L.—*Derivatives of Taurine. Part II.*

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THE preparation of trimethyltaurine by the action of a concentrated alcoholic solution of trimethylamine on the corresponding salt of β -chlorethylsulphonic acid has been already described (Trans., 1885, 372). I have since then made larger quantities of this substance, and carried out a few experiments with a view to determine whether trimethyltaurine is to be regarded as the methyl ether of dimethyltaurine, $C_2H_4\langle\begin{smallmatrix} NMe_2 \\ SO_2 \cdot OMe \end{smallmatrix}\rangle$, as is warranted by its synthetical formation, or as a compound containing pentad nitrogen, $C_2H_4\langle\begin{smallmatrix} NMe_3 \\ -SO_2- \end{smallmatrix}\rangle O$, analogous to trimethylglycocine, $C_2H_4\langle\begin{smallmatrix} NMe_3 \\ -CO_2- \end{smallmatrix}\rangle O$ (betaïne).

Decomposition of Trimethyltaurine with Alkalis.

15 grams of pure trimethyltaurine were dissolved in water, 20 grams of crystallised barium hydroxide added, and the mixture boiled in a flask until the steam was neutral to litmus-paper. The evolved gases were passed through a well-cooled U-tube containing dilute hydrochloric acid. This solution was afterwards distilled very carefully to one-third, the distillate twice distilled to one-third, potassium carbonate added, and again distilled; on testing this last distillate for methyl alcohol, no trace of it could be detected. A portion of the hydrochloric acid solution was then precipitated with platinum tetrachloride in three equal portions, and the dried platinochloride analysed with the following results:—

Fraction I.	1.	0.2474 gram substance, after ignition, yields	
		0.0909 gram platinum.	
	2.	0.3272 gram substance, after ignition, yields	
		0.1204 gram platinum.	
Fraction II.		0.2141 gram substance, after ignition, yields	
		0.0790 gram platinum.	
Fraction III.		0.243 gram substance, after ignition, yields	
		0.089 gram platinum.	

Calc. for trimethylammonium platinochloride, $2N(CH_3)_3HCl, PtCl_4$.		Found. Fraction.		
		I.	II.	III.
Pt.	36.81 p. c.	1. 36.74	36.89	36.62
		2. 36.79	—	—

These numbers leave no doubt that the gas evolved in the decomposition of trimethyltaurine is nothing but pure trimethylamine.

The residue in the flask containing the barium was heated to boiling with addition of more water, and then poured into a hot aqueous solution of 6.28 grams of concentrated sulphuric acid to remove the barium. After filtering off the barium sulphate, the strongly acid liquid was evaporated to a syrup on the water-bath, diluted with water, neutralised with potassium carbonate, and evaporated to dryness. The residue of crude potassium salt was well ground up with strong alcohol and digested with it for some time; on filtering the solution, silky needles were soon deposited which resembled potassium isethionate both in appearance and in being sparingly soluble in alcohol. The substance after recrystallisation was dried at 100°, and a complete analysis has shown that it consisted of the above salt in a state of purity.

I. 0.2054 gram substance burnt with CuO, PbCrO₄ and Cu gave 0.0590 gram H₂O and 0.1065 gram CO₂.

II. 0.205 gram substance fused with KHO and KNO₃ produced 0.3006 gram BaSO₄.

III. 0.1786 gram substance produced 0.095 gram K₂SO₄.

	Calculated for		Found.		
	potassium isethionate, OH·C ₂ H ₄ ·SO ₃ K.		I.	II.	III.
C ₂	24	14.63	14.14	—	—
H ₅	5	3.05	3.19	—	—
S	32	19.51	—	20.13	—
O	64	39.03	—	—	—
K	39	23.78	—	—	23.84
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	164	100.00			

From the above experiment it follows that trimethyltaurine when boiled with excess of alkali decomposes, according to the equation—

into trimethylamine and isethionic acid.

Cyanamide and Trimethyltaurine.

1.5 gram of trimethyltaurine and 0.37 gram cyanamide were allowed to stand in concentrated aqueous solution for some days, but no action took place: the mixture was afterwards heated in a sealed tube for four hours at 120°; on evaporating the liquid, a crystalline substance separated, insoluble in alcohol, and having a sweet taste:

an estimation of the nitrogen proved it to be unaltered trimethyltaurine.

0.1616 gram substance produced 12.3 c.c. moist nitrogen at 15° and 757.7 mm.

	Calculated for trimethyltaurine.	Found.
N	8.4	8.73

Hydriodic Acid and Trimethyltaurine.

So far as is known, compounds containing a methoxyl-group are decomposed by boiling with hydriodic acid, sp. gr. 1.68, with formation of methyl iodide, and the number of methoxyl-groups can be easily estimated by converting the methyl iodide into silver iodide as described in a recent paper by Zeisel (*Monats. Chem.*, **6**, 989; Abstr., 1886, 493). An experiment carried out precisely as described in this memoir gave no trace of methyl iodide after boiling for an hour; this appears to me to exclude the formula $\text{NMe}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_2 \cdot \text{OMe}$ (Trans., 1885, 367), as such a compound would undoubtedly yield methyl iodide under this treatment.

On heating trimethyltaurine with hydriodic acid in a sealed tube at 200°, a reaction takes place with separation of iodine; a strong odour of mercaptan compounds is produced, but no methyl iodide even under these circumstances could be detected.

Constitution of Taurine and its Alkyl-derivatives.

The ease with which trimethyltaurine is decomposed by alkalis into trimethylamine and isethionic acid seems to show conclusively that it must have a constitution very different from taurine and its derivatives with monamines and diamines, for had these compounds a similar constitution there is no reason why they should not also be decomposed by boiling with alkalis into monamines and diamines and isethionic acid, but it has already been shown that such is not the case (Trans., 1885, 368).

Again, the acid reaction of taurine, mono- and di-substituted taurines, and their behaviour with cyanamide strongly supports the above supposition, as all these substances unite with it forming well characterised crystalline compounds (Engel, *Ber.*, **8**, 1597; Dittrich, *J. pr. Chem.* [2], **18**; James, Trans., 1885, 373). Trimethyltaurine, on the other hand, is neutral to litmus, and forms no combination with cyanamide under similar conditions.

It follows then that trimethyltaurine is to be represented as a saturated compound containing pentad nitrogen and analogous to

trimethylglycocine (betaïne), whereas taurine and mono- and di-substituted taurines containing triad nitrogen are capable of combining with a molecule of cyanamide. The following general formulæ for taurine and its alkyl-derivatives,

would then be in accordance with the experimental evidence, and a trialkyl taurine, as a compound containing pentad nitrogen, would presumably decompose more or less readily into two molecules, which has been shown to be true of the trimethyl-derivative.

Action of Ammonia on β -Chlorethylsulphonic Chloride, $\text{Cl}\cdot\text{C}_2\text{H}_4\cdot\text{SO}_2\text{Cl}$.

Some time ago I investigated this reaction with the intention of preparing the amide of β -chlorethylsulphonic acid, but only succeeded in obtaining an oily substance free from chlorine (Trans., 1883, 47), and in such small quantities that I was unable at the time to study it further. Working now with larger quantities of pure β -chlorethylsulphonic chloride, I have obtained satisfactory results. 30 grams of the chloride were dissolved in 300 c.c. of absolute ether and dry ammonia gas passed in to thorough saturation, the flask being well cooled during the experiment. The precipitate which had formed was collected, dried over sulphuric acid, and analysed.

- I. 0.398 gram substance burnt with CuO , PbCrO_4 , and Cu gave 0.2265 gram H_2O and 0.1852 gram CO_2 .
- II. 0.2454 gram substance burnt with CuO and copper gauze with sodium hydrogen carbonate, produced 44 c.c. of moist nitrogen at 19°C . and 767 mm.
- III. 0.581 gram substance dissolved in water and acidified with nitric acid, produced 0.775 gram AgCl .
- IV. 0.528 gram substance treated similarly gave 0.7025 gram AgCl .

Calculated for NH ₂ ·C ₂ H ₄ ·SO ₂ NH ₂ + 2NH ₄ Cl.		Calculated for C ₂ H ₄ <div style="display: inline-block; vertical-align: middle;"> $\left\{ \begin{array}{c} \text{NH} \\ \\ \text{SO}_2 \end{array} \right.$ </div> + 2NH ₄ Cl.	Found.			
			I.	II.	III.	IV.
C....	10.39	11.21	12.69	—	—	—
H...	6.92	6.07	6.32	—	—	—
N...	24.24	19.62	—	20.36	—	—
Cl...	30.73	33.17	—	—	32.99	32.89
S....	13.85	14.95	—	—	—	—
O...	13.87	14.98	—	—	—	—
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100.00		100.00				

From these numbers, it is clear that the precipitate consisted of a mixture of a substance of the formula $C_2H_5NSO_2$ with ammonium chloride: this is specially apparent from the nitrogen and chlorine determinations. Its formation is expressed by the following simple

unless indeed the compound, $NH_2 \cdot C_2H_4 \cdot SO_2NH_2$ (the amide of taurine, $NH_2 \cdot C_2H_4 \cdot SO_2OH$), is so unstable that it decomposes on standing over sulphuric acid in the cold, which seems hardly probable.

The ammonium chloride was easily removed from this precipitate by adding silver oxide in slight excess, evaporating the mixture to dryness on the water-bath, taking up with water, and filtering off the silver chloride. The filtrate was found to still contain a small quantity of silver which was got rid of by hydrogen sulphide; on evaporating the liquid, now free from silver, to dryness, and drying at 100° , the new substance was obtained as a yellowish oil which, on cooling, set to a hard mass resembling gum arabic.

An analysis (I and II) gave the following numbers, and they agree as well as can be expected with *ethanesulphonimide*, $C_2H_4 \begin{array}{c} \text{NH} \\ | \\ SO_2 \end{array}$ (anhydrotaurine). The other nitrogen determinations (III, IV, and V) were made from separately prepared samples.

- I. 0.4604 gram substance burnt with CuO , $PbCrO_4$, and Cu produced 0.2312 gram H_2O and 0.359 gram CO_2 .
 II. 0.3562 gram substance burnt with CuO and copper gauze with sodium hydrogen carbonate, gave 43 c.c. moist nitrogen at 10° and 763 mm.
 III. 0.178 gram substance similarly treated gave 21 c.c. moist nitrogen at 16° and 765 mm.
 IV. 0.147 gram substance by the soda-lime method yielded 0.137 gram platinum.
 V. 0.113 gram substance by the soda-lime method yielded 0.110 gram platinum.

Calculated for ethanesulphonimide.

			Found.				
			I.	II.	III.	IV.	V.
C_2	24	22.43	21.26	—	—	—	—
H_5	5	4.67	5.57	—	—	—	—
N	14	13.06	—	14.34	13.60	12.9	13.7
S	32	29.92	—	—	—	—	—
O_2	32	29.92	—	—	—	—	—
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	107	100.00

Ethanesulphonimide is a solid resembling gum arabic in appearance: it melts between 45° and 50° , and at 100° becomes more or less mobile. It has a bitter taste. In cold water, it is scarcely soluble, but mixes with hot water in all proportions: it is insoluble in alcohol or ether.

No taurine was formed on heating it with water alone in a sealed tube at 150° , neither did the addition of a drop of hydrochloric acid bring about a reaction. No compound with hydrochloric acid and platinum tetrachloride could be obtained. It is not decomposed by boiling with barium hydroxide, and this may be taken advantage of for obtaining this substance from its admixture with ammonium chloride, the barium being subsequently removed by sulphuric acid.

Metallic Derivatives of Ethanesulphonimide.

If freshly precipitated mercuric oxide is gradually added to a hot concentrated aqueous solution of ethanesulphonimide, it is dissolved, and on filtering the liquid, after a slight excess of the oxide has been added, the mercury compound separates on cooling as an amorphous white precipitate which aggregates into several semi-solid globules on standing. The precipitate was washed once or twice with distilled water and dried over sulphuric acid.

I have not been able to prepare this mercury compound in a state of purity, it is always mixed with more or less of the original substance, probably carried down with it mechanically, but the following numbers obtained on the analysis of a sample can leave no doubt but that the hydrogen of the imide-group has been replaced by mercury—two molecules of imide being required for one molecule of mercuric oxide—

- I. 0.2300 gram substance burnt with CuO and copper gauze produced 15.6 c.c. moist nitrogen at 13° and 757 mm. = 7.86 per cent. N.
- II. 0.1185 gram substance dissolved in hydrochloric acid with addition of a drop of nitric acid, gave 0.0548 gram HgS = 0.04724 gram Hg = 39.86 per cent.

If the excess of nitrogen over that required by the formula of the mercury compound be calculated to ethanesulphonimide and subtracted, the percentage of mercury is as near as possible the theoretical.

0.1185 — 0.0213 (admixture of imide calculated from excess of N)
= 0.0972 gram pure mercury compound.

	Calculated for (C ₂ H ₄ NSO ₂) ₂ Hg.	Found.
Hg	48.54	48.60

Silver oxide is also dissolved by the aqueous solution of ethanesulphonimide, and doubtless forms a compound analogous to the above.

In the *Berichte*, 18, 869, Leymann describes experiments with β -chloroethylsulphonic chloride and aniline: he obtained three substances in this reaction—

I have found no indication of any analogues of the two first compounds, but this ethanesulphonimide is the compound corresponding to the latter substance, which Leymann has named *anhydrophenyltaurine*. It is true such a compound and water should yield phenyltaurine or phenyltaurine on hydrolysis, but there is no evidence to support these assumptions, and I have in vain endeavoured to prepare taurine from ethanesulphonimide by heating it with water and dilute acid under pressure. The name *anhydro* is therefore misleading and should be discontinued in connection with this new class of substances, for they are neither acids or anhydrides, but simply analogous to the imides of the fatty series with carboxyl. Leymann's body should be called phenylethanesulphonimide, and the relation between taurine and ethanesulphonimide is plainly seen from the following formulæ:—

NH₂·C₂H₄·SO₂·OH, amidoethanesulphonic acid (taurine).

NH₂·C₂H₄·SO₂NH₂, amidoethanesulphonamide (unknown).

C₂H₄ $\begin{array}{l} \text{NH} \\ | \\ \text{SO}_2 \end{array}$, ethanesulphonimide.