CVIII.—*The Application of Powerful Optically Active Acids to the Resolution of Externally Compensated Basic Substances. Resolution of Tetrahydroquin-aldine.*

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IN the present communication, we describe the separation of compensated tetrahydroquinaldine into its optically active components by means of Reychler's dextrocamphorsulphonic acid ; we have previously discussed the reasons for using this acid in preference to tartaric acid (Trans., 1898, **73**, 893). The new method adopted, which is a generally applicable one, is based upon the following considerations.

The solubilities of the salts $(dB\ dA$ and $lB\ dA)$ of a dextrorotatory acid $(dA)$ with a dextro- and a lævo-base $(dB$ and $lB)$ 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, $lB\ dA$, is the less soluble and only sufficient of the active acid, $dA$, necessary to the formation of this salt is added, the balance of acid required to dissolve the base being made up by adding the requisite amount of an optically inactive acid, such as hydrochloric acid, which forms com-

paratively soluble salts with the base, it would be expected that on crystallisation the greater part of the lævo-base would separate as the sparingly soluble salt, $lB\ dA$, whilst the mother liquors would retain the dextro-base of which the hydrochloride, $dB$ HCl, is very soluble. The disadvantage of the ordinary method of separating externally compensated bases by crystallisation with excess of tartaric acid lies very largely in the fact that the solubilities of the two salts, $dB\ dA$ and $lB\ dA$, are not sufficiently different to permit of the pure salts being easily isolated by fractional crystallisation ; this is illustrated by Ladenburg's observation (*Ber.*, 1894, **27**, 77) that the crude dextro-tetrahydroquinaldine dextrobitartrate obtained from the inactive base must be recrystallised many times before it is obtained pure. By applying our method to this base (using one molecular proportion each of dextro-α-bromocamphorsulphonic acid and of hydrochloric acid for the dissolution of two molecular proportions of externally compensated base) and crystallising the first separation twice from alcohol to remove mechanically retained impurities, a pure sample of lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate is obtained.

Although the separation was best effected in this way, instructive results were obtained by modifying the method of applying the principle above explained.

Thus, hot aqueous solutions of one molecular proportion of ammonium dextro-α-bromocamphorsulphonate and of two molecular proportions of racemic tetrahydroquinaldine hydrochloride were mixed and the liquid allowed to cool ; a large separation of lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate was thus obtained in a practically pure condition, this being the least soluble salt which could be formed.

A further great advantage of making use of the formation of a sparingly soluble salt of a strong acid in the resolution of externally compensated bases is found in the fact that such sparingly soluble salts are not decomposed by feeble acids. Thus, a fairly serviceable method of obtaining lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate consists in adding an aqueous solution of one molecular proportion of ammonium dextro-α-bromocamphorsulphonate to an acetic acid solution of two molecular proportions of the externally compensated base ; the solution soon affords a copious deposit of crystals of lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate.

### I. Lævotetrahydroquinaldine.

*Lævotetrahydroquinaldine Dextro-α-bromocamphorsulphonate,*
$$C_{10}H_{13}N, C_{10}H_{14}BrO \cdot SO_3H.$$

The most convenient method of preparing lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate consists in mixing a hot con-

centrated solution of one molecular proportion of crude externally compensated tetrahydroquinaldine hydrochloride with a hot concentrated solution of one molecular proportion of the base in one molecular proportion of a concentrated dextro-α-bromocamphorsulphonic acid solution prepared as we have previously described (Trans., 1898, **75**, 895). By the time the solution has cooled to the ordinary temperature, the greater part of the salt of the lævo-base has crystallised ; the separation is filtered off, washed with dilute alcohol, and recrystallised from boiling absolute alcohol. After two recrystallisations, the substance is obtained as a mass of colourless needles melting at 223—225°. It is sparingly soluble in cold, and moderately so in hot alcohol or water ; it is more soluble in glacial acetic acid, but nearly insoluble in acetone or ethylic acetate.
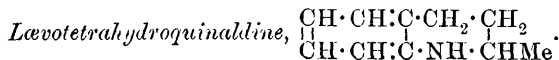
The crystals deposited as the hot alcoholic solution cools are long, flattened needles with obliquely placed end faces ; the extinction in the large flat face is straight with the sides, and through this face the bisectrix of a large optic axial angle emerges nearly normally. The double refraction is negative in sign and the optic axial dispersion is marked, the optic axial angle for red light being greater than that for blue ; the optic axial plane is parallel to the long edges of the crystals. No goniometrical measurements could be obtained. After melting the salt on a microscope slide under a cover slip and subsequently cooling quickly, it remains amorphous, and signs of crystallisation only appear at the edges of the preparation after several days preservation at the ordinary temperature. By alternately cooling and heating the liquid film several times, crystallisation may be started, and once started proceeds rapidly at temperatures not much below the melting point ; at the ordinary temperature, however, the crystallisation proceeds with extreme slowness even after it has been started at a higher temperature. The crystalline film thus obtained consists of a radiate mass of long needles which crack across the direction of growth as cooling proceeds ; these needles are crystallographically identical with the crystals deposited from the alcoholic solution, and mostly show the optically negative bisectrix of a large optic axial angle emerging nearly normally to the plate.

The following analytical results were obtained :

0·1969 gave 0·3793 $CO_2$ and 0·1104 $H_2O$.   C $= 52·54$ ; H $= 6·23$.
0·1986   „   0·3843 $CO_2$   „   0·1111 $H_2O$.   C $= 52·77$ ; H $= 6·22$.
0·9654   „   25·9 c.c. of dry nitrogen at 16° and 749 mm.   N $= 3·14$.
0·6144   „   0·2534 AgBr and 0·3172 $BaSO_4$.   Br $= 17·55$ ; S $= 7·09$.
$C_{20}H_{28}O_4NBrS$ requires C $= 52·40$ ;  H $= 6·11$ ; N $= 3·06$ ; Br $= 17·47$ ;
S $= 6·99$ per cent.

The specific rotatory power of the salt was determined in absolute

alcohol and in glacial acetic acid solutions. A solution in glacial acetic acid of $0.5005$ gram in $25.2$ c.c. gave $a_D + 1.54°$ at $21.2°$ in a 200 mm. tube, whence $[a]_D + 38.8°$ and $[M]_D + 177.6°$. A solution in absolute alcohol of $0.2005$ gram in $25.2$ c.c. gave $a_D + 0.66°$ at $21°$ in a 200 mm. tube, whence $[a]_D + 41.5°$ and $[M]_D + 190°$.

$$Lævotetrahydroquinaldine, \begin{array}{l} CH \cdot CH \vdots C \cdot CH_2 \cdot CH_2 \\ CH \cdot CH \vdots C \cdot NH \cdot CHMe \end{array}.$$

Carefully purified lævotetrahydroquinaldine dextro-α-bromocamphor-sulphonate is distilled in a current of steam with a slight excess of soda ; the base is obtained as a colourless oil suspended in the aqueous distillate and is extracted with ether. The ethereal solution is dried with potash and the solvent distilled off ; the residual pale yellow oil is then distilled under reduced pressure. It passes over as a colourless oil boiling at $158°$ under 59 mm. pressure, and is sparingly soluble in water, but miscible with the ordinary organic solvents ; it has a faint basic odour and gradually becomes yellow on exposure to the air. The following analytical results were obtained :

$0.1876$ gave $0.5593$ $CO_2$ and $0.1511$ $H_2O$.   $C = 81.31$ ; $H = 8.95$.
$0.2977$  ,,  $24.6$ c.c. of dry nitrogen at $21°$ and $761$ mm.   $N = 9.65$.
$C_{10}H_{13}N$ requires $C = 81.63$ ; $H = 8.84$ ; $N = 9.52$ per cent.

The base has $a_D - 59.24°$ in a 100 mm. tube at $20°$; whence $[a]_D - 58.12°$ and $[M]_D - 85.44°$ at $20°$. The relative density is $1.02365$ at $14.5°/4°$. Further details as to the physical properties are given in a subsequent paper (this vol., p. 1111).

*Lævotetrahydroquinaldine Hydrochloride*, $C_{10}H_{13}N,HCl + H_2O$.

A warm solution of pure lævotetrahydroquinaldine in excess of concentrated hydrochloric acid yields on cooling a large separation of the hydrochloride as a white, crystalline powder ; this is filtered on the pump, washed with concentrated hydrochloric acid, in which the salt is moderately soluble, and recrystallised from absolute alcohol. It melts at $196.5—197.5°$ and is fairly soluble in water, less so in absolute alcohol, and sparingly soluble in acetone. The following analyses of the air-dried material show it to contain $1H_2O$ which is lost at $100°$ :

$0.1428$ gave $0.1021$ $H_2O$ and $0.3118$ $CO_2$.   $C = 59.55$ ; $H = 7.94$.
$0.3162$  ,,  $0.2258$ AgCl.   $Cl = 17.66$.
$1.9828$ lost $0.1765$ $H_2O$ in 4 hours at $100°$.   $H_2O = 8.90$.
$C_{10}H_{13}N,HCl + H_2O$ requires $C = 59.58$ ; $H = 7.94$ ; $Cl = 17.57$ ;
$H_2O = 8.93$ per cent.

On prolonged heating at $100°$, the material volatilises slowly, and afterwards does not melt so sharply as before.

The alcoholic solution, on spontaneous evaporation, deposits the hydrated salt as large, transparent, lustrous tablets belonging to the orthorhombic system (Fig. 1). The form $c\{001\}$ is dominant and gives very good results on measurement; the forms $q\{011\}$ and $r\{101\}$ are the next largest and are well developed. The pyramid $o\{561\}$ is always present and fairly large, but the dome $r'\{501\}$ is very rarely observed. There is a perfect cleavage parallel to $r\{101\}$, and the optic axial interference figure may be observed through a flake hacked parallel to $b\{010\}$. The axis-$b$ is the acute bisectrix, and the optic axial plane is $a\{100\}$; the optic axial angle is not large, and the double refraction is fairly strong and negative in sign. The optic axial dispersion is marked, the angle for red light being greater than that for blue.
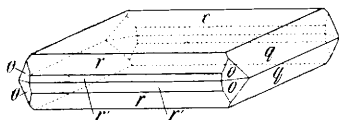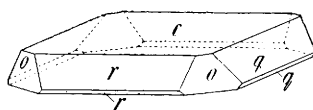
FIG. 1.                                   FIG. 2.



No evidence of the sphenoidal hemihedrism was obtained. The form $o\{561\}$ is never completely developed, but usually only one half of its total number of faces is present; this, however, is apparently due to the crystal growing whilst resting upon the face $c\{00\overline{1}\}$, which results in an imperfect development of those faces cutting the negative end of the $c$-axis. Thus the crystals very usually present the appearance shown in Fig. 2, only the four faces (561), (5̄61), (56̄1), and (5̄6̄1) of the form $o\{561\}$ being present. We were unable to obtain any evidence of enantiomorphous hemihedrism by etching; the action of water and alcohol upon the faces of the pinacoid $c\{001\}$ gives rise to etch-figures having the appearance shown in Figs. 3 and 4 respectively, whilst upon a cleavage plate parallel to $r\{101\}$ water produces etch-figures of the outline shown in Fig. 5. These figures appear to be quite in accordance with holohedral symmetry.
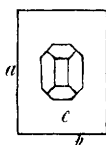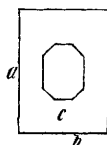
FIG. 3.                FIG. 4.                FIG. 5.



Crystalline System.—Orthorhombic.

$$a : b : c = 0.8627 : 1 : 1.4124.$$

Forms observed.—$c\{001\}$, $q\{011\}$, $r\{101\}$, $r'\{501\}$, and $o\{561\}$.

The following angular measurements were obtained :

| Angle. | Number of observations. | Limits. | Mean observed. | Calculated. |
|---|---|---|---|---|
| $cq = 001 : 011$ | 37 | $54°19' — 55°11'$ | $54°42'$ | — |
| $qq = 011 : 01\bar{1}$ | 14 | $70\ 8 — 71\ 5$ | $70\ 40$ | $70°36_{\jmath}$ |
| $cq = 00\bar{1} : 011$ | 12 | $124\ 42 — 125\ 37$ | $125\ 15$ | $125\ 18$ |
| $cr = 001 : 101$ | 41 | $57\ 59 -- 59\ 1$ | $58\ 35$ | — |
| $rr = 101 : 10\bar{1}$ | 16 | $62\ 9 — 63\ 18$ | $62\ 47$ | $62\ 50$ |
| $cr = 00\bar{1} : 101$ | 24 | $121\ 4 — 122\ 0$ | $121\ 31$ | $121\ 25$ |
| $cr' = 001 : 501$ | 19 | $82\ 16 — 83\ 25$ | $82\ 54$ | $83\ 2$ |
| $rr' = 101 : 501$ | 11 | $23\ 54 — 24\ 50$ | $24\ 20$ | $24\ 27$ |
| $rr' = 10\bar{1} : 501$ | 14 | $38\ 0 — 39\ 4$ | $38\ 26$ | $38\ 23$ |
| $qr = 011 : 101$ | 6 | $72\ 6 — 72\ 57$ | $72\ 31$ | $72\ 28$ |
| $qo = 011 : 561$ | 18 | $50\ 2 — 51\ 8$ | $50\ 35$ | $50\ 40$ |
| $co = 001 : 561$ | 15 | $84\ 36 — 85\ 41$ | $85\ 4$ | $85\ 9$ |
| $co = 00\bar{1} : 561$ | 7 | $94\ 40 — 95\ 27$ | $94\ 59$ | $94\ 51$ |

After cautiously melting anhydrous lævotetrahydroquinaldine hydro-chloride under a cover slip on a microscope slide, it begins to crystallise quite readily at about 60°, yielding a film which is macroscopically very transparent. As the temperature falls, however, the speed of growth decreases, and at the ordinary temperature crystallisation proceeds so slowly that it cannot be followed microscopically. Further, the crystalline material obtained at temperatures not far removed from the melting point, consists of long needles or of large square plates showing straight extinction ; these are striated parallel to one side and the striæ are the trace of the optic axial plane, a bisectrix of positive double refraction emerging normally to the large square face. The optic axes emerge outside the microscope field, and this material is of orthorhombic crystalline form.

As the very transparent film cools, large patches of it successively change with great rapidity, becoming very white and opaque ; in a thick film, the change is almost explosive in character, sometimes even throwing the cover slip into the air. Notwithstanding this, it is very improbable that the change is due to polymorphism, as, although the material becomes so opaque, yet the optical properties can still be made out and are not appreciably altered ; the rupture is apparently due to strain set up during cooling. At a little below the temperature at which the hydrochloride solidifies most readily, crystallisation still proceeds, although more slowly, the same modification being produced as at higher temperatures ; the crystallisation proceeds from centres just as before with production of radiate aggregates of long needles, showing well-defined extinction and optical properties. These aggre-gates, however, do not fly to pieces on cooling, but remain transparent, merely cracking across the longer dimensions of the needles. At the

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ordinary temperature, the substance crystallises very sluggishly (about 1 mm. in 3 days), yielding a very opaque film showing aggregate polarisation ; this confused crystallisation is structurally identical with the broad needles produced so easily just below the melting point, because here and there in the mass transparent fragments may be observed having optical properties identical with those of the material produced at the higher temperature, and also because no conversion of the one material into the other occurs on standing.   Since crystallisation only occurs readily at about 60°, it is necessary, in order to obtain a crystalline film rapidly, to allow the hot molten film to cool until crystallisation starts from centres, and then to warm it over the lamp until the whole has solidified.

The rotatory power of the hydrated salt, $C_{10}H_{13}N,HCl + H_2O$, was determined in aqueous and absolute alcoholic solutions.   0·4932 gram, made up to 25·15 c.c. with water at 18·9°, gave $a_D - 2·37°$ in a 200 mm. tube ;  0·5451 gram, made up to 25·15 c.c. with absolute alcohol at 18·9°, gave $a_D - 3·03°$ in a 200 mm. tube ; whence the following values :

|  | In aqueous solution. | In alcoholic solution. |
|---|---|---|
| $C_{10}H_{13}N,HCl + H_2O$ ............... | $[a]_D - 60·4°$ | $[a]_D - 69·9°$ |
| $C_{10}H_{13}N,HCl$ ......................... | $[a]_D - 66·4$ | $[a]_D - 77·4$ |
| $C_{10}H_{13}N,HCl$ ......................... | $[M]_D - 121·7$ | $[M]_D - 140·8$ |

*Lævotetrahydroquinaldine  Picrate*,  $C_{10}H_{13}N,C_6H_2(NO_2)_3 \cdot OH$.

Lævotetrahydroquinaldine picrate is prepared by crystallising a mixture of the lævo-base and picric acid in the requisite proportion from hot alcohol ; it forms dark yellow plates or needles melting at 148—150°, but crystals suitable for goniometrical examination could not be obtained.   It is sparingly soluble in water and moderately so in alcohol, acetone, benzene, or ethylic acetate.   The following analytical results were obtained with material crystallised from absolute alcohol :

0·1693 gave 0·3145 $CO_2$ and 0·0670 $H_2O$.   C = 50·66 ; H = 4·39.
0·2146   ,,    0·4003 $CO_2$  ,,   0·0838 $H_2O$.   C = 50·87 ; H = 4·34.
      $C_{16}H_{16}O_7N_4$ requires C = 51·06 ;  H = 4·26 per cent.

A solution of 0·5014 gram, made with 25·2 c.c. of absolute alcohol at 20°, gave $a_D - 1·31°$ in a 200 mm. tube, whence $[a]_D - 33·0°$ and $[M]_D - 124°$.   Since the molecular rotatory power of lævotetrahydroquinaldine in absolute alcohol is $[M]_D - 94·1°$, it would appear that the picrate for the most part is not dissociated in alcoholic solution.

*Benzoyllævotetrahydroquinaldine*, $C_{10}H_{12}N \cdot CO \cdot C_6H_5$.

On suspending purified lævotetrahydroquinaldine in warm caustic soda solution and running in rather more than the calculated quantity of benzoic chloride with continual agitation, an opaque, yellowish oil separates which rapidly solidifies to a hard, crystalline mass ; this is ground in a mortar and filtered, being well washed with water and dilute hydrochloric acid. The substance is best purified by crystallisation from acetone ; if, as sometimes happens, a green colouring matter is produced, this is best destroyed by crystallisation from ethylic acetate. After ultimately crystallising from absolute alcohol, the benzoyl derivative is obtained in colourless crystals melting at 117·5—118°. It is very soluble in benzene and moderately soluble in cold alcohol, less so in cold acetone or ethylic acetate ; it is nearly insoluble in light petroleum or boiling water. This substance is, as would be expected, appreciably more soluble than the corresponding racemic compound. The following results were obtained on analysis :

0·1996 gave 0·5934 $CO_2$ and 0·1230 $H_2O$. C = 81·08 ; H = 6·84.

0·2066 ,, 0·6139 $CO_2$ ,, 0·1276 $H_2O$. C = 81·04 ; H = 6·86.

0·6108 ,, 30·0 c.c. of dry nitrogen at 21° and 7·55 mm. N = 5·69.

$C_{17}H_{17}ON$ requires C = 81·27 ; H = 6·77 ; N = 5·58 per cent.

In order to obtain evidence as to the racemic nature of externally compensated benzoyltetrahydroquinaldine, it was necessary to compare the densities and crystalline forms of the active and inactive substances. The densities were determined by Retgers' method (*Zeit. physikal. Chem.*, 1889, **3**, 497), using a solution of barium mercuric iodide diluted with water ; the results seem slightly more accurate than those obtained by Retgers with isomorphous mixtures, using organic liquids. The following results were obtained with crystals of benzoyllævo-tetrahydroquinaldine deposited from acetone or ethylic acetate solutions :

$$d_{4°}^{14·5°} = 1·2119 ; \ 1·2113 ; \ 1·2116 ; \ \text{mean} = 1·2116 ;$$

the molecular volume of the crystalline material is thus 207·16 at 14·5°/4°.

The crystallographic properties of the benzoyl derivatives of lævo- and dextro-tetrahydroquinaldine were fully studied and compared ; the crystals of the two substances being enantiomorphously related, as was to be expected, the following crystallographic description includes both compounds.

The optically active benzoyltetrahydroquinaldines are so soluble in benzene that good crystals could not be obtained from this solvent ;

cold solutions in acetone or ethylic acetate, however, deposit on spon-
taneous evaporation well-developed crystals suitable for goniometrical
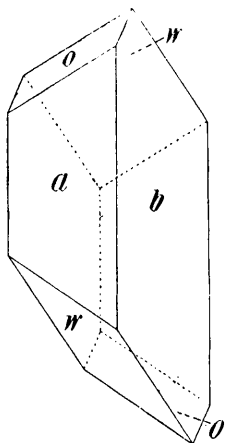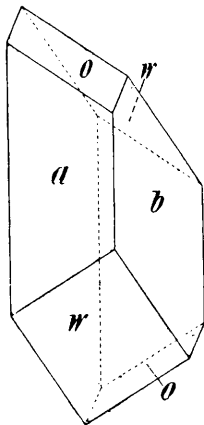examination. The crystals are usually elongated in the direction of



FIG. 6.

FIG. 7.

the c-axis, and then are generally developed only at one end ; fre-
quently, however, crystals of the typical habit shown in Figs. 6 and 7
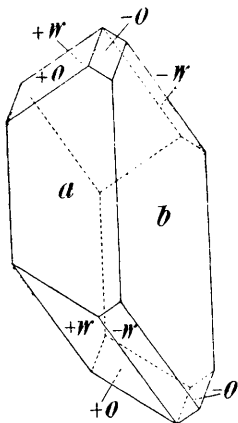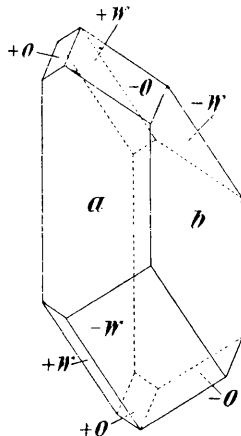are obtained, and the examination of these crystals shows them to be



FIG. 8.

FIG. 9.

hemimorphic, the b-axis being polar. The pinacoids $a\{100\}$ and $b\{010\}$
are predominant, and generally of about the same facial development ;
neither of these forms gives very good reflections. The form $\rho w\{\bar{1}11\}$
is usually fairly large, whilst the pyramid $\rho o\{111\}$ is quite small ;

crystals exhibiting the number of faces required in the holohedral division of the monosymmetric system are often deposited from ethylic acetate solution, but the hemimorphism is generally betrayed by the unequal sizes of the faces, as in Figs. 8 and 9.

There is a very perfect cleavage parallel to $a\{100\}$, and the acute bisectrix emerges through a cleavage fragment at the edge of the field ; observation of the extinction in $b(010)$ shows that the acute bisectrix lies in the plane of symmetry at $17.5°$ to the face—normal to $a(100)$. Both optic axes are visible in convergent light under a 1/12th inch oil immersion objective ; the optic axial dispersion is marked, the optic axial angle for red being greater than that for blue light. The double refraction is positive in sign, and the optic axial plane is perpendicular to the plane of symmetry.

Crystalline system.—Monosymmetric : Hemimorphic.

$$a : b : c = 1.0277 : 1 : 0.4261.$$

$$\beta = 88° 15'.$$

Forms present on benzoyllævotetrahydroquinaldine (Figs. 6 and 8). —$a\{100\}$, $b\{010\}$, $+\rho o\{111\}$ and $+\rho w\{\bar{1}11\}$ ; sometimes also $-\rho o\{111\}$ and $-\rho w\{\bar{1}11\}$.

Forms present on benzoyldextrotetrahydroquinaldine (Figs. 7 and 9).—$a\{100\}$, $b\{010\}$, $-\rho o\{111\}$, $-\rho w\{111\}$ ; sometimes also $+\rho o\{111\}$ and $+\rho w\{\bar{1}11\}$.

The following angular measurements were obtained :

| Angle. | Number of measurements. | Limits. | Mean observed. | Calculated. |
|---|---|---|---|---|
| $ao = 100 : 111$ | 36 | $67°15' — 67°59'$ | $67°43'$ | — |
| $ow = 111 : \bar{1}11$ | 38 | $41\ 7 — 42\ 15$ | $41\ 45$ | — |
| $aw = \bar{1}00 : \bar{1}11$ | 29 | $70\ 3 — 71\ 0$ | $70\ 31$ | $70°32'$ |
| $bo = 010 : 111$ | 26 | $68\ 16 — 69\ 11$ | $68\ 44$ | — |
| $oo = 111 : 1\bar{1}1$ | 21 | $41\ 56 — 43\ 5$ | $42\ 28$ | $42\ 32$ |
| $bw = 010 : \bar{1}11$ | 24 | $67\ 44 — 68\ 39$ | $68\ 16$ | $68\ 18$ |
| $ww = \bar{1}11 : \bar{1}\bar{1}1$ | 19 | $43\ 8 — 44\ 12$ | $43\ 31$ | $43\ 23$ |
| $ow = 111 : 11\bar{1}$ | 8 | $117\ 4 —118\ 46$ | $117\ 56$ | $117\ 52$ |
| $ow = 111 : \bar{1}\bar{1}1$ | 11 | $61\ 24 — 62\ 30$ | $61\ 59$ | $62\ 8$ |

After melting the substance on a microscope slide under a cover slip, the liquid film can usually be cooled to the ordinary temperature without any solidification occurring ; sometimes, however, crystallisation sets in whilst the film is very hot and then proceeds rapidly at the high temperature, but stops entirely when the slide cools. The crystallisation, having once started, can be caused to proceed rapidly until complete by cautiously heating the film at a temperature

below its melting point. The crystalline film consists of large, well-defined individual flakes ; the larger faces of some of these are nearly perpendicular to the acute bisectrix of a fairly small optic axial angle showing positive double refraction, but those of others are nearly perpendicular to the obtuse bisectrix, in which the double refraction is apparently negative in sign. The optic axial dispersion is marked, the optic axial angle for red being greater than that for blue light. At the ordinary temperature, the liquid film solidifies very slowly indeed to a mass of interlaced needles showing aggregate polarisation ; some of these needles can be seen to lie perpendicularly to the optically negative bisectrix of a large optic axial angle. Both the films obtained at high and low temperatures are probably structurally identical and also identical with the crystals deposited from solution.

The rotation constants of benzoyllævotetrahydroquinaldine are of considerable interest, and show that the introduction of the acidic group has converted the lævorotatory base into a highly dextrorotatory compound. This is the more remarkable since the piperidine bases, dextro $\alpha$-pipecoline, dextroisopipecoline, coniine, and dextroisoconiine, have the specific rotatory powers $[\alpha]_D$ $+36\cdot9°$, $+33\cdot29°$, $+13\cdot79°$, and $+8\cdot19°$ respectively, whilst their benzoyl derivatives are also dextrorotatory and have the values $[\alpha]_D + 35\cdot3°$, $+33\cdot35°$, $+37\cdot7°$, and $+29\cdot1°$ respectively ; the introduction of the benzoyl group into the pipecolines scarcely alters the specific rotatory power (Ladenburg, *Ber.*, 1893, **26**, 854). A case somewhat similar to that of lævotetrahydroquinaldine and its benzoyl derivative has been investigated by Forster (Trans., 1898, **73**, 386), who finds that dextrobornylamine having $[M]_D + 69\cdot6°$ yields a benzoyl derivative having the molecular rotatory power in alcoholic solution of $[M]_D - 56\cdot0°$, the molecular rotatory power thus changing by $125\cdot6°$ ; in the case now recorded, a change of nearly $1000°$ in molecular rotatory power attends the conversion of the base into its benzoyl derivative. It is further of interest to note that, whilst the change of rotatory power occurs in the same sense on passing from either bornylamine or neobornylamine to its hydrochloride and then to its benzoyl derivative, the direction of the change in rotatory power alters in the case of tetrahydroquinaldine, as is shown in the following table :

|  | $l$-Tetrahydro-quinaldine $[M]_D$. | Bornylamine, $[M]_D$. | Neobornyl-amine, $[M]_D$. |
|---|---|---|---|
| Base ............................... | $-85\cdot4°$ | $+69\cdot6°$ | $-47\cdot9°$ |
| Hydrochloride in alcohol............ | $-140\cdot8$ | $+43\cdot0$ | $-73\cdot8$ |
| ,,        ,,     water.............. | $-121\cdot7$ | — | — |
| Benzoyl derivative in alcohol...... | $+814\cdot7$ | $-56\cdot0$ | $-114\cdot8$ |

The variation of the rotation constants of non-electrolytes with change of solvent has up to the present been but little studied, as, with the exception of the work of Freundler (*Ann. Chim. Phys.*, 1895, [vii], **4**, 286), few results of theoretical importance have been derived from such determinations. As, however, we show in a subsequent paper (this vol., p. 1111) that valuable information concerning the state of molecular aggregation of optically active substances is derivable from the variations in rotation constants referred to, a series of determinations of the specific rotatory powers of benzoyllævotetrahydroquinaldine in various solvents has been made. The results are stated in the following table, in which $w$ denotes the weight of substance contained in $v$ c.c. of solution at temperature $t$, and $c$ is the concentration in grams per 100 c.c. of solution :

| Solvent. | $w$. | $v$. | $c$. | $t$. | $\alpha_D$. | $[\alpha]_D$. | $[M]_D$. |
|---|---|---|---|---|---|---|---|
| Benzene ............ | 0·2502 | 25·24 | 0·991 | 28·0° | +4·96° | +250·2° | +628·0° |
| ,, ............ | 0·5007 | 25·17 | 1·989 | 27·5 | +9·98 | +250·8 | +629·6 |
| ,, ............ | 1·0008 | 25·24 | 3·965 | 23·0 | +19·93 | +251·3 | +630·8 |
| Chloroform ......... | 0·5010 | 25·10 | 1·989 | 25·5 | +12·08 | +303·7 | +762·2 |
| Acetone............... | 0·4993 | 25·19 | 1·982 | 25·0 | +12·55 | +316·6 | +794·6 |
| Ethylic alcohol ... | 0·5002 | 25·19 | 1·986 | 25·0 | +12·89 | +324·6 | +814·7 |
| Ethylic acetate ... | 0·5009 | 25·17 | 1·990 | 26·0 | +13·00 | +326·6 | +819·8 |
| Acetic acid ...... .. | 0·5000 | 25·19 | 1·985 | 25·0 | +14·41 | +363·0 | +911·1 |

*Hydrolysis of Benzoyllævotetrahydroquinaldine.*—Since we proposed to prepare pure dextrotetrahydroquinaldine by hydrolysing its benzoyl derivative, and since racemisation frequently accompanies chemical change, it was desirable to ascertain whether benzoyl-lævotetrahydroquinaldine yields only the parent base on hydrolysis. The powdered benzoyl derivative was hydrolysed by boiling for some days with concentrated hydrochloric acid ; after rendering alkaline with soda, and extracting with ether, the ethereal solution was washed with water and evaporated to dryness, hydrochloric acid being added towards the end. The crystalline hydrochloride was then ground up with acetone in an agate mortar, separated by filtration, and spread on a porous plate ; it was colourless, and 0·5009 gram, dissolved in water and made up to 25·2 c.c. at 23·0°, gave $\alpha_D - 2·63°$ in a 200 mm. tube, whence $[\alpha]_D - 66·2°$. This being the specific rotatory power of the lævohydrochloride, it is obvious that no racemisation attends the hydrolysis.

II. EQUILIBRIA BETWEEN OPTICAL ISOMERIDES AND THEIR SOLUTIONS.

*Fractional Crystallisation of Crude Dextrotetrahydroquinaldine Dextrocamphorsulphonate.*

Preliminary experiments showed that, on crystallising externally compensated tetrahydroquinaldine with dextro-α-bromocamphorsulphonic acid, the first separation of crystals yielded a lævorotatory base on treatment with alkali ; similarly, it was found that, on crystallising the inactive base with Reychler's dextrocamphorsulphonic acid, the first separation of crystals gave a dextrorotatory base when rendered alkaline with soda and distilled in steam.   We consequently expected that, after separating the major part of the lævo-isomeride as bromocamphorsulphonate, pure dextrotetrahydroquinaldine would be readily obtainable from the mother liquors by isolating the base and converting it into dextrocamphorsulphonate ; by recrystallising this salt, we expected easily to obtain a pure salt of dextrotetrahydroquinaldine, and to dispense with the rather tedious process originally employed by Ladenburg (*Ber.*, 1894, **27**, 77) for preparing the dextrorotatory base.   Singularly enough, however, this plan was a failure, but the results obtained are of sufficient interest to merit description.

The crude dextro-base was separated from the mother liquors and dissolved in a hot ethylic acetate solution of a molecular proportion of Reychler's dextrocamphorsulphonic acid.   On cooling, a copious separation of the camphorsulphonate occurred, and this was repeatedly crystallised from hot ethylic acetate, the salt separating in colourless, acicular aggregates.   The fresh crystals melt at $65-80°$, but after preliminary drying in a vacuum the melting point is $125-127°$ ; the lower melting point is due apparently to mechanically retained solvent, because the crystals do not lose appreciably in weight at $100°$.   The salt was recrystallised four times from ethylic acetate, the melting points, after drying, being (1) $121-123°$, (2) $125-127°$, (3) $125-127°$, and (4) $125-127°$, so that the material had been recrystallised twice after attaining the constant melting point $125-127°$, and might reasonably be expected to be a pure salt. After treatment with soda and distillation in steam, the base was obtained as a colourless oil boiling at $156°$ under $54$ mm. pressure.   It gave the rotatory power $a_D + 39·44°$ in a $100$ mm. tube, and since the pure lævo-base gives $a_D - 59·24°$ in a $100$ mm. tube, still contains about one-sixth of its weight of lævo-base.

The base was therefore again converted into dextrocamphorsulphonate and crystallised from boiling acetone ; the salt is very sparingly soluble in hot dry acetone, but dissolves readily if the solvent contains several per cent. of water.   The first separation melted at $125-127°$,

and after drying at 100°, a solution of 1 gram made up to 25 c.c. with water gave $a_D + 3·60°$ in a 200 mm. tube, whence $[a]_D + 45·0°$; the mother liquor gave a separation melting at 125—127°, and after drying at 100° an aqueous solution of 0·4374 gram of this, made up to 25 c.c. with water, gave $a_D + 1·53$ in a 200 mm. tube, whence $a_D + 44·3°$. The main separation having $[a]_D + 45·0°$ was once more crystallised from acetone and again melted at 125—127°; an aqueous solution of 0·4374 gram of this in 25 c.c. gave $a_D + 1·57°$ in a 200 mm. tube, whence $[a]_D + 44·9°$. These three fractions having identical melting points and practically the same specific rotatory power, the base was again separated as before from the fraction having $[a]_D + 44·9°$. After distillation under reduced pressure, the base had the rotatory power $a_D + 53·04°$ in a 100 mm. tube, a value considerably below that obtained for the pure lævo-isomeride, namely, $a_D - 59·24°$.

These results illustrate well the extreme difficulty which may be met with in isolating a pure salt of the type $dB\ dA$, from a mixture of the types $dB\ dA$ and $lB\ dA$. Had we not possessed previous knowledge of the specific rotatory power of dextrotetrahydroquinaldine, we should, on the basis of the above results, have been justified in supposing the rotatory power of the dextro-base to be $a_D + 53°$ in a 100 mm. tube. It is therefore necessary to emphasise the fact that in separating a mixture of the type $dB\ dA$, $lB\ dA$, no criterion of purity is necessarily afforded by the identity of melting point or rotatory power of several consecutive fractions.

## *Fractional Crystallisation of Crude Dextrotetrahydroquinaldine Hydrochloride.*

We have shown that lævotetrahydroquinaldine hydrochloride has the composition $C_{10}H_{13}N,HCl + H_2O$, whilst the racemic isomeride is anhydrous; it might therefore be expected that by crystallising the hydrochloride of the dextro-base containing a little of the lævo-isomeride, dextrotetrahydroquinaldine hydrochloride could easily be obtained in a pure state. Here again we met with failure, and again the failure was more interesting than success would have been.

A quantity of crude dextrotetrahydroquinaldine obtained in the manner described above from the mother liquors remaining after the preparation of lævotetrahydroquinaldine dextro-a-bromocamphorsulphonate was converted into hydrochloride, which was then fractionally crystallised from absolute alcohol. The first fractions consisted almost entirely of the racemic hydrochloride, which would be expected to be less soluble than its optically active components; they had $[a]_D + 6°$ or $+ 7°$, and were only mechanically contaminated with the dextro-hydrochloride by reason of adherent mother liquor. These fractions

were recrystallised from absolute alcohol, and readily yielded pure racemic hydrochloride ; the mother liquors in which the dextro-hydrochloride had concentrated were then added to the main mother liquor, and the fractionation continued. After a series of deposits had been obtained of this low rotatory power ($[a]_D + 6°$ to $7°$), the specific rotatory power suddenly rose considerably ; thus a separation having $[a]_D + 6\cdot28°$ was followed by one having $[a]_D + 41\cdot90°$, and the succeeding fractions had specific rotatory powers varying from $[a]_D + 55°$ to $+58°$ in 2 per cent. aqueous solutions. Further, the repeated recrystallisation of these fractions failed on all occasions, with one exception, to yield a product having the specific rotatory power of dextrotetrahydroquinaldine hydrochloride, namely, $[a]_D + 62\cdot8°$ in aqueous solution, the specific rotatory power of the deposits varying from $[a]_D + 55°$ to $+58°$.

This behaviour showed that fractional crystallisation of a mixture of racemic and dextrorotatory tetrahydroquinaldine hydrochlorides from alcohol could not be used as a practical method for obtaining the pure dextro-salt ; the racemic hydrochloride can be separated from the mixture until only a few per cent. of it remains with the dextro-salt, and further crystallisation fails to sensibly reduce this proportion. The explanation of this behaviour is to be found in Roozeboom's lucid discussion of the isothermals for systems consisting of a solvent, a racemic compound and its optically active components (*Zeit. physikal. Chem.*, 1899, **28**, 494). In Fig. 10 the ordinates denote

FIG. 10.
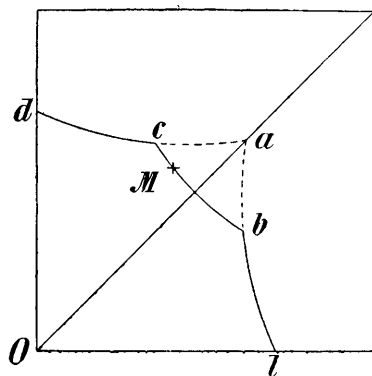


the quantity of dextro-compound, and the abscissæ the quantity of lævo-compound in the saturated solution ; the curve *lbcd* is an iso-thermal representing the composition of saturated solutions of the dextro- and lævo-compound and their mixtures at some particular temperature. The branches *lb* and *dc* of the curve represent solutions

in contact with lævo- or dextro-material respectively, in contact, therefore, with one solid phase; the branch $bc$ represents solutions in equilibrium with the racemic compound, again, therefore, with one solid phase. The points $b$ and $c$, however, represent solutions which are in equilibrium with two solid phases, namely, the racemic and one optically active component. Suppose we start with a solution containing both dextro- and lævo-material in the proportion corresponding to the point $M$ on the curve; on crystallisation, the solution will deposit racemic compound, and the composition of the saturated mother liquor will change in the direction of the point $c$; after the composition at $c$ is reached, the subsequent fractions will be of identical composition and specific rotation, both dextro- and racemic salt being deposited in a fixed proportion, and the solution retaining the composition at $c$ until the whole of the solvent has evaporated. These considerations hold if the temperature of crystallisation remains constant, and in our attempts to isolate the dextro-salt from the mixture, crystallisation always occurred at the ordinary temperature; in spite of slight temperature fluctuations, we were in general unable to change the composition of the mixture to any serviceable extent from that at the point $c$. This is apparently the first recorded instance in which equilibrium in contact with an optically active and racemic phase at the point $c$ has interposed practical difficulty, and we hoped to overcome the difficulty by sowing dextro-hydrochloride into supersaturated solutions obtained by lowering the temperature or by cooling saturated solutions in contact with the dextro-salt so that the solution becomes a labile one of composition lying upon the branch $ac$. Only on one occasion, however, did we succeed in getting a separation of pure dextrotetrahydroquinaldine hydrochloride. This is somewhat noteworthy, because Kipping and Pope observed just the converse behaviour with mixtures of potassium sodium dextro- and lævo-tartrates (Trans., 1899, **77**, 45), and pointed out the ease with which "a racemic compound might, under certain conditions, be resolved into its optically active components by simple crystallisation at temperatures at which the racemic compound is more stable than the mixture of the two optically active salts."

Attempts were made to change the composition of the solutions of the mixed hydrochlorides from that represented by the point $c$ by alternate crystallisations from two solvents, on the supposition that the composition at this point would differ for various solvents; our efforts in this direction were not successful, the only useful solvent besides alcohol being a mixture of alcohol and acetone.

*Fractional Crystallisation of Mixtures of Dextro- and Racemic Benzoyl-tetrahydroquinaldine.*

In spite of our failure to isolate pure dextrotetrahydroquinaldine hydrochloride in quantity from its mixture with the racemic compound and the consequent expectation of a similar behaviour with the benzoyl derivatives, we were able easily to obtain benzoyldextrotetrahydroquinaldine in quantity by fractionally crystallising a mixture of this substance with its racemic isomeride. Since we have previously shown that no racemisation occurs on hydrolysing benzoyllævotetrahydroquinaldine, we could readily obtain pure dextrotetrahydroquinaldine in quantity from its benzoyl derivative.

The conversion of the mixture of dextro-base with a much smaller proportion of its lævo-isomeride into benzoyl derivative is effected as previously described (p. 1073) ; the benzoyl derivative is then systematically fractionated from its hot acetone solution by recrystallising the early separations, which consist largely of the racemic compound, and adding the optically active mother liquors to the main solution. After the greater part of the racemic material present has been eliminated, the subsequent deposits consist of nearly pure benzoyldextrotetrahydroquinaldine,whilst occasionally a separation of low specific rotatory power occurs ; by continuing the fractionation and determining the specific rotatory power of each deposit, practically all of the original benzoyl derivative may be obtained in two lots, the one inactive, and the other having $[a]_D - 247.4°$ in a 2 per cent. benzene solution at 16°. Since our specimen of pure benzoyllævotetrahydroquinaldine had $[a]_D + 247.3°$ at 15° in benzene solution, the material of $[a]_D - 247.4°$ is obviously a pure substance. In this case, therefore, the existence of the equilibrium point $c$ (Fig. 10) causes no practical difficulty, owing, doubtless, to a greater facility of supersaturation.

### III. DEXTROTETRAHYDROQUINALDINE.

#### *Benzoyldextrotetrahydroquinaldine.*

The general properties of benzoyldextrotetrahydroquinaldine need no separate description ; its crystalline form has already been discussed (p. 1074), and analytical results proving its composition have been obtained.

The determinations of the density of benzoyldextrotetrahydroquinaldine were made in the same way as were those of the antipodes and with the following results :

$$d_4^{14.5°} = 1.2111 ; 1.2115 ; 1.2115.    \text{Mean} = 1.2114.$$

The molecular volume at $14.5°/4°$ is thus $207.20$ ; the mean density and

molecular volume differ by only 0·02 per cent. from the corresponding values obtained for benzoyllævotetrahydroquinaldine.

Benzoyldextrotetrahydroquinaldine is highly lævorotatory, and its rotation constants are given in the following table :

| Solvent. | $w$. | $v$. | $c$. | $t$. | $\alpha_D$. | $[\alpha]_D$. | $[M]_D$. |
|---|---|---|---|---|---|---|---|
| Benzene ............... | 0·2502 | 25·24 | 0·991 | 18° | − 4·88° | − 246·1° | − 617·7° |
| ,, ............... | 0·5007 | 25·24 | 1·984 | 18 | − 9·80 | − 247·0 | − 620·0 |
| ,, ............... | 1·0005 | 25·24 | 3·964 | 18 | − 19·70 | − 248·5 | − 623·7 |
| ,, ............... | 0·5000 | 25·24 | 1·981 | 17 | − 9·76 | − 246·3 | − 618·2 |
| ,, ............... | 1·0000 | 25·24 | 3·962 | 17 | − 19·77 | − 249·5 | − 626·2 |
| Chloroform............ | 0·5000 | 25·25 | 1·980 | 17 | − 12·23 | − 308·8 | − 775·1 |
| Acetone ............... | 0·5000 | 25·25 | 1·980 | 17 | − 12·64 | − 319·2 | − 801·1 |
| Ethylic alcohol ...... | 0·5000 | 25·25 | 1·980 | 17 | − 12·97 | − 327·5 | − 822·0 |
| Ethylic acetate ...... | 0·4995 | 25·24 | 1·979 | 17 | − 13·12 | − 331·5 | − 832·0 |
| Acetic acid ............ | 0·5000 | 25·25 | 1·980 | 17 | − 14·60 | − 368·6 | − 925·2 |

A comparison of these numbers with those obtained with the antipodes shows that the two sets differ arithmetically but slightly, the difference being attributable to the different working temperature. In both cases, the solutions in glacial acetic acid show far the highest rotation constants.

### Dextrotetrahydroquinaldine.

For the preparation of this base, finely-powdered benzoyldextrotetrahydroquinaldine is heated in a reflux apparatus with excess of concentrated hydrochloric acid ; after several days' heating, a copious separation of benzoic acid occurs on cooling, and the hydrolysis is complete. Slight excess of soda is added and the product distilled in a current of steam ; the base is extracted with ether and purified as before described ; the purity of the product was ascertained by a determination of its density and specific rotatory power. The density was found to be $d_4^{20}$ 1·01926, and the rotatory power was $a_D + 59·21°$ in a 100 mm. tube at 20°, whence $[a]_D + 58·09$ at 20°. Ladenburg gives the rotatory power, $a_D + 58·35°$ in a 100 mm. tube at 16°, for this base, and calculates the specific rotatory power as $[a]_D + 55·99°$ ; the density number, $d_4^{16}$ 1·042, which he uses is somewhat too high (*Ber.*, 1894, **27**, 76).

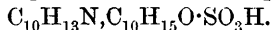### Dextrotetrahydroquinaldine Hydrochloride, $C_{10}H_{13}N,HCl + H_2O$.

The hydrochloride of dextrotetrahydroquinaldine was prepared in the same way as that of the lævo-isomeride. It crystallises in large, orthorhombic monohydrated tablets which melt at 196·5—197·5°, and are crystallographically indistinguishable from the crystals of the lævo-isomeride (Figs. 1 and 2, p. 1070).

The specific rotatory power of the salt dried at 100° was determined in aqueous solution; 0·4806 gram of the anhydrous salt, made up to 25·3 c.c. with water at 21·4°, gave $\alpha_D + 2\cdot51°$ in a 200 mm. tube. The specific rotatory power is thus $[\alpha]_D + 66\cdot1°$, which compares perfectly well with the value $[\alpha]_D - 66\cdot4°$ obtained for lævotetrahydroquinaldine hydrochloride (p. 1072).

## IV. MOLECULAR ROTATORY POWERS OF SALTS OF OPTICALLY ACTIVE BASES WITH OPTICALLY ACTIVE ACIDS.

A simple law should connect the molecular rotatory powers of optically active salts of the type $dB\ dA$ and $lB\ dA$, in fairly dilute aqueous solutions, provided that the base and acid, $B$ and $A$, are so strong that the salts are practically wholly dissociated. The algebraic difference between the molecular rotatory powers of the two salts should be equal to twice the molecular rotatory powers of the hydrochloride or similar salt of the active base, whilst the algebraic sum should be equal to twice the molecular rotatory power of a metallic salt of the active acid. Since the truth of this consequence of the electrolytic dissociation hypothesis has previously only been tested by Walden upon salts of feeble bases, like morphine (*Zeit. physikal. Chem.*, 1894, **15**, 206), it seemed desirable to prepare salts of the strong bases, dextro- and lævo-tetrahydroquinaldine, with a powerful optically active acid, when the principle enunciated above should be found to hold even more rigidly than in the case referred to. For this purpose, the salts of dextro- and lævo-tetrahydroquinaldine with Reychler's dextro-camphorsulphonic acid were prepared; the former salt was also required in order to compare its properties with those of the impure compound obtained in the fractional crystallisation of the mixture.

*Dextrotetrahydroquinaldine Dextrocamphorsulphonate,*
$$C_{10}H_{13}N,C_{10}H_{15}O\cdot SO_3H.$$

Dextrotetrahydroquinaldine dextrocamphorsulphonate is obtained by crystallising a benzene solution of the component base and acid in long, colourless, flat prisms melting at 128—129°; the prism zone is composed of six faces, whilst rather obliquely placed end faces complete the crystal. An optic axis is observed to emerge through the large face, and the extinction in this face is practically parallel with the longer sides; the crystals are very possibly anorthic, but good crystals could not be obtained for measurement. The salt is soluble in the ordinary organic solvents, including carbon bisulphide and ethylene dibromide. The following analytical results were obtained with material dried at 100°:

0.1246 gave 0.2887 $CO_2$ and 0.0879 $H_2O$.   C = 63.18 ; H = 7.84.
0.1317 ,,  0.3054 $CO_2$  ,,  0.0923 $H_2O$.   C = 63.24 ; H = 7.79.
0.4162 ,,  0.2699 $BaSO_4$.   S = 8.93.
  $C_{20}H_{29}O_4NS$ requires C = 63.32 ; H = 7.65 ; S = 8.64 per cent.

The specific rotation was determined in aqueous solution : 0.5077 gram, made up to 25 c.c. with water at 19.1°, gave $a_D + 1.85°$ in a 200-mm. tube ; whence $[a]_D + 45.7°$ and $[M]_D + 173.3°$.

In discussing the fractional crystallisation of a mixture of the dextro-camphorsulphonates of dextro- and lævo-tetrahydroquinaldine, it was pointed out (p. 1079) that we were unable to obtain the dextrocamphor-sulphonate of a higher specific rotatory power than $[a]_D + 45.0°$ in aqueous solution, and that this salt yielded a base having the rotatory power $a_D + 53°$ in place of  + 59° ; since it is now shown that dextro-tetrahydroquinaldine dextrocamphorsulphonate has $[a]_D + 45.7°$, it is evident that the material previously obtained was, as we stated, still contaminated with salt of the lævo-base.

*Lævotetrahydroquinaldine Dextrocamphorsulphonate,*
$C_{10}H_{13}N, C_{10}H_{15}O \cdot SO_3H$.
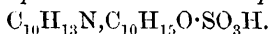
Lævotetrahydroquinaldine dextrocamphorsulphonate is prepared by crystallising the requisite quantities of the base and acid together from benzene solution ; it separates in colourless, flattened needles melting at 137—138°. The needles are square ended with truncated corners ; the extinction in the large face is straight with the sides, and a bisectrix emerges perpendicularly through the face. The following analytical results were obtained with material dried at 100° :

0.2022 gave 0.4680 $CO_2$ and 0.1416 $H_2O$.   C = 63.12 ; H = 7.78.
0.1209 ,,  0.2802 $CO_2$  ,,  0.0882 $H_2O$.   C = 63.21 ; H = 7.83.
0.4415 ,,  0.2838 $BaSO_4$.   S = 8.85.
  $C_{20}H_{29}O_4NS$ requires C = 63.32 ; H = 7.65 ; S = 8.64 per cent.

0.5073 gram, made up to 25 c.c. with water at 19.1°, gave $a_D - 0.74°$ in a 200 mm. tube, whence $[a]_D - 18.3°$ and $[M]_D - 69.5°$.

*Ammonium Dextrocamphorsulphonate,* $C_{10}H_{15}O \cdot SO_3NH_4$.

The ammonium salt of dextrocamphorsulphonic acid has been described by Reychler (*Bull. Soc. Chim.,* 1898, [iii], **19,** 120) ; we obtained it in long, colourless needles which, after drying at 100°, gave analytical results agreeing with those required for the above formula. The following rotation determinations were made :

0.2503 gram, made up to 25 c.c. with water at 16°, gave $a_D + 0.12°$ in a 200 mm. tube ; whence $[a]_D + 21.0°$.

POPE AND PEACHEY :

0·5000 gram, made up to 25 c.c. with water at 18°, gave $a_D + 0·83°$ in a 200 mm. tube ; whence $[a]_D + 20·7°$.

1·0008 grams, made up to 25 c.c. with water at 18°, gave $a_D + 1·65°$ in a 200 mm. tube ; whence $[a]_D + 20·6°$.

Since we are dealing all through with solutions of about 2 per cent., we may take for comparison with other salts the values $[a]_D + 20·7°$ and $[M]_D + 51·7°$. The following table gives the specific and molecular rotatory powers of the various salts of dextrocamphorsulphonic acid with which we are concerned :

| Salt. | $[a]_D.$ | $[M]_D.$ |
|---|---|---|
| $d\text{-}C_{10}H_{13}N, d\text{-}C_{10}H_{15}O\cdot SO_3H$ ................. | $+ 45·7°$ | $+ 173·3°$ |
| $l\text{-}C_{10}H_{13}N, d\text{-}C_{10}H_{15}O\cdot SO_3H$ .. ............... | $- 18·8$ | $- 69·5$ 7 / |
| $l\text{-}C_{10}H_{13}N, HCl$ ................................... | $- 66·4$ | $- 121·7$ |
| $NH_3, d\text{-}C_{10}H_{15}O\cdot SO_3H$ ........................ | $+ 20·7$ | $+ 51·7$ |

The algebraic difference between the molecular rotatory powers of salts (1) and (2) is 242·8° and the half of this, namely, 121·4°, should be equal to the molecular rotatory powers of active tetrahydroquinaldine hydrochloride, namely, 121·7°. Further, the algebraic sum of molecular rotatory powers (1) and (2) is 103·8, and the half of this, namely, 51·9°, should be equal to the molecular rotatory power of ammonium dextrocamphorsulphonate, namely, 51·7°. The agreement even in these comparatively concentrated solutions is very close.

## V. EXTERNALLY COMPENSATED TETRAHYDROQUINALDINE.

For the preparation of the tetrahydroquinaldine used in the present work, quinaldine was reduced with tin and hydrochloric acid essentially as described by Walter (*Ber.*, 1892, **25**, 1261) ; when the reduction was complete, slight excess of soda was added and the liquid subjected to prolonged distillation in a current of steam. The tetrahydroquinaldine was extracted from the distillate with ether, the ethereal solution dried over potash and fractionally distilled ; the fraction boiling at 240—250° was taken as containing all the hydroquinaldine and is sufficiently pure for immediate resolution into its optically active components as described above.

### *Racemic Tetrahydroquinaldine Hydrochloride,* $C_{10}H_{13}N, HCl.$

A quantity of the crude base boiling at 240—250° was dissolved in large excess of hydrochloric acid and the solution allowed to crystal-

lise ; the deposited hydrochloride was crystallised a number of times from absolute alcohol and then melted at 196—197·5°. This salt was prepared by Fischer and Steche (*Annalen*, 1887, **242**, 358) and described as not very soluble in water, but easily soluble in alcohol ; it is, however, less soluble in alcohol than in water. Our analytical results show that the salt has the composition $C_{10}H_{13}N,HCl$, as deposited from aqueous or alcoholic solutions ; it is consequently a true racemic compound, because its optically active components under similar conditions crystallise with water. It separates on spontaneous evaporation of its pure aqueous or alcoholic solution either in small, colourless, transparent crystals of rhombohedral habit, or in long, thin needles, both melting at 196—197·5°. These crystals are very poorly developed and the faces show considerable striation ; on microscopic examination, they are usually found to be composite, a lamellated twin structure somewhat resembling that characteristic of labradorite being observed. The goniometrical examination of these crystals gave no result other than that the crystals are geometrically pseudorhombohedral in accordance with the lamellation detected microscopically. Large crystals better suited for measurement are obtained by spontaneous evaporation of a solution of the salt in hydrochloric acid ; these consist of large, colourless, transparent tablets of poor facial development. The form $c\{001\}$ is dominant (Fig. 11) and the

FIG. 11.
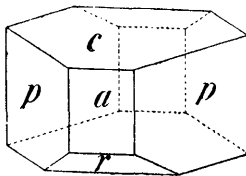


prism $p\{110\}$ is also well developed ; the pinacoid $a\{100\}$ is usually smaller, and the faces of the dome $r\{\bar{1}01\}$ are only observed as narrow replacements. There is an extremely perfect cleavage parallel to $c\{001\}$ and, when hacked in other directions, the crystals merely shear parallel to the cleavage. A bisectrix of positive double refraction emerges nearly normally to $c(001)$, but the orientation of the optic axial plane could not be ascertained.

Crystalline system.—Monosymmetric.

$$a : b : c = 0.934 : 1 : 0.935.$$

$$\beta = 71° 46'.$$

Forms observed.—$a\{100\}$, $c\{001\}$, $p\{110\}$, and $r\{101\}$.

4 D 2

The following angular measurements were obtained:

| Angle. | Number of observations. | Limits. | Mean. | Calculated. |
|---|---|---|---|---|
| $ap = 100 : 110$ | 31 | $40°48' — 42° \ 7'$ | $41°35'$ | — |
| $pp = 110 : \bar{1}10$ | 18 | $96 \ \ 4 — 97 \ 52$ | $96 \ 53$ | $96°50'$ |
| $pp = 110 : 1\bar{1}0$ | 15 | $82 \ 26 — 84 \ \ 1$ | $83 \ 19$ | $83 \ 10$ |
| $ac = 100 : 001$ | 42 | $70 \ 47 — 72 \ 12$ | $71 \ 32$ | $71 \ 46$ |
| $cr = 001 : \bar{1}01$ | 31 | $53 \ 42 — 55 \ 26$ | $54 \ 42$ | $54 \ \ 9$ |
| $ar = 100 : 10\bar{1}$ | 38 | $53 \ \ 6 — 55 \ 13$ | $54 \ \ 5$ | — |
| $cp = 001 \cdot 110$ | 44 | $75 \ 19 — 77 \ 14$ | $76 \ 28$ | — |
| $cp = 00\bar{1} : 110$ | 14 | $102 \ 54 — 104 \ \ 7$ | $103 \ 29$ | $103 \ 32$ |
| $pr = 110 : 10\bar{1}$ | 8 | $63 \ \ 0 — 64 \ 56$ | $63 \ 49$ | $63 \ 58$ |

After melting the racemic hydrochloride, it solidifies whilst hot less readily than the lævo-isomeride, but when cold solidifies with distinctly greater rapidity; it is quite easy to obtain a liquid film of the racemic substance at the ordinary temperature, but after 48 hours most of the liquid has crystallised. On allowing the liquid film to cool considerably below the melting point and then again warming, the whole may soon be made to crystallise; crystallisation proceeds from centres and results in the production of broad, individual flakes, which are usually striated in a direction parallel to the extinction. The striæ are parallel to the trace of the optic plane in the fragment, and a bisectrix emerges nearly normally to the face; the optic axial axes are outside the field, and the double refraction of the bisectrix, probably the obtuse one, is of positive sign. As cooling proceeds, the plates crack considerably along lines perpendicular to the direction of growth. Optically, this material is very similar to the orthorhombic plates of the lævo-hydrochloride, but morphologically it seems very different, the square plates never being observed; the inactive material produced at the high temperature does not fall to pieces during cooling in the violent manner affected by the optically active substance.

On rapidly cooling the molten film to the ordinary temperature, it remains liquid, but after a day or so a fringe of the modification described above, which polarises brilliantly, forms round the edge of the preparation and subsequently a macroscopically opaque growth makes its appearance in the body of the film; this growth consists of minute, square-ended needles showing oblique extinction and, being of low double refraction, polarises far less brilliantly than the first-described modification; the needles exhibit an oblique optic axial emergence and are interlaced in a highly confused manner. After several days, this modification occupies nearly the whole of the film and encroaches upon the brilliantly polarising fringe, the latter

apparently becoming converted into the former. The externally compensated hydrochloride is therefore almost certainly dimorphous.

### Racemic Tetrahydroquinaldine Picrate, $C_{10}H_{13}N,C_6H_2(NO_2)_3 \cdot OH$.

Racemic tetrahydroquinaldine picrate is obtained by crystallising the externally compensated base with the requisite quantity of picric acid from absolute alcohol ; it is more sparingly soluble in organic solvents and in water than the picrate of the lævo-base. The crystals deposited from the alcoholic solution melt at 153—154° and do not give good results on measurement ; they are apparently anorthic and consist of a predominant form $a\{100\}$, a smaller one, $c\{001\}$, and still smaller ones, $p\{110\}$ and $p'\{\bar{1}10\}$. The approximate angles are :

$$ac = 100 : 001 = 74° \ 54' \qquad ap = 100 : 110 = 32° \ 13'$$
$$cp = 001 : 110 = 81 \quad 20 \qquad pp' = 110 : \bar{1}10 = 79 \quad 0$$
$$cp' = 001 : \bar{1}10 = 78 \quad 6 \qquad ap' = \bar{1}00 : \bar{1}10 = 68 \quad 47$$

There is a perfect cleavage parallel to $c(001)$ and the acute bisectrix emerges through $c(001)$ ; the optic axial angle is large, the double refraction is negative in sign, and the optic axial dispersion is so marked that no definite extinction is observed for white light in $c(001)$. The extinction in $a(100)$ is nearly straight with the edge $ac$, and the optic axial plane is nearly parallel to $a(100)$. The following analytical results were obtained with material crystallised from alcohol :

0·2055 gave 0·3823 $CO_2$ and 0·0829 $H_2O$.   C = 50·74 ; H = 4·48.
0·2107  ,,   0·3933 $CO_2$  ,,  0·0825 $H_2O$.   C = 50·91 ; H = 4·35.
$C_{10}H_{16}O_7N_4$ requires C = 51·06 ; H = 4·26 per cent.

### Externally Compensated Tetrahydroquinaldine, $C_{10}H_{13}N$.

Carefully purified racemic tetrahydroquinaldine hydrochloride is distilled in a current of steam with addition of a slight excess of soda ; the distillate is extracted with purified ether, the ethereal solution dried with potash, and the ether distilled off. The residual nearly colourless oil is then distilled under reduced pressure and practically all distils at 196° under 207·5 mm. pressure. The base has the same density as its lævo-component, and its physical properties are dealt with fully in a subsequent paper, in which it is shown that this base is merely a mixture of the two optically active constituents.

### Racemic Benzoyltetrahydroquinaldine, $C_{10}H_{12}N \cdot CO \cdot C_6H_5$.

This substance has been prepared from tetrahydroquinaldine by Walter (*Ber.*, 1892, **25**, 1293), using the Schotten-Baumann reaction. It separates on spontaneous evaporation of its cold ethylic acetate

solutions in magnificent, lustrous, monosymmetric prisms (Fig. 12) melting at 117—118°, and showing the form $b\{010\}$ dominant ; the forms $p\{110\}$ and $q\{011\}$ are the next largest forms present, whilst the pinacoid $a\{100\}$ is always small and frequently absent. The pinacoid $c\{001\}$ is well developed and gives good results on measurement ; the form $r\{101\}$ is generally well represented, whilst the form $r'\{\bar{1}01\}$ is
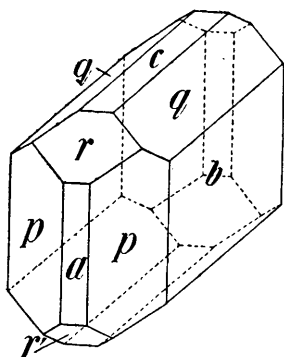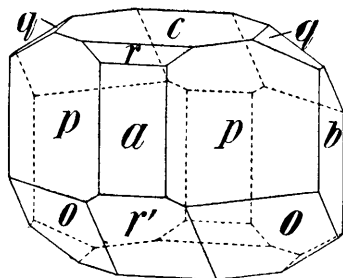
FIG. 12.                FIG. 13.



poorly developed and rarely observed. The crystals deposited from solutions in benzene (Fig. 13) differ greatly in habit from those obtained from ethylic acetate, and lend themselves better to crystallographic measurement than do the latter ; they exhibit the form $p\{110\}$ predominant, and also show $r'\{\bar{1}01\}$ and $o\{\bar{1}11\}$ well developed, whilst the pinacoids $a\{100\}$ and $b\{010\}$ are comparatively small and frequently

FIG. 14.
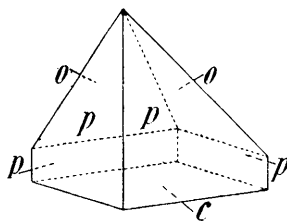


absent. The facial development of the form $r\{101\}$ is less than that of $r'\{\bar{1}01\}$. Crystals are frequently deposited from benzene solution of the hemihedral habit depicted in Fig. 14 ; these consist of parts of the forms $c\{001\}$, $o\{\bar{1}11\}$, and $p\{110\}$. No indications of pyroelectrical properties could be obtained to show that this habit is due to hemihedrism, so that it is probably due merely to abnormal conditions of growth.

Crystalline system.—Monosymmetric.

$$a : b : c = 0.6768 : 1 : 0.6675.$$

$$\beta = 81° 4'.$$

Forms observed.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$, $r\{101\}$, $r'\{\bar{1}01\}$ and $o\{\bar{1}11\}$.

The following angular measurements were obtained :

| Angle. | Number of observations. | Limits. | Mean. | Calculated. |
|---|---|---|---|---|
| $ap = 100 : 110$ | 7 | 33°16′—34° 9′ | 33°42′ | 33°46′ |
| $bp = 010 : 110$ | 42 | 56 0 —56 39 | 56 17 | 56 14 |
| $pp = 110 : 1\bar{1}0$ | 35 | 67 7 —67 54 | 67 29 | 67 31 |
| $cq = 001 : 011$ | 48 | 33 15 —33 34 | 33 24 | — |
| $bq = 010 : 011$ | 17 | 56 1 —56 59 | 56 27 | 56 36 |
| $qq = 011 : 0\bar{1}1$ | 34 | 66 17 —67 20 | 66 51 | 66 48 |
| $qr = 011 : 101$ | 25 | 49 57 —50 45 | 50 19 | 50 23 |
| $pq = 110 : 011$ | 22 | 78 16 —79 0 | 78 38 | 78 34 |
| $pr = 110 : 101$ | 51 | 50 38 —51 32 | 51 3 | — |
| $pr' = 110 : 10\bar{1}$ | 12 | 57 0 —58 2 | 57 33 | 57 38 |
| $pq = 110 : 010$ | 16 | 65 3 —65 58 | 65 37 | 65 34 |
| $qr' = 011 : \bar{1}01$ | 7 | 56 22 —57 6 | 56 49 | 56 48 |
| $ar = 100 : 101$ | 9 | 40 12 —41 1 | 40 41 | 40 52 |
| $cr = 001 : 101$ | 52 | 39 29 —40 56 | 40 12 | — |
| $cr' = 001 : \bar{1}01$ | 4 | 48 41 —49 12 | 48 56 | 49 0 |
| $ar' = 100 : 10\bar{1}$ | 6 | 49 36 —50 14 | 49 57 | 49 55 |
| $aq = 100 : 011$ | 11 | 82 19 —82 54 | 82 36 | 82 33 |
| $qo = 011 : \bar{1}11$ | 24 | 41 58 —42 55 | 42 24 | 42 26 |
| $ao = \bar{1}00 : \bar{1}11$ | 8 | 54 47 —55 10 | 54 59 | 55 1 |
| $co = 001 : \bar{1}11$ | 19 | 53 42 —54 32 | 54 10 | 54 15 |
| $op = \bar{1}11 : \bar{1}10$ | 19 | 42 54 —43 39 | 43 14 | 43 10 |
| $cp = 001 : 110$ | 26 | 82 4 —83 6 | 82 33 | 82 35 |
| $r'o = \bar{1}01 : \bar{1}11$ | 4 | 26 55 —27 30 | 27 14 | 27 3 |
| $oo = \bar{1}11 : \bar{1}\bar{1}1$ | 12 | 53 29 —54 26 | 53 58 | 54 7 |
| $bo = 010 : \bar{1}11$ | 15 | 62 18 —63 25 | 62 55 | 62 57 |

The extinctions in the faces $b(010)$ and $p(110)$ are practically straight with the side $ap$. The obtuse bisectrix emerges nearly normally through $a\{100\}$ and the obtuse bisectrix is observed through a section hacked nearly perpendicular to the zone [001]; the optic axial angle is large and the double refraction is negative in sign. The optic axial dispersion is slight and the angle for blue light is greater than that for red ; the plane of symmetry is the optic axial plane.

After melting, the substance solidifies fairly readily at high temperatures, and the whole film may be caused to crystallise by alternate heating and cooling; if, however, the film be rapidly cooled, it may be obtained at the ordinary temperature as a liquid film which crystallises extremely sluggishly. The crystalline film obtained at high temperatures is composed of long needles radiating from centres ;

these extinguish nearly straight with the direction of growth and, on cooling, crack extensively in different directions. Most of the crystalline individuals lie nearly perpendicular to the positive obtuse bisectrix of the optic axial angle and the optic axial plane is parallel to the direction of growth. Sometimes the acute bisectrix emerges nearly normally to the surface of the crystal fragment; the optic axial angle is large and the optic axial dispersion slight. The double refraction is negative in sign. The optical properties of this modification agree closely with those of the crystals deposited from solution, and the two are structurally identical, so that externally compensated benzoyltetrahydroquinaldine melts and solidifies as a racemic compound. The molten film at ordinary temperatures crystallises very slowly, yielding a mass of needles which shows aggregate polarisation.

The density of the crystals was determined as in the case of those of the optically active constituents with the following results :

$$d_4^{14\cdot5^\circ} = 1\cdot2373 \; ; \; 1\cdot2380 \; ; \; 1\cdot2373. \quad \text{Mean} = 1\cdot2375.$$

The molecular volume at $14\cdot5^\circ/4^\circ$ is thus $202\cdot8$. Since the optically active benzoyltetrahydroquinaldines have the molecular volume $207\cdot2$ at the same temperature in the crystalline state, it is obvious that the crystals of the racemic substance conform to Liebisch's rule (*Annalen,* 1895, **286**, 140), their density being greater than that of their optically active components. In the formation of crystalline racemic benzoyltetrahydroquinaldine from its crystalline optically active components at $14\cdot5^\circ$, a contraction of about $2\cdot14$ per cent. in volume occurs.


## VI. Melting Points of Optically Active and Externally Compensated Isomerides.

The great interest which has been imported into the question of the melting points of optically active and externally compensated isomerides by the recent work of Roozeboom (*Zeit. physikal. Chem.,* 1899, **28**, 505) rendered desirable the investigation of the melting points of the hydrochlorides and benzoyl derivatives of the tetrahydroquinaldines.

Careful determinations of the melting points of highly purified racemic and optically active tetrahydroquinaldine hydrochlorides gave the values $196—197\cdot5^\circ$ and $196\cdot5—197\cdot5^\circ$ respectively; the melting point of the racemic material is not quite so sharp as that of the dextro- or lævo-component. An intimate mixture of about equal weights of racemic and lævo-material melted at $180—184^\circ$.

Similarly, active benzoyltetrahydroquinaldine melted at $117\cdot5—118\cdot5^\circ$ and the racemic material at $117—118^\circ$, the racemic again melting less sharply than the active isomerides. A mixture of about equal parts of each melted at $108—110^\circ$.

Although the active and inactive isomerides melt at practically the same temperature, the externally compensated substance melts as a racemic compound, and the melting point curves for the mixtures would seem to belong to Roozeboom's Type 2 ; attention does not seem to have been drawn previously to examples of this type.

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