

LXXIII.—*Studies in Asymmetric Synthesis. V. Asymmetric Syntheses from l-Bornyl Pyruvate.*

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OPTICALLY active lactic acids are formed by a variety of methods, which may be sharply differentiated from one another as follows :

I. *Production from Substances Already Optically Active.*

Under this heading are embraced such cases as the formation of "fermentation" lactic acid from carbohydrates by the agency of micro-organisms (compare Trans., 1905, 87, 1373), the production of *d*-lactic acid from meat extract, the formation of *d*-lactic acid in the organism (Saito and Katsuyama, *Zeit. physiol. Chem.*, 1901, 32, 214), and the formation of *d*-lactic acid from *d*-alanine (Fischer and Skita, *Zeit. physiol. Chem.*, 1901, 33, 177).

II. *Production by Resolution of the Inactive Variety into its Optically Active Components.*

(a) Biological method by moulds (Lewkowitsch, *Ber.*, 1883, 16, 2720; Linossier, *Bull. Soc. Chim.*, 1891, [iii], 6, 10; McKenzie and Harden, Trans., 1903, 83, 424) and by bacteria (P. F. Frankland and MacGregor, Trans., 1893, 63, 1028).

(b) Crystallisation method, by separation of alkaloidal salts (Purdie and Walker, Trans., 1892, 61, 754; Jungfleisch, *Compt. rend.*, 1904, 139, 56).

(c) Crystallisation method, by the addition of a nucleus of active zinc ammonium lactate to a supersaturated solution of zinc ammonium *i*-lactate (Purdie, Trans., 1893, 63, 1143).

(d) Fractional saponification method from *l*-menthyl *dl*-lactate (McKenzie and Thompson, Trans., 1905, 87, 1004).

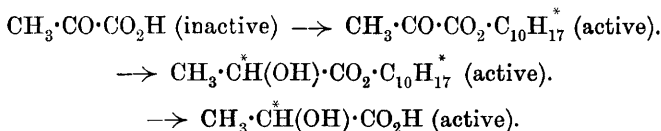
III. *Production by Asymmetric Synthesis.*

The asymmetric synthesis of *l*-lactic acid by the reduction of *l*-menthyl pyruvate has recently been described (Trans., 1905, 87, 1373).

Lactic acid is the only compound containing an asymmetric carbon atom which can be obtained in its optically active forms by such a variety of methods.

The authors have therefore considered it of interest to record in the

present paper another instance of the asymmetric synthesis of lactic acid in accordance with the following scheme :



Pyruvic acid is inactive, and does not contain an asymmetric carbon atom. Its *l*-bornyl ester is active in virtue of the *l*-bornyl group. When this ester is reduced, a new asymmetric carbon atom is generated, and a mixture of unequal amounts of *l*-bornyl *d*-lactate and *l*-bornyl *l*-lactate, containing an excess of the latter, is formed. When the latter mixture is saponified by an excess of alkali and the resulting *l*-borneol completely removed, the aqueous solution of potassium salt is dextrorotatory, and contains a mixture of potassium *d*- and *l*-lactates with an excess of the latter, since on acidification by mineral acid it becomes lævorotatory (*l*-lactic acid forms dextrorotatory salts). On extracting the lactic acid and converting it into its lithium salt, the latter is found to be dextrorotatory.

In a recent paper by one of us (this vol., p. 365), the action of magnesium alkyl (or aryl) halides on *l*-menthyl benzoylformate, *l*-bornyl benzoylformate, and *l*-menthyl pyruvate respectively was investigated with the view of contrasting the effect, firstly, of the active menthyl and bornyl groups, and, secondly, of the various alkyl (or aryl) halides used, on the extent of the asymmetric syntheses of the resulting substituted glycollic acids. The direction of rotation of the mixture of *d*- and *l*-substituted glycollic acids, resulting from the esters in question by variation of the Grignard reagent, is indicated in the table on p. 690.

From the rotation values quoted (*loc. cit.*) it appears that, in the actions in which *l*-menthyl benzoylformate is involved, the increase in weight of the hydrocarbon group of the Grignard reagent has the effect of diminishing the lævorotation of the mixture of unequal amounts of the substituted glycollic acid obtained in each case. With *l*-bornyl benzoylformate the lævorotation is actually transformed into a dextro one with the increase in weight of the hydrocarbon group of the Grignard reagent, and the mixture of phenyl- α -naphthylglycollic acids obtained is more dextrorotatory than the mixture of phenylisobutylglycollic acids. In the two actions quoted with *l*-menthyl pyruvate, the substitution of the phenyl for the ethyl group in the Grignard reagent very considerably increases the dextrorotation of the acid mixture.

If the influence of the bornyl group be contrasted with that of the menthyl group, the atrolactic acid mixture obtained from *l*-bornyl

Ester.	Magnesium alkyl halide.	Acid mixture.	Sign of rotation.
<i>l</i> -C ₆ H ₅ •CO•CO ₂ •C ₁₀ H ₁₉	CH ₃ •Mg•I	$\begin{array}{c} \text{CH}_3 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	Lævo
" "	C ₂ H ₅ •Mg•Br	$\begin{array}{c} \text{C}_2\text{H}_5 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"
" "	<i>n</i> -C ₃ H ₇ •Mg•I	$\begin{array}{c} n\text{-C}_3\text{H}_7 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"
" "	<i>iso</i> -C ₄ H ₉ •Mg•I	$\begin{array}{c} iso\text{-C}_4\text{H}_9 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"
" "	<i>tert.</i> -C ₄ H ₉ •Mg•I	$\begin{array}{c} tert\text{-C}_4\text{H}_9 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"
" "	α -C ₁₀ H ₇ •Mg•Br	$\begin{array}{c} \alpha\text{-C}_{10}\text{H}_7 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"
<i>l</i> -C ₆ H ₅ •CO•CO ₂ •C ₁₀ H ₁₇	CH ₃ •Mg•I	$\begin{array}{c} \text{CH}_3 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"
" "	C ₂ H ₅ •Mg•I	$\begin{array}{c} \text{C}_2\text{H}_5 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"
" "	<i>iso</i> -C ₄ H ₉ •Mg•I	$\begin{array}{c} iso\text{-C}_4\text{H}_9 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	Dextro
" "	α -C ₁₀ H ₇ •Mg•Br	$\begin{array}{c} \alpha\text{-C}_{10}\text{H}_7 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"
<i>l</i> -CH ₃ •CO•CO ₂ •C ₁₀ H ₁₉	C ₂ H ₅ •Mg•Br	$\begin{array}{c} \text{CH}_3 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_2\text{H}_5 \end{array}$	"
" "	C ₆ H ₅ •Mg•Br	$\begin{array}{c} \text{CH}_3 > \text{C} < \begin{array}{l} \text{OH} \\ \text{CO}_2\text{H} \end{array} \\ \text{C}_6\text{H}_5 \end{array}$	"

benzoylformate is seen to be much less lævorotatory than that obtained from *l*-menthyl benzoylformate. The effect of the bornyl group is to increase the proportion of the *d*-acid in the acid mixture.

The present paper contains an account of the action of magnesium ethyl iodide, magnesium *isobutyl* iodide, magnesium phenyl bromide, and magnesium α -naphthyl bromide respectively on *l*-bornyl pyruvate, whilst the action of magnesium *isobutyl* iodide and magnesium α -naphthyl bromide respectively on *l*-menthyl pyruvate has also been examined. The sign of rotation of the acid mixture obtained in each case is indicated in the table on p. 691.

Whilst the results obtained by the application of the Grignard action to *l*-bornyl pyruvate are, considered by themselves, not of much interest as typical examples of asymmetric syntheses owing to the feeble optical activity of the resulting substituted glycollic acids, they are in striking uniformity with the results quoted in the former paper (*loc. cit.*), and bear out in a remarkable degree the influences of mass and other factors, to which attention has just been drawn. For example, the mixture of *d*- and *l*-atrolactic acids, resulting from the action of magnesium methyl iodide on *l*-bornyl benzoylformate, is much less lævorotatory than the mixture resulting from *l*-menthyl benzoylformate and magnesium methyl iodide: a similar effect of the *l*-bornyl as contrasted with the *l*-menthyl group is seen when the

Ester.	Magnesium alkyl halide.	Acid mixture.	Sign of rotation.
$l\text{-CH}_3\cdot\text{CO}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{17}$	$\text{C}_2\text{H}_5\cdot\text{Mg}\cdot\text{I}$	$\begin{array}{c} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{array} > \text{C} \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$	Dextro
" "	$iso\text{-C}_4\text{H}_9\cdot\text{Mg}\cdot\text{I}$	$\begin{array}{c} \text{CH}_3 \\ \text{C}_4\text{H}_9 \end{array} > \text{C} \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$	"
" "	$\text{C}_6\text{H}_5\cdot\text{Mg}\cdot\text{Br}$	$\begin{array}{c} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array} > \text{C} \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$	"
" "	$\alpha\text{-C}_{10}\text{H}_7\cdot\text{Mg}\cdot\text{Br}$	$\begin{array}{c} \text{CH}_3 \\ \alpha\text{-C}_{10}\text{H}_7 \end{array} > \text{C} \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$	Lævo
$l\text{-CH}_3\cdot\text{CO}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$	$iso\text{-C}_4\text{H}_9\cdot\text{Mg}\cdot\text{I}$	$\begin{array}{c} \text{CH}_3 \\ iso\text{-C}_4\text{H}_9 \end{array} > \text{C} \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$	Dextro
" "	$\alpha\text{-C}_{10}\text{H}_7\cdot\text{Mg}\cdot\text{Br}$	$\begin{array}{c} \text{CH}_3 \\ \alpha\text{-C}_{10}\text{H}_7 \end{array} > \text{C} \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$	"

action of magnesium phenyl bromide on *l*-menthyl pyruvate and *l*-bornyl pyruvate is contrasted. We should expect that the mixture of atrolactic acids obtained from *l*-bornyl pyruvate would be much less dextrorotatory than that obtained from *l*-menthyl pyruvate, and this on experiment was found to be the case. Again, the effect of increasing the mass of the hydrocarbon group in the magnesium alkyl (or aryl) halide in the actions on *l*-bornyl benzoylformate is to cause a change in sign from lævo- to dextro-rotation. A similar effect is found with *l*-bornyl pyruvate; whilst dextrorotatory acid mixtures are obtained by the application of magnesium ethyl iodide, magnesium *isobutyl* iodide and magnesium phenyl bromide respectively, the sign of the acid mixture changes from dextro to lævo when magnesium α -naphthyl bromide is employed.

The results obtained with *l*-menthyl pyruvate are also in harmony with the previous observations. The acid mixture obtained by the action of magnesium *isobutyl* iodide on *l*-menthyl pyruvate was, as was expected, slightly dextrorotatory, whilst the influence of the heavier α -naphthyl group is seen by the marked dextrorotation of the acid mixture, resulting from the action of magnesium α -naphthyl bromide on *l*-menthyl pyruvate.

EXPERIMENTAL.

Pyruvic acid was heated with three times its weight of *l*-borneol for ten hours at 100° , a current of dry hydrogen chloride having been passed at intervals of three hours into the mixture. After the product had been washed with water several times, it was submitted to distillation in steam in order to remove the bulk of the borneol. The residual oil was washed with very dilute sodium carbonate, and its ethereal solution dried with anhydrous sodium sulphate. After expulsion of the ether, the borneol was separated from the ester

by allowing the mixture to rise almost to the boiling point under diminished pressure, when the borneol sublimed and was removed from time to time from the side-tube of the distilling flask. The removal of the last traces of borneol in this manner is a tedious process, but presents no difficulty.

l-Bornyl pyruvate, $\text{CH}_3 \cdot \text{CO} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{17}$, is a colourless oil and boils at 143—144° under 18 mm. pressure.

0.1473 gave 0.3760 CO_2 and 0.1212 H_2O . C = 69.6; H = 9.2.

$\text{C}_{13}\text{H}_{20}\text{O}_3$ requires C = 69.6; H = 9.0 per cent.

A determination of its specific rotation gave the result: $l = 1$, d 19.9°/4° 1.0467, $\alpha_D^{19.9^\circ} - 54.82^\circ$, $[\alpha]_D^{19.9^\circ} - 52.4^\circ$.

Reduction of l-Bornyl Pyruvate. The Asymmetric Synthesis of l-Lactic Acid.

A solution of 12.5 grams of *l*-bornyl pyruvate in 50 c.c. of moist ether was added to an excess of aluminium amalgam. A vigorous evolution of hydrogen quickly took place. More ether and a little water were added from day to day during four days. The ethereal solution was drained off and the residue washed with ether. The oil, resulting from the ethereal solution, was dissolved in a solution of 6.5 grams of potassium hydroxide in 70 c.c. of methyl alcohol and allowed to remain overnight at the ordinary temperature. To ensure complete saponification, the liquid was then boiled for one hour under a reflux condenser. The methyl alcohol was expelled, water added, and the precipitated borneol drained off. The filtrate, which was strongly alkaline to litmus, was acidified by the addition of dilute sulphuric acid and made faintly alkaline by potassium hydroxide, since it was desirable that, during the subsequent prolonged evaporation, the solution should not be too strongly alkaline; the presence of a large excess of alkali might tend to racemise any active potassium lactate present, although this racemising effect of alkali on active potassium lactate is slight (Trans., 1905, 87, 1373; compare also Godchet and Jungfleisch, *Compt. rend.*, 1905, 140, 719). The aqueous solution of potassium salt was then extracted with ether and decolorised by being heated on the water-bath for several hours with animal charcoal. By this treatment the borneol was completely removed. The solution was then filtered and sterilised. The polarimetric determination, made two days later, showed that the solution was dextrorotatory, 28 c.c. in a 4-dm. tube giving $\alpha_D^{20^\circ} + 0.44^\circ$. The solution was then concentrated and dilute sulphuric acid added in excess as indicated by Congo red paper; the precipitated potassium sulphate was removed, and the filtrate, when made up to 28 c.c. and examined in a 4-dm. tube,



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proved to be lævorotatory, giving $\alpha_D^{20} -0.17^\circ$. The lactic acid present in this solution was then extracted with ether by aid of a continuous extraction apparatus, the ether was expelled and the aqueous solution of the resulting syrup neutralised by the exact amount of lithium carbonate. The aqueous solution of lithium salt, after evaporation on the water-bath for one hour, measured 30 c.c.; it was dextrorotatory, 28 c.c. of it in a 4-dcm. tube giving $\alpha_D^{20} + 0.22^\circ$. The concentration of the solution as estimated by withdrawing an aliquot portion, evaporating off the water and drying the residue at 100° until constant in weight was 13.46.

A portion of the solution was evaporated to dryness and the residue on analysis shown to consist of lithium lactate.

0.3892, dried at $120-125^\circ$, gave $0.2206 \text{ Li}_2\text{SO}_4$. $\text{Li} = 7.24$.

$\text{C}_3\text{H}_5\text{O}_3\text{Li}$ requires $\text{Li} = 7.32$ per cent.

The specific rotation of the mixture of lithium *d*- and *l*-lactates prepared in the manner indicated is $+0.4^\circ$ at 20° , whereas the value for the pure active lithium lactate as deduced from Purdie and Walker's determinations (Trans., 1895, 67, 616) is 12.0° for an *N*-solution at about 10° .

In the asymmetric synthesis described, the necessary precautions were taken to ensure that the rotations observed were not due to a resolution of *l*-bornyl *dl*-lactate by fractional saponification or to a resolution of potassium *r*-lactate by the growth of micro-organisms.

Action of Magnesium Alkyl (or Aryl) Halides on l-Bornyl Pyruvate.

A solution of magnesium ethyl iodide ($1\frac{1}{4}$ mol.) in 25 c.c. of ether was added by means of a siphon within an interval of forty-five minutes to a solution of 10 grams (1 mol.) of *l*-bornyl pyruvate in 30 c.c. of ether. The saponification of the oil, obtained by decomposing the product resulting from the Grignard action by ice and mineral acid, was conducted with a solution of 5 grams of potassium hydroxide in 100 c.c. of ethyl alcohol. The ethyl alcohol and borneol were removed as previously described (this vol., p. 374), and the acid, obtained from the potassium salt, decolorised in aqueous solution. A crop of inactive acid was separated, and the filtrate proved to be feebly dextrorotatory, giving $\alpha_D + 0.06^\circ$ in a 2-dcm. tube.

A solution of magnesium isobutyl iodide ($2\frac{1}{2}$ mol.) in 30 c.c. of ether was added within an interval of twenty minutes to a solution of 10 grams (1 mol.) of *l*-bornyl pyruvate in 30 c.c. of ether. The saponification of the ester mixture, obtained in the usual manner, was conducted by allowing it to remain for two hours at the ordinary

temperature in contact with a solution of 5.4 grams of potassium hydroxide in 100 c.c. of ethyl alcohol and then boiling for one hour with the addition of 5 c.c. of water. The ethyl alcohol and borneol were removed, and the acid, obtained from the potassium salt by acidification and extraction with ether, was converted into barium salt; the aqueous solution of the latter, when decolorised, proved to be dextrorotatory, the observed rotation in a 2-dcm. tube being only $\alpha_D + 0.10^\circ$. The concentration of this solution as estimated by withdrawing an aliquot portion, evaporating to dryness and then heating at 130° until constant in weight, was 5.47. An estimation of barium gave $\text{Ba} = 38.2$ per cent., a value which indicated that some barium pyruvate was present in the solution together with the barium methyl-isobutylglycollate.

A solution of magnesium phenyl bromide ($1\frac{1}{4}$ mol.) in 25 c.c. of ether was added drop by drop within an interval of seventy minutes to a solution of 10 grams (1 mol.) of *l*-bornyl pyruvate in 30 c.c. of ether. After a night, the product was boiled for fifteen minutes and decomposed by the successive addition of crushed ice and dilute mineral acid. The oil, resulting from the ethereal solution, was allowed to remain for two hours at the ordinary temperature in contact with a solution of 4.9 grams of potassium hydroxide in 100 c.c. of ethyl alcohol, and, after the addition of 5 c.c. of water, the solution was boiled for one hour. After the removal of the ethyl alcohol and borneol, the aqueous solution of potassium salt could not be sufficiently decolorised to permit of accurate polarimetric observation. It was accordingly acidified by mineral acid and the solution extracted with ether. The resulting atrolactic acid was partially decolorised in aqueous solution and then converted into barium salt by boiling with an excess of barium carbonate. The filtrate (15 c.c.) was slightly but distinctly dextrorotatory, giving $\alpha_D + 0.08^\circ$ in a 2-dcm. tube.

This slight dextrorotation was confirmed by a second experiment, where magnesium phenyl bromide was used in the proportion of $2\frac{1}{2}$ mols. to 1 mol. of ester.

A solution of magnesium α -naphthyl bromide ($2\frac{1}{2}$ mol.) in 50 c.c. of ether was added within an interval of twenty minutes to a solution of 10 grams (1 mol.) of *l*-bornyl pyruvate in 30 c.c. of ether. The action was vigorous. After remaining at the laboratory temperature overnight, the product was decomposed by ice and dilute hydrochloric acid, and the oil, resulting from the ethereal solution, submitted to distillation in steam in order to remove naphthalene. The residue in the distilling flask was extracted with ether, the ether expelled and the oil dissolved in a solution of 6 grams of potassium hydroxide in 100 c.c. of ethyl alcohol. After two hours at the ordinary temperature, the solution was boiled for one hour. The ethyl alcohol and borneol were then

removed in the customary manner. The aqueous solution of potassium salt, which was rather highly coloured, was decomposed by an excess of sulphuric acid, and the acid, resulting from the extraction with ether, was directly converted into barium salt by the addition of a solution of 15 grams of crystallised barium hydroxide in 100 c.c. of water. The excess of barium hydroxide was removed by carbon dioxide, and, when the solution had been filtered off from barium carbonate, it was decolorised by animal charcoal. This method was found to be a convenient one for obtaining a solution sufficiently colourless for accurate polarimetric observation. It is practically impossible to decolorise the aqueous solution of potassium salt directly resulting from the saponification, nor can the acid, obtained from the potassium salt, be itself conveniently decolorised. The aqueous solution of barium salt was concentrated to 32 c.c., of which 15 c.c. in a 2-dcm. tube gave $\alpha_D - 0.14^\circ$. The concentration of this solution, as estimated for anhydrous salt, was 7.54. An estimation of barium gave Ba = 31.3 per cent., a result which indicated that the interaction between the magnesium α -naphthyl bromide and *l*-bornyl pyruvate had been incomplete.

A second experiment yielded a similar result, a λ evorotatory acid mixture again being obtained. As a product from this experiment, *i*- α -naphthylmethylglycollic acid was isolated; when crystallised from benzene and then dried at 100° , it melted at $138-139^\circ$, whereas Grignard (*Ann. Chim. Phys.*, 1902, [vii], 27, 548) gives 143° .

Action of Magnesium isobutyl Iodide on l-Menthyl Pyruvate.

A solution of magnesium isobutyl iodide ($2\frac{1}{2}$ mol.) in 30 c.c. of ether was added within an interval of thirty minutes to a solution of 10 grams (1 mol.) of *l*-menthyl pyruvate in 30 c.c. of ether. The product was treated as in the case of the corresponding experiment with *l*-bornyl pyruvate. The barium salt obtained (21 c.c.) was dextro-rotatory, 14 c.c. in a 2-dcm. tube giving $\alpha_D + 0.13^\circ$. The concentration of this solution, as estimated for anhydrous salt, was 4.85. The anhydrous salt contained 40.4 per cent. of barium, a result which indicated the presence of barium pyruvate in the solution.

Action of Magnesium α -Naphthyl Bromide on l-Menthyl Pyruvate.

A solution of magnesium α -naphthyl bromide ($2\frac{1}{2}$ mol.) in 25 c.c. of ether was added within an interval of twenty minutes to a solution of 10 grams (1 mol.) of *l*-menthyl pyruvate in 30 c.c. of ether. The action was vigorous. After twenty-four hours, the product was decomposed and the naphthalene removed as described for the corresponding experiment with the bornyl ester. The ester mixture was

dissolved in a solution of 5.2 grams of potassium hydroxide in 100 c.c. of ethyl alcohol, the solution allowed to remain for two hours at the ordinary temperature and then boiled for one hour. The ethyl alcohol and menthol were then removed by the usual method. The acid, obtained by acidifying the aqueous solution of potassium salt and extracting with ether, was converted into barium salt by the addition of baryta water, the excess of which was removed by carbon dioxide and the resulting barium salt decolorised by charcoal. The aqueous solution of barium salt was concentrated to a bulk of 22 c.c., of which 15 c.c. in a 2-dm. tube gave $\alpha_D^{15} + 0.89^\circ$. The concentration of this solution as determined by withdrawing an aliquot portion, evaporating off the water and drying the residue at 130° was 6.43.

The authors desire to thank the Research Fund Committee of the Chemical Society for a grant in aid of this research.

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