

CVI.—*Racemisation Phenomena during the Hydrolysis of Optically Active Menthyl and Bornyl Esters by Alkali.*

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IN the course of work previously communicated by one of us to this Society (Trans., 1904, 85, 378), the fractional hydrolysis of the partially racemic esters formed by the combination of *r*-mandelic acid with *l*-menthol and *l*-borneol respectively was investigated. *r*-Mandelic acid, for instance, was completely esterified by *l*-borneol by the hydrogen chloride method, and the resulting *l*-bornyl *dl*-mandelate (in admixture with *l*-borneol) was submitted to fractional hydrolysis by being heated with an amount of alcoholic potassium hydroxide insufficient for its complete hydrolysis; the potassium salt prepared in this manner yielded a *l*-ævorotatory acid. Since a solution of *l*-bornyl *dl*-mandelate in alcohol may be regarded as containing equal amounts of *l*-bornyl *d*-mandelate and *l*-bornyl *l*-mandelate, the result that the initial hydrolysis by alkali yielded a *l*-ævorotatory acid (a mixture of *r*- and *l*-acids) can be accounted for by the experiments of Marckwald and one of us on the fractional esterification and hydrolysis of stereoisomerides (*Ber.*, 1899, 32, 2130; 1900, 33, 208; 1901, 34, 469). The velocity of formation of the *d*-mandelate differs from that of the *l*-mandelate, as also does the velocity of hydrolysis. The product which remained after the removal of the solution of potassium salt accordingly consisted of unequal amounts of *d*- and *l*-esters together with *l*-borneol, and this mixture, when heated with an excess of alkali, formed an inactive potassium salt, from which the inactive acid was prepared. The acid obtained was not accordingly dextrorotatory, as might have been expected.

As a result of this and other experiments, it was concluded (*loc. cit.*) that racemisation occurs during the hydrolysis by alkali of the menthyl and bornyl esters of *d*- and *l*-mandelic acids respectively. That this view is correct was recently proved in connection with attempts to realise the asymmetric synthesis of mandelic acid (Trans., 1904, 85, 1249), when the action of alkali on *l*-menthyl *d*-mandelate and on *l*-menthyl *l*-mandelate was studied. The acid obtained on hydrolysing either of these esters was invariably found to be either totally or partially racemised according to the experimental conditions.

The total or the partial racemisation of an optically active compound is often attributed either to the action of heat on it or

to its production by a vigorous action. It is certain that those factors do actually in many cases induce racemisation, and the dynamical interpretation of the transformation as consisting in the direct interchange of two of the groups attached to the asymmetric carbon atom appears to be sufficiently simple and adequate. The fact, however, that such a large number of active compounds can be raised to elevated temperatures without undergoing any optical inversion suggests that many cases of racemisation which are ascribed to the action of heat may, oftener than not, be conditioned by other influences. Indeed, cases are known of active compounds which can be prepared and redistilled at elevated temperatures without diminishing in activity, but which racemise when left at the ordinary temperature. This phenomenon of autoracemisation, first observed by Wallach (*Annalen*, 1892, **270**, 190) with *d*-limonene monohydrochloride, has been examined in some detail by Walden (*Ber.*, 1898, **31**, 1416), who finds, for example, that ethyl *d*-bromosuccinate, when freshly prepared, has $[\alpha]_D$ 40.96° , and after a lapse of four years at the ordinary temperature has $[\alpha]_D$ $+9^\circ$, whilst *d*-phenylbromoacetic acid under similar conditions becomes quite inactive. Walden suggests that such results may have been caused by the catalytic action of a trace of halogen hydride.

The racemising effect of alkali during the hydrolysis of optically active esters cannot be ascribed either to the influence of temperature or of vigorous action, and we considered the subject to be of sufficient novelty to warrant its further study.

Racemisation in the presence of alkali has been observed by several investigators. Schulze and Bosshard (*Zeit. physiol. Chem.*, 1886, **10**, 135) found that active leucine retains its activity when heated with water at 170 — 180° , but loses it when heated at 150 — 160° with an aqueous solution of barium hydroxide. Purdie and Williamson (*Trans.*, 1896, **69**, 818) obtained ethyl *i*- α -ethoxypropionate by the action of sodium ethoxide on ethyl *d*- α -chloropropionate at the ordinary temperature. P. F. Frankland and Price (*Trans.*, 1897, **71**, 255) found that commercial amyl alcohol is only partially racemised when heated at 170° in a sealed tube for 7 hours, but is completely racemised when converted into sodium amyloxide, which is then heated for 3 hours at 206° (compare Borucki, *Inaug. Diss., Berlin*, 1886; Walden, *Zeit. physikal. Chem.*, 1895, **17**, 711). Holleman (*Rec. Trav. chim.*, 1898, **17**, 323) was the first to observe that *l*-mandelic acid is racemised when heated with alkalis. In the benzoylation of *d*-glutaminic acid by benzoyl chloride and sodium hydrogen carbonate, E. Fischer (*Ber.*, 1899, **32**, 2464) notes that partial racemisation occurred; when *l*-leucine is benzoylated by the same method, no racemisation occurs, but when sodium hydroxide is substituted for sodium hydrogen carbonate, a

mixture of benzoyl-*r*-leucine and benzoyl-*l*-leucine is formed (E. Fischer, *Ber.*, 1900, **33**, 2370). Partial racemisation also occurs when *d*- α -amino-*n*-hexoic acid is benzoylated by sodium hydrogen carbonate and benzoyl chloride (E. Fischer and Hagenbach, *Ber.*, 1901, **34**, 3764). Finally, J. W. Walker (Trans., 1903, **83**, 472) has shown that the catalytic racemisation of amygdalin takes place when the glucoside is heated with an aqueous solution of barium hydroxide, and has proved that Liebig and Wöhler's amygdalinic acid is racemoid as regards the mandelic asymmetric carbon atom, whilst Dakin (Trans., 1904, **85**, 1512) has amplified Walker's results by isolating *iso*amygdalin (*i*-mandelonitrile *d*-malto-side).

In the work described in this paper, the partially racemic esters formed by the complete esterification of a number of externally compensated acids by optically active alcohols were submitted to fractional hydrolysis by an inactive base, with the expectation that abnormal results would, in certain cases, be obtained in consequence of the racemising influence of alkali. It was found possible, for instance, to convert an inactive acid into a mixture of *i*- and *l*-acids without the evident formation of the corresponding amount of the *d*-enantiomorph.

When *l*-menthyl *dl*-phenylethoxyacetate is hydrolysed by an amount of alkali requisite for the hydrolysis of half the amount of ester used, a *l*ævorotatory potassium salt is produced. The product which survived the attack of the alkali in this initial hydrolysis was then hydrolysed by an excess of alkali, when a *l*ævorotatory potassium salt was again obtained and not a *d*extrorotatory one.

The interpretation of this result is as follows. When *i*-phenylethoxyacetic acid is partially esterified by being heated with *l*-menthol at 155°, the unesterified acid is *l*ævorotatory, from which it is inferred that the velocity of formation of *l*-menthyl *d*-phenylethoxyacetate is greater than that of *l*-menthyl *l*-phenylethoxyacetate (Marckwald and McKenzie, *Ber.*, 1901, **34**, 469). Since of two isomeric esters of this type, the one which is the more readily formed is, as a rule, the more readily hydrolysed, it is likely that the *d*-ester is hydrolysed more quickly than the *l*-ester. If the initial hydrolysis of the *dl*-ester is considered, where a mixture of equal amounts of *d*-ester and *l*-ester is hydrolysed by an amount of potassium hydroxide insufficient for the complete hydrolysis, the *d*-ester is more quickly hydrolysed than the *l*-ester, whilst the potassium *d*- and *l*-salts formed are, of course, racemised at the same rate, since they are mirror images of one another. If it were the case that the alkali present exercised no racemising effect, the potassium salt formed in the earlier stages of the initial hydrolysis would accordingly be a mixture of *d*- and *l*-salts containing an excess of the former; the excess of hydroxyl ions at this stage is

so great, however, as to render the mixture of potassium salts inactive or nearly so. As the initial hydrolysis proceeds, the concentration of hydroxyl ions diminishes, and the racemising effect of alkali, which is directly proportional to the concentration of hydroxyl ions, becomes less and less marked until in the later stages of the initial hydrolysis it is practically negligible. During the earlier stages of the initial hydrolysis, therefore, an excess of *d*- over *l*-salt is formed, but the racemising effect of the alkali on this mixture is pronounced; during the later stages of the initial hydrolysis, the ester mixture consists of an excess of *l*-ester over *d*-ester, and, although the latter is more quickly hydrolysed than the former, the difference in the relative masses of the two esters leads to the production of an excess of *l*-salt over *d*-salt, on which mixture the alkali has at this stage little racemising effect. The final result of the initial hydrolysis is accordingly the formation of a levorotatory salt.

The ester mixture remaining after the initial hydrolysis contains an excess of *l*-ester and, when completely hydrolysed by alkali, yields a levorotatory salt. The racemising effect of alkali in this case is not such as to cause the formation of a potassium inactive salt, since at the earlier stages of this final hydrolysis a considerable excess of *l*-salt over *d*-salt is present. At the earlier stages of the initial hydrolysis, on the other hand, the excess of *d*-salt over *l*-salt was not so great as was the excess of *l*-salt over *d*-salt in this case.

This interpretation throws light on a result previously obtained with *l*-menthyl *dl*-mandelate (Trans., 1904, 85, 378). When this ester is submitted to fractional hydrolysis, it generally yields a dextrorotatory potassium salt as the product of the initial hydrolysis by an insufficiency of alkali, but in certain rare cases a levorotatory salt was formed.

The conversion of an inactive substance into one of its optically active isomerides with the apparent disappearance of the corresponding amount of the other isomeride recalls the experience of Pope and Peachey (*Proc.*, 1900, 16, 42) in their preliminary note on the preparation of *d*-methylethyl-*n*-propyl tin iodide. These authors found that when *i*-methylethyl-*n*-propyl tin iodide was agitated with a warm aqueous solution of silver *d*-camphorsulphonate, *d*-methylethyl-*n*-propyl tin *d*-camphorsulphonate separated. When the mother liquor, however, was allowed to crystallise, it did not deposit a mixture of the camphorsulphonates containing an excess of the salt of the *l*-base but, instead of this, a mixture containing an excess of the salt of the *d*-base.

When *i*-phenylethoxyacetic acid was partially esterified by *l*-borneol, the unesterified acid was dextrorotatory, whilst the mixture of esters formed yielded a dextrorotatory acid on hydrolysis with an excess of

alkali. The *l*-acid is accordingly esterified more quickly than the *d*-acid. That the ester mixture, in which the *l*-ester preponderated, yielded a dextrorotatory acid is due to the racemising effect of alkali as indicated in the discussion of the fractional hydrolysis of *l*-menthyl *dl*-phenylethoxyacetate.

The fractional hydrolysis of *l*-bornyl *dl*-phenylethoxyacetate proceeded in such a manner that both the initial and the final hydrolysis yielded levorotatory potassium salts. The fractional esterification of the acid itself indicated that the *l*-ester would be hydrolysed more quickly than the *d*-ester since it is formed more quickly. The racemising effect of the alkali in the initial hydrolysis was not, under the conditions employed, sufficient to effect the formation of a dextrorotatory salt, so that the direction of the rotation of the salt from the initial hydrolysis is normal. In the final hydrolysis, however, the racemising effect is seen, since the potassium salt was levorotatory and not dextrorotatory.

The fractional hydrolysis of *l*-bornyl *dl*-mandelate gave, under the conditions employed, a levorotatory acid as the product of the initial hydrolysis, whilst the acid obtained from the final hydrolysis was inactive. From the result of the initial hydrolysis, it might be concluded that the *l*-ester is more readily hydrolysed than the *d*-ester, but we are inclined to believe that the reverse is the case since the *d*-ester is the more readily formed of the two (McKenzie, *loc. cit.*). The production of a levorotatory salt from the initial hydrolysis is easily accounted for on the assumption that the racemisation gradually diminishes as the hydrolysis proceeds. It may be possible to alter the experimental conditions in such a manner that a dextrorotatory acid will result from the initial hydrolysis, and measurements of the velocity of hydrolysis of the *d*-, *l*-, and *dl*-esters respectively are at present in progress with this aim in view.

The racemisation phenomena described are much influenced by the concentration of the alkali and by the temperature conditions. The variation of the latter factor was examined in the case of *l*-bornyl *l*-mandelate. When molecular amounts of *l*-mandelic acid and *l*-borneol were heated at 155°, the unesterified acid was practically unchanged in rotation. When the ester formed was hydrolysed by being boiled with alcoholic potassium hydroxide, the resulting acid had $[\alpha]_D^{20} - 49^\circ$ in aqueous solution; when the hydrolysis was conducted at 25° with the same amount of alkali and in the same dilution, the rotation of the resulting acid was $[\alpha]_D^{20} - 65^\circ$, whilst the original *l*-mandelic acid had $[\alpha]_D^{20} - 158^\circ$.

The resolution effected in the case of *l*-bornyl *dl*-lactate was a very slight one; the product of the initial hydrolysis was inactive, whilst

the product of the final hydrolysis was feebly, although distinctly, lævorotatory. No resolution was effected with *l*-menthyl *dl*- α -hydroxybutyrate, *l*-bornyl *dl*- α -hydroxybutyrate, and *l*-menthyl *dl*- β -hydroxybutyrate respectively.

The initial hydrolysis of *l*-menthyl *dl*-lactate yielded a mixture of *i*- and *d*-lactic acids, whilst the final hydrolysis yielded a mixture of *i*- and *l*-acids. With *l*-menthyl *dl*- α -ethoxypropionate, a lævorotatory acid was obtained from the initial hydrolysis and a dextrorotatory one from the final hydrolysis, whilst with the corresponding bornyl ester the initial hydrolysis yielded a dextrorotatory acid, and the final hydrolysis a lævorotatory one. There was no evidence that the alkali had exerted any racemising effect in those instances.

In the course of his remarkable experiments on the optical inversion of the malic acids, Walden (*Ber.*, 1899, 32, 1833) discusses the possibility of the racemising action of alkali in the formation of malic acid from halogen succinic acid, and quotes experiments which show that under the conditions he employed the active malic acid formed was not racemised by the alkali present. We find, however, that a solution of potassium *l*-malate becomes quite inactive in the presence of an excess of alkali under the conditions quoted in the experimental portion of this paper. If this result is due to the formation of *i*-malate, it has an important bearing on Walden's interconversion of the active malic acids.

When *r*-mandelic acid is partially esterified by being heated with *l*-menthol at 155°, the unesterified acid is lævorotatory, whilst the esters formed yield, on hydrolysis by an excess of alkali, either an inactive or a feebly lævorotatory acid, and not a dextrorotatory one as was at first expected (Marckwald and McKenzie, *loc. cit.*). Since the *d*-acid is esterified more quickly than the *l*-acid, a mixture of unequal amounts of *d*- and *l*-esters, containing an excess of the former, would have been produced on the assumption that no racemisation or decomposition had attended the formation of the esters. It was formerly concluded that the *d*-mandelate is racemised by heat more quickly than the *l*-mandelate to such an extent that the ester mixture did not contain an excess of the former ester. This view must now be modified, as the most important factor in the production of an inactive or a feebly lævorotatory acid from the hydrolysis of the ester mixture is the racemising effect of the alkali used. Definite proof, however, is given in this paper that the *d*- and *l*-mandelates are actually racemised by heat at different rates.

It will be seen from the following table that the values for the molecular rotations of the esters prepared by us are of the same order as those obtained by Tschugaeff for other menthyl and bornyl esters

(*Ber.*, 1898, **31**, 360, 1775; *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606).

	$[M]_D^{20}$	$[M]_D$ (in ethyl-alcoholic solution)
<i>l</i> -Menthyl <i>dl</i> - β -hydroxybutyrate	152°	159°
<i>l</i> -Menthyl <i>dl</i> - α -ethoxypropionate	154	164
<i>l</i> -Menthyl <i>dl</i> - α -hydroxybutyrate	—	170
<i>l</i> -Menthyl <i>dl</i> -lactate	166	173
* <i>l</i> -Menthyl <i>dl</i> -mandelate	—	215
<i>l</i> -Menthyl <i>dl</i> -phenylethoxyacetate	209	218
<i>l</i> -Bornyl <i>dl</i> - α -ethoxypropionate	84	78
<i>l</i> -Bornyl <i>dl</i> -lactate.....	89	82
<i>l</i> -Bornyl <i>dl</i> - α -hydroxybutyrate	92	83
<i>l</i> -Bornyl <i>dl</i> -mandelate	—	88
<i>l</i> -Bornyl <i>dl</i> -phenylethoxyacetate.....	87	92

* *Trans.*, 1904, **85**, 378.

Tschugaeff found that whilst the molecular rotation of *l*-menthyl formate was -146.3° , the acetate had $[M]_D - 157.3^\circ$, a value which remained practically constant for the six succeeding members of the series. The mean of his values was -157.8° . Subsequent examination of aromatic esters showed that the influence of the phenyl group was such as to increase the molecular rotation. This influence is also indicated by the numbers quoted above for the mandelate and phenylethoxyacetate. The *l*-bornyl esters of acids of the formic acid series examined by Tschugaeff have the mean value $[M]_D - 87.9^\circ$. The influence of the phenyl group on the rotation of bornyl esters does not appear to have been examined by Tschugaeff; in the cases examined by us it is very slight.

EXPERIMENTAL.

Fractional Hydrolysis of l-Menthyl dl-Phenylethoxyacetate.

i-Phenylethoxyacetic acid, prepared by the alkylation of *r*-mandelic acid by silver oxide and ethyl iodide (McKenzie, *Trans.*, 1899, **75**, 756), was heated for 20 hours on a boiling water-bath with three times its weight of *l*-menthol, a current of dry hydrogen chloride having been passed at intervals into the mixture. After the ethereal solution of the product had been agitated, first with a dilute aqueous solution of sodium carbonate and then with water, it was dried by anhydrous sodium sulphate. The esterification was regarded as complete, since, when an excess of dilute sulphuric acid was added to the united aqueous solutions from which the ester had been completely separated and the solution then extracted quantitatively with ether in a continuous extraction apparatus for several hours, the residue obtained on evaporation of the ether was so small as to be negligible. After removal of the ether from the ethereal solution containing the ester and excess of

menthol, the menthol was readily separated from the ester by distillation under diminished pressure.

1-Menthyl dl-phenylethoxyacetate, $\text{OEt} \cdot \text{CHPh} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, is a colourless, viscid oil which boils at 205° under 17 mm. pressure.

0.1937 gave 0.1660 H_2O and 0.5336 CO_2 . $\text{H} = 9.6$; $\text{C} = 75.1$.

$\text{C}_{20}\text{H}_{30}\text{O}_3$ requires $\text{H} = 9.5$; $\text{C} = 75.4$ per cent.

It has $\alpha_D^{20} = -65.65^\circ$ ($l = 1$) and $d_{20}^{20}/4 = 1.0007$; whence $[\alpha]_D^{20} = -65.6^\circ$.

A determination of its specific rotation in ethyl alcohol gave the following result:

$$l = 2, c = 4.3200, \alpha_D^{20} = -5.91^\circ, [\alpha]_D^{20} = -68.4^\circ.$$

When the ester was heated in a current of steam for 1 hour, it was not appreciably hydrolysed.

Initial Hydrolysis.—10.6 grams of the ester were boiled in a reflux apparatus for 4 hours with 140 c.c. of a solution of potassium hydroxide in ethyl alcohol containing an amount of alkali sufficient to hydrolyse half the ester used. The alcohol was removed by evaporation and water added to the product. The mixture of residual esters and menthol was then extracted with ether and, after the expulsion of the ether, was retained for the final hydrolysis.

After the aqueous solution of potassium phenylethoxyacetate formed had been concentrated by evaporation, it contained no menthol, the latter having been completely removed, first by extracting the solution with ether and then by evaporating the solution. The solution was decolorised by animal charcoal and, when examined in a 4-dm. tube, was found to be distinctly levorotatory, giving $\alpha_D^{20} = -0.26^\circ$ for $c = 11.107$. In confirmation of this activity observed, the acid was prepared from the potassium salt by acidification and extraction with ether and then converted into the barium salt, the aqueous solution of which gave $l = 4$, $c = 11.096$, $\alpha_D^{20} = -0.31^\circ$.

Final Hydrolysis.—The mixture of residual esters and menthol was boiled in a reflux apparatus for 4 hours with 120 c.c. of standard alkali, containing 0.025 gram of potassium hydroxide more than the amount necessary for the hydrolysis of 5.3 grams of the ester. The alcohol was expelled, water added to the residue, and the menthol drained off. The filtrate was completely freed from menthol in the usual manner and then clarified by charcoal. The solution of potassium salt thus obtained was slightly alkaline; it measured 20 c.c., of which 14 c.c. in a 2-dm. tube gave $\alpha_D^{20} = -0.90^\circ$ ($c = 15.559$); whence $[\alpha]_D^{20} = -2.9^\circ$.

The aqueous solution of barium salt, formed as indicated in the initial hydrolysis, gave

$$l = 4, c = 9.566, \alpha_D^{20} = -1.07^\circ, [\alpha]_D^{20} = -2.8^\circ.$$

Fractional Hydrolysis of l-Bornyl dl-Phenylethoxyacetate.

l-Bornyl *dl*-phenylethoxyacetate, $\text{OEt} \cdot \text{CHPh} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{17}$, was prepared by a method similar to that used for the corresponding menthyl ester. The excess of *l*-borneol was not, however, in this case removed under diminished pressure, since it tends to condense in such a manner as to choke up the side-tube of the distilling flask. It is best separated from the ester by distillation in a current of steam, a preliminary experiment having indicated that the ester is not appreciably hydrolysed under such treatment.

The ester is a viscid, colourless oil which boils at 204° under 20 mm. pressure.

0.2057 gave 0.1629 H_2O and 0.5707 CO_2 . $\text{H} = 8.9$; $\text{C} = 75.7$.

$\text{C}_{20}\text{H}_{28}\text{O}_3$ requires $\text{H} = 8.9$; $\text{C} = 75.9$ per cent.

It has $\alpha_D^{20} = -28.63^\circ$ ($l = 1$) and $d_{20}^{20}/4^\circ = 1.0407$; whence $[\alpha]_D^{20} = -27.5^\circ$.

A determination of its specific rotation in ethyl alcohol gave the following result: $l = 2$, $c = 4.2388$, $\alpha_D^{20} = -2.47^\circ$, $[\alpha]_D^{20} = -29.1^\circ$.

Initial Hydrolysis.—A solution of 4.4 grams of the ester in 50 c.c. of ethyl alcohol was heated for 4 hours with 28 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0139 KOH), an amount requisite for the hydrolysis of half the ester used. After removal of the alcohol, the aqueous solution of potassium salt was completely separated from the mixture of residual esters and borneol and was found to be slightly laevorotatory: $l = 1$, $c = 5.346$, $\alpha_D^{20} = -0.15^\circ$. The barium salt of the acid obtained from this solution was also found to be laevorotatory in aqueous solution: $l = 2$, $c = 7.932$, $\alpha_D^{20} = -0.20^\circ$.

Final Hydrolysis.—The ether was expelled from the solution of borneol and esters remaining from the initial hydrolysis, and the resulting oil dissolved in 50 c.c. of ethyl alcohol and then boiled for 4 hours with 29 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0139 KOH). After complete removal of the borneol, the aqueous solution of potassium salt gave: $l = 1$, $c = 7.856$, $\alpha_D^{20} = -0.21^\circ$, whilst an aqueous solution of the barium salt, obtained from it, gave $l = 1$, $c = 5.605$, $\alpha_D^{20} = -0.11^\circ$.

Special precautions were taken in this and in other cases to ensure that the activity observed with the potassium salts resulting from the hydrolysis was not due to traces of the active alcohols. From the aqueous solutions separated by filtration from the precipitated menthol or borneol, the last traces of the alcohols may be removed by extracting the solutions with ether and then evaporating them until the odour of the alcohols has entirely disappeared.

Fractional Esterification of i-Phenylethoxyacetic Acid by l-Borneol.

i-Phenylethoxyacetic acid (18.3 grams), prepared by the action of sodium ethoxide on ethyl phenylchloroacetate, was heated with an equal weight of *l*-borneol at 150–155° for 4½ hours. The product was dissolved in ether and the unesterified acid removed by means of an aqueous solution of sodium carbonate. The solution of sodium salt thus obtained was completely freed from borneol and bornyl esters by extraction with ether, the ethereal extracts being added to the main ethereal solution from which the sodium salt in question had been removed.

The sodium salt was then decomposed by the addition of mineral acid, the liberated phenylethoxyacetic acid extracted with ether, and then converted into its barium salt, a solution of which in water proved to be dextrorotatory:

$$l = 2, c = 11.95, [\alpha]_D^{20} + 1.15^\circ, [\alpha]_D^{20} + 4.8^\circ.$$

The mixture of esters and borneol was then heated with an excess of alcoholic potassium hydroxide for 2 hours, the alcohol was evaporated off, water was added, and the borneol, which was precipitated, was drained off. The filtrate was then completely separated from the traces of borneol present and decomposed by mineral acid. The phenylethoxyacetic acid obtained by extraction with ether was converted into barium salt, a solution of which in water proved to be dextrorotatory:

$$l = 2, c = 16.39, \alpha_D^{20} + 1.40^\circ, [\alpha]_D^{20} + 4.3^\circ.$$

Fractional Hydrolysis of l-Bornyl dl-Mandelate.

l-Bornyl *dl*-mandelate, prepared by the complete esterification of *r*-mandelic acid by *l*-borneol by the hydrogen chloride method, was first obtained as a viscid oil which boiled at 204° under 14 mm. pressure and slowly crystallised as a felted mass of fine needles; it melts at 45–47° and is readily soluble in the ordinary organic solvents.

0.2176 gave 0.1635 H₂O and 0.5978 CO₂. H = 8.4; C = 74.9.

C₁₈H₂₄O₃ requires H = 8.4; C = 75.0 per cent.

A determination of its specific rotation in ethyl alcohol gave the following value: $l = 2, c = 6.6876, \alpha_D^{20} - 4.07^\circ, [\alpha]_D^{20} - 30.4^\circ$.

When this ester was submitted to fractional hydrolysis in a manner indicated in the foregoing cases, the acid obtained from the initial hydrolysis was *lævorotatory*, whilst that obtained from the final hydrolysis was inactive. Details need not be quoted, as the result

confirmed the experiments formerly conducted by one of us (Trans., 1904, 85, 378), where the fractional hydrolysis was carried out with a mixture of *l*-bornyl *dl*-mandelate and *l*-borneol.

Esterification of l-Mandelic Acid by l-Borneol.

l-Mandelic acid (10 grams), prepared from amygdalin, was heated with 10 grams of *l*-borneol for 2 hours in an oil-bath at 155°. The ethereal solution of the product was shaken with aqueous sodium carbonate, and the aqueous solution, from which the borneol and bornyl ester had been completely removed, yielded, on acidification and extraction with ether, 3 grams of unesterified mandelic acid, the rotation of which was practically identical with that of the original acid. The solution of the esterified product in 100 c.c. of ethyl alcohol was divided into two equal portions, to each of which were added 106 c.c. of standard alcoholic potassium hydroxide (1 c.c. = 0.0133 KOH), an amount in excess of that required for the complete hydrolysis of the ester in each case. The hydrolysis was conducted, in the one case, by boiling the mixture for 4 hours in a reflux apparatus, and in the other by allowing the solution to remain in a thermostat at 25° for 24 hours. The mandelic acid was recovered in each instance from the solutions of potassium salt which had been freed from borneol; in the former case, the acid gave the following result: $l = 2$, $c = 4.988$, $\alpha_D^{20} = -4.89^\circ$, $[\alpha]_D^{20} = -49.0^\circ$, and in the latter case, $l = 2$, $c = 4.7296$, $\alpha_D^{20} = -6.12^\circ$, $[\alpha]_D^{20} = -64.7^\circ$. The original *l*-mandelic acid in a 5 per cent. solution had $[\alpha]_D^{20} = -158^\circ$.

The borneol was recovered in each case, and was found not to have undergone racemisation.

Fractional Hydrolysis of l-Bornyl dl-Lactate.

l-Bornyl *dl*-lactate, prepared by the complete esterification of *i*-lactic acid by *l*-borneol by the hydrogen chloride method, is a viscid, colourless oil which boils at 136° under 10 mm. pressure.

0.2023 gave 0.1793 H₂O and 0.5109 CO₂. $H = 9.9$; $C = 68.9$.

C₁₃H₂₂O₃ requires $H = 9.8$; $C = 69.0$ per cent.

It has $\alpha_D^{20} = -40.71^\circ$ ($l = 1$) and $d_{20}^{20} 1.0370$; whence $[\alpha]_D = -39.3^\circ$.

A determination of its specific rotation in ethyl alcohol gave the following result: $l = 2$, $c = 5.2600$, $\alpha_D^{20} = -3.83^\circ$, $[\alpha]_D^{20} = -36.4^\circ$.

Initial Hydrolysis.—Forty-three grams of ester were dissolved in 100 c.c. of ethyl alcohol and heated for 7 hours with 69 c.c. of standard alcoholic potassium hydroxide (1 c.c. = 0.07729 KOH), an amount requisite for the hydrolysis of half of the ester used. The alcohol

was then removed, and, after the addition of water, that portion of the ester which had not undergone hydrolysis was separated, together with the precipitated borneol, from the aqueous solution of potassium lactate by means of ether. The aqueous solution of potassium lactate was acidified by sulphuric acid and the lactic acid liberated was quantitatively extracted in a continuous extraction apparatus. The acid obtained in this manner was converted into zinc salt, from the aqueous solution of which a crop of 11 grams of *r*-salt was withdrawn, whilst the filtrate, when examined in a 4-dcm. tube, proved to be inactive.

Final Hydrolysis.—The mixture of residual esters and borneol was dissolved in 100 c.c. of ethyl alcohol and boiled for 7 hours with 71 c.c. of alkali (1 c.c. = 0.07729 KOH). From the resulting potassium lactate, the acid was liberated as in the initial hydrolysis and converted into zinc salt. The aqueous solution of the latter was allowed to crystallise; a crop of crystals (10 grams) was separated, whilst the filtrate, when examined in a 4-dcm. tube, proved to be feebly dextro-rotatory, giving $\alpha_D + 0.08^\circ$, and containing therefore a slight excess of the dextrorotatory zinc *l*-lactate. This observation was confirmed by dissolving the crop (10 grams) in dilute hydrochloric acid and examining the solution in a 4-dcm. tube, when the value $\alpha_D - 0.17^\circ$ was noted. In this case, some of the *l*-salt had apparently crystallised along with the *i*-salt, and when the mixture is acidified the presence of *l*-lactic acid in the solution is indicated.

Cases where no Resolution was effected by Fractional Hydrolysis.

l-Menthyl *dl*- α -hydroxybutyrate, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, prepared by the complete esterification of α -hydroxybutyric acid by *l*-menthol in the usual manner, was first obtained as an oil which boiled at 161° under 17 mm. pressure, and which, after 24 hours, solidified to a mass of fine needles melting at 37° . It was analysed by hydrolysis with standard alcoholic potassium hydroxide.

0.5180 required 0.1190 potassium hydroxide for complete hydrolysis, the theoretical amount being 0.1199.

A determination of its specific rotation in ethyl alcohol gave the following result:

$$l = 2, c = 4.6988, \alpha_D^{20} - 6.62^\circ, [\alpha]_D^{20} - 70.4^\circ.$$

Twelve grams of ester were dissolved in 100 c.c. of ethyl alcohol and submitted to fractional hydrolysis with 23 c.c. of alkali (1 c.c. = 0.0606 KOH) in the usual manner. The acid obtained from

the potassium salt thus produced was inactive, as also was that obtained as the product of the final hydrolysis.

The result was the same when the fractional hydrolysis of twelve grams of the ester was conducted in a thermostat at 25° for 40 hours instead of at the temperature of a boiling water-bath, as in the previous experiment.

l-Bornyl *dl*- α -hydroxybutyrate, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{17}$, prepared in the usual manner, is an oil which boils at 157° under 17 mm. pressure; it was analysed by hydrolysis with standard alcoholic potassium hydroxide:

0.5345 required 0.1251 potassium hydroxide for complete hydrolysis, the theoretical amount being 0.1247.

It has $\alpha_D^{20} - 39.28^\circ$ ($l=1$) and $d_{20}^{20}/4^\circ 1.0250$; whence $[\alpha]_D^{20} - 38.3^\circ$. Its specific rotation in ethyl alcohol was determined:

$$l=2, c=4.7344, \alpha_D^{20} - 3.27^\circ, [\alpha]_D^{20} - 34.5^\circ.$$

The fractional hydrolysis proceeded as in the case of the menthyl ester, no resolution having been effected.

l-Menthyl *dl*- β -hydroxybutyrate, $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, prepared by the complete esterification of β -hydroxybutyric acid by *l*-menthol in the usual manner, is an oil which boils at 169° under 17 mm. pressure.

0.2132 gave 0.2078 H_2O and 0.5396 CO_2 . $\text{H}=10.9$; $\text{C}=69.0$.

$\text{C}_{14}\text{H}_{26}\text{O}_3$ requires $\text{H}=10.8$; $\text{C}=69.4$ per cent.

It has $\alpha_D^{20} - 30.90^\circ$ ($l=0.5$) and $d_{20}^{20}/4^\circ 0.9859$; whence $[\alpha]_D^{20} - 62.7^\circ$.

Its specific rotation in ethyl alcohol was determined:

$$l=2, c=5.0816, \alpha_D^{20} - 6.69^\circ, [\alpha]_D^{20} - 65.8^\circ.$$

No resolution was obtained when this ester was submitted to fractional hydrolysis.

Fractional Hydrolysis of l-Menthyl dl-Lactate.

l-Menthyl *dl*-lactate, prepared by the complete esterification of *i*-lactic acid by *l*-menthol by the hydrogen chloride method, was first obtained as an oil, which boiled at 142° under 15 mm. pressure and gradually solidified to a mass of stellate needles; these melt at 32° and are very readily soluble in ethyl alcohol, ether, benzene, chloroform, ethyl acetate, acetone, ligroin, or carbon tetrachloride.

0.2157 gave 0.2093 H_2O and 0.5413 CO_2 . $\text{H}=10.9$; $\text{C}=68.4$.

$\text{C}_{13}\text{H}_{24}\text{O}_3$ requires $\text{H}=10.6$; $\text{C}=68.4$ per cent.

Its specific rotation in the superfused state was determined :

$$l = 1, \alpha_D^{20^\circ} - 71.61^\circ, d \ 20^\circ/4^\circ \ 0.9835, [\alpha]_D^{20^\circ} - 72.8^\circ.$$

Its specific rotation in ethyl alcohol was as follows :

$$l = 2, c = 5.0488, \alpha_D^{20^\circ} - 7.66^\circ, [\alpha]_D^{20^\circ} - 75.9^\circ.$$

Initial Hydrolysis.—Forty-two grams of ester were dissolved in 100 c.c. of ethyl alcohol and hydrolysed in the usual manner for $3\frac{1}{2}$ hours with 67 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.07729 KOH), the total amount necessary for complete hydrolysis being 134 c.c. From the potassium lactate formed, the lactic acid was prepared in the manner already indicated in connection with the fractional hydrolysis of the bornyl lactate and was converted into zinc salt, the aqueous solution of which was allowed to crystallise; 11 grams of hydrated *r*-salt were withdrawn, whilst 28 c.c. of the filtrate (34 c.c.), when examined in a 4-dm. tube, gave $\alpha_D^{18^\circ} - 0.33^\circ$ for $c = 1.6885$, whence $[\alpha]_D^{18^\circ} - 4.9^\circ$. The concentration of this solution was determined by evaporating an aliquot portion of it to dryness and then heating the residue at 117 — 120° until constant in weight. The solution accordingly contained a considerable amount of zinc *d*-lactate, the specific rotation of which is much influenced by temperature and has been found by Purdie and Walker (Trans., 1895, **67**, 621) to be -5.8° at 14° for $c = 8.002$.

Final Hydrolysis.—The mixture of residual esters and menthol was dissolved in 100 c.c. of ethyl alcohol and hydrolysed by heating with 70 c.c. of alkali (1 c.c. = 0.07729 KOH) for 4 hours. After removal of the menthol, the solution was acidified and extracted with ether. The lactic acid obtained was converted into its zinc salt, from the aqueous solution of which a crop of 9.5 grams of hydrated *r*-salt was withdrawn, whilst the filtrate (28 c.c.) gave the result :

$$l = 4, c = 2.2975, \alpha_D^{20^\circ} + 0.34^\circ, [\alpha]_D^{20^\circ} + 3.7^\circ.$$

The filtrate accordingly contained a considerable amount of zinc *l*-lactate.

Fractional Hydrolysis of 1-Menthyl dl- α -Ethoxypropionate.

Marckwald and McKenzie have shown that when *i*- α -ethoxypropionic acid is heated with *l*-menthol at 155° , the unesterified acid is dextrorotatory, whereas the esterified portion yielded, on complete hydrolysis by an excess of alkali, a levorotatory acid (*Ber.*, 1901, **34**, 469). Since the amount of *l*-acid in the latter mixture of *i*- and *l*-acids corresponded to the amount of *d*-acid in the unesterified portion, it was obvious that in this special case no racemisation had occurred

during the hydrolysis by alkali. It was accordingly of interest to examine the fractional hydrolysis of the menthyl and bornyl esters of the acid in question.

The acid used was prepared by the action of sodium ethoxide on ethyl α -bromopropionate (Schreiner, *Annalen*, 1879, 197, 13). 1-Menthyl dl- α -ethoxypropionate, $\text{CH}_3 \cdot \text{CH}(\text{OEt}) \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, prepared by the complete esterification of the acid by menthol, is an oil, which boils at 140° under 13 mm. pressure.

0.2080 gave 0.2085 H_2O and 0.5338 CO_2 . $\text{H} = 11.2$; $\text{C} = 70.0$.

$\text{C}_{15}\text{H}_{28}\text{O}_3$ requires $\text{H} = 11.0$; $\text{C} = 70.3$ per cent.

It has $\alpha_D^{20} - 28.23^\circ$ ($l = 0.5$) and $d_{20}^{20}/4^\circ$ 0.9363; whence $[\alpha]_D^{20} - 60.3^\circ$.

A determination of its specific rotation in ethyl alcohol gave the result:

$$l = 2, c = 4.6616, \alpha_D^{20} - 5.99^\circ, [\alpha]_D^{20} - 64.2^\circ.$$

Initial Hydrolysis.—The solution of 21 grams of the ester in 100 c.c. of ethyl alcohol was boiled for 6 hours with 40 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0565 KOH), the amount necessary for complete hydrolysis being 81.3 c.c. The aqueous solution of potassium salt, obtained in the usual manner entirely free from menthol, gave $\alpha_D^{14} - 0.70^\circ$ when examined in a 2-dcm. tube containing 14 c.c. The ethoxypropionic acid, prepared by acidifying this solution by dilute sulphuric acid and extracting with ether in a continuous extraction apparatus, was converted into its calcium salt, from the aqueous solution of which 2 grams of hydrated r -salt were withdrawn, whilst the filtrate (15 c.c.) gave the result:

$$l = 2, c = 20.724, \alpha_D^{20} - 0.61^\circ, [\alpha]_D^{20} - 1.5^\circ.$$

The concentration of the salt was determined by evaporating an aliquot portion of the solution to dryness and then heating the residue at 120° until constant.

Final Hydrolysis.—The mixture of residual esters and menthol was dissolved in 80 c.c. of ethyl alcohol and heated with 50 c.c. of alkali (1 c.c. = 0.0565 KOH) for 7 hours. The aqueous solution of potassium salt (25 c.c.), from which the menthol had been removed, gave $\alpha_D + 0.56^\circ$ in a 2-dcm. tube containing 14 c.c. The aqueous solution of calcium salt, prepared as in the initial hydrolysis, was concentrated, a crop of 1.5 grams of hydrated r -salt withdrawn, whilst the filtrate (15 c.c.) gave the result:

$$l = 2, c = 20.739, \alpha_D^{20} + 0.78^\circ, [\alpha]_D^{20} + 1.9^\circ.$$

These results show, therefore, that *l*-menthyl *l*-ethoxypropionate is hydro-

lysed by alkali more quickly than is *l*-menthyl *d*-ethoxypropionate. The former ester is produced more readily than the latter during the esterification of the *i*-acid; that it is more quickly hydrolysed is in accordance with the usual experience that, of two isomeric esters, the one which is formed more quickly is also more quickly hydrolysed.

Fractional Hydrolysis of l-Bornyl dl-α-ethoxypropionate.

l-Bornyl *dl*-α-ethoxypropionate, $\text{CH}_3 \cdot \text{CH}(\text{OEt}) \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{17}$, prepared by the complete esterification of *i*-ethoxypropionic acid by *l*-borneol, is an oil which boils at 135° under 10 mm. pressure.

0.2069 gave 0.1905 H_2O and 0.5367 CO_2 . $\text{H} = 10.3$; $\text{C} = 70.7$.

$\text{C}_{15}\text{H}_{26}\text{O}_3$ requires $\text{H} = 10.3$; $\text{C} = 70.8$ per cent.

It has $\alpha_D^{20} - 32.70^\circ$ ($l = 1$) and $d \ 20^\circ/4^\circ \ 0.9858$; whence $[\alpha]_D^{20} - 33.2^\circ$.

A determination of its specific rotation in ethyl alcohol gave:

$l = 2$, $c = 4.9320$, $\alpha_D^{20} - 3.03^\circ$, $[\alpha]_D^{20} - 30.7^\circ$.

Initial Hydrolysis.—26.5 grams of ester were dissolved in 100 c.c. of ethyl alcohol and boiled for 3 hours with 52 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0565 KOH), the amount required for complete hydrolysis being 103.6 c.c. After the mixture of esters and borneol had been removed, the aqueous solution of potassium salt (14 c.c.), when examined in a 2-dcm. tube, gave $\alpha_D + 2.44^\circ$. The acid formed from it was converted into calcium salt, from the aqueous solution of which a crop of 3.8 grams of hydrated *r*-salt was separated, whilst the filtrate (15 c.c.), when examined in a 2-dcm. tube containing 14 c.c., gave $\alpha_D^{20} + 1.61^\circ$, $c = 20.685$, $[\alpha]_D^{20} + 3.9^\circ$.

Final Hydrolysis.—The mixture of residual esters and borneol was dissolved in 100 c.c. of ethyl alcohol and boiled for 4 hours with 60 c.c. of standard alkali (1 c.c. = 0.0565 KOH). The resulting potassium salt, after having been separated from borneol, was decolorised in aqueous solution by charcoal and then concentrated to 15 c.c., of which 6 c.c. in a 1-dcm. tube gave $\alpha_D - 0.75^\circ$. The aqueous solution of calcium salt obtained from it was concentrated, a crop of 2.5 grams of hydrated *r*-salt removed, whilst the filtrate (14 c.c.) gave $l = 2$, $c = 21.227$, $\alpha_D^{20} - 1.33^\circ$, $[\alpha]_D^{20} - 3.1^\circ$.

Racemisation of l-Malic Acid by Alkali.

Whilst racemisation takes place with remarkable ease during the hydrolysis of *l*-menthyl *d*-mandelate or of *l*-menthyl *l*-mandelate by alkali, the racemisation of the active acids themselves by alkali is not

nearly so pronounced. Thus, when either of the esters mentioned is hydrolysed by the calculated amount of alcoholic potassium hydroxide even in dilute solution and at 25°, the mandelic acid obtained has a rotation of about one-quarter of that of the pure active acid (Trans., 1904, 85, 1249). As contrasted with this result, the following experiment on the gradual racemisation of potassium *l*-mandelate may be quoted: 0.983 gram of *l*-mandelic acid was dissolved in ethyl alcohol, 10 c.c. of standard alcoholic potassium hydroxide (1 c.c. = 0.06935 KOH) were added (the amount necessary for the neutralisation of the acid being 5.2 c.c.), and the solution then made up to 50 c.c. with ethyl alcohol. This solution gave $\alpha_D^{20} - 1.95^\circ$ in a 1-dm. tube, a value which was unchanged after a lapse of 24 hours. After having been maintained at 80° for 2 hours, the solution exhibited a slight diminution in activity, giving $\alpha_D^{20} - 1.74^\circ$ ($l = 1$); it was then heated to boiling for 7 hours, evaporated to dryness, and the solid made up to 50 c.c. with ethyl alcohol, when the resulting solution gave $\alpha_D^{20} - 1.64^\circ$ ($l = 1$). The whole was then evaporated to dryness and the residue dissolved in a mixture of 20 c.c. of ethyl alcohol and 30 c.c. of alkali (1 c.c. = 0.06935 KOH); this solution, when boiled for 2½ hours, had very slightly diminished in volume and, when made up to 50 c.c., gave $\alpha_D^{20} - 0.87^\circ$ ($l = 1$).

The action of alkali on *l*-malic acid was investigated as follows. *l*-Malic acid (2 grams) and potassium hydroxide (5.5 grams) were made up to 50 c.c. with water. The solution gave $\alpha_D^{20} - 0.76^\circ$ in a 2-dm. tube, a value which did not change after the solution had been kept in a thermostat at 25° for seven weeks. It was then evaporated to dryness on the water-bath and the residue made up to 50 c.c. with water, by which treatment it was found that considerable racemisation had occurred, the solution giving $\alpha_D^{18} - 0.29^\circ$ ($l = 2$). When the solution was again subjected to a similar treatment, it became quite inactive.

In a second experiment, malic acid (16 grams) was dissolved in 200 c.c. of potassium hydroxide solution, containing 41 grams of alkali. The initial rotation was $\alpha_D^{20} - 1.09^\circ$ ($l = 2$). The solution was then heated on a boiling water-bath, the necessary precautions being taken to prevent any alteration in the concentration of the solution, and portions were withdrawn from time to time for polarimetric observations. After 5, 10, 26, 62, 102, and 162 hours' heating respectively, the observed angles of rotation were -0.98° , -0.91° , -0.67° , -0.35° , -0.19° , and -0.05° respectively ($l = 2$).

Action of Heat on the Isomeric Menthyl Mandelates.

After the removal of the unesterified levorotatory acid from the mixture of esters obtained by heating *r*-mandelic acid with *l*-menthol

at 155°, the latter mixture was found by Marckwald and McKenzie to yield on hydrolysis by alkali an acid which was generally inactive and in some cases feebly lævorotatory. This result is due much more to the racemising effect of alkali than to the partial racemisation by heat of the isomeric esters. Marckwald and McKenzie (*Ber.*, 1901, **34**, 472) quote the following experiment. Molecular weights of *l*-mandelic acid and *l*-menthol were heated for 1 hour at 155°, when it was found that the unesterified acid had not undergone any racemisation; when the esterified portion, however, was hydrolysed by alcoholic potassium hydroxide, the *l*-menthol recovered had undergone no racemisation, but the acid gave the value $[\alpha]_D - 55^\circ$, the value for *l*-mandelic acid being -153° in aqueous solution. When one of us repeated this experiment, using the same amount of alkali for the hydrolysis but varying the conditions of temperature and concentration, the acid recovered had $[\alpha]_D - 6^\circ$, whilst the unesterified acid and the menthol had not undergone any racemisation.

The action of heat on *l*-menthyl *d*-mandelate and on *l*-menthyl *l*-mandelate respectively was examined in order to show that those esters actually underwent partial racemisation by heat, but that the difference in the rate of racemisation was in itself insufficient to account for the results obtained on the hydrolysis of mixtures of unequal amounts of those two esters. *l*-Menthyl *d*-mandelate, having $[\alpha]_D^{10^\circ} - 7.6^\circ$ for $c = 3.5956$ in ethyl alcohol (*Trans.*, 1904, **85**, 1254), was heated in an oil-bath at 155° for 4 hours; the product, when dissolved in ethyl alcohol, then gave $l = 2$, $c = 5.279$, $\alpha_D^{20^\circ} - 1.91^\circ$, $[\alpha]_D^{20^\circ} - 18.1^\circ$. When the same ester was heated for a longer time, namely, for 16 hours at 150°, the product then gave in ethyl alcohol $l = 2$, $c = 8.610$, $\alpha_D^{20^\circ} - 4.67^\circ$, $[\alpha]_D^{20^\circ} - 27.1^\circ$. When *l*-menthyl *l*-mandelate, having $[\alpha]_D^{17^\circ} - 138.6^\circ$ for $c = 4.3732$ in ethyl alcohol, was heated at 155° for 4 hours, the rotation of the product in ethyl-alcoholic solution was $l = 1$, $c = 5.580$, $\alpha_D^{18^\circ} - 7.64^\circ$, $[\alpha]_D^{18^\circ} - 136.9^\circ$. When the same ester was heated for 16 hours at 150°, the rotation of the product in ethyl-alcoholic solution was :

$$l = 2, c = 10.191, \alpha_D^{20^\circ} - 26.83^\circ, [\alpha]_D^{20^\circ} - 131.6^\circ.$$

These isomeric esters are, accordingly, partially racemised by heat in such a manner that the optical inversion takes place round the asymmetric carbon atom to which the mandelic complex is attached, whilst no inversion takes place in the menthyl grouping. The rotation of the *d*-mandelate rises during the inversion to an extent greater than the fall of the value of the *l*-mandelate. The inference is that if *l*-menthyl *dl*-mandelate were heated, a mixture of unequal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate containing an excess of the latter ester would be formed. This was the case, since, when

l-menthyl *dl*-mandelate (Trans., 1904, 85, 384) was heated for 4 hours at 155°, its specific rotation increased to the extent of -1.5° .

Before the racemising effect of alkali during the hydrolysis of the menthyl esters of the active mandelic acids was known, several unsuccessful attempts were made by one of us to prepare *l*-mandelic acid from the *r*-acid by converting the latter into *l*-menthyl *dl*-mandelate, heating the latter at 155° for 3 hours, and then hydrolysing the product with an excess of alkali. Although unequal amounts of the *d*- and *l*-mandelates were undoubtedly formed by the action of heat on the partially racemic ester, the acid obtained was invariably quite inactive. This negative result is of some interest, however, in connection with the recent publication of Marckwald and Paul (*Ber.*, 1905, 38, 810), who describe a novel method of obtaining an active compound from its inactive form, and employ it in converting *r*-mandelic acid into the *d*-acid with the aid of anhydrous brucine.

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