# 35. Studies in Stereochemical Structure. Part VI. The Isomeric (-)Menthyl a-Naphthylglycollates. 

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The dispersion of the ( - )menthyl mandelates has been described by one of us (Roger, J., 1932, 2168), who also found that the superposition of the slightly complex dispersion of $(-)$ menthyl $(-)$ mandelate on the anomalous dispersion of the $(-)$ menthyl ( + )mandelate reproduced the simple dispersion of $(-)$ menthyl $r$-mandelate. The connexion between optical superposition and the fact that ( - menthyl $r$-mandelate could not be resolved by crystallisation was discussed at the time. Meanwhile, McKenzie and Gow (J., 1933, 32) have shown that the diastereoisomeric constituents of ( - menthyl $d l-\alpha$-naphthylglycollate can be separated either by crystallisation or distillation, and an examination of the dispersions of the isomeric ( - )menthyl $\alpha$-naphthylglycollates described by these authors offered a chance of investigating the question already dealt with in the case of the mandelates. Moreover, McKenzie and Gow have shown that there is a definite difference between the derivatives of the optically active $\alpha$-naphthylglycollic acids and the mandelic acids as regards racemisation and other phenomena.

The following results have now been obtained.
(-) $\alpha$-Naphthylglycollic Acid.-This acid is much more lævorotatory than (-)mandelic acid in acetone. It exhibits a greater variance with solvent and a similar temperature effect to mandelic acid. The Rupe criteria (see Table I) for the two acids were very similar and the dispersion is very like that of mandelic acid, i.e., normal and slightly complex.
(-)Menthyl ( - ) $\alpha$-Naphthylglycollate. -The rotatory power of solutions of this ester varied somewhat with solvent but not with temperature. Concentration had a slight effect in carbon disulphide and in benzene solution. One-term Drude equations expressed the dispersions between $\lambda 6563$ and $\lambda 4358$. The Rupe criteria (see Table I) were similar to those of ( - menthyl ( - mandelate except that the values for the alcoholic solutions did not depart markedly from those for the other solutions. The dispersion is normal but slightly complex.
$(-)$ Menthyl ( + ) $\alpha-$ Naphthylglycollate.-The rotatory powers (always + ) varied markedly with solvent and were also affected by temperature and concentration. One-term Drude equations did not express the dispersions, and the Rupe criteria (see Table I) for the $(-)$ menthyl $(+) \alpha$-naphthylglycollate showed a certain regularity that was entirely lacking in the corresponding mandelate. The dispersion is definitely complex (much more so than that of its diastereoisomeride) but normal, whilst that of ( - )menthyl ( + )mandelate is anomalous. The " totale intramolekulare Anomalie" of Tschugaev is, therefore, not realised in the visible spectrum in this case (cf. Rupe and Kägi, Annalen, 1920, 420, 33).
(-)Menthyl dl- $\alpha$-Naphthylglycollate.-This compound was obtained by McKenzie and Gow (loc. cit.) as a low-melting solid (m. p. $38 \cdot 5-39 \cdot 5^{\circ}$ ) after standing for several weeks. It cannot be purified, however, by distillation or crystallisation, for both these operations cause separation into the constituent diastereoisomerides. With the unpurified ester, the coloured solutions made accurate readings impossible for the blue and violet lines. Samples of the crude ester were therefore dissolved in dry ether, and treated with animal charcoal for 2 minutes, 2 hours, and 2 weeks. The dispersions of each of these samples were determined, and although values for the longer wave-lengths did not alter much, yet those for $\lambda 4358$ were much improved after 2 weeks, and the dispersion was almost simple and normal, and agreed with the values found by superposition of the rotatory powers of the diastereoisomerides. Whilst the rotatory powers in acetone, chloroform, and alcohol did not vary greatly, that in carbon disulphide showed a depression. This was also shown in the Rupe criteria. The dispersion may be regarded as normal and almost simple, and is similar to that of $(-)$ menthyl $\boldsymbol{r}$-mandelate.

The dispersions of ( - )menthyl $(+) \alpha$-naphthylglycollate and ( - )menthyl ( + )mandelate also form an interesting contrast with the (-)menthyl esters of benzoyl- and $\alpha$-naphthoylformic acid. (-)Menthyl $\alpha$-naphthoylformate showed anomalous dispersion, whilst the

Table I.
Dispersion criteria for ( - ) $\alpha$-naphthylglycollic acid and ( - menthyl $\alpha$-naphthylglycollates.

| Solvent. | $\lambda_{0}^{2}$. | $\begin{gathered} \lambda_{a} . \\ (-) \text { Acid. } \end{gathered}$ | P.R.D. | $\lambda_{0}^{2}$. | $\begin{gathered} \lambda_{\alpha} . \\ (-) \text { Ester. } \end{gathered}$ | P.R.D. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{COMe}_{2}$ | $0 \cdot 06096$ | 628 | 155 | 0.05200 | 642 | 146 |
| $\mathrm{C}_{6} \mathrm{H}_{6}$ | - |  | - | 0.05666 | 633 | 151 |
| $\mathrm{CHCl}_{3}$ | 0.05792 | 633 | 152 | 0.05720 | 633 | 151 |
| $\mathrm{CS}_{2}$ | - | - | - | 0.06099 | 629 | 155 |
| EtOH | $0 \cdot 06005$ | 630 | 154 | 0.05551 | 636 | 150 |
| $\mathrm{H}_{2} \mathrm{O}$ | 0.05332 | 637 | 147 | - | - | - |
|  |  | $(+)$ Ester. |  |  | $d l$-Ester. |  |
| $\mathrm{COMe}_{2}$ | $0 \cdot 1285$ | 550 | 197 | 0.03038 | 676 | 118 |
| $\mathrm{C}_{6} \mathrm{H}_{6}$ | $0 \cdot 1360$ | 541 | 199 | 0.02230 | 687 | 103 |
| $\mathrm{CHCl}_{3}$ | $0 \cdot 1141$ | 563 | 190 | 0.02581 | 682 | 110 |
| $\mathrm{CS}_{2} \ldots$ | $0 \cdot 1064$ | 575 | 188 | * 0.01924 | 690 | 96 |
| EtOH | $0 \cdot 1106$ | 566 | 188 | 0.02978 | 679 | 117 |

* The ester used in the carbon disulphide solution was decolorised for 2 weeks, that used in the other solvents for 2 hours.
benzoylformate had only a normal and complex dispersion (Roger and Ritchie, Biochem. $Z$., 1932, 253, 240), i.e., the relative effects of the phenyl and the $\alpha$-naphthyl group are reversed in the two sets of compounds.

The rotatory power of ( - menthyl $d l-\alpha$-naphthylglycollate can be calculated from the values of the diastereoisomerides, and agrees with that determined experimentally for the ester itself. The values from an equimolar solution of the diastereoisomerides also agreed, as did those when separate equimolar solutions were superimposed in the polarimeter, e.g., in carbon disulphide (see Table II). It will be seen, therefore, that the Rupe criteria obtained by superposition agree remarkably well with those obtained from the $d l$ ester.

Table II (all rotations negative).

|  | $\lambda 6563$. | $\lambda 6162$. | $\lambda 5893$. | $\lambda 5461$. | $\lambda 5106$. | $\lambda 4861$. | $\lambda 4358$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I | $35.5{ }^{\circ}$ | $40 \cdot{ }^{\circ}$ | $44.4{ }^{\circ}$ | $52.3{ }^{\circ}$ | $60 \cdot 3^{\circ}$ | $66.7{ }^{\circ}$ | $84.6{ }^{\circ}$ |
| II | $35 \cdot 4$ | $40 \cdot 3$ | $44 \cdot 4$ | $52 \cdot 3$ | $60 \cdot 5$ | 66.9 | 83.5 |
| III | $35 \cdot 3$ | $40 \cdot 2$ | $44 \cdot 1$ | $52 \cdot 0$ | $60 \cdot 1$ | 66.9 | 83.8 |
| IV | 35•3 | $40 \cdot 2$ | 44.2 | $52 \cdot 0$ | $60 \cdot 0$ | $67 \cdot 0$ | $83 \cdot 9$ |

I. Values calculated from the superposition of the diastereoisomerides.
II. Superposition of equimolar solutions of the diastereoisomerides.
III. One solution composed of equal amounts of the diastereoisomerides.
IV. Observed values for ( - )menthyl $d l$-a-naphthylglycollate.

Table III.
Dispersion criteria calculated from II in Table II.

| Solvent. | $\lambda_{0}^{2}$. | $\lambda_{a}$. | P.R.D. | Solvent. | $\lambda_{0}^{2}$. | $\lambda_{\alpha}$. | P.R.D. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{COMe}_{2}$ | 0.02966 | 676 | 117 | $\mathrm{CS}_{2}$ | $0 \cdot 02005$ | 692 | 99 |
| $\mathrm{C}_{6} \mathrm{H}_{8}$ | 0.02794 | 681 | 114 | EtOH | $0 \cdot 03146$ | 675 | 120 |
| $\mathrm{CHCl}_{3} \ldots \ldots$. | 0.02735 | 676 | 112 |  |  |  |  |

This same superimposability was found with the ( - )menthyl mandelates, but there is one important difference between the two sets of esters, inasmuch as ( - )menthyl dl- $\alpha-$ naphthylglycollate can be resolved into its diastereoisomerides by recrystallisation or by distillation (McKenzie and Gow, loc. cit.), whilst (-)menthyl $r$-mandelate is partially racemic. This definitely shows that there is no connexion between the optical superposition exhibited by these esters and the question whether they are partially racemic compounds or not. Rupe and Kägi (loc. cit.) obtained perfect superposition with an equimolar mixture of their diastereoisomerides, and it was found that the rotatory powers of this mixture obeyed a one-term Drude equation. Tschugaev and Glebko (Ber., 1913, 46, 2752 ) found the principle to hold in the ( - menthylurethanes of $d$ - and $l$-tartaric acids and meso-tartaric acid, and we find that the rotatory powers of the meso-derivative obey
approximately a one-term Drude equation. Patterson and Buchanan (J., 1924, 125, 2579) have examined the di(-)sec.-octyl dimethoxysuccinates, and find superposition in the homogeneous state, but not in o-nitrotoluene. In both circumstances, however, we find that one-term Drude equations approximately express the calculated values for the $i$-ester; for instance (in $o$-nitrotoluene) :

| [a]. | $\lambda 6716$. | $\lambda 5790$. | $\lambda 5461$. | $\lambda 4960$. |
| :---: | :---: | :---: | :---: | :---: |
| Calc. from $\frac{1}{2}(d+l)$ | $3.76{ }^{\circ}$ | $4 \cdot 67{ }^{\circ}$ | $5.68{ }^{\circ}$ | $8.46{ }^{\circ}$ |
| Calc. from [a] $=1 \cdot 252 /\left(\lambda^{2}-0.08984\right)$ | $3 \cdot 47$ | $5 \cdot 09$ | $6 \cdot 0$ | $8 \cdot 02$ |
| Obs. for $i$-ester | $2 \cdot 46$ | $3 \cdot 08$ | $3 \cdot 37$ | $4 \cdot 26$ |

It may so happen, however, that in the homogeneous state the rotatory powers of the meso- and $r$-esters are by chance identical, but it does not follow that they should be identical in solution. This question has been examined by Walden ( $Z$. physikal. Chem., 1896, 20, 377; cf. Patterson and Patterson, J., 1915, 107, 142) with the amyl tartrates. He found no agreement between the meso- and the $r$-ester, but his experiment is not conclusive. He distilled the $r$-ester repeatedly, and may have partially separated his product; moreover, the amyl alcohol was not pure. The first of these points is important, since the resolution of racemic acid has been effected by borneol and menthol (Wren, Williams, and Myddleton, J., 1920, 117, 191; cf. Wren and Still, J., 1917, 111, 513 ; Wren and Hughes, J., 1924, 125, 1739).

Wood, Such, and Scarf (J., 1926, 1928) also found no superposition with the sec.-butyl lactates, but once again we find that a one-term Drude equation approximately fits the dispersion of the values calculated from the diastereoisomeric esters, as shown below :

| [a]. | $\lambda 6708$. | $\lambda 5893$. | $\lambda 5461$. | $\lambda 4861$. | $\lambda 4358$. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Calc. from $\frac{1}{2}(d+l)$ | $7.79^{\circ}$ | $10.06^{\circ}$ | $11.85{ }^{\circ}$ | $15.33^{\circ}$ | $18.91{ }^{\circ}$ |
| Calc. from $[a]=3 \cdot 317 /\left(\lambda^{2}-0 \cdot 1929\right)$ | $7 \cdot 71$ | $10 \cdot 13$ | $11 \cdot 89$ | 15.29 | $19 \cdot 3$ |
| Obs. ......... | $6 \cdot 79$ | $8 \cdot 47$ | $9 \cdot 60$ | 11.34 | $12 \cdot 9$ |

Here the dl-sec.-butyl $l$-lactate might have undergone a partial separation during distillation, but the authors showed that this was not so by saponifying their ester, thus obtaining an optically inactive alcohol. Hydrolysis of the $d$-sec.-butyl $l$-lactate gave a pure $d$-sec.-butyl alcohol. In this case, however, there are no complications arising from the existence of a meso- and a racemic form of the acid. The "Entfernungsatz" (Freudenberg, Ber., 1933, 66, 190) offers an explanation, since in the lactates the asymmetric centre of the sec.-butyl alcohol is directly linked to the carboxyl group and is thus comparable with the sec.-octyl tartrates where superposition does not hold, although it occurs with the amyl tartrates. The ( - )menthyl esters of mandelic and $\alpha$-naphthylglycollic acid do not apparently fall in with the "Entfernungsatz" as here the asymmetric carbinol centre is directly united to the carboxyl group (cf. Roger and Ritchie, loc. cit.).

The exceptions to the superposition rule are capable of other interpretations. In the few cases where data are available we have shown that the dispersion calculated from superposition values should be simple or almost simple, a prediction not always fulfilled in practice. In cases such as that of the homogeneous $d l$-sec.-butyl $l$-lactate the physical state is that of the solution of one compound in another, and solvent effect may have to be considered. The dispersion of one diastereoisomeride in solution in the other may be so altered by the act of solution that the dispersions of both may no longer be superimposed to give a simple dispersion. With the $d l$ - $\alpha$-naphthylglycollate in solvents, this solution effect apparently is not marked.

On the basis of asymmetric induction, the following configurations are possible for

$$
\begin{array}{rlrl}
\text { (I.) } \mathrm{C}_{10} \mathrm{H}_{7} \cdot \mathrm{CH}(\mathrm{OH})-\mathrm{C}-\mathrm{OC}_{10} \mathrm{H}_{19} & \text { (II.) } \mathrm{C}_{10} \mathrm{H}_{7} \cdot \mathrm{CH}(\mathrm{OH})-\mathrm{C}-\mathrm{OC}_{10} \mathrm{H}_{19} \\
& \text { (+) } & (+) & (-)
\end{array}
$$

$(-)$ menthyl $(+) \alpha$-naphthylglycollate and a solution would probably consist of an equilibrium mixture of the two forms. This equilibrium would readily be displaced by alter-
ation of physical conditions. Now, if the ( + ) $\alpha$-naphthylglycollyl complex has a greater dextro-inducing influence than the ( + )mandelyl complex, then there should be a definite preponderance of one of the forms under all conditions. It would appear that in chloroform solutions of $(-)$ menthyl $(+)$ mandelate the contributions of the separate centres (real and induced) to the optical activity of the molecule balance one another under certain conditions of wave-length and temperature. On the other hand, solutions of esters of the type under consideration may be homogeneous, and the phenomena described may depend on the extent to which induction of the carbonyl groups takes place. This group in any of these compounds may be capable of exhibiting a " maximum " induction, but under conditions of examination it may seldom be able to attain this " maximum " and therefore is only "partially" induced. The extent of the contribution of this induced centre to the optical activity of such esters will, therefore, vary and be influenced by physical conditions and by the variation of R in the $\mathrm{R} \cdot \mathrm{CH}(\mathrm{OH})$ complex (cf. work of W . Kuhn on the "Vizinalregel," Hand- und Jahrbuch der chemischen Physik, 1932, 8, III, 121).

## Experimental.

(一) $\alpha$-Naphthylglycollic Acid. (All rotations are negative.)
(1) In acetone $\left(c=3 \cdot 2375, l=2, t=20^{\circ}\right) ;[\alpha]=53.77 /\left(\lambda^{2}-0.06096\right)$.

|  |  | $\lambda 6563$. | $\lambda 6162$. | $\lambda 5893$. | $\lambda 5461$. | $\lambda 5106$. | $\lambda 4861$. | $\lambda 4358$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $145 \cdot 8^{\circ}$ | $168 \cdot 7^{\circ}$ | $187 \cdot 4^{\circ}$ | $226 \cdot 4^{\circ}$ | $269 \cdot 6^{\circ}$ | $306 \cdot 8^{\circ}$ | $416 \cdot 2^{\circ}$ |
| $[\alpha]$ calc. $\ldots \ldots \ldots .$. | $145 \cdot 5$ | $168 \cdot 8$ | $187 \cdot 8$ | $226 \cdot 8$ | $269 \cdot 3$ | $306 \cdot 8$ | $416 \cdot 9$ |  |

(2) In chloroform * $\left(c=0.9805, l=2, t=3.5^{\circ}\right)$.
$\left[\begin{array}{llllllllll}{[\alpha] \text { obs. }} & \ldots \ldots . . . & 166.7 & 190.7 & 212.6 & 254.0 & 303.4 & 349.3 & -\end{array}\right.$

Same solution, $t=20^{\circ} ;[\alpha]=59.43 /\left(\lambda^{2}-0.05792\right)$.

| [ $\alpha$ ] obs. | 161.2 | 183.5 | $204 \cdot 5$ | 246.8 | 292.7 | 334-5 | $452 \cdot 3$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $[\alpha]$ calc. | $159 \cdot 4$ | 184.8 | $205 \cdot 3$ | $247 \cdot 4$ | 293•1 | $333 \cdot 2$ | $450 \cdot 0$ |
| Same solution, $t=35^{\circ}$. |  |  |  |  |  |  |  |
| [ $\alpha$ ] obs. | $149 \cdot 4$ | 171.3 | $191 \cdot 7$ | 231.5 | $272 \cdot 9$ | 313.0 | - |

(3) In ethyl alcohol $\left(c=2 \cdot 779, l=2, t=0^{\circ}\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | 154.5 | $177 \cdot 6$ | 197.9 | $239 \cdot 6$ | 283.9 | 323.2 | - |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

Same solution, $t=20^{\circ} ;[\alpha]=53.41 /\left(\lambda^{2}-0.06005\right)$.

| [ $\alpha$ ] obs. | $144 \cdot 0$ | $166 \cdot 6$ | 186.7 | 224.4 | $266 \cdot 7$ | $302 \cdot 6$ | 411.8 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| [ $\alpha$ ] calc. | $144 \cdot 1$ | $167 \cdot 1$ | 186.0 | 224.3 | $266 \cdot 3$ | 303•1 | 411.1 |
| Same solution, $t=38^{\circ}$. |  |  |  |  |  |  |  |
| $[\alpha]$ obs. | $137 \cdot 1$ | $160 \cdot 5$ | $177 \cdot 4$ | 211.9 | $253 \cdot 5$ | 287.2 | - |

(4) In water ${ }^{*}\left(c=1 \cdot 195, l=2, t=20^{\circ}\right) ;[\alpha]=45 \cdot 66 /\left(\lambda^{2}-0.05332\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots \ldots$ | 120.9 | $138 \cdot 9$ | 156.5 | $185 \cdot 8$ | $220 \cdot 1$ | $250 \cdot 6$ | 336.4 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots$. | $121 \cdot 0$ | 139.9 | 155.3 | 186.5 | $220 \cdot 2$ | $249 \cdot 6$ | 334.4 |

$(+) \alpha-$ Naphthylglycollic Acid. (All rotations are positive.)
(1) In ethyl alcohol ( $c=2.804, l=2, t=20^{\circ}$ ); $[\alpha]=52.91 /\left(\lambda^{2}-0.06302\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $144 \cdot 2$ | $166 \cdot 5$ | $186 \cdot 3$ | $225 \cdot 4$ | $268 \cdot 0$ | $304 \cdot 5$ | $414 \cdot 8$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots .$. | 143.9 | $167 \cdot 0$ | $186 \cdot 1$ | $225 \cdot 0$ | $267 \cdot 7$ | $305 \cdot 4$ | $417 \cdot 0$ |

[^0](1) In acetone $\left(c=2 \cdot 525, l=2, t=1^{\circ}\right)$.

|  |  | $\lambda 6563$. | $\lambda 6162$. | $\lambda 5893$. | $\lambda 5461$. | $\lambda 5106$. | $\lambda 4861$. | $\lambda 4358$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $101 \cdot 0^{\circ}$ | - | $129 \cdot 4^{\circ}$ | $155 \cdot 0^{\circ}$ | - | $206 \cdot 6^{\circ}$ | $275 \cdot 0^{\circ}$ |

Same solution, $t=21^{\circ} ; \quad[\alpha]=36.85 /\left(\lambda^{2}-0.05373\right)$.

| $[\alpha]$ obs. | $\ldots \ldots . . . .$. | $98 \cdot 0$ | $112 \cdot 7$ | $125 \cdot 7$ | $150 \cdot 5$ | $178 \cdot 2$ | $202 \cdot 2$ | $268 \cdot 3$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots . . . . .$. | 97.7 | $113 \cdot 1$ | $125 \cdot 5$ | $150 \cdot 8$ | $178 \cdot 0$ | $201 \cdot 8$ | $270 \cdot 4$ |

Same solution, $t=40^{\circ}$.
$[\alpha]$ obs.......... $.100 .6 \quad 128.7 \quad 155.6 \quad$ - $\quad 207.7$ -
The concentration effect in this solvent was negligible :

$$
c=10 \cdot 123, l=1, t=20^{\circ}, \alpha_{5893}=-12 \cdot 78^{\circ},[\alpha]_{5893}=-126 \cdot 3^{\circ} .
$$

(2) In benzene ( $c=1.8065, l=2, t=21^{\circ}$ ); $[\alpha]=33 \cdot 13 /\left(\lambda^{2}-0.05588\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $88 \cdot 8$ | $102 \cdot 1$ | $113 \cdot 4$ | $137 \cdot 0$ | $162 \cdot 4$ | $182 \cdot 6$ | $245 \cdot 5$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $[\alpha]$ calc. | $\ldots \ldots \ldots .$. | $88 \cdot 4$ | $102 \cdot 3$ | 113.7 | $136 \cdot 8$ | 161.7 | 183.7 | $247 \cdot 1$ |

The concentration effect was much more evident in this solvent :
$c=10 \cdot 102, l=1, t=20^{\circ},[\alpha]=34.46 /\left(\lambda^{2}-0.05666\right)$.

| $[\alpha]$ obs. | $\ldots \ldots . . . .$. | $92 \cdot 39$ | 106.5 | $118 \cdot 5$ | $142 \cdot 3$ | $168 \cdot 9$ | $192 \cdot 4$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $[\alpha]$ calc. | $\ldots \ldots . . .$. | $92 \cdot 12$ | 106.7 | 118.7 | 142.8 | $169 \cdot 0$ | 191.9 |

(3) In chloroform ( $c=2.4595, l=2, t=21^{\circ}$ ); $[\alpha]=40.23 /\left(\lambda^{2}-0.05776\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $107 \cdot 7$ | $125 \cdot 6$ | $139 \cdot 8$ | 167.9 | 199.2 | 225.6 | - |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots .$. | 107.8 | 124.9 | $139 \cdot 1$ | $167 \cdot 3$ | 198.3 | $225 \cdot 4$ | - |

Same solution, $t=55^{\circ}$.
$[\alpha]$ obs. $\quad . . . . . . . . . . \quad 104 \cdot 0 \quad 119 \cdot 1 \quad 135 \cdot 3 \quad 161 \cdot 0 \quad 193 \cdot 1 \quad 221 \cdot 1$
There was no temperature effect at $-13^{\circ}$ and $0^{\circ}$ : $[\alpha]_{5833^{\circ}}^{-130}-140 \cdot 2^{\circ},[\alpha]_{5693}^{0^{\circ}}-140 \cdot 2^{\circ}$.
Same solvent ( $c=8.562, l=1, t=20^{\circ}$ ) ; $[\alpha]=41.21 /\left(\lambda^{2}-0.0572\right)$.


There is, therefore, a small concentration effect in this solvent.
(4) In carbon disulphide ( $c=1 \cdot 687, l=2, t=0^{\circ}$ ).

Same solution, $t=20^{\circ} ; \quad[\alpha]=45.82 /\left(\lambda^{2}-0.05388\right)$.

| $[\alpha]$ obs. | $\ldots \ldots . . .$. | $121 \cdot 3$ | 140.5 | 156.8 | $188 \cdot 6$ | $220 \cdot 9$ | 250.8 | $338 \cdot 8$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots . . .$. | 121.6 | 140.6 | 156.2 | 187.6 | $221 \cdot 6$ | 251.2 | $337 \cdot 0$ |

Same solvent ( $c=10 \cdot 7, l=1, t=20^{\circ}$ ); $[\alpha]=43.64 /\left(\lambda^{2}-0.06099\right)$.

| [ $\alpha$ ] obs. | 118.4 | 136.5 | $2 \cdot 5$ | 184.0 | 218.5 | $249 \cdot 0$ | 339 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| [ $\alpha$ ] calc. | 118.0 | 137.0 | 152.4 | 184.0 | 218.5 | 249.0 | 338 |

In this case the temperature does not influence the rotation, whereas increase of concentration causes a noticeable diminution in rotatory power.
(5) In ethyl alcohol $\left(c=10.675, l=1, t=20^{\circ}\right) ;[\alpha]=42.65 /\left(\lambda^{2}-0.05551\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $114 \cdot 0$ | $131 \cdot 1$ | $146 \cdot 2$ | $175 \cdot 6$ | $207 \cdot 8$ | $236 \cdot 2$ | 316.6 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots$. | $114 \cdot 0$ | $131 \cdot 6$ | $146 \cdot 2$ | $175 \cdot 8$ | $207 \cdot 8$ | $235 \cdot 9$ | 317.4 |

$(-)$ Menthyl $(+) \alpha-$ Naphthylglycollate. (All rotations are positive.)
(1) In acetone ( $c=3 \cdot 622, l=2, t=20^{\circ}$ ).

|  |  | $\lambda 6563$. | $\lambda 6162$. | $\lambda 5893$. | $\lambda 5461$. | $\lambda 5106$. | $\lambda 4861$. | $\lambda 4358$. |
| ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| $[\alpha]$ obs. | $\ldots \ldots . . .$. | $14 \cdot 2^{\circ}$ | $17 \cdot 0^{\circ}$ | $19.9^{\circ}$ | $25 \cdot 3^{\circ}$ | $32 \cdot 9^{\circ}$ | $39 \cdot 8^{\circ}$ | $61 \cdot 3^{\circ}$ |

Same solvent ( $c=10.0505, l=2, t=21^{\circ}$ ).
$\begin{array}{llllllllll}{[\alpha] \text { obs. }} & \ldots \ldots . . . . & 15.0 & 17.7 & 20.7 & 26.9 & 34.3 & 40.8 & 60.9\end{array}$
(2) In benzene ( $\left.c=10 \cdot 2885, l=2, t=20^{\circ}\right)$.

| $[\alpha]$ obs. | $\ldots \ldots . . . .$. | 14.8 | 17.9 | 20.9 | 27.5 | 35.3 | 42.8 | 67.2 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

Same solution, $t=35^{\circ}$.
$\begin{array}{llllllllll}{[\alpha] \text { obs. }} & \ldots \ldots . . . . . . & 16.5 & 19.6 & 22.9 & 29.6 & 37.9 & 45.9 & -\end{array}$
(3) In chloroform ( $c=10 \cdot 244, l=2, t=1^{\circ}$ ).


Same solution, $t=20^{\circ}$.
$[\alpha]$ obs. $\qquad$ $25 \cdot 4$
$30 \cdot 0 \quad 34 \cdot 6$
$44.0 \quad 55.0 \quad 65.0$
$96 \cdot 7$
(4) In carbon disulphide ( $c=10 \cdot 261, l=2, t=1^{\circ}$ ).

| $[\alpha]$ obs. | $\cdots \cdots \cdots . . .$. | 49.3 | 58.4 | 66.8 | 83.5 | 103.1 | 121.2 | - |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

Same solution, $t=20^{\circ}$.

| $[\alpha]$ obs. | $\ldots . . . . . .$. | 47.4 | 56.0 | 63.8 | 79.5 | 98.0 | 115.5 | 169.7 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

Same solution, $t=31^{\circ}$.
$[\alpha]$ obs.
$46 \cdot 0$
$\begin{array}{lll}54.5 & \mathbf{6 2 . 4} & \mathbf{7 7 . 7}\end{array}$
$95 \cdot 7$
112.0
(5) In ethyl alcohol ( $c=10 \cdot 2865, l=2, t=0^{\circ}$ ).
[ $\alpha$ ] obs.
$25 \cdot 4$
$30 \cdot 0$
$34 \cdot 2$
$43 \cdot 2$
$53 \cdot 6$
$63 \cdot 2$
Same solution, $t=21^{\circ}$.

| $[\alpha]$ obs. $\ldots \ldots . . .$. | 24.4 | 28.7 | 33.2 | 41.9 | 52.1 | 61.5 | 90.2 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Same solution, $t=39^{\circ}$. |  |  |  |  |  |  |  |
| $[\alpha]$ obs. $\ldots \ldots \ldots .$. | 23.9 | 27.8 | 32.3 | 40.5 | 50.8 | 59.3 | - |

(-)Menthyl dl- $\alpha$-Naphthylglycollate. (All rotations are negative.)
After two minutes' decolorisation with animal charcoal (see p. 130); solutions still slightly coloured :
(1) In acetone ( $c=3.3685, l=2, t=21^{\circ}$ ); $[\alpha]=16.82 /\left(\lambda^{2}-0.0292\right)$.

| $[\alpha]$ obs. | $\ldots \ldots . . .$. | 42.0 | 47.9 | 52.8 | 62.7 | 72.7 | 80.9 | 98.7 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | ---: |
| $[\alpha]$ calc. | $\ldots \ldots \ldots .$. | 41.9 | 48.0 | 52.9 | 62.5 | 72.7 | 81.2 | 104.6 |

(2) In benzene ( $c=3 \cdot 5135, l=2$ ), $\alpha_{5883}^{20^{\circ}}-3 \cdot 34^{\circ},[\alpha]_{5893}^{20^{\circ}}-47 \cdot 5^{\circ}$.
(3) In chloroform ( $c=3 \cdot 2885, l=2$ ), $\alpha_{5093}^{20^{\circ}}-3 \cdot 51^{\circ},[\alpha]_{5893}^{20^{\circ}}-53 \cdot 4^{\circ}$.
(4) In carbon disulphide ( $c=2 \cdot 93, l=2$ ), $\alpha_{2893}^{219}-2 \cdot 66^{\circ},[\alpha]_{5993}^{21 \cdot}-45 \cdot 4^{\circ}$.
(5) In ethyl alcohol $(c=3 \cdot 33, l=2), \alpha_{593}^{2)^{\circ}}-3 \cdot 83^{\circ},[\alpha]_{5993}^{21}-57 \cdot 5^{\circ}$.

After 2 hours' decolorisation; solutions practically colourless :
(1) In acetone ( $\left.c=3.52, l=2, t=20^{\circ}\right) ;[\alpha]=16.75 /\left(\lambda^{2}-0.03038\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $42 \cdot 1$ | $48 \cdot 0$ | $52 \cdot 6$ | $62 \cdot 9$ | $72 \cdot 4$ | $81 \cdot 3$ | $102 \cdot 0$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots . .$. | $41 \cdot 8$ | $48 \cdot 0$ | $52 \cdot 9$ | $62 \cdot 6$ | $72 \cdot 7$ | $81 \cdot 3$ | $105 \cdot 0$ |

(2) In benzene $\left(c=4 \cdot 1415, l=2, t=20^{\circ}\right)$; $[\alpha]=15.83 /\left(\lambda^{2}-0.0223\right)$.

| $\lambda 6563$. | $\lambda 6162$. | $\lambda 5893$. | $\lambda 5461$. | $\lambda 5106$. | $\lambda 4861$. | $\lambda 4358$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $38 \cdot 8^{\circ}$ | $44 \cdot 3^{\circ}$ | $48 \cdot 8^{\circ}$ | $57 \cdot 5^{\circ}$ | $66 \cdot 3^{\circ}$ | $74 \cdot 0^{\circ}$ | $91 \cdot 6^{\circ}$ |
| $38 \cdot 8$ | $44 \cdot 3$ | $48 \cdot 7$ | $57 \cdot 4$ | $66 \cdot 4$ | $74 \cdot 0$ | $94 \cdot 5$ |

(3) In chloroform ( $c=3.6115, l=2, t=20^{\circ}$ ); $[\alpha]=17.6 /\left(\lambda^{2}-0.02581\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $43 \cdot 3$ | $50 \cdot 0$ | $54 \cdot 7$ | $64 \cdot 8$ | $\mathbf{7 5 \cdot 0}$ | $83 \cdot 3$ | $102 \cdot 6$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots .$. | $43 \cdot 5$ | $49 \cdot 7$ | $54 \cdot 8$ | $64 \cdot 6$ | $\mathbf{7 4 \cdot 9}$ | $83 \cdot 6$ | $107 \cdot 3$ |

(4) In carbon disulphide $\left(c=3 \cdot 3195, l=2, t=20^{\circ}\right)$; $[\alpha]=14 \cdot 15 /\left(\lambda^{2}-0.03265\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $35 \cdot 3$ | $41 \cdot 1$ | $45 \cdot 0$ | $53 \cdot 8$ | $61 \cdot 9$ | $69 \cdot 1$ | $83 \cdot 3$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots$. | $35 \cdot 6$ | $40 \cdot 8$ | $45 \cdot 0$ | $53 \cdot 3$ | $62 \cdot 1$ | $69 \cdot 5$ | $90 \cdot 0$ |

(5) In ethyl alcohol $\left(c=3 \cdot 1395, l=2, t=20^{\circ}\right) ;[\alpha]=18 \cdot 34 /\left(\lambda^{2}-0.02978\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | 45.9 | 52.4 | 57.7 | 68.5 | 79.6 | 88.4 | 110.5 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots$. | 45.7 | 52.6 | 57.8 | 68.3 | 79.4 | 88.8 | 114.5 |

After two weeks' decolorisation :
(1) In benzene $\left(c=5 \cdot 6025, l=2, t=20^{\circ}\right) ;[\alpha]=15 \cdot 71 /\left(\lambda^{2}-0.01923\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | 37.8 | 43.8 | $48 \cdot 0$ | 56.3 | $65 \cdot 0$ | 72.4 | 92.5 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots$. | 38.2 | 43.6 | 47.9 | 56.3 | $65 \cdot 1$ | 72.4 | 92.0 |

(2) In carbon disulphide ( $c=6.2435, l=2, t=20^{\circ}$ ); $[\alpha]=14.51 /\left(\lambda^{2}-0.01924\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $35 \cdot 3$ | $40 \cdot 0$ | $44 \cdot 2$ | $52 \cdot 0$ | $60 \cdot 0$ | $67 \cdot 0$ | $83 \cdot 9$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. $\ldots \ldots \ldots$. | $\mathbf{3 5 \cdot 3}$ | $\mathbf{4 0 \cdot 2}$ | $44 \cdot 2$ | $52 \cdot 0$ | $60 \cdot 0$ | $66 \cdot 8$ | $85 \cdot 0$ |  |

The dispersion of the ester was determined by the superposition of separate equimolecular solutions of the two diastereoisomeric esters.
(1) In acetone $\left(c=10.123, l=1, t=20^{\circ}\right)^{*} ;[\alpha]=16.75 /\left(\lambda^{2}-0.02966\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | 41.8 | 47.7 | 52.8 | 62.4 | 72.5 | $81 \cdot 0$ | 102.3 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. $\ldots \ldots \ldots .$. | 41.8 | 47.9 | 52.7 | 62.4 | 72.5 | $81 \cdot 1$ | $104 \cdot 5$ |  |

(2) In benzene ( $\left.c=10 \cdot 103, l=1, t=20^{\circ}\right)^{*}$; $[\alpha]=15 \cdot 52 /\left(\lambda^{2}-0.02794\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots$. | 38.7 | $43 \cdot 9$ | $48 \cdot 6$ | $57 \cdot 4$ | 66.8 | $74 \cdot 3$ | $94 \cdot 8$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. $\ldots \ldots \ldots$. | $38 \cdot 5$ | $44 \cdot 1$ | $48 \cdot 6$ | $57 \cdot 4$ | $66 \cdot 7$ | $74 \cdot 5$ | $95 \cdot 8$ |  |

(3) In chloroform $\left(c=8.562, l=1, t=20^{\circ}\right)^{*} ;[\alpha]=17.24 /\left(\lambda^{2}-0.02735\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | 42.6 | $49 \cdot 0$ | $54 \cdot 0$ | 63.4 | 74.0 | 82.8 | 105.6 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. $\ldots \ldots \ldots$. | 42.7 | 48.9 | 53.9 | 63.6 | 73.9 | 82.5 | 106.0 |  |

(4) In carbon disulphide $\left(c=10.698, l=1, t=20^{\circ}\right)^{*} ;[\alpha]=14.51 /\left(\lambda^{2}-0.02005\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | $35 \cdot 4$ | $40 \cdot 3$ | $44 \cdot 4$ | $52 \cdot 3$ | $60 \cdot 5$ | $67 \cdot 1$ | $83 \cdot 5$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots .$. | $\mathbf{3 5 \cdot 4}$ | $40 \cdot 4$ | $44 \cdot 4$ | $52 \cdot 3$ | $60 \cdot 4$ | $67 \cdot 3$ | $85 \cdot 7$ |

(5) In ethyl alcohol $\left(c=10 \cdot 675, l=1, t=20^{\circ}\right)^{*} ; \quad[\alpha]=17.73 /\left(\lambda^{2}-0.03146\right)$.

| $[\alpha]$ obs. | $\ldots \ldots \ldots .$. | 44.4 | 50.8 | 56.4 | 66.6 | 77.6 | 86.2 | 110.8 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $[\alpha]$ calc. | $\ldots \ldots \ldots .$. | 44.4 | 50.9 | 56.1 | 66.5 | 77.4 | 86.6 | 111.9 |

The dispersion of the ester was also determined by making one solution composed of equal amounts of the two diastereoisomerides.
(1) In carbon disulphide ( $c=10.014, l=2, t=20^{\circ}$ ); $[\alpha]=14.45 /\left(\lambda^{2}-0.02037\right)$.

| [ $\alpha$ ] obs. | $35 \cdot 3$ | $40 \cdot 2$ | $44 \cdot 1$ | 52.0 | $60 \cdot 1$ | 66.9 | 83.8 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| [ $\alpha$ ] calc. | $35 \cdot 2$ | $40 \cdot 2$ | $44 \cdot 2$ | $52 \cdot 0$ | $60 \cdot 1$ | 66.9 | $85 \cdot 2$ |

(2) In ethyl alcohol $\left(c=8.512, l=2, t=20^{\circ}\right) ;[\alpha]=17.77 /\left(\lambda^{2}-0.03011\right)$.

|  | $\lambda 6563$. | $\lambda 6162$. | $\lambda 5893$. | $\lambda 5461$. | $\lambda 5106$. | $\lambda 4861$. | $\lambda 4358$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $[\alpha]$ obs. | $44.6{ }^{\circ}$ | $50.8{ }^{\circ}$ | $56.4{ }^{\circ}$ | $66.4{ }^{\circ}$ | $77.4{ }^{\circ}$ | $86.8^{\circ}$ | $111.2^{\circ}$ |
| [ $\alpha$ ] calc. | $44 \cdot 4$ | $50 \cdot 8$ | 56.0 | $66 \cdot 3$ | $77 \cdot 0$ | 86.2 | 111.2 |

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[^0]:    * The optically active forms of this acid are not readily soluble in chloroform or water.

