water. For small quantities such as may be found in U. S. P. chloroform as an impurity, we prefer this test due to its simplicity.

It will be noted that other ketones give, in the presence of chloroform, a reaction with Nessler's reagent that is similar to the acetone reaction. The colors, however, as a rule are paler, shading toward white. The reaction is therefore not qualitatively positive for acetone, but for ketones in general.

Acetone alone, in water solutions, of less than 5 per cent concentration, will form a permanent white or pale yellow precipitate with Nessler's reagent. Higher aliphatic and aromatic ketones give the reaction in higher concentratons as well.

Aldehydes alone, and in the presence of chloroform, yield by this test an orange precipitate immediately becoming dark red and finally black. Chloroform alone, in aqueous solution, yields after ten minutes, a red turbidity that eventually becomes a red and finally a black precipitate. This action of chloroform alone is due doubtless to alkaline hydrolysis of the chloroform to potassium formate, which subsequently reduces the mercury salt to metallic mercury.

It is believed that the test with Nessler's reagent, with the immediate production of a turbidity or precipitate, is the most satisfactory means of detecting the presence of aldehydes and ketones in chloroform.

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(1) Middleton and Hymas, *Analyst*, 56 (1931), 238.
(2) Gros, *Ann. fals.*, 18 (1925), 39–42.
(3) Kolthoff, *Pharm. Weekblad*, 55 (1918), 1021–1029.
(4) Van Slyke, *J. Biol. Chem.*, 32 (1917), 455–493.
(5) Pittarelli, *Paliclinico*, 28 (1921), 621; through *J. Am. Med. Assoc.*, 76 (1921), 1803.

August 17, 1932.

PHYTOCHEMICAL TERMINOLOGY.*,[1]

BY EDWARD KREMERS AND COLABORERS.

Terpene.[2,3]

The object of this brief essay is not to define the word terpene, neither to outline a classification of the hydrocarbons known as terpenes. All that is intended is to show the reader who is not a specialist in the field how the word has

* Section on Historical Pharmacy, A. PH. A., Toronto meeting, 1932. See also 21 (1932), 252.

[1] For introductory remarks, see THIS JOURNAL, 21 (1932), 252.

[2] Copies of a first draft of this paper were submitted to a number of persons whose criticism was invited. Without going into details, the reader may be interested in two comments quite opposite in tendency. The first of these is by Dr. Francis D. Dodge. His comments are herewith quoted:

"In regard to the article on 'Terpenes,' the older classifications, based on incomplete knowledge have of course only historical interest. Even Wallach's classification seems to me of doubtful value. For example, Limonene and Dipentene appear at present to be identical in structure.

"The properties given under Limonene could apply only to one compound, not to a group.

"One might set up some such classification as single ring, double ring, triple ring, etc., but I fail to see any advantage in it.

originated and how it has changed its meaning with changes in nomenclature and even within the same system of nomenclature. To the student who endeavors to acquire an insight into the so-called terpene literature this change in the meaning of the word is confusing. Moreover, the confusion is not made clear by any one of the several dogmatic definitions found in textbooks. There is no thought of even indicating to the reader which of the several definitions or modifications thereof he should accept for himself. As for the writer, while he uses the word in its conventional sense as a matter of convenience, he long ago arrived at the conclusion that the group name terpene, however defined, had better be eliminated

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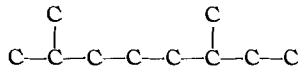
"In my opinion, the term Terpene should be applied to those hydrocarbons $C_{10}H_{16}$, which occur in the volatile oils, and contain the atomic grouping:



which is also characteristic of the open chain, Geraniol-Citral-Linalool group.

"To call all $C_{10}H_{16}$ compounds Terpenes seems to me unnecessary and undesirable.

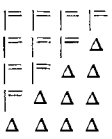
"Nor does it seem advisable to have the term Terpene cover the $(C_5H_8)_n$ groups.

"I would approve the following classification:

1. Hemi Terpene—C_5H_8—Isoprene (1 member)
2. Terpenes $C_{10}H_{16}$
3. Sesqui-terpenes $C_{15}H_{24}$
4. Diterpenes $C_{20}H_{32}$

"A sub-classification of Terpenes seems unnecessary, and a sub-classification of Sesquiterpenes, which may later be advisable, must be postponed until further knowledge has been accumulated."

As early as 1904 (O. Schreiner, The *Sesquiterpenes*, page 17) and, some years before that date, the writer pointed out the practical results accruing from a classification of the sesquiterpenes according to the configurations



This was years before our present structural knowledge had been acquired in this field. The early adoption of this classification by European chemists, also more recent developments have proven the soundness of the reasoning involved. As a matter of fact even at that time it involved nothing really new but the application, to this group, of well-understood considerations.

[3] The other comment is from the pen of Dr. Eduard Gildemeister. Parts of it are here given:

"In Ihrem Manuskript ueber die Terpene schreiben Sie, dass Beilstein dieses Wort schon frueher gebraucht hat als Kekulé. Nun bleibt aber doch noch die Moeglichkeit, dass der Ausdruck von Kekulé herruehrt. Soweit ich mich erinnere, war auch Wallach dieser Ansicht. Ich vermute, dass Beilstein, ehe er im Jahre 1866 seine Professur am technologischen Institut in Petersburg antrat, in Bonn gearbeitet hat. Als naemlich Beilstein i. J. 1887 das Bonner Laboratorium besuchte, wurde er von Anschuetz als alter Laboratoriumskollege begruesst. Da mag er dann bei seinen Arbeiten das Wort Terpen von Kekulé gehoert haben, das er dann in der von Ihnen erwaehnten Abhandlung gebraucht hat. Ob dem nun wirklich so ist, koennten Sie am besten von Anschuetz, dem alten Mitarbeiter Kekulés, selbst, der jetzt in Darmstadt (Hermannstrasse 16) lebt, erfahren.

"Die Auseinandersetzung darueber, wie die verschiedenen Autoren den Begriff Terpen gefasst und angewandt haben, sind recht interessant, aber auch ziemlich verwickelt, und deshalb ist es dankbar zu begruessen, dass Sie das Problem mit Erfolg in Angriff genommen haben."

from our organic systematics if not from our vocabulary. The individual "terpenes," old style as well as new style, should be considered as representatives of the hydrocarbons at large rationally classified. Such a classification, built upon the ideas of Kekulé, does away with the obsolete terminology of aliphatic and aromatic, and is based on the degree of saturation as its first principle, and secondarily upon the chain or cyclic character of the hydrocarbons.[1]

The German word *Terpen*, Eng. terpene, is no doubt, derived from the German word *Terpentin*, Eng. turpentine, Fr. *térébenthine* and is commonly attributed to Kekulé[2] who is said to have introduced it as a generic term for hydrocarbons $C_{10}H_{16}$ to take the place of such words as terebene,[3] camphene,[4] etc., which,

[1] See E. K. *Classification of Carbon Compounds. Bull. Univ. of Wisc.* No. 528, 1912, reprinted 1924.

[2] The following passage from Kekulé's *Lehrbuch d. org. Chemie* (1866), Band II, page 437, is quoted by Gildemeister and Hoffmann [*Die aeth. Oele* 3te Aufl. Bd. I (1928), page 91]: ".... anderseits das Terpentinoel und die zahlreichen mit ihm isomeren Kohlenwasserstoffe, welche im allgemeinen als Terpene bezeichnet werden moegen." However, if priority is dependent on publication, the credit for having used the work first should, possibly, be attributed to Beilstein, for in an article published in 1864 in the *Annalen* [Vol. 133, page 35], he makes the following statement: "Die andere Beimengung unseres Xylols besteht offenbar aus einer aeusserst geringen Menge eines Terpens." A terpene boiling between 270° and 300° (*sic*) is referred to. Again in 1865 he uses the word: "Sehr bald gelang es, zwei ganz constant bei 166 bis 170° siedende Kohlenwasserstoffe zu isoliren, von denen der erste Cumol, der zweite ein Terpin $C_{10}H_{16}$..." [*Ann.*, 137, page 320]. Again: "Der ganz constant bei 171° siedende Antheil des Steinkohlentheers ist ein Terpen von der Formel $C_{10}H_{16}$.... Das Terpen des Steinkohlentheers absorbirt...." [*Ibid.*, page 133.] It is apparent that the first reference is not to a terpene, $C_{10}H_{16}$, but possibly to a sesquiterpene as now understood. In the second reference the spelling "Terpin" occurs with that of "Terpen." This may be a printer's error. Comp. also Gildemeister's comment in footnote No. 3.

[3] Terebene was regarded by Berthelot [*Compt. rend.*, 55 (1862), pages 496 and 544; also *Ann.*, Suppl. II (1862–1863), page 226], as a chemical unit, but now is regarded as a mixture. The generic sense is brought out in sesquiterebene, $C_{15}H_{24}$, diterebene, $C_{20}H_{32}$, and polyterebene. For further details see Gildemeister, *Die aeth. Oele*, 3te Aufl. Bd. III, pages 89 and 90.

As early as 1840, Soubeiran [*Ann.*, 34, page 311] had employed the word camphene in a generic sense to designate all hydrocarbons C_5H_8. In 1862 Berthelot (*l. c.*) used the word to designate "camphene proper" the hydrocarbon derived from artificial camphor, $C_{10}H_{16}.HCl$. Our *l*-camphene he designated terecamphene, our *d*-camphene austracamphene. See also Gild., *l. c.;* also footnote No. 7.

[4] Thus Gerhardt in 1846, following the general system of classification according to the number of carbon atoms classifies the hydrocarbons $(C_5H_8)_x$ into camphenes, $C_{10}H_{16}$; para camphenes, $C_{15}H_{24}$; and meta camphenes, $C_{20}H_{32}$. [*Grundriss d. org. Chemie*, 2, pages 242 and 413; see also *Arch. d. Pharm.*, 4, page 144.]

Having, in 1860, proposed a detailed classification of the hydrocarbons $C_{10}H_{16}$ in his *Chimie organique fondée sur la synthese* (page 733), Berthelot, in 1869, showed how the hydrocarbons terebene, $C_{10}H_{16}$; sesquiterebene, $C_{15}H_{24}$; and diterebene, $C_{20}H_{32}$, isolated by him previously [*Ann. Suppl.*, 2 (1862–1863), page 228; from *Compt. rend.*, 55 (1862), pages 496 and 544] could be related to isoprene, C_5H_8, isolated by Greville Williams a few years before [Jahresb. 1860, page 495]. Regarding his terebenes as polymeres of isoprene, he names them accordingly:

Monomeres	C_5H_8		
Dimeres	$2C_5H_8$	=	$C_{10}H_{16}$ or terebene
Trimeres	$3C_5H_8$	=	$C_{15}H_{24}$ or sesquiterebene
Tetrameres	$4C_5H_8$	=	$C_{20}H_{32}$ or diterebene

Gladstone, in 1864 [*J. Chem. Soc.*, 17, page 1; also 25 (1872), page 1], arranged the volatile oil hydrocarbons into like groups but uses no group designations.

while used in a generic sense at times, had primarily a specific meaning. Much later it was used to designate certain, not all, hydrocarbons $C_{10}H_{18}$ with one double bond, referable to terpane or menthane (Methyl *p*-sec. propyl cyclohexane). With the subclassification of "terpenes" into hemiterpenes, terpenes proper, sesquiterpenes, etc., it is used to designate all hydrocarbons $(C_5H_8)_x$. Finally, it has been used, *e. g.*, in such designations as terpene literature, to include not only all hydrocarbons $(C_5H_8)_x$, but their derivatives as well. At the present time the concept has, therefore, a fourfold significance.

I. Terpenes: All Isomeric Hydrocarbons $C_{10}H_{16}$.[1]—As already pointed out, the older usage of the word comprising all hydrocarbons $C_{10}H_{16}$ is commonly attributed to Kekulé and dates back to the middle of the sixties of the past century. The numerical relationship of these natural hydrocarbons $C_{10}H_{16}$ to hydrocarbons C_5H_8 on the one hand, also to $C_{15}H_{24}$ and $C_{20}H_{32}$ on the other hand, was recognized at an early date and made use of in nomenclature.[1] Just as the older designations terebene, etc., have given way to terpene, so such words as sesquiterebene, etc., have given way to sesquiterpene since Wallach in 1885 adapted Kekulé's term to the older nomenclature. He recognizes three groups, *viz.*, hemiterpene, terpene and polyterpene.[2] The classification of Baker in his "Natural Terpenes" is essentially the same.[3]

All of the names suggested emphasize the group $(C_5H_8)_x$ and remove its representatives from their relationship to innumerable members of the organic type hydrocarbon, irrespective of whether they be natural or artificial, isomers or homologues. This unfortunate segregation has been emphasized by referring to such a hydrocarbon as C_9H_{14} (Santene-Norcamphene) as a homologue. Homologue of what? But even if it be regarded as a homologue in the crude empirical sense of

[1] Dodge would restrict the usage of the term "to those hydrocarbons $C_{10}H_{16}$, which occur in volatile oils." (See footnote No. 2.) This is in harmony with certain textbook definitions, but not in accordance with its earliest usage. Thus Beilstein (see footnote No. 5) designates as a terpene a hydrocarbon $C_{10}H_{16}$ isolated from coal tar. Dodge goes even a step farther and places additional restrictions upon its usage by demanding a certain configuration. In this he appears to be alone. (Comp. also Pseudoterpenes, and Aliphatic Terpenes.)

[2] The details of Wallach's early classification are herewith given:

A. Hemiterpene or Pentene C_5H_8 (isoprene).

B. Terpene $C_{10}H_{16}$.

1. Pinene group. Boiling point around 160°, unites with one molecule of HCl and the nitrosoderivative melts at 129°.
2. Camphene group. Solid terpenes melting about 50° and boiling under 160°.
3. Limonene group. Have citron-like odor and boil at 175° to 177°, the nitroso derivative melts at 104–105°, and they yield a dihydrochloride melting at 50°.
4. Dipentene group. Boiling at 180° to 182°, odor like limonene; tetrabromide melts at 125° to 126°; the dihydrochloride melts at 49° to 50°; etc.

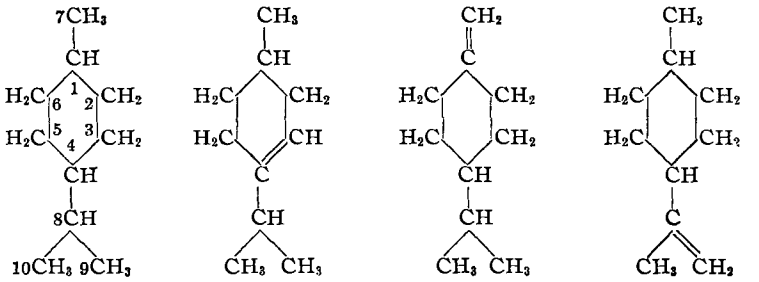
C. Polyterpene $(C_5H_8)_x$.

1. Sesquiterpene or tripentene. Boiling 250° to 260°; formula $C_{15}H_{24}$ as cedrene and cubebene.
2. Diterpene or tetrapentene. Boiling over 300°; formula $C_{20}H_{32}$. Example is colophene.
3. Polyterpene $(C_{10}H_{16})_x$ as caoutchouc (polymerized isoprene).

[3] A very recent classification is that of Baker [*Natural Terpenes* (1920), page 7] who bases his particular classification on structural relationship.

difference of CH_2, it will be seen that the recognition of homologues destroys the relationship based on isomerism of $(C_5H_8)_x$. The simplest way in which this difficulty can be obviated, is to classify these hydrocarbons as all hydrocarbons should be classified, *viz.*, in a rational system based on structural relations.

II. Terpenes: Hydrocarbons $C_{10}H_{18}$ with One Double Bond Derived from Terpane.—In accordance with the principles adopted by the Geneva Congress in 1893, the designation terpene has been applied to hydrocarbons $C_{10}H_{18}$ with one double bond derived by the removal of two hydrogen atoms from neighboring carbon atoms of the hydrocarbon terpane, $C_{10}H_{20}$, methyl-*p*-sec. propylcyclohexane.[1] The symbol used to designate "double bond" by v. Baeyer in his menthene synonyms is the capital Greek delta.[2] The position of the double bond is indicated by numbers, thus



The numbers indicating carbon atoms of the side chain are placed in parentheses.

Comp. Menthene.

III. Terpenes $(C_5H_8)_x$.—The original application of the term to hydrocarbons $C_{10}H_{16}$ was extended to all hydrocarbons $(C_5H_8)_x$ after the numerical relation of the terpenes proper to the larger group had been recognized. In his

[1] The minutes of the Geneva Congress were published by Tiemann, the secretary in the *Berichte*, Vol. 26, page 1595. A summary may be found in Meyer und Jacobsen, *Handbuch der Organischen Chemie*, Bd. I, page 1091, also in the corresponding volume of subsequent editions [*e. g.*, Vol. 1, page 147 of the second edition]. The 1893 Congress adjourned without having come to any decision concerning the nomenclature of cyclic compounds, expecting to take up the problem at a later session. Such a session was never held. Several attempts, however, were made by individuals to supplement the rules, adopted by the Geneva Congress with reference to chain compounds, by suggesting rules for cyclic compounds. Such an attempt for mono- and dicyclic compounds referred to in the literature of volatile oils was made by Semmler in his four volume work on "Die aetherischen Oele," 1906. [Vol. II, page 32.] The attempt, however, did not meet with favor on the part of workers in this field. Less ambitious, but more successful was the suggestion made by Adolf von Baeyer, a member of the Geneva Congress when later he proposed the term menthane for the hydrocarbon $C_{10}H_{20}$ underlying menthol and the term menthene as a group name for derivable hydrocarbons $C_{10}H_{18}$ with one double bond. (Ref.) Wagner proposed the designation terpane for the same saturated cyclic hydrocarbon $C_{10}H_{20}$ because it is the hydrocarbon underlying terpin, the diatomic alcohol or glycol, now better known as terpane diol- 1,8. The derivable hydrocarbons $C_{10}H_{18}$ with one double bond thus became terpenes, former dihydroterpenes.

[2] Confusion may arise when in place of the capital Greek delta the symbol Δ is employed since this is used to designate a cycle in contrast to double bond ⟊.

classical series in the Annalen on "Terpene und Campher"[1] Wallach uses the term in this, its broadest sense. In this sense it has also been used recently in an advertisement "Curcumen, Terpen $C_{15}H_{24}$, das neue Cholagogum."[2]

IV. Terpenes $(C_5H_8)_x$ *and Their Derivatives.*—Not only have Wallach's students been dubbed "Terpenkuenstler" even though the material upon which they worked were not hydrocarbons, but related oxygenated compounds, Fr. Heusler in 1895[3] contributed the article "Terpene" to the *Handwoerterbuch der Chemie* in which more space is devoted to related oxygenated compounds than to the hydrocarbons. As late as 1829 Ossian Aschan dedicated his treatise on Naphtenverbindungen, Terpene und Campherarten to Otto Wallach, "dem Altmeister der Terpenchemie." Hence, although in the title he differentiates between terpenes and camphors, he refers to Wallach's special field as terpene chemistry. These two illustrations of rather loose usage might be multiplied.

EXTERNAL EMULSIONS WITH A NEW EMULSIFIER.*

BY L. G. FREEMAN[1] AND E. L. SCHWABE.

The frequency with which prescriptions occur calling for oil, limewater and one or more impalpable powders such as zinc oxide, calamine, etc., presents a problem of finding a method which will give sufficient saponification to completely emulsify all of the oil and suspend these impalpable powders.

A number of series of emulsions were prepared without the incorporation of the impalpable powders, varying in oil content from 15–85%, some two hundred emulsions in all.

Olive oil, being most frequently prescribed, was used with the idea of developing a standard method of procedure, which, with modifications, could be applied to other oils. Twelve series of emulsions were prepared by the bottle method, English and Continental mortar methods, and the electric mixer, with and without added emulsifiers. Observations of separations occurring were made at varying intervals from twenty-four hours to six months. The following key being used to identify the oil–water ratios:

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[1] The same words are used in his book title "Terpene und Campher. Zusammenfassung eigener Untersuchungen auf dem Gebiete der alicyclischen Kohlenstoffverbindungen von Otto Wallach." Leipzig, 1909.

[2] Cover page of *Pharm. Zentralh.* for Dec. 19, 1926.

[3] This article was published in book form in the following year. In the preface thereto the following passage occurs: "Dem Umstande Rechnung tragend, dass die *Chemie der Terpene* (Italics the writers) zur Zeit im Vordergrund des wissenschaftlichen Interesses steht...." The table of contents refers to the following chapters:

Hemiterpene
Eigentliche Terpene
Kohlenwasserstoffe $C_{10}H_{18}$
Kohlenwasserstoffe $C_{10}H_{20}$
Anhang: Glieder der Terpengruppe mit offener Kohlenstoffkette
Sesquiterpene und Polyterpene.

* Section on Practical Pharmacy and Dispensing, A. PH. A., Toronto meeting, 1932.

[1] Asst. Prof. of Pharmacy, University of Buffalo.