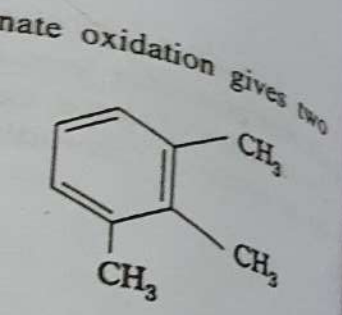
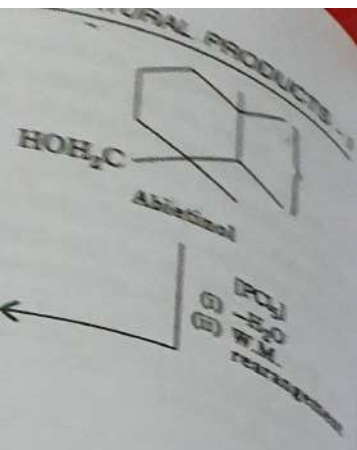
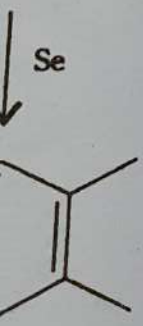
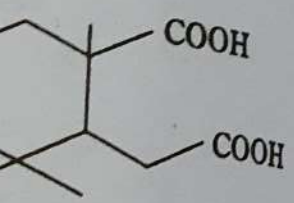




be having the following



Illitene

anhydride at above
was observed that at
it is just possible
then forms adduct.

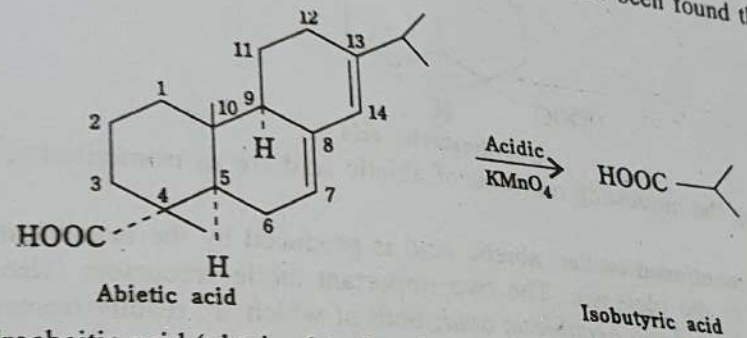
REFERENCES

However, abietic acid shows a maximum at 238 nm in the ultraviolet region which coincides with the structure of abietic acid having heteroannular conjugation (calculated value $214 + (4 \times 5) + 5 = 239 \text{ nm}$). From the oxidation of abietic acid in point 6 it is obvious that the ring A has no double bond, since if the double bond would have been present in ring A the latter must have been ruptured. Moreover, since the rings B and C are never obtained as such during oxidation these must be having double bonds i.e. in abietic acid one double bond is present in ring B and the other in ring C.

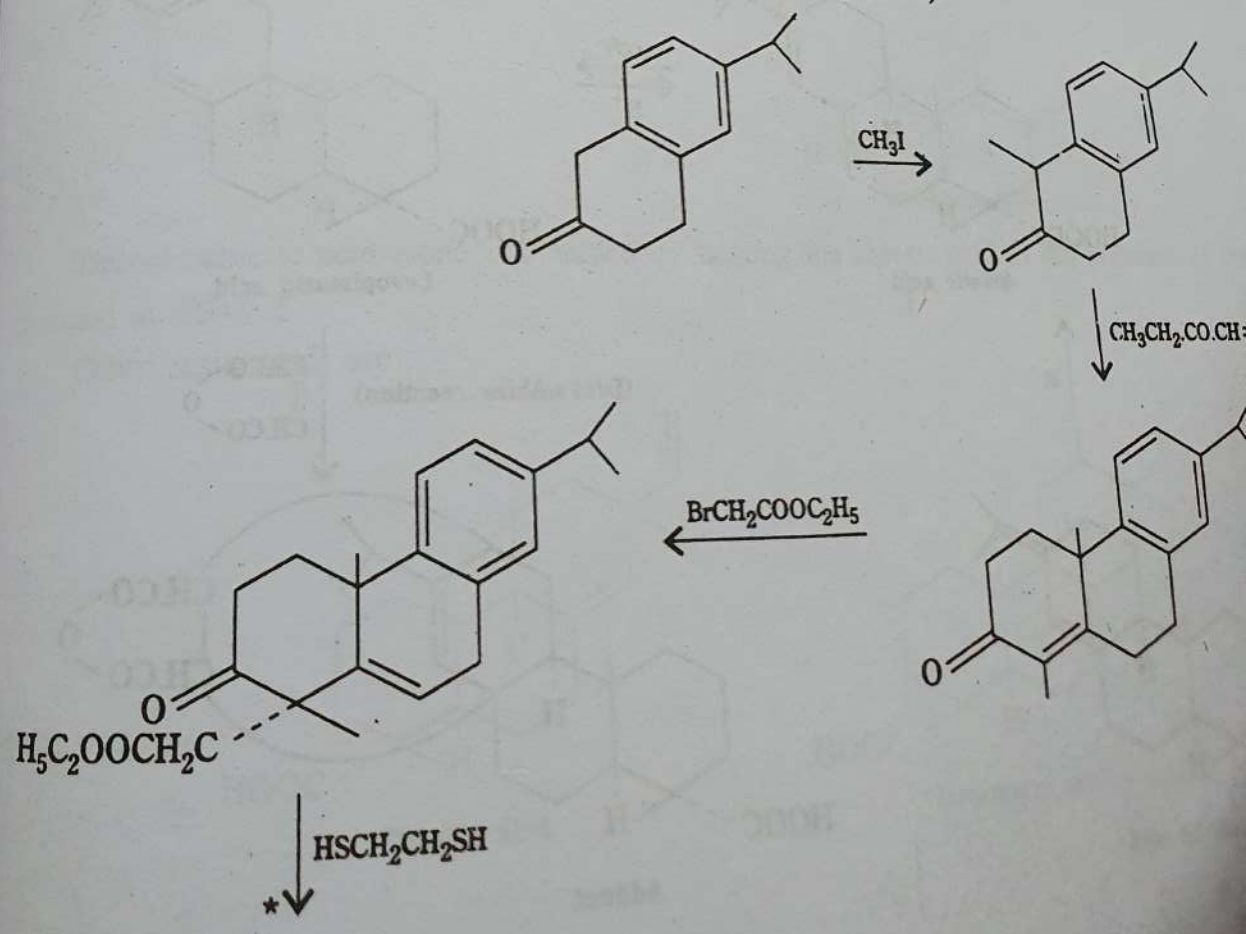
Abietic acid on acidic permanganate oxidation gives isobutyric acid ($\text{HO}_2\text{C} \cdot \text{CHMe}_2$) as one of the products which indicates that one of the double bonds must be present in ring C either between C₆ and C₇ or C₇ and C₈. The former possibility is discarded since it will give a homoannular conjugated structure, and hence one of the double bonds must be present between C₇ and C₈ which will assign position of the other double bond between C₁₃ and C₁₄.

8. Thus on the basis of the above points, abietic acid is assigned the following structure.

The stereochemistry of abietic acid has been elucidated and has been found the following absolute configuration.



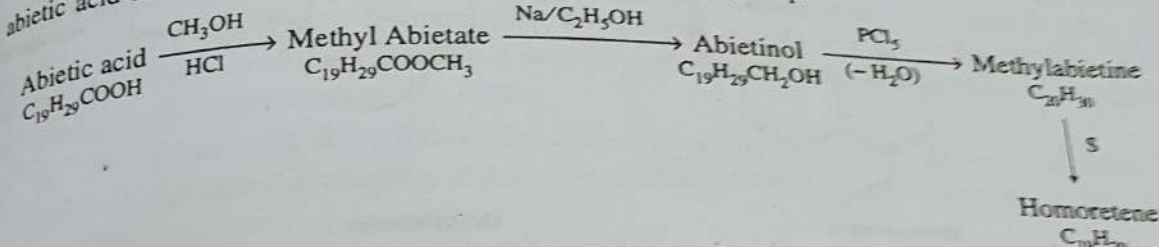
9. The dehydroabietic acid (obtained by heating abietic acid in the presence of palladium on charcoal at 250-275°C) has been synthesised by Stork and Schulenberg (1956).



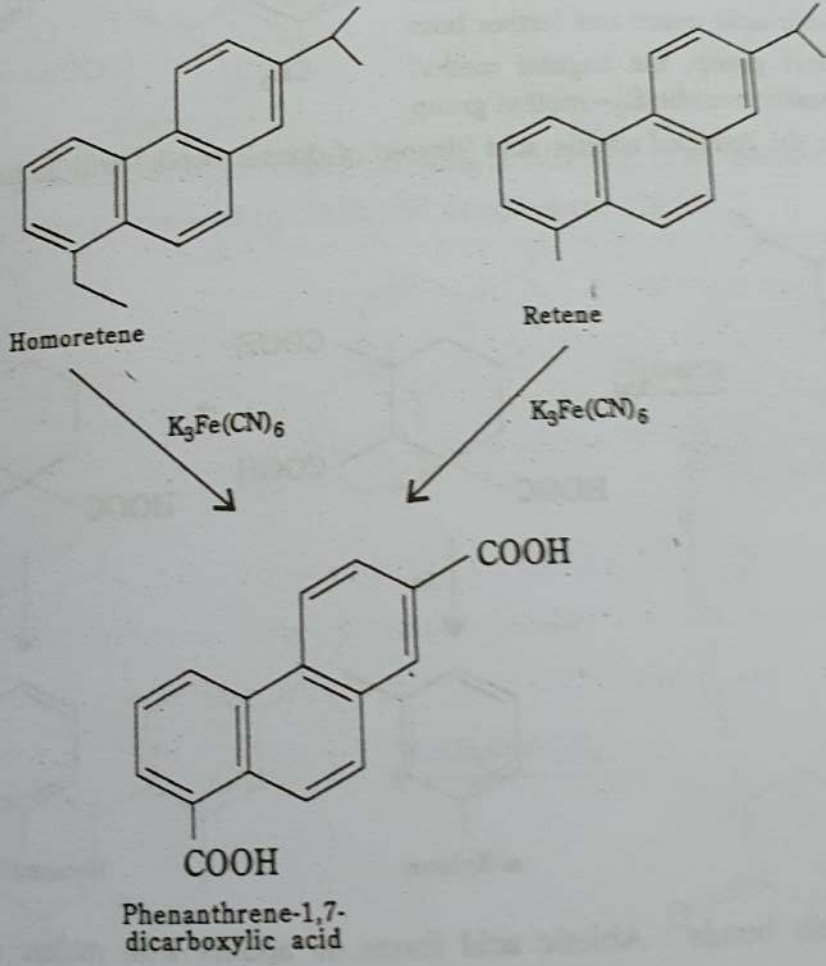
The formation of retene from the abietic acid suggests that the latter has retene carbon skeleton.

5. Now as the abietic acid has 20 carbon atoms the positions of 18 of which have been established by retene formation, one as tertiary carboxyl group (see point 2), the last i.e. 20th must be present as an angular methyl group which is expected to be lost during sulphur dehydrogenations. Hence for elucidating the exact structure of abietic acid we must know (i) the position of tertiary carboxyl group, (ii) the position of the angular methyl group, and (iii) position of the two double bonds (see point 2).

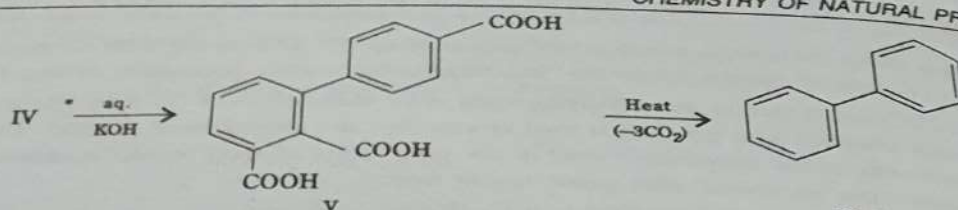
6. Position of the carboxyl group : Ruzicka *et al.* (1922) carried out the following set of reactions on abietic acid for establishing the position of tertiary carboxyl group.



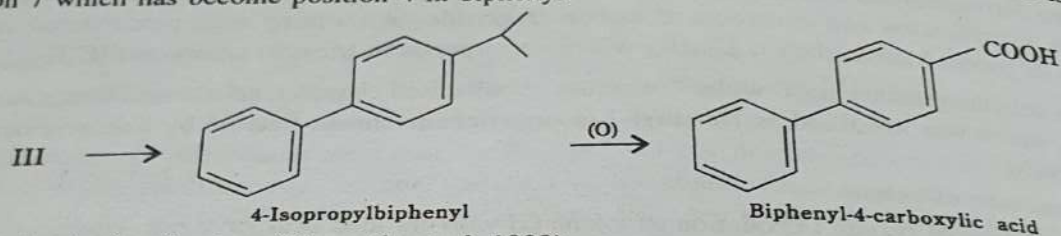
Now since homoretene $\text{C}_{19}\text{H}_{20}$ contains one CH_2 more than retene ($\text{C}_{18}\text{H}_{18}$), and on oxidation with alkaline potassium ferricyanide gives phenanthrene-1, 7-dicarboxylic acid which is also obtained from the oxidation of retene, the homoretene must be 1-ethyl-7-isopropylphenanthrene which has been confirmed by its synthesis (Haworth *et al.* 1932).



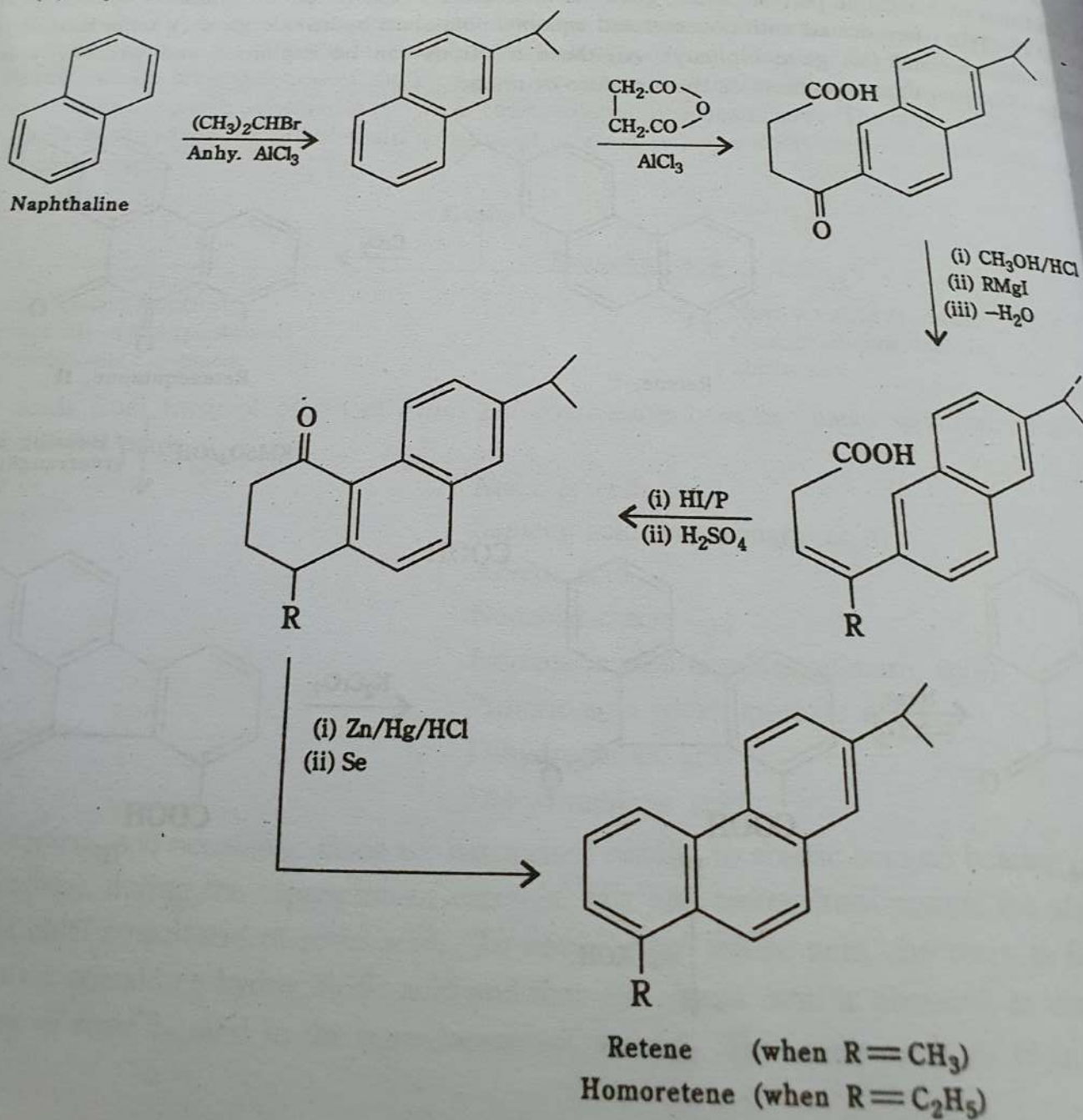
The position of ethyl group in homoretene suggests that the carboxyl and methyl groups are on the same carbon atom (C_1) in abietic acid. The formation ethyl group in homoretene can be explained by assuming that abietinol first undergoes dehydration and then Wagner-Meerwein rearrangement.

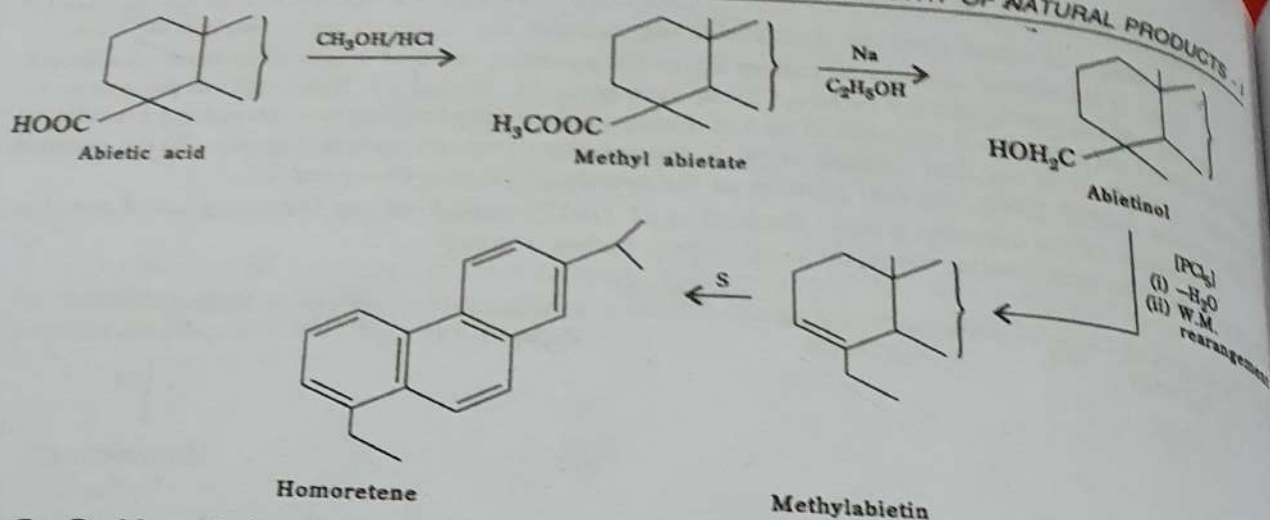


Position of the isopropyl group was established by fusing (III) with potassium hydroxide followed by oxidation to give biphenyl-4-carboxylic acid indicating that isopropyl group in retene is followed position 7 which has become position 4 in biphenyl.



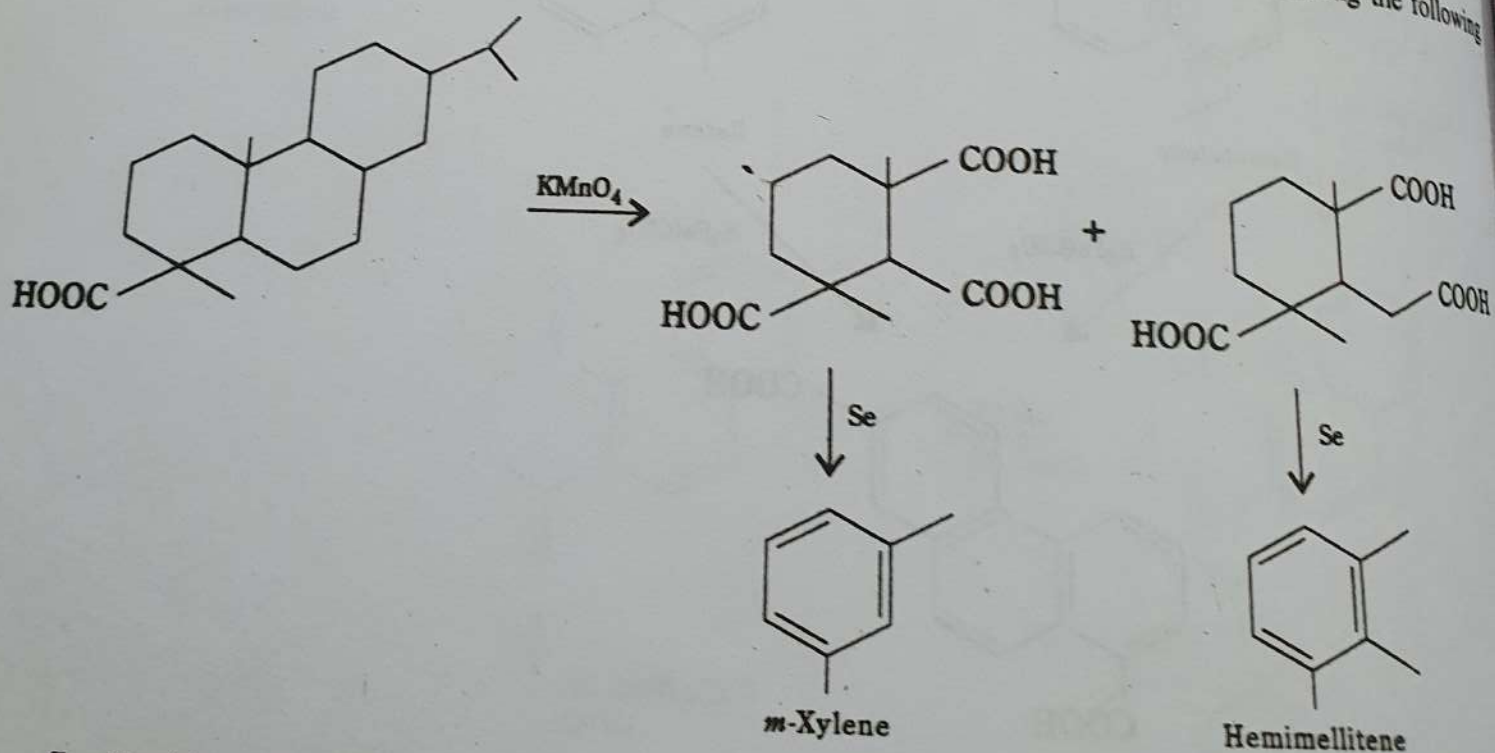
(ii) Synthesis of retene (Haworth *et al.* 1932)





7. Position of the angular methyl groups : Abietic acid on permanganate oxidation gives two tricarboxylic acids, one of which on selenium dehydrogenation gives, *m*-xylene and the other, 1, 2, 3-trimethylbenzene (hemimellitene).

Now since the above two hydrocarbons have C_1 -methyl group of abietic acid intact and further both of them have a *m*-methyl group, the angular methyl group must be in the *m*-position to the C_1 -methyl group of abietic acid and hence the reduced abietic acid (devoid of double bonds) will be having the following structure.



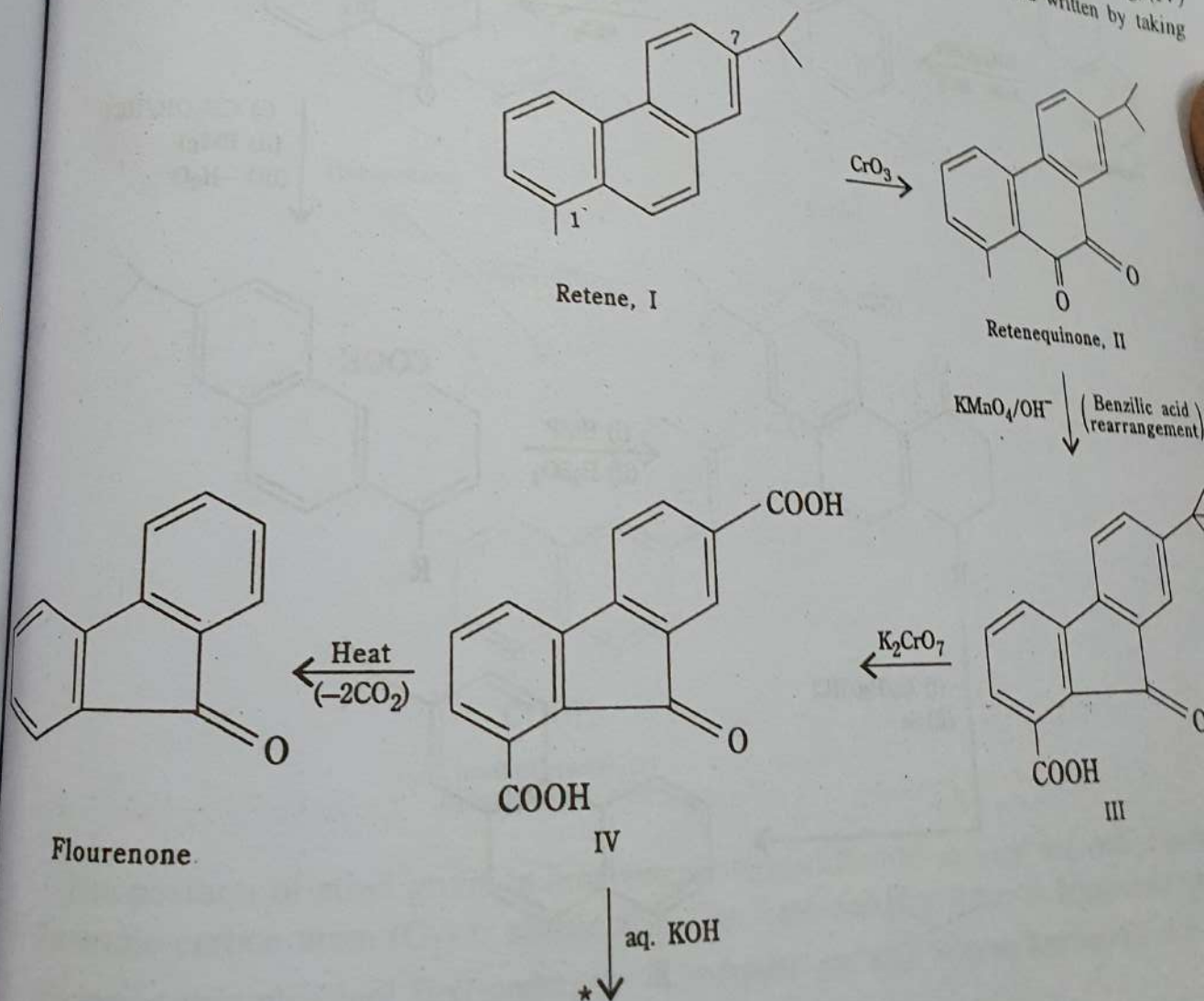
7. Position of the double bonds : Abietic acid forms an adduct with maleic anhydride at 100° , suggesting the presence of conjugation in abietic acid. However, later on it was observed that above 100°C , the levopimaric acid also forms adduct with maleic anhydride and thus it is just that under the conditions the abietic acid first isomerises to levopimaric acid which then forms

for sizing paper and in the manufacture of yellow laundry soap. The sodium salt is the disproportionated abietic acids (a mixture of dihydro, tetrahydro-, and dehydro-abietic acids, obtained by heating the abietic acid to about 225°) and is used as an emulsifying agent in the manufacture of GR-S-10 synthetic rubber. Ester gum (rosin esterified with glycerol) is used in varnishes and nitrocellulose lacquers. The reaction product of rosin with maleic anhydride is used in the manufacture of alkyl resins. In addition to these main applications, there are several other minor uses of rosin.

Constitution : 1. Its molecular formula is $C_{20}H_{30}O_2$.
2. By the usual tests, abietic acid is found to possess two double bonds (shown by the formation of tetrahydro derivative) and a tertiary carboxylic group (shown by effervescences with sodium bicarbonate, difficulty in esterification and evolution of carbon monoxide on warming with concentrated sulphuric acid). Thus its parent hydrocarbon is $C_{19}H_{34}$ which corresponds to tricyclic compound (C_nH_{2n-4}).
3. On dehydrogenation with sulphur, selenium or palladised charcoal, abietic acid forms an aromatic hydrocarbon which was identified as 1-methyl-7-isopropylphenanthrene (retene) by oxidative degradation (Bucherer, 1910).

4. Structure of retene

(i) **Degradation of retene :** Oxidation of retene (I) with chromic acid gave retenequinone (II) which, on oxidation with alkaline permanganate, gave the intermediate (III) which on oxidation with dichromate gave fluorenone (IV). (IV), when heated with concentrated aqueous potassium hydroxide gave (V). On heating, (IV) gave fluorenone and (V) gave biphenyl. All these reactions can be explained and written by taking 1-methyl-7-isopropylphenanthrene as the structure of retene.



ANNEXURE - B

SEMESTER - II (2017-119)

Paper XIV. C. = Natural Products -

TERPENOIDS

Most of this class of compounds occur in the plant Kingdom. Simpler terpenoids are the main constituents of the volatile essential oils, mostly used in the perfumery industry.

Basic structural units of the terpenoids are Isoprene, as the thermal decomposition of nearly all the terpenoids give isoprene as one of the products. (Wallach - 1887)

Details of Isoprene Rule etc. were part of your semester - II syllabus. So I am not going into details.

Naturally occurring terpenoid hydrocarbons have the molecular formula - $(C_5H_8)_n$. Value of (n) is used as a basis of classification. —

No. of C-atoms	Class
i) 10	Mono terpenoids. $(C_{10}H_{16})$
ii) 15	Sesquiterpenoids $(C_{15}H_{24})$
iii) 40	Tetra terpenoids (Carotenoids) $(C_{40}H_{64})$
iv) >40	Poly terpenoids. $(C_5H_8)_n \Rightarrow$ Rubber.

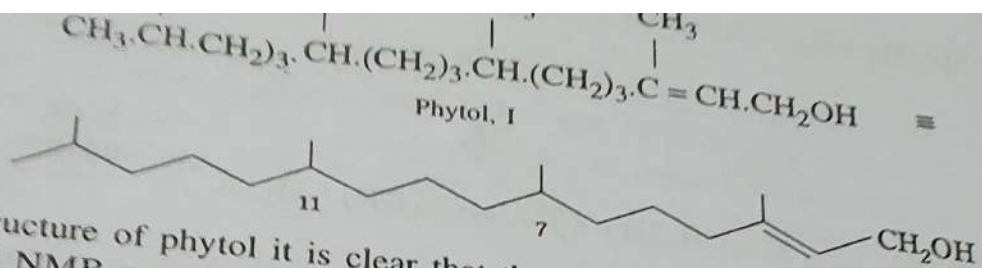
Isolation of Terpenoids

Plants containing essential oils usually have the greatest concentration at some particular time, e.g. jasmine at sunset.

Our Methods of Extraction of Terpenoids

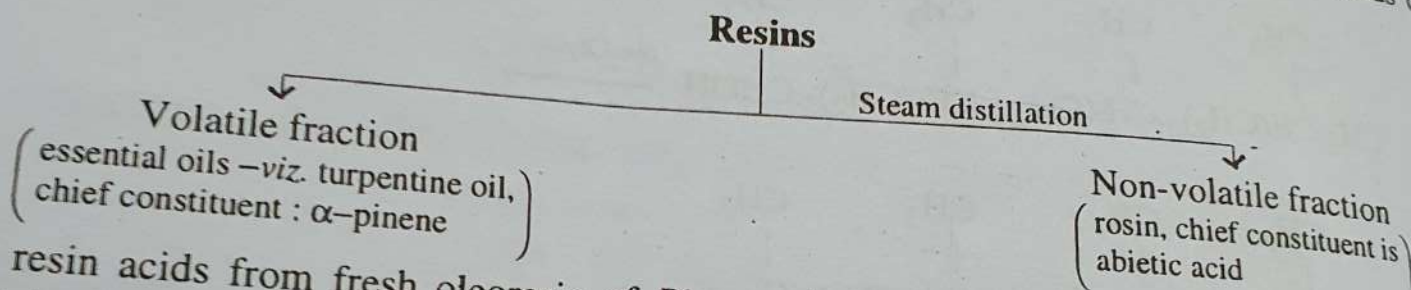
(i) Expression (ii) Steam distillation (iii) extraction by means of volatile solvents (iv) adsorption in purified fats. Method (v) is the most widely used process. Chromatography has been used both for isolation and separation of terpenoids. Gas chromatography has been particularly useful for isolating pure configurational forms of a given terpenoid from mixture produced by synthesis.

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From the structure of phytol it is clear that the double bond can give rise to *cis-trans* isomers with the help of NMR spectroscopy the configuration at the double bond was shown to be *cis*. Furthermore, the two asymmetric carbon atoms, viz. C₇ and C₁₁, can give rise to optical isomers. Natural phytol is weakly dextrorotatory.

(ii) **Abietic acid** : Abietic acid is the most important diterpenoid from the commercial point of view. It is the chief constituent of **rosin or colophony** which in turn is obtained by the steam distillation of resins. Resins, which are exudation of the pine trees, on steam distillation give volatile essential (turpentine oils) and nonvolatile substances known as rosin, colophony or resin acids. The main constituent of turpentine oils is α -pinene while the main constituent of rosin or resin acids (organic acids from resin) is abietic acid.



The resin acids from fresh oleoresin of *Pinus palustrica* have been estimated spectroscopically and consist of the following acids.

Percentage	Name of resin acid
30-35	Sapietic acid (levopimaric acid)
15-20	Abietic acid
15-20	Neoabietic acid
8	Isopimaric acid (isodextropimaric acid)
8	Pimaric acid (dextropimaric acid)
8	Dihydroabietic acid
4	Dehydroabietic acid

But since the sapietic and neoabietic acids are isomerised readily to abietic acid on heating (in the presence of acids), during the separation of essential oils and rosins from resins, they are considered as the chief constituent of resin acids. To obtain pure abietic acid, the rosin is dissolved in an alcoholic solution containing hydrochloric acid and then the abietic acid is obtained by crystallisation. A large amount of rosin is used in the manufacture of varnish. The crude sodium