

THE TERPENES

VOLUME I

*The Simpler Acyclic and Monocyclic Terpenes
and their Derivatives*

BY

J. L. SIMONSEN

SECOND EDITION REVISED

BY

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PREFACE

Although the constituents of the various essential oils have been adequately dealt with in the English language by Parry, *The Chemistry of Essential Oils*, and by Finnemore, *Essential Oils*, with the exception of Brooks' monograph, *The Non-Benzenoid Hydrocarbons*, which covers a somewhat wider field, no book is available which deals with the chemistry of the terpenes. An attempt has been made in this volume to supply this deficiency, a description being given of the more important properties of the simpler acyclic and monocyclic terpenes and their derivatives. In order to keep the size of the book within reasonable limits it has been found necessary to include only those terpenes, containing ten carbon atoms, which occur in nature, although exception has been made in a few cases (sylvestrene, carvenone, terpin hydrate, etc.). Special attention has been directed to the methods used in the determination of constitution and synthesis, and it is hoped that the information which has been collected may stimulate research by British chemists in this important branch of organic chemistry, which owes so much to the pioneering investigations of Sir William Tilden and the synthetic researches of W. H. Perkin, jun.

It is proposed in a succeeding volume to discuss the dicyclic terpenes and sesquiterpenes.

The writer is indebted to Dr T. A. Henry for reading much of the book in manuscript and for many valuable suggestions; he desires also to acknowledge the valuable assistance rendered by Professor C. S. Gibson, O.B.E., and Dr R. S. Cahn in the reading of the proofs. He has further to thank Professor J. Read and the Council of the Chemical Society for their permission to reproduce the table on page 213.

J. L. S.

BANGOR

January 1931

PREFACE TO SECOND EDITION

The enhanced interest displayed in recent years in the chemistry of natural products has made it desirable to issue a revised edition of "The Terpenes." No attempt has been made to alter either the plan or the scope of the book. The literature, so far as the difficulties arising out of the war have permitted, has been consulted up to the end of 1945 and it has proved possible to include also some work of later date.

We are greatly indebted to Lt. Col. H. J. Holman, B.Sc., A.R.I.C. for undertaking the laborious task of checking all the literature references and also for the preparation of the author and subject indexes.

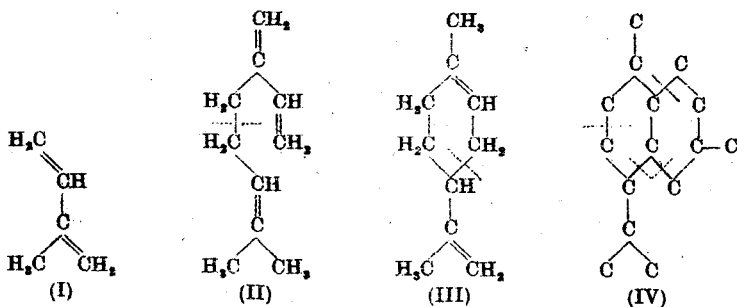
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May 1946

INTRODUCTION

The essential oils of plants, which are present mainly in the flowers, fruits and leaves and also occasionally in the wood (camphor wood, sandalwood), consist of a complex mixture of ingredients comprising acyclic, alicyclic and aromatic substances. They are separated as a rule by distillation in steam, in which they are volatile, or by extraction with volatile or fixed solvents (enfleurage). In no case is the product so obtained homogeneous, but occasionally one ingredient may predominate, as is the case with oil of cloves, which consists almost entirely of eugenol.

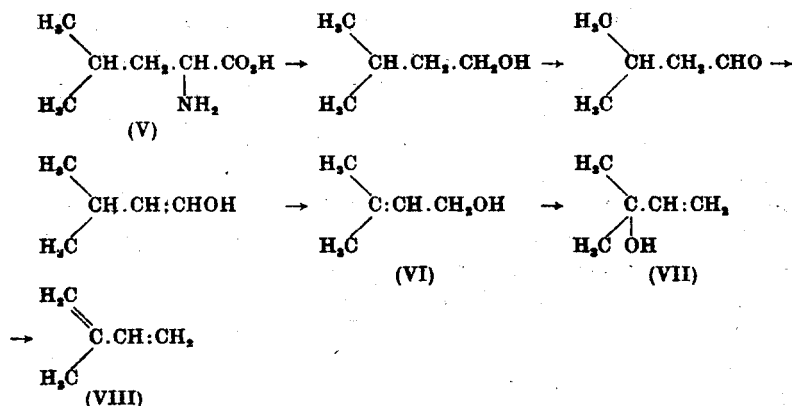
A consideration of the carbon skeleton of the acyclic and cyclic hydrocarbons and their derivatives, whether simple or complex, has revealed the interesting feature that they contain a repeated isopentane skeleton and that they may be regarded as derivatives of *isoprene*, C_5H_8 (I) (see below). Thus, for example, the simple hydrocarbons, *myrcene* (II) and *limonene* (III) may be constructed by the fusion of two isoprene nuclei, whilst sesquiterpenes (cadinene type (IV)) contain three such nuclei.



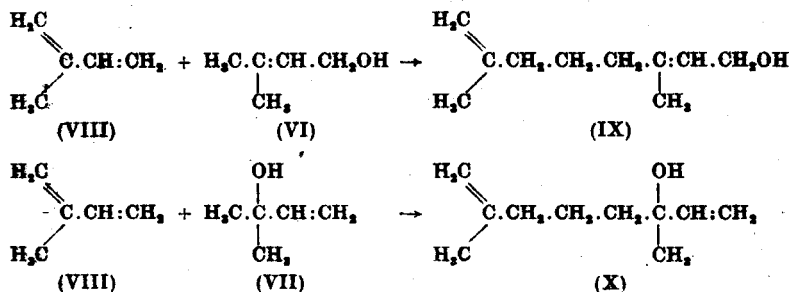
The so-called "isoprene rule" deduced from these observations has proved a most valuable working hypothesis for the elucidation of the structure, not only of the simpler terpenes, but also of the more complex sesquiterpenes and polyterpenes. It can, however, only be regarded as a working hypothesis, since several anomalous examples are known, including one which has been observed in the sesquiterpene series.* It does not, therefore, appear unlikely that other exceptions to the rule will be encountered.

* Gillam, Lynas-Gray, Penfold and Simonsen, *J.C.S.* 1941, p. 80.

The actual precursor of the terpenes is still obscure, and the part which they play in the plant metabolism unknown. Two views, which may ultimately prove to be complementary, have been advanced regarding their formation. Favorsky and Lébédéva* suggest that the parent substance of the terpenes is the amino-acid, *leucine* (V), formed by the degradation of proteins, which is converted into isoprene (VIII) by the reactions shown below:



The condensation of isoprene (VIII) with (VI) would then lead to *geraniol* (IX), or with (VII) to *linalool* (X). The facile polymerisation of isoprene to terpene hydrocarbons, alcohols and sesquiterpenes has been recorded by Wagner-Jauregg† and Lennartz.*



* *Bull. Soc. chim.* 1939 [v], 6, 1350.

† *Ber.* 1943, 76, 831.

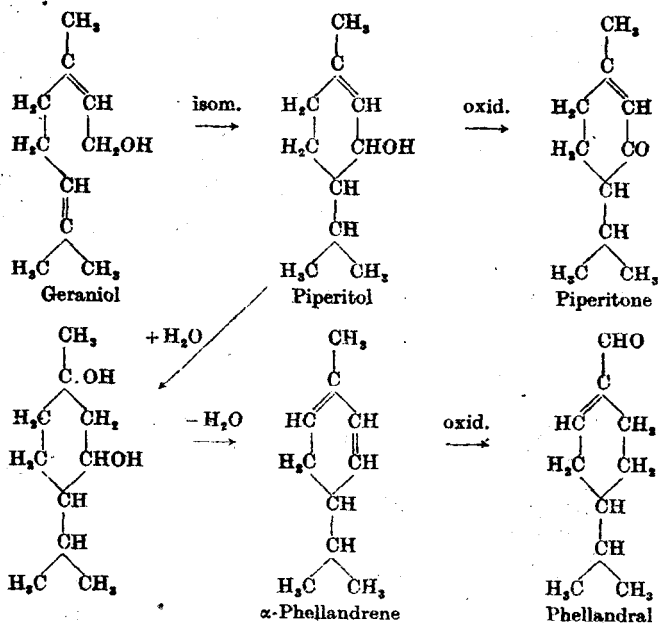
† *Annalen*, 1932, 496, 52.

The suggestion that *l*-leucine might be the precursor of the terpenes had been made previously by Leeman,* on the cytological evidence that the destruction of protoplasm precedes the formation of terpenes in certain plants. This simple mechanism for the formation of geraniol from leucine is of interest since, as pointed out by Read,† the alcohol possesses an unusual molecular structure; it contains a primary alcohol group activated by an $\alpha\beta$ -ethylenic linkage ($-\text{C}:\text{CH}.\text{CH}_2\text{OH}$) situated in close



proximity to a second active group $\left(\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \right) > \text{C}:\text{CH}-$ also containing an ethylenic linkage. Owing to the great mobility of this grouping geraniol can be regarded as the parent substance of a great variety of cyclic terpenes and related bodies, the joint occurrence of which has been observed in plant products. The

(A) α -Phellandrene and related substances

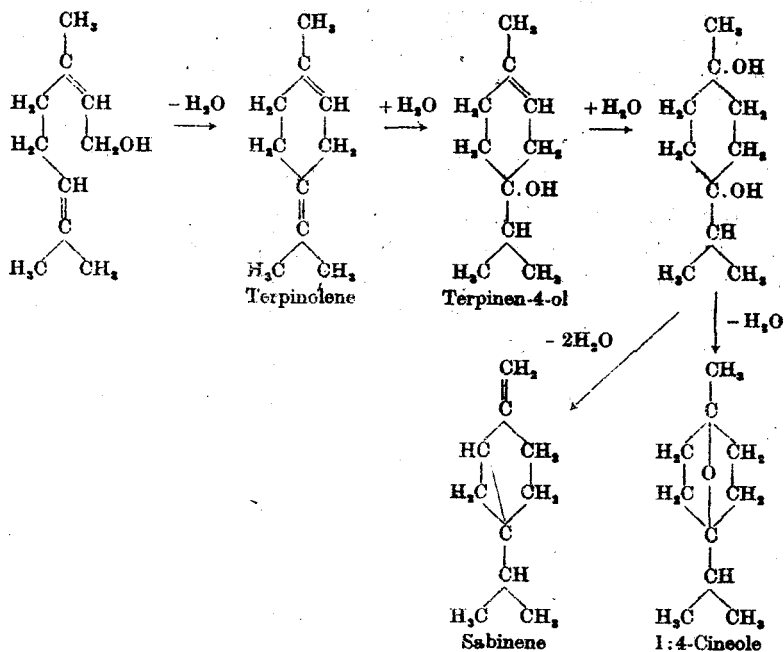


* *Nature*, 1929, 124, 946.

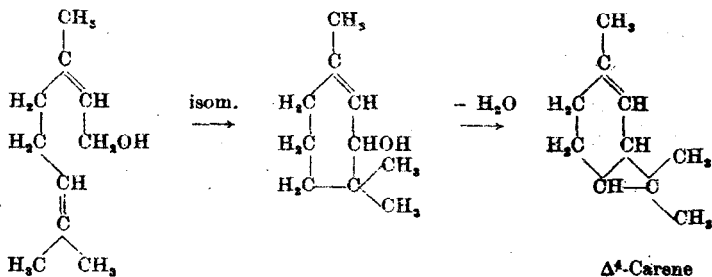
† *J.S.C.I.* 1929, 43, 786.

examples (A), (B) and (C), with some additions, are quoted from Read's memoir. (Substances to which no names are attached have not been found to occur in nature.)

(B) *Sabinene and related substances*



(C) Δ^4 -Carene*

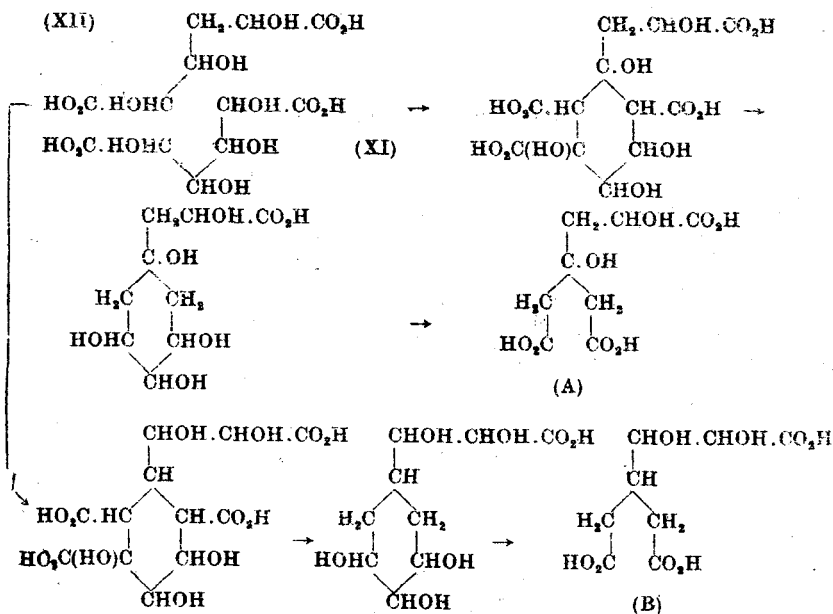


* An alternative and possibly simpler method involves the dehydration of piperitol (compare p. 287).

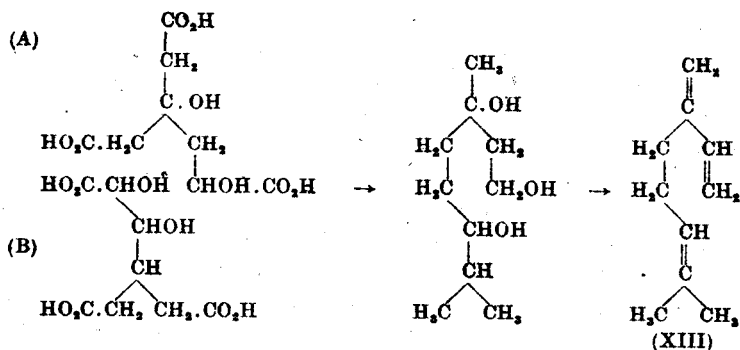
These examples, which could be extended to include also α -pinene, limonene, α -terpineol, etc., are sufficient to indicate that, starting from geraniol, it is possible by a single series of reactions to account theoretically not only for the formation, but also for the joint occurrence, of a number of terpenes and their derivatives.

It is not certain how far Leeman's observation can be generally applied and it is therefore not possible to reject a carbohydrate source. The most complete theory for a carbohydrate origin of the terpenes is due to Hall.* This may perhaps be most simply illustrated by his scheme for the formation of myrcene (XIII) from one molecule of *saccharic acid* (XI) and one of *meta-saccharonic acid* (XII). By variations of the process outlined below, the postulated intermediates (A) and (B) can give rise to all the known naturally occurring terpenes.

Little is known as to the function of terpenes in the plant economy. Whilst the odoriferous principles of the leaves and



* *Chem. Reviews*, 1933, 13, 479; 1937, 20, 305; compare Singleton, *J.S.C.I.* 1931, 50, 989.



flowers can be assumed to be of use in the attraction of insects to the pollen, no such property can be ascribed to the oils present in other parts of the plant. In the latter case it is possible that they act as a protection against insect attack, but it would appear more satisfactory, in the absence of definite proof, to regard essential oils as waste products of the plant metabolism. Tyndall's theory that they have a "heat screening" effect is devoid of experimental justification.*

Attention may be directed here to one side of the study of essential oils which has aroused interest,[†] namely, the possibility of the use of these highly characteristic constituents as an aid to the differentiation of plant species. As the outcome of the important work of Smith on the constituents of the oils from the different species of *Eucalyptus*, Baker and Smith[‡] largely based their classification of the genus on the chemical characteristics of the oil derived from each species. The use of this method as an aid to the ordinary morphological classification has been advocated by Simonsen,[§] and would appear to be especially applicable in the case of grasses, such as the *Cymbopogons*, where the ordinary botanical methods have encountered great difficulties. Systematic work in this field with the refined methods now available should open up a wide and profitable field of research.

* Nicol, *Perfum. essent. Oil Rec.* 1936, 27, 328.

† Barger, Presidential Address, Brit. Assoc., Section B, 1929; Hill, Presidential Address, Brit. Assoc., Section K, 1930; Parry, *Perfum. essent. Oil Rec.* 1941, 32, 267; Penfold, *ibid.* 1942, 33, 78.

‡ *A Research on the Eucalypts and their Essential Oils.*

§ Presidential Address, Indian Science Congress, 1928.

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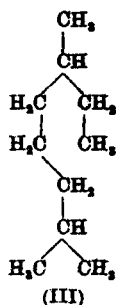
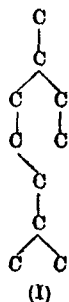
PART I

THE SIMPLER ACYCLIC TERPENES AND THEIR DERIVATIVES

INTRODUCTION

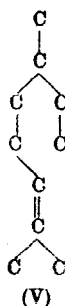
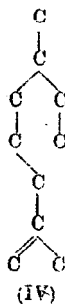
Although the acyclic terpenes and their derivatives, which occur in nature, are somewhat limited in number, they possess a wide scientific and technical interest. The fundamental investigations in this field were made during the decade 1890-1900 by Tiemann and Semmler in Germany and by Barbier, Bouveault and their collaborators in France. As a perhaps not unnatural outcome of the difficulty of this pioneering work, a controversy arose between these two schools. Subsequent research has shown that, although there may have been errors in detail, the work was in the main correct and the conflict in reality illusory. It lies beyond the scope of this monograph to discuss fully this controversy, and those interested should refer to the account given by one of the participants.*

As already mentioned, the simpler acyclic terpenes may be regarded as being formed by the union of two isoprene nuclei and may be represented by the skeleton formula (I), which, it will be observed, would pass by ring closure into the *p*-cymene structure (II). They can therefore be considered to be derivatives of the paraffinoid hydrocarbon 2:6-dimethyloctane (III).



* Semmler, *Die Ätherischen Öle*, vol. I.

In such derivatives as contain one ethylenic linkage, this linkage is apparently, with one exception only, situated between the 1:2 or the 2:3 carbon atoms, so that they have the structures represented by the formulae (IV) and (V), designated by Semmler the dipentene (*isopropenyl*) and terpinene (*isopropylidene*) forms respectively.



Much of the early controversy ranged round the position of this ethylenic linkage and in spite of numerous investigations the situation cannot yet be regarded as completely clarified. Since the majority of substances which have been examined are oils, adequate proof of homogeneity has been lacking, but the final conclusion reached, with which the authors concur, is that in nearly all cases these oils consist of a mixture of the *isopropenyl* and *isopropylidene* forms in varying proportions. The proportion in which each form is present has, as a general rule, been determined by oxidation, the yield of acetone and formaldehyde being estimated. In a few cases crystalline and apparently homogeneous solids have been examined and these would appear also to be inseparable mixtures. This has been shown to be the case with citronellal semicarbazone (p. 74), and two further interesting examples are dehydrogeranic acid and α -santalylmalonic acid.

Both natural and synthetic *dehydrogeranic acids* give on ozonolysis acetone and formaldehyde, the yield of acetone being approximately 60 per cent.* It is natural to deduce therefore that this acid is a mixture of (VI) and (VII).

* Cahn, Penfold and Simonsen, *J.C.S.* 1931, p. 3134; Kuhn and Roth, *Ber.* 1932, 65, 1285.