XLVII.—*Studies in the Phenylsuccinic Acid Series.*
Part IV. The l-Menthyl Esters of the Diphenyl-
succinic Acids.

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THE experiments which are described in the present communication were undertaken with the primary object of examining the action of alkali on the *l*-menthyl diphenylsuccinates, and in this connexion particular interest appeared to be attached to the behaviour of di-*l*-menthyl mesodiphenylsuccinate. It has been previously shown that ethyl mesodiphenylsuccinate is converted by an excess of boiling aqueous alcoholic potassium hydroxide solution into a mixture of the potassium salts of *r*- and meso-diphenylsuccinic acids (Wren and Still, T., 1915, **107**, 447), whilst, according to Anschütz and Bendix (*Annalen*, 1890, **259**, 90), the former is the sole product of the action of alcoholic potassium hydroxide on the meso-ester. Since, in these experiments, a molecule which is inactive by reason of internal compensation is transformed into one which is externally compensated, it appeared of interest to apply the reaction to a case in which the inactive ethyl groups were replaced by an optically active radicle, such as *l*-menthyl. In the circumstances, it seemed possible that the mixture of potassium salts of the *d*- and *l*-acids which would be produced might contain an excess of one isomeride; although our previous experience of the hydrolysis of methyl and ethyl *d*-diphenylsuccinates (Wren and Still, T., 1915, **107**, 1454) had shown that there was a probability of moderately extensive racemisation, nevertheless the unusually high specific rotation of the active acids led us to hope that the presence of even a slight excess of one of the isomerides would be easily detected. Unfortunately, this primary object has proved incapable of realisation, since the *l*-menthyl esters are so resistant to the action of alcoholic alkali that their complete hydrolysis cannot be effected under conditions which would lend any interest to the acids that might be formed. On the other hand, certain rather unusual features have been encountered in the preparation of the esters.

The diphenylsuccinic acids are esterified only with great difficulty by *l*-menthol in the presence of hydrogen chloride. In the case of the *r*-acid (and therefore in all probability in the cases of the *d*- and *l*-acids also), a limit is placed on the temperature which can be used, since this substance is immediately transformed at its first melting point, 183°, into a mixture of *r*-diphenylsuccinic

anhydride and *mesodiphenylsuccinic acid*, and this decomposition also occurs more slowly at a lower temperature (Anschütz and Bendix, *loc. cit.*). Experiments with the *r*-acid and its active components have been uniformly effected at a temperature not exceeding 120°; in the case of the *meso*-acid, no such limit is imposed, and it has been found advantageous to operate at a considerably higher temperature (150°).

When *l*-diphenylsuccinic acid is heated with an excess of *l*-menthol during seventeen hours at 115–120° in a slow current of dry hydrogen chloride, a mixture of acid and normal *l*-menthyl esters is formed. Di-*l*-menthyl *l*-diphenylsuccinate crystallises from ethyl alcohol in long, colourless needles which melt at 160–161°, and have $[\alpha]_D^{16.5} - 214.8^\circ$ in acetone. *l*-Menthyl hydrogen *l*-diphenylsuccinate separates from alcohol in felted masses of fine needles which contain one molecule of solvent of crystallisation. It melts at 158.5–159.5°. The specific rotations of the crystalline and dried products in acetone are $[\alpha]_D^{19.5} - 240.3^\circ$ and $[\alpha]_D^{19} - 266.9^\circ$ respectively.

If *d*-diphenylsuccinic acid is heated with *l*-menthol under conditions precisely the same as those adopted for the *l*-isomeride, but for a longer period (twenty-seven hours instead of seventeen), a somewhat different result is obtained. The only product that has been isolated is *l*-menthyl hydrogen *d*-diphenylsuccinate. This substance crystallises from light petroleum in short needles which melt at 144–145°, and have $[\alpha]_D^{16} + 179.5^\circ$ in acetone solution. Attempts to obtain the normal ester of the *d*-acid in a state of optical purity were unsuccessful, but, in the course of these attempts, small quantities of pure di-*l*-menthyl *mesodiphenylsuccinate* were isolated. (The appearance of the *meso*-ester is of some interest, as it affords the only direct evidence which has been obtained of any racemisation during the esterification of these acids under the experimental conditions adopted. It is quite possible that a similar formation of *meso*-ester occurs with the *l*- and *r*-acids, but its detection, if present in relatively small amount, would be a matter of considerable difficulty, as its solubility does not differ greatly from that of the *l*-ester.)

As the preparation of di-*l*-menthyl *d*-diphenylsuccinate by the above method seemed to present considerable difficulties, attempts were made to employ other means. The action of *l*-menthol on *d*-diphenylsuccinyl chloride could not be investigated, since the *d*-acid passes into the corresponding anhydride under conditions which would appear likely to lead to the chloride (Wren and Still, T., 1915, 107, 1458). It appeared probable, however, that *l*-menthyl hydrogen *d*-diphenylsuccinate would be converted by

thionyl chloride into the corresponding chloride, which might subsequently react with *l*-menthol to give the desired normal ester. Preliminary experiments, carried out with the more readily accessible *l*-menthyl hydrogen *l*-diphenylsuccinate, showed that the reaction follows an unexpected course; the substance reacts slowly with thionyl chloride and yields diphenylmaleic anhydride.

Another possibility appeared to lie in the replacement of the alkyl group of the methyl or ethyl *d*-diphenylsuccinates by the *l*-menthyl radicle in a manner similar to that used by Cohn (*Monatsh.*, 1900, **21**, 200), Lapworth and Hann (*T.*, 1902, **81**, 1499), and McKenzie (*T.*, 1906, **89**, 379) in the preparation of *l*-menthyl acetoacetate. Preliminary experiments, however, with ethyl *r*-diphenylsuccinate showed this substance to be unaffected by being heated with an excess of *l*-menthol in a current of dry hydrogen chloride during twelve hours at 115–120°.

Lastly, it appeared possible that the racemisation noticed during attempts to obtain the normal ester from the acid might occur during the initial stages of the esterification, and that a pure product might be obtainable by the action of *l*-menthol on pure *l*-menthyl hydrogen *d*-diphenylsuccinate. Experiments have confirmed this view to some extent, and a more highly active product has been prepared than that obtained by direct crystallisation in the attempt to which reference has already been made. It has not been found possible, however, either by crystallisation or by mechanical means, to obtain a substance of constant specific rotation from the limited amount of product at our disposal. As soon as it is possible to accumulate the requisite material, it is hoped to continue the investigation.

The action of *l*-menthol on *r*-diphenylsuccinic acid at 120–125° in the presence of hydrogen chloride has also been studied. The substances which are isolated from this action depend greatly on the mode of treatment of the crude material. In different experiments, the following compounds have been obtained: di-*l*-menthyl *l*-diphenylsuccinate, *l*-menthyl hydrogen *l*-diphenylsuccinate, *l*-menthyl hydrogen *r*-diphenylsuccinate, *l*-menthyl hydrogen *d*-diphenylsuccinate (m. p. 144–145°), and a substance melting at 154–154·5°, which has been shown to be a second crystalline form of the latter ester. In all cases the same method of esterification has been used, and the relative quantities of material, duration of heating, and temperature have been approximately the same.

In the first experiments, attempts were made to separate the normal and acidic products by agitating the ethereal solution of the crude material with aqueous sodium carbonate. After this treatment, the only compounds which were isolated were *l*-menthyl

hydrogen *l*-diphenylsuccinate and di-*l*-menthyl *l*-diphenylsuccinate. The physical constants of these substances show them to be identical with those obtained by the action of *l*-menthol on the *l*-acid, and the identity is confirmed by the melting points of mixtures of them.

The separation of the normal and acidic products of reaction by means of sodium carbonate was found to be attended by considerable difficulty, and in subsequent experiments attempts were made to employ other methods. For this reason, the crude material, obtained as previously described, was dissolved in alcohol, the solution exactly neutralised with aqueous alcoholic potassium hydroxide, and evaporated to dryness. The dry residue, consisting of a mixture of normal ester (or esters) and potassium salts of the acid esters, was extracted with dry ether in the expectation that the former alone would be dissolved. This was found not to be the case. Suitable treatment of the ethereal solution led to the isolation of di-*l*-menthyl *l*-diphenylsuccinate and *l*-menthyl hydrogen *d*-diphenylsuccinate, whilst the portion which did not pass into the ethereal solution consisted mainly of potassium *l*-menthyl *l*-diphenylsuccinate mixed with quantities of material from which a homogeneous substance could not be isolated.

In another experiment, the only modification introduced consisted in the employment of a somewhat greater volume of ether in the extraction of the crude product. This slight variation, however, had a considerable effect on the nature of the substances isolated, since, from the portion soluble in ether, di-*l*-menthyl *l*-diphenylsuccinate, *l*-menthyl hydrogen *r*-diphenylsuccinate, and a substance which melted at 154—154.5°, and proved to be a second crystalline form of *l*-menthyl hydrogen *d*-diphenylsuccinate, were obtained. An exhaustive examination of the mother liquors obtained from the crystallisation of the first-named substance failed to yield indications of the presence of the normal esters of the *d*- or *r*-acids.

With regard to the mechanism of the process, it may be noted that the first stage of the action of *l*-menthol on the diphenylsuccinic acids may either follow the lines of a normal esterification or consist in a preliminary formation of acid anhydride, and subsequent union of this substance with *l*-menthol to yield the acid ester. Several considerations render the latter course the more probable: (1) Repeated attempts to isolate unaltered acid have been uniformly unsuccessful, even in those cases in which the duration of the reaction has been limited to four hours. (2) In the very early stages of the reaction there is an abundant separation of water; esterification, if normal, must therefore have occurred

very readily, and in consequence the acid ester would be expected to be very readily saponified by alkali. Direct experiment shows that this is by no means the case. In the second phase of the reaction, the *l*-menthol appears to react far more readily with *l*-menthyl hydrogen *l*-diphenylsuccinate than with the derivative of the *d*-acid, so that an excess of the di-*l*-menthyl *l*-ester is produced. This result is to be expected from the behaviour of the *d*- and *l*-acids when esterified separately with an excess of *l*-menthol under similar conditions; after seventeen hours, the *l*-acid yields a considerable proportion of the normal *l*-ester, whilst after twenty-seven hours the formation of the normal *d*-ester could not be established. Further confirmation is to be found in experiments on the esterification of *l*-menthyl hydrogen *r*-diphenylsuccinate by *l*-menthol at 130—140° during ten hours; the product was, unfortunately, too discoloured to permit of direct polarimetric observation, and was recrystallised from alcohol, when the only definite product which could be isolated was di-*l*-menthyl *l*-diphenylsuccinate. This result can scarcely be attributed to a possible resolution of the *r*-ester by crystallisation, since a careful examination of the residues obtained from the filtrate failed to disclose the presence of any normal *d*-ester. In a number of cases it has been shown by Marckwald and McKenzie (*Ber.*, 1899, **32**, 2130; 1901, **34**, 469), and by McKenzie and his co-workers (*T.*, 1902, **81**, 1411; 1904, **85**, 380; 1915, **107**, 712), that the enantiomorphous forms of which a racemic acid may be considered to be composed are esterified with different velocities by an optically active alcohol. When, therefore, a deficiency of alcohol is used or the process is interrupted before completion, an excess of the ester of one form must be produced. In the present instance, an excess of alcohol was used in every case, and the remarkable feature appears to be the magnitude of the disparity between the rates of esterification of the two acid esters.

A series of experiments on the resolution of *l*-menthyl hydrogen *r*-diphenylsuccinate and its alkali salts has greatly helped to explain the isolation of the various acid esters from the products of the action of *l*-menthol on the *r*-acid. It has been found that: (i) *l*-Menthyl hydrogen *r*-diphenylsuccinate is not resolved by crystallisation from light petroleum. (ii) Sodium *l*-menthyl *dl*-diphenylsuccinate is resolved into its diastereoisomerides by crystallisation from water, in which the derivative of the *d*-acid is the more soluble. (iii) Sodium *l*-menthyl *dl*-diphenylsuccinate can be partly resolved by suspending it in water and agitating the suspension with ether; an excess of the derivative of the *d*-acid passes into the ethereal layer. (iv) Potassium *l*-menthyl *dl*-diphenyl-

succinate can be resolved by fractional extraction with boiling ether, an excess of the ester salt of the *d*-acid passing into solution.

The action of *l*-menthol on *r*-diphenylsuccinic acid appears therefore most probably to take the following course. The initial step consists in the formation of *r*-diphenylsuccinic anhydride, which subsequently reacts with *l*-menthol to give the *l*-menthyl hydrogen esters of *d*- and *l*-diphenylsuccinic acids. These are then further esterified, but owing to the greatly superior velocity of esterification of the *l*-acid ester, the normal *l*-ester is formed in large excess, so that the crude, unesterified acid ester probably contains an excess of the *d*-acid derivative. When the acid esters are converted into their potassium salts and treated with ether, a partial resolution occurs, and the ethereal solution contains a greater or less excess of potassium *l*-menthyl *d*-diphenylsuccinate. With a moderate bulk of solvent, conditions may be such that comparatively little potassium *l*-menthyl *l*-ester passes into solution, so that, on acidification of the dissolved portion, the *l*-menthyl hydrogen *d*-diphenylsuccinate is greatly in excess of the *r*-acid ester, and separates in the pure condition when the product is repeatedly crystallised from light petroleum; on the other hand, with a greater quantity of ether, so much potassium *l*-menthyl *l*-diphenylsuccinate may also be dissolved that the acidified product consists of a mixture of *d*-acid ester with considerable quantities of *r*-acid ester, and, on crystallisation, the latter compound just separates, leaving the former in the mother liquors.

Finally, it should be noticed that the compounds enumerated are only those which have been isolated and characterised. They do not account for the whole of the material, but, although the mother liquors from the various products have been exhaustively examined, it has not been found possible to obtain any other substance in even an approximately homogeneous condition.

In the course of the above discussion, it has been pointed out that the two esters which are most readily isolated from the products of the action of *l*-menthol on *r*-diphenylsuccinic acid are identical with those obtained from the alcohol and the *l*-acid. They might, therefore, possibly be derivatives of either the *r*- or *l*-acid, their formation being due to a combination of the effect of fractional esterification and partial resolution on the one hand or of racemisation on the other. The acid ester is doubtless a derivative of the *l*-acid, however, since when mixed with an equal quantity of *l*-menthyl hydrogen *d*-diphenylsuccinate it gives *l*-menthyl hydrogen *r*-diphenylsuccinate, which forms fine needles, m. p. 134—135°, $[\alpha]_D^{25} - 43.7^\circ$ in acetone solution. This substance behaves as a definite chemical compound, and can be crystallised

from light petroleum without undergoing change in its physical constants. The normal ester has not been quite so definitely characterised, but the following considerations appear to leave little doubt that it also is derived from the *l*-acid: (i) The specific rotation is unusually high for the *l*-menthyl ester of a racemic acid. (ii) The difference between the specific rotation of this ester (-214.0°) and that of di-*l*-menthyl *mesodiphenylsuccinate* (-68.5°) is much greater than that generally observed between the activities of similar optically active derivatives of stereoisomeric acids. Instances of this kind have been investigated by Walden (*Zeitsch. physikal. Chem.*, 1896, **20**, 377), who finds that the amyl esters of racemic and *mesotartaric* acids have respectively $[\alpha]_D +3.37^\circ$ and $+4.77^\circ$, whilst the similar esters of *r*- and *meso*-dimethylsuccinic acids have $[\alpha]_D +3.66^\circ$ and $+3.42^\circ$; similarly, according to Patterson and Kaye (T., 1906, **91**, 710), the molecular rotations of *l*-menthyl diacetyl-*i*-tartrate is -274° , whereas the mean of the molecular rotations of *l*-menthyl diacetyl-*d*- and -*l*-tartrates is -307.5° . (iii) If extensive racemisation had occurred during the esterification of the *l*-acid, it is scarcely probable that the pure *l*-acid ester could have been readily isolated; in these circumstances, also, the normal ester would probably contain very considerable amounts of di-*l*-menthyl *mesodiphenylsuccinate*, which does not appear to be the case. Under similar conditions, but with greatly prolonged heating, some racemisation does occur during the analogous action of *l*-menthol on *d*-diphenylsuccinic acid, but even then the proportion of *meso*-ester formed is very slight, and racemisation is not in any sense complete. (iv) Experiments on the esterification of the optically active acids with *l*-menthol show that the second phase of the process (conversion of acidic into normal ester) occurs much more readily with *l*-menthyl hydrogen *l*-diphenylsuccinate than with the derivative of the *d*-acid. The action, therefore, of *l*-menthol on a molecular mixture of the two substances, if interrupted before completion, would lead to the production of an excess of the normal *l*-ester.

Di-*l*-menthyl *mesodiphenylsuccinate* is slowly formed by the esterification of the corresponding acid by *l*-menthol at 150° . It forms long, silky needles which melt at 178 – 179° and have $[\alpha]_D^{16.5} -68.5^\circ$ in acetone solution.

As already indicated, the normal *l*-menthyl esters of the diphenylsuccinic acids are hydrolysed with extreme difficulty by slightly aqueous ethyl-alcoholic potassium hydroxide solution. Thus, the *meso*-ester is practically unattacked when boiled for two hours with an excess of *N*-alkali, and is only hydrolysed to a very limited extent by treatment with approximately 10 per cent. boiling

aqueous alcoholic alkali during eighteen hours. Under the latter conditions, however, the unsaponified portion appears to be partly converted into the racemic ester, which may possibly contain an excess of the normal ester of the *d*- or *l*-acid. The amount of material at our disposal was insufficient to allow a complete examination of this point, but the reverse change can readily be established, since di-*l*-menthyl mesodiphenylsuccinate readily separates, even from the boiling solution, when di-*l*-menthyl *l*-diphenylsuccinate is treated with an excess of aqueous alcoholic potassium hydroxide solution.

The action of alkali on *l*-menthyl hydrogen *l*-diphenylsuccinate has also been investigated. This substance is partly hydrolysed when treated during four hours with approximately normal boiling aqueous alcoholic potassium hydroxide solution. The unattacked portion appears to consist mainly of unchanged ester, whilst from the hydrolysed part it has been found possible to isolate small amounts of *l*-diphenylsuccinic acid in an approximately pure condition.

EXPERIMENTAL.

Action of l-Menthol on l-Diphenylsuccinic Acid.

A mixture of *l*-diphenylsuccinic acid ($[\alpha]_D -386.7^\circ$ in acetone solution, 10.2 grams) and *l*-menthol (30.6 grams) was heated during seventeen hours at $115-120^\circ$ in a slow stream of dry hydrogen chloride. The product, which solidified when preserved overnight, was distilled in a current of steam until excess of *l*-menthol was removed and the residual solid was dissolved in ether. The ethereal solution was gently agitated with very dilute potassium carbonate solution (about 1 per cent.), which caused the separation of a bulky, somewhat slimy precipitate (*A*) in the aqueous layer. The ethereal portion was dried over calcium chloride; after removal of the solvent, the residue readily solidified and was purified by repeated crystallisation from ethyl alcohol until the specific rotation of successive crops in acetone was constant.

Di-l-menthyl l-diphenylsuccinate separates readily from its solution in boiling alcohol in well-defined, colourless needles. It is moderately soluble in the boiling solvent, very sparingly so in the cold. It dissolves freely in cold acetone, benzene, chloroform, or light petroleum (b. p. $60-80^\circ$). It melts at $160-161^\circ$:

0.1655 gave 0.4788 CO_2 and 0.1350 H_2O . $\text{C}=78.9$; $\text{H}=9.1$.

$\text{C}_{36}\text{H}_{50}\text{O}_4$ requires $\text{C}=79.1$; $\text{H}=9.2$ per cent.

The specific rotation was determined in a number of solvents.

In acetone solution :

$$l = 2, c = 1.720, \alpha_D^{17.4} - 7.37^\circ, [\alpha]_D^{17.4} - 214.2^\circ$$

$$l = 2, c = 1.6895, \alpha_D^{16.3} - 7.26^\circ, [\alpha]_D^{16.3} - 214.8^\circ.$$

In benzene solution :

$$l = 2, c = 2.475, \alpha_D^{16.3} - 12.04^\circ, [\alpha]_D^{16.3} - 243.2^\circ.$$

In chloroform solution :

$$l = 2, c = 1.7320, \alpha_D^{15.4} - 7.77^\circ, [\alpha]_D^{15.4} - 224.3^\circ.$$

In ethylene bromide solution :

$$l = 2, c = 1.7265, \alpha_D^{17} - 8.27^\circ, [\alpha]_D^{17} - 239.5^\circ.$$

l-Menthyl hydrogen *l*-diphenylsuccinate was obtained by the addition of mineral acid to the precipitate (*A*) and purified by repeated crystallisation from ethyl alcohol until successive crops had a constant specific rotation. It is freely soluble in the boiling solvent, very sparingly so in the cold, and the solutions show a marked tendency to remain supersaturated; it separates in felted masses of colourless needles which contain one molecule of alcohol of crystallisation. It dissolves readily in cold acetone, benzene, or ether, and melts at 158.5—159.5°:

0.2959 lost 0.0302 at 100—105°. EtOH = 10.2.

$C_{26}H_{32}O_4$, EtOH requires EtOH = 10.1 per cent.

0.1336 * gave 0.3752 CO_2 and 0.0957 H_2O . C = 76.6; H = 8.0.

$C_{26}H_{32}O_4$ requires C = 76.4; H = 7.9 per cent.

The specific rotation was observed in acetone solution :

$$l = 2, c = 1.5750, \alpha_D^{18.5} - 7.57^\circ, [\alpha]_D^{18.5} - 240.3^\circ$$

$$l = 2, c = 1.8295, \alpha_D^{20} - 8.30^\circ, [\alpha]_D^{20} - 239.9^\circ.$$

The material, which had been heated at 100—105° until constant in weight, was optically examined in acetone and in benzene solution.

In acetone solution :

$$l = 2, c = 1.3095, \alpha_D^{19} - 6.99^\circ, [\alpha]_D^{19} - 266.9^\circ.$$

In benzene solution :

$$l = 2, c = 2.1425, \alpha_D^{15.2} - 13.39^\circ, [\alpha]_D^{15.2} - 315.4^\circ.$$

Action of l-Menthol on d-Diphenylsuccinic Acid.

d-Diphenylsuccinic acid ($[\alpha]_D + 387.4^\circ$ in acetone solution, 10.2 grams) was heated with *l*-menthol (30.6 grams) during twenty-seven hours in a slow current of dry hydrogen chloride. After removal of excess of menthol by distillation with steam, the product was dissolved in ether and the ethereal solution shaken with aqueous sodium carbonate, which remained alkaline; in this instance, separa-

* Dried at 100—105° until constant in weight.

tion of the sodium salt of the acid ester was not observed. The ethereal solution left, after evaporation, 9.7 grams of solid residue, which was purified by repeated crystallisation from boiling light petroleum (b. p. 60—80°) until successive crops showed a constant specific rotation in acetone solution. The ultimate product proved to be *l*-menthyl hydrogen *d*-diphenylsuccinate instead of the normal ester which would be expected after the treatment outlined above.

l-Menthyl hydrogen *d*-diphenylsuccinate separates from boiling light petroleum (b. p. 60—80°) in soft aggregates of minute, colourless needles. It dissolves readily in the boiling, rather sparingly in the cold solvent. It is readily soluble in the usual organic media and melts at 144—145°:

0.2343 neutralised 5.3 c.c. 0.108*N*-alkali. Calc., 5.3 c.c.

0.2080 gave 0.5804 CO₂ and 0.1467 H₂O. C=76.1; H=7.9.

C₂₆H₃₂O₄ requires C=76.4; H=7.9 per cent.

The specific rotation was determined in acetone solution:

$$l = 2, c = 1.5710, \alpha_D^{16} + 5.64^\circ, [\alpha]_D^{16} + 179.5^\circ$$

$$l = 2, c = 1.5495, \alpha_D^{18.2} + 5.56^\circ, [\alpha]_D^{18.2} + 179.4^\circ.$$

In the hope of obtaining the normal ester, the entire residues from the experiment described above were re-esterified with *l*-menthol for a further period of nineteen hours. After removal of excess of menthol and treatment of the residue dissolved in ether with sodium carbonate solution, a solid product was obtained which was repeatedly crystallised from ethyl alcohol, whereby colourless prisms were obtained. Successive crops had the following physical constants, the specific rotations being determined in acetone solution: Crop II, m. p. 93—94°, $[\alpha]_D^{17} + 54.3^\circ$; Crop III, m. p. 94.5—95.5°, $[\alpha]_D^{17.5} + 52.5^\circ$; Crop IV, m. p. 94.5—95°, $[\alpha]_D^{20} + 50.3^\circ$; Crop V, m. p. 95—96°, $[\alpha]_D^{21} + 41.7^\circ$. The last fraction was obviously not homogeneous, and, by suitably adjusting the temperature at which crystallisation occurred, it was found possible to cause the separation of a small crop of long, shining needles from which, after recrystallisation, a small amount of substance was obtained which was identified as di-*l*-menthyl *meso*-diphenylsuccinate; it melted at 178—179°, and the melting point was unchanged by admixture with the synthetic *meso*-ester (see later). It was laevorotatory in acetone solution, but the amount available was too minute to permit an accurate determination of the specific rotation. The ethyl-alcoholic mother liquors from which the crops described above had been obtained were united and allowed to evaporate to dryness at the ordinary temperature. In this manner, well-defined double pyramids mixed with a few needles were obtained. The former were separated mechanically and crystallised from methyl

alcohol; the product thus obtained melted at $98.5-99^\circ$, and had $[\alpha]_D^{15.5} + 75.0^\circ$ in acetone solution ($l=2$, $c=1.8325$, $\alpha_D^{15.5} + 2.75^\circ$). After a further crystallisation from the same solvent, the specific rotation of the substance had diminished to $+72.3^\circ$ ($l=2$, $c=1.252$, $\alpha_D^{16.5} + 1.81^\circ$). It was apparently still not homogeneous, and the amount of material was insufficient for further purification. On analysis, results were obtained which are in agreement with those required for a normal ester. (Found, $C=79.1$; $H=9.2$. $C_{36}H_{50}O_4$ requires $C=79.1$; $H=9.2$ per cent.)

Action of l-Menthol on l-Menthyl Hydrogen d-Diphenylsuccinate.

A mixture of the acid ester (2.5 grams) and *l*-menthol (7.5 grams) was heated at $115-120^\circ$ during twenty-five hours in a slow stream of dry hydrogen chloride. After removal of excess of menthol, the crude product was repeatedly crystallised from methyl alcohol. The fourth crop had m. p. $98-99^\circ$ and $[\alpha]_D^{12} + 72.7^\circ$. Attempts were made to obtain well-defined crystals from it and to effect further purification mechanically, as described in the foregoing experiment. The most highly active product obtained in this manner had $[\alpha]_D^{15.2} + 73.7^\circ$ in acetone solution, a figure which is slightly lower than the highest value observed in the previous experiment.

Preparation of l-Menthyl Hydrogen r-Diphenylsuccinate.

Equal quantities of *l*-menthyl hydrogen *d*-diphenylsuccinate and *l*-menthyl hydrogen *l*-diphenylsuccinate (heated at $100-105^\circ$) were dissolved in acetone, the solutions mixed, and allowed to evaporate spontaneously to dryness. The product melted at $134-135^\circ$. It was polarimetrically examined in acetone solution:

$$l=2, c=1.4775, \alpha_D^{18.6} - 1.30^\circ, [\alpha]_D^{18.6} - 43.99^\circ.$$

The substance is readily soluble in the usual organic media. It may, however, be readily crystallised from light petroleum (b. p. $60-80^\circ$), from which it separates in short, well-defined needles melting sharply at $134-135^\circ$. The specific rotation in acetone remains unchanged:

$$l=2, c=1.4060, \alpha_D^{18.5} - 1.23^\circ, [\alpha]_D^{18.5} - 43.7^\circ.$$

This value is in exact agreement with the mean (-43.7°) of the specific rotations of *l*-menthyl hydrogen *d*-diphenylsuccinate ($+179.5^\circ$) and *l*-menthyl hydrogen *l*-diphenylsuccinate (-266.9°) under similar conditions:

0.1541 gave $0.4299 CO_2$ and $0.1119 H_2O$. $C=76.1$; $H=8.1$.

$C_{26}H_{32}O_4$ requires $C=76.4$; $H=7.9$ per cent.

Partial Resolution of Potassium l-Menthyl dl-Diphenylsuccinate by Fractional Solution in Ether.

Equal quantities (each 0.2 gram) of *l*-menthyl hydrogen *l*-diphenylsuccinate and *l*-menthyl hydrogen *d*-diphenylsuccinate were dissolved in alcohol, and the solution exactly neutralised with aqueous alcoholic potassium hydroxide solution in the presence of phenolphthalein. The solid residue, obtained after removal of alcohol, was heated under reflux with dry ether (30 c.c.) from which every trace of acid had been previously removed. A portion dissolved. The solution was filtered and the filtrate shaken with dilute hydrochloric acid. The ethereal layer was dried over sodium sulphate and the ether removed. The solid residue was polarimetrically examined in acetone solution:

$$l=2, c=0.196, \alpha_D + 0.47^\circ, [\alpha]_D + 119.9^\circ.$$

The residue, which remained undissolved in ether, was agitated with dilute hydrochloric acid and ether, when two clear solutions were ultimately obtained. The ethereal portion was evaporated to dryness and the residue heated at 100° . The optical activity was determined in acetone solution:

$$l=2, c=0.7275, \alpha_D - 2.30^\circ, [\alpha]_D - 158.1^\circ.$$

After being recrystallised from rectified spirit and dried at $100-105^\circ$, the product had $[\alpha]_D - 240.3^\circ$ ($l=2, c=0.231, \alpha_D - 1.11^\circ$), whereas the value $[\alpha]_D^{19} - 266.9^\circ$ has been found for pure *l*-menthyl hydrogen *l*-diphenylsuccinate under approximately the same conditions.

Partial Resolution of Sodium l-Menthyl dl-Diphenylsuccinate.

(a) *By Crystallisation from Water.*—Dry sodium *l*-menthyl *dl*-diphenylsuccinate (0.5 gram) was dissolved in hot water (20 c.c.) and the solution cooled at first to the temperature of the laboratory, and subsequently during one hour in ice-water. The very gelatinous, white precipitate (*A*) was removed, and the filtrate acidified with dilute hydrochloric acid, yielding thereby a white, caseous precipitate which readily passed into solution in ether. After removal of the solvent, a small amount of a varnish-like residue was obtained which was polarimetrically examined in acetone solution:

$$l=2, c=0.1725, \alpha_D + 0.35^\circ, [\alpha]_D + 101.4^\circ.$$

The precipitate (*A*) was suspended in water, decomposed by dilute hydrochloric acid, and the liberated menthyl hydrogen ester extracted with ether. After removal of the solvent and desicca-

tion of the residue in a vacuum over calcium chloride, it was examined in acetone solution:

$$l=2, c=1.0405, \alpha_D - 1.78^\circ, [\alpha]_D - 85.5^\circ.$$

(b) *By Extraction of the Aqueous Suspension with a Limited Amount of Ether.*—The dry sodium salt (0.5 gram) was dissolved in hot water (50 c.c.), and the solution cooled to the ordinary temperature, when partial separation occurred. The suspension was thoroughly agitated with ether (50 c.c.) which had been repeatedly shaken with sodium hydroxide solution and subsequently with water. The ethereal layer was treated with dilute hydrochloric acid, dried, and the ether removed. The small solid residue thus obtained was examined in acetone solution:

$$l=2, c=0.097, \alpha_D + 0.03^\circ, [\alpha]_D + 15.4^\circ.$$

The aqueous suspension was acidified with dilute hydrochloric acid and extracted with ether. After removal of the solvent, the residue was optically investigated in acetone solution:

$$l=2, c=1.680, \alpha_D - 1.76^\circ, [\alpha]_D - 52.4^\circ.$$

Action of Thionyl Chloride on l-Menthyl Hydrogen l-Diphenylsuccinate.

l-Menthyl hydrogen *l*-diphenylsuccinate which had been heated for two hours at 90–100° (3 grams) was covered with an excess of thionyl chloride. The ester immediately passed into solution, but after half an hour the evolution of hydrogen chloride was not perceptible. The temperature was slowly raised to 40°, when gas commenced to be freely evolved. The solution was subsequently heated at its boiling point during ten hours, at the end of which period there was practically no further disengagement of hydrogen chloride. Excess of thionyl chloride was removed in an exhausted desiccator over soda-lime, leaving a deeply coloured, crystalline residue mixed with a small quantity of oily matter. After being twice crystallised from a mixture of benzene and light petroleum (b. p. 60–80°), it yielded well-defined, yellowish-green prisms which melted at 158–158.5°, were optically inactive in chloroform solution, and were free from chlorine. The product was readily soluble in dilute, aqueous alcoholic potassium hydroxide solution, from which it was immediately precipitated by an excess of mineral acid as a mass of pale yellow needles. Analysis showed the substance to be diphenylmaleic anhydride. (Found, C=76.87, 76.93; H=4.29, 4.31. Calc., C=76.77; H=4.04 per cent.) It has been previously described by Reimer (*Ber.*, 1880, **13**, 742) and Rügheimer (*Ber.*, 1882, **15**, 1626), who gave 155° and 156° respectively for the melting point.

Action of l-Menthol on r-Diphenylsuccinic Acid.

A mixture of dehydrated *r*-diphenylsuccinic acid (10 grams) and *l*-menthol (30 grams) was heated in an oil-bath at 120—125° in a slow current of dry hydrogen chloride. After half an hour the acid had completely dissolved and, later, oily drops were found to have collected on the bottom and sides of the flask. Heating was continued during fifteen hours. The viscous, brown oil thus obtained was distilled with steam to remove excess of menthol, and the residue, which formed a hard cake when cold, was dissolved in ether. The ethereal solution was washed with water and then with dilute sodium carbonate solution, which caused the separation of a bulky, white, gelatinous precipitate (*A*), rendering the subsequent separation of the two layers a matter of considerable difficulty. The ethereal solution was dried over calcium chloride, and the residue, left after removal of the solvent, purified by repeated crystallisation from rectified spirit until successive crops showed a constant specific rotation in acetone solution, ten crystallisations being necessary to produce this result. The product thus isolated formed well-defined, colourless needles which melted at 160—161°, and the melting point was unchanged when the substance was mixed with an approximately equal quantity of the normal ester prepared by the action of *l*-menthol on *l*-diphenylsuccinic acid. In acetone solution it had $[\alpha]_D^{16} - 214.0^\circ$ ($l=2$, $c=1.785$, $\alpha_D^{16} - 7.64^\circ$). For the reasons stated in the introductory portion of the paper, the substance is regarded as di-*l*-menthyl *l*-diphenylsuccinate. (Found, C=79.2; H=9.1. $C_{36}H_{50}O_4$ requires C=79.1; H=9.2 per cent.)

The bulky, white precipitate (*A*) was filtered, dried, and thoroughly extracted with ether. The undissolved portion was suspended in water and decomposed by an excess of dilute hydrochloric acid. The liberated acid ester was extracted with ether and, after removal of the solvent, purified by crystallisation from rectified spirit. It was obtained in this way as a mass of colourless needles which melted at 158.5—159.5°, had $[\alpha]_D^{16.5} - 241.3^\circ$ in acetone solution ($l=2$, $c=1.3810$, $\alpha_D^{16.5} - 5.70^\circ$), and were in all respects identical with *l*-menthyl hydrogen *l*-diphenylsuccinate, $C_{26}H_{32}O_4 \cdot C_2H_5 \cdot OH$, obtained by the esterification of *l*-diphenylsuccinic acid with *l*-menthol.

In a second experiment the same conditions of esterification were adopted, but the products were worked up in a different manner. The *r*-acid (21 grams) was treated as previously described with three times its weight of *l*-menthol and excess of the latter removed with steam. The crude product remaining in the distilling flask was dissolved in ether and the supernatant aqueous layer extracted with the same solvent. After removal of ether from the

combined extracts, the residue was dissolved in alcohol and exactly neutralised with aqueous alcoholic potassium hydroxide solution in the presence of phenolphthalein. During the process a considerable quantity of gelatinous precipitate separated. The alcohol was completely removed on the water-bath and the solid residue ground to a fine powder and dried in a vacuum over calcium chloride. It was then repeatedly extracted with small quantities of boiling dry ether and the extracts filtered and united. The undissolved portion was repeatedly washed with cold ether and the washings added to the ethereal extracts. In all, 500 c.c. of ether were employed. The operations of extraction and washing are rendered somewhat difficult by the property of the residue of swelling up greatly and obstinately retaining ether.

Treatment of Undissolved Portion.—The residue was suspended in water, decomposed with an excess of dilute hydrochloric acid, and the liberated acid ester was extracted with ether. After desiccation of the ethereal solution and removal of the solvent, 12.5 grams of substance were obtained, which had $[\alpha]_D - 159.4^\circ$ in acetone solution. The product was completely and readily soluble in a small quantity of cold benzene, and nothing separated from the cold solution even after long keeping, so that the presence of an appreciable amount of unchanged acid is improbable. The benzene was removed and the residue crystallised from rectified spirit; after one treatment, which involved a very considerable loss of material, the value for the specific rotation in acetone had increased to -210.7° and, after two further crystallisations, pure *l*-menthyl hydrogen *l*-diphenylsuccinate (3.8 grams) was obtained which melted at $158.5-159.5^\circ$ and had $[\alpha]_D - 239.3^\circ$ when dissolved in acetone.

The mother liquor obtained from the first crystallisation of the *l*-menthyl hydrogen ester left a considerable solid residue when evaporated to dryness. A long series of crystallisations of the product from boiling light petroleum failed to yield any homogeneous product, the melting points of the various fractions lying indefinitely between 90° and 152° .

Treatment of Ethereal Solution.—The residue obtained after removal of ether formed a slightly viscid mass with a very faint odour of menthol. It weighed 17.7 grams, was neutral in reaction, and only slowly soluble in acetone. When dissolved in the latter solvent, it had $[\alpha]_D + 35.4^\circ$ ($c=1.2715$). It dissolved readily in boiling rectified spirit and, on cooling the solution, needles separated which ultimately became a pasty, felted mass. The crop (3.7 grams) was laevorotatory in acetone ($l=2$, $c=0.5195$, $\alpha_D - 0.18^\circ$, $[\alpha]_D - 17.3^\circ$), and was found to be contaminated with a quantity of a potassium salt. It was therefore redissolved in boiling recti-

fied spirit containing a small proportion of glacial acetic acid; the cooled solution readily deposited well-defined needles (1.2 grams), which after being washed successively with alcohol, water, and alcohol had $[\alpha]_D - 208.8^\circ$ in acetone; after a further crystallisation, pure di-*l*-menthyl *l*-diphenylsuccinate, m. p. $160-161^\circ$, $[\alpha]_D^{13.5} - 213.9^\circ$ in acetone solution ($l=2$, $c=1.3255$, $\alpha_D^{13.5} - 5.67^\circ$), was isolated.

The filtrate obtained after the crystallisation from rectified spirit of the material which had $[\alpha]_D + 35.4^\circ$ in acetone was evaporated to dryness, leaving a slightly viscid mass, in which the presence of potassium was readily detected. It was heated with a considerable volume of water, yielding thereby a very soapy solution containing a small quantity of slimy, white precipitate, which was removed and not further examined. The filtrate was acidified with dilute hydrochloric acid, and the heavy, white precipitate which was produced was dissolved in ether. After removal of the solvent, the residue consisted of an oil, which intumesced strongly and slowly solidified to a porous, friable varnish-like mass (6.8 grams) when preserved in a vacuum over calcium chloride. It had $[\alpha]_D + 92.0^\circ$ when dissolved in acetone ($l=2$, $c=1.1515$, $\alpha_D + 2.12^\circ$). It dissolved readily in boiling light petroleum (b. p. $60-80^\circ$) and, after two crystallisations from this solvent, yielded pure *l*-menthyl hydrogen *d*-diphenylsuccinate, m. p. $144-145^\circ$, $[\alpha]_D^{12} + 181.1^\circ$, in acetone solution ($l=2$, $c=1.5545$, $\alpha_D^{12} + 5.63^\circ$). The melting point was unchanged by admixture with an approximately equal quantity of the acid ester obtained from *l*-menthol and *d*-diphenylsuccinic acid.

In a third experiment, the *r*-acid (20 grams) was esterified with *l*-menthol (60 grams), the excess of menthol removed, and the acid esters converted into their potassium salts in exactly the same manner as in the experiment just described. A somewhat larger volume of dry ether (700 c.c. instead of 500 c.c.) was used for the extraction of the solid residue. The portion which remained undissolved was treated with dilute hydrochloric acid and ether, and the ethereal solution was evaporated to dryness. After a single crystallisation from rectified spirit, the residue yielded almost pure *l*-menthyl hydrogen *l*-diphenylsuccinate, which, after being heated at 100° , had $[\alpha]_D^{11} - 262.1^\circ$ in acetone solution ($l=2$, $c=1.5165$, $\alpha_D^{11} - 7.95^\circ$), the value observed for the pure ester under similar conditions being -266.9° .

The portion soluble in ether, after removal of the solvent, was extracted with warm water; the part which remained undissolved yielded di-*l*-menthyl *l*-diphenylsuccinate after purification from alcohol and contained small quantities of material, from which a homogeneous substance could not be isolated in addition to a little potassium salt which had escaped extraction; it did not give any

indication of the presence of di-*l*-menthyl *d*-diphenylsuccinate or of the corresponding ester of the *r*-acid. The portion which dissolved in water was decomposed by dilute hydrochloric acid, and the caseous precipitate of acid esters was dissolved in ether. The ethereal solution left, on evaporation, an oily residue, which ultimately solidified to a brittle, varnish-like mass. The latter was purified by two crystallisations from boiling light petroleum (b. p. 60—80°), when well-defined, needle-shaped crystals (4 grams) were isolated, which were found to consist of *l*-menthyl hydrogen *r*-diphenylsuccinate. They melted at 134—135°, and the melting point remained unaltered by admixture with an approximately equal quantity of the *r*-ester prepared from its two components. The specific rotation was determined in acetone solution:

$$l=2, c=1.9135, \alpha_D -1.68^\circ, [\alpha]_D -43.9^\circ.$$

The synthetic *r*-ester has $[\alpha]_D^{18.5} -43.7^\circ$ under similar conditions.

The mother liquor from the first crystallisation of the *r*-ester from light petroleum was allowed to evaporate spontaneously at the ordinary temperature; the brittle, glassy, yellow solid thus obtained weighed 8 grams and had $[\alpha]_D +79.0^\circ$ in acetone solution ($l=2, c=1.791, \alpha_D +2.83^\circ$). It was heated with a small quantity of boiling light petroleum and the solution filtered from a small amount of sparingly soluble matter; the well-cooled filtrate slowly deposited a crop (2.5 grams), which melted at 151.5—152.5° and had $[\alpha]_D +170.3^\circ$ in acetone solution. After repeated recrystallisation, well-defined, transparent prisms were obtained, which melted constantly at 154—154.5° and had $[\alpha]_D^{14} +178.4^\circ$ ($l=2, c=1.513, \alpha_D^{14} +5.40^\circ$):

0.1505 gave 0.4226 CO₂ and 0.1073 H₂O. C=76.6; H=8.0.

C₂₆H₃₂O₄ requires C=76.4; H=7.9 per cent.

The analytical results show the substance to be a *l*-menthyl hydrogen diphenylsuccinate, and the practical identity of the specific rotations of this substance and of *l*-menthyl hydrogen *d*-diphenylsuccinate in acetone (+178.4° and +179.5° respectively) points to the existence of the latter in two different crystalline forms; this conclusion is confirmed by the observation that, in one case, a specimen of the substance (m. p. 144—145°) had become spontaneously converted into the form of higher melting point when preserved for some months in a desiccator over calcium chloride. Also, the melting point of a mixture of approximately equal quantities of the two esters lies at 154—154.5°, and, further, if the ester of lower melting point is maintained at about 146° for some minutes, it gradually solidifies and subsequently melts at 154—154.5°, whilst the same change can be instantaneously induced

by seeding the molten ester with a small quantity of the ester of higher melting point.

Further Attempts to Prepare Di-l-menthyl r-Diphenylsuccinate.

I. *By the Action of l-Menthol on l-Menthyl Hydrogen r-Diphenylsuccinate.*—A mixture of the acid ester (2 grams) and *l*-menthol (6 grams) was heated at 130–140° during twenty hours in a slow stream of dry hydrogen chloride. The product, after removal of excess of *l*-menthol by steam, solution in ether, and removal of the solvent in the usual manner, formed a discoloured, slightly viscid mass which was too dark to permit of direct polarimetric investigation. It was crystallised from boiling rectified spirit, when well-defined needles (0.8 gram) were deposited, which melted at 160–161° after slight previous softening and had $[\alpha]_D - 208.7^\circ$ in acetone solution ($l=2$, $c=0.908$, $\alpha_D - 3.79^\circ$). After two more recrystallisations from the same solvent, pure di-*l*-menthyl *l*-diphenylsuccinate was obtained in colourless needles melting at 161–162°. The specific rotation was determined in acetone solution:

$$l=2, c=1.645, \alpha_D^{13} - 7.04^\circ, [\alpha]_D^{13} - 214.0^\circ.$$

The mother liquor from the first crystallisation of the *l*-ester was decolorised with animal charcoal and the solution evaporated to dryness. A transparent, brittle, yellow solid (1.2 grams) remained, which had $[\alpha]_D + 14.3^\circ$ in acetone solution. It dissolved readily in boiling light petroleum, but nothing separated when the solution was cooled in a freezing mixture of ice and salt, the conditions employed being those under which *l*-menthyl hydrogen *d*-diphenylsuccinate is fairly readily deposited even when in an impure condition. It was also readily soluble in boiling methyl alcohol, and the cooled solution slowly deposited a small crop of somewhat discoloured needles, which melted indefinitely at 87–120° and had $[\alpha]_D + 5.2^\circ$ in acetone solution, thus giving no indication of the presence of any considerable amount of di-*l*-menthyl *d*-diphenylsuccinate.

II. *By the Action of l-Menthol on Ethyl r-Diphenylsuccinate.*—The mixture of ester (1 gram) and *l*-menthol (3 grams) was heated in a slow current of dry hydrogen chloride during twelve hours at 115–120°; the product was worked up in the usual manner, and, after being crystallised from light petroleum (b. p. 60–80°), was identified by crystalline form, melting point (84–85°), alone and when mixed with the synthetic ether, as unchanged ethyl *r*-diphenylsuccinate. It was optically inactive in acetone solution ($c=1.327$).

Action of l-Menthol on mesoDiphenylsuccinic Acid.

A mixture of *mesodiphenylsuccinic acid* (7.9 grams) and *l*-menthol (23.7 grams) was heated at 150° during twenty hours in a slow current of dry hydrogen chloride. After removal of excess of *l*-menthol by steam, the residue was dissolved in a large volume of ether. The ethereal solution was shaken with aqueous sodium carbonate and the ether removed. The crystalline residue was decolorised with animal charcoal and crystallised from alcohol. After two crystallisations, the substance was optically pure.

Di-l-menthyl mesodiphenylsuccinate separates from alcohol in long, silky needles. It is rather sparingly soluble in the boiling, very sparingly so in the cold, solvent. It dissolves readily in cold chloroform, carbon tetrachloride, or benzene, sparingly in cold acetone or boiling light petroleum (b. p. 40—60°). It melts at 178—179°:

0.1542 gave 0.4460 CO₂ and 0.1270 H₂O. C=78.9; H=9.2.

C₃₆H₅₀O₄ requires C=79.1; H=9.2 per cent.

The specific rotation was determined in a number of solvents.

In acetone solution:

$$l = 2, c = 1.5175, \alpha_D^{16.5} - 2.08^\circ, [\alpha]_D^{16.5} - 68.5^\circ$$

$$l = 2, c = 1.2275, \alpha_D^{9.4} - 1.68^\circ, [\alpha]_D^{9.4} - 68.4^\circ.$$

In ethylene dibromide solution:

$$l = 2, c = 1.1530, \alpha_D^{16.2} - 1.56^\circ, [\alpha]_D^{16.2} - 67.6^\circ.$$

In benzene solution:

$$l = 2, c = 1.0420, \alpha_D^{15} - 1.91^\circ, [\alpha]_D^{15} - 91.7^\circ.$$

In chloroform solution:

$$l = 2, c = 1.2780, \alpha_D^{12.7} - 1.97^\circ, [\alpha]_D^{12.7} - 77.1^\circ.$$

Attempts to Hydrolyse the l-Menthyl Esters of the Diphenylsuccinic Acids with Aqueous Alcoholic Potassium Hydroxide Solution.

A. Action of Alkali on Di-l-menthyl mesoDiphenylsuccinate.—Preliminary experiments having shown that this substance is only very slowly attacked by alkali, the ester (1 gram) was heated under reflux with a solution of potassium hydroxide (11 grams), ethyl alcohol (100 c.c.), and water (20 c.c.) during eighteen hours. The progress of some change was indicated by the ultimate failure of the solution to deposit a crystalline precipitate when cooled, whereas in the earlier stages of the experiment, the slightly cooled solution readily deposited needles of unchanged *meso*-ester. The

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alcohol was removed on the water-bath, when the odour of menthol became definite but not strong. The aqueous alkaline liquid was extracted with a large volume of ether and the solvent removed. The residue was recrystallised from alcohol, and, when polarimetrically examined in ethylene dibromide solution, had $[\alpha]_D -113.4^\circ$. Since the meso-ester has $[\alpha]_D^{16.2} -67.6^\circ$ in this solvent, it is evident that the normal product must have undergone alteration, but the amount of material was too small to permit further investigation.

B. Action of Alkali on Di-l-menthyl 1-Diphenylsuccinate.—The pure *l*-ester (1 gram) was heated to boiling under reflux with aqueous ethyl-alcoholic potassium hydroxide solution (approx. 2*N*, 25 c.c.). The substance did not immediately dissolve, but, after a few minutes, a change in the nature of the undissolved portion became apparent, and, after two and a-half hours, the original precipitate seemed to have been completely replaced by a mass of very fine needles. These were filtered from the hot solution, washed with a little alcohol, and crystallised from a considerable volume of the same solvent. On cooling, silky needles (about 0.25 gram) separated from the solution, which were identified as di-*l*-menthyl mesodiphenylsuccinate. They melted at 178–179°, and the melting point was unaltered by admixture with an approximately equal quantity of the synthetic meso-ester. The specific rotation was determined in acetone solution:

$$l=2, c=1.005, \alpha_D -1.37, [\alpha]_D -68.2^\circ.$$

Synthetic di-*l*-menthyl mesodiphenylsuccinate has $[\alpha]_D^{9.4} -68.4^\circ$ for $c=1.2275$ in acetone.

C. Action of Alkali on l-Menthyl Hydrogen 1-Diphenylsuccinate.—The acid ester ($[\alpha]_D -237.3^\circ$ in acetone, 3 grams) was boiled under reflux with aqueous ethyl-alcoholic potassium hydroxide solution (0.99*N*, 30 c.c.) during four hours. The resulting solution was heated on the water-bath until the alcohol was completely removed and the odour of menthol had disappeared. Excess of hydrochloric acid was now added, and the mixture was thoroughly extracted with ether. The residue obtained from the ethereal solution, after being dried at 100°, had $[\alpha]_D -224.4^\circ$ in acetone. It was dissolved in boiling rectified spirit; the thoroughly cooled solution deposited a small crop of crystals (*A*), whilst the filtrate, when evaporated to dryness, left a glassy residue (*B*). The former, after being heated at 105°, melted at 155.5–156.5° and had $[\alpha]_D -257.5^\circ$ in acetone solution ($l=2, c=1.233, \alpha_D -6.35^\circ$), and thus consisted of nearly pure unchanged *l*-menthyl hydrogen *l*-diphenylsuccinate. The residue (*B*) was recrystallised from benzene, from which a white, apparently amorphous, precipitate

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slowly separated. It melted at 180—182°, resolidified, and again melted at 220—223°. It had $[\alpha]_D - 342.2^\circ$ in acetone solution ($l=2$, $c=0.431$, $\alpha_D - 2.95^\circ$), and thus appeared to consist of somewhat impure *l*-diphenylsuccinic acid (the pure *d*-diphenylsuccinic acid has $[\alpha]_D^{17} + 397.3^\circ$ in this solvent; Wren and Still, T., 1915, 107, 450). On titration with standard alkali, 0.0805 gram of substance was found to neutralise 5.45 c.c. of 0.0957 *N*-alkali, the quantities theoretically required for this weight of pure acid and *l*-menthyl hydrogen ester being respectively 6.23 c.c. and 2.06 c.c. The residue obtained from the benzene mother liquor melted indefinitely at 122—145°, and a homogeneous substance could not be isolated from it.

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