

CHAPTER VIII

TERPENES

§1. **Introduction.** The terpenes form a group of compounds the majority of which occur in the plant kingdom; a few terpenes have been obtained from other sources. The simpler mono- and sesqui-terpenes are the chief constituents of the essential oils; these are the volatile oils obtained from the sap and tissues of certain plants and trees. The essential oils have been used in perfumery from the earliest times. The di- and tri-terpenes, which are not steam volatile, are obtained from plant and tree gums and resins. The tetraterpenes form a group of compounds known as the *carotenoids*, and it is usual to treat these as a separate group (see Ch. IX). Rubber is the most important polyterpene.

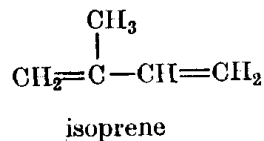
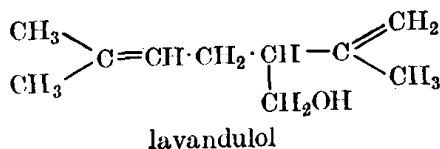
Most natural terpene hydrocarbons have the molecular formula $(C_5H_8)_n$, and the value of n is used as a basis of classification. Thus we have the following classes (these have already been mentioned above):

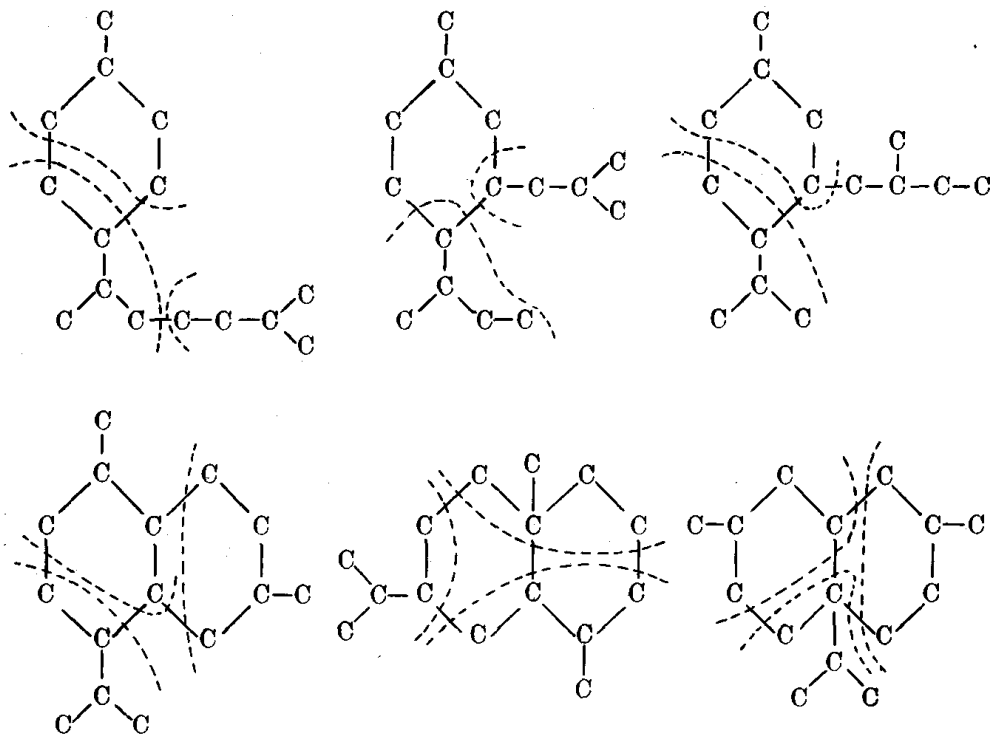
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| (i) Monoterpenes, $C_{10}H_{16}$. | (ii) Sesquiterpenes, $C_{15}H_{24}$. |
| (iii) Diterpenes, $C_{20}H_{32}$. | (iv) Triterpenes, $C_{30}H_{48}$. |
| (v) Tetraterpenes, $C_{40}H_{64}$ (these are the carotenoids). | |
| (vi) Polyterpenes, $(C_5H_8)_n$. | |

In addition to the terpene hydrocarbons, there are the oxygenated derivatives of each class which also occur naturally, and these are mainly alcohols, aldehydes or ketones.

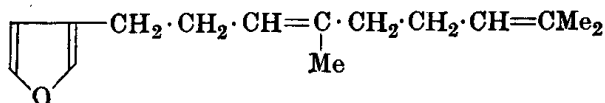
The term *terpene* was originally reserved for those hydrocarbons of molecular formula $C_{10}H_{16}$, but by common usage, the term now includes all compounds of the formula $(C_5H_8)_n$. There is, however, a tendency to call the whole group *terpenoids* instead of *terpenes*, and to restrict the name *terpene* to the compounds $C_{10}H_{16}$.

The thermal decomposition of almost all terpenes gives isoprene as one of the products, and this led to the suggestion that the skeleton structures of all naturally occurring terpenes can be built up of isoprene units; this is known as the **isoprene rule**, and was first pointed out by Wallach (1887). Thus the divisibility into isoprene units may be regarded as a necessary condition to be satisfied by the structure of any plant-synthesised terpene. Furthermore, Ingold (1925) pointed out that the isoprene units in natural terpenes were joined "head to tail" (the head being the branched end of isoprene). This divisibility into isoprene units, and their head to tail union, may conveniently be referred to as the *special isoprene rule*. It should be noted, however, that this rule, which has proved very useful, can only be used as a guiding principle and not as a fixed rule. Several exceptions to it occur among the simpler terpenes, e.g., lavandulol is composed of two isoprene units which are not joined head to tail; also, the carotenoids are joined tail to tail at their centre (see Ch. IX).





Recently some furano-terpenes have been isolated, *e.g.*, dendrolasin, which is believed to have the following structure (Quilico *et al.*, 1957); it contains three isoprene units joined head to tail.



§2. Isolation of monoterpenes and sesquiterpenes. Plants containing essential oils usually have the greatest concentration at some particular time, *e.g.*, jasmine at sunset. In general, there are four methods of extraction of the terpenes: (i) expression; (ii) steam distillation; (iii) extraction by means of volatile solvents; (iv) adsorption in purified fats (*enfleurage*). Method (ii) is the one most widely used; the plant is macerated and then steam distilled. If the compound decomposes under these conditions, it may be extracted with light petrol at 50°, and the solvent then removed by distillation under reduced pressure. Alternatively, the method of adsorption in fats is used. The fat is warmed to about 50°, and then the flower petals are spread on the surface of the fat until the latter is saturated. The fat is now digested with ethanol, any fat that dissolves being removed by cooling to 20°. The essential oils so obtained usually contain a number of terpenes, and these are separated by fractional distillation. The terpene hydrocarbons distil first, and these are followed by the oxygenated derivatives. Distillation of the residue under reduced pressure gives the sesquiterpenes, and these are separated by fractional distillation.

§3. General methods of determining structure. The following brief account gives an indication of the various methods used in elucidating the structures of the terpenes (see the text for details).

(i) A pure specimen is obtained, and the molecular formula is ascertained by the usual methods. If the terpene is optically active, its specific rotation

is measured. Optical activity may be used as a means of distinguishing structures (see, *e.g.*, §12).

(ii) If oxygen is present in the molecule, its functional nature is ascertained, *i.e.*, whether it is present as hydroxyl, aldehyde, ketone, etc. (*cf.* alkaloids, §4. XIV).

(iii) The presence of olefinic bonds is ascertained by means of bromine, and the number of double bonds is determined by analysis of the bromide, or by quantitative hydrogenation, or by titration with monoperphthalic acid. These facts lead to the molecular formula of the parent hydrocarbon, from which the number of rings present in the structure may be deduced.

(iv) The preparation of nitroschlorides and a study of their behaviour (see also the nitroso compounds, Vol. I).

(v) Dehydrogenation of terpenes with sulphur or selenium, and an examination of the products thereby obtained (see also §2 vii. X).

(vi) Measurement of the refractive index leads to a value for the molecular refractivity. From this may be deduced the nature of the carbon skeleton (see, in particular, sesquiterpenes). Also, optical exaltation indicates the presence of double bonds in conjugation (*cf.* §11. I).

(vii) Measurement of the ultraviolet, infra-red and Raman spectra. More recently X-ray analysis of crystals has also been used.

(viii) Degradative oxidation. The usual reagents used for this purpose are ozone, acid or alkaline permanganate, chromic acid and sodium hypobromite. In general, degradative oxidation is the most powerful tool for elucidating the structures of the terpenes.

(ix) After the analytical evidence has led to a tentative structure (or structures), the final proof of structure depends on synthesis. In terpene chemistry, many of the syntheses are ambiguous, and in such cases analytical evidence is used in conjunction with the synthesis. Many terpenes have not yet been synthesised.

MONOTERPENES

The monoterpenes may be subdivided into three groups: acyclic, monocyclic and bicyclic. This classification affords a convenient means of study of the monoterpenes.

ACYCLIC MONOTERPENES

§4. **Myrcene**, $C_{10}H_{16}$, is an acyclic monoterpene hydrocarbon which occurs in verbena and bay oils. It is a liquid, b.p. 166–168°. Catalytic hydrogenation (platinum) converts myrcene into a decane, $C_{10}H_{22}$; thus myrcene contains three double bonds, and is an open-chain compound. Furthermore, since myrcene forms an adduct with maleic anhydride, two of the double bonds are conjugated (Diels *et al.*, 1929; see the Diels–Alder reaction, Vol. I). This conjugation is supported by evidence obtained from the ultraviolet spectrum of myrcene (Booker *et al.*, 1940). These facts, *i.e.*, that myrcene contains three double bonds, two of which are in conjugation, had been established by earlier investigators (*e.g.*, Semmler, 1901). Ozonolysis of myrcene produces acetone, formaldehyde and a ketodialdehyde, $C_5H_8O_3$, and the latter, on oxidation with chromic acid, gives succinic acid and carbon dioxide (Ruzicka *et al.*, 1924). These results can be explained by assigning structure I to myrcene. In terpene chemistry it has become customary to use conventional formulæ rather than those of the type I. In these conventional formulæ only lines are used; carbon atoms are at the junctions of pairs of lines or at the end of a line, and unsaturation is indicated by double bonds. Furthermore, the carbon skeleton is usually