LXXXVIII.—*Experiments on the Synthesis of the Terpenes. Part VIII. Synthesis of the Optically Active Modifications of Δ^3 -p-Menthenol(8) and $\Delta^{3.8(9)}$ -p-Menthadiene.*

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THE terpenes and their derivatives which have so far been obtained synthetically (Trans., 1904, 85, 654; 1905, 87, 639, 655, 661, 1067, and 1083; *Proc.*, 1905, 21, 255) have always been inactive, and, while engaged in further researches on this subject, it was thought that it would be interesting to undertake a series of experiments with the object of synthesising some optically active members of this important group. Our first intention was to resolve *dl*- Δ^3 -tetrahydro-*p*-toluic acid,

into its active components by the fractional crystallisation of a suitable salt formed by combining it with some active base such as strychnine or brucine. The next step would be to treat the esters of the *d*- and *l*-acids with magnesium methyl iodide in ethereal solution, a process which should lead to a synthesis of the *d*- and *l*-modifications of terpineol and limonene,

(compare Trans., 1904, 85, 663—668). Since, however, it is extremely difficult to prepare Δ^3 -tetrahydro-*p*-toluic acid in the quantities required for a research of this kind, and it moreover appeared to us that it would be even more interesting to synthesise the optically active modifications of some terpene which had not been met with in Nature, we have, in the meantime, postponed our intention of preparing optically active terpineol synthetically, and carried out instead the following series of experiments.

Hexahydro-*p*-toluic acid was prepared in quantity from *p*-toluic acid by reduction with sodium and *iso*amylic alcohol, and converted first into α -bromohexahydro-*p*-toluic acid and then into *dl*- Δ^1 -tetrahydro-*p*-toluic acid,

by a process which has already been described (Perkin and Pickles, Trans., 1905, 87, 643—645). A series of experiments on the behaviour of this *dl*-acid towards active bases showed that, when treated with brucine, it yields a salt, *lBla*, which crystallises well and is somewhat less soluble than the salt *lBdA*.

By taking advantage of this property, and after many fractional crystallisations, we were ultimately successful in separating the *lBla* salt in a state of purity, and from this we obtained *l*-tetrahydro-*p*-toluic acid, the rotation of which was found to be $[\alpha]_D - 100.8^\circ$.

The ester of this acid has $[\alpha]_D - 83.5^\circ$, and reacts readily with an ethereal solution of magnesium methyl iodide with formation of *l*- Δ^3 -*p*-menthenol(8),

a colourless syrup which distils at 102° (14 mm.) and has a rotation of $[\alpha]_D - 67.3^\circ$. When this *l*-menthenol was digested with potassium hydrogen sulphate, it decomposed in the usual manner with elimination of water and formation of the corresponding *l*- $\Delta^{3.8(9)}$ -*p*-menthadiene,

but the rotation of the hydrocarbon obtained in this way was only $[\alpha]_D - 10.0^\circ$. This result, taken in connection with the high rotation of the corresponding *d*- $\Delta^{3.8(9)}$ -*p*-menthadiene ($+98.2^\circ$), clearly proves that optical inversion must have taken place to a considerable extent during the heating with potassium hydrogen sulphate, a change which is somewhat similar to that observed in the case of *d*-limonene, which, when strongly heated, is converted into dipentene.

During the course of our experiments on the resolution of *dl*-tetrahydro-*p*-toluic acid, we made the further fortunate discovery that the

comparative solubilities of the strychnine salts are of the reverse order to those observed in the case of the brucine salts.

It has just been stated that the *dl*-acid combines with brucine and yields a salt, *lBIA*, which is less soluble than the salt *lBdA*.

In the case of strychnine, on the other hand, it is the salt *lBdA* which is the more sparingly soluble. The difference in the solubilities of the strychnine salts was, moreover, sufficient to allow of the ultimate separation of the salt *lBdA* in a state of purity, and from this salt we obtained pure *d*- Δ^1 -*tetrahydro-p-toluic acid*.

This acid has $[\alpha]_D + 101.1^\circ$, a rotation which compares very favourably with that of the corresponding *l*-acid, for which the value -100.8° had been observed. From this pure *d*-acid, *ethyl d*- Δ^1 -*tetrahydro-p-toluate* was now prepared in the usual manner and found to have a rotation of $[\alpha]_D + 86.5^\circ$, a number slightly higher than that which had been observed in the case of the ester of the *l*-acid (-83.5°). When *ethyl d*-*tetrahydro-p-toluate* is treated with magnesium methyl iodide, it is doubtless converted, in the first instance, into *d*- Δ^3 -*p*-menthenol(8), the rotation of which, judging from that observed in the case of the *l*-modification, should be about $[\alpha]_D + 67^\circ$. Since, however, it seemed more important to obtain the *d*- $\Delta^{3.8(9)}$ -*p*-menthadiene in a pure condition, and our supply of material was limited, we decided not to attempt to prepare the *d*-menthenol in a state of purity, but to proceed at once to the preparation of the hydrocarbon.

The difficulty in obtaining the *d*-hydrocarbon from the *d*-menthenol lies in the fact, mentioned above, that when the usual procedure (digesting with potassium hydrogen sulphate) is adopted optical inversion takes place. It was therefore obvious that, if the pure *d*-hydrocarbon was to be obtained, every care would have to be taken to avoid a high temperature during the elimination of water. Fortunately, during the course of other researches of this series (compare *Trans.*, 1905, 87, 1100), the observation had been made that the menthenols are converted into the menthadienes when left in contact with an ethereal solution of magnesium methyl iodide at the ordinary temperature.

When this method was applied in the present instance to *d*- Δ^3 -*p*-menthenol(8), the result was most successful, since an almost quantitative yield of *d*- $\Delta^{3.8(9)}$ -*p*-menthadiene was obtained, which distilled at 184° and had $[\alpha]_D + 98.2^\circ$, a rotation which is approximately the same as that of *d*-limonene ($+105^\circ$).*

* This interesting result seems to indicate that magnesium methyl iodide may often prove to be a valuable agent for the elimination of water, especially in cases such as the above, where it is necessary for the operation to take place at the ordinary temperature.

EXPERIMENTAL.

*1- Δ^1 -Tetrahydro-*p*-toluic Acid.*

The resolution of *dl*-tetrahydro-*p*-toluic acid may be accomplished, as stated in the introduction to this paper, by the fractional crystallisation of the brucine, quinine, or strychnine salts. In the case of the two first mentioned, the more sparingly soluble salts are the salts of the *l*-acid; the strychnine salt which is the least soluble is, on the other hand, the salt of the *d*-acid.

I. *Experiments with Brucine*.—When equivalent quantities of brucine and *dl*-tetrahydro-*p*-toluic acid are separately dissolved in pure ethyl acetate and the solutions mixed and allowed to stand, a solid cake of brucine tetrahydro-*p*-toluate is gradually deposited, and in this the salt of the *l*-acid predominates. After many fractional crystallisations, this salt may ultimately be obtained in a pure condition.

A convenient amount of acid for one operation is 20 grams, and this is heated on the water-bath with brucine (70 grams) and pure ethyl acetate (500 c.c.) until solution is complete. The liquid is then set aside until crystallisation is complete, which is usually the case in two to three days, care being taken that the solvent does not evaporate during the crystallisation. The mother liquor is decanted and the pale yellow crystals washed with ethyl acetate, the crude salt is then systematically recrystallised from the same solvent until the acid has a constant rotation. As the separation proceeds, the salt loses its original sticky nature, and, especially during the later stages, crystallisation, which at first is always slow, takes place rapidly. Each crop of crystals was tested in the following manner. About one gram was ground to a fine paste with water, warmed on the water-bath with excess of sodium carbonate, and the precipitated base filtered off. The acid obtained by acidifying the filtrate was recrystallised from dilute acetic acid and its rotation determined in ethyl acetate solution in the usual manner. This rather tedious procedure had to be adopted because measurements of the brucine salt itself were not found to be sufficiently reliable.

The following are the rotations of three of the last crystallisations, the acid, in each case, being dissolved in ethyl acetate (20 c.c.) at a temperature of 17° and the measurement made in a 100 mm. tube.

Crop 17.	0.4004	gave a rotation of	-2.02°.	$[\alpha]_D$	-100°
Crop 18.	0.3844	„ „ „	-1.92°.	„	-99.9°
Crop 20.	0.3951	„ „ „	-2.00°.	„	-100.8°

In the hope of shortening the process of separation, experiments were next carried out on the fractional crystallisation of

the brucine salts from water, instead of from ethyl acetate, but, although the salts separated readily, the number of crystallisations necessary before the *l*-acid was obtained pure was about the same as when ethyl acetate was employed as the solvent.

Ultimately, however, by employing a method recommended by Pope and Peachey (Trans., 1899, 75, 1066), we obtained a much more satisfactory result and were able to prepare the *l*-acid in sufficient quantity for our subsequent synthetical experiments. This important method of separation depends, as its authors state, on the following considerations. The solubilities of the salts (*lBdA* and *lBIA*) of a laevorotatory base (*lB*) with a dextro- and a laevo-acid (*dA* and *lA*) would hardly be expected to differ considerably, because the solubility is partly a function of the chemical nature of the salts.

If, however, the salt *lBIA* is the less soluble, and only sufficient of the active base *lB* necessary for the formation of this salt is added, the balance of base required to dissolve the acid being made up by adding the requisite amount of an optically inactive base, such as caustic soda or ammonia, which forms comparatively soluble salts with the acid, it would be expected that on crystallisation the greater part of the laevo-acid would separate as the sparingly soluble salt, *lBIA*, whilst the mother liquors would retain the very soluble sodium or ammonium salts of the dextro-acid, *dA*.

In applying this method, *dl*- Δ^1 -tetrahydro-*p*-toluic acid (14 grams) was exactly neutralised with sodium carbonate and diluted to one litre with boiling water, a boiling concentrated alcoholic solution of brucine (60 grams) and *dl*-acid (14 grams) was slowly poured in, and the liquid boiled until practically all the alcohol had been removed. The solution was then allowed to cool slowly, when a mass of beautiful dagger-shaped crystals rapidly separated and were collected at the pump and washed with a little water. The filtrate and washings were concentrated and precipitated by hydrochloric acid, the acid being collected and again treated with sodium carbonate and brucine exactly as before. The brucine salt was then divided into two equal parts, one of which was ground to an exceedingly fine paste with water and then warmed with an excess of sodium carbonate. The filtrate from the precipitated base was heated to boiling and the excess of alkali exactly neutralised by the cautious addition of dilute hydrochloric acid. The second half of the brucine salt, dissolved in the minimum quantity of boiling alcohol, was then mixed with the aqueous sodium salt and the liquid allowed to stand until crystallisation was complete. After this operation had been repeated five times, the brucine salt of the *l*-acid was obtained quite pure and yielded an acid with a rotation of $[\alpha]_D - 100.8^\circ$.

The acid present as sodium salt in the mother liquors from each

crystallisation was worked up systematically by the same process, and ultimately more than 25 per cent. of the original *dl*-acid was obtained in the form of the pure *l*-acid.

II. *Experiments with Quinine*.—The experiments just described show that when the laevorotatory base brucine is combined with *dl*-tetrahydro-*p*-toluic acid, the more sparingly soluble salt formed is the salt *lBIA*. It seemed possible that quinine (*dB*), under similar conditions, might yield a salt with the *d*-acid which was less soluble than the corresponding salt of the *l*-acid, and that, in this way, a separation of the pure *d*-acid might prove to be possible. The following experiment showed, however, that the reverse is the case and that the more sparingly soluble quinine salt is the salt *dBIA*.

Quinine (19 grams) was dissolved in alcohol and digested with 14 grams of impure lævo-acid ($[\alpha]_D - 9^\circ$) until solution was complete. A further 14 grams of the same specimen of acid (exactly neutralised with carbonate of soda and dissolved in the minimum amount of water) was added, when a precipitate was produced which was dissolved by the addition of small quantities of alcohol. The copious crystalline precipitate which separated on standing was collected at the pump, washed with water, and decomposed by sodium carbonate, with the result that an acid was obtained which had a rotation of $[\alpha]_D - 20.9^\circ$. This process was not continued as it had no advantages over the separation by means of brucine. In our subsequent experiments on the behaviour of *dl*-tetrahydro-*p*-toluic acid towards optically active bases we made the observation that the strychnine salt of the *d*-acid is less soluble than that of the *l*-acid, and this led to a process of separation of the pure *d*-acid which is described on p. 845.

l- Δ^1 -Tetrahydro-*p*-toluic acid melts at $133\text{--}134^\circ$, or at exactly the same temperature as the *dl*-acid, a fact which seems to indicate that the latter is a racemic modification and not merely a mixture of the *d*- and *l*-components. An analysis of a sample of the *l*-acid which had a rotation of $[\alpha]_D - 100.1^\circ$ gave the following results :

0.3050 gave 0.7700 CO_2 and 0.2394 H_2O . $\text{C} = 68.8$; $\text{H} = 8.8$.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires $\text{C} = 68.6$; $\text{H} = 8.8$ per cent.

This acid separates from dilute acetic acid in slender, prismatic needles and is obtained in large, transparent prisms when its solution in ethyl acetate is allowed to evaporate slowly under ordinary conditions. It dissolves freely in acetic acid, ethyl acetate, or light petroleum, less readily in chloroform, and is rather sparingly soluble in cold alcohol.

Ethyl l- Δ^1 -Tetrahydro-*p*-toluate.—In the preparation of this ester and also of the corresponding ester of the *d*-acid (p. 847), the use of hydrogen chloride was avoided and every care was taken to prevent

any optical inversion by keeping the temperature as low as possible. *l*-Tetrahydro-*p*-toluic acid (15 grams) was dissolved in boiling absolute alcohol (100 c.c.) and the solution cooled quickly under the tap in order that the acid might separate in as finely divided a state as possible. A mixture of concentrated sulphuric acid (10 c.c.) and alcohol (20 c.c.) was gradually added, any rise in temperature being checked by immersing the flask in cold water. The mixture was then set aside and shaken from time to time, when, after five days, all the acid was found to have passed into solution and esterification was practically complete. The oily ester, which separated on the addition of water, was extracted with ether, the ethereal solution washed well with water and dilute sodium carbonate, dried over calcium chloride, and evaporated. The residual oil distilled at 154° (100 mm.) and had $[\alpha]_D - 83.5^\circ$ in a 100 mm. tube at 18°.

d- Δ^1 -Tetrahydro-*p*-toluic Acid.

When equivalent quantities of strychnine and *dl*-tetrahydro-*p*-toluic acid are digested in ethyl acetate solution, only a portion of the acid combines with the base, and the crystalline deposit which separates contains an excess of the salt of the *d*-acid.

dl-Tetrahydro-*p*-toluic acid (14 grams) and finely-divided strychnine (35 grams) were boiled together with one litre of ethyl acetate in a reflux apparatus for one hour. The hot solution was then filtered at the pump and set aside for two or three days and until crystallisation was complete. The crystalline mass, which consisted of large, transparent, rhomboid plates, was collected at the pump, washed with ethyl acetate, and the filtrate and washings were used to extract the strychnine and salt which had remained undissolved in the first instance. By repeating this operation several times, a considerable additional quantity of the sparingly soluble salt was obtained.

The crops of crystals were combined and recrystallised twice from ethyl acetate, a little chloroform being added to assist solution.

The acid, separated in the usual manner, had a rotation of $[\alpha]_D + 55.9^\circ$. The acetic ester mother liquors were concentrated and allowed to crystallise, when long needles separated, which were found to consist of the free *laevo*-acid with a rotation of $[\alpha]_D - 32^\circ$. Attempts to purify the crude *d*-salt by further recrystallisation did not lead to a satisfactory result, owing to the ease with which the salt dissociates* in solution, and this method of purification had therefore to be abandoned.

After many unsuccessful experiments, however, we were ultimately able, by employing a slight modification of the method of Pope and

* It seems remarkable that the strychnine salts of the *d*- and *l*-tetrahydro-*p*-toluic acids should dissociate so much more readily than the corresponding brucine salts.

Peachey (compare p. 843), to separate the strychnine salt of the *d*-acid in a state of purity.

The separation could, however, not be carried out in aqueous solution owing to the insolubility of the strychnine salt in water, and, as the sodium salt of the acid is very sparingly soluble in organic solvents, the method of half neutralisation with sodium carbonate could not be employed. When, however, the *dl*-acid and strychnine, in the proportion of two molecules of the former to one of the latter, were dissolved in chloroform and ethyl acetate, dissociation was largely prevented by the presence of the excess of the acid, and thus a satisfactory separation became possible.

Strychnine (35 grams), dissolved in the least possible quantity of chloroform (1 vol.), was mixed with a hot solution of the *dl*-acid (28 grams) in acetic ester (4 vols.), and the solvent distilled off until minute crystals began to form. After standing until crystallisation was complete, the salt was collected at the pump and washed once with ethyl acetate. The mother liquors were then treated with half the previous quantity of strychnine, and this operation repeated until no further separation of the crude salt of the *d*-acid took place.

The various crops of crystals of this salt were combined, divided into two equal parts, one of which was converted into the acid by treatment with sodium carbonate in the usual way; the second half and the free acid were then mixed and crystallised from chloroform and acetic ester as before. After repeating this separation five or six times, the strychnine salt of the *d*-acid was obtained pure.

If all the mother liquors are carefully collected and systematically treated with strychnine in the way just described, the yield of this salt is at least equal to that of the brucine salt of the *l*-acid obtained as described on p. 844.

Strychnine d-Δ¹-tetrahydro-p-toluate crystallises readily from acetic ester, in which it is sparingly soluble, in colourless, transparent, glistening plates frequently half a centimetre in length.

It dissolves sparingly in alcohol, but very readily in chloroform, and separates from the latter solvent in aggregates of large, transparent, hexagonal tablets. This salt shows a marked tendency to dissociate, especially when its solutions are boiled for a considerable time.

d-Δ¹-Tetrahydro-p-toluic acid was readily obtained by decomposing the pure strychnine salt with sodium carbonate and then recrystallising from dilute acetic acid.

0.2201 gave 0.5561 CO₂ and 0.1757 H₂O. C = 68.9; H = 8.9.

C₈H₁₂O₂ requires C = 68.6; H = 8.8 per cent.

In order to determine the rotation as accurately as possible, two

different specimens of the acid were prepared and examined in the usual manner, with the result that the values $[\alpha]_D + 101.1^\circ$ and $+100.9^\circ$ were obtained in the two cases. It will thus be seen that the rotation of this *d*-acid compares well with that of the corresponding *l*-acid, for which the value $[\alpha]_D - 100.8^\circ$ was obtained (p. 842).

The other physical properties of the *d*-acid are identical with those of the *l*-acid. It melts at 133° , and when it is mixed with an equal quantity of the *l*-acid (m. p. $133-134^\circ$) the mixture melts lower, namely, at about 129° . This seems to confirm the suggestion (p. 844) that the original *dl*-acid from which the active acids had been prepared is the racemic modification.

Ethyl d-Δ¹-Tetrahydro-p-toluate.—This ester, which was prepared in exactly the same manner as the corresponding ester of the *l*-acid (p. 844), distilled at 154° (100 mm.) and had $[\alpha]_D + 86.5^\circ$, a value which is rather higher than that observed in the case of the ester of the *l*-acid (-83.5°).

l-Δ³-p-Menthenol(8) and l-Δ^{3.8(9)}-p-Menthadiene.

The preparation of *l-Δ³-p-menthenol* was conducted under the following conditions. Magnesium (7.5 grams) was covered with dry ether (250 c.c.) and converted into magnesium methyl iodide in the usual manner. The solution was cooled in ice-water and gradually poured into ethyl *l-Δ¹-tetrahydro-p-toluate* (16 grams) diluted with ether (100 c.c.), any rise of temperature being carefully avoided. After remaining for twenty-four hours, the product was decomposed by water and dilute hydrochloric acid, the ethereal solution washed with a little sodium hydrogen sulphite to remove some iodine, and evaporated. The oil was then freed from any unchanged ester by digesting for half an hour with methyl-alcoholic potash (5 grams KOH), again extracted with ether, and, after washing well and drying over calcium chloride, the ether was evaporated and the residue fractionated under reduced pressure.

0.1091 gave 0.3130 CO_2 and 0.1144 H_2O . $\text{C} = 78.3$; $\text{H} = 11.7$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C} = 77.9$; $\text{H} = 11.7$ per cent.

l-Δ³-p-Menthenol(8) distils at $101-102^\circ$ (14 mm.) and was obtained as a thick, colourless syrup which would doubtless have solidified had a crystal been available with which to start the crystallisation.*

It has a penetrating but pleasant odour which somewhat resembles

* Unfortunately the whole of this menthenol had been used up in preparing *l-Δ^{3.8(9)}-p-menthadiene* before we succeeded in obtaining *dl-Δ³-p-menthenol(8)* in a crystalline form (p. 851).

that of terpineol, and its other properties are similar to those of *dl*- Δ^3 -*p*-menthenol(8), which had previously been prepared by Perkin and Pickles (Trans., 1905, 87, 647; compare also the present paper, p. 851).

Its rotation, determined in benzene solution in a 100 mm. tube at 18°, was found to be $[\alpha]_D - 67.3^\circ$.

The whole of the *l*-menthenol was next heated to boiling with twice its weight of powdered potassium hydrogen sulphate in a reflux apparatus heated by means of an oil-bath. The product was then mixed with water, distilled in steam, the distillate extracted with ether, and, after drying over calcium chloride, the ether was evaporated and the hydrocarbon fractionated. Almost the whole quantity passed over at 175—185°, and after twice distilling over sodium an oil was obtained which boiled constantly at 182—183° (748 mm.) and had an odour resembling that of dipentene.

0.2353 gave 0.7610 CO₂ and 0.2497 H₂O. C = 88.1; H = 11.8.

C₁₀H₁₆ requires C = 88.2; H = 11.8 per cent.

When this hydrocarbon (0.6111 gram), diluted with benzene (20 c.c.), was examined at 18°, it was found to have a rotation of only -0.31° , or $[\alpha]_D - 10.0^\circ$. Since, however, the rotation of *d*- $\Delta^{3.8(9)}$ -*p*-menthadiene (see below) is $+98.2^\circ$, it is clear that the value observed for the above menthadiene from *l*- Δ^3 -*p*-menthenol(8) is much too low, and that optical inversion must have taken place to a considerable extent during the preparation under the conditions described above.

Conversion of Ethyl d- Δ^1 -Tetrahydro-*p*-toluate into *d*- $\Delta^{3.8(9)}$ -*p*-Menthadiene.

It has just been shown that boiling with potassium hydrogen sulphate had the effect of partially inverting *l*- $\Delta^{3.8(9)}$ -*p*-menthadiene, and since it seemed probable that the high temperature employed had contributed largely to this result, we were careful to avoid this in the present case by using as the dehydrating agent an excess of magnesium methyl iodide at the ordinary temperature.

A solution of magnesium methyl iodide, prepared from magnesium (9 grams), was gradually poured into ethyl *d*- Δ^1 -tetrahydro-*p*-toluate (21 grams), and, after remaining for a couple of days, the product was decomposed by dilute hydrochloric acid in the usual manner. After removing any traces of unchanged ester which might be present by hydrolysis with methyl-alcoholic potash, the oil was extracted and distilled under reduced pressure, when most of it passed over at 80° (15 mm.). There was, however, a higher fraction which without doubt consisted of *d*- Δ^3 -*p*-menthenol(8), but the quantity was small and it was not further examined.

The oil of lower boiling point was distilled at the ordinary pressure and the fraction 178—187° digested twice with sodium and again distilled.

0.1973 gave 0.6343 CO₂ and 0.2110 H₂O. C = 87.9; H = 11.9.

C₁₀H₁₆ requires C = 88.2; H = 11.8 per cent.

d-Δ^{3.8(9)}-p-Menthadiene boils at 184° (756 mm.) and has an odour closely resembling that of d-limonene. When examined in benzene solution at 18° in a 100 mm. tube, it had a rotation of $[\alpha]_D + 98.2^\circ$.

Densities, Magnetic Rotations, and Refractive Powers of d-Δ^{3.8(9)}-p-Menthadiene, Ethyl dl-Δ¹-Tetrahydro-p-toluate, dl-Δ³-p-Menthenol(8), dl-Δ^{3.8(9)}-p-Menthadiene, Terpeneol, and Dipentene.

In the present communication, as well as during the course of some of the other researches of this series, terpenes and their derivatives have been described which, so far, have not been met with in Nature. Prof. H. E. Armstrong and others interested in this matter were good enough to suggest to us that valuable results might be expected if it were found possible to prepare some of these new substances in sufficient quantity to allow of their physical properties being carefully examined.

In the first instance, we prepared a very pure specimen of d-Δ^{3.8(9)}-p-menthadiene and sent it to Dr. W. H. Perkin, sen., for examination, but as the results obtained were found to be quite abnormal it was thought necessary, for the sake of comparison, to prepare very pure specimens of the other substances mentioned at the head of this section and examine them. The determination of the whole of the physical constants which are given below was undertaken by Dr. W. H. Perkin, sen., and this laborious investigation has added greatly to the value of the present research.

d-Δ^{3.8(9)}-p-Menthadiene.

This hydrocarbon was prepared by the process described on p. 848, and the analysis there given was carried out with the specimen used in the determination of the following physical constants.

Density: $d_{4^\circ/4^\circ} = 0.8712$; $d_{15^\circ/15^\circ} = 0.8634$; $d_{25^\circ/25^\circ} = 0.8574$.

Magnetic rotation :

<i>t</i> .	Sp. rot.	Mol. rot.
13.6°	1.4941	13.061

Refractive power :

$$t = 12.7^\circ; d_{12.7^\circ/4^\circ} = 0.86483.$$

	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1.49434	0.57161	77.739
β	1.50913	0.58871	80.064
γ	1.51849	0.59953	81.536

Dispersion $\gamma - \alpha = 3.797$.

dl- $\Delta^{3,8(9)}$ -p-Menthadiene.

The specimen of this hydrocarbon employed in the following determinations was prepared from crystalline *dl- Δ^3 -p-menthenol*(8) (see p. 851) by digesting with potassium hydrogen sulphate. It was twice distilled over sodium and boiled constantly at 184—185°.

Density: $d_{10}^{10}/10^\circ = 0.8425$; $d_{15}^{15}/15^\circ = 0.8390$; $d_{20}^{20}/20^\circ = 0.83579$.

Magnetic rotation :

t .	Sp. rot.	Mol. rot.
16.2°	1.4356	12.939

Refractive power :

$$t = 17.2^\circ; d_{17.2}^{17.2}/4^\circ = 0.83659.$$

	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1.46945	0.56114	76.315
β	1.48113	0.57510	78.213
γ	1.48824	0.58360	79.369

Dispersion $\gamma - \alpha = 3.054$.

Dipentene.

This hydrocarbon was prepared from terpineol (from Schimmel) and distilled twice over sodium in an atmosphere of carbon dioxide. It boiled constantly at 180—181°.

Density: $d_4^{4^\circ}/4^\circ = 0.8627$; $d_{15}^{15}/15^\circ = 0.8548$; $d_{25}^{25}/25^\circ = 0.8486$.

Magnetic rotation :

t .	Sp. rot.	Mol. rot.
15.7°	1.2796	11.315

Refractive power :

$$t = 14.4^\circ; d_{14.4}^{14.4}/4^\circ = 0.85457.$$

	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1.47506	0.55590	75.602
β	1.48629	0.56905	77.391
γ	1.49367	0.57768	78.564

Dispersion $\gamma - \alpha = 2.962$.

Terpineol.

The specimen examined was prepared by distilling terpeneol (from Schimmel) under reduced pressure. It melted at 35° and boiled at 120—122° (25 mm.).

Density: (surfused) $d_{10^{\circ}}/10^{\circ} = 0.9448$; $d_{15^{\circ}}/15^{\circ} = 0.9415$; $d_{25^{\circ}}/25^{\circ} = 0.9355$.

(Fused) $d_{40^{\circ}}/40^{\circ} = 0.9282$; $d_{45^{\circ}}/45^{\circ} = 0.9256$.

Magnetic rotation :

<i>t</i> .	Sp. rot.	Mol. rot.
16°	1.1923	10.841
50.5	1.1676	10.823

Refractive power : (a) surfused.

$t = 18.4^{\circ}$; $d_{18.4^{\circ}}/4^{\circ} = 0.93831$.

	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1.48064	0.51224	78.885
β	1.49028	0.52251	80.466
γ	1.49627	0.52890	81.450

Dispersion $\gamma - \alpha = 2.565$.

(b) Fused.

$t = 43.75^{\circ}$; $d_{43.75^{\circ}}/4^{\circ} = 0.91770$.

	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1.47018	0.51234	78.900
β	1.47966	0.52267	80.491
γ	1.48527	0.52879	81.433

Dispersion $\gamma - \alpha = 2.533$.

dl- Δ^3 -p-Menthenol(8).

This substance was prepared by the action of magnesium methyl iodide on ethyl *dl*- Δ^1 -tetrahydro-*p*-toluate. When first obtained (Perkin and Pickles, *Trans.*, 1905, **87**, 650), it was described as a syrup, but the specimen prepared on the present occasion solidified during the winter months to a hard, crystalline mass which closely resembled terpeneol in appearance.* It melted at 38—40° and distilled at 102° (14 mm.).

* Attention has already been directed (*Trans.*, 1905, **87**, 1100, footnote) to the difficulty experienced in obtaining the viscid menthenols in a crystalline condition. This was well instanced in the case of the pure specimens of terpeneol and

Density: (surfused) $d_{10^{\circ}/10^{\circ}} = 0.9251$; $d_{15^{\circ}/15^{\circ}} = 0.9217$; $d_{25^{\circ}/25^{\circ}} = 0.9158$; (fused) $d_{40^{\circ}/40^{\circ}} = 0.9080$; $d_{45^{\circ}/45^{\circ}} = 0.9055$.

Magnetic rotation:

t .	Sp. rot.	Mol. rot.
16.4°	1.2002	11.150
50.5	1.1700	11.085

Refractive power: (a) surfused.

$$t = 16.3^{\circ}; d_{16.3^{\circ}/4^{\circ}} = 0.9200.$$

	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1.47545	0.51679	79.585
β	1.48522	0.52741	81.221
γ	1.49105	0.53375	82.197

Dispersion $\gamma - \alpha = 2.612$.

(b) Fused.

$$t = 43.4^{\circ}; d_{43.4^{\circ}/4^{\circ}} = 0.90131.$$

	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1.46341	0.51415	79.179
β	1.47329	0.52511	80.867
γ	1.47897	0.53142	81.838

Dispersion $\gamma - \alpha = 2.659$.

Ethyl dl- Δ^1 -Tetrahydro-p-toluate.

This ester was prepared from pure *dl- Δ^1 -tetrahydro-p-toluic acid* by means of alcohol and sulphuric acid. It distilled at $152-153^{\circ}$ under 100 mm. pressure.

Density: $d_{4^{\circ}/4^{\circ}} = 0.9877$; $d_{15^{\circ}/15^{\circ}} = 0.9792$; $d_{25^{\circ}/25^{\circ}} = 0.9726$.

Magnetic rotation:

t .	Sp. rot.	Mol. rot.
16.3°	1.1576	11.043

Refractive power:

$$t = 15.3^{\circ}; d_{15.3^{\circ}/4^{\circ}} = 0.97813.$$

	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1.46539	0.47580	79.935
β	1.47604	0.48668	81.762
γ	1.48259	0.49338	82.887

dl- Δ^3 -p-menthenol(8) described in the present communication. During the investigation of their physical properties, the specimens were fused and subsequently sent by post, in cold weather, from Sudbury to Manchester without again solidifying. They remained in this condition for several days, and it was not until a crystal of each had been introduced that crystallisation took place.

In discussing the above results it will be convenient to consider, in the first instance, the effect which slight differences in constitution have on the densities of the substances examined. In the case of terpineol (Δ^1 -*p*-menthenol(8)) and *dl*- Δ^3 -*p*-menthenol(8),

we have the following numbers for comparison :

Terpineol	$d_{15^\circ}/15^\circ = 0.9415$	} Difference.
<i>dl</i> - Δ^3 - <i>p</i> -Menthenol(8)	$d_{15^\circ}/15^\circ = 0.9217$	
		+ 0.0198

It is therefore evident that the change of the double-linking from the Δ^1 - to the Δ^3 -position has, in the case of these substances, only brought about a slight difference in the density.

Turning next to the hydrocarbons, dipentene (*dl*- $\Delta^{1.8(9)}$ -*p*-menthadiene) and *dl*- $\Delta^{3.8(9)}$ -*p*-menthadiene,

we obtain the following comparison :

Dipentene	$d_{15^\circ}/15^\circ = 0.8548$	} Difference.
<i>dl</i> - $\Delta^{3.8(9)}$ - <i>p</i> -Menthadiene	$d_{15^\circ}/15^\circ = 0.8390$	
		+ 0.0158

Here again the change of density, due to the alteration of the position of the double linking in the ring, is very small, a fact which is interesting when taken in connection with the great difference observed in the magnetic rotation values of these two hydrocarbons. The difference in density is, in fact, less than that between the *dl*- and *d*-modifications of $\Delta^{3.8(9)}$ -*p*-menthadiene :

<i>dl</i> - $\Delta^{3.8(9)}$ - <i>p</i> -Menthadiene	$d_{15^\circ}/15^\circ = 0.8390$	} Difference.
<i>d</i> - " " " "	$d_{15^\circ}/15^\circ = 0.8634$	
		- 0.0244

When these last figures are compared with the corresponding values in the limonene series :

Dipentene	$d_{15^\circ}/15^\circ = 0.8548$	} Difference.
<i>d</i> -Limonene*	$d_{15^\circ}/15^\circ = 0.8498$	
		+ 0.005

it is seen that the difference between the two sets of externally compensated and dextro-modifications is not only considerably larger in the former than in the latter, but also that in the first pair the *d*-modification has the higher density, whereas the reverse is the case in the limonene series.

* Trans., 1902, **81**, 315.

Taking next into consideration the magnetic rotation values of the menthenols, the following numbers are available for comparison :

Terpineol	10·841	} Difference.
<i>dl</i> - Δ^3 - <i>p</i> -Menthenol(8)	11·150	
		- 0·309

In other words, the change of the double linking from the Δ^1 - to the Δ^3 -position has had a distinct but relatively small influence on the magnetic rotation of these substances. It is in the magnetic rotations of the hydrocarbons derived from these menthenols that the most striking differences are to be observed. This was first noticed during a comparison of the values obtained for the magnetic rotations of *d*- $\Delta^{3.8(9)}$ -*p*-menthadiene and *d*-limonene (*d*- $\Delta^{1.8(9)}$ -*p*-menthadiene) :

<i>d</i> - $\Delta^{3.8(9)}$ - <i>p</i> -Menthadiene.....	12·939	} Difference.
<i>d</i> -Limonene*.....	11·246	
		+ 1·693

This great difference between the values of two hydrocarbons so closely related is one of the most remarkable observations which has been made during the investigation of the magnetic rotations of organic substances. In order to be certain that this difference was not due to some experimental error, it was thought advisable to prepare pure specimens of dipentene and *dl*- $\Delta^{3.8(9)}$ -*p*-menthadiene and examine their rotations and also to investigate the physical constants of ethyl *dl*- Δ^1 -tetrahydro-*p*-toluate, from which the latter hydrocarbon is derived. The values found for the inactive hydrocarbons are the following :

<i>dl</i> - $\Delta^{3.8(9)}$ - <i>p</i> -Menthadiene.....	12·939	} Difference.
Dipentene†	11·315	
		+ 1·624

This comparison shows that the difference between the rotations of the inactive hydrocarbons is again abnormal and practically the same as that observed in the case of the active modifications. There can therefore be no doubt that this remarkable difference [which is larger than would be required for the introduction of two additional double

* The magnetic rotation of *L*-limonene is 11·162 (Trans., 1902, **81**, 315).

† It may be readily shown that the rotation of dipentene is normal, that is to say, that the value actually observed agrees with that which would be expected as the magnetic rotation of a tetrahydrocymene. The difference between the rotation of benzene (11·284) and hexahydrobenzene (5·664) is 5·620, a number which may be taken as generally representing the effect produced when a benzene hydrocarbon is converted into its hexahydro-derivative.

The magnetic rotation of hexahydrocymene, deduced from that of cymene (15·255) by subtracting the value 5·620, is therefore 9·635.

If to this be added the effect of introducing two double linkings ($2 \times 0·720$; compare Trans., 1902, **81**, 300), the calculated rotation of a tetrahydrocymene will be approximately 11·075, a number which agrees well with that actually found in the case of dipentene (11·246).

linkings (2×0.720) into the molecule] is not due to experimental error, and the question naturally arises, what explanation can be offered to account for a difference of this magnitude? It was pointed out on p. 853 that, except in respect of the position of the double linking in the ring, the hydrocarbons $\Delta^{3.8(9)}$ -*p*-menthadiene and dipentene are exactly similarly constituted, therefore any variation in properties can only be due to a difference in the position of this double linking. Previous researches have, however, shown that the mere alteration of the position of a double linking does not bring about any great change in magnetic rotation.

This fact is well seen from a comparison of the values of *dl*- Δ^3 -*p*-menthenol(8) and terpineol (see p. 854), the difference being only 0.309. But this small difference is due to precisely the same change in the position of the double linking as the great difference (1.624) between the values of $\Delta^{3(9)}$ -*p*-menthadiene and dipentene. Since, then, mere change of the position of the double linking is not sufficient to account for the remarkable alteration in magnetic rotation, the reason must, apparently, be sought in the relative positions of the double linkings.

It has already been pointed out (Perkin, Pickles, and Tattersall, *Trans.*, 1905, **87**, 641; compare also 1077 and 1101) that dipentene and $\Delta^{3.8(9)}$ -*p*-menthadiene,

while very similar in most of their properties, exhibit a remarkable difference in their behaviour towards bromine, hydrogen bromide, and hydrogen chloride.

Dipentene, as is well known, combines with *two* molecules of bromine or of hydrogen bromide or chloride to yield the derivatives $\text{C}_{10}\text{H}_{16}\text{Br}_4$, $\text{C}_{10}\text{H}_{16}2\text{HBr}$, or $\text{C}_{10}\text{H}_{16}2\text{HCl}$. $\Delta^{3.8(9)}$ -*p*-Menthadiene, on the other hand, is only capable of combining with *one* molecule of bromine, hydrogen bromide, &c., and when the compounds $\text{C}_{10}\text{H}_{16}\text{Br}_2$ and $\text{C}_{10}\text{H}_{16}\text{HBr}$ have been produced the additive capacity of the hydrocarbon is exhausted. This striking difference in behaviour was attributed to the fact that the formula of $\Delta^{3.8(9)}$ -*p*-menthadiene has two double linkings in the position $-\text{C}:\text{C}:\text{C}:\text{C}-$, whilst the formula of dipentene does not contain this grouping. It is well known that substances containing the above conjugated system of double linkings have unusual properties and are only capable of uniting with one molecule of bromine (or HBr or HCl) to form derivatives in which this grouping becomes $-\text{CBr}:\text{C}:\text{C}:\text{CBr}-$. It seems clear that the remarkably high value for the magnetic rotation of $\Delta^{3.8(9)}$ -*p*-menthadiene must also be ascribed to the presence of this grouping. Future investiga-

tion will probably show that other terpenes of similar constitution will yield magnetic rotations higher by about 1.63 than those of hydrocarbons which, whilst in other respects similarly constituted, do not contain this conjugated grouping.

It is rather curious that no correspondingly great difference should have been observed between the permanent rotations of $d\text{-}\Delta^{3.8(9)}\text{-}p\text{-menthadiene}$ and $d\text{-limonene}$, and that the values actually observed should be so nearly the same. Again, it is interesting to note that the comparison of the refractive powers of the $dl\text{-hydrocarbons}$:

	$\frac{\mu-1}{d}p.$	
$dl\text{-}\Delta^{3.8(9)}\text{-}p\text{-Menthadiene}$	76.315	} Difference. + 0.713
Dipentene	75.602	

exhibits only a very small and not unusual difference, which cannot, of course, be compared with that observed in the case of the magnetic rotations.

For reasons stated on p. 849, the physical constants of ethyl $\Delta^1\text{-tetrahydro-}p\text{-toluate}$ were included in this investigation.

The numbers obtained (p. 852) are quite normal and do not call for special comment.

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