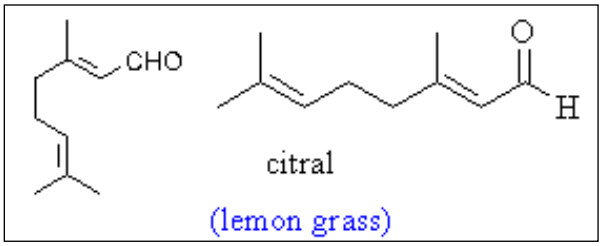
Citral



SOURCE OF CITRAL

Name of drug	Part of plant	Biological source	Active constituents	use
Lemon grass oil	Lemon grass oil is the oil distiiled	Cymbopogan flexuosus (Gramineae)	Citral , citronellal, geraniol	Flavouring agent, mosquitorepellent, source for preparation of beta ionone and vitamin A

Citral is acyclic monoterpenoids, it is a major constituent of lemon grass oil in which it occurs to an extent of 60-80%. It is a pale yellow liquid having strong lemon like odor and can be obtained by fractional distillation under reduced pressure from lemon grass oil. Since the structures of most of the other compounds in this group are based on that of citral ($C_{10}H_{16}O$). Citral is widely distributed and occurs to an extent of 60-80 percent in lemon grass oil. Citral is a liquid which has the smell of lemons.

EXTRACTION AND ISOLATION

Transfer 10ml of lemon grass oil, 100ml of water to a 250 ml round bottom flask. Place a boiling chip into the flask. Connect the flask to a simple distillation apparatus. Heat the mixture to boiling, and collect the distillate at graduated cylinder. Isolate the citral obtained from mixture of water and citral by extracting it with diethyl ether. Evaporate the ether layer to get citral.

1) Molecular formula of citral is ($C_{10}H_{16}0$), bp-77 c and Chemical name 3, 7-dimethyl -2, 6-0ctadienal.
2) Nature of oxygen atom include formation of oxime of citral indicate presence of an Oxo group in citral molecules.

$C_{10}H_{16}0 + NH_2OH \longrightarrow C_{10}H_{16} ==NOH$ (oxime)

On reduction with Na/Hg it gives geraniol and on oxidation with silver oxide it give geranic acid,

$C_{10}H_{16}02$ (geranic acid), $\xleftarrow{Ag_20}$ CITRAL ($C_{10}H_{16}0$) $\xrightarrow{Na/Hg}$ $C_{10}H_{18}0$ geraniol.

Both these reaction reveal that Oxo group in citral is therefore an aldehyde group. Citral reduces Fehling solution, furthermore confirm the presence of aldehyde group.

3) Presence of two double bond: when citral is treated with two molecules of to form citral tetra bromide.

$C_{10}H_{16}0 \xrightarrow{Br_2} C_{10}H_{16}0Br_4$ (citral tetra bromide)

On ozonolysis, it gives acetone, Laevualdehyde and glyoxal.

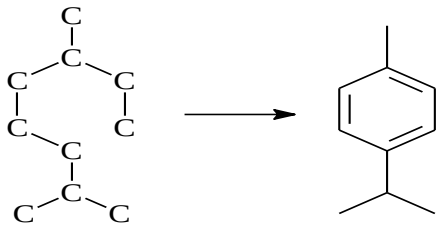
$CH_3\text{-}C(=O)(CH_3)$ + CHO-CH_2-CH_2-$C(=O)(CH_3)$ + CHO-CHO

Formation of above products shows that citral is an acyclic compound containing two double bond. Corresponding saturated hydrocarbon of citral (molecular formula $C_{10}H_{22}$) corresponds to the general formula CnH2n+2 for acyclic compound, indicating that citral must be an acylic compound.

4- C-skeleton of citral: when citral is heated with potassium hydrogen sulfate, it cyclises to p-cymene, indicate that citral is a acylic compound,.

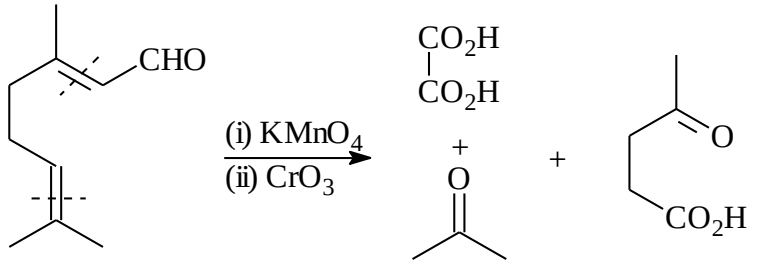
$C_{10}H_{16}0 \xrightarrow{KHSO_4} C_{10}H_{14}$ (p-cymene)

(II) Stuructre is para-cymene.



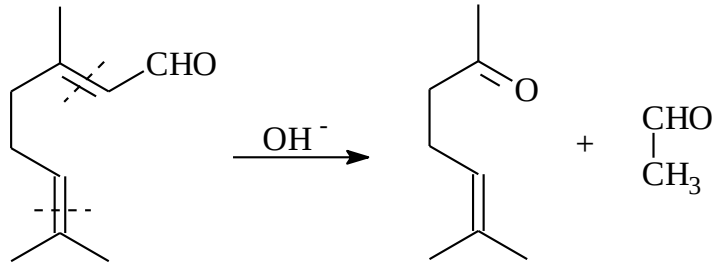
(I) **(II)**

5- Oxidation of citral with alkaline permanganate, followed by chromic acid, gives acetone, oxalic and laevulic acids.



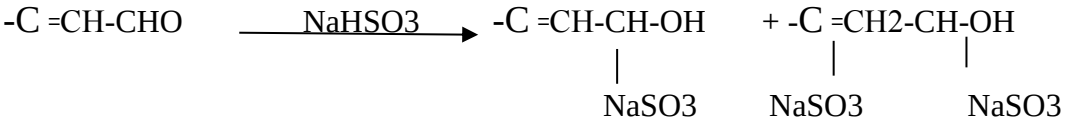
(III)

6- Citral on boiling with aqueous potassium carbonate converted into 6-methylhept-5-en-2-one (**IV**) and acetaldehyde. The formation of these products is readily explained that citral is product of aldol condensation of these two

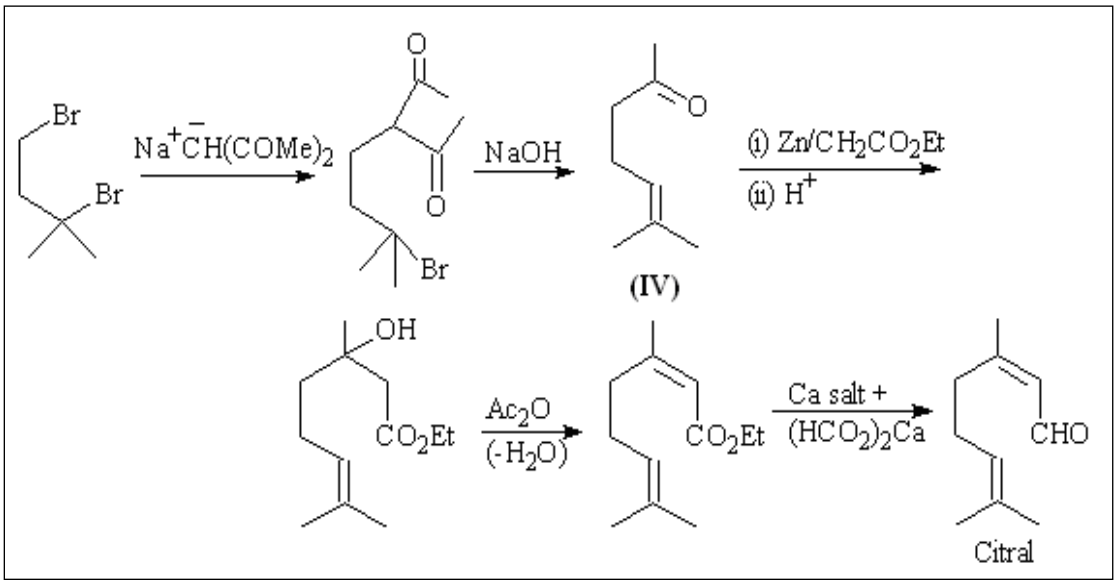


(III) **(IV)**

7-Citral is treated with sodium bisulfate to forms mono as well as bisulfite addition product, which indicates that one of the double bond is conjugated with carbonyl group.



8- The structure of citral was confirmed by the synthesis of methylheptenone, the conversion of this into geranic ester, which was then converted into citral by heating a mixture of the calcium salts of geranic and formic acids.



MENTHOL

Menthol is a 10 carban monocylic terpenes alcohol with a molecular wt. of 156 and chemical formula **$C_{10}H_{20}O$.** It is obtained from the fresh flowering tops of mentha piperita.(labiate) . The active constituent is menthol, menthone, and limonene.

SOURCE OF MENTHOL

Name of drug	Part of plant	Biological source	Active constituents	use
PEPPERMINT	Fresh flowering top	Mentha piperita (Labiatae)	menthol , menthone, limonene	Flavouring agent,carminative. Used in tooth paste. Tooth poweder, shaving cream

Properties of menthol. Menthol is a covalent organic compound made synthetically or obtained from peppermint or other mint oils. It is a waxy, crystalline substance, clear or white in color, which is solid at room temperature and melts slightly above. The main form of menthol occurring in nature is (-)-menthol, Menthol has local anesthetic and counterirritant qualities, and it is widely used to relieve minor throat irritation.

EXTRACTION AND ISOLATION.

Extraction and isolation of menthol is done through steam distillation. Steam from a boiler is allowed in the vessel from the bottom, above which the plant material is placed on a grid and the steam carries the vapours of the essential oil to the condenser where they are condensed and collected.

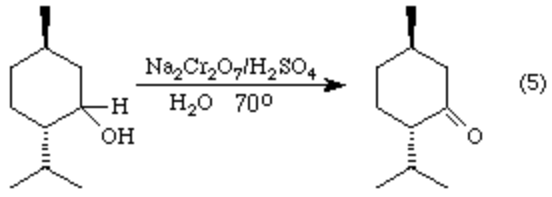
ELUCIDATION OF MENTHOL

Menthol, $C_{10}H_{20}O$.

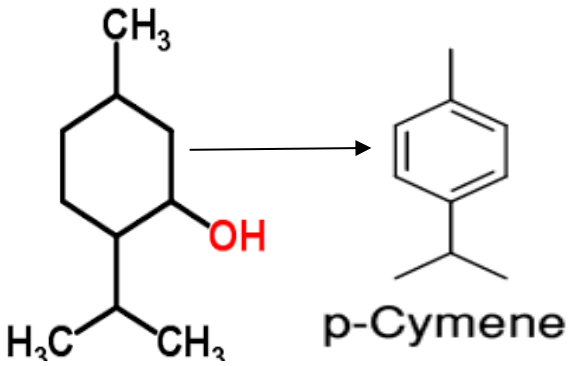
1- Molecular formula of menthol was determined as $C_{10}H_{20}O$.

2- On treatment with phosphorus pentachloride and phosphorus pentoxide menthol gave a chloride $C_{10}H_{19}Cl$ and a hydrocarbon $C_{10}H_{18}$ respectively, inferring that it is an alcohol.

3- Menthol was oxidized by chromic acid to a ketone, Menthone to prove that menthol contained a secondary hydroxyl group



4-On dehydration followed by dehydrogenation, it yields p- cymene.

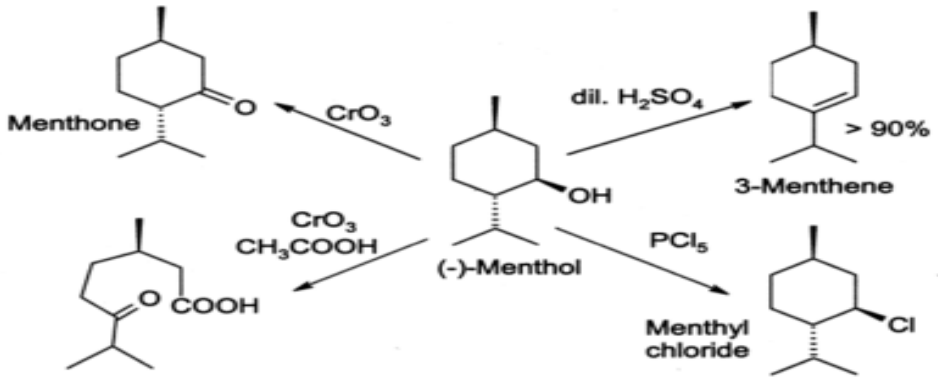


It Show the presence of cymene nucleus in menthol.

5-Menthone on oxidation with $KMNO_4$ yield keto acid $C_{10}H_{18}O_3$, which readily oxidized to 3- methyl adipic acid. These reaction can be explained by considering the following structure of menthol

$C_{10}H_{20}O \xrightarrow{KMnO4}$ COOH-CH_2-CH_2-CH(-CH_3)-CH_2-COOH(3-MAA)

6-Menthol was converted to para cymene (1-methyl 4-isopropyl benzene), which was also obtained by dehydrogenation of pulegone. Pulegone on reduction yielded menthone, which on further reduction yielded menthol



MENTHOL SYNTHESIS

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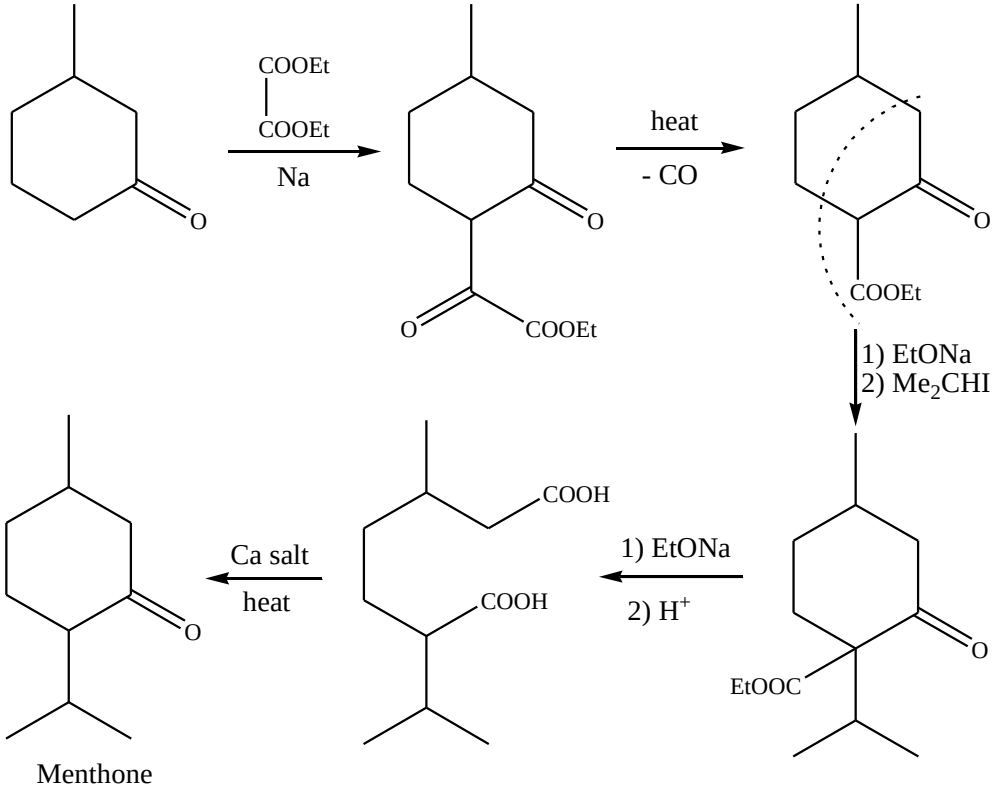
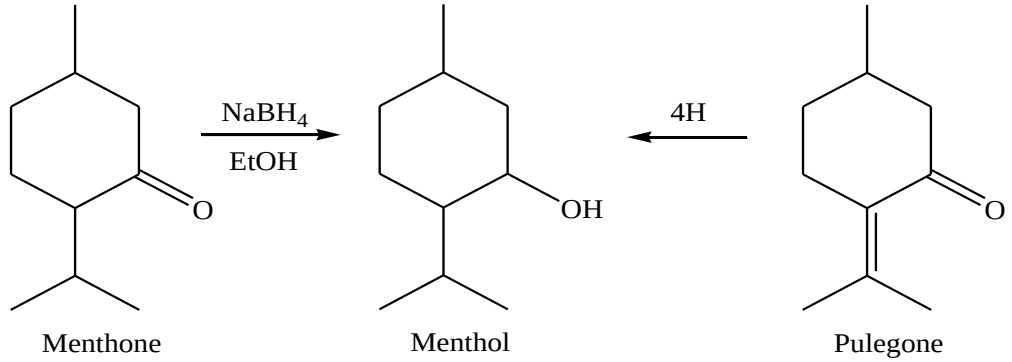


The reduction of menthone using $NaBH_4$ in alcohol or pulegone in the presence of reduced catalyst gave the corresponding menthol



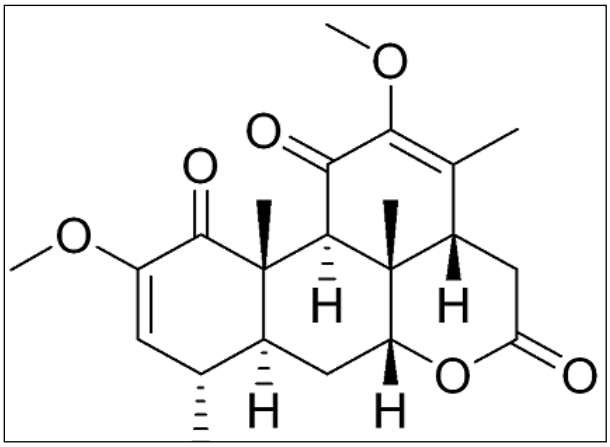
QUASSINOIDS

Quassinoids are degraded triterpene lactones (similar to limonoids) of the Simaroubaceous plant family grouped into C-18, C-19, C-20, C-22 and C-25 types. The prototypical member of the group, quassin, was first described in the 19th century from plants of the genus Quassia from which it gets its name.

It is one of the most bitter substance found in nature , with a bitter thresh old of 0.008 ppm and it is 50 times more bitter than quinine.

Among them C-20 quassinoids have especially been the subject of extensive investigations to dig their biological activities partially due to the discovery in the early 1970s by National Cancer Institute that some of these compounds possess marked antileukemic activity. The C-20 quassinoids can be further classified into two types, tetracyclic and the pentacyclic. The tetracyclic variety does not have oxygenationat C-20, while the pentacyclic quassinoids possess additional oxygenation at C-20 that allows for the formation of an additional ring. As studies on these compounds progress, however,other groups, especially C-19 quassinoids, have recently received more attention .Many of these quassinoids display a wide range of biological activities in vitro and/or invivo, including antitumor, antimalarial, antiviral, anti-inflammatory, antifeedant, insecticidal,amoebicidal, antiulcer and herbicidal activities.

It is white crystalline substance. It is bitter in taste and odorless



Protocol for isolation of Simalikalactone from *Quassia amara*

1kg dry leaves defatted for 24h in cyclohexane

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Filter, dry plant powder, boil in distilled water

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At half liquid volume, filter decoction, boil, reduce to half, cool

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Extract decoction twice with hot chloroform under reflux

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Cool, separate organic phase, evaporate to obtain extract.

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Dissolve extract in n-heptane-ethyl acetate-methanol-water (3:2:3:2)

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Remove upper phase containing pigments, lower phase concentrated

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Dissolve in ethyl acetate and wash with water, ethyl acetate removed under pressure

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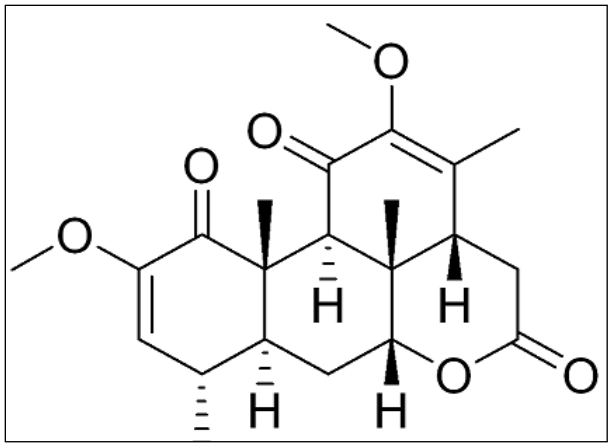
Extract containing concentrated quasinoids.

EXTRACTION AND ISOLATION'



Structure elucidation- . for methoxy , ketonic and lactone and alkene.