Studies in the Stereochemistry of Quinquevalent Nitrogen. II.

Resolution of the Asymmetric Quarternary Ammonium Compounds.

By

Shigeru Komatsu.

(Received February 23, 1915.)

The author has already shown in his previous article[1], that the four negative valences of the nitrogen atom in the quaternary ammonium compounds are of the same value, but it has still remained as a question that the melting point of compound formed by one and the same method is different in the statements of different investigators.

Hence, the present work was undertaken to decide whether the author's substance is a true asymmetric compound or not, and at the same time to study the spatial configuration of atoms or atomic groups in the molecule.

Pure methyl n-propyl phenyl benzyl ammonium iodide prepared from methyl n-propyl aniline and benzyl iodide, was mixed with equimolecular quantity of anhydrous silver salt of dextro bromocamphorsulphonic acid in an acetone ethyl acetate solution, and boiled on a water bath for 2 hours. The filtrate separated from silver iodide was subjected to distillation to remove the solvent, and the yellow syrupy residue changed to a solid mass on allowing to stand in a desiccator over a night. The crystalline mass consisting of a mixture of dextro and lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate, was dissolved in hot acetone and left in a desiccator.

The crystals melting at 161–162° gave the specific rotatory power $[\alpha]_D^{25} = +51.68°$ in an aqueous solution, which corresponds to that of the racemic ammonium dextro-bromocamphorsulphonate.

Then, the whole mass was dissolved in ethyl acetate, and from such a solution lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate isolated in white needle-shaped crystals. The

---

[1] Mem. Coll. Sci. Engin., Kyoto, **3**, 371 (1912).

mother liquor was made to evaporate down to a small bulk, and some ether added in order to promote the further crystallisation. Adding more ether to the filtrate from the second crop of the crystals, we have obtained hygroscopic needle-shaped crystals, and finally a syrupy residue containing dextro methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate. To the syrup dissolved in water, was added a potassium iodide solution in order to precipitate all the sulphonate present as the crystalline iodide, and methyl n-propyl phenyl benzyl ammonium iodide thus formed was allowed to recrystallize from alcohol.

It melts at 148°, and its specific rotatory power in its alcoholic solution was found to be $[\alpha]_D^{25} = +90.90°$.

The three fractions of the active bromocamphorsulphonate crystallized out from the ethyl acetate regularly increase their hygroscopic character from the first to the third, also showing the difference in the specific rotatory power in their aqueous solutions, i.e., $[\alpha]_D^{25} = +1.48°$, $[\alpha]_D^{25} = -0.87$ and $[\alpha]_D^{25} = -2.57°$ respectively.

Repeating the recrystallisation of the first fraction several times from ethyl acetate, finally it was found to possess the constant rotatory power $[\alpha]_D^{25} = -2.57°$ which agrees with that of the pure lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate. The substance thus obtained was no longer hygroscopic as was observed by Jones,[1] and has no definite melting point. Colourless crystals when heated at 80° for a while became opaque, and the cause of such a phenomena is due to the escape of the ethyl acetate of crystallisation which is contained in the molecule, as was ascertained by the author by the usual method.

The melting points and rotatory powers in the alcoholic solutions of the active ammonium iodide, bromide and chloroplatinate derived from optically active ammonium dextro-bromocamphorsulphonates, have been studied , and the results of the experiments by the author together with those of Wedekind and Fröhlich,[2] will be shown in the table I :

---

[1] J. Chem. Soc., 89, 281 (1906).

[2] Zur Stereochemie d. funfwertigen Stickstoffes, 1907, S. 49.

TABLE I.

Wedekind & Fröhlich.   Author.

l-$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N \cdot C_{10}H_{14}BrSO_4$ $[\alpha]_D^{25} = -2.67°$ $[\alpha]_D^{25} = -2.57°$

l-$(CH_3)(C_3H_7)(C_6H_5)C_7H_7)NI$ $\begin{cases} [119-150°]: & [146-147°]; \\ [\alpha]_D = -96.47° & [\alpha]_D^{25} = -93.63° \end{cases}$

l-$(CH_3)(C_3H_7)C_6H_5)(C_7H_7)NBr$ $\begin{cases} - & [166-167°]; \\ - & [\alpha]_D^{25} = -124.3° \end{cases}$

l-$[(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NCl]_2PtCl_4$ — $[164.5-164°]$

d-$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NI$ $[\alpha]_D = +86.74°$ $[\alpha]_D^{25} = +90.90°$

The author has attempted to resolve *α* methyl allyl phenyl benzyl ammonium iodide prepared from methyl benzyl aniline and allyl iodide, into its optical antipodes by means of silver dextro-bromocamphorsulphonate in an acetone or ethyl acetate solution, and the white platy crystals obtained by the fractional crystallisation of the racemic methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate in the acetone solution, melted at 135–136° and gave the specific rotatory power, $[\alpha]_D^{25} = +51.59°$, in an aqueous solution. After a repeated crystallisation from acetone, the rotatory power of the substance was again determined, and observed to be $[\alpha]_D^{25} = +52.28°$, and *γ* methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate like the *α* compound, also melted at 135–136° and gave the specific rotatory power, $[\alpha]_D^{25} = +52.77°$.

Thus the author's endeavour to resolve methyl allyl phenyl benzyl ammonium iodides (both *α* and *γ* forms) by means of bromocamphorsulphonic acid, into optically active compounds has not been succeeded.

The author, therefore, used Pope and Peachey's[1] method, and fortunately succeeded in resolving both ammonium iodides into their optically active forms.

Pure *α* methyl allyl phenyl benzyl ammonium iodide and anhydrous silver dextro-camphorsulphonate mixed in equimolecular quantities in an acetone ethyl acetate solution, was heated over a water bath for 1½ hours. After separating silver iodide, the solution was subjected to distillation, and the residue consisting of a viscid liquid, when

---

[1] J. Chem. Soc., **75**, 1127 (1899); **79**, 828 (1901).

was allowed to stand over sulphuric acid in a dark and cold place for a week, deposited crystals. By repeating fractional crystallisation from acetone six times, there were obtained white needle-shaped crystals melting at 161–162°, which gave the mean specific rotatory power of $[\alpha]_D^{25} = +46.48°$ in an aqueous solution. From the mother liquor, crude lævo a methyl allyl phenyl benzyl ammonium iodide was isolated by the aid of a potassium iodide solution, which was utilized for the preparation of the pure lævo isomeride.

In the winter time when the author repeated the same experiment, the yield of the crystalline mass consisting of a mixture of dextro and lævo methyl allyl phenyl benzyl ammonium dextro-camphorsulphonates was more fruitful, owing to the influence of the external conditions—temperature and humidity of the atomosphere. In the fractional crystallisation, of the racemic camphorsulphonates, ethyl acetate was used as a solvent according to Pope and Harvey.[1]

The first crop of the crystals consisted of almost pure dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate which when recrystallized from ethyl acetate 5 times and then from acetone twice, formed white needle-shaped crystals melting at 162–163°, whose specific rotatory power in an aqueous solution was found to be $[\alpha]_D^{25} = +46.71°$ as the mean value. The second crop consisted of white needle-shaped crystals, and the third hygroscopic rhombic crystals, and their rotatory powers, determined in aqueous solutions, were observed to be $[\alpha]_D^{25} = +38.27°$ and $[\alpha]_D^{25} = -1.28°$ respectively.

The crude lævo ammonium iodide separated from the mother liquor from the last crop was treated with an equimolecular silver lævo-camphorsulphonate. Carrying out the process of the crystallisation of the reaction product as described in its optical antipode, pure lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was obtained in white needle-shaped crystals melting at 160–161° which in an aqueous solution gave the mean specific rotatory power of $[\alpha]_D^{25} = -46.49$.

In another experiment, pure lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was prepared from the externally compensated ammonium iodide and silver lævo-camphorsulphonate; it consisted of white needles which were found to have the melting point 162–163° and the specific rotatory power, $[\alpha]_D^{25} = -46.69°$.

---

[1] *Loc. cit.*

Now, the author, expecting that stereoisomers may exist in the active forms of the ammonium compound, has undertaken the resolution of γ methyl allyl phenyl benzyl ammonium iodide by means of anhydrous silver dextro-camphorsulphonate, and γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained and recrystallized from acetone, consisted of white needles which melt at 162°, and its mean specific rotatory power in an aqueous solution was found to be $[\alpha]_D^{25} = +58.46°$.

Since the specific rotatory power of the γ form is not altered by recrystallisation, it is noteworthy that the pure sample of α methyl allyl phenyl benzyl ammonium compound has lower specific rotatory power than that of the γ isomer.

Now, the author has to ascribe the difference of the specific rotatory powers in α and γ isomerides to the different configurations of the atomic groups in their molecules.

For the confirmation of this view, the author has conducted the experiment to be described below:

In the experiment, the racemic dextro-camphorsulphonate was macerated with ethyl acetate according to Pope and Harvey,[1] and the purified γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate used had the properties already stated, i.e., the white needle-shaped crystals melted at 163°, and the specific rotatory power of the well purified sample in an aqueous solution was found to be $[\alpha]_D^{25} = +58.76°$ as the mean value.

To the crude γ lævo methyl allyl phenyl benzyl ammonium iodide obtained from the impure dextro methyl allyl phenyl benzyl ammonium dextro camphorsulphonate, an equimolecular silver dextro-camphorsulphonate was added, and the reaction product was subjected to fractional crystallisation using acetone as the solvent. And pure γ lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate, thus obtained, was found to be white needle-shaped crystals which had the properties similar to those of the enantiomorphous compound; it melted at 163–164° and its specific rotatory power was shown to be $[\sigma]_D^{25} = -56.21°$, which is lower than that of its enantiomorph.

γ lævo methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate prepared from racemic γ methyl allyl phenyl benzyl ammonium iodide and silver lævo-camphorsulphonate was observed to have the same

[1] *Loc. cit.*

melting point, the same specific rotatory power and the same crystalline form as those of the compound above mentioned.

The author has prepared several other optically active ammonium compounds of the α and γ series; and compared their melting point, specific rotatory power in alcohol or chloroform solutions with those of the same substances stated by Pope and Harvey,[1] as shown in the table II.

<div align="center">

TABLE II.

</div>

α Compounds.	Pope and Harvey.	Author.
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot C_{10}H_{15}SO_4$	$\begin{cases}[171-173°]\\ [\alpha]_D^{11}=+46.6°\end{cases}$	$\begin{matrix}[162-163°]\\ [\alpha]_D^{25}=+46.71°\end{matrix}$
d-$(CH_5)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I$	$\begin{cases}[147°]\\ \\ [\alpha]_D^{17}=+55.4°\end{cases}$	$\begin{matrix}[135-136°]\\ [\alpha]_D^{25}=+68.28°[2]\\ [\alpha]_D^{25}=+51.72°[3]\end{matrix}$
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot Br$	$\begin{cases}[165-167°]\\ [\alpha]_D^{16.2}=+64.1°\\ \text{(chloroform)}\end{cases}$	$\begin{matrix}[155-156°]\\ [\alpha]_D^{25}=+67.44°\\ \text{(alcohol)}\end{matrix}$
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI,HgI_2$	$\begin{cases}[124-125°]\\ [\alpha]_D^{11}=+24.3°\end{cases}$	$\begin{matrix}[119-120°]\\ [\alpha]_D^{25}=+24.86°\end{matrix}$
d-$[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NCl]_2PtCl_4$	$[166°]$	$[149-150°]$
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot C_{10}H_{15}SO_4$	$\begin{cases}[171-173°]\\ [\alpha]_D^{10}=-45.5°\end{cases}$	$\begin{matrix}[162-163°]\\ [\alpha]_D^{25}=-46.59°\end{matrix}$
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI$	$\begin{cases}147°\\ [\alpha]_D^{17}=-53.4°\\ \text{(chloroform)}\end{cases}$	$\begin{matrix}[134-135°]\\ [\alpha]_D^{25}=-51.34°\\ \text{(alcohol)}\end{matrix}$
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI,HgI_2$	$\begin{cases}[125-126°]\\ [\alpha]_D^{11.5}=-23.5°\end{cases}$	$\begin{matrix}[119-120°]\\ [\alpha]_D^{25}=-24.12°\end{matrix}$

---

[1] *Loc. cit.*

[2] In chloroform.

[3] In alcohol.

γ-Compounds.	Author.	
	Melting point.	$[\alpha]_D^{25}$
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot S_{10}H_{15}SO_4$	$[163°]$	$+58 \cdot 61°$
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I$	$[134-135°]$	$\begin{cases} +73 \cdot 98^{01} \\ +65 \cdot 54^{02} \end{cases}$
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot Br$	$[155-156°]$	$+81 \cdot 80°$
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I, HgI_2$	$[120-121°]$	$+39 \cdot 51°$
d-$[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot Cl]_2PtCl_4$	$[148-149°]$	
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot C_{10}H_{15}SO_4$	$[163-165°]$	$-56 \cdot 21°$
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I$	$[135-135,5°]$	$-63 \cdot 15°$
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I, HgI_2$	$[120°]$	$-39 \cdot 60°$

From the experimental results so far obtained the following conclusions are drawn:

1. The asymmetrical ammonium compounds, prepared by the author, may directly resolve into optically active antipodes by means of optically active acids.

2. Whilst the melting points of the same optically active compounds obtained by the same method, do not agree with those of the other investigators, their specific rotatory powers are concordant to each other.

3. In the optically active methyl allyl phenyl benzyl ammonium compounds, there exist optical isomers in σ and γ forms, which possess the same melting points but the different specific rotatory powers.

The optically active acids used for the resolution were dextro-camphorsulphonic, lævo-camphorsulphonic and dextro-bromocamphorsulphonic acids. And dextro-camphorsulphonic acid was prepared according to Reychler[3] from Japan camphor purified by sublimation and by treating with conc. sulphuric acid and acetic anhydride, and it was obtained in the form of hygroscopic crystals melting at 192–193°, showing its specific rotatory power as $[\alpha]_D^{25} = +23 \cdot 14°$ in its aqueous solution. Lævo-

---

[1] In chloroform.

[2] In alcohol.

[3] Bull. Soc. Chim., 19, 120 (1898).

camphorsulphonic acid used in the expeiment was prepaied according to Pope and Harvey[1] fiom lævo-borneol from Kahlbaum, and its melting point was found to be 190° and the specific rotatoiy power of its ammoninm salt in the aqueous solution to be $[a]_D^{25} = -21\cdot35°$. Dextio-bromocamphorsulphonic acid obtained accordiug to the method suggested by Morsh and Cousins,[2] from dextro-bromocamphor ciystallized fiom methyl alcohol and chlorosulphonic acid, was purified by converting it into the ammonium salt which possessed the specific rotatory power, $[a]_D^{25} = +85\cdot54°$, in an aqueous solution.

EXPERIMENTAL PART.

1. Dextro-Camphorsulphonic Acid, $C_{10}H_{15}O\cdot SO_3H$.

The substance was prepared by Reychlei's method,[3] and the process will be mentioned below :

152 paits Japan camphor purified by sublimation were tieated with the mixture of 204 paits acetic anhydride from Meick and 98 parts pure conc. sulphuric acid. After a while dextio-camphorsulphonic acid ciystallized out in needles, which were separated from the mother liquor by filtration, washed with ether and then recrystallized from acetic acid. The substance dried at 100° for 3 hours and obseived to melt at 192–193°, was analysed and gave the following results :

0·1953 grm. substance gave 0·1916 grm. BaSO₄.

	Calc. for $C_{10}H_{16}O_4S$.	Found.
Sulphur	13·79	13·46

The optical rotation of the free acid in an aqueous solution was determined :

A solution of 0·8751 grm. acid made up to 25 c.c. with water at 25°, gave $a_D^{25} = +1\cdot62°$ in a 20 cm. tube ; whence $[a]_D^{25} = +23\cdot14°$.

2. Lævo-Comphorsulphonic Acid, $C_{10}H_{15}O\cdot SO_3H$

l-Camphor prepared accoiding to Pope and Harvey[4] from l-borneol from Kahlbaum by oxidation with nitric acid (sp. gr. 1·42) was converted into lævo-camphorsulphonic acid by the usual way.

1 J. Chem. Soc., **79**, 76, 80 (1901).
2 J. Chem. Soc., **59**, 966 (1891).
3 Bull. Soc. Chim.; [III], **19**, 120 (1898).
4 J. Chem. Soc., **79**, 76 (1901).

The acid purified by crystallisation from acetic acid was found to melt at 190°. Converting it into the ammonium salt, its analysis and optical determination were carried on, with the following results :

0·4098 grm. substance gave 0·3896 grm. BaSO$_4$.

	Calc. for C$_{10}$H$_{19}$O$_4$SN.	Found.
Sulphur	13·61	13·06

A solution of 0·3981 grm. of the ammonium salt made up to 25 c.c. with water at 25° gave $a_D^{25} = -0.68°$ in a 20 cm. tube ; whence $[a]_D^{25} = -21.35°$. Pope and Harvey gave for its value $[a]_D = -20.7°$.

3. *Dextro-Bromocamphorsulphonic Acid and its Salts.*

The following experiments were conducted according to the method suggested by Marsh and Cousins.[1] To prepare the acid, 100 grms. dextro-bromocamphor purified by recrystallisation from methylated alcoholic solution and dissolved in 200 grms. pure dried chloroform were mixed with 75 grms. of fresh distilled chlorosulphonic acid prepared after Muller,[2] and the whole contents of a vessel were heated over a water bath for 15 hours. The brown solution was then poured into cold water, and the chloroform separated from the brownish-yellow aqueous part. The acidic aqueous solution was neutralized with calcium carbonate ; removeing calcium sulphate by filtration, a brownish-yellow solution containing crude calcium bromocamphorsulphonate was obtained The calcium salt was converted into the ammonium salt which crystallized out from hot water in white needle-shaped crystals.

The analysis of the pure ammonium salt gave the following value for sulphur :

0·1996 grm. substance gave 0·1274 grm. BaSO$_4$.

	Calc. for C$_{10}$H$_{18}$O$_4$NSBr.	Found.
Sulphur	9·76	9·74

A solution of 1·27 grm. of the ammonium salt made up to 25 c.c. with water at 25°, gave $a_D^{25} = +8.69°$ in a 20 cm. tube, whence $[a]_D^{25} = +85.54°$ and $[M]_D^{25} = +280.59°$, while Marsh and Cousins[3] gave $[a]_D^{25} = +87.52°$ and Kipping and Pope[4] $[a]_D^{25} = +84.78°$ for its specific rotation in the aqueous solution.

1 J. Chem. Soc., **59**, 970 (1891).
2 Ber. D. Chem. Ges., **6**, 227 (1878).
3 J. Chem. Soc., **59**, 966 (1891).
4 *Ibid.*, **67**, 354 (1895).

Starting from the ammonium salt the author has prepared the barium salt, fiee acid and silver salt successively, and used the silver salt for the iesolution of the asymmetiic ammonium iodide.

4. Resolution of Methyl n-Propyl Phenyl Benzyl Ammonium Iodide into its Optically Active Components.

A. Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Dextro-Bromocamphorsulphonate,

$$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N \cdot O \cdot SO_2 \cdot C_{10}H_{14}Bi O, CH_3 \cdot CO_2 \cdot C_2H_5.$$
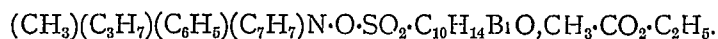
One molecule of methyl n-propyl phenyl benzyl ammonium iodide prepared from methyl n-propyl aniline and benzyl iodide, was mixed with one molecule of anhydrous silver dextro-bromocamphorsulphonate, and boiled in a mixture of acetone and ethyl acetate for 2 houis over a water bath. After the reaction has been completed, the silver iodide was separated, the solvent distilled off and a brown syrupy residue allowed to stand, solidifing in a crystalline mass. The crystalline mass, thus formed, was dissolved in acetone, from which white ciystals were obtained. The crystals purified by recrystallisation from acetone, melted at 141–142° and were analysed:

0·235 grm. of the substance gave 0·1028 grm. BaSO$_4$.

	Calc. for C$_{27}$H$_{36}$O$_4$NSBr.	Found.
Sulphur	5·81	6·01

The rotatory power of the pure preparations a and b was determined in the aqueous solutions with the following results:

a). A solution of 0·866 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +3·50°$ in a 20 cm. tube; whence $[a]_D^{25} = +51·68°$ and $[M]_D^{25} = +284·2°$.

b). A solution of 0·7021 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +3·15°$ in a 20 cm. tube; whence $[a]_D^{25} = +56·26°$.

From the analytical results and polaiimetric measurements above stated, it is quite evident that the substance would be the racemic one from which racemic methyl n-propyl phenyl benzyl ammonium iodide has been derived as will be shown in the following polarimetric experiment:

A solution of 0·1084 grm. of the iodide made up to 25 c c. with alcohol at 25°, gave $a_D^{25} = +0·02°$ in a 20 cm. tube, whence $[a]_D^{25} = +1·4°$.

By the fractional crystallisation of the racemic bromocamphorsulphonate in ethyl acetate, lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate separated out in white needle-shaped crystals, and the mother liquor, on evaporation, yielded platy crystals; adding ether to the second filtrate, the third crop in the hygroscopic crystals and finally a syrupy residue were obtained. To the latter dissolved in water, was added an excess of a potassium iodide solution to, precipitate the base as iodide.

The rotatory power of the crystallized fractions above mentioned, were determined in their aqueous solutions, and the results will be shown as follows:

1. *The first fraction*, recrystallized from ethyl acetate three times:

A solution of 1·1807 grm. substance made up to 25 c.c. with water at 25°, gave $[a]_D^{25} = -0·14°$ in a 20 cm. tube, whence $[a]_D^{25} = -1·48°$.

2. *The second fraction:*

A solution of 0·5738 grm. of the substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = -0·04$ in a 20 cm. tube; whence $[a]_D^{25} = -0·09°$.

3. *The third fraction:*

A solution of 0·7836 grm. of the substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +0·15$ in a 20 cm. tube; whence $[a]_D^{25} = +2·07°$.

In order to fix the optical rotation constant, the first crop was re-crystallized several times from ethyl acetate, and the rotatory powers of the purified different preparations were determined in aqueous solutions and the results will be seen in the following statements:

a). A solution of 0·8157 grm. of the substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = -0·16°$ in a 20 cm. tube; whence $[a]_D^{25} = -2·45°$.

b). A solution of 0·6316 grm. of the substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = -0·13°$ in a 20 cm. tube; whence $[a]_D^{25} = -2·57°$.

Pure lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate has the mean specific rotatory power $[a]_D^{25} = -2·51°$ in an aqueous solution, but no definite melting point; it was soluble in acetone, ethyl acetate, alcohol and water but not in ether.

Since the crystals when heated at 80° became opaque, the author was led to the suspicion that they might contain solvent in the molecule.

When 1·419 grm. of the pure crystals obtained from the ethyl acetate solution, were heated in an air bath at 80° for 5 hours, it was observed that the loss of weight amounted to 0·1821 grm. which just correspond to the calculated value of ethyl acetate of crystallisation (1 mole.) for one molecule of the active substance.
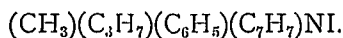
$$\text{Calc. for } C_{29}H_{36}O_4NSBr.CH_3CO_2C_2H_5. \qquad \text{Found.}$$

Ethyl acetate   13·79   12·83

The substance gave the following analytical result :
0·27 grm. the substance gave 0·0385 grm. BaSO$_4$.

$$\text{Calc. for } C_{31}H_{42}O_6NSBr. \qquad \text{Found.}$$

Sulphur   5·02   5.02

B.   Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Iodide,

$$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NI.$$

Adding a potassium iodide solution to an aqueous solution of pure dextro methyl n-propyl phenyl benzyl ammonium dextro-bromocamphor-sulphonate, white crystalline precipitate of lævo methyl n-propyl phenyl benzyl ammonium iodide soon began to separate out; it was recrystallized from hot alcohol in a dark place with the protection of optical inversion by the sun light. The platy crystals, thus obtained, were *soluble in alcohol and acetone, and most easily in chloroform,* and melted at 146–147°.

The analysis and determination of the rotatory power of the substance were made, and the results will be shown as follows;
0·2481 grm. of the substance gave 0·1592 grm. AgI.

$$\text{Calc. for } C_{17}H_{22}NI. \qquad \text{Found.}$$

Iodine   34·62   34·68

a). A solution of 0·991 grm. iodide made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0.68°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -93.31°$.
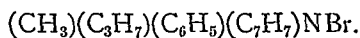
b). A solution of 0·1028 grm. iodide made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0.77°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -93.63°$.

c). A solution of 0·1016 grm. iodide made up to 25 c.c. with

alcohol at 25°, gave $a_D^{25} = -0.76°$ in a 20 cm. tube; whence $[a]_D^{25} = -93.51°$.

Consequently the mean specific rotatory power of the iodide is $[a]_D^{25} = -93.48°$.

C. *Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Bromide,*

$$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NBr.$$

The substance prepared from pure dextro methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate and potassium iodide, crystallized in rhombic prisms from alcoholic solution. It melts at 166–167° and is more soluble in organic solvents than the corresponding iodide.

The analytical result of the substance will be mentioned below:

0.2244 grm. substance gave 0.1317 grm. AgBr.

	Calc. for $C_{17}H_{22}NBr$.	Found.
Bromine	25.00	24.98

The determination of the rotatory power was conducted with the purified substance, and the result is as follows:

A solution of 0.116 grm. bromide made up to 25 c.c. with alcohol at 25°, gave $a_D^{22} = -1.06°$ in a 20 cm. tube; whence $[a]_D^{25} = -114.2°$.

D. *Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Chloroplatinate,*

$$[(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N \cdot Cl]_2Pt \cdot Cl_4.$$
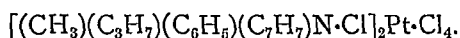
Lævo methyl n-propyl phenyl benzyl ammonium hydroxide obtained by the interaction of pure lævo methyl n-propyl phenyl benzyl ammonium iodide and moist silver oxide, was neutralized with hydrochloric acid; the ammonium chloride thus formed was converted into the double salt with platinic chloride.

The double salt recrystallized from a large quantity of hot water, was yellow fine needle-shaped crystals, melting at 163.5–164°, while the corresponding inactive salt melts at 159–160°.

The salt, dried at 100°, was analysed and gave the following result:

0.1824 grm. double salt gave 0.039 grm. Pt on ignition.

	Calc. for $C_{34}H_{44}N_2Cl_6Pt$.	Found.
Platinum	22.01	21.49

E.   Dextro Methyl n-Propyl Phenyl Benzyl Ammonium Iodide,

$$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N \cdot I.$$

Evaporating the filtrate from lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate, there was left a syrupy residue from which dextro methyl n-propyl phenyl benzyl ammonium iodide was obtained in white crystalline form.   It crystallizes from alcohol in white plates which melt at 146–147° as observed in its antipode.

The analysis of the substance gave the following result:

0·3449 grm. substance gave 0·2182 grm. AgI.

	Calc. for $C_{17}H_{22}NI$.	Found.
Iodine	34·62	34·19

a).   A solution of 0·098 grm. iodide made up to 25 c.c. with alcohol at 25°, gave $a_D^{25} = +0\cdot70°$ in a 20 cm. tube; whence $[a]_D^{25} = +89\cdot28°$.

b).   A solution of 0·0977 grm. iodide recrystallized from alcohol, made up to 25 c.c. with alcohol at 25°, gave $a_D^{25} = +0\cdot71$ in a 20 cm. tube; whence $[a]_D^{25} = +90\cdot84°$.

F.   Dextro Methyl n-Propyl Phenyl Benzyl Ammonium Chloroplatinate,

$$[(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N \cdot Cl]_2 \cdot PtCl_4.$$
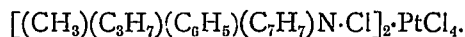
The double salt with platinic chloride prepared from dextro methyl n-propyl phenyl benzyl ammonium iodide by the usual method, consists of yellow fine needle-shaped crystals which melt at 163–164°.   Its analysis gave the following result:

0·1906 grm. of the double salt gave 0·0416 grm. Pt on ignition.

	Calc. for $C_{31}H_{44}N_2Cl_6Pt$.	Found.
Platinum	22·01	21·84

5.   Resolution of Methyl Allyl Phenyl Benzyl Ammonium Iodide into its Optically Active Components.

A.   a Methyl Allyl Phenyl Benzyl Ammonium Dextro-Bromocamphorsulphonate,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot O \cdot SO_2C_{10}H_{14}BrO.$$

a Methyl allyl phenyl benzyl ammonium iodide prepared from methyl benzyl aniline and allyl iodide, was boiled with an equi-

molecular silver dextro-bromocamphorsulphonate in an acetone-ethyl acetate solution on a water bath for 2 hours.

By the recrystallisation of the reaction product three times from acetone, α methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate was obtained in white plates which melt at 133–134°.

It is soluble in acetone, ethyl acetate, alcohol and water, dried at 100° it was analysed:

0 2054 grm. substance gave 0·082 grm. BaSO$_4$.

	Calc. for $C_{27}H_{34}O_4NSBr$.	Found.
Sulphur	5·84	5·48

a). A solution of 0·94 grm. of the substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +3·86°$ in a 20 cm. tube; whence $[a]_D^{25} = +51·33°$.

b). A solution of 0·8142 grm. of the substance recrystallized from acetone, made up to 25 c.c. with water at 25°, gave $a_D^{25} = +3·36°$ in a 20 cm. tube; whence $[a]_D^{25} = +51·56°$.

c). A solution of 0·3493 grm. of the substance (the sample b recrystallized three times from ethyl acetate) made up to 25 c.c. with water at 25°, gave $a_D^{25} = +1·37°$ in a 20 cm. tube; whence $[a]_D^{25} = +49·63°$.

d). A solution of 0·263 grm. of the substance (the sample c recrystallized 4 times from ethyl acetate) made up to 25 c.c. with water at 25°, gave $a_D^{25} = +1·10°$ in a 20 cm. tube; whence $[a]_D^{25} = +52·28°$.

The ammonium iodide derived from the ammonium bromocamphorsulphonate was observed to be optically inactive.

B. γ *Methyl Allyl Phenyl Benzyl Ammonium Dextro-Bromocamphorsulphonate,*

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot O \cdot SO_2 \cdot C_{10}H_{14}BrO.$$

By the interaction of γ methyl allyl phenyl benzyl ammonium iodide, prepared from methyl allyl aniline and benzyl iodide, and silver dextro-bromocamphorsulphonate, γ methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate was obtained, which crystallizes in white crystals from acetone. It melts at 135–136°, and its analysis gave the following result.

0·2251 grm. of the substance gave 0·0941 grm. BaSO$_4$.

	Calc. for $C_{27}H_{34}O4NSBr$.	Found.
Sulphur	5·84	5·74

The optical measurement of 2 prepaiations, a and b was conducted, and the results aie as follows:

a). A solution of 1·0086 grm. of the substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +4.01°$ in a 20 cm. tube; whence $[a]_D^{25} = +50.81°$.

b). A solution of 0·7699 gim. of the substance obtained by the crystallisation of the pieparation a, made up to 25 c.c. with water at 25°, gave $a_D^{25}+ = 3.25°$ in a 20 cm tube; whence $[a]_D^{25} = +52.77°$.

C. a Dextro Methyl Allyl Phenyl Benzyl Ammonium Dextro-Camphorsulphonate,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N·O·SO_2C_{10}H_{15}O.$$
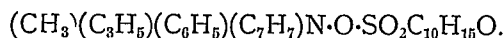
In June, the author attempted the resolution of a methyl allyl phenyl benzyl ammonium iodide by means of dextro-camphorsulphonate[1], and on standing the acetone solution of the reaction product in a desiccater, kept in a dark and cold place for a week, the crystals began to separate out from the solution, but its yield was very poor. The substance recrystallized five times from acetone consisted of colourless needles which were found to melt at 161–162°. They are soluble in water, acetone, ethyl acetate and alcohol; their analysis gave the following result:

0·178 grm. substance gave 0·0878 grm. BaSO₄.

	Calc. for $C_{27}H_{33}O_4NS$.	Found.
Sulphur	6·82	6·78

The rotatory power of the substance was determined in an aqueous solution, with the following results:

a). A solution of 0·8525 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +3.17°$ in a 20 cm. tube; whence $[a]_D^{25} = +46.48°$.

b). A solution of 0·5327 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +2.02°$ in a 20 cm. tube; whence $[a]_D^{27} = +47.40°$.

Adding potassium iodide to the mother liquor separated from dextro methyl-allyl phenyl benzyl ammonium d-camphorsulphonate, lævo methyl allyl phenyl benzyl ammonium iodide was obtained in an impuie state;

---

[1] Pope and Harvey, J. Chem. Soc. **75,** 1127 (1899).

the substance recrystallized from ethyl alcohol was found to melt at 127–128° and the specific rotatoly power to be $[a]_D^{25} = -29.33°$ in alcoholic solution.

In the second expeiiment peiformed in winter, the yield of iacemic methyl allyl phenyl benzyl ammonium dextio-camphorsulphonate was more fruitful than in the previous experiment ; it was macerated with ethyl acetate according to Pope and Harvey[1].

The first crop consisted of colouiless needles ; after evaporating the mother liquor to a small bulk, and then on standing it over sulphuric acid, we get the second crop.

From the mother liquor of the second crop, rhombic crystals deposited as the third ciop. Evaporating the residual liquor almost to dryness, and then adding a large quantity of ether, hygroscopic crystals were formed, and finally the syrupy residue was dissolved in watei and converted into the iodide.

For each fraction the optical measurement was made in its aqueous solution and the results will be mentioned below :

The first fraction :

The crystals obtained by recrystallizing from ethyl acetate 5 times melted at 162°, and the optical iotation for each of 4 pure pieparations a, b, c and d was determined.

a). A solution of 0·2082 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +0.77°$ in a 20 cm. tube ; whence $[a]_D^{25} = +46.23°$·

b). A solution of 0·1423 grm. substance obtained by the recrystallisation twice from acetone, made up to 25 c.c with water at 25°, gave $a_D^{25} = +0.54°$ in a 20 cm. tube; whence $[a]_D^{25} = +47.43°$.

c) A solution of 0·3132 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +1.17°$ in a 20 cm. tube; whence $[a]_D^{25} = +46.67°$.

d). A solution of 0·3176 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{26} = +1.20°$ in a 20 cm. tube ; whence $[a]_D^{25} = +47.23°$.

The mean value is, therefore, $[a]_D^{26} = +46.91°$, while Jone[2] in one hand and Pope and Harvey[3] on the other gave $[a]_D = +46.8$ and $[a]^D = +46.6°$ iespectively.

---

1 *J oc. cit.*

2 *Loc. cit.*

3 *Loc. cit.*

The second fraction :

A solution of 0·3168 grm. substance made up to 25 c.c. with water at 25°, gave $v_D^{25} = +0·97°$ in a 20 cm. tube ; whence $[a]_D^{25} = +38·27°$
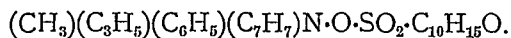
The third fraction :

A solution of 0·1983 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = 0$ in a 20 cm. tube.

The fourth fraction :

A solution of 0·2382 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = -0·07°$ in a 20 cm. tube ; whence $[a]_D^{25} = -1.32°$.

D.　γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Dextro Cᴀmphorsulphonate,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N·O·SO_2·C_{10}H_{15}O.$$

A.　Equimolecular mixture of γ methyl allyl phenyl benzyl ammonium iodide and silver dextro-camphorsulphonate was heated in a acetone-ethyl acetate solution for 2½ hours on a water bath. From the reaction product, dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate was obtained in the like manner as was descɪibed in the case of the α compound, the substance crystallizing from acetone in white needles and melting at 162°.

It is soluble in alcohol, acetone, ethyl acetate and water but not in ether. The sulphur contents and the rotatory power of the substance were determined with the following results :

0·2101 grm of the substance gave 0·1043 grm. BaSO₄

	Calc. for $C_{27}H_{35}O_4NS$.	Found.
Sulphur	6·82	6·82

a).　A solution of 0·8444 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +3·87°$ in a 20 cm. tube; whence $[a]_D^{25} = +57·29°$.

b).　A solution of 0·9161 grm. the substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = +4·37°$ in a 20 cm. tube ; whence $[a]_D^{25} = +59·63°$. The mean value of the rotatory power is, therefore, accounted for as $[a]_D^{25} = +58·46°$.

The filtrate from the crystals of dextro ammonium dextro-camphorsulphonate was dissolved in water, and then potassium iodide solution added to transform the base contained in it into the iodide whose rotatory power in an alcoholic solution has been observed to be $[a]_D^{25} = -25·0°$.

B. As the second experiment, the racemic dextro-camphorsul-phonate was subjected to the fractional crystallisation in ethyl acetate, and the pure γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained, consisted of white needles which melt at 163–164°. The deter mination of the rotatory power of the substance was conducted with the purified different preparations a, b and c in their aqueous solutions.

a). A solution of 0·2532 grm. substance made up to 25 c c with water at 25°, gave $a_D^{25} = +$ 1·20° in a 20 cm. tube; whence $[a]_D^{25} = +$ 59·24°.

b). A solution of 0·2342 grm. substance obtained by the recı ystal-lisation of the preparation a) from acetone, made up to 25 c.c. with water at 25°, gave $a_D^{25} = +$ 1·10° in a 20 cm. tube; whence $[a]_D^{25} = +$ 58·71°.

c). A solution of 0·3572 grm. of the same preparation as used in b) made up to 25 c.c. with water at 25°, gave $a_D^{25} = +$ 1·67° in a 20 cm. tube; whence $[a]_D^{25} = +$ 58·44°.

The mean value of the specific rotatory power is, therefore, accounted for as $[a]_D^{25} = +$ 58·66°.

E a Lævo Methyl Allyl Phenyl Benzyl Ammonium Lævo Camphorsulphonate,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot O \cdot SO_2 \cdot C_{10}H_{15}O.$$
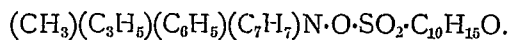
A. By the interaction of 5 grm. raw a lævo methyl allyl phenyl benzyl ammonium iodide and 5 grm. silver lævo-camphorsulphonate, 2·5 grm. lævo methyl allyl phenyl benzyl ammonium lævo-camphorsul-phonate was obtained in pure state.

The substance recrystallized from acetone three times, melts at 160–161°, and has the same chemical and physical properties as its enantiomorphous salt. The specific rotatory power in its aqueous solu-tion was determined to be opposite in its sign to that of its antipode but with the same magnitude as will be shown in the following state-ments:

a). A solution of 0·3069 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = -$ 1·14° in a 20 cm. tube; whence $[a]_D^{25} = -$ 46·43°.

b). A solution of 0·2927 grm. substance made up to 25 c.c. with

water at 25°, gave $a_D^{25} = -1\cdot09^\circ$ in a 20 cm. tube; whence $[a]_D^{25} = -46\cdot55^\circ$.

The analytiscal result is as follows:

0·3097 grm. of the substance gave 0·1533 grm. BaSO$_4$,

	Calc. for C$_{27}$H$_{35}$O$_4$NS.	Found.
Sulphur	6·82	6·80

B. The substance, also, prepared from 6 grm. a methyl allyl phenyl benzyl ammonium iodide and 6 grm. silver lævo camphoisulphonate in an acetone-ethyl acetate solution, and its yield in pure state was found to be about 1 grm.

The pure preparation melting at 162–163° gave the following value of the optical rotatory power in an aqueous solution.

A solution of 0·2249 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = -0\cdot84^\circ$ in a 20 cm. tube; whence $[a]_D^{25} = -46\cdot69^\circ$.

F. γ Lævo Methyl Allyl Phenyl Benzyl Ammonium Lævo-Camphorsulphonate.

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N\cdot O\cdot SO_2\cdot C_{10}H_{15}O.$$
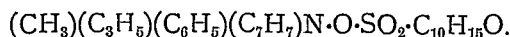
A. 4 grm. crude γ l methyl allyl phenyl benzyl ammonium iodide (its specific rotatoiy power in alcohol solution being $[a]_D^{25} = -25\cdot0^\circ$) was made to react with 4 grm. silver l-camphorsulphonate in an acetone-ethyl acetate solution, and 1 grm. pure γ l methyl allyl phenyl benzyl ammonium l-camphorsulphonate was obtained. It crystallizes from acetone in white needle-shaped crystals which melt at 163–164°, possessing all the other same chemical and physical properties as those of its antipode.

0·357 grm. of ths substance, gave 0·1792 grm. BaSO$_4$ by analysis.

	Calc. for C$_{27}$H$_{35}$O$_4$NS.	Found.
Sulpdur	6.82	6.89

A solution of 0·2581 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = -1\cdot09^\circ$ in a 20 cm. tube; whence $[a]_D^{25} = -55\cdot70^\circ$.

A solation of 0·2422 grm. substance made up to 25 c.c. with water at 25°, gave $a_D^{25} = -1\cdot09^\circ$ in a 20 cm. tube; whence $[a]_D^{25} = -56\cdot21^\circ$.

B. Pure γ lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was also prepared by the interaction of 6·5 grm. γ racemic methyl allyl phenyl benzyl ammonium iodide and 6 grm. silver lævo camphorsulphonate, and its yield was found to be about 1·5 grm.

The melting point of the substance was observed to be 162–163° and its specific rotatory power was determined in an aqueous solution.

A solution of 0·2244 grm. substance made up to 25 c.c. with water at 25°C, gave $\alpha_D^{25} = -1\cdot02°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -56\cdot82°$.

G. α Dextro Methyl Allyl Phenyl Benzyl Ammonium Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I.$$
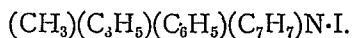
A. By adding potassium iodide to an aqueous solution of pure α dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate prepared in the first experiment, α dextro methyl allyl phenyl benzyl ammonium iodide precipitated as a white crystalline powder, which was separated from the mother liquor and recrystallized from an alcoholic solution in a dark place.

The white needle-shaped crystals melt at 135–136° with some decomposition and were found to have the same chemical properties with its inactive isomer.

A solution of 0·1211 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\sigma_D^{25} = +0\cdot50°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51\cdot61°$.

B. The pure active iodide also prepared from the active ammonium dextro-camphorsulphonate obtained in the second experiment, consists of white needles melting at 135–136°.

The specific rotatory powers of the two preparations were determined in the alcohol and chloroform solutions with the following results:

a). A solution of 0·1254 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0\cdot52°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51\cdot84°$.

b). A solution of 0·2102 grm. substance made up to 25 c.c. with chloroform at 25°, gave $\alpha_D^{25} = +0\cdot92°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +58\cdot28°$.

Its analysis gave the result recorded below:
0·22 grm. substance gave 0·1398 grm. AgI.

	Calc. for $C_{17}H_{20}NI$.	Found.
Iodine	34·79	34·34

H. γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I.$$

A. The substance was prepared by the action of potassium iodide upon pure γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained in the first experiment, and that crystallized from alcohol in a dark place, has the same melting point (134–135°), crystalline form and chemical properties as those of the a compound.

The specific rotatory power of the substance was determined in an alcohol solution.

A solution of 0·1254 grm. substance made up to 25 c.c. with alcohol at 25°, gave $a_D^{25} = +0.64°$ in a 20 cm. tube; whence $[a]_D^{25} = +63.64°$.

B. The active iodide obtained from the corresponding active ammonium dextro-camphorsulphonate prepared in the second experiment, melts at 135–136° in a capilary tube.

Its analysis and polarimetric measurement gave the following results :

0·2235 grm. substance gave 0·1438 grm. AgI.

	Calc. for $C_{17}H_{20}NI$.	Found.
Iodine	34.79	34.68

A solution of 0·1281 grm. substance made up to 25 c.c with alcohol at 25°, gave $a_D^{25} = +0.65°$ in a 20 cm. tube; whence $[a]_D^{25} = +63.45°$.

A solution of 0·2112 grm. substance made up to 25 c.c. with chloroform at 25°, gave $a_D^{25} = +1.25°$ in a 20 cm. tube; whence $[a]_D^{25} = +73.98°$.

It is noteworthy that the iodide of γ form has a higher specific rotatory power than that of a form just as γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate has a higher value than the corresponding a compound.

I. a Lævo Methyl Allyl Phenyl Benzyl Ammonium Iodide,

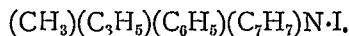$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N·I.$$
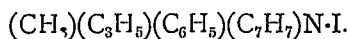
The substance formed by the interaction of potassium iodide and pure a lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate, crystallizes in white plates from alcohol in a dark place.

It melts at 134–135° and its chemical properties are same as those of its antipode.

A solution of 0·1047 grm. substance made up to 25 c.c. with alcohol at 25°, gave $a_D^{25} = -0.43°$ in a 20 cm. tube; whence $[a]_D^{25} = -51.34°$.

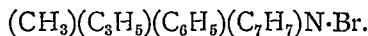### J.   γ *Lævo Methyl Allyl Phenyl Benzyl Ammonium Iodide,*

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I.$$

The iodide prepared from the corresponding pure γ lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate, crystallizes in white plates melting at 135–135 5°, and all other properties are same as those of the α isomer.

A solution of 0·1062 grm. substance made up to 25 c.c. with alcohol at 25°, gave $a_D^{25} = -0.54°$ in a 20 cm. tube ; whence $[a]_D^{25} = -63.14°$.

K.   α *Dextro Methyl Allyl Phenyl Benzyl Ammonium Bromide,*

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot Br.$$

By the action of potassium bromide upon pure α dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, α dextro methyl allyl phenyl benzyl ammonium bromide was obtained, which crystallizes in colourless rhombic prisms from aqueous alcohol in a dark place, and melts at 155–156°. It is more soluble in organic solvents than the corresponding iodide.
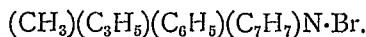
0·18 grm. substance gave 0·1054 grm. AgBr.

	Calc. for $O_{17}H_{20}NBr$.	Found.
Bromine	25·15	24·75

A solution of 0·1075 grm. substance made up to 25 c.c. with alcohol at 25°, gave $a_D^{25} = +0.57°$ in a 20 cm. tube ; whence $[a]_D^{15} = +67.44°$.

A solution of 0·116 grm. substance made up to 25 c.c. with alcohol at 25°, gave $a_D^{25} = +0.63°$ in a 20 cm. tube ; whence $[a]_D^{25} = +67.89°$.

L.   γ *Dextro Methyl Allyl Phenyl Benzyl Ammonium Bromide,*

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot Br.$$

The substance was prepared by the action of potassium bromide upon pure γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate.

It crystallizes in colourless rhombic prisms from aqueous alcohol and melts at 155–156°.

It is soluble in alcohol, acetone and chloroform.

The analysis of the substance is as follows :

0·21 grm. substance gave 0·1249 grm. AgBr.

	Calc. for $C_{17}H_{20}NBr$.	Found.
Bromine	25·15	25·31

A solution of 0 136 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0.89°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +81.80°$.

A solution of 0·11 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0.77°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +82.95°$.
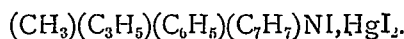
M. α Lævo Methyl Allyl Phenyl Benzyl Ammonium Bromide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot Br.$$
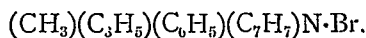
The bromide obtained from α lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate consists of colourless rhombic prisms, and its melting point was found to be 149–150° showing the lower value than that of its antipode. Its optical rotatory power was determined.

A solution of 0·1185 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0.60°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -63.29°$.

N. α Dextro Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI, HgI_2.$$

The substance was prepared by the method of Hope and Harvey[1] by the interaction of equimolecular quantities of pure α dextro methyl allyl phenyl benzyl ammonium iodide and mercuric iodide.

It is soluble in acetone, ethylacetate and alcohol, and crystallizes in yellow plates from ethyl acetate and melts at 119–120°.

A solution of 0·112 grm. substance made up to 25 c.c. with ethyl acetate at 26°, gave $\alpha_D^{25} = +0.22°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = + 24.56°$.

A solution of 0·1142 grm. substance made up to 24 c.c. with ethyl acetate at 25°; gave $\alpha_D^{25} = +0.23°$ in a 20 cm. tube; whence $\alpha_D^{25} = +25.17°$.

P. γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I \cdot HgI_2.$$

---
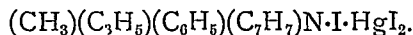
[1] *Loc. cit.*

The substance was prepared from γ dextro methyl allyl phenyl benzyl ammonium iodide and mercuric iodide, and crystallizes in yellow plates from ethyl acetate. Its melting point was found to be 120–121°.

A solution of 0·123 grm. substance 'made up to 25 c.c. with ethyl acetate at 25°, gave $a_D^{25} = +0.39°$ in a 20 cm. tube; whence $[a]_D^{25} = +39.63°$.

A solution of 0·1006 grm. substance made up to 25 c.c. with ethyl acetate at 25°, gave $a_D^{25} = +0.32°$ in a 20 cm. tube; whence $[a]_D^{15} = +39.39°$.
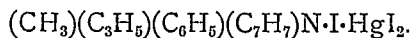
Q. *a Lævo Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide,*

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I \cdot HgI_2.$$
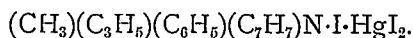
The substance prepared from the corresponding iodide by the usual method consists of yellow plates. It is soluble in alcohol and ethyl acetate, and melts at 119–120°.

A solution of 0·114 grm. substance made up to 25 c.c. with ethyl acetate at 25°, gave $a_D^{24} = -0.22°$ in a 20 cm. tube; whence $[a]_D^{25} = -24.12°$.
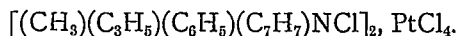
R. *γ Lævo Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide,*

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot I \cdot HgI_2.$$

The substance prepared by the action of mercuric iodide upon the corresponding lævo iodide, crystallizes in yellow plates from ethyl acetate and melts at 120°.

A solution of 0·1219 grm. substance made up to 25 c.c. with ethyl acetate at 25°, gave $a_D^{25} = -0.39°$ in a 20 cm. tube; whence $[a]_D^{25} = -39.99°$.

S. *a Dextro Methyl Allyl Phenyl Benzyl Ammonium Chloroplatinate,*

$$[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NCl]_2, PtCl_4.$$

The chloride obtained by treating the aqueous solution of pure a dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate with sodium chloride solution, was converted into its platinum double salt by the usual method. It crystallizes in yellow fine needles from hot aqueous solution, and melts at 149–150°.

The substance dried at 100° was analysed.

0·2526 grm. double salt gave 0·0565 grm. Pt on ignition.

	Calc. for $C_{34}H_{40}N_2Cl_6Pt$.	Found.
Platinum	22·08	22·40

T. γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Chloroplatinate,

$$[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N \cdot Cl]_2PtCl_4.$$
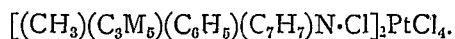
The substance was prepared from the chloride formed from γ dextro methyl allyl phenyl benzyl ammonium dextro camphorsulphonate, and crystallizes in yellow fine needles from hot aqueous solution. Its melting point was found to be 148–149°.

The analytical result of the substance is as follows:

0·1174 grm. substance gave 0·0264 grm. Pt on ignition.

	Calc. for $C_{34}H_{40}N_2Cl_6Pt$.	Found.
Platinum	22·08	22·49