12. *The Isomeric (−)Menthyl α-Naphthylglycollates.*

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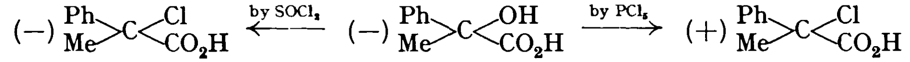
The phenyl and the α-naphthyl group have been contrasted in this laboratory from the point of view of saturation capacity and migrational aptitude, the compounds selected for this purpose being derived mainly from the isomeric mandelic acids and the analogous α-naphthylglycollic acids (McKenzie and Roger, J., 1924, **125**, 844; 1927, 571; McKenzie and Dennler, J., 1924, **125**, 2105; 1926, 1596; *Ber.*, 1927, **60**, 220; McKenzie and Mills, *Ber.*, 1929, **62**, 1784). Now, whilst the optically active mandelic acids and their derivatives have been studied in considerable detail with respect to the Walden inversion and racemisation phenomena, no such study has been made hitherto with the optically active α-naphthylglycollic acids. Derivatives of the latter acids have accordingly been investigated, more particularly with respect to displacement reactions, and certain pronounced differences have emerged between them and the corresponding mandelates.

In connexion with the interconversion of the optically active atrolactinic acids by the Walden inversion, the divergence between the behaviour of phosphorus pentachloride on the one hand and of thionyl chloride on the other towards optically active hydroxy-compounds containing a phenyl group directly attached to the asymmetric carbon atom, was described by McKenzie and Clough (J., 1910, **97**, 1016, 2564), thus:



$$(-)\,\substack{\text{Ph}\\ \text{Me}}\!>\!\text{C}\!<\!\substack{\text{Cl}\\ \text{CO}_2\text{H}} \xleftarrow{\text{by SOCl}_2} (-)\,\substack{\text{Ph}\\ \text{Me}}\!>\!\text{C}\!<\!\substack{\text{OH}\\ \text{CO}_2\text{H}} \xrightarrow{\text{by PCl}_5} (+)\,\substack{\text{Ph}\\ \text{Me}}\!>\!\text{C}\!<\!\substack{\text{Cl}\\ \text{CO}_2\text{H}}$$

and this observation was extended *inter alia* to ethyl (−)mandelate (J., 1911, **99**, 1910) and (+)phenylmethylcarbinol (J., 1913, **103**, 687). The substitution of chlorine for the hydroxy-group was also studied under the asymmetric environment of the (−)menthyl group, and for this purpose the diastereoisomeric (−)menthyl mandelates were examined (McKenzie and Smith, J., 1923, **123**, 1962), and the work was further prosecuted, more particularly on the side of asymmetric catalytic racemisation (McKenzie and Smith, J., 1924, **125**, 1582; *Ber.*, 1925, **58**, 894; Smith, *Ber.*, 1931, **64**, 427, 1115).

The (−)menthyl α-naphthylglycollates have now been brought within the scope of these investigations.

(−)Menthyl *r*-mandelate had previously been shown to be partially racemic, and to crystallise unchanged under various conditions of temperature above − 15° (McKenzie, J., 1904, **85**, 378; Findlay and Hickmans, J., 1907, **91**, 905; 1909, **95**, 1386). It is now found that (−)menthyl *dl*-α-naphthylglycollate (m. p. 38·5—39·5°) is not partially racemic but can be resolved, giving the optically pure ester (m. p. 71—72°) of the (+)acid after two crystallisations from light petroleum. For the preparation of the diastereoisomeric esters in quantity it was found, however, more practical to esterify the (+) and (—)acids separately.

(—)Menthyl *dl*-phenylchloroacetate is crystalline, and can be resolved in ethyl-alcoholic solution (McKenzie and Smith, *loc. cit.*). But (—)menthyl *dl*-α-naphthylchloroacetate (prepared by esterifying the *r*-acid) at the ordinary temperature is an oil ($[\alpha]_{5461}$ — 74·9° in acetone) which has not been obtained crystalline, and difficulties have also been met in preparing the optically pure α-naphthylchloroacetic acids. Accordingly, the diastereoisomeric (—)menthyl esters of the latter acids are not so far available for the direct comparison of their rotatory powers with those of the products from the action of phosphorus pentachloride and of thionyl chloride respectively on the (—)menthyl hydroxy-esters.

The action of thionyl chloride on the latter esters gave the following results, the rotatory powers being determined in acetone :

$$\underset{(-)}{C_{10}H_7\cdot CH(OH)}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}} \xrightarrow{\text{by SOCl}_2} C_{10}H_7\cdot CHCl\cdot CO_2\cdot C_{10}H_{19},\ [\alpha]_{5461} - 120\cdot4^\circ$$

$$\underset{(+)}{C_{10}H_7\cdot CH(OH)}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}} \xrightarrow{\text{by SOCl}_2} C_{10}H_7\cdot CHCl\cdot CO_2\cdot C_{10}H_{19},\ [\alpha]_{5461} - 23^\circ$$

The full significance of these results is not apparent until the action of thionyl chloride on (—)menthyl *dl*-α-naphthylglycollate (which in the melted state is regarded as consisting of equal amounts of the diastereoisomerides) is considered, whereby the chloro-ester formed had $[\alpha]_{5461}$ — 75·5°, which agrees very closely with the value quoted above, *viz.*, $[\alpha]_{5461}$ — 74·9°, for (—)menthyl *dl*-α-naphthylchloroacetate. This result, in conjunction with those just quoted for the diastereoisomeric esters, clearly indicates that the displacement racemisation is negligible during the action of thionyl chloride. From previous experience with menthyl esters, it can safely be concluded that no racemisation took place at the (—)menthyl complex. It therefore follows that the values $[\alpha]_{5461}$ — 120·4° and — 23° will probably approximate to those of the optically pure chloro-esters. Further support to this conclusion is obtained from a consideration of the optical rotatory power of (—)menthyl *dl*-α-naphthylchloroacetate, *viz.*, $[\alpha]_{5461}$ — 74·9°. Using the principle of optical superposition and calculating from the figures — 120·4° and — 23°, we obtain the value $[\alpha]_{5461}$ — 71·7°, which is not far removed from that of the ester of the *dl*-chloro-acid.

The action of thionyl chloride on the diastereoisomeric (—)menthyl esters of α-naphthylglycollic acid differs in a very marked manner from that on the mandelates (McKenzie and Smith, *loc. cit.*), where a considerable amount of displacement racemisation has been shown to occur, thus :

$$\underset{(-)}{CHPh(OH)}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}} \xrightarrow{\text{by SOCl}_2} \overset{70\%}{\underset{(-)}{CHPhCl}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}}} + \overset{30\%}{\underset{(+)}{CHPhCl}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}}}$$

$$\underset{(+)}{CHPh(OH)}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}} \xrightarrow{\text{by SOCl}_2} \overset{68\%}{\underset{(+)}{CHPhCl}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}}} + \overset{32\%}{\underset{(-)}{CHPhCl}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}}}$$

Phosphorus pentachloride on the α-naphthylglycollates gave :

$$\text{(a)}\quad \underset{(-)}{C_{10}H_7\cdot CH(OH)}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}} \xrightarrow{\text{by PCl}_5} C_{10}H_7\cdot CHCl\cdot CO_2\cdot C_{10}H_{19},\ [\alpha]_{5461} - 78\cdot3^\circ$$

$$\text{(b)}\quad \underset{(+)}{C_{10}H_7\cdot \overset{*}{C}H(OH)}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}} \xrightarrow{\text{by PCl}_5} C_{10}H_7\cdot CHCl\cdot CO_2\cdot C_{10}H_{19},\ [\alpha]_{5461} - 79\cdot1^\circ$$

In (a) the displacement racemisation was almost complete, whereas in (b) a *slight* swing round of sign actually occurred at the complex *. Here also we have a marked contrast with the mandelates (McKenzie and Smith, *loc. cit.*), thus :

$$\underset{(-)}{CHPh(OH)}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}} \xrightarrow{\text{by PCl}_5} \overset{35\%}{\underset{(-)}{CHPhCl}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}}} + \overset{65\%}{\underset{(+)}{CHPhCl}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}}}$$

$$\underset{(+)}{CHPh(OH)}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}} \xrightarrow{\text{by PCl}_5} \overset{31\%}{\underset{(+)}{CHPhCl}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}}} + \overset{69\%}{\underset{(-)}{CHPhCl}\cdot CO_2\cdot\underset{(-)}{C_{10}H_{19}}}$$

In both of these cases, a *pronounced* swing round of sign occurred at the mandelyl complexes.

The action of phosphorus pentachloride on (—)menthyl *dl*-α-naphthylglycollate gave a product which contained a slight preponderance of (—)menthyl (—)α-naphthylchloroacetate.

Now, according to Clough (J., 1918, **113**, 526), (—)mandelic acid belongs to the *d*-series (cf. Freudenberg, Brauns, and Siegel, *Ber.*, 1923, **56**, 193; Freudenberg and Markert, *ibid.*, 1925, **58**, 1753), and (—)phenylchloroacetic acid is also assumed by the same author to have the same configuration as (—)mandelic acid. The latter conclusion is also arrived at by Kenyon, Lipscomb, and Phillips (J., 1930, 415) from a study of the interaction of ethyl (—)mandelate and thionyl chloride in the presence of pyridine. If this conclusion is accepted, along with the assumption that (—)mandelic and (—)α-naphthylglycollic acid have the same configuration and belong to the *d*-series, then the actions of thionyl chloride described in the present paper are not accompanied by configurational change, whereas some evidence is given that a Walden inversion occurs with phosphorus pentachloride.

Since the (—)menthyl α-naphthylglycollates differed from the mandelates in the manner described, the contrast between the phenyl and the α-naphthyl group has been extended further. Thus the fractional esterification of *r*-mandelic acid by (—)menthol by the method of Marckwald and McKenzie showed that the acid which had escaped esterification was *lævorotatory*. On the other hand, when *r*-α-naphthylglycollic acid was heated at 155° with (—)menthol, the unesterified acid was *dextrorotatory*, the (—)acid being here esterified more quickly than the (+)acid. The ester mixture gave after saponification and removal of the menthol, an acid which was practically optically inactive, as was anticipated. From previous work, only a single example is available where the phenyl and the α-naphthyl group have been contrasted with regard to catalytic racemisation by alcoholic alkali, an alcoholic solution of (—)α-phenyl-γ-benzyl-γ-α′-naphthylacetone, $CH_2Ph{\cdot}CO{\cdot}CH(C_{10}H_7){\cdot}CH_2Ph$ (I) (*Ber.*, 1927, **60**, 220), gradually becoming optically inactive when a trace of alcoholic alkali was added, whilst the analogous (+)*a*γ-diphenyl-γ-benzylacetone, $CH_2Ph{\cdot}CO{\cdot}CHPh{\cdot}CH_2Ph$ (II) (Roger and McKenzie, *Ber.*, 1929, **62**, 272), exhibits a similar behaviour. But the velocity of racemisation was much greater with (II) than with (I) when a few drops of alcoholic potash (0·4487*N*) were added to ethyl-alcoholic solutions. Thus, for (II) ($c = 1{\cdot}103$, $l = 2$) the dextrorotation fell from α_{5893} + 4·17° to + 3·88° in 45 minutes and the solution was optically inactive after 100 hours, whereas with (I) ($c = 0{\cdot}5187$, $l = 2$) the lævorotation fell from — 3·38° to only — 3·33° after 1 hour, and the solution was optically inactive after 216 hours. Now, in the esters in question we have an α-naphthyl group in direct attachment to the asymmetric carbon atom and at the same time a hydrogen atom in the α-position to the carbonyl group, and it might be expected that the α-naphthyl group would exercise an influence similar to that of the phenyl group so far as catalytic racemisation by alcoholic alkali is concerned. This was borne out by results. Not only do the (—)menthyl esters of the optically active α-naphthylglycollic acids yield partially racemised acids after saponification, but the extent of this racemisation is *less pronounced* than with the corresponding mandelates, as was expected from the observations made with the two ketones just mentioned.

The fractional esterification of *r*-α-naphthylglycollic acid by (+)menthol showed that the unesterified acid was *lævorotatory*.

Finally, the effect of a trace of potassium ethoxide on alcoholic solutions of the diastereoisomeric esters was examined. With a solution of (—)menthyl (—)α-naphthylglycollate giving the initial value $[\alpha]_{5461}$ — 177·7°, a fall of rotation gradually took place, the constant value $[\alpha]_{5461}$ — 166·2° being attained. On evaporation of the alcohol from this solution, the odour of menthol was perceptible. The amount of saponification was negligible, but the menthyl group of the ester had to some extent been displaced by the ethyl group on the lines of Purdie's reaction, where a trace of ethoxide causes an interchange of radicals in alcoholic solutions of esters, thus :

$$\underset{(-)}{C_{10}H_7}{\cdot}CH(OH){\cdot}CO_2{\cdot}\underset{(-)}{C_{10}H_{19}} + EtOH \longrightarrow \underset{(-)}{C_{10}H_7}{\cdot}CH(OH){\cdot}CO_2Et + \underset{(-)}{C_{10}H_{19}}{\cdot}OH$$

" Umesterung " has recently been observed by McKenzie and Mitchell (*Biochem. Z.*, 1930, **224**, 242) with (—)menthyl benzoylformate. Again, with (—)menthyl (+)α-naphthylglycollate under similar conditions, the rotation rose from $[\alpha]_{5461}$ + 41·8° to + 47·8°, an observation which can be attributed to the same cause. With the two glycollates, it is very likely that two distinct reactions were progressing simultaneously, *viz.*, asymmetric catalytic racemisation and " Umesterung." Asymmetric catalytic racemisation alone would cause the lævorotation of (—)menthyl (—)α-naphthylglycollate in ethyl-alcoholic solution to decrease in value, as was actually observed, but on the other hand the dextrorotation of the (—)menthyl ester of the (+)acid would fall in value, whereas it actually rises. We have thus no experimental evidence which suggests that asymmetric catalytic racemisation had actually taken place.

EXPERIMENTAL.

The method of resolving *r*-α-naphthylglycollic acid (m. p. 98·5—99·5°) as described by McKenzie and Dennler (*loc. cit.*) was modified with advantage as follows. With the proportions formerly quoted, the cinchonine dissolves readily in the hot alc. solution of the acid, and the separation of the salt of the (+)acid takes place very quickly thereafter, even in the hot solution. It is not necessary to dissolve this deposit several times in more EtOH—an inconvenient procedure owing to the large quantities of solvent required—but the mixture is kept at 0° for about 4 hr. The mixture of alkaloidal salts (needles) is then decomposed with dil. H_2SO_4, and the acid after extraction with Et_2O gives the optically pure (+)acid after 2—4 crystns. from C_6H_6.

The prepn. of the (—)acid, which had not been previously carried out by McKenzie and Dennler, was conducted as follows. From the filtrate from which the crude salt of the (+)acid had been removed, crystals gradually separated containing a preponderance of the salt of the (—)acid. The latter was not removed, but the EtOH was expelled, and the residue decomposed by dil. H_2SO_4. The acid was extracted with Et_2O, and crystallised 4—6 times from C_6H_6 until optically pure.

(—)α-Naphthylglycollic acid crystallises from C_6H_6 in leaflets, m. p. 124—125°, identical with the m. p. for the (+)acid. The rotatory power in EtOH also agreed closely with that for the (+)enantiomorph.

(—)*Menthyl* (+)α-*Naphthylglycollate*.—The (+)acid (5 g.) was heated on the water-bath with 3 times its weight of (—)menthol, in the presence of HCl for 12 hr. The ethereal solution of the product was shaken with dil. $NaHCO_3$ aq., the Et_2O expelled, and the menthol removed by steam distillation. The residual oil solidified on trituration with 66% EtOH, and the solid was crystallised from light petroleum (b. p. 40—60°). Glassy octahedra, m. p. 71—72°. Yield, 5 g. (Found : C, 77·8; H, 8·0. $C_{22}H_{28}O_3$ requires C, 77·6; H, 8·3%). In acetone ($l = 2$, $c = 3·573$) :

λ	6563.	6162.	5893.	5461.	5106.	4861.	4358.
$a^{20°}$	+ 1·16°	+ 1·35°	+ 1·53°	+ 1·97°	+ 2·45°	+ 2·93°	+ 4·26°
$[a]^{20°}$	+ 16·2°	+ 18·9°	+ 21·4°	+ 27·6°	+ 34·3°	+ 41·0°	+ 59·6°

(—)*Menthyl* (—)α-*Naphthylglycollate*.—Esterification as above. The oil which remained after removal of the menthol did not, however, solidify on treatment with EtOH, and was distilled under diminished press.; b. p. 220°/4 mm. Yield, 6 g. The resulting oil, which was optically pure, was triturated with light petroleum (b. p. 40—60°), and crystallised from the same solvent. Rectangular needles, m. p. 62—63° (Found : C, 77·6; H, 8·4%). In acetone ($l = 2$, $c = 3·281$) :

λ	6563.	6162.	5893.	5461.	5106.	4861.
$a^{20°}$	— 6·32°	— 7·35°	— 8·20°	— 9·76°	— 11·68°	— 13·23°
$[a]^{20°}$	— 96·3°	— 112·0°	— 125·0°	— 148·7°	— 178·0°	— 201·6°

(—)*Menthyl* dl-α-*Naphthylglycollate*.—The *r*-acid was esterified as above : heating, 16 hr. The esterification was practically complete. The ester, which stood at room temp. for 3 weeks before it solidified, has m. p. 38·5—39·5°. In acetone ($l = 2$, $c = 4·096$) $\alpha^{21°}_{5893}$ — 4·23°, $[\alpha]^{21°}_{5893}$ — 51·6°; $\alpha^{21°}_{5461}$ — 5·03°, $[\alpha]^{21°}_{5461}$ — 61·4°. The former value is in good agreement with the value $[\alpha]_{5893}$ — 51·7° calc. from the figures for the diastereoisomeric esters on the basis of optical superposition. The rotatory power of the ester prepared by mixing equal wts. of the diastereoisomerides dissolved in acetone was also in close accordance.

Resolution of (—)*Menthyl* dl-*α-Naphthylglycollate into its Diastereoisomerides.*—To a solution of the ester (1 g.) in light petroleum (b. p. 40—60°) at − 14°, a nucleus of (—)menthyl (+)α-naphthylglycollate was added. The crystals (0·5 g.) which separated had m. p. 55—59°, and gave an optically inactive solution in acetone ($c = 1{\cdot}946$) for λ5893. These crystals consisted of a mixture of (—)menthyl (+)α-naphthylglycollate (85%) and (—)menthyl (—)α-naphthylglycollate (15%), the original ester being lævorotatory with $[\alpha]_{5893} - 51{\cdot}6^\circ$. After one more crystn. from light petroleum, the product (0·2 g.) was now dextrorotatory and consisted of the optically pure (—)menthyl (+)α-naphthylglycollate; in acetone, $[\alpha]_{5893}^{20^\circ} + 21{\cdot}2^\circ$ ($c = 0{\cdot}9175$). The m. p. was not depressed on admixture with the ester already described.

Evidence of resolution was also afforded when (—)menthyl *dl*-α-naphthylglycollate was distilled under diminished press. The first fraction (b. p. 214°/3 mm.) had $[\alpha]_{5893}^{20^\circ} - 55{\cdot}4^\circ$ ($c = 2{\cdot}368$), whereas the second fraction (b. p. 214—216°/3 mm.) gave a lower value, *viz.*, $[\alpha]_{5893}^{21^\circ} - 48{\cdot}9^\circ$ ($c = 3{\cdot}755$) in acetone.

Action of Thionyl Chloride on the (—)*Menthyl α-Naphthylglycollates.*—(1) $SOCl_2$ (12 g.) was added to a solution of (—)menthyl (—)α-naphthylglycollate (1·8 g.) in 5 c.c. of Et_2O. After heating for 2 hr. on the water-bath, the excess of $SOCl_2$ was removed in vac., and the Et_2O solution washed with $NaHCO_3$ aq. and dried by Na_2SO_4. The resulting oil was dried over soda-lime and $CaCl_2$ until const. in wt. (1·6 g.). Vac. distillation was not adopted in this and subsequent expts. (Found : Cl, 9·6. Calc., 9·9%). In acetone ($l = 2$, $c = 1{\cdot}0335$) : $\alpha_{5893}^{21^\circ} - 2{\cdot}01^\circ$, $[\alpha]_{5893}^{21^\circ} - 97{\cdot}2^\circ$; $\alpha_{5461}^{21^\circ} - 2{\cdot}49^\circ$, $[\alpha]_{5461}^{21^\circ} - 120{\cdot}5^\circ$.

(2) (—)Menthyl (+)α-naphthylglycollate (2 g.) was treated similarly. Yield of chloro-esters, 2 g. (Found : Cl, 9·7. Calc., 9·9%). In acetone ($l = 2$, $c = 5{\cdot}292$) : $\alpha_{5893}^{20{\cdot}7^\circ} - 2{\cdot}11^\circ$, $[\alpha]_{5893}^{20{\cdot}7^\circ} - 19{\cdot}9^\circ$; $\alpha_{5461}^{20{\cdot}7^\circ} - 2{\cdot}44^\circ$, $[\alpha]_{5461}^{20{\cdot}7^\circ} - 23{\cdot}1^\circ$.

(3) (—)Menthyl *dl*-α-naphthylglycollate (2·5 g.) was treated similarly. Yield of chloro-esters, 2·2 g. (Found : Cl, 10·0. Calc., 9·9%). In acetone ($l = 2$, $c = 1{\cdot}807$) : $\alpha_{5893}^{20{\cdot}5^\circ} - 2{\cdot}25^\circ$, $[\alpha]_{5893}^{20{\cdot}5^\circ} - 62{\cdot}3^\circ$; $\alpha_{5461}^{20{\cdot}5^\circ} - 2{\cdot}73^\circ$, $[\alpha]_{5461}^{20{\cdot}5^\circ} - 75{\cdot}5^\circ$.

Action of Phosphorus Pentachloride on the (—)*Menthyl α-Naphthylglycollates.*—(1) PCl_5 (6 g.) was gradually added to a solution of (—)menthyl (—)α-naphthylglycollate (2·7 g.) in $CHCl_3$ (15 c.c.). Heating, 6 hr. The $CHCl_3$ solution was washed with H_2O, then with $NaHCO_3$ aq., and dried with Na_2SO_4. The product (2·2 g.) after expulsion of the $CHCl_3$ was an oil, which was dried in vac. until const. (Found : Cl, 10·1. Calc., 9·9%). In acetone ($l = 2$, $c = 3{\cdot}626$) : $\alpha_{5893}^{20{\cdot}6^\circ} - 4{\cdot}78^\circ$, $[\alpha]_{5893}^{20{\cdot}6^\circ} - 65{\cdot}9^\circ$; $\alpha_{5461}^{20{\cdot}6^\circ} - 5{\cdot}68^\circ$, $[\alpha]_{5461}^{20{\cdot}6^\circ} - 78{\cdot}3^\circ$.

(2) (—)Menthyl (+)naphthylglycollate (2·2 g.) on similar treatment gave 1·8 g. of chloro-esters (Found : Cl, 9·7. Calc., 9·9%). In acetone ($l = 2$, $c = 2{\cdot}513$) : $\alpha_{5893}^{20{\cdot}8^\circ} - 3{\cdot}36^\circ$, $[\alpha]_{5893}^{20{\cdot}8^\circ} - 66{\cdot}9^\circ$; $\alpha_{5461}^{20{\cdot}8^\circ} - 3{\cdot}98^\circ$, $[\alpha]_{5461}^{20{\cdot}8^\circ} - 79{\cdot}2^\circ$.

(3) (—)Menthyl *dl*-α-naphthylglycollate (2·5 g.) on similar treatment gave 2 g. of chloro-esters (Found : Cl, 10·1. Calc., 9·9%). In acetone ($l = 2$, $c = 2{\cdot}447$) : $\alpha_{5893}^{20{\cdot}5^\circ} - 3{\cdot}17^\circ$, $[\alpha]_{5893}^{20{\cdot}5^\circ} - 64{\cdot}8^\circ$; $\alpha_{5461}^{20{\cdot}5^\circ} - 3{\cdot}78^\circ$, $[\alpha]_{5461}^{20{\cdot}5^\circ} - 77{\cdot}2^\circ$.

r-*α-Naphthylchloroacetic Acid.*—$SOCl_2$ (100 g.) was added gradually to α-naphthylglycollic acid (30 g.); heating, 4½ hr. Excess of $SOCl_2$ was removed by warming in vac., and the acid chloride was kept in contact with excess of H_2O for 4 hr. The chloro-acid, obtained by extraction with Et_2O as an oil, was dissolved in light petroleum (b. p. 80—100°), from which 13 g. of acid, m. p. 126—129°, crystallised. This was refluxed with light petroleum insufficient to dissolve the whole (undissolved oil A). The crystals which separated were recrystallised.

r-α-*Naphthylchloroacetic acid*, $C_{10}H_7{\cdot}CHCl{\cdot}CO_2H$, forms rosettes of needles, m. p. 131·5—132·5° (Found : C, 65·2; H, 4·1; Cl, 16·0. $C_{12}H_9O_2Cl$ requires C, 65·3; H, 4·1; Cl, 16·1%).

The acid is dimorphous. A was dissolved in light petroleum, but the needles which now separated had m. p. 111—112°; on cooling the m. p. tube and again heating, the m. p. had now risen to 131·5—132·5° (Found : Cl, 16·0. Calc., 16·1%). In subsequent prepns. the higher-melting form was generally got.

(—)*Menthyl* dl-*α-Naphthylchloroacetate.*—This *ester* was prepared by esterifying the *r*-acid (10 g.) with (—)menthol (30 g.) in the presence of HCl by heating at 100° for 13 hr.; no unesterified acid was then recovered. The ester (13 g.) was obtained as an oil and attempts to crystallise it failed (Found : Cl, 9·6. $C_{22}H_{27}O_2Cl$ requires Cl, 9·9%). In acetone ($l = 2$, $c = 2{\cdot}594$) : $\alpha_{5893}^{20{\cdot}8^\circ} - 3{\cdot}27^\circ$, $[\alpha]_{5893}^{20{\cdot}8^\circ} - 63{\cdot}0^\circ$; $\alpha_{5461}^{20{\cdot}8^\circ} - 3{\cdot}89^\circ$, $[\alpha]_{5461}^{20{\cdot}8^\circ} - 75{\cdot}0^\circ$. After distillation at 228—230°/4 mm. these values remained const.

Fractional Esterification of r-*α-Naphthylglycollic Acid by* (—)*Menthol.*—The *r*-acid (5 g.) was esterified at 155° by (—)menthol for 1¼ hr. (cf. Marckwald and McKenzie, *Ber.*, 1899, **32**, 2130). The unesterified acid (2·9 g.) was *dextrorotatory* in EtOH ($l = 2$, $c = 2{\cdot}532$), $\alpha_{5893}^{21{\cdot}5^\circ}$

+ 0·31°, $[\alpha]_{5893}^{21\cdot5^\circ}$ + 6·1°. The mixture of esters gave, after hydrolysis with alc. KOH and removal of the menthol, an acid which was practically inactive: in EtOH ($l = 2$, $c = 1\cdot2173$), α_{5893} − 0·05°.

Fractional Esterification of r-α-*Naphthylglycollic Acid by* (+)*Menthol*.—The acid was esterified as above with (+)menthol, for a specimen of which we are indebted to Professor John Read. The unesterified acid (3 g.) was *lævorotatory* in EtOH ($l = 2$, $c = 2\cdot811$), $\alpha_{5893}^{21^\circ}$ − 0·26°, $[\alpha]_{5893}^{21^\circ}$ − 4·6°. The ester mixture from which the menthol had been separated by steam distillation gave in acetone ($l = 2$, $c = 2\cdot44$), $\alpha_{5893}^{21^\circ}$ + 2·87°, $[\alpha]_{5893}^{21^\circ}$ + 58·8°. This value shows that the mixture contained a preponderance of (+)menthyl (+)α-naphthylglycollate, since the value for (−)menthyl *dl*-α-naphthylglycollate in the same solvent is $[\alpha]_{5893}$ − 51·6°.

Saponification of (−)*Menthyl* (+)α-*Naphthylglycollate*.—(1) *With excess of alcoholic potash.* A solution of the ester (1·3 g.) in EtOH (32 c.c.) to which 5·2 c.c. of alc. KOH (0·91*N*) had been added (calc., 4·2 c.c.) was heated for 2 hr. on the water-bath. The acid (0·5 g.) recovered gave in EtOH ($l = 2$, $c = 1\cdot743$), α_{5893} + 3·70°, $[\alpha]_{5893}$ + 106°, whereas the pure (+)acid has $[\alpha]_{5893}$ + 193°. The racemisation was more pronounced when (−)menthyl (+)mandelate was saponified under comparable conditions to the preceding, since the recovered mandelic acid had only $[\alpha]_{5893}$ + 29° in aq. solution (J., 1904, **85**, 1249), the pure (+)mandelic acid having $[\alpha]_{5893}$ + 158°.

(2) *With insufficient alcoholic potash.* A solution of the ester (3 g.) in EtOH (30 c.c.) to which 5 c.c. of alc. KOH (0·8886*N*) had been added (calc., 9·9 c.c.) was heated for 2 hr. The acid (1 g.) obtained after removal of the unsaponified esters and menthol gave in EtOH ($l = 2$, $c = 1\cdot813$), α_{5893} + 5·26°, $[\alpha]_{5893}$ + 145°.

Action of a Trace of Alcoholic Potassium Hydroxide on (−)*Menthyl* (−)α-*Naphthylglycollate*.—The solution of the ester in EtOH ($l = 2$, $c = 2\cdot6585$) gave $\alpha_{5893}^{20\cdot4^\circ}$ − 7·89°, $[\alpha]_{5893}^{20\cdot4^\circ}$ − 148·4°; $\alpha_{5461}^{20\cdot4^\circ}$ − 9·45°, $[\alpha]_{5461}^{20\cdot4^\circ}$ − 177·7°. The addition of 5 drops of alc. KOH (0·88*N*) caused the rotation to fall, after 3¼ hr. to $\alpha_{5461}^{20\cdot4^\circ}$ − 9·37°, after 23½ hr. to − 8·99°, after 99 hr. to 8·85°. After 7 days, the value was − 8·84°, and the solution was still alkaline. On evaporation, an oil was left with an odour of menthol.

Action of a Trace of Alcoholic Potassium Hydroxide on (−)*Menthyl* (+)α-*Naphthylglycollate*.—The solution of the ester in EtOH ($l = 2$, $c = 4\cdot159$) gave $\alpha_{5893}^{20^\circ}$ + 2·93°, $[\alpha]_{5893}^{20^\circ}$ + 35·2°; ($l = 2$, $c = 3\cdot629$) $\alpha_{5461}^{20^\circ}$ + 3·04°, $[\alpha]_{5461}^{20^\circ}$ + 41·9°. Six drops of alc. KOH (0·88*N*) were added to the latter solution, and a rise of rotation was detected: after 45 min. $\alpha_{5461}^{20^\circ}$ was + 3·10°, after 4¼ hr. + 3·34°, after 28 hr. + 3·47°. After 7 days, the value was + 3·46°, and the solution was still alkaline. On evaporation, an oil with an odour of menthol was left.

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