VIII.—*Studies in Optical Superposition. Part VIII. The* l-*Menthylamine, Brucine, and Strychnine Salts of Mucic and* allo*Mucic Acid.*

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In Part VII (J., 1926, 3224) and previous papers attempts were made to attack the problem of optical superposition by what seemed the simplest method capable of yielding positive results, namely, the preparation of esters formed from the *d*-, the *l*-, and the *i*-modifications of tartaric acid or some of its derivatives, with an active alcohol such as *l*-menthol or one of the methyl-*n*-hexylcarbinols. If the principle of optical superposition really holds, the mean of the rotations of such *d*- and *l*-compounds should be identical with that of the *i*-compound. This method sometimes presents considerable practical difficulties, and of course involves in the end result a possible summation of the experimental errors for the three different esters.

A method of obtaining further data on this problem would be the comparison of the rotations of esters of mucic and *allo*mucic acid, respectively, with active alcohols. These two acids are both optically inactive, their inactivity being due to compensation, in two different ways, of the activities due to the asymmetric carbon atoms. If the rotation of, say, *l*-menthyl mucate is different from that of *l*-menthyl *allo*mucate, this difference can hardly be ascribed to anything else than the different arrangement of the groups attached to the asymmetric carbon atoms in the mucic and *allo*mucic acids; and such a difference, we consider, would be a sound disproof of van 't Hoff's conception. Unfortunately, our attempts to prepare menthyl mucate and menthyl *allo*mucate by heating together the respective acids and the alcohol, under the influence of dry hydrogen chloride, have failed, but we have prepared some salts of these acids with active bases as described below. The salts of active acids are not so suitable for our purpose as the esters would have been; the results arrived at from rotation values obtained in aqueous solution, on the one hand, might easily be complicated by the influence of electrolytic dissociation, whilst, on the other, the solubility of such salts as we have been able to prepare is usually only slight in non-dissociating solvents. Nevertheless, we have determined the rotations of the brucine, the strychnine, and the *l*-menthylamine salts of mucic acid and of *allo*mucic acid, either in methyl alcohol or in benzyl alcohol. We prepared also the corresponding salts of nicotine, codeine, and morphine, but these were difficult to purify in a satisfactory manner and were not further examined. As a check on our results, the preparation of each salt and its optical examination were carried out twice; these preparations are indicated below as *A* and *B*.

allo*Mucic acid* was prepared according to Emil Fischer (*Ber.*, 1891, **24**, 2136) by heating mucic acid in aqueous pyridine solution in a copper autoclave. M. p. 172—173°.

Menthylamine Mucate.—To the acid (1 mol.) in hot water was added menthylamine (2 mols.), $\alpha_{5461}^{19^\circ}$ (homogeneous: $l = 100$ mm.) $-35{\cdot}31^\circ$, d 0·8574, $[\alpha]_{5461}^{19^\circ}$ $-41{\cdot}2^\circ$. This furnished a salt which, after two crystallisations from water, formed plates, m. p. 198° (decomp.) [Found: N, (*A*) 5·4, 5·4, (*B*) 5·4. $C_6H_{10}O_8,2C_{10}H_{21}N$ requires N, 5·4%]. $\alpha_{5461}^{19\cdot5^\circ}$ (methyl alcohol: $c = 1$; $l = 400$ mm.) $= -1{\cdot}29^\circ$ for *A* and $-1{\cdot}27^\circ$ for *B*.

Menthylamine allo*mucate* was prepared in the same way as the mucate. Fine needles, m. p. 173° (decomp.) [Found: N, (*A*) 5·5, 5·4, (*B*) 5·4%]. $\alpha_{5461}^{19\cdot5^\circ}$ (methyl alcohol: $c = 1$; $l = 400$ mm.) $=$ $-1{\cdot}26^\circ$ for *A* and $-1{\cdot}24^\circ$ for *B*.

The brucine salts were prepared similarly from purified brucine of m. p. 177—178° and $\alpha_{5461}^{17\cdot3}$ (ethyl alcohol: $c = 3{\cdot}008$; $l = 100$ mm).

$= -2{\cdot}97°$, whence $[\alpha]^{17{\cdot}3°}_{5461} = -98{\cdot}74°$; after recovery from the salts, its m. p. was 176° and $\alpha^{18°}_{5461}$ (ethyl alcohol: $c = 3{\cdot}008$; $l = 100$ mm. $= -2{\cdot}94°$, whence $[\alpha]^{18°}_{5461} = -97{\cdot}75°$.

Brucine mucate, crystallised twice from water, formed needles which commenced to froth about 150° [Found in specimens dried for a long time in a vacuum over sulphuric acid: N, (*A*) 5·6, 5·8, (*B*) 5·7. $2C_{23}H_{26}O_4,C_6H_{10}O_8$ requires N, 5·6%]. In benzyl alcohol ($c = 5$; $l = 400$ mm.), $\alpha^{17°}_{5461}$ for $A = +0{\cdot}27°$ and $\alpha^{20°}_{5461}$ for $B = +0{\cdot}23°$, whence $[\alpha]^{17°}_{5461}$ and $[\alpha]^{20°}_{5461} = +\,1{\cdot}35°$ and $+1{\cdot}15°$, respectively. After some time, a fine precipitate settled on the walls of the tube and the rotation altered.

Brucine allo*mucate* formed needles which, after two crystallisations from water, decomposed at 170°, softening at a lower temperature [Found: N, (*A*) 5·7, 5·8, (*B*) 5·7%]. In benzyl alcohol ($c = 5$; $l = 400$ mm.), $\alpha^{17°}_{5461}$ for $A = -0{\cdot}22°$ and $\alpha^{20°}_{5461}$ for $B = -0{\cdot}19°$, whence $[\alpha]^{17°}_{5461}$ and $[\alpha]^{20°}_{5461} = -1{\cdot}10°$ and $-0{\cdot}95°$, respectively.

The *strychnine* salts were prepared from purified strychnine of m. p. 284° and $\alpha^{20°}_{5461}$ (chloroform: $l = 100$ mm.; $c = 5{\cdot}02) = -8{\cdot}61°$, whence $[\alpha]^{20°}_{5461} = -171{\cdot}5°$; after recovery from the salts, its m. p. was unchanged and $[\alpha]^{19{\cdot}5°}_{5461} = -169{\cdot}7°$.

Strychnine mucate, twice recrystallised from water, formed fine needles which became brown at 200° and decomposed at 273°. The compound had previously been prepared by Ruhemann and Dufton (J., 1891, **59**, 750) [Found: N, (*A*) 6·35, 6·4, (*B*) 6·4. Calc. for $2C_{21}H_{22}O_2N_2,C_6H_{10}O_8$: N, 6·4%]. $\alpha^{17{\cdot}5°}_{5461}$ (benzyl alcohol: $l = 400$ mm.; $c = 3{\cdot}5$) for $A = +1{\cdot}11°$, whence $[\alpha]^{17{\cdot}5°}_{5461} = +7{\cdot}93°$, and $\alpha^{21{\cdot}5°}_{5461}$ (benzyl alcohol: $l = 400$ mm.; $c = 5$) for $B = +1{\cdot}06°$, whence $[\alpha]^{21{\cdot}5°}_{5461} = +\,7{\cdot}57°$.

Strychnine allo*mucate*, twice crystallised from water, formed needles turning brown at 189°, and decomposing at 269° [Found: N, (*A*) 6·4, 6·45, (*B*) 6·4%]. In benzyl alcohol ($c = 3{\cdot}5$; $l = 400$ mm.), $\alpha^{17{\cdot}5°}_{5461}$ for $A = +\,0{\cdot}99°$ and $\alpha^{21{\cdot}5°}_{5461}$ for $B = +\,0{\cdot}96°$, whence $[\alpha]^{17{\cdot}5°}_{5461}$ and $[\alpha]^{21{\cdot}5°}_{5461} = +7{\cdot}07°$ and $+6{\cdot}86°$, respectively.

The results of these experiments are tabulated:

Specific Rotation for Mercury Green Light. Temperature about 20°.

	Menthylamine.	*Δ*.	Brucine.	*Δ*.	Strychnine.	*Δ*.
First series.						
Mucic acid	−32·25°	0·75°	+1·35°	2·45°	+7·93°	0·86°
*allo*Mucic acid	−31·50		−1·10		+7·07	
Second series.						
Mucic acid	−31·75	0·75	+1·15	2·11	+7·57	0·71
*allo*Mucic acid	−31·00		−0·96		+6·86	

Regarding these results, it may be noted particularly that the rotations of the brucine and strychnine salts of mucic and *allo*mucic acid are remarkably low in view of the highly active character of the bases and the inactivity of the acids. This might well suggest the idea that in combination with certain active bases the asymmetric carbon atoms of the acid molecule no longer neutralise each other in pairs, but that the acid part of the molecule has become active and is contributing to the rotation. This, if it be the case, is, of course, in strong opposition to the principle of optical superposition. A similar observation was made in Part V of this series (J., 1924, **125**, 578), where the specific rotation, $[\alpha]^{17^\circ}_{5461}$, of *d-sec.*-octyl *i*-tartrate was found to be only 0·18°. The menthylamine salts show a similar tendency, but not so markedly.

It will be seen from the third column of the table that the difference found between the specific rotations of the menthylamine salts of mucic and *allo*mucic acid is only small, 0·75°, but it is the same in both series, and greater, although not much, than the difference which was found between the rotations for like salts of one of the acids in the two series of experiments. It is, therefore, presumably greater than the experimental error.

The difference for the brucine salts is also nearly the same in the two series of experiments, but it is specially remarkable that the two salts are active in opposite senses. This seems to be a really strong argument against the principle of optical superposition. With reference to the strychnine salts, it may be noted, firstly, that the rotations are both positive, and secondly, that although the absolute difference is not very great, it is at least twice the probable experimental error and fairly large in proportion to the actual rotations of the individual compounds.

Thus, although the results for the menthylamine and strychnine salts are hardly as definite as might be desired, they certainly do not seem to support the idea that the configuration of mucic acid has exactly the same effect as that of *allo*mucic acid in determining the rotation of compounds formed from these acids and one and the same active base, whilst the results with the brucine salts are definitely in conflict with van 't Hoff's supposition.

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