# Molecular Rotations of Terpenes in Relation to their Structures. I. The Internal Conformation of Isopropyl Group in Menthol-like Substance[1)]

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In liquid or dissolved state, $C^9H_3$ and $C^{10}H_3$ in the isopropyl group of menthol-like substance are considered to be free to rotate about the axis of $C^4$–$C^8$ bond and the position which has minimal potential and makes these methyl groups rest, may be decided by steric repulsions and intramolecular van der Waals' forces etc. between the atoms in the molecule (Fig. 1).

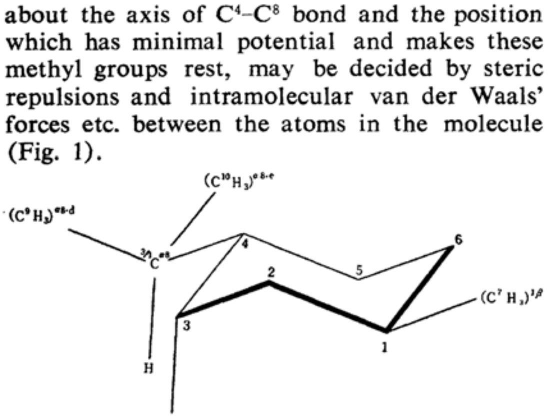


Fig. 1[2)]. Perspective drawing of the molecular model of (+)neomenthol.

On the other hand, by uing the PM-method, the author recently tried to explain the molecular rotations of polyhydroxycyclohexanes[3,4)]. From the standpoint of the fact that a menthol-like substance is a kind of polyhydroxy (or monohydroxy)-cyclohexane, the type of the internal conformation of its isopropyl group at an equilibrium state, above mentioned, is discussed in this article.

## Molecular Model and Data Used

According to Jefferies' investigation of menthol-like substances by infrared spectrum[5)], it was concluded that in their molecules, isopropyl group usually takes equatorial orientation and that two methyl groups repulse each other. Referring to Jefferies' work, only the compounds which have a six-membered ring of C 1 conformation are treated in this article.

The unit groups in their molecules and their corresponding molecular rotations are given in Table I.

The molecular model and the optical properties of the hydroxyl group (except the value of ζ-coefficient), used in the preceding article[3)] were adopted here without any correction. Values of mean polarizability $\alpha$ and of anisotropy ratio $\beta$ of methyl group are $2.27\times10^{-24}$ (cc.) and 0.35 respectively[17)]. The optical

1) Presented at the Symposium on the Structural Chemistry of the Chemical Society of Japan, Sapporo, August, 1960.

2) $C^{\alpha8}$-Atom is $C^8$-atom which is situated in α-orientation (i. e. under the cyclohexane-ring in Fig. 1). $(CH_3)^{\alpha8}$ means the $CH_3$ group which combines with $C^{\alpha8}$-atom. Concerning the symbols, d- and e-, refer to "Method Proposed" in this article.

3) S. Yamana, This Bulletin, 33, 1741 (1960).

4) In the previous paper[3)], by using $[M]^{20}_{D}(W)$ of (−) 1, 3/2, 4 cyclohexanetetrol, the value of $(\zeta_{OH})^2$ was calculated as 3.6402 $\{3/(n^2+2)\}$. But strictly speaking, it was apparent there that if 3.6402 $\{3/(n^2+2)\}$ is used, $\sum[\mu]^{20}_{D\,obs}$ of (−)1/2 cyclohexanediol becomes somewhat smaller than its corresponding $[M]^{20}_{D}(W)$ and $\sum[\mu]^{20}_{D\,obs}$ of (+) 3, 5, 6/1, 2, 4 cyclohexanehexitol becomes somewhat larger than its corresponding $[M]^{20}_{D}(W)$. That fact can be explained superficially by the assumption of the changeability of $(\zeta_{OH})^2$ according to the number of hydroxyl groups in a molecule. When $[M]^{20}_{D}(W)$ of (−) 1/2 cyclohexanediol is used, the value of $\zeta_{OH}{}^2$ is calculated as follows;

$$\sum[\mu]^{20}_{D\,obs} \text{ of } (-)\ 1/2 \text{ cyclohexanediol} = (OH)\cdot{}^{1\beta}\Lambda(OH)^{2\alpha}+(OH)^{1\beta}\Lambda ch.R+(OH)^{2\alpha}\Lambda ch.R$$

$$=-11.73\{(n^2+2)/3\}\zeta_{OH}{}^2+0+0\equiv-48.2$$

$$\therefore\ \zeta_{OH}{}^2=4.1091\{3/(n^2+2)\} \qquad (4)^*$$

(Ref. Tables I and II of the previous paper[3)]).

5) A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 1956, 4391.

TABLE I.

| Name | Unit groups | | | | | $[M]^{20}_{D}$ [6] |
|---|---|---|---|---|---|---|
| $(-)$1/2 Cyclohexanediol | $[(OH)^{1\beta}$, | $(OH)^{2\alpha}$, | | | ch. R[7]] | $-48.2_{w}$[8] |
| $(-)$*trans*-2-Methylcyclohexanol | $[(OH)^{1\beta}$, | $(CH_3)^{2\alpha}$, | | | ch. R ] | $-42.4$[9] |
| $(+)$Neomenthol | $[(CH_3)^{1\beta}$, | | $(OH)^{3\alpha}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | 30.6[10] |
| $(-)$*cis*-2-Hydroxyneomenthol | $[(CH_3)^{1\beta}$, | $(OH)^{2\alpha}$, | $(OH)^{3\alpha}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $-50.6_{ch}$[11] |
| $(+)$*trans*-2-Hydroxyneomenthol | $[(CH_3)^{1\beta}$, | $(OH)^{2\beta}$, | $(OH)^{3\alpha}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $70.3_{ch}$[11] |
| $(-)$*trans*-2-Hydroxymenthol | $[(CH_3)^{1\beta}$, | $(OH)^{2\alpha}$, | $(OH)^{3\beta}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $-16.0_{ch}$[11] |
| $(-)$*cis*-2-Hydroxymenthol | $[(CH_3)^{1\beta}$, | $(OH)^{2\beta}$, | $(OH)^{3\beta}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $-56.7_{ch}$[11] |
| $(-)$Isomenthol | $[(CH_3)^{1\alpha}$, | | $(OH)^{3\beta}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $-39.4_{ch}$[12] |
| $(-)$Menthol | $[(CH_3)^{1\beta}$, | | $(OH)^{3\beta}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $-77.5_{et}$[13] |
| $(-)$Carvomenthol | $[(CH_3)^{1\beta}$, | $(OH)^{2\alpha}$, | | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $-41.2$[14] |
| $(+)$*cis*-1,2-Menthanediol | $[(CH_3)^{1\beta}$, | $(OH)^{1\alpha}$, | $(OH)^{2\alpha}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $24.1_{ac}$[15] |
| $(+)$Neocarvomenthol | $[(CH_3)^{1\beta}$, | $(OH)^{2\beta}$, | | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | 65.2[14] |
| $(+)$*trans*-1-Hydroxyneo-carvomenthol | $[(CH_3)^{1\beta}$, | $(OH)^{1\alpha}$, | $(OH)^{2\beta}$, | $(iso\text{-}C_3H_7)^{4\alpha}$, | ch. R ] | $79.2_{ac}$[16] |

w: water solution, ch: chloroform solution, et: ethyl alcohol solution, ac; acetone solution.

center of a unit group is located at the center of the mass of its corresponding bond. In order to simplify the calculations, the refractive indices of the homogeneous substances and of the solutions under discussion are all assumed to be about 1.46[18].

## Method Proposed

Strictly speaking, as isopropyl group has no optical axis of cylindrical symmetry, the calculations of $[\mu]^{20}_{D\,\mathrm{calcd}}$ which are concerned with isopropyl group are impossible. In order to avoid this difficulty, the following two simplifications are introduced.

Simp. I

$$(iso\text{-}C_3H_7)^{4\alpha}=(C^8H)^{4\alpha}+(C^9H_3)^{\alpha 8}+(C^{10}H_3)^{\alpha 8}$$
$$\simeq^{2)}(C^8H_3)^{4\alpha}+(C^9H_3)^{\alpha 8}+(C^{10}H_3)^{\alpha 8}$$

Simp. II

$$(iso\text{-}C_3H_7)^{4\alpha}\,\bar{\chi}\,A=\{(C^8H)^{4\alpha}+(C^9H_3)^{\alpha 8}+(C^{10}H_3)^{\alpha 8}\}\,\bar{\chi}\,A\simeq(C^8H)^{4\alpha}\,\bar{\chi}\,A+(C^9H_3)^{\alpha 8}\,\bar{\chi}\,A+(C^{10}H_3)^{\alpha 8}\,\bar{\chi}\,A$$

From Simps. I and II,

$$(iso\text{-}C_3H_7)^{4\alpha}\,\bar{\chi}\,A\simeq(C^8H_3)^{4\alpha}\,\bar{\chi}\,A+(C^9H_3)^{\alpha 8}\,\bar{\chi}\,A+(C^{10}H_3)^{\alpha 8}\,\bar{\chi}\,A \tag{1}$$

Next, the positions of minimal potential for $(C^9H_3)^{\alpha 8}$ or $(C^{10}H_3)^{\alpha 8}$ will be mentioned. Referring to the steric repulsion between one of these methyl groups and the C-atom in the cyclohexane-ring ($C^3$- and $C^5$-atoms), it can be easily understood that there should be three positions of minimal potential for methyl groups. The author names these three positions d-, e- and f-positions, respectively (Fig. 2).

But, d-position is trans to $C^4$–$C^5$ bond and e-position is trans to $C^4$–$C^3$ bond and f-position is gauche to both $C^4$–$C^5$ and $C^4$–$C^3$ bonds. As

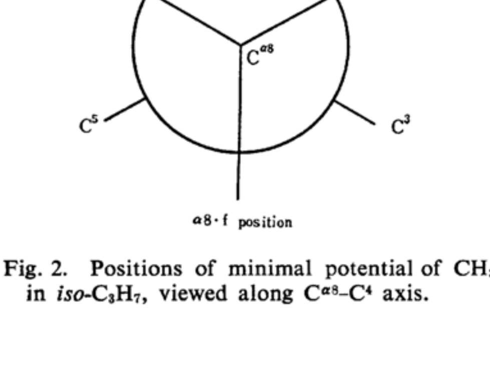


Fig. 2. Positions of minimal potential of $CH_3$ in *iso*-$C_3H_7$, viewed along $C^{\alpha 8}$–$C^4$ axis.

6) $[M]^{20}_{D}$ of pure materials in liquid state or of chloroform solutions are adopted, preferentially. Some values were presumed from $[M]_D$ which had been observed in the neighborhood of 20°C. (Ref. 3).

7) ch. R is an abbreviated symbol of a cyclohexane-ring.

8) Th. Posternak, D. Reymond and H. Friedli, *Helv. Chim. Acta*, **38**, 205 (1955).

9) G. A. C. Gough, H. Hunter and J. Kenyon, *J. Chem. Soc.*, **1926**, 2052.

10) O. Zeitshel and H. Schmidt, *Ber.*, **59**, 2298 (1926).

11) P. R. Jefferies and B. Milligan, *J. Chem. Soc.*, **1956**, 2363.

12) W. Hückel and H. Miggemeyer, *Ber.*, **72**, 1354 (1939).

13) J. Read and W. J. Grubb, *J. Chem. Soc.*, **1934**, 313.

14) R. G. Johnston and J. Read, ibid., **1935**, 1138.

15) H. Schmidt, *Suomen Kemistilehti B.*, **31**, 61 (1958); *Chem. Abstr.*, **52**, 20226 (1958).

16) P. Ham, G. Dupont, J. Wiemann and R. Dulou, *Compt. rend.*, **249**, 700 (1959).

17) S. Yamana, This Bulletin, **31**, 564 (1958).

18) The refractive index, $n$, is as follows; homogeneous state (1.46), chloroform solution (1.45), acetone solution (1.36), ethyl alcohol solution (1.36). If $n$ changes from 1.46 to 1.36, $\{(n^2+2)/3\}$ changes by $\partial/\partial n\{(n^2+2)/3\}\delta n\simeq 0.0973$. The magnitude of this value of $\{(n^2+2)/3\}$-change is about 7% of the value of $\{(n^2+2)/3\}\simeq 1.3772$.

movable groups in isopropyl group are $(C^9H_3)^{\alpha 8}$, $(C^{10}H_3)^{\alpha 8}$ and one H atom, it is obvious that any two of these three positions (d-, e- and f-positions) must be occupied by two methyl groups and the remaining one position should be occupied by one H atom. Then, the following three types of the internal conformation of $(iso\text{-}C_3H_7)^{4\alpha}$ are possible (Table II).

TABLE II. THE TYPE OF THE INTERNAL CONFORMATION OF $(iso\text{-}C_3H_7)^{4\alpha}$

| Name of type | $\alpha 8\cdot$d-Position | $\alpha 8\cdot$e-Position | $\alpha 8\cdot$f-Position |
|---|---|---|---|
| Symmetrical | $CH_3$ | $CH_3$ | H |
| Unsymmetrical I | H | $CH_3$ | $CH_3$ |
| Unsymmetrical II | $CH_3$ | H | $CH_3$ |

**Substances which Have $(OH)^{3\alpha}$.**—It is apparent in Table III that the distance between O-atom in $(OH)^{3\alpha}$ and f-position is 2.52 Å and is shorter than the sum of van der Waals' radius of methyl group and that of $(OH)^{3\alpha}$.

TABLE III. THE DISTANCES BETWEEN O-ATOM IN $(OH)^3$ AND THREE POSITIONS OF MINIMAL POTENTIAL OF METHYL GROUP IN $(iso\text{-}C_3H_7)^{4\alpha}$

| | $\alpha 8\cdot$d-Position | $\alpha 8\cdot$e-Position | $\alpha 8\cdot$f-Position |
|---|---|---|---|
| $(OH)^{3\alpha}$ | 3.49 Å | 4.30 Å | 2.52 Å |
| $(OH)^{3\beta}$ | 2.52 Å | 4.30 Å | 3.49 Å |

Then, owing to the steric repulsion, $(OH)^{3\alpha}$ may refute the idea that any movable methyl group in isopropyl group stays at f-position. In this case, the symmetrical type is only one possible type of the internal conformation of isopropyl group. For these reasons, it is concluded that in $(iso\text{-}C_3H_7)^{4\alpha}$ of (+)neomenthol in the liquid or dissolved state, two $(CH_3)^{\alpha 8}$'s are forced to stay at d- and e-positions (Fig. 1).

$$\therefore\quad (iso\text{-}C_3H_7)^{4\alpha}=(C^8H)^{4\alpha}+(C^9H_3)^{\alpha 8\cdot d}\,{}^{20)}+(C^{10}H_3)^{\alpha 8\cdot e}\simeq(C^8H_3)^{4\alpha}+(C^9H_3)^{\alpha 8\cdot d}+(C^{10}H_3)^{\alpha 8\cdot e}\,{}^{21)} \qquad (2)$$

Referring to Table I and Eq. 2, $\sum[\mu]^{20}_{D\ obs}$ of (+)neomenthol can be calculated by the following equation.

$$\begin{aligned}\sum[\mu]^{20}_{D\ obs}\text{ of }(+)\text{neomenthol}&=(CH_3)^{1\beta}\,\lambda\,(OH)^{3\alpha}+(CH_3)^{1\beta}\,\lambda\,(CH_3)^{4\alpha}+(CH_3)^{1\beta}\\&\lambda\,(CH_3)^{\alpha 8\cdot d}+(CH_3)^{1\beta}\,\lambda\,(CH_3)^{\alpha 8\cdot e}\\&+(CH_3)^{1\beta}\,\lambda\,\text{ch. R}+(OH)^{3\alpha}\,\lambda\,(CH_3)^{4\alpha}\\&+(OH)^{3\alpha}\,\lambda\,(CH_3)^{\alpha 8\cdot d}+(OH)^{3\alpha}\,\lambda\,(CH_3)^{\alpha 8\cdot e}\\&+(OH)^{3\alpha}\,\lambda\,\text{ch. R}+(CH_3)^{4\alpha}\,\lambda\,(CH_3)^{\alpha 8\cdot d}\\&+(CH_3)^{4\alpha}\,\lambda\,(CH_3)^{\alpha 8\cdot e}+(CH_3)^{4\alpha}\,\lambda\,\text{ch. R}\\&+(CH_3)^{\alpha 8\cdot d}\,\lambda\,(CH_3)^{\alpha 8\cdot e}+(CH_3)^{\alpha 8\cdot d}\,\lambda\,\text{ch. R}\\&+(CH_3)^{\alpha 8\cdot e}\,\lambda\,\text{ch. R}\end{aligned}\qquad (3)$$

On the other hand, $[\mu]^{20}_{D\ calcd}\{3/(n^2+2)\}$, caused by the dynamical coupling effect between any two members of unit groups in menthol-like substance, can be calculated by using the theoretical formulae[19]. The results of calculation are shown in Table IV.

By using Table IV, Eq. 3 is rewritten as follows;

$$\begin{aligned}\sum[\mu]^{20}_{D\ obs}&\text{ of }(+)\text{neomenthol}\\&=(-4.04\zeta'_{CH_3}\zeta'_{OH}{}^{22)}+0-4.41\zeta'^2_{CH_3}\\&+4.41\zeta'^2_{CH_3}+0+25.30\zeta'_{CH_3}\zeta'_{OH}\\&+3.09\zeta'_{CH_3}\zeta'_{OH}-4.04\zeta'_{CH_3}\zeta'_{OH}+0+0+0\\&+0+0)\{(n^2+2)/3\}+D-D\\&=20.31\zeta'_{CH_3}\zeta'_{OH}\{(n^2+2)/3\}\end{aligned}$$

The corresponding observed value is 30.6[23].

$$\therefore\quad 20.31\zeta'_{CH_3}\zeta'_{OH}\{(n^2+2)/3\}\equiv 30.6$$

or

$$\zeta'_{CH_3}\zeta'_{OH}=1.5066\{3/(n^2+2)\} \qquad (4)$$

On the other hand, the value of $\zeta_{CH_3}\zeta_{OH}$ in the case of hydroxycyclohexane can be calculated by using (−)*trans*-2-methylcyclohexanol as below;

$$\begin{aligned}\sum[\mu]^{20}_{D\ obs}&\text{ of }(-)trans\text{-2-methylcyclohexanol}\\&=(OH)^{1\beta}\,\lambda\,(CH_3)^{2\alpha}+(OH)^{1\beta}\,\lambda\,\text{ch. R}\\&+(CH_3)^{2\alpha}\,\lambda\,\text{ch. R}^{23)}\\&=-25.30\{(n^2+2)/3\}\zeta_{CH_3}\zeta_{OH}+0+0^{24)}\\&\equiv-42.4\end{aligned}$$

$$\therefore\quad \zeta_{CH_3}\zeta_{OH}=1.6759\{3/(n^2+2)\} \qquad (5)$$

The value of $\zeta'_{CH_3}\zeta'_{OH}$ of menthol-like substance, shown in Eq. 4 is almost equal to that of $\zeta_{CH}\zeta_{OH}$ of methylcyclohexanol given in Eq. 5. This fact indicates that the value of $\zeta'_{CH_3}\zeta'_{OH}$ in Eq. 4 is trustworthy. Moreover, by using Eq. 4, $\sum[\mu]^{20}_{D\ obs}$ of (+)*trans*-2-hydroxyneomenthol which has $(OH)^{3\alpha}$ in its molecule is calculated to be 69.5. This calculated value is almost equal to the corresponding observed value, 70.3. This fact may mean that the value of $\zeta'_{CH_3}\zeta'_{OH}$ in Eq. 4 is a suitable one for the calculation of $\sum[\mu]^{20}_{D\ obs}$ of menthol-like substances.

Next, by using a method similar to that described above, an equation can be obtained as follows;

19) S. Yamana, This Bulletin, 30, 203 (1957).

20) $(CH_3)^{\alpha 8\cdot d}$ means $(CH_3)^{\alpha 8}$ which stays at d-position, and so on (Ref. 2).

21) Simp. I is used here.

22) $\zeta'$ is $\zeta$-coefficient of a unit group in the case of menthol-like substance.

23) Ref. Table I.

24) Table IV is used, here.

TABLE IV. $[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}}\{3/(n^2+2)\}$, CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS IN MENTHOL-LIKE SUBSTANCE OF C 1 CONFORMATION

| | $(CH_3)^{\alpha 8 \cdot f}$ | $(CH_3)^{\alpha 8 \cdot e}$ | $(CH_3)^{\alpha 8 \cdot d}$ | $(CH_3)^{4\alpha}$ | $(OH)^{3\beta}$ | $(OH)^{3\alpha}$ | $(OH)^{2\beta}$ | $(OH)^{2\alpha}$ |
|---|---|---|---|---|---|---|---|---|
| ch. R | 0 | $-D$ | $D$ | 0 | 0 | 0 | 0 | 0 |
| $(OH)^{1\alpha}$ | 0 | −0.74 | 0.74 | 0 | 1.88 | 0 | 0 | 11.73 |
| $(CH_3)^{1\alpha}$ | 0 | −1.75 | 1.75 | 0 | 4.20 | 0 | 0 | 25.30 |
| $(CH_3)^{1\beta}$ | 0 | 4.41 | −4.41 | 0 | 0 | −4.04 | 25.30 | −25.30 |
| $(OH)^{2\alpha}$ | −4.74 | 0 | 4.74 | 0 | 11.73 | −11.73 | | |
| $(OH)^{2\beta}$ | 0 | 4.64 | −0.11 | −4.04 | −11.73 | 0 | | |
| $(OH)^{3\alpha}$ | 0 | −4.04 | 3.09 | 25.30 | | | | |
| $(OH)^{3\beta}$ | −3.07 | 4.04 | 0 | −25.30 | | | | |
| $(CH_3)^{4\alpha}$ | 0 | 0 | 0 | | | | | |
| $(CH_3)^{\alpha 8 \cdot d}$ | 0 | 0 | 0 | | | | | |
| $(CH_3)^{\alpha 8 \cdot e}$ | 0 | 0 | 0 | | | | | |
| $(CH_3)^{\alpha 8 \cdot f}$ | 0 | 0 | 0 | | | | | |

Note: $D$ cannot be calculated, theoretically.

TABLE V. $\sum[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$ OF MENTHOL-LIKE SUBSTANCE

| Name | Type | | |
|---|---|---|---|
| | S | I | II |
| (−)*trans*-2-Hydroxymenthol | −12.8 | $-29.4-D$ | $-33.0+D$ |
| (−)*cis*-2-Hydroxymenthol | −43.4 | $-45.5-D$ | $-63.4+D$ |
| (−)Isomenthol | −25.7 | $-31.3-D$ | $-35.5+D$ |
| (−)Menthol | −32.0 | $-34.3-D$ | $-45.1+D$ |
| (−)Carvomenthol | −31.0 | $-42.9-D$ | $-40.5+D$ |
| (+)*cis*-1,2-Menthanediol | 19.2 | $6.2-D$ | $10.8+D$ |
| (+)Neocarvomenthol | 38.9 | $41.4-D$ | $29.5+D$ |
| (+)*trans*-1-Hydroxyneocarvomenthol | 38.9 | $40.3-D$ | $30.6+D$ |

S: Symmetrical type, I: Unsymmetrical I type, II: Unsymmetrical II type.

$$\sum[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}} \text{ of } (-)cis\text{-2-hydroxyneomenthol} \equiv(-11.73\zeta'^{2}_{\mathrm{OH}}-0.25\zeta'_{\mathrm{CH_3}}\zeta'_{\mathrm{OH}}) \times\{(n^2+2)/3\}\equiv-50.6 \tag{6}$$

Combining Eq. 4 with Eq. 6,

$$\zeta'^{2}_{\mathrm{OH}}=4.2796\{3/(n^2+2)\} \tag{7}$$

or

$$\zeta'_{\mathrm{OH}}=2.0687\{3/(n^2+2)\}^{1/2} \tag{7'}$$

The value of $\zeta'^{2}_{\mathrm{OH}}$ in Eq. 7 is nearly equal to that of $\zeta^{2}_{\mathrm{OH}}$, $4.1091\{3/(n^2+2)\}$ which was obtained for the case of (−)1/2 cyclohexanediol[25]. This fact can easily be understood by considering that both (−)*cis*-2-hydroxyneomenthol and (−) 1/2 cyclohexanediol have only two hydroxyl groups which are adjacent to each other in their molecules. Thus, the value of $\zeta'^{2}_{\mathrm{OH}}$ Eq. 7 seems to be reliable. From Eqs. 4 and 7′,

$$\zeta'_{\mathrm{CH_3}}=0.7283\{3/(n^2+2)\}^{1/2}$$

and

$$\zeta'^{2}_{\mathrm{CH_3}}=0.5304\{3/(n^2+2)\} \tag{8}$$

**Substances which Have $(OH)^{3\beta}$.** — Referring to Table III, the nearest position from O-atom in $(OH)^{3\beta}$ is $\alpha 8\cdot$d-position. Then, owing to the steric repulsion, $(OH)^{3\beta}$ may refute the idea that any movable $(CH_3)^{\alpha 8}$ in $(iso\text{-}C_3H_7)^{4\alpha}$ stays at $\alpha 8\cdot$d-position. In this case, the internal conformation of $(iso\text{-}C_3H_7)^{4\alpha}$ may be forced to take the unsymmetrical I type. But if an atom or group which combines whith $C^2$-atom attracts $(OH)^{3\beta}$ off $\alpha 8\cdot$d-position, the influence of $(OH)^{3\beta}$ on the type of the internal conformation of $(iso\text{-}C_3H_7)^{4\alpha}$ may be greatly weakened. Now, by using Eqs. 4 and 7, $\sum[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$ of the menthol-like substances which have $(OH)^{3\beta}$ are calculated in each type of the internal conformation of $(iso\text{-}C_3H_7)^{4\alpha}$. The results of calculation are shown in the upper part of Table V.

For lack of experimental data in relation to the cyclohexane-ring, $D$ cannot be calculated theoretically. Then, the author resorted to a quasi-empirical evaluation of it. (−)Menthol has $(OH)^{3\beta}$ but it has no atom or group which combines with the $C^2$-atom and attracts $(OH)^{3\beta}$. And moreover, as the orientation of its $(CH_3)^{1\beta}$ is equatorial, the influence of $(CH_3)^{1\beta}$ on the type of the internal conformation of its $(iso\text{-}C_3H_7)^{4\alpha}$ will be very small. Then, the internal conformation of its $(iso\text{-}C_3H_7)^{4\alpha}$ is expected

25) Ref. Eq. 4* in the foot-note 4.

TABLE VI. COMPARISON OF $[M]_D^{20}$ WITH $\sum[\mu]_D^{20}{}_{obs}$

| Name | at $C^3$ | $[M]_D^{20}$ [23] | $\sum[\mu]_D^{20}{}_{obs}$ S | I | II | % |
|---|---|---|---|---|---|---|
| (+)Neomenthol | $(OH)^{3\alpha}$ | 30.6 | 30.6 | | | 100% S |
| (−)*cis*-2-Hydroxyneomenthol | $(OH)^{3\alpha}$ | −50.6 | −50.6 | | | 100% S |
| (+)*trans*-2-Hydroxyneomenthol | $(OH)^{3\alpha}$ | 70.3 | 69.5 | | | 100% S |
| (−)*trans*-2-Hydroxymenthol | $(OH)^{3\beta}$ | −16.0 | −12.8 | −72.6 | 10.2 | 95% S + 5% I |
| (−)*cis*-2-Hydroxymenthol | $(OH)^{3\beta}$ | −56.7 | −43.4 | −88.7 | −20.2 | 71% S +29% I |
| (−)Isomenthol | $(OH)^{3\beta}$ | −39.4 | −25.7 | −74.5 | 7.7 | 72% S +28% I |
| (−)Menthol | $(OH)^{3\beta}$ | −77.5 | −32.0 | −77.5 | −1.9 | 100% I |
| (−)Carvomenthol | none | −41.2 | −31.0 | −86.1 | 2.7 | 82% S +18% I |
| (+)*cis*-1,2-Menthanediol | none | 24.1 | 19.2 | −37.0 | 54.0 | 86% S +14% II |
| (+)Neocarvomenthol | none | 65.2 | 38.9 | −1.8 | 72.7 | 22% S +78% II |
| (+)*trans*-1-Hydroxyneo-carvomenthol | none | 79.2 | 38.9 | −2.9 | 73.8 | 100% II |

S: Symmetrical type, I: Unsymmetrical I type, II: Unsymmetrical II type.

to be of the unsymmetrical I type. Accordingly, by referring to Table V, $\sum[\mu]_D^{20}{}_{obs}$ of (−) menthol should be $(-34.3-D)$. The corresponding observed value is $-77.5$[23].

$$\therefore \quad -34.3-D \equiv -77.5$$

or

$$D=43.2 \qquad (9)$$

By using Eq. 9, Table V can be rewritten into Table VI.

The seventh column of Table VI indicates the percentage of two types in order to explain the corresponding observed value. But, as the observed value, $[M]_D^{20}$, has some probable errors and the calculated value, $\sum[\mu]_D^{20}{}_{obs}$, was obtained by using some assumptions, the absolute values of the percentage in the seventh column should not be considered to be conclusive. Thus, it becomes apparent that even in this series, the symmetrical type can be prevalent when there are some groups which attract $(OH)^{3\beta}$ or to not allow any $(CH_3)^{\alpha 8}$ to say at the $\alpha$8·f-position. But the ratio of these two types is affected greatly by the orientations of the other atoms or groups in the molecules.

**Substances which Have no (OH)$^3$.**—By using a method similar to those mentioned above, $\sum[\mu]_D^{20}{}_{obs}$ of the substances which have not $(OH)^3$ are calculated and the results are shown in the lower parts of Tables V and VI. In this case also, the symmetrical type is prevalent. But it is strange that in (+)neocarvomenthol and (+)*trans*-1-hydroxyneocarvomenthol, the unsymmetrical II type is prevalent among the three types. This may mean that there is a kind of intramolecular (or intermolecular) van der Waals' attractive force between $(CH_3)^{\alpha 8}$ and the hydroxyl group which combines with the $C^2$- or $C^1$-atom, but this point is left for future study.

## Summary

From the standpoint of the fact that a menthol-like substance is a kind of hydroxycyclohexane, the molecular rotations of menthol-like substances are calculated by using the PM-method. A comparison of the calculated values with the corresponding observed values seems to make it possibe to presume the type of the internal conformation of $(iso\text{-}C_3H_7)^{4\alpha}$.

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