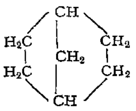
THE STEREO-CHEMISTRY OF PINANE AND ITS DERIVATIVES.

By K. Ganapathi.

I. Introduction.

The properties of pinene cannot be adequately explained by the ordinary graphic formula.[1] Therefore, an attempt is here made to study in detail the spatial arrangement of the atoms of compounds of the pinane group with a view to elucidating their isomerism as also their characteristic chemical reactions.

Sachse postulated that the strain (in Baeyers's sense) in the polymethylene rings can be relieved by their assuming multiplanar configurations. Investigations by Ruzicka, Huckel, Rao, Kandiah and Linstead have confirmed the validity of Sachse's postulates as extended by Mohr to the (1 ; 2 fused) bicyclic systems. These concepts have been extended to the bicyclo-(1 : 2 : 2)-heptane or norcamphane (norbornylan) system (I)[2], but the bicyclo-(1 : 1 : 3)-heptane or norpinate group (II) has not formed the subject of a detailed study.[3, 4]



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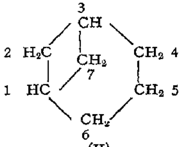
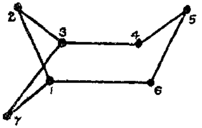


(II)

2. The Space model of the norpinane ring system.

The remarkable stability of pinane[5] requires that the ring system (II) should be free from strain - i. e., the valencies of the carbon atoms should not be too much deflected from their normal tetrahedral positions. All the carbon atoms of norpinane system cannot lie in one plane, since this arrangement not only involves much of strain but also cannot explain the existence of two isomers of pinane, nopinol, myrtanol, etc. The second possibility,[6, 7] in which the six membered ring is uniplanar with the other portion of the *cyclo*butane ring being inclined to the former, also involves considerable amount of strain at C_1 and C_3 (fig. II). A strainless model is possible in which both the rings are multiplanar, with the *cyclo*hexane ring existing in the strainless Sachse forms. As regards the locking of the two rings in this system, it has been shown by a study of the model as well as by experimental evidence,[8] that the *trans* fusion of the two rings cannot form the bicyclic ring system (II) capable of existence, whereas by the *cis*-locking, the system becomes quite stable. With the two forms of *cyclo*hexane, "the chair" and "the boat," the *cyclo*butane ring can be constructed (by *cis* valencies in the *meta* positions) with an additional carbon atom (7), to give rise correspondingly to two strainless forms (III) and (IV); the third possible structure (V) arising from 'the boat' (wherein, unlike "the chair," all the carbon atoms are not identical), being too strained, either may not form or rearrange to (III) or (IV).



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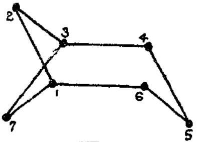

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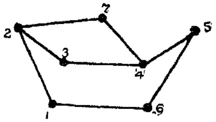
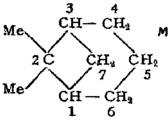


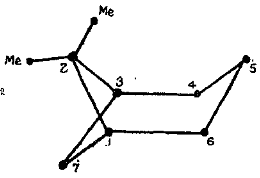
V

3. The Phenomena of Isomerism.

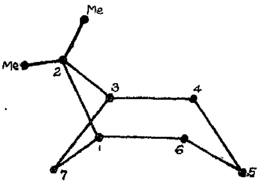
(a) *Norpinane and nopinane.*—The two forms (III) and (IV), in which the fourth valencies of C_1 and C_3 lie almost in the plane of $C_1C_3C_4C_6$, become identical if C_2 and C_7 are identical as in norpinane (II) which can exist in one form only. But, when the carbon atoms (2) and (7) are not identical, as in nopinane (VI), the two arrangements (VII) and (VIII) are different, the existence of two forms of nopinane being thus possible.



(VI)



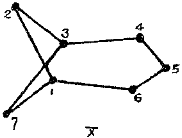
VII



VIII

The non-isolation of two Sachse forms of *cyclo*hexane has been explained on theoretical grounds[9] as being due to the easy interconvertibility of one form into the other, probably through the intermediate little strained form (IX) which, by strain-free relative rotations about C_4 and C_6 (fig. IX), can pass either into the chair or the boat form. It is only when these relative rotations are arrested by appropriate attachment to a ring, e. g., in the decalins, or probably by substitution of some groups, that the two forms (each getting stabilised) are capable of isolation.[10] Though the original claims of Khudha[10] regarding the isolation of derivatives of two forms of *cyclo*hexane (C & Z) have been contradicted, recently, some communications[10a] are appearing wherein experimental evidence has been provided for the existence of the methyl *cyclo*hexane ring in at least two distinct multiplanar forms. Thus, in the case of the nopinane system, though the carbon atoms (4) and (6) are free to rotate so that the two forms (VII) and (VIII) are interconvertible (through the " liegessel form " (X) of Bredt[4]), yet, the distortion in the *cyclo*hexane ring produced by (the steric and polar effects of) the *cyclo*butane ring and also the *gem*-dimethyl group,[11] can stabilise to the same extent (as in the substituted *cyclo*hexane derivatives) the two forms (VII) and (VIII) which should be capable of isolation. Since the difference in physical properties between the two forms will be very little and the one can easily isomerise to the other, the nopinane that can be isolated in our usual experiments may either be a mixture of both forms or consist of only the stabler form (VIII).* Though it cannot be definitely proved at present, there are

IX



X

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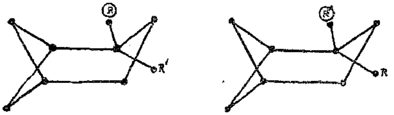
*Jatkar (Indian J. Physics, IX, p. 550) has observed from a study of the Raman spectra the two 1:2-dimethyl-*cyclo*hexanes to resemble the two decalins. Desai (J. C. S., 1932, 1053) from a study of the derivatives of methyl *cyclo*hexanes concludes that the methyl *cyclo*hexane ring is strainless. Mills and Keats (J. C. S., 1935, 1373) assign to the two hexahydroterephthalic acids the two Sachse configurations to be compatible with the physical data. These indicate that the *cyclo*hexane is probably existing in the Sachse forms in all its derivatives.

indications to believe from what follows (section 4c) that the *cyclo*hexane ring in these compounds can be existing in the strainless forms.

(b) *Compounds substituted at one of the carbon atoms* 4 *or* 5.—When the hydrogen atoms attached to one of the carbon atoms (4) or (5) of norpinane are substituted by different atoms or groups (R and R^1), such a derivative can give rise to two forms (XI) and (XII). In the case of nopinane, by a similar substitution by (R) and (R^1), four isomers should be possible from the two forms (VII) and (VIII) of nopinane. So far, only two isomers are definitely known in the cases of pinane, nopinol, methylnopinol and myrtanal. This cannot be taken to indicate that nopinane can be isolated in only one form (X), for there is no reason why, by very careful experiments as in the *cyclo*hexane series,[10a] four isomers should not be isolated.



(figs. rounded lie in the plane of $C_1C_3C_4C_8$)

Lipp[6], by the systematic reduction of α- and β- pinenes under different conditions, has reported to have isolated two forms of pinane (XIII and XIV)* which he has designated '*cis*' and '*trans*' by the application of Auwers-Skita Rule.‡ Nothing definite being known regarding the configurations of these compounds, it is quite desirable to study their properties and characterise them more thoroughly.[12] If

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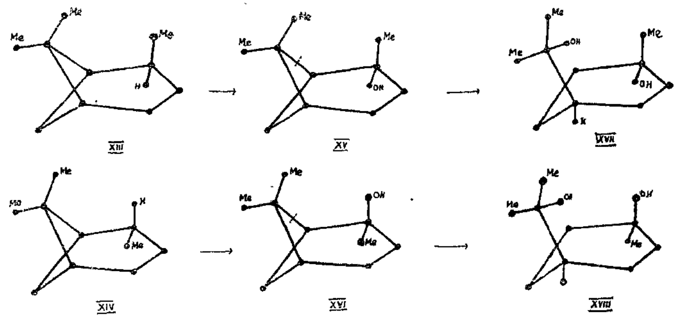
* In this section, for convenience of representation, unless otherwise stated, nopinane is taken to be of the form (X) which only cannotes the average state between (VII) and VIII) but does bar the possibility of the compound existing in two forms.

‡ The adoption of the terms '*cis*' and '*trans*' in this case, as also with other derivatives, is purely arbitrary and does not convey any definite meaning. In the bicyclic and polycyclic systems these terms are adopted to denote the nature of locking of the two rings. It seems to be better to use α, β, as in nopinol.

Huckel (*Annalen*, 1935, **517**, 229) has shown that the Auwers-Skita rule does not give any unequivocal answer as to spatial structures in all cases (cf. Ruzicka, Furter and Goldberg, *Helv. Chim. Acta.*, 1938, **21**, 498).

these two forms are not easily interconvertible, on oxidation with permanganate under suitable conditions, they should yield the two corresponding stereoisomeric methylnopinols (XV) and (XVI), one of which may be identical with the product, m. p. 58–59° (b. p., 204°–205°; α_D–4.90°) obtained by Wallach[13] from nopinone. Lipp, without stating which form of pinane was oxidised by him, has obtained apparently only one product, m. p., 79° (b.p.$_{721}$204°–204°.5: α_D–24.39°), which he considers to be probably a stereoisomer of Wallach's compound. Austerweil[14] has prepared by the hydration of β-pinene with (45 per cent.) sulphuric acid, methyl nopinol, m. p., 62°, which he believes to be identical with Wallach's compound. In view of the fact that nopinene on hydration, or nopinone by the action of magnesium methyl iodide, can give rise to (at least) two methyl-nopinols (or pinene hydrates) (see section 4c), it appears essential to carefully search for the other isomers in the above reactions. If, during the process of hydration of methyl nopinol, the bond between C_2 and C_8 breaks directly to yield (1 : 8)-terpin, then, the two stereoisomeric forms of methylnopinol should yield correspondingly the *trans* and *cis* terpins (XVII and XVIII) as shown below. But, by shaking



with 5 per cent. sulphuric acid, both the methyl nopinols of Wallach and of Lipp are described to yield only *cis*-terpin (XVIII). This anomaly can be explained as due to any of the following reasons : (i) the methylnopinols of Lipp and Wallach are the same (XVI) but with different degrees of optical purity or both are derivatives of one of the forms (VII) or (VIII) of nopinane; (ii) the conversion of the form (XV) of methylnopinol to (XVI) takes place before hydration; (iii) the isomerisation of *trans*-terpin initially formed to the *cis* form takes place in one case, (which is not likely since only the reverse change is observed); [15,16] and (iv) the formation of (1 : 8)- terpin from both the methyl nopinols takes place through the intermediate *α*-terpineol [14] (see section 4c). It is not quite likely that the *trans*-terpin formed from the form (XV) of methylnopinol first undergoes dehydration to *α*-terpineol[15] which on subsequent hydration furnishes *cis*-terpin. In view of these possibilities, it is quite essential that the reactions of the methyl nopinols should be thoroughly studied. If, by controlled reactions, the two pinanes are oxidised to the corresponding methyl nopinols and the latter converted into two stereo–isomeric *cyclo*hexane compounds, the configurations of the pinanes and methyl-nopinols can possibly be fixed.

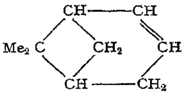
Nopinone, on reduction, gives two nopinols ($R = H$, $R^1 = OH$ in XIII and XIV)—*α*-form, m. p., 102° and *β*-form, m. p., 5-7°. These two are stereoisomers, *α*-form isomerising to the *β*-form by the action of dilute, sulphuric acid or zinc chloride [13,17]. By the action of hydrochloric acid on apopinene (XXIII), Komppa and Hasselstroem[17] have obtained two isomeric chlorides (probably $R = H$, $R^1 = Cl$ in XIII and XIV)-one, m. p., 59-6°, and the other, a liquid. Myrtenol on reduction is shown by Dupont and Zacherewics[18] to give rise to two stereoisomers, myrtanol and isomyrtanol ($R = H$; $R^1 = CH_2OH$ in XIII and XIV) which the authors consider to be '*trans*' and '*cis*' by a study of their Raman spectra. Pinocamphone has also been isolated in the '*cis*' and '*trans*' forms by Schmidt and Schulz[19]. A detailed study has been proposed to be made in this direction to isolate the (four) possible isomers in the case of nopinic acid, myrtanal, myrtanic acid etc. and also to fix up their configurations.

(c) *Compounds substituted at two of the carbon atoms 4, 5 or 6.*—When two of the carbon atoms 4, 5 or 6 are substituted as in pinocampheol, verbanol, pinylamine, etc., eight isomers should be possible from the two forms (VII) and (VIII) of nopinane. Schmidt and

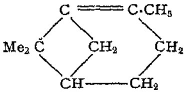
Schulz[7] have obtained two forms of pinocampheol (m.p., 57° and 67°) which on oxidation have furnished two ('*cis*' and '*trans*') pinocamphones. The '*cis*' pinocampheol (m.p. 57°), is described to lose water more easily than the '*trans*' (m.p. 67°) but the dehydrated products do not seem to have been examined (*α* or δ-pinene?). Kahnamann,[20] by the reduction of verbanone (*cis* or *trans*?), obtained two verbanols, '*cis*' (m.p.74-75°) and '*trans*' (m.p. 67-70°). By the reduction of the other isomeric verbanone two more forms should be obtainable. These compounds and also the reactions require a more detailed study.

(d) *Compounds substituted at* C_2 *or* C_3. The isomerism becomes more interesting if the carbon atoms (2) and (7) in the ring system (II) are not identical. Thus, 2-methyl-norpinane can exist in four forms, while 2 : 7-dimethyl-norpinane also in four forms. Though compounds of this type are not known to occur in nature, a practical realisation of these possibilities will be of considerable interest from the stereochemical point of view.

(e) *Compounds with double bonds.*—The double bond present in the *cyclo*hexane ring between C_4 and C_5, as for example in *α*-pinene and "apopinene" (XIX), brings to the same plane the carbon atoms 3, 4, 5 and 6, as also the fourth valencies attached to C_4 and C_5, so that any atom or group attached to C_4 or C_5, cannot cause spatial or geometric isomerism. Thus, *α*-pinene, wherein the *cyclo*hexane ring cannot assume the Sachse forms, can exist in only one form.[21] This is supported by the fact that Komppa and Hasselstroem[17] have observed that the dehydration of either of the nopinols furnishes the same homogenous apopinene (XIX). Thus, myrtenol, myrtenal, etc., should exist in only one form though δ-pinene where the methyl group is unconnected with the double bond should be isolated in two stereoisomeric forms.



(XIX)



(XX)

In the case of *β*-pinene, wherein the double bond is semicyclic, the *cyclo*hexane ring can exist in the Sachse forms, the exocyclic carbon atom connected by a double bond to C_4 being in the same plane as C_3, C_4 and C_5. So, corresponding to the two forms of nopinane (VII) and (VIII), two β-pinenes can theoretically exist.

The presence of the double bond between C_3 and C_4 as in the hypothetical " isopinene " (XX), causes a lot of strain to the ring system and especially at C_3 so that it is doubtful whether such a compound can have even a momentary existence (Bredt's rule). Under such conditions of strain, the *cyclo*butane ring will undergo fission to give rise to a *cyclo*hexane derivative.* In view of this, the structure assigned to carvopinone (which, though easily isomerises to carvone, is capable of existence) seems to require confirmation.

4. The bearing of the space configuration on the chemistry of these compounds.

(A) *The stability of pinane and its derivatives.*—Though, ordinarily, the *cyclo*butane ring is known to be unstable, the valency deflection hypothesis has shown[22] that the presence of the *gem*-dimethyl group stabilises the ring to a great extent as is evidenced by the fact that norpinic acid is remarkably stable[23, 24]. However, in the construction of the additional six membered ring from such a *cyclo*butane ring to form the nopinane skeleton, the two valencies of the

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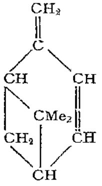
* The formation of verbenene (i) (Ruzicka and Trebler[3]) by the dehydration of verbenol cannot satisfactorily be assumed to proceed through (ii) which may undergo fission of the *cyclo*butane ring rather than isomerise to (i). Since the dehydration of verbenol is effected by the action of acetic anhydride, the author assumes the intermediate formation of (iii) by an anionotropic change, which gets dehydrated to (i).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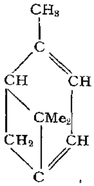
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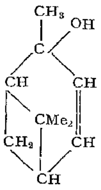

(iii)

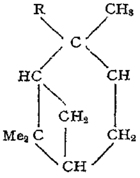
dimethyl*cyclo*butane ring that participate have to be deflected towards each other appreciably from their stablest positions (as in norpinic acid) and the strain involved therein is relieved by the two rings becoming multiplanar. Nopinane, pinane and norpinane are, therefore, expected to be very stable. Lipp[5] has observed pinane to be remarkably stable both to mineral acids and oxidising agents.

(B) *Isomerisation of β- to α-pinene*:—Since the construction of the additional six membered ring from the *cyclo*butane derivative to give rise to a strainless form of nopinane has been shown to draw closer towards each other the two valencies C_3-C_4 and C_1-C_6 (fig. VI), any decrease in the angle subtended by C_4 or C_6 and to a less extent C_5 in the *cyclo*hexane ring causes strain to the *cyclo*butane ring at C_3 or C_1. So, for a compound of this group to be least strained, the maximum possible angle should be subtended by the carbon atoms 4 or 6 in the *cyclo*hexane ring. In β-pinene, since the double bond is semicyclic, the angle which C_4 subtends in the ring (110°) is far less than in the case of α-pinene (125°) where the double bond is *endo*cyclic. α-Pinene, being, therefore, the less strained form of the two, the semicyclic bond in β-pinene enters the ring with great ease to relieve the strain. It is thus easy to understand why β-pinene readily isomerises to the α-form though the reverse change is yet unknown[25] and β-pinene undergoes hydration with greater ease than α-pinene. The researches of Kon[26] and Linstead[27] in the analogous *cyclo*hexane derivatives have clearly shown the great tendency of the exocyclic double bond to enter the ring undoubtedly to relieve the strain.

(C) *Ring fission and Isomerisation.*—The remarkable stability of pinane gives us to understand that the instability met with in some of its derivatives—wherein, except in the oxidation of the double bonds, the *cyclo*butane ring always undergoes fission—is not to be attributed to any inherent instability of the ring system itself but to the modifying influences of the atoms or groups present therein. When the carbon atom (4) directly attached to the *cyclo*butane ring is substituted by two heavy groups, according to the valency deflection hypothesis of Thorpe and Ingold, the angle subtended by C_4 with the other carbon atoms in the *cyclo*hexane ring decreases. This, as shown above, causes the instability of the *cyclo*butane ring at the strained carbon atom (3). This effect will be more marked if one or both of the groups attached to C_4 are of the polar type as OH, Cl or Br. Under such circumstances of strain at C_3, two types of allied changes can occur—(a) the fission of the *cyclo*butane ring at C_3 to give rise to a 1:4-substituted *cyclo*hexane derivative, or (b) the isomerisation of the compound to a stabler structure. A study of the model now enables us to understand the stereochemical conditions under which these two types of reactions can proceed on.

(a) It is known that methylnopinol on being shaken with 5 per cent. dilute sulphuric acid yields terpin hydrate,[13, 5] whereas nopinol is not at all affected by the same reagent. Wallach[13] explains the stability of nopinol as being due to the secondary alcoholic grouping whereas Perkin and Simonsen[24] have remarked "it seems very difficult to see why the substitution of a hydrogen atom by a methyl group in nopinol should bring about such a remarkable change in the condition of stability." In the case of nopinol, there being only one (bulky or polar) group attached to C_4, there is no appreciable difference in the angle subtended by C_4 in the *cyclo*hexane ring as compared with the case of pinane, and so nopinol is expected to be quite stable. It should be noted that the polar hydroxy group, *by itself*, has got no effect in causing the fission of the *cyclo*butane ring. The action of hydrochloric acid on apopinene gives two stereoisomeric chlorides corresponding to nopinol and these also do not seem to undergo ring fission.[17] Similarly, all mono-substituted products (at C_4) e.g., myrtanal, myrtanol, myrtanic acid, etc., should not easily undergo fission. But, in the case of methylnopinol, the additional methyl group makes all the difference, because, as shown above, the two groups CH_3 and OH decrease the angle subtended by C_4 in the *cyclo*hexane ring, thereby causing the *cyclo*butane ring get strained and break at C_3. Pinene glycol, nopinic acid, etc., are all thus known to furnish *cyclo*hexane derivatives. The ketonic group has a similar effect from the point of view of strain as the attachment of two polar groups to C_4 and so we find that nopinone is also unstable. The unique case of verbanone yielding Δ^4-*ortho*menthene-3-one[28] can now be realised to be due to the ketonic group at C_6 which causes strain at C_1 so that the bond C_1C_2 undergoes fission. It can be concluded that the *cyclo*butane ring undergoes fission only if C_4 or C_6 carries two groups (one of them being preferably polar) and not otherwise. In the case of the hydration of α- and β-pinenes, it is definite that initial addition to the double bond takes place as a preliminary to further changes[29]. In all such cases where a *cyclo*hexane derivative is produced, the fission always occurs between the strained carbon atoms C_3 or C_1 and C_2 which carries the *gem*dimethyl group. This is probably because of the steric effects of the *gem*-dimethyl group which makes this valency more strained than that between C_3 or C_1 and C_7 (see later on).*

(b) One of the remarkable changes recorded in the chemistry of the bicyclic terpenes is the Wagner-Meerwein rearrangement—the ready isomerisation of pinene or its derivatives by means of acids to camphane or fenchane derivatives. This rearrangement has formed the subject of intense practical and theoretical study but the stereochemical conditions involved therein have not till now been taken into account.[30] By the addition of water or a halogen acid (a complex H.R.), as a preliminary to the rearrangement, both α- and β-pinenes initially get the double bond saturated forming the compound (XXI) which, becomes strained at C_8. In this case, under particular conditions, the isomerisation of (XXI) to a camphane or fenchane derivative takes place.



XXI

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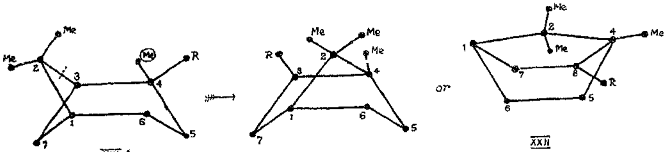
* Ingold (*J. Chem- Soc.*, 1921, *119*, 952) has stated that 1:1-dialkyl groups have a destabilising action on the (uniplanar) *cyclo*hexane ring also.

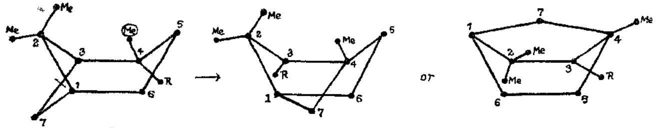
The strain at C_8 causing the *cyclo*butane ring to break and the tendency of (R) to split off as a potential anion are the driving forces of the ring isomerisation of (XXI) to a stabler structure[31], the mechanism being visualised somewhat like this: the group (R) splits off from C_4, as also C_2 or C_7 from C_8 and the structural and spatial dispositions of the two free valencies created are such that C_2 or C_7 attaches to C_4 filling the place of (R), while (R) simultaneously joins C_8 so that the isomerisation involves simply a reciprocal interchange in positions of the two groups concerned. The factor which mostly decides the breaking of the *cyclo*butane ring strained at C_8 by the fission from it of C_2 or C_7 appears to be the "direct effect" of the proximate polar group (R)[32]. This group (R), can occupy two different positions as shown in the space representations (A) and (B) of (XXI), wherein it can be seen that the bond breaking and the group (R) are in *cis*- positions of the two directly attached carbon atoms. As a result of this exchange,



XXI A

XXII

(Figures rounded lie in the same plane as $C_1C_3C_4C_6$)

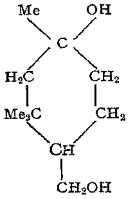


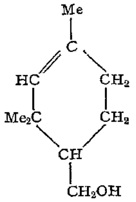
XXI B

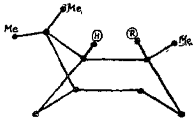
XXIII

form (A) gives rise to a camphane derivative (XXII), while form (B) to a fenchane derivative (XXIII). These two forms (A) and (B) which give a rational explanation of the formation of camphane and fenchane derivatives are believed by the author to be the precursors of these isomerised compounds during the hydration of *α*- or *β*-pinene. An examination of the two forms (A) and (B) indicates it as quite probable that by the action of the complex H. R. on *α*- or *β*-pinene, form (A) will be formed in greater amount than (B), so that the formation of the camphane derivative as the major product in such an isomerisation is easily explainable.

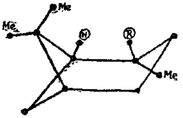
(c) The last important and allied question to be satisfactorily answered is—why is it that by the similar addition of water to the double bond to α- or β-pinenes, in some cases, only the 1 : 4 *cyclo*hexane derivatives are produced and the bond between C_2 and C_3 only undergoes fission ? The products (XXIV or XXV) never seem to have been obtained.


XXIV


XXV



XXI C



XXI D

It was pointed out previously that substitution at carbon atom (4) in nopinane can give rise to four isomers. Thus when HR adds on to the double bond in pinene to furnish (XXI), in addition to the forms (A) and (B), the isomeric forms (C) and (D) can also be produced, wherein (H) and (R) can be seen to be in the same plane as C_1 C_3 C_4 and C_6 and in the *cis*- positions. The influence of (R) on the bonds C_2-C_3 and C_7-C_3 being the same, the inherently strained of the above two bonds, C_2-C_3, due to the *gem*-dimethyl group, easily breaks. Since C_2 is in *trans*-position to (R), the interchange postulated in the Wagner rearrangement is not easy to take place here; but, on the other hand, (R) and (H) being contiguous and also being reactive, a double bond is created by their elimination as HR while the ruptured valency C_2C_3 is satisfied by hydration thus furnishing α-terpineol. There is the alternative mechanism that C_2, having split off from C_3, can unite with the group (R) also split off as an ion so that a double bond is created between C_3 and C_4. This leads us to suggest that the methyl nopinol of Wallach, and probably of Lipp, which on dehydration furnish α-terpineol, terpenene, dipentene, limonene, etc., but not known till now to yield camphene or fenchene or the pinenes, may therefore possess the configurations (C) and (D), while the hydration products of the pinenes which immediately isomerise to borneol or fenchyl alcohol, (A) and (B). The forms (A) and (B) are therefore difficult to isolate and a close examination of the four forms reveals that (A) can isomerise to (D) by simple rotation about C_4 and C_6, and so also (B) to (C). The compound (XXI) is here postulated to be existing in four forms in accordance with the two forms (VII) and (VIII) of nopinane which indicates that the *cyclo*hexane ring in nopinane may be existing in the Sachse forms.

5. Conclusion

It is now quite evident, that the space model of the ring system of nopinane gives us a better understanding of the chemistry of pinene and its derivatives and correlates a series of apparently unconnected facts. The foregoing is not claimed to be the last word in the subject, but only a working hypothesis and the ideas may have to be modified in the light of fresh facts to come.

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