - $C_{16}H_{32}O_2$)	☐	☐	☐
stearic acid (octadecanoic acid - $C_{18}H_{36}O_2$)	☐	☐	☐
oleic acid (9-octadecenoic acid - $C_{18}H_{34}O_2$)	☐		
linoleic acid (9,12-octadecadienoic acid - $C_{18}H_{32}O_2$)	☐		☐

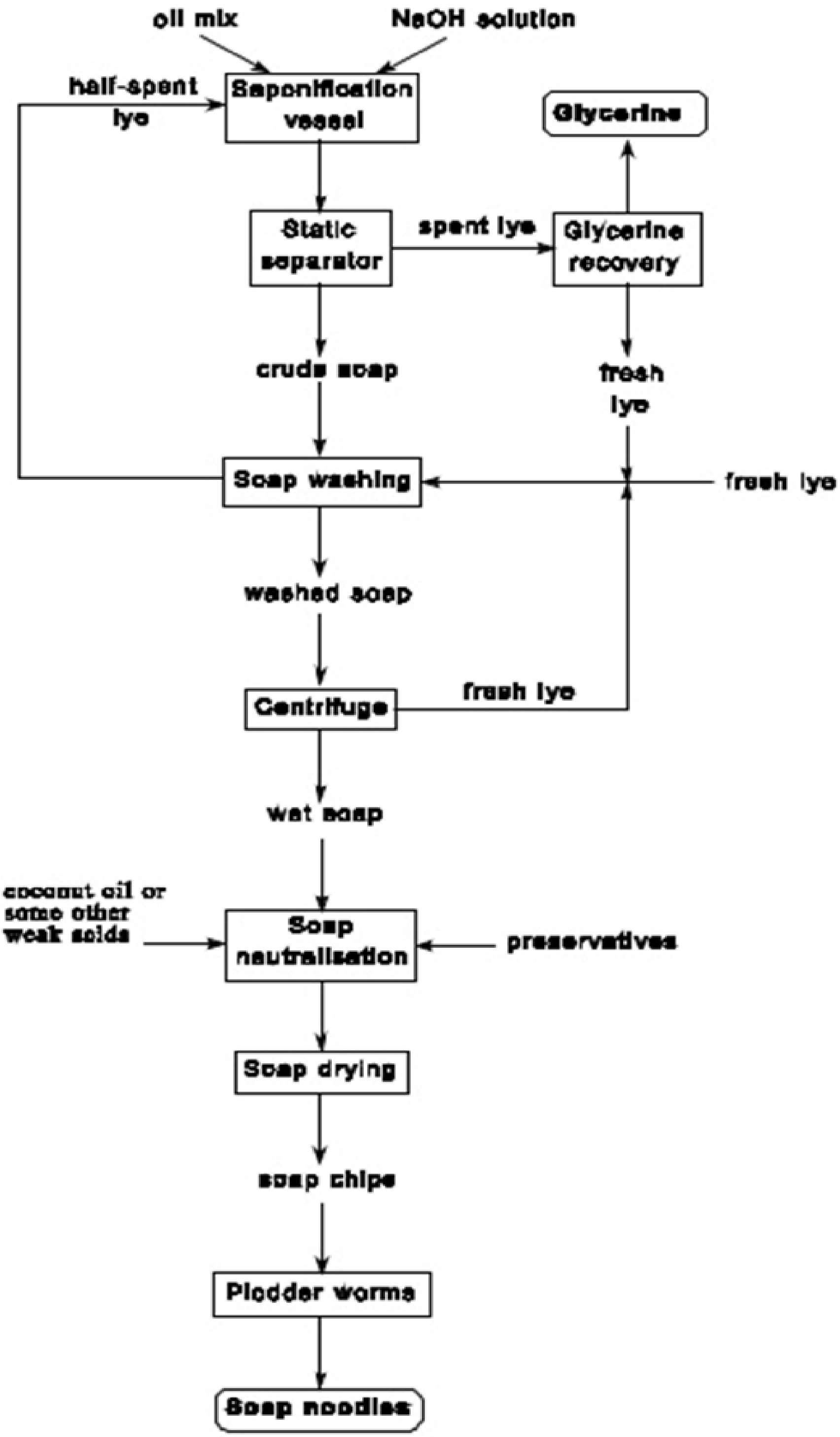


Figure 1 - The Colgate Palmolive continuous soap manufacturing process

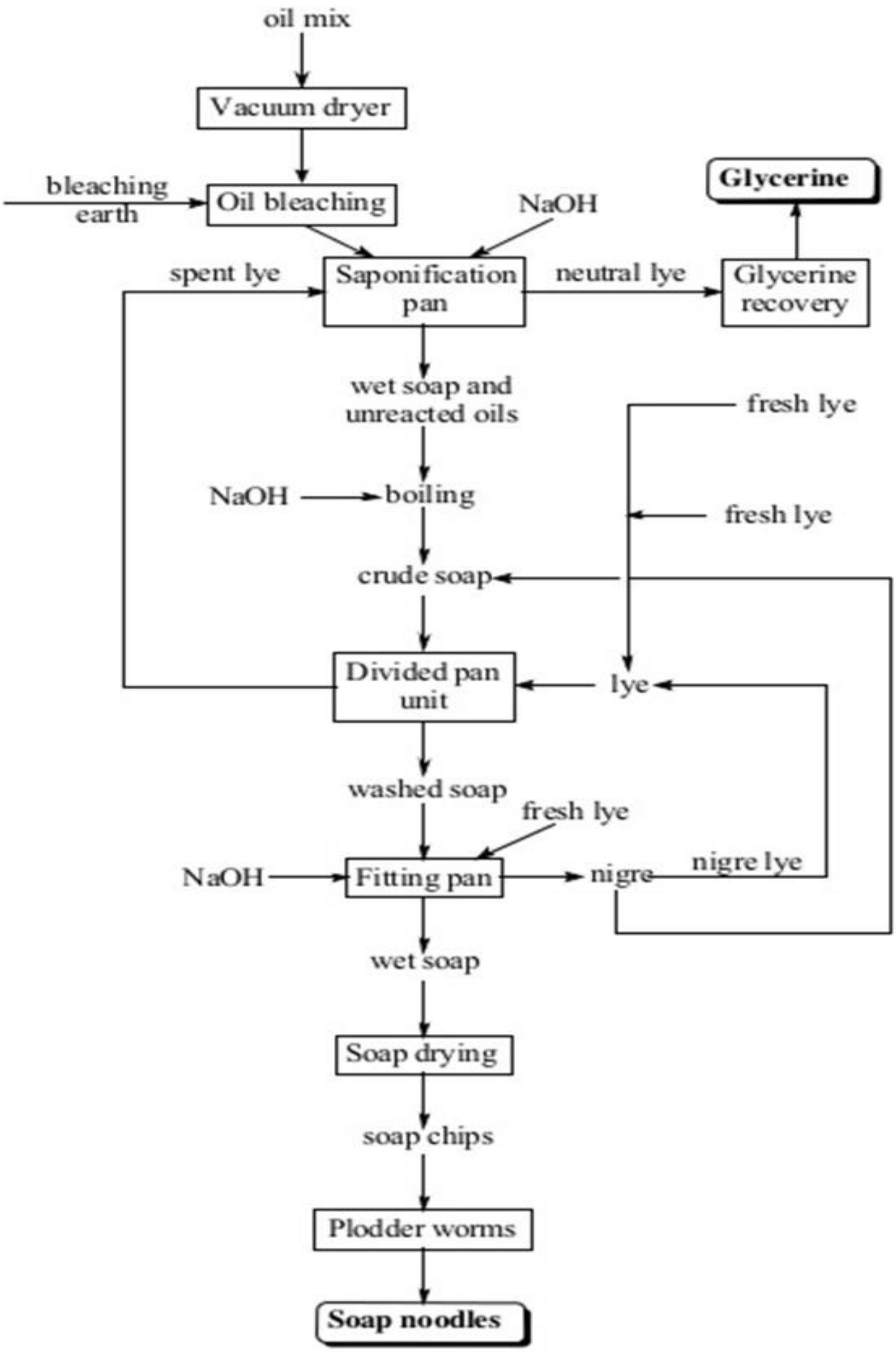


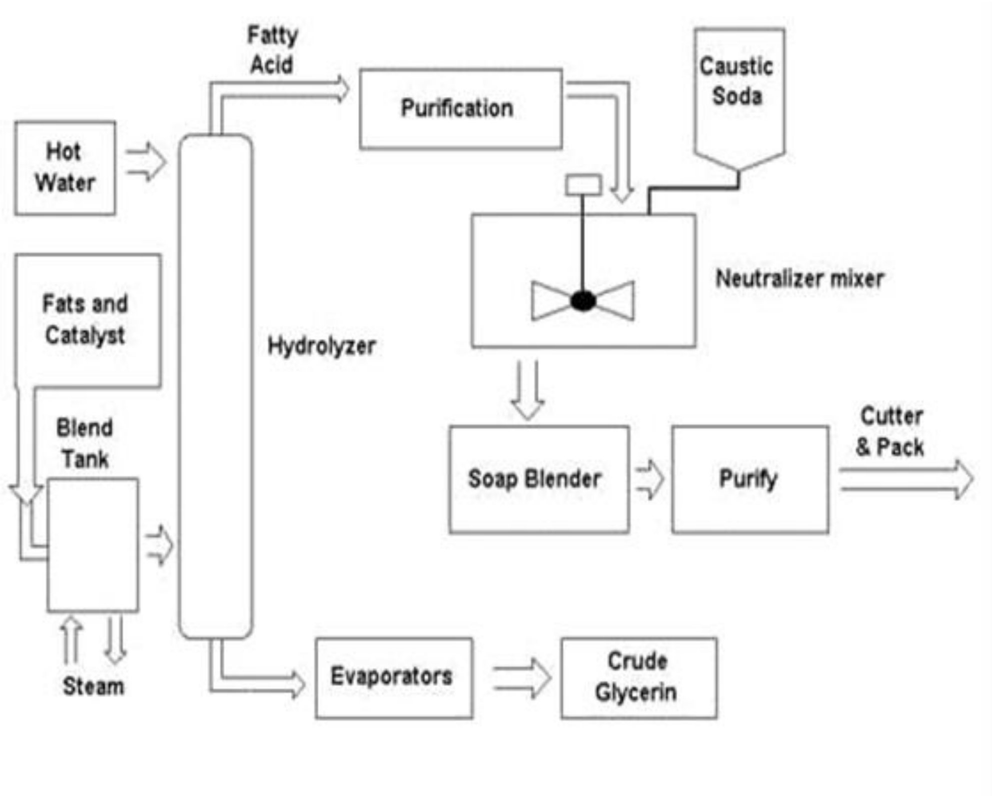
Figure 2 - The Lever Rexona soap manufacturing batch process

Step 1 - Saponification The raw materials are continually fed into a reactor in fixed proportions. Assuming a production rate of 1000 kg wet soap per hour and a 80:20 tallow:coconut oil mix, the raw materials would be fed in at the following rates:

coconut oil 525.9 kg

tallow 131.5 kg

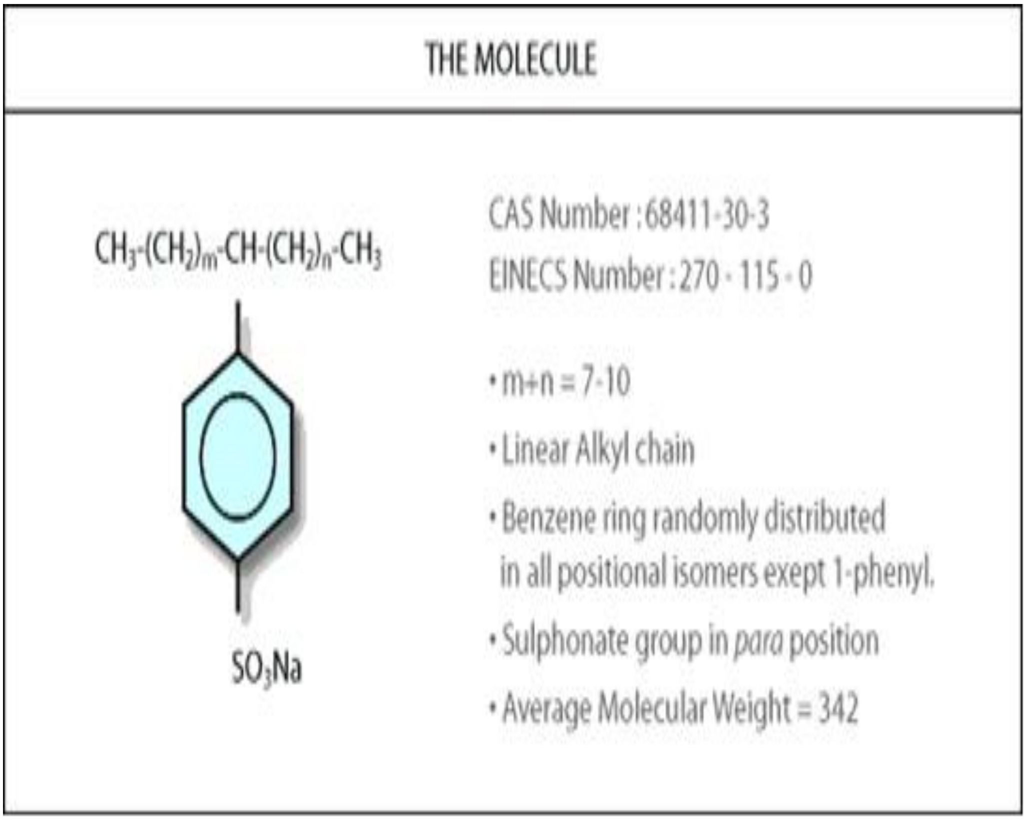
NaOH solution 101 kg



Process diagram of Soap

Detergents

Composition	% by weight
Alkyl benzene sulphonate	9.8
Nonionic surfactant 1)	13.1
Sodium triphosphate	40.9
Sodium carbonate	8.2
CP5-polymer ex BASF 2)	1.7
Alkaline sodium silicate	7.4
Minors	1.6
Moisture	17.3



CAS Number : 68411-30-3
EINECS Number : 270 - 115 - 0

- m+n = 7-10
- Linear Alkyl chain
- Benzene ring randomly distributed in all positional isomers exept 1-phenyl.
- Sulphonate group in *para* position
- Average Molecular Weight = 342

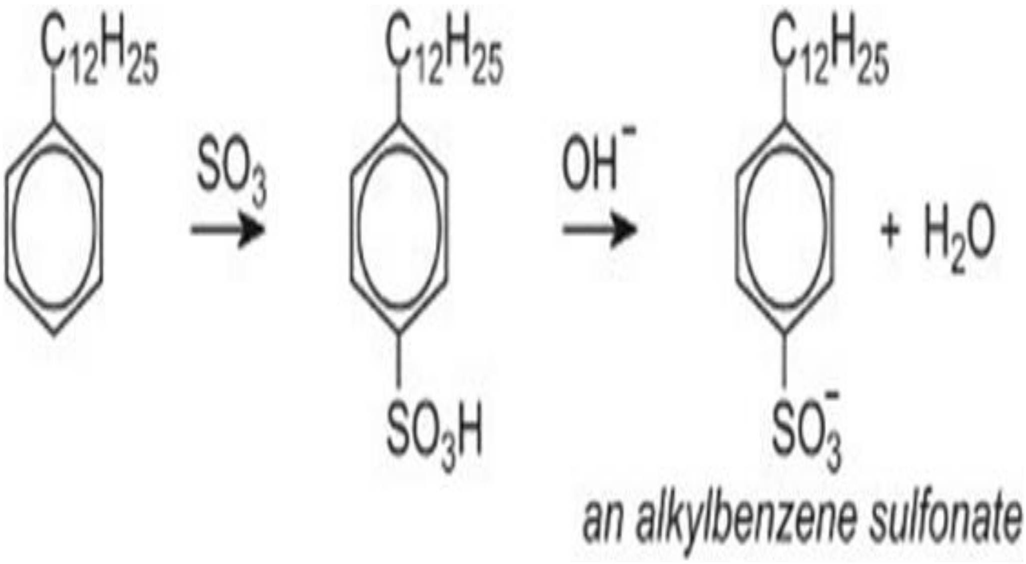
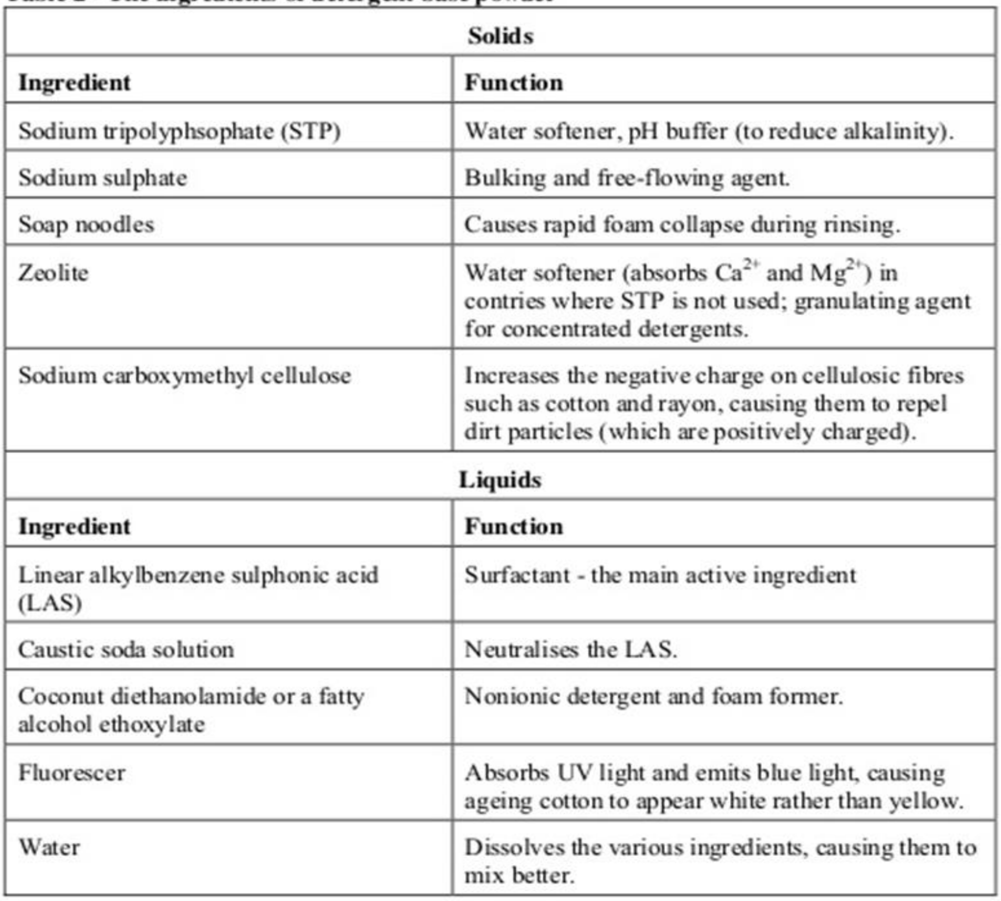


Table 2 - The ingredients of detergent base powder



Solids	
Ingredient	**Function**
Sodium tripolyphsophate (STP)	Water softener, pH buffer (to reduce alkalinity).
Sodium sulphate	Bulking and free-flowing agent.
Soap noodles	Causes rapid foam collapse during rinsing.
Zeolite	Water softener (absorbs Ca^{2+} and Mg^{2+}) in contries where STP is not used; granulating agent for concentrated detergents.
Sodium carboxymethyl cellulose	Increases the negative charge on cellulosic fibres such as cotton and rayon, causing them to repel dirt particles (which are positively charged).
Liquids	
Ingredient	**Function**
Linear alkylbenzene sulphonic acid (LAS)	Surfactant - the main active ingredient
Caustic soda solution	Neutralises the LAS.
Coconut diethanolamide or a fatty alcohol ethoxylate	Nonionic detergent and foam former.
Fluorescer	Absorbs UV light and emits blue light, causing ageing cotton to appear white rather than yellow.
Water	Dissolves the various ingredients, causing them to mix better.

THE PULP AND PAPER INDUSTRY

In New Zealand, paper is made from wood using the "Kraft" process. This is a part mechanical, part chemical process that produces a strong pulp. It has several disadvantages, in terms of complexity and set up costs as well as having a low pulp yield and producing unpleasant-smelling sulfur compounds, but it is still internationally the most widely used pulp and paper process. The manufacturing process is outlined below.

Step 1 - Wood preparation:

The bark is removed from in-coming logs, and these are then chipped. Sometimes, the wood arrives at the plant already chipped, meaning that this step is unnecessary.

Step 2 – Cooking:

The wood chips are heated in a solution of NaOH and Na2S in a pressure cooker, during which time a lot of the lignin (the reinforcing susbstance that make tree cells wood hard and 'woody' rather than soft like those of other plants) is removed from the wood. The pressure is then released suddenly, causing the chips to fly apart into fibres.

Step 3 - Pulp washing:

The pulp is washed with water to wash out the cooking chemicals and lignin from the fibre so that they will not interfere with later process steps.

Step 4 - Pulp screening:

A sieve is used to remove knots and clumped-together uncooked fibres from the pulp.

Step 5 – Bleaching:

This is done in two stages. Firstly the pulp is treated with NaOH in the presence of O2. The NaOH removes hydrogen ions from the lignin and then the O2 breaks down the polymer. Then, the pulp is treated with ClO2 then a mixture of NaOH, O2 and peroxide and finally with ClO2 again to remove the remaining lignin.

Step 6 - Paper making:

The fibres are mechanincally treated to make them bond better to each other (strengthening the paper), chemicals added to provide special properties such as colour or water resistance, and then the water is squeezed out and the pulp is rolled smooth and dried.

Various ancilliary processes result in the recovery of CaO, NaOH and Na2S, the major chemicals used in the process. Various utilities ensure that such conditions as sufficient reaction times and adequate mixing are met.

On site processing removes the lignin from the liquid wastes, and solid wastes are generally taken to a landfill. Efforts continue to be made to reduce water consumption by recycling, as smaller volumes are easier to process. The most obvious environmental problem continues to be the sulfurous emissions that give Kraft pulping plants their characteristic smell. These are decreased by gas incineration, but are not able to be wholly eliminated.

INTRODUCTION:

Paper is a major product of the forestry industry, and is used widely in our society. Paper products are used not only in their obvious applications in the publishing industry and for writing on, but also in a variety of specialty papers, cardboards, brown papers etc. In addition, various chemicals are produced as a byproduct of the pulp and paper industry (see articles).

Paper is made by pulping wood, bleaching this pulp and then spreading it out into sheets to make it into paper. At various stages of the process, chemicals are used to give the paper particular properties, such as the bleaching chemicals that make paper white (and which also enable it to subsequently be coloured). The pulping process that is used in New Zealand is known as "kraft pulping" which relies on a combination of heat, chemicals and mechanical pulping to convert the wood into a smooth, soft pulp suitable for use in paper making.

Kraft pulping is the main pulping process (together with mechanical pulping) used today, and is the only one discussed below. The kraft process has several advantages:

It can be used with virtually all wood species

It can easily handle the extractives in most coniferous wood

The pulp has very good strength (the word 'kraft' means 'strong' in Swedish)

The recovery process for the chemicals is well established

However, there are also disadvantages:

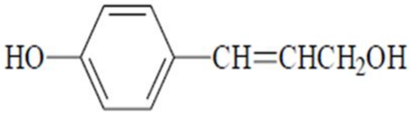
The pulp yield is quite low at about 45 - 50% • The equipment used for the chemical recovery is extensive and costly to install

Sulphurous compounds, which are odorous in the parts per billion range, are formed in the process

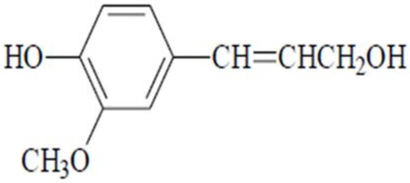
Fairly complicated processes are required for bleaching the pulp

Lignin:

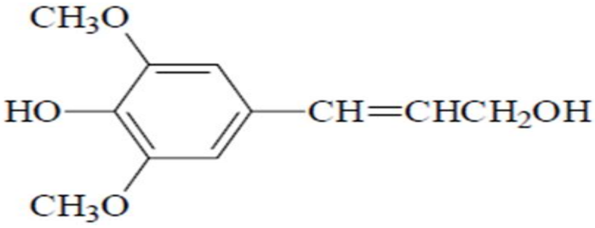
The main component of wood that needs to be removed to turn it into paper is a compound known as lignin. This name refers to a group of chemicals that are essentially three dimensional polymers of trans-coniferol, trans-sinapol and trans-p-coumarol (see below), along with hemicelluloses and aromatic carboxylic acids. Lignin is the reinforcing compound that is deposited on tree cell walls to make the wood strong enough to carry the weight of the tree crown. However, it is also the compound that makes wood pulp brown, so it is removed from all wood pulp except that used to make brown paper and some cardboards



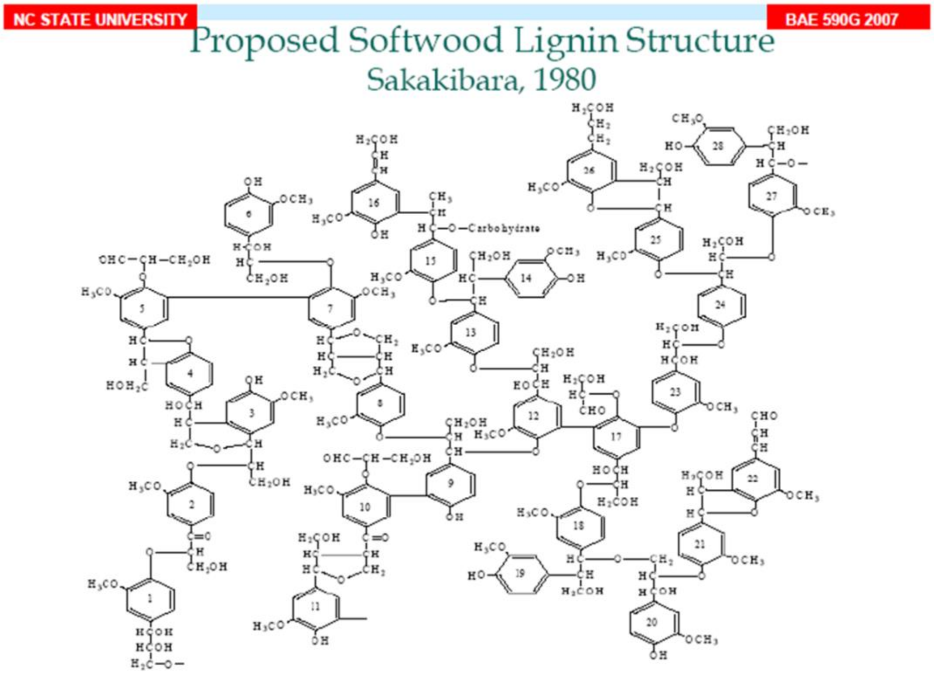
trans-p-coumarol



trans-coniferol



trans-sinapol



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Proposed Softwood Lignin Structure

Sakakibara, 1980

Final bleaching:

The final bleaching is always carried out in several stages to improve the efficiency of the chemicals used, and to decrease the strength loss of the pulp. There are quite a number of bleaching chemicals used commercially, and many more have been tried in the laboratory. The chemicals used are:

Chlorine • Chlorine dioxide • Sodium hypochlorite • Oxygen • Peroxide • Ozone

The following reactions very simply explain the combustion of the combustible organic compounds:

$C + O_2 \rightarrow CO_2 + \text{heat}$

$2C + O_2 \rightarrow 2CO + \text{heat}$

$CO + \frac{1}{2}O_2 \rightarrow CO_2 + \text{heat}$

$2H_2 + O_2 \rightarrow 2H_2O + \text{heat}$

$H_2S + 1\frac{1}{2}O_2 \rightarrow SO_2 + H_2O$

$Na_2O + SO_2 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$

$NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

$Na_2O + CO_2 \rightarrow Na_2CO_3$

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

The chemical transformation that takes place in the recovery boiler is not just due to combustion, but also involves the reduction of sodium sulfate to sodium sulfide. The main reaction is:

$Na_2SO_4 + 2C + \text{heat} \rightarrow Na_2S + 2CO_2$

This reaction consumes heat, i.e. it is endothermic

Since sodium sulfate does not help in the cooking process, it is important to obtain maximum reduction of sulfate into sulfide within the recovery boiler. A measure of the quality of this reduction (in the smelt or green liquor) is called reduction efficiency. It is expressed as follows:

$$\text{Reduction efficiency (\%)} = \frac{Na_2S \times 100}{Na_2S + Na_2SO_4}$$

What About Fiberboard For Green Building

Cellulosic fiberboard panels are ideal green building components. They are manufactured with natural and recycled fibers and bonded with renewable vegetable binders. "Green building (also known as green construction or sustainable building) refers to a structure and using process that is environmentally responsible and resource-efficient throughout a building's life-cycle: from site to design, construction, operation, maintenance, renovation, and demolition." (Wikipedia—Green Building). An important start to any green building strategy is to choose environmentally responsible and resource efficient building materials. Cellulosic Fiberboard, a/k/a "Fiberboard," fits the bill.

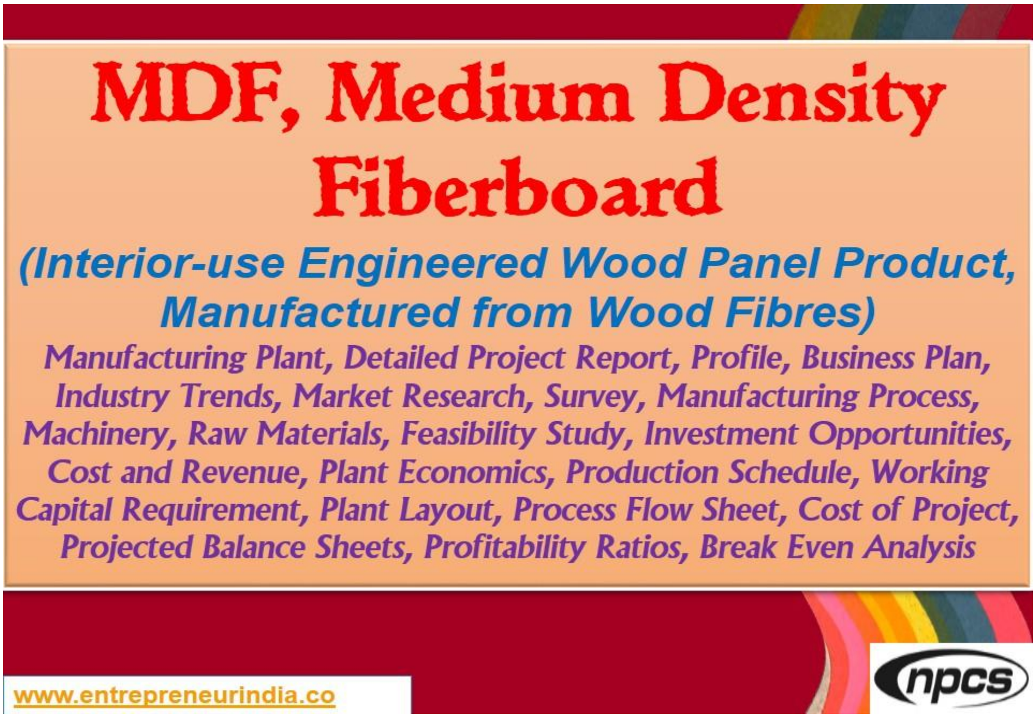
Fiberboard panels are manufactured with natural cellulose fibers, from renewable, reused and recyclable materials. No virgin old growth timber or tropical forest fiber content are found in these panels. Recycled content in the form of saw mill trim, sawdust, planer shavings and whole wood chips are put to good use. Other recycled material may include construction waste, demolition wood, postconsumer kraft paper, newsprint, and office paper. In fact, virtually any cellulosic fiber of acceptable geometry can be utilized for fiberboard, either alone or as a supplement to more commonly available wood fiber. Non-wood fiber sources such as wheat straw, rice straw, kenaf, and other plant fibers have also been used.

Fiberboard composition is achieved through wet process fiber-to-fiber hydrogen bonding and integral inter-knitting of the fibers during panel formation. Eco-friendly vegetable-based starch binders (adhesives) add

to the product‟s renewable content and desired properties. Consequently, synthetic adhesives like phenol and urea-formaldehyde are not used in the process. Chlorinated hydrocarbons or other ozone-depleting chemicals are not used. Blowing agents like pentane are unnecessary. The continuously-formed fibrous "mats" (unfinished panels) are dried via gradual drying. The product is not subject to high pressure and temperature to cure a resinous adhesive binder.

Wet process fiberboard manufacturing utilizes closed-loop water systems that recycle large volumes of water. These closed-loop water systems eliminate discharge of process water. Some participating companies collect wood sugars released in the manufacturing process for use as livestock feed supplements.

Recycled content in fiberboard eliminates the necessity of burning and/or disposal of the waste materials by other means. Thus, release of carbon to the atmosphere is decreased and the carbon cycle is extended for the life of the product. In addition, fiberboard is landfill friendly. These panels release no toxic chemicals. Alternatively, fiberboard can be reduced to fibers and reintroduced into the fiberboard manufacturing process as a supplemental material much like kraft paper or other reused or recycled content.



MDF, Medium Density Fiberboard

(Interior-use Engineered Wood Panel Product, Manufactured from Wood Fibres)

Manufacturing Plant, Detailed Project Report, Profile, Business Plan, Industry Trends, Market Research, Survey, Manufacturing Process, Machinery, Raw Materials, Feasibility Study, Investment Opportunities, Cost and Revenue, Plant Economics, Production Schedule, Working Capital Requirement, Plant Layout, Process Flow Sheet, Cost of Project, Projected Balance Sheets, Profitability Ratios, Break Even Analysis

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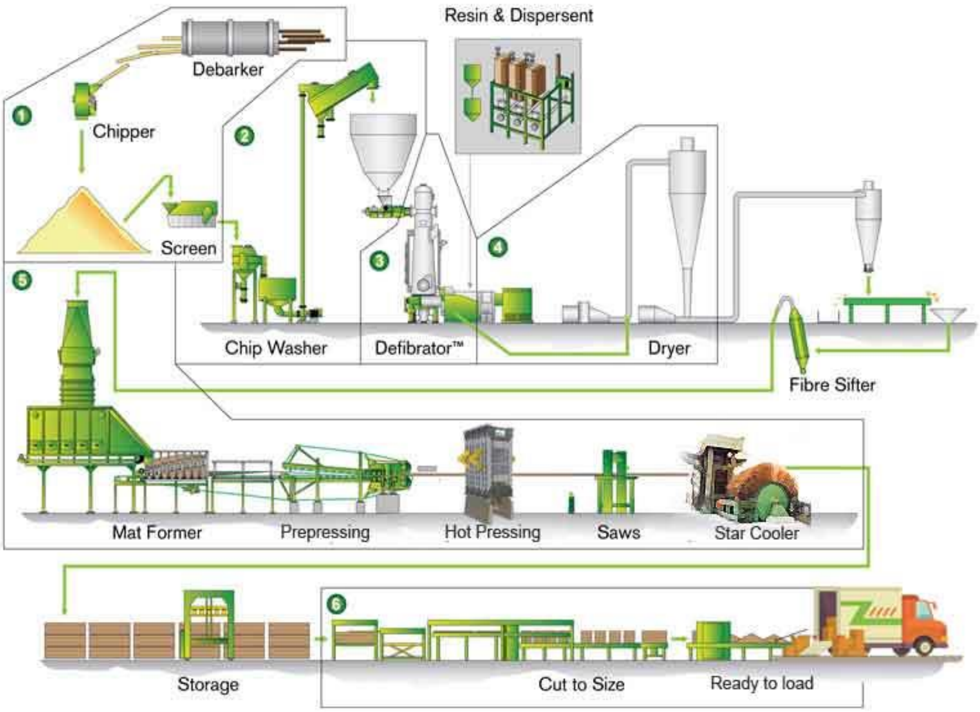
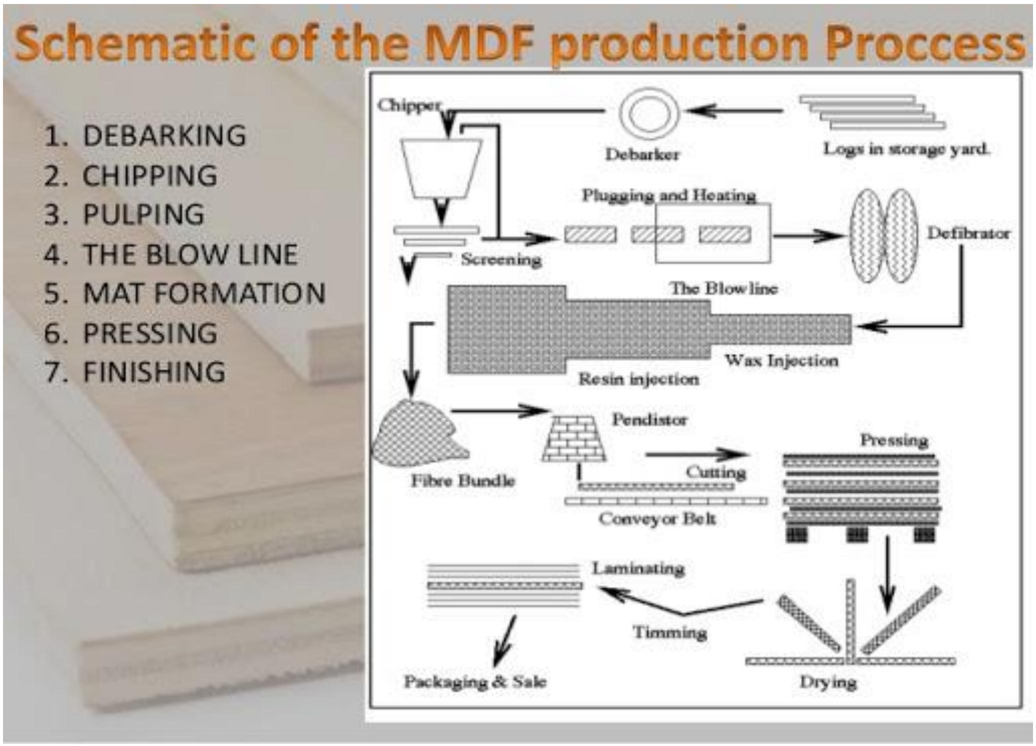
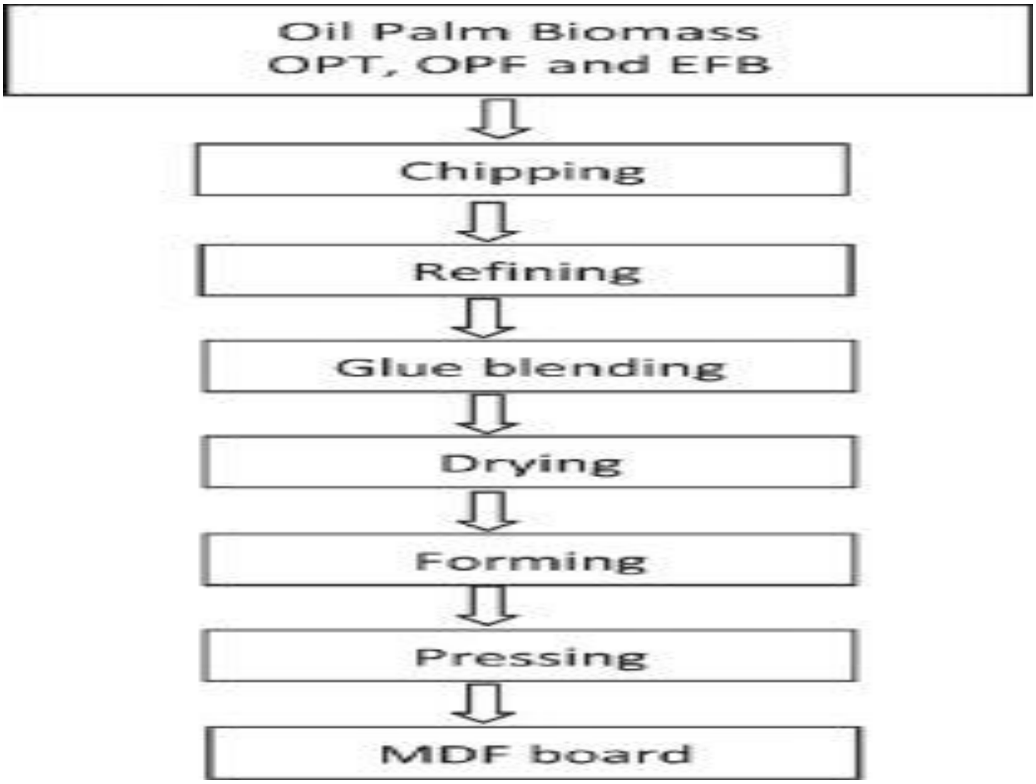
npcs





Schematic of the MDF production Proccess

1. DEBARKING
2. CHIPPING
3. PULPING
4. THE BLOW LINE
5. MAT FORMATION
6. PRESSING
7. FINISHING



Wood Plastic Composite Decking Manufacturing Process

What are Wood-Plastic Composites (WPC)?

Combination of Wood-Plastic n

Thermoplastic- HDPE, LDPE, PP, PVC n

Wood Flour- 20 to 60 mesh- Pine, Oak, Maple n

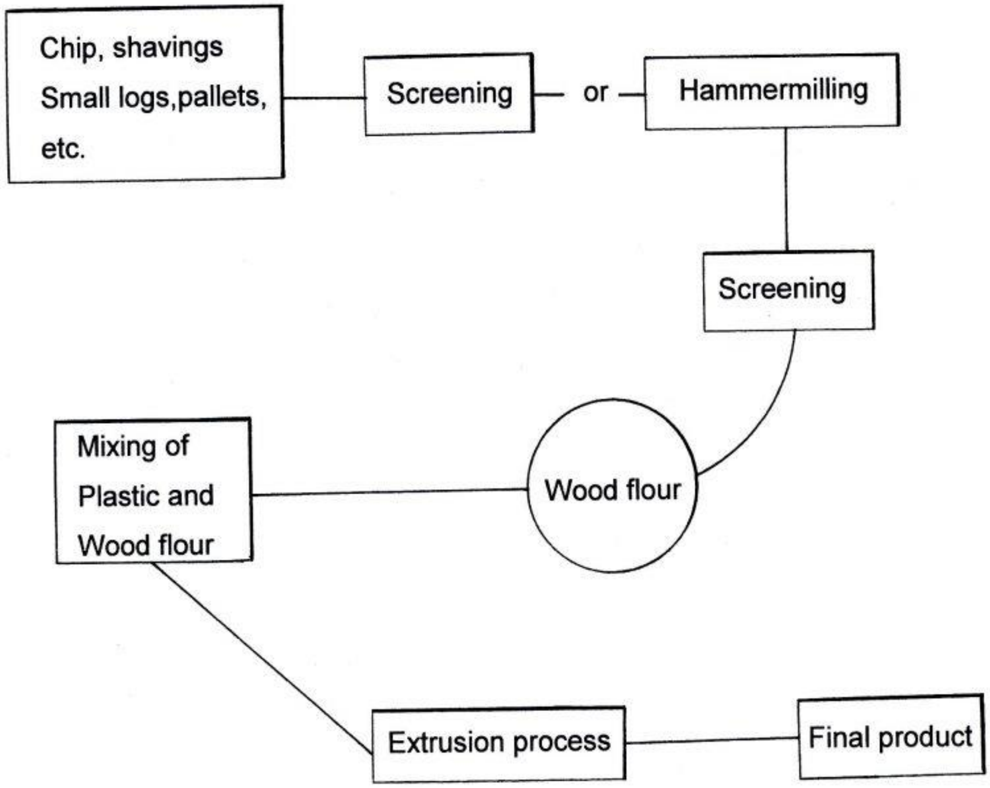
Lubricants, Pigments, Coupling agents, other additives

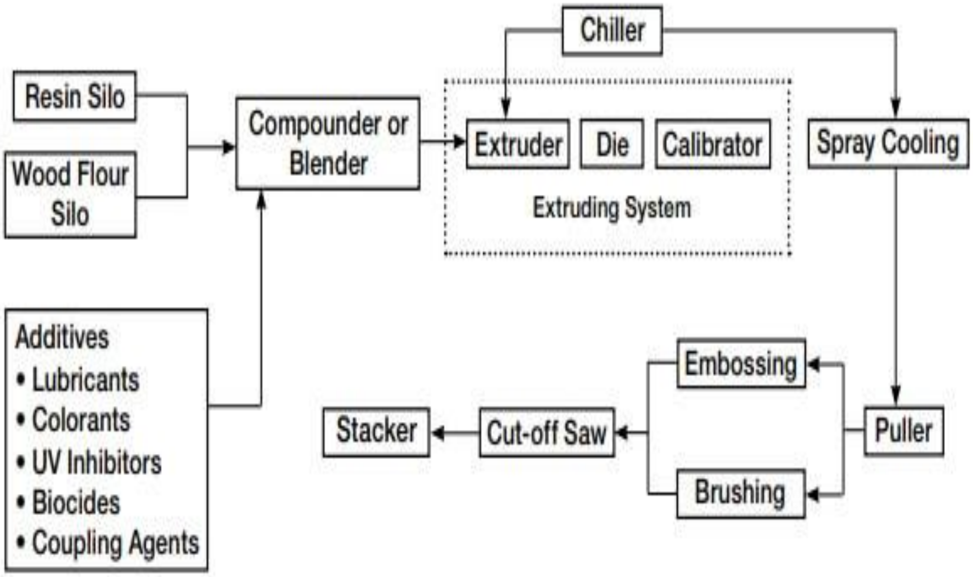
Technology.

Extrusion, Injection or Compression molding n

Pre-Compounding

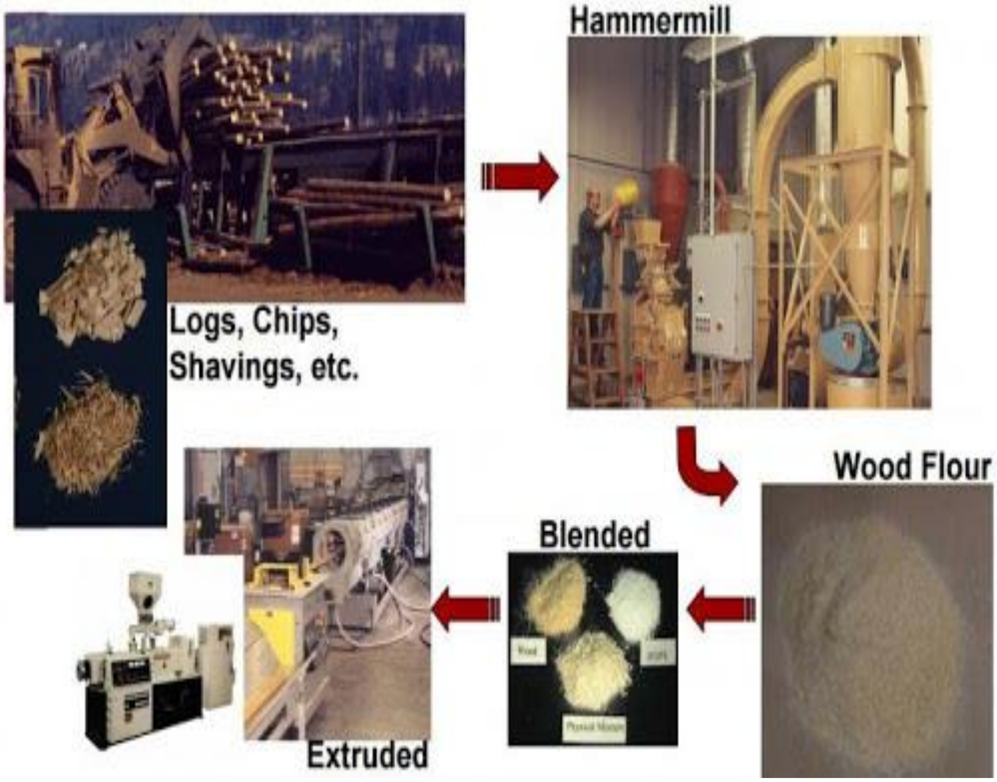
How are WPCs manufactured:

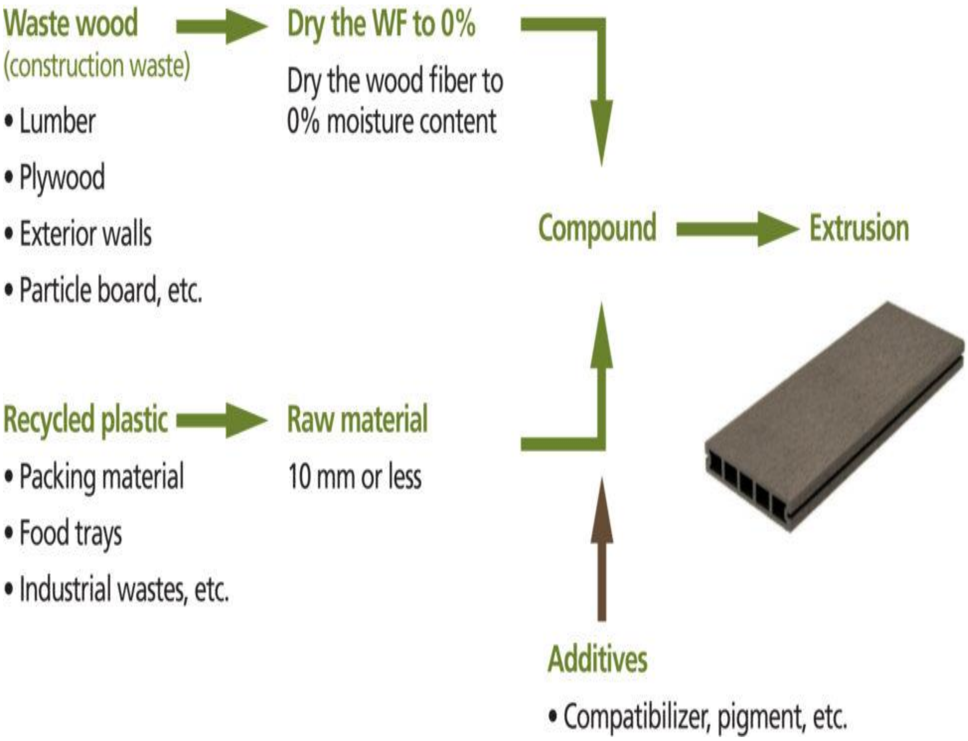




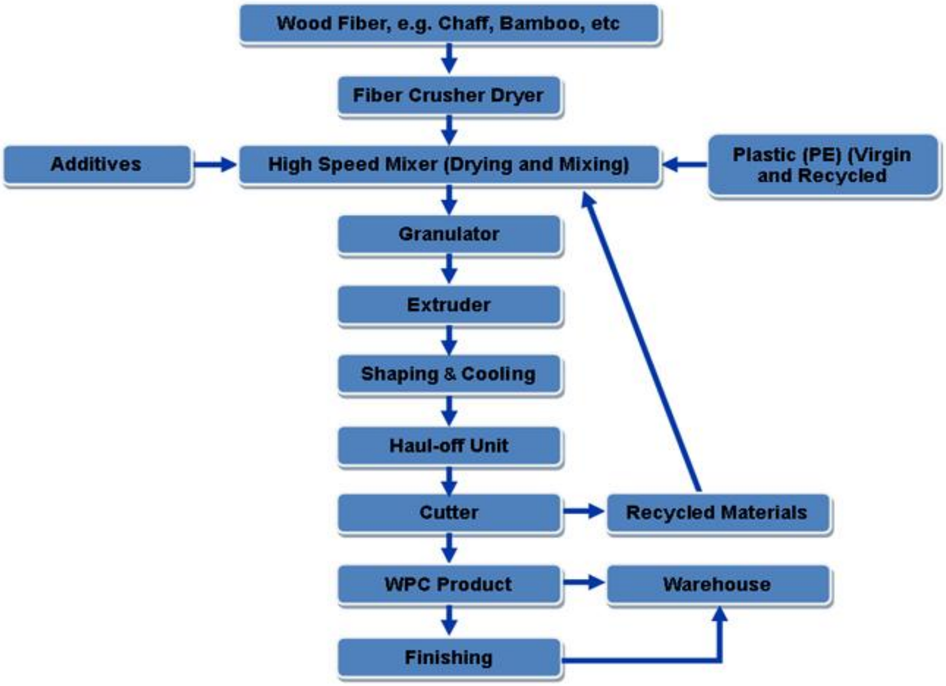
The WPC manufacturing process, with extrusion forming


Organic Fiber
/Saw Dust
Plastic
/ Virgin polymer
PP/PE
AB Wood ™ Manufacturing Technology
ABWOOD
Application
100% Water Proof Warranty
100% Termite Damage Proof Warranty


Logs, Chips, Shavings, etc.
Hammermill
Wood Flour
Blended
Extruded


Waste wood
(construction waste)
• Lumber
• Plywood
• Exterior walls
• Particle board, etc.
Dry the WF to 0%
Dry the wood fiber to 0% moisture content
Compound
Extrusion
Recycled plastic
• Packing material
• Food trays
• Industrial wastes, etc.
Raw material
10 mm or less
Additives
• Compatibilizer, pigment, etc.


Wood Plastic Composites
(WPC) Market


Wood Fiber, e.g. Chaff, Bamboo, etc
Fiber Crusher Dryer
Additives
High Speed Mixer (Drying and Mixing)
Plastic (PE) (Virgin and Recycled
Granulator
Extruder
Shaping & Cooling
Haul-off Unit
Cutter
Recycled Materials
WPC Product
Warehouse
Finishing

Perfume Production Process

Notes

Perfume is a fragrant liquid made from an extract that has been distilled in alcohol and water. A perfume is composed of three notes. The base note is what a fragrance will smell like after it has dried. The smell that develops after the perfume has mixed with unique body chemistry is referred to as the middle note. And the top note is the first smell experienced in an aroma. Each perfumery has a preferred perfume manufacturing process, but there are some basic steps.

Collection

Collection of raw materials is the first step in the perfume making process. Fragrance can be obtained from flowers, grasses, mosses, leaves, tree barks and fruit peels. Once raw materials are collected, the fragrance is extracted by distillation, absorption or extraction using solvents.

Aromatherapy for your Home or Place Containing Cosmetic Grade Fragrance.

Distillaton

In the distillation method, raw materials are steamed. As the steam rises, the scent is carried into a glass tube where the mixture condenses as it cools. The mixture is then put into flask where the essential oil naturally rises to the top and is skimmed off for use in the perfume.

Absorption

Absorption is used for raw materials that can't with stand the heat of the distillation process. They are steeped in

heated fats or oils, then filtered through fabric to obtain the scented solid. The solid is then washed in alcohol. When the fat is removed, the perfumed alcohol remains.

Extraction

Fragrance also is drawn when plant matter and volatile solvents are combined in a rotating tank. The solvent extracts the essential oils and dissolves the plant matter, leaving a wax-like oil. Once the oil has evaporated, a perfume paste remains.

Aromas

Musk and castor are animal secretions frequently used in perfume making. Synthetically produced aromas also are used.

Blending

Once the perfume oil is extracted, the blending process commences. A perfumer, known as "a nose," uses an extensive knowledge of fragrance characteristic to blend anywhere from 20 to 800 raw materials to compose a scent. Once the scent is developed and tested, batches are robotically mixed.

The pure perfume oil is then diluted with alcohol and water. If a full perfume is desired, 10 to 20 percent of the oil is dissolved in alcohol with a minute amount of water. Cologne is 3 to 5 percent oil, 80 to 90 percent alcohol and 10 percent water. An eau de toilette is 2 percent oil, 60 to 80 percent alcohol and 20 percent water. Then the perfume is ready to be aged, filtered and bottled.

Putting the Theory to Use

If want to create your own fragrance, essential and synthetic oils can be obtained from perfume making suppliers. Experiment by combining oils, then smell and test the combinations on your skin. Once the desired aroma is achieved, mix the oils with the appropriate ratios of alcohol and water. Purchase perfume alcohol from perfume materials suppliers. Or clear drinking alcohol that has no smell, such as vodka, can be substituted. Once poured into a bottle, the fragrance is ready to be enjoyed.

Ink Manufacturing and the Dispersion of Pigment into Printing Ink

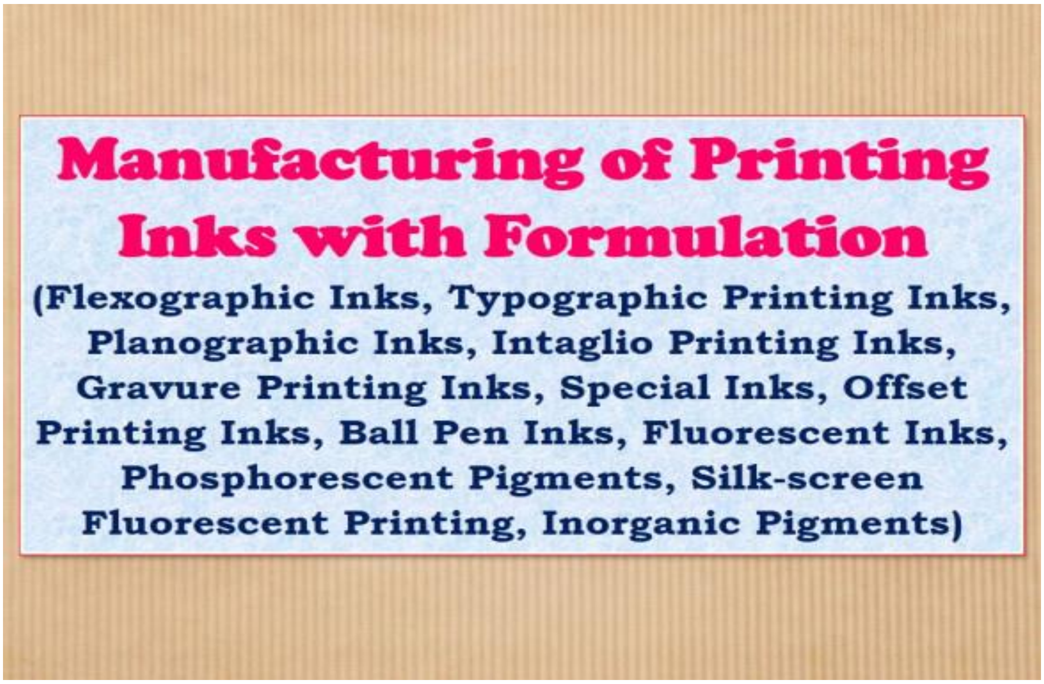
Introduction:

Printing of one form or another has been with us for centuries, and whilst the technologies of both the printing process and the ink formulations have changed considerably, the main functions of decoration and information remain. Nowadays, printing inks are composed of a pigment, a binder (an oil, resin or varnish of some kind), a solvent and various additives such as drying and chelating agents.

Raw materials:

The raw materials for ink production are pigments, binders, solvents and additives

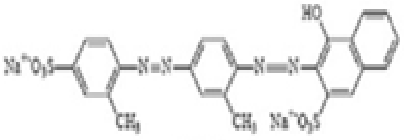
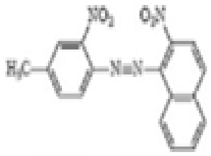
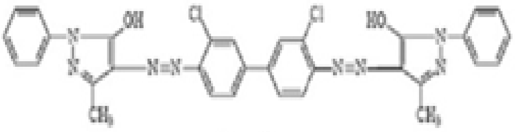
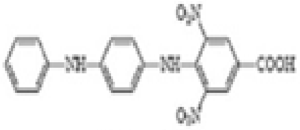
2.1 Pigments The most obvious role of a pigment is to color the ink. However, pigments can also provide gloss, abrasiveness, and resistance to attack by light, heat, solvents, etc. Special pigments known as extenders and opacifiers are also used. Extenders are transparent pigments which make the colors of other pigments appear less intense, while opacifiers are white pigments, which make the paint opaque so that the surface below the paint cannot be seen. Common pigments used in the manufacture of printing inks are listed in Table 1.

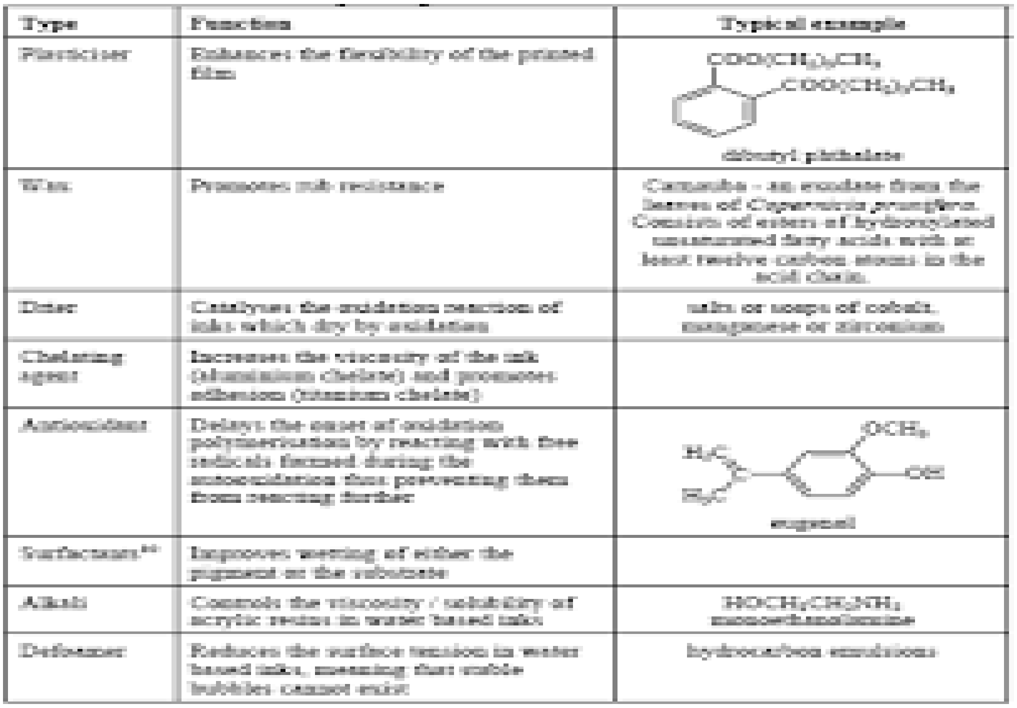


Manufacturing of Printing Inks with Formulation

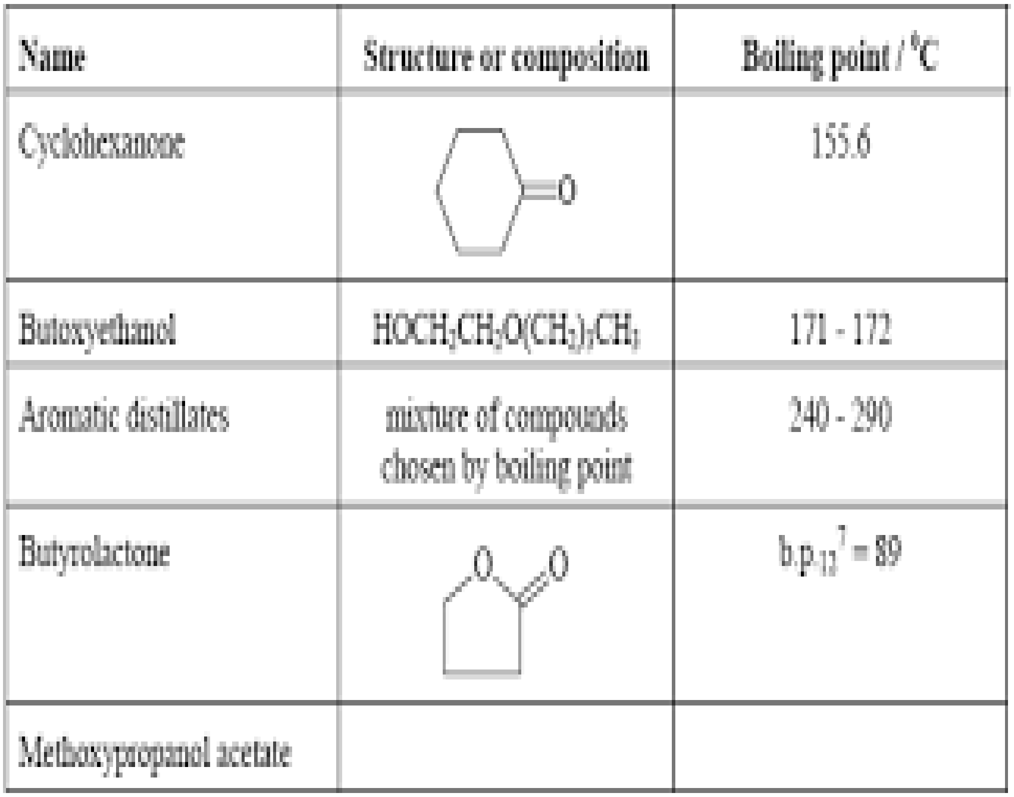
(Flexographic Inks, Typographic Printing Inks, Planographic Inks, Intaglio Printing Inks, Gravure Printing Inks, Special Inks, Offset Printing Inks, Ball Pen Inks, Fluorescent Inks, Phosphorescent Pigments, Silk-screen Fluorescent Printing, Inorganic Pigments)

Table 1 - Common printing ink pigments

Class	Examples	
Inorganic white (opacifiers)	Titanium dioxide (TiO_2) - in either rutile or anatase form	Zinc oxide (ZnO)
Extenders	Calcium carbonate ($CaCO_3$)	Talc - mixed oxides of magnesium, calcium, silica and aluminium
Inorganic black	Carbon black	
Organic red	 Lithol (C.I. 26670^5)	 Toluidine derivative (C.I. 12120)
Organic orange	 Pyrazolone (C.I. 21110)	 Dinitroaniline (C.I. 10390)



Type	Function	Typical example
Plasticiser	Enhances the flexibility of the printed film	$COO(CH_2)_3CH_3$ $COO(CH_2)_3CH_3$ dibutyl phthalate
Wax	Promotes rub resistance	Carnauba - an exudate from the leaves of Copernicia prunifera. Consists of esters of hydroxylated unsaturated fatty acids with at least twelve carbon atoms in the acid chain.
Drier	Catalyses the oxidation reaction of inks which dry by oxidation	salts or soaps of cobalt, manganese or zirconium
Chelating agent	Increases the viscosity of the ink (aluminium chelate) and promotes adhesion (titanium chelate)	
Antioxidant	Delays the onset of oxidation polymerisation by reacting with free radicals formed during the autooxidation thus preventing them from reacting further	OCH_3 H_3C H_3C OH eugenol
Surfactant**	Improves wetting of either the pigment or the substrate	
Alkali	Controls the viscosity / solubility of acrylic resins in water based inks	$HOCH_2CH_2NH_2$ monoethanolamine
Defoamer	Reduces the surface tension in water based inks, meaning that stable bubbles cannot exist	hydrocarbon emulsions



Name	Structure or composition	Boiling point / ^{0}C
Cyclohexanone	O	155.6
Butoxyethanol	$HOCH_2CH_2O(CH_2)_3CH_3$	171 - 172
Aromatic distillates	mixture of compounds chosen by boiling point	240 - 290
Butyrolactone	O O	$\text{b.p.}_{12}{}^{7} = 89$
Methoxypropanol acetate		

A lightfast red ink suitable for outdoor use on acrylic or PVC sheet would be :

Quinacridone pigment (CI Pigment Red 122)	10.0
Ethyl methacrylate copolymer	25.0
Vinyl resin	7.0
Methyl propoxol acetate	20.0
Aromatic hydrocarbon (186-214°C)	20.0
Cyclohexanone	10.0
Diacetone alcohol	7.0
Silicone anti-foam	1.0
	100.0

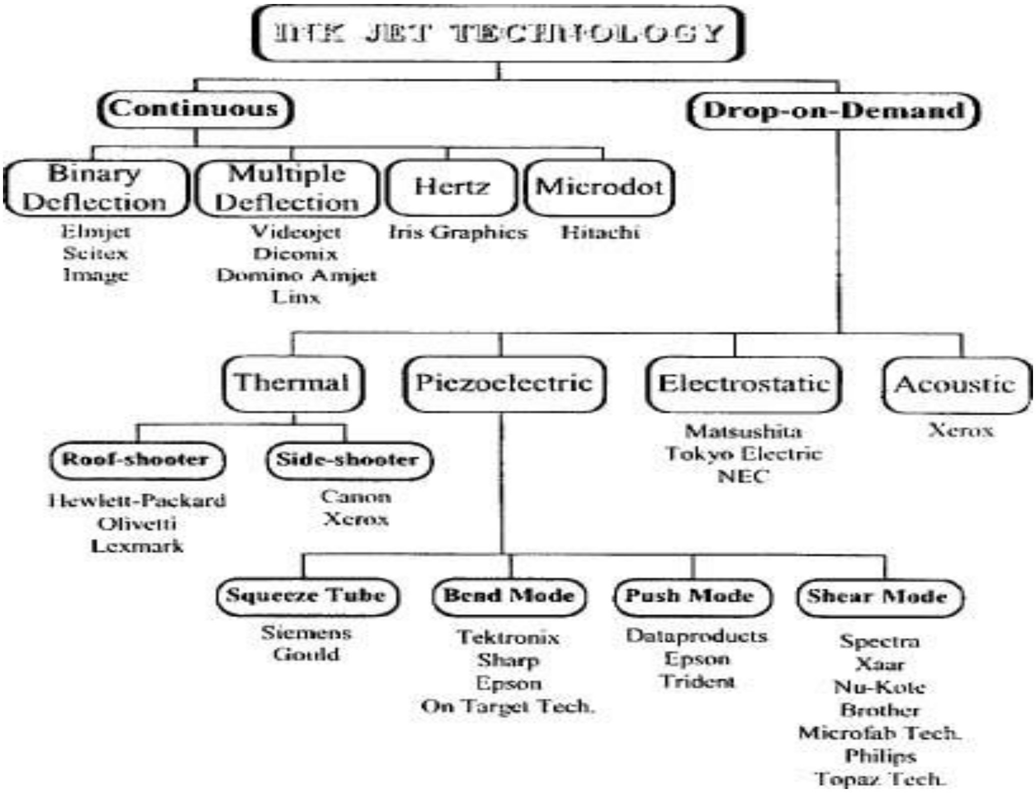
Typical formulations for a matt and gloss ink for either plasticised or rigid PVC are

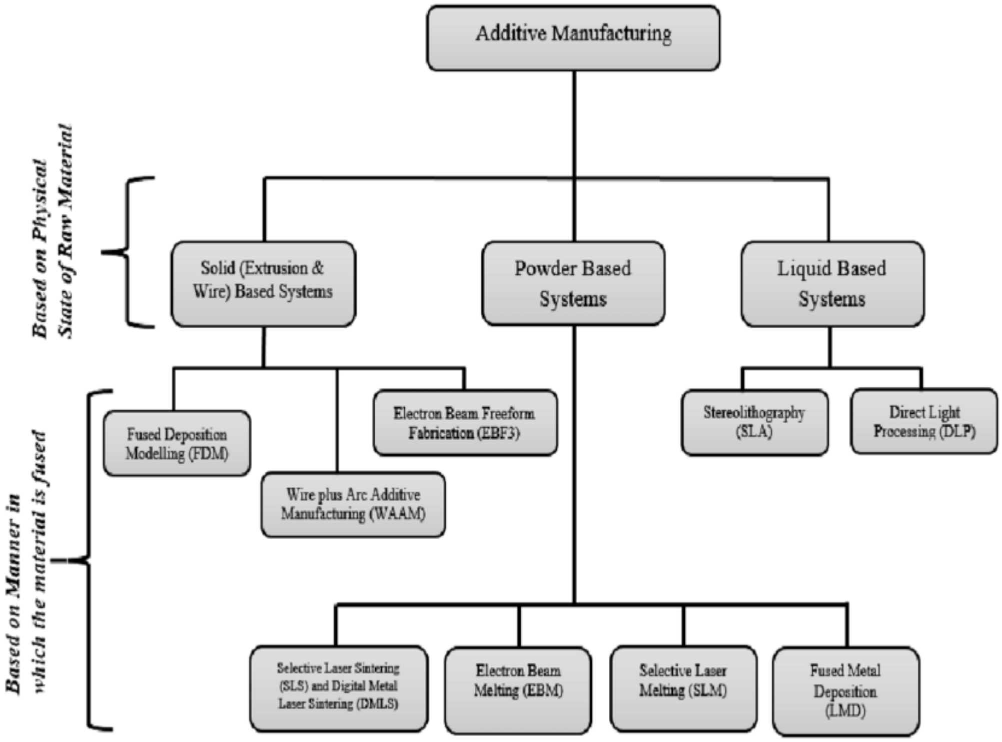
Matt ink for PVC sheet

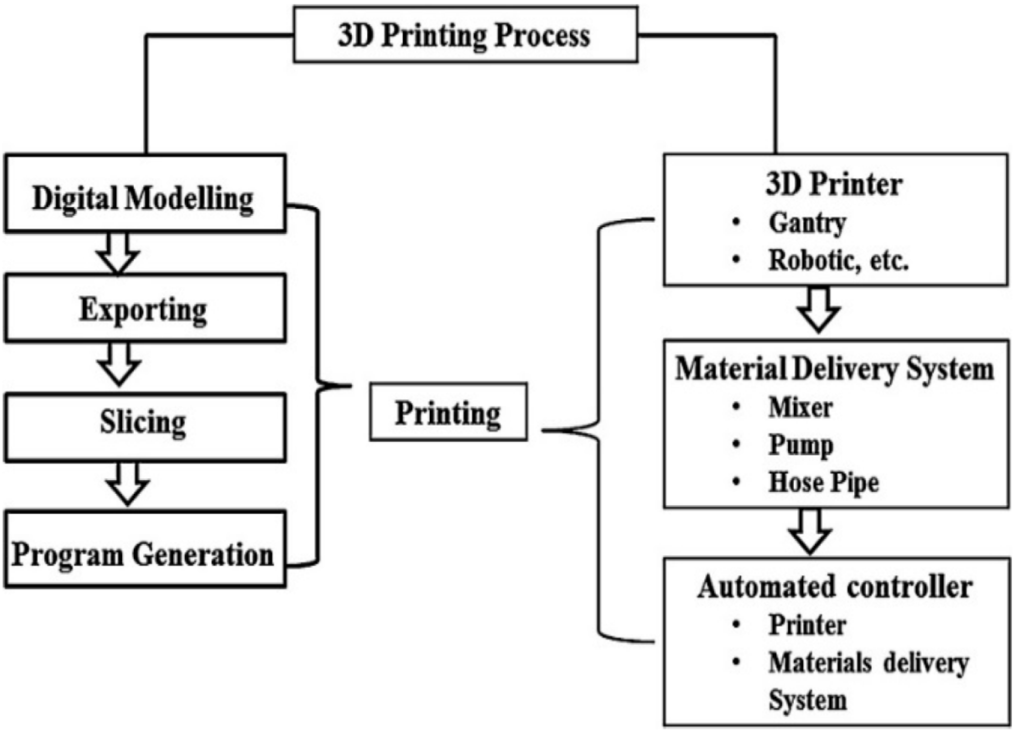
Permanent Yellow H10G (CI Pigment yellow 3)	5.0
Titanium dioxide (CI Pigment White 6)	7.0
China clay (CI Pigment White 6)	30.0
PVC/PVA copolymer	15.0
Aromatic hydrocarbon (160-180°C)	20.0
Pentoxone	16.0
Cyclohexanone	7.0
	100.0

Gloss ink for PVC sheet

Rutile titanium dioxide (CI Pigment white 6)	27.0
PVC/PVA copolymer	19.0
methyl/butyl methacryalate	7.0
Cyclohexanone	20.0
Aromatic hydrocarbon (160-180°C)	18.0
2-butoxyethyl acetate	8.5
Silicone anti-foam	0.5
	100.0




Additive Manufacturing
Based on Physical State of Raw Material
Solid (Extrusion & Wire) Based Systems
Powder Based Systems
Liquid Based Systems
Based on Manner in which the material is fused
Fused Deposition Modelling (FDM)
Wire plus Arc Additive Manufacturing (WAAM)
Electron Beam Freeform Fabrication (EBF3)
Stereolithography (SLA)
Direct Light Processing (DLP)
Selective Laser Sintering (SLS) and Digital Metal Laser Sintering (DMLS)
Electron Beam Melting (EBM)
Selective Laser Melting (SLM)
Fused Metal Deposition (LMD)


3D Printing Process
Digital Modelling
Exporting
Slicing
Program Generation
Printing
3D Printer
• Gantry
• Robotic, etc.
Material Delivery System
• Mixer
• Pump
• Hose Pipe
Automated controller
• Printer
• Materials delivery System

South Valley university

Faculty of Education

Chemistry Department

Petroleum Chemistry

4^{th} year students Faculty of Education South Valley University

Second term 2022/2023

Dr/ Ibrahim Abdul-Motaleb Mousa

Contents

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- **Petroleum exploration operations**
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- **Petroleum evaluation**
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- **Petroleum Products**
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- **Treatment of Petroleum Products**
- **Petrochemicals**
- **Oil and energy problems**

Definition of Petroleum

- **Petroleum is defined as a metallic liquid present naturally in the core of the earth.**
- **Its color is differs from light brown color to dark black color and it has a characteristic sulfuric smell.**
- **The word petroleum is called from two latin words are oil (oleum) and rock (petro), so it is called rock oil.**
- **While the word (naft) is an arabic word.**
- **Petroleum is the common nomenclature for a huge number mix of naturally chemical substances which defined as hydrocarbons.**

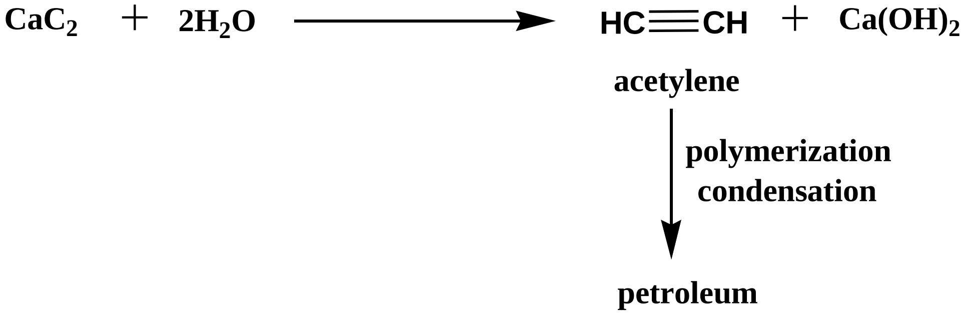
These substances is formed from carbon atoms and hydrogen atoms in different ratios

The importance of Petroleum

- **The importance of petroleum is due to:**
- **One of the most important and basic sources of energy but it is non-renewable energy.**
- **All machines today depend on petroleum as a source of energy and lubricants.**
- **Also, petrochemicals depend on petroleum to produce chemical substances as basic petrochemicals, intermediate petrochemicals and final petrochemicals.**

The origin of petroleum

- **1- Inorganic theory:**
- **Wohler 1828:**
- **He formed urea in the laboratory by heating of ammonium cyanate. Urea is an organic substance which in this time it can not be prepared in the lab but prepared only in the living organs.**
- **NH_4NCO --------------- NH_2CONH_2**
- **- In 1866:**
- **Acetylene is prepared from the reaction of calcium carbonate with alkali metals, so calcium carbide is formed which reacts with water to produce acetylene.**
- **Petroleum is formed from acetylene by a series of reactions such as alkylation, polymerization and condensation.**



$$CaC_2 + 2H_2O \longrightarrow \underset{\text{acetylene}}{HC{\equiv}CH} + Ca(OH)_2$$

$$\text{acetylene} \xrightarrow{\text{polymerization, condensation}} \text{petroleum}$$

- 1876:

- **Mandalev suggested that the hydrocarbons of petroleum are formed in the core of the earth by the effect of hot water vapor on metals carbide, the reactions are done by temperature and catalysts.**
- **Methane can be prepared from the reaction of alminium carbide and water.**
- $Al_4C_2 + 12H_2O \longrightarrow 4Al(OH)_3 + 4CH_4$

The organic theory

- **1886:**
- **They assumed that the crude oil is formed as a result of decomposition of huge marine animals by the temperature of the core of the earth, which decomposed to small fatty molecules after a series of chemical reactions converted to the crude oil ingredients.**
- **Some of researchers considered the origin of petroleum is plant substances due to:**

- **1- Presence of natural naphtha as a result of thermal decomposition of plants and fallen forests in the core of the earth.**
- **2- Thermal decomposition of coal, which converted to hydrocarbon ingredients.**
- **3- Breakdown of cellulose give methane gas.**
- **4- Bacterial decomposition of carbohydrates give methane.**
- **5- Presence of some plants pigments as chlorophyl and carotene.**
- **6- Presence of some living creatures in the crude oil.**

Stages of petroleum Formation

- **- First stage:**
- **The parts of dead plants and animals are congregated in the bottom of lakes and seas and bury them by sand and rocks.**
- **After that bacteria and micro-organisms reacted with most of simple carbohydrates and proteins which soluble in water, then decomposed them to water soluble compounds.**

Then the residue collected and bury in various depth in case of precipitation

The second stage:

- **The plants and animals residue are composed to different rates of pressure and temperature, to evolve CO_2 gas from aliphatic carboxylic acids and evolve water from alcohols, to form hydrocarbon mixture.**
- **In case of the hydrocarbons composed to a lot of temperature and pressure, these compounds breakdown to hydrocarbons with low molecular weights and unsaturated.**

The third stage:

- **When the formed petroleum is composed continuously to more of pressure and temperature, when moved from the pore of sedimentary rocks, the petroleum reacted with natural catalysts which present in the core of the earth, which reacted as catalysts in a lot of chemical reactions as polymerization, alkylation, condensation and hydrogenation, to form several parafins and naphthens.**
- **Also, heterocyclic compounds are formed which contains sulfur, nitrogen and oxygen.**
- **In the principle, from the different of plants and animals and sedimentary rocks, the crude oil is differs in a lot of physical and chemical properties.**

Petroleum exploration operations

Types of oil wells

- **1- Gushing well:**
- **This well is present in the surface of the earth, it has no economic significance for several reasons related to the quality and quantity of oil, and it may be:**
- **a- stagnant oil. b- flowing oil.**
- **2- underground petroleum:**
- **Existence of natural fisheries with buffer sides in which oil collects.**

Petroleum exploration operations

- **In the past, it was based on surface indications of the effects of petroleum, and with the advancement of science, there are several methods used, including:**
- **1- Aerial Survey:**
- **Filming is done from the air using specially equipped aircraft in air corridors and takes from interlaced images or by satellite. And it is used in:**
- **Knowing the arrangement of the ground layers.**
- **Soil Forms.**
- **Water tracts.**
- **Effects of gases and petroleum.**
- **2- Ground studies:**
- **The study of maps is prepared by the science of geology to know the arrangement according to the earth and its ages, and to determine the places in which the petroleum and its forms are located, as well as chemical analyzes to know the chemical**

composition of these rocks and the extent of their ability to collect oil within them.

- **3- Use of geophysical methods:**
- **It is used on the foundations of physics to study the geology of the earth and to measure the thickness and shapes of ground deposits. Such as:**
- **a- Gravity measurement:**
- **The gravity of the Earth's layers is measured as it is found that the sedimentary layers are less than the Earth's gravity than the rest of the layers.**
- **b- Magnetic field measurement:**
- **It is found that the magnetic field of the sedimentary layers is less than the rest of the layers.**
- **c- Seismic survey:**
- **And it is done by inserting amplifiers or explosives at different dimensions into the depths of the ground layers and detonating them from a distance and receiving the sounds emanating from them and reflected.**

Drilling oil wells

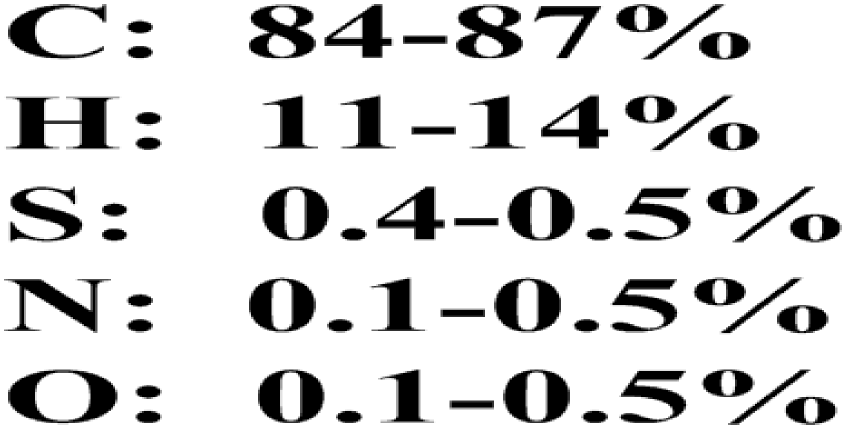
- **1- Drilling by pounding:**
- **This method is summarized in raising the drilling machine above the surface of the soil and then dropping it on it, then part of it crumbled and the drilling machine is re-lifted and dropped several times until the soil crumbles and the fragmented parts come out and hammering is repeated many times until the drilling process is completed.**
- **2- Rotary drilling:**
- **Drilling is done in this method by rotating the drilling machine over the surface of the soil, so that part of the soil is broken up by the effect of the pressure on it, and another part of it is separated in the form of flakes by the sharpening of the teeth of the drilling machine.**

Petroleum production methods

- **1- Flowing wells:**
- **Most of the oil fields at the dawn of their life are of high pressures. Therefore, when drilling any well, the oil is pushed with enough force to lift it to the surface of the earth through a tube running close to the bottom of the well.**
- **2- Gas Lift:**
- **Some gases extracted from a nearby well are compressed into the liner pipelines to compress the oil and push it into the production pipelines.**
- **3- Lifting by pumps:**
- **Crude oil is raised by installing automatic cranes or pumps instead of gas or any other method.**

The chemical composition of petroleum

- **Petroleum is composed of hydrocarbon materials, and these materials are a mixture of organic chemical compounds (solid, liquid and gas) and each compound consists of the union of two elements of carbon and hydrogen in varying proportions, as these two elements sometimes combine with many types of other elements such as (nitrogen and sulfur) And oxygen) to form hydrocarbon derivatives.**



C: 84-87%
H: 11-14%
S: 0.4-0.5%
N: 0.1-0.5%
O: 0.1-0.5%

- **And the crude oil that contains sulfur compounds such as (H_2S) and the two compounds are called bitter oil.**

- **While the crude contains a very small amount of sulfur compounds such as (H_2S) and the two compounds in sweet oil.**
- **Petroleum is distinguished by the presence of three types of hydrocarbons that are included in its composition:**
- **Paraffins.**
- **Naphthenate.**
- **Aromatic compounds (aromatics).**
- **Petroleum can be divided into four sections according to the nature of the predominant carbon and hydrogen compounds:**
- **1- Paraffin crude oil Composition:**
- **It contains a high percentage of paraffins with straight or branched chains, and these chains are composed of more than 44 carbon atoms linked by single bonds.**
- **These chains are found in the gaseous state (C1-C4).**
- **And the liquid state (C5-C15)**

- **And solid state (C16- ---)**
- **All of them are soluble in petroleum, such as methane, ethane, propane, and butane ....**
- **Paraffinic petroleum is called light crude, and its most important component is natural gasoline**
- **2- Naphthenic base crude oil:**

This type contains a high percentage of naphthenes or cyclo-paraffins such as cyclopentane and cyclohexane

- **The presence of these compounds in a large proportion makes the crude oil more viscous, so it is called heavy crude.**
- **The main components of this group are high-octane gasoline, kerosene, diesel, lubricant, and bitumen (asphalt).**

- **3- Mixed Crude Oil:**
- **Crude oil of this type contains a mixture of paraffin components and naphthenic components in close proportions and few aromatic hydrocarbons, and this type of crude oil represents most of the crude oil.**
- **4- Crude Oil Asphalt Composition:**
- **This type of crude oil is dominated by aromatic compounds and contains a high percentage of asphalt.**

Petroleum evaluation

- **Petroleum raw materials vary in their natural and chemical properties according to:**
- **Diversity of rock production sources.**
- **The ages of rock formation.**
- **Natural properties.**
- **Chemical properties of the rocks that contain it.**
- **The different depths of the ore-containing layers and their geological and mineral structures.**

1- Determination of the specific density of crude oil:

2- Absolute density (w): The mass of a unit of volume of a given substance at a given temperature and its unit is g / cm^3.

3- Specific density (G): is the quotient of dividing the absolute density of a substance by the density of water at the same temperature.

4- Specific density degree (API):

$$\text{API Gravity} = \frac{141.5}{G} - 131.5$$

- **Where G: density of petroleum at a temperature of 15 ° C.**
- **When the quality density is high, it is of the finest and highest price.**

Determination of the viscosity coefficient of crude oil:

- **Viscosity coefficient (VI): It describes the extent of change in the viscosity of petroleum products such as lubricants with the change in temperature.**
- **It is a measure of the oil’s resistance to flow and its ability to lubricate surfaces.**
- **Petroleum products that have a high viscosity coefficient have the least effect of changing with temperature, and vice versa.**

- **Standard temperatures are 40-100 ° C.**

$$VI = \frac{L - U}{L - H} X 100$$

- **L = value estimated in the table corresponding to the value of viscosity measured at 100 m.**
- **H = a value estimated in the table corresponding to the value of the measured viscosity at 100 M.**
- **U = viscosity measured at 40 m.**

3- point of pouring (F)

- **point of pouring (F):**
- **It is the lowest temperature at which the movement of liquids stops during cooling.**
- **Cloudiness point: is the temperature at which fine particles of waxes and paraffins are formed.**

4- Determination of aniline point

It is the temperature at which two equal volumes -5
of the aniline and the petroleum product are
mixed.

Describes hydrocarbons in their pure or blended -6
form of petroleum products and hydrocarbon
solvents that have significance in kerosene.

The aniline point is inversely proportional to the -7
proportion of aromatic hydrocarbons in
petroleum products.

Diesel coefficient (D.I.): This indicates the -8
combustion efficiency of diesel fuel

Diesel modulus = (aniline point X specific density -9
degree (API)) ÷ 150

5- Coefficient of Excellence (K)

$$K = \frac{(T_B)^{1/3}}{G}$$

Where: •

TB: average boiling point. •

G: the specific density at 15 pm. •

The higher the value (K) the paraffinic oil is the composition. •

6- Relationship Evidence (CI)

$$C.I. = \frac{87552}{T_B} + (473.7 x G - 456.8$$

- **TB: average boiling point.**
- **G: the specific density at 15 pm.**
- **The smaller the CI value, the paraffinic oil is in the composition.**
- **The higher the CI value, the greater the oil is an aromatic or paraffinic composition.**

7- Residual carbon

The carbon remaining from the carbonization process after distillation in the absence of air has to do with the asphalt content, and in general, low-carbon materials are considered more valuable ores.

Crude oil processing operations

- **Accompanying petroleum while leaving the well:**
- **Gases.**
- **Salts.**
- **water.**
- **Mechanical impurities (sand and mud).**
- **So these things must be separated partly in the field, and then completely in the refinery.**
- **The associated gases in the oil fields are separated in special devices (traps) and then paid to the gasoline unit to separate the light condensate that are often associated with the gases, which are separated by condensation and called (natural gasoline).**

- **The ore is then driven into sedimentation depots, where mechanical impurities are separated by sedimentation.**
- **After that, the salts are removed from the petroleum by washing the salts with fresh water in a ratio of 10-15% of the water two or three times.**
- **It separates water from petroleum at times relatively easily. But it is often stable emulsions (water in petroleum or petroleum in water) that are difficult to separate, especially during pumping and pipelining operations very quickly, which is difficult to dispose of.**

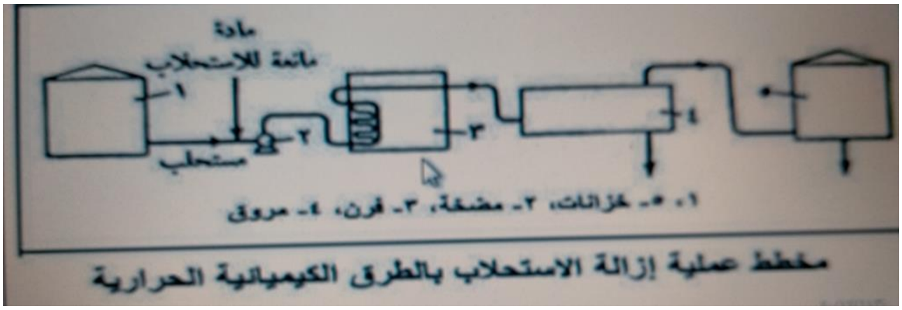
Industrial methods for removing petroleum emulsification

1- Mechanical methods:

- **It is carried out by filtering, centrifugation, or filtering, but these methods are widely used.**

2- Thermal methods:

- **The emulsion is heated, and the fixative layer of the emulsion expands, breaks down, strikes off water, and collects in tanks. This method is used for treating unstable emulsions only, and it leads to a large amount of light petroleum cuttings being lost in the event of insufficient sealing.**
- **3- Chemical methods:**
- **By using cheap and sufficiently effective anti-emulsification chemicals, these materials weaken the water droplets' membrane so that the water is easily separated.**
- **4- thermochemical methods:**



مخطط عملية إزالة الاستحلاب بالطرق الكيميائية الحرارية

Why are the impurities removed from the ore before the refining process?

- **1- If the impurities are not separated from the ore, they will settle on the heating surface, which leads to lowering the efficiency of the heat exchangers.**

- **2- During the passage of petroleum through the pipelines at high speeds, the particles have an effect on the corrosion of the equipment.**

- **3- The survival of mechanical impurities (sand and mud) in petroleum residues after distillation leads to a decrease in the quality of these residues and an increase in the proportion of ash in them (boiler and coke fuel), which leads to their non-conformity with international standards.**

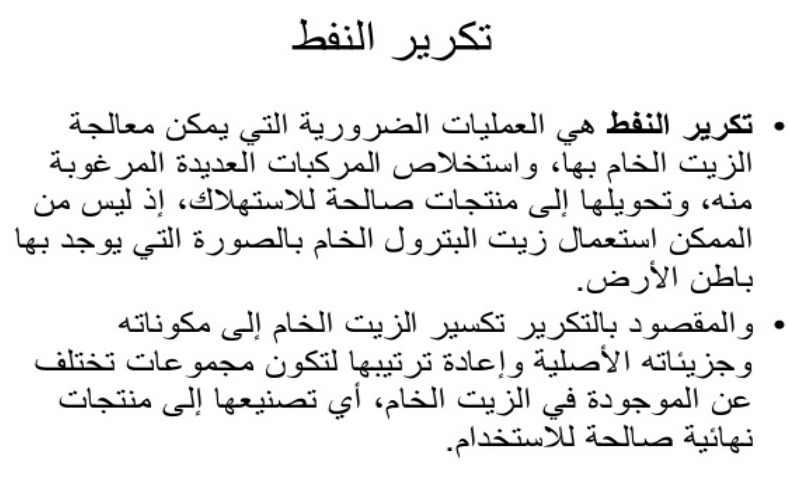
- **4- The water in the raw material evaporates inside the heating devices, which leads to an increase in the pressure in the devices and a disturbance to the unit.**

- **5- The water in the raw material contains large amounts of salts such as ($NaCl$, $MgCl_2$, CaI_2).**

- **6- Hydrochloric acid is formed from the decomposition of these salts, which causes corrosion processes of the devices.**

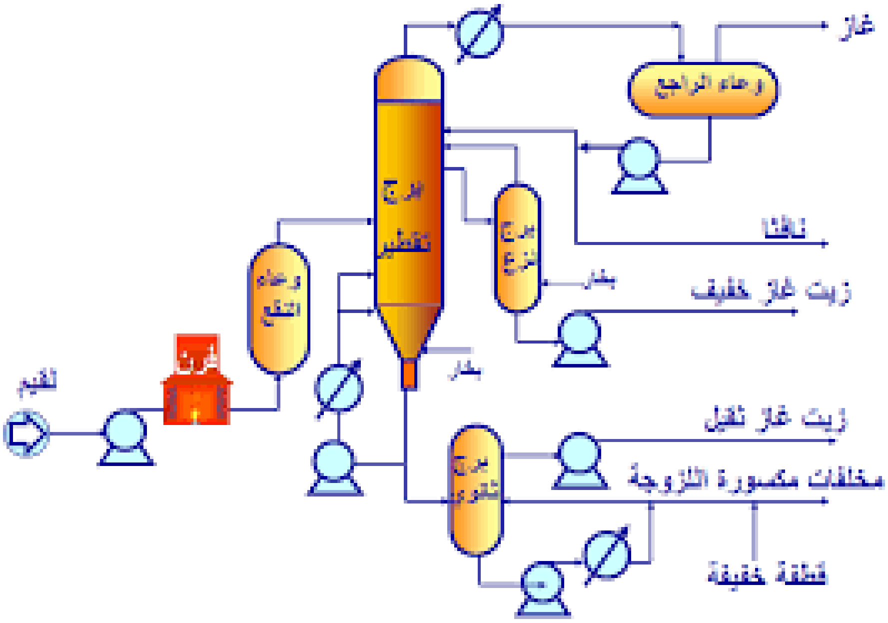
- **It is evident from the foregoing that the oil, after obtaining it from the wells, must undergo a preparatory treatment to provide the required degree of purity.**

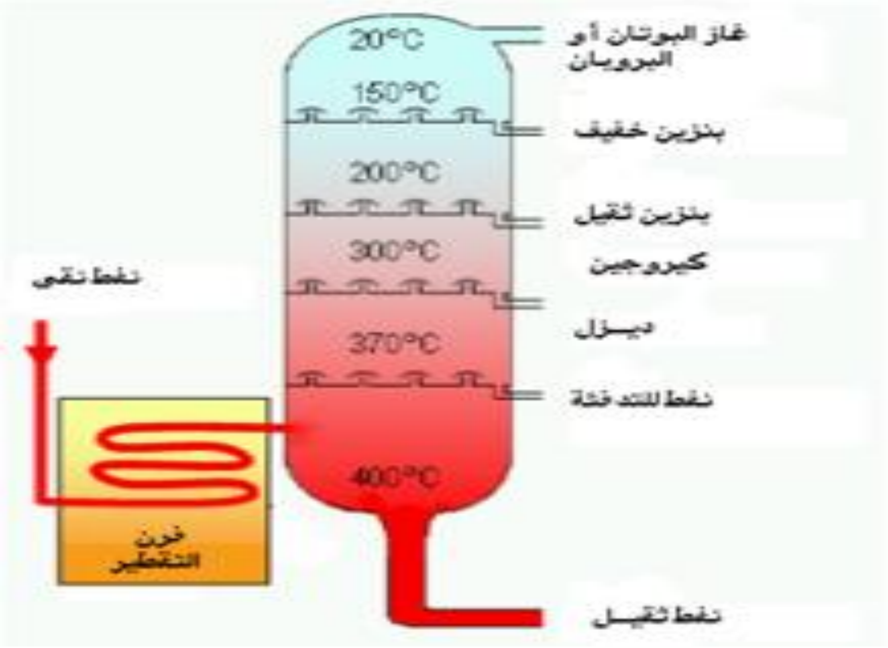
Petroleum Products

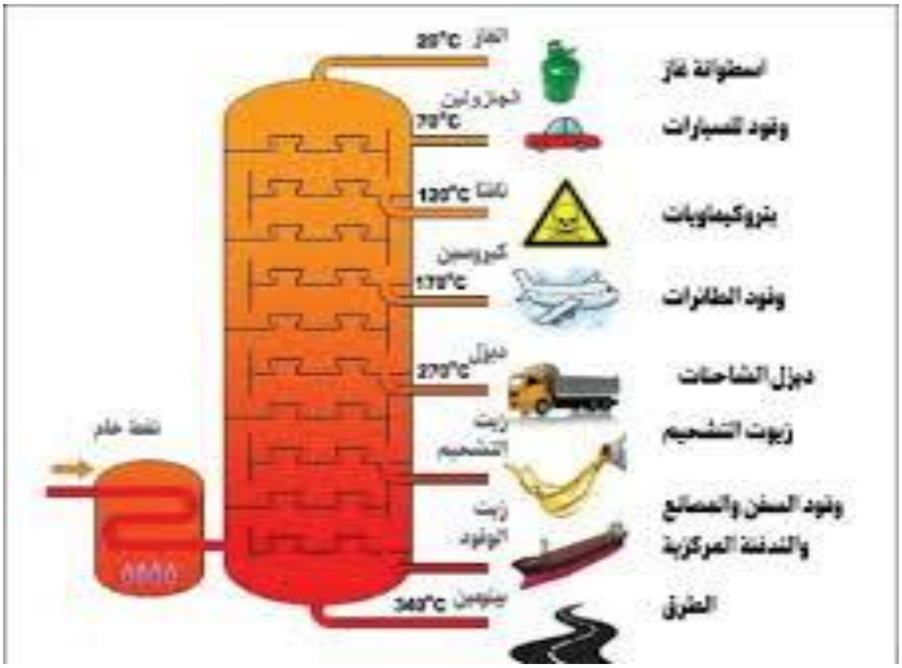


تكرير النفط

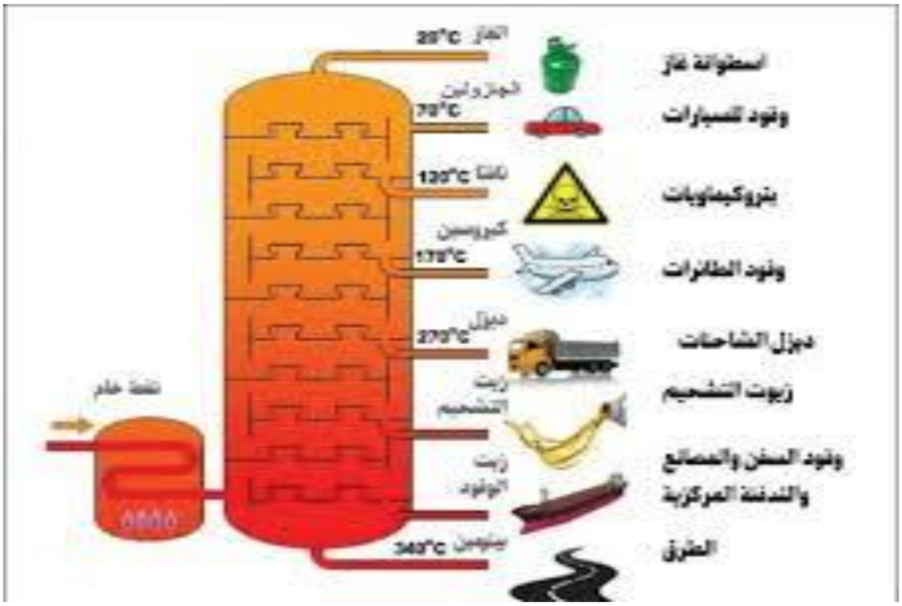
- **تكرير النفط** هي العمليات الضرورية التي يمكن معالجة الزيت الخام بها، واستخلاص المركبات العديدة المرغوبة منه، وتحويلها إلى منتجات صالحة للاستهلاك، إذ ليس من الممكن استعمال زيت البترول الخام بالصورة التي يوجد بها باطن الأرض.
- والمقصود بالتكرير تكسير الزيت الخام إلى مكوناته وجزيئاته الأصلية وإعادة ترتيبها لتكون مجموعات تختلف عن الموجودة في الزيت الخام، أي تصنيعها إلى منتجات نهائية صالحة للاستخدام.


غاز
وعاء الراجع
برج تقطير
برج نزع
نافثا
بخار
زيت غاز خفيف
وعاء النقع
فرن
لقيم
بخار
زيت غاز ثقيل
برج ثانوي
مخلفات مكسورة اللزوجة
قطفة خفيفة

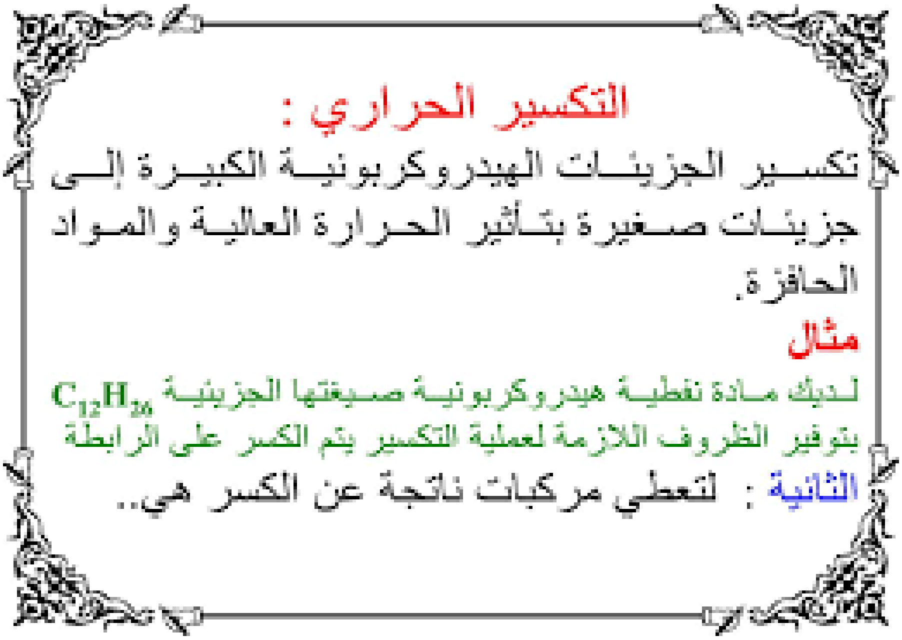

20°C
150°C
200°C
300°C
370°C
400°C
غاز البوتان أو البروبان
بنزين خفيف
بنزين ثقيل
كيروجين
ديـــزل
نفط للتدفئة
نفط نقي
فرن التقطير
نفط ثقيــل


الغاز 20°C
الجازولين 70°C
نافثا 120°C
كيروسين 170°C
ديزل 270°C
زيت التشحيم
زيت الوقود
بيتومين 340°C
نفط خام
اسطوانة غاز
وقود للسيارات
بتروكيماويات
وقود الطائرات
ديزل الشاحنات
زيوت التشحيم
وقود السفن والمصانع والتدفئة المركزية
الطرق

Conversions of petroleum Products



Thermal Cracking:



التكسير الحراري :

تكسير الجزيئات الهيدروكربونية الكبيرة إلى جزيئات صغيرة بتأثير الحرارة العالية والمواد الحافزة.

مثال

لديك مادة نفطية هيدروكربونية صيغتها الجزيئية $C_{12}H_{26}$ بتوفير الظروف اللازمة لعملية التكسير يتم الكسر على الرابطة

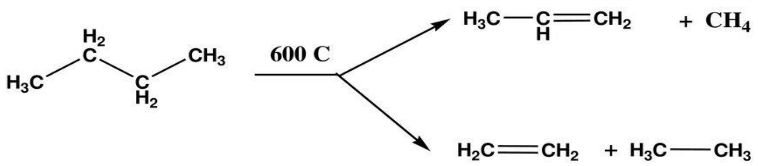
الثانية : لتعطي مركبات ناتجة عن الكسر هي..

تكسير النواتج الثقيلة

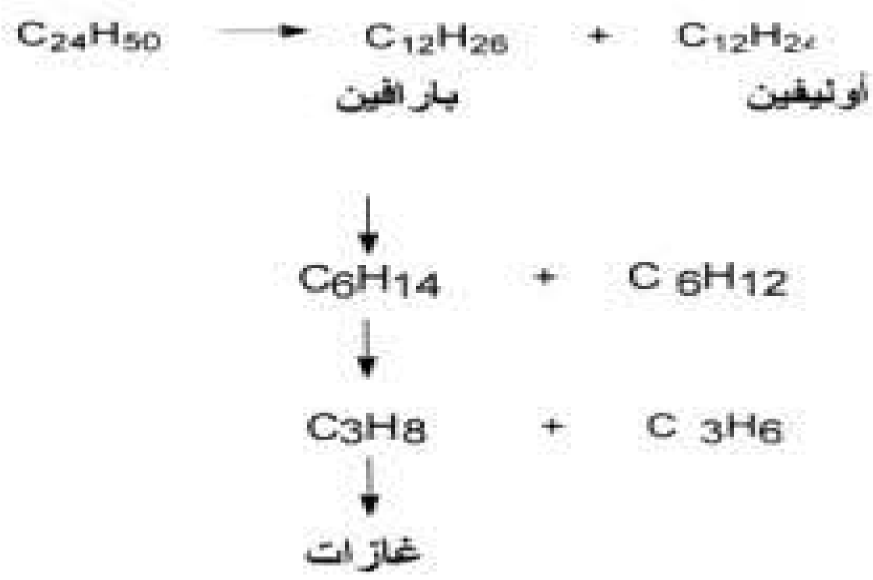
أ- التكسير الحرارى Thermal Cracking

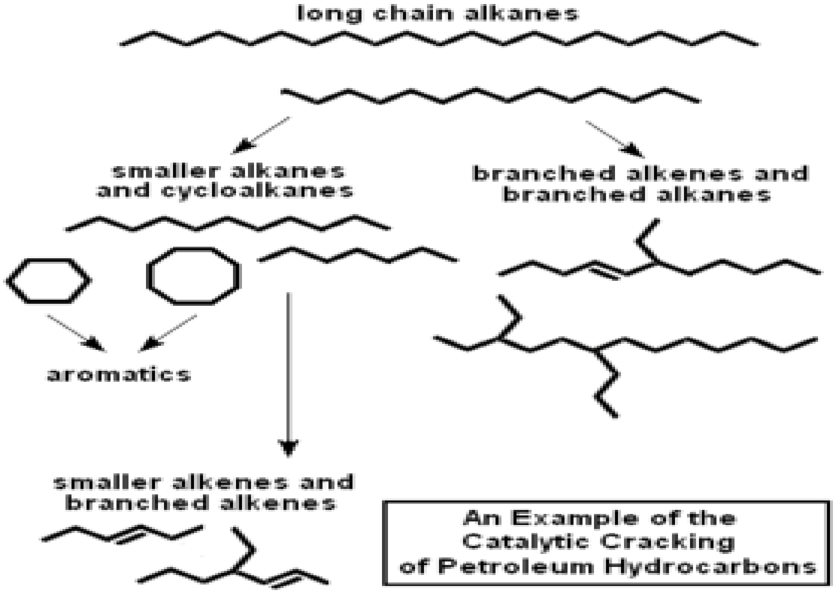
وقد استخدمت طريقة التكسير على نطاق تجاري للمرة الأولي فى عام 1913م، فبتعرض الزيت الخام إلى درجات حرارة مرتفعة (600-500)، وتحت ضغوط عالية تحدث عملية تكسير الجزيئات الهيدروكربونية الكبيرة إلى جزيئات أصغر. وبهذه الطريقة، أمكن تحويل المنتجات الثقيلة إلى منتجات خفيفة مثل الجازولين. ومن أهم نواتج التكسير الحرارى التى تحتوى على ذرات كربون لا تزيد عن 4 ذرات مثل الميثان والإيثان والبروبان والبيوتان.

مثال : تكسير البيوتان العادى عند 600 درجة مئوية.



Catalytic Cracking:




long chain alkanes
smaller alkanes and cycloalkanes
branched alkenes and branched alkanes
aromatics
smaller alkenes and branched alkenes
An Example of the Catalytic Cracking of Petroleum Hydrocarbons

Treatment of Petroleum Products

- **Treatment of water, CO_2, and H_2S.**
- **Water: By Al_2O_3 or H_2SO_4.**
- **CO_2: By methanol gas.**
- **H_2S: By dry method:**
- **$3H_2S + Fe_2O_3$ ------------ $Fe_2S_3 + 3H_2O$**
- **$2Fe_2S_3 + 3O_2$ ------------ $2Fe_2O_3 + 6S$**

Octane Number

- **The percentage between isooctane and heptane in gasoline, this for the quality of gasoline.**
- **For example: gasoline 90 means:**
- **This gasoline is mixture of 90% isooctane and 10% of heptane.**

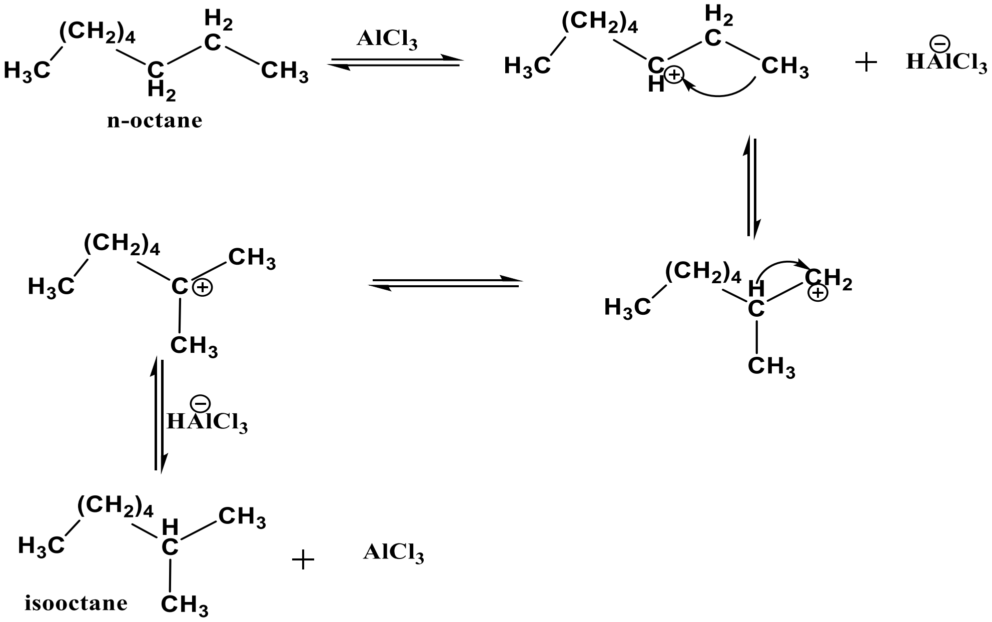
Methods for improvement of gasoline

- **1- Addition of $(Et)_4Pb$:**
- **5 ml for each galon.**
- **2- By catalysts:**
- **By heating low gasoline octane number in high temperature and high pressure in the presence of**

catalyst as ammonium silicate to convert the straight chains to branched chains.

- **3- Tanning:**

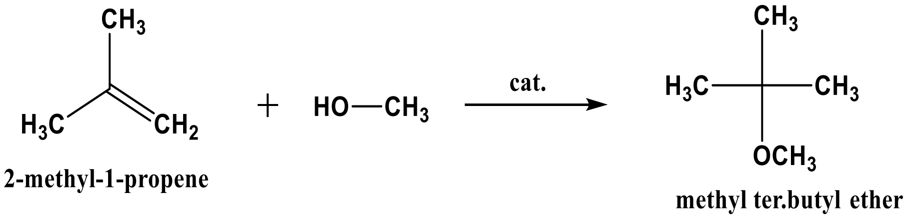
- **This is to convert the straight chains in gasoline to branched chains by heating with $AlCl_3$. But it is cost.**



- **4-Alkylation:**

- **This method used to convert small alkenes to long branched aliphatic chains in the presence of a catalyst.**

- **5- Addition of methyl ter.butyl ether:**
- **Add 5-10% to improve octane number, it prepared from the reaction of isobutene with methanol.**



Petrochemicals

These processes which use petroleum or natural gas or its derivatives to produce many of chemical compounds are called petrochemicals.

Steps for manufacture of petrochemicals

- **First step:**
- **Convert petroleum derivatives as methane, ethane, butane and naphtha to basic petrochemicals as methanol, ammonia, ethylene, propylene, butadiene and benzene.**
-

- **Second step:**
- **Production of intermediate petrochemicals by conversion of basic petrochemicals to intermediate petrochemicals as vinyl chloride and ethylene oxide.**
- **Third step:**
- **Production of final petrochemicals by conversion of intermediate petrochemicals to final petrochemicals as polyethylene, polypropylene, PVC., and polystyrene.**
- **Fourth step:**
- **Production of consumed materials by conversion of final petrochemicals to consumed materials as plastics and water bottles.**

Petrochemicals from Methane:

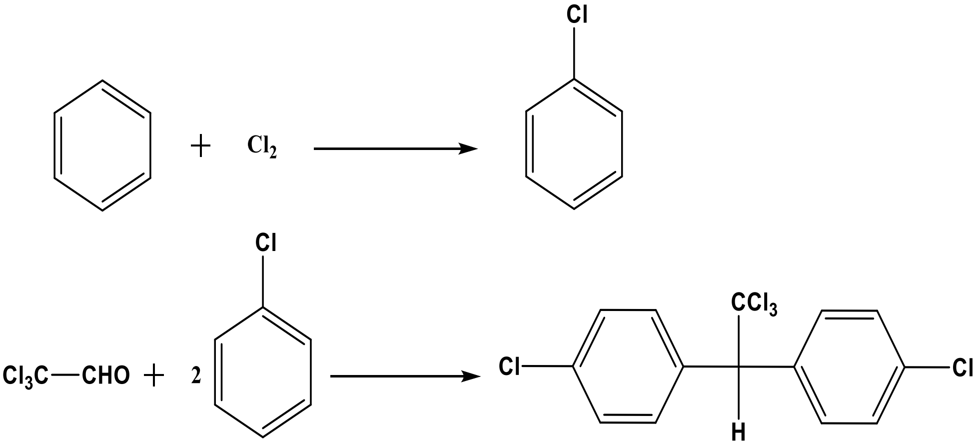
- **1- Synthesis gas:**
- $CH_4 + H_2O$ ------------- $3H_2 + CO$
- $CH_3\text{-}CH_2\text{-}CH_3 + 3H_2O$ ----------- $7H_2 + 3CO$
- $2CH_4 + O_2$ ------------- $4H_2 + 2CO$

- **2- Methanol:**

$2H_2 + CO$ ---------------- CH_3OH

<u>Petrochemicals from Methanol:</u>

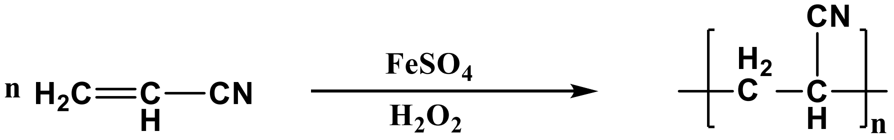
- **CH_3OH ---------------- HCHO**
- **CH_3OH --------------- CH_3COOH**
- **<u>Insecticide:</u>**



D.D.T
dichlorodiphenyl-trichloro ethane

<u>Synthetic Fibers:</u>

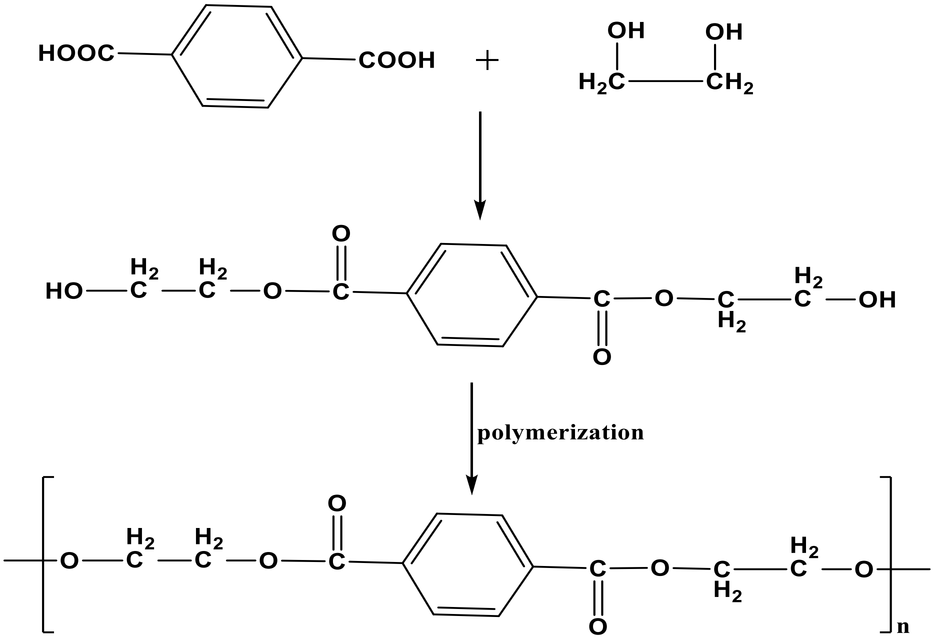
- **1- Acrylic fibers:**



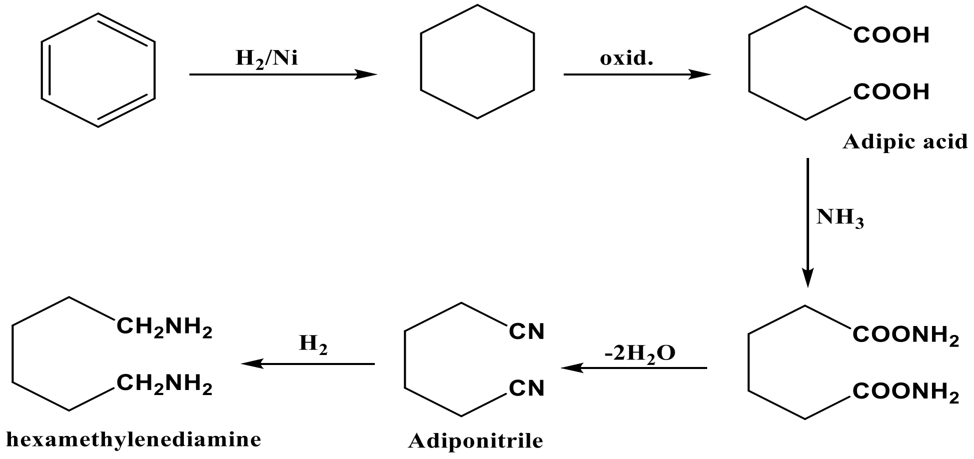
$$n\ H_2C{=}CH{-}CN \xrightarrow[H_2O_2]{FeSO_4} \left[-\overset{H_2}{C}-\underset{H}{\overset{CN}{C}}- \right]_n$$

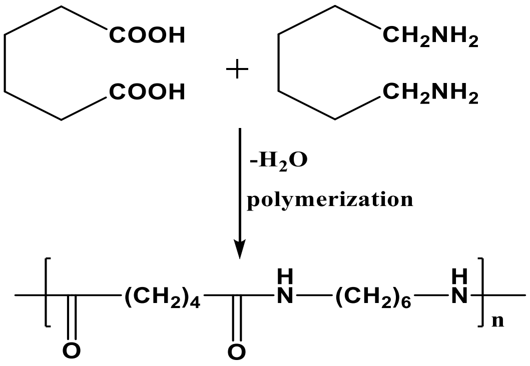
Arolon (Acrylic)

2- **Polyester fibers:**



3- **Nylon6,6 fibers:**


H2/Ni
oxid.
COOH
COOH
Adipic acid
NH3
COONH2
COONH2
-2H2O
CN
CN
Adiponitrile
H2
CH2NH2
CH2NH2
hexamethylenediamine


COOH
COOH
+
CH2NH2
CH2NH2
-H2O
polymerization
(CH2)4
H
N
(CH2)6
H
N
O
O
n

Oil and energy problems

- **an introduction:**
- **Solar energy: for heating, food heating and drying purposes.**
- **Tree fires: for heating, boiling water, cooking food and lighting.**
- **Coal: the steam engine.**
- **Petroleum: The most important source of energy in the year today.**

Oil-based energy problems

- **1- Emission of quantities of gases to the air (such as, CO_2, NO_2, NO, CO and some hydrocarbons) at the free oil fuel or natural gas that cause a number of environmental phenomena, including:**
- **(Global warming - acid rain - smog)**
- **The solution:**
- **1- Development of internal combustion machines in engines (fuel combustion complete combustion) to convert carbon into carbon dioxide, not the most toxic carbon monoxide.**

- **2- Development of exhaust filters for transport and factories.**
- **3- Using petroleum fuels from energy production with an environmentally friendly composition or less harmful to the environment.**
- **4- At the international level: international cooperation in facing global environmental risks.**
- **5- At the local level: Enacting local laws and regulations that prevent the occurrence of all kinds of pollution.**
- **6- At the level of individuals: Recommendations for individuals to follow lifestyle habits that reduce pollution, including:**
- **Reducing car use and encouraging walking and cycling.**

The second problem:

- **The spillage of large quantities of petroleum into the seas and oceans during its transportation.**
- **The spread of large layers of petroleum over the sea level as a result of cleaning operations of**

tankers' tanks or after emptying them from the balance water.

- **These problems cause a deterioration of the marine environment and damage to the organisms that live in it or depend on it.**
- **The solution:**
- **Enactment of international laws and regulations:**
- **To regulate the disposal of balance water in oil tankers.**
- **Imposing maximum penalties for those who pollute the waters of the seas and oceans with oil or other oil.**
- **2- Tightening control over oil tankers and imposing severe penalties for the violation.**

<u>The third problem:</u>

- **Petroleum is a non-renewable energy source (expected to be depleted within a specific period of time), so what is the alternative:**
- **The solution:**
- **Searching for alternative energy sources such as:**

- **1- Solar energy.**
- **2- Water energy (converting kinetic energy into electricity)**
- **3- Steam energy: produced when sea water is desalinated.**
- **4- Wind energy.**
- **5- Nuclear energy.**

The energy cycle in the universe

- **Energy is transformed from plants (photosynthesis) to the herbivore, and thus the transfer of energy from one creature to another through the food chain is sequenced until the organism dies and its body decomposes and buries in the ground and then turns into organic remains over time and under pressure and heat isolated from the air, it returns Energy and is formed in the ground in the form of oil and natural gas.**

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- **4- Chemistry of petrochemical processes 2nd edition, Sami Matar and Lewis F. Hatch 2001.**
- **5- Chemistry of fossil fuels and biofuels, Harold H. Schobert 2013.**