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SOME NEW GOLD SALTS
OF
HYOSCINE, HYOSCYAMINE, AND ATROPINE

BY

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Some New Gold Salts of Hyoscine, Hyoscyamine, and Atropine.

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IN the course of some work necessitating the preparation of the aurichloride from the hyoscine hydrobromide of commerce (which, it may be remarked, is really scopolamine hydrobromide), it was observed that, on mixing aqueous solutions of this salt with auric chloride, a red precipitate was formed instead of the characteristic yellow aurichloride. Experiments made to determine the composition of this precipitate showed that it is an additive compound of gold chloride with the hydrobromide, and may thus be termed hyoscine hydrobromide gold chloride $[B, HBr, AuCl_3]$. In studying the conditions of formation of this salt, the auribromide $[B, HBr, AuBr_3]$ was also prepared, and it was further observed that the other solanaceous alkaloids, atropine and hyoscyamine, react in a similar manner, forming analogous compounds.

Hyoscine hydrobromide gold chloride, $C_{17}H_{21}NO_4, HBr, AuCl_3$, is formed when aqueous solutions of hyoscine hydrobromide and auric chloride are mixed either in equivalent proportions or with a slight excess of auric chloride, the red, amorphous precipitate which is formed becoming crystalline on standing, or, better, by heating the mixture to boiling and then cooling, when a crop of dark red, prismatic crystals separate. The salt is best recrystallised from boiling water acidified with a little hydrochloric acid, when it separates in red prisms which melt and decompose at about 215° . The salt is soluble in boiling

water or acetone, and sparingly so in hot and cold alcohol or cold water. On analysis it gave the following results :

Found : Gold (i) 29.08 ; (ii) 28.95 per cent. Mixed silver haloid salts, 90.4 per cent. of salt taken.

Calculated for $C_{17}H_{21}NO_4, HBr, AuCl_3$: Au = 28.60 per cent. ; mixed silver salts, 90.2 per cent.

The silver salts tested in the usual way were found to contain both chlorine and bromine.

In order to be certain that the salt was homogeneous, and also to determine whether, under any conditions, the aurichloride is formed, the experiment was repeated in solutions of varying strength, both acid and neutral, and the percentage of gold in the product determined by ignition. In no case was the aurichloride formed, and except in presence of excess of hydrobromic acid, this new compound was obtained in every case.

These results may be tabulated as follows :

Conditions of experiment.	Percentage of gold found in salt.
(i) By mixing concentrated solutions in presence of considerable excess of hydrochloric acid	28.69
(ii) As above, with specially prepared auric chloride.....	28.38
(iii) By mixing 10 per cent. neutral solutions	28.10
(iv) „ „ 1 „ „ „	28.10
(v) „ „ 0.5 solutions acidified with HCl	28.10

In all the above experiments except (ii), the double gold salt of commerce was used, but parallel experiments, with specially prepared auric chloride yielded identical results. In some experiments, the product seemed lighter in colour, but on analysis yielded the same results :

Hyoscine auribromide, $C_{17}H_{21}NO_4, HBr, AuBr_3$.—When, in place of excess of hydrochloric acid in the above experiment, hydrobromic acid is used, a chocolate-coloured precipitate is formed, which may be recrystallised from boiling water acidified with hydrobromic acid, when it is obtained in chocolate-coloured prisms sparingly soluble in cold water. This salt melts with decomposition at about 210° , and on analysis was found to contain bromine but no chlorine, and to be the auribromide of the base. It must thus be formed by the interaction of auric chloride and hydrobromic acid. On analysis, the recrystallised salt gave the following results :

Found : Au (i) 23.68 ; (ii) 23.64 per cent. Br 39.09 per cent.

$C_{17}H_{21}NO_4, HBr, AuBr_3$ requires Au = 23.93 ; Br = 39.07 per cent.

The corresponding salts of hyoscyamine and atropine are prepared in precisely the same manner, and possess similar chemical and physical properties.

Hyoscyamine hydrobromide gold chloride, $C_{17}H_{23}NO_3, HBr, AuCl_3$, is a yellowish-red salt which crystallises from boiling acidified water in scales, melting sharply at 164° (corr.) and on analysis was found to contain 28.00 per cent. of gold. Calculated for $C_{17}H_{23}NO_3, HBr, AuCl_3$: Au = 27.76 per cent.

Hyoscyamine auribromide, $C_{17}H_{23}NO_3, HBr, AuBr_3$, is prepared by the method described for hyoscine auribromide, and is in appearance exactly similar to that salt. It melts at 115° — 120° (corr.) and is soluble in hot water, but only sparingly in cold water. On analysis, the recrystallised salt was found to contain 23.75 per cent. of gold. Calculated for $C_{17}H_{23}NO_3, HBr, AuBr_3$: Au = 24.3 per cent.

Atropine hydrobromide gold chloride, $C_{17}H_{23}NO_3, HBr, AuCl_3$. This salt is precipitated as an oil when prepared in the usual manner, but crystallises from boiling acidified water in reddish brown scales, which melt sharply at 144° (corr.) and contain 27.20 per cent. of gold. $C_{17}H_{23}NO_3, HBr, AuCl_3$ requires 27.76 per cent. gold.

Atropine auribromide, $C_{17}H_{23}NO_3, HBr, AuBr_3$.—This salt is also precipitated as an oil when prepared in the usual manner, and crystallises from boiling acidified water in chocolate prisms, similar in appearance to the other auribromides, and melts at 120° (corr.) On analysis, it was found to contain 23.6 per cent. of gold. Calculated for $C_{17}H_{23}NO_3, HBr, AuBr_3$: Au = 24.3 per cent.

It will be noticed that the gold chloride compounds have in every case a melting point slightly higher than that of the aurichloride, whilst the auribromides of atropine and hyoscyamine melt at a lower temperature.

The salts having the composition $B, HBr, AuCl_3$ offer some analogies to a platinum salt first prepared by Pitkin by the interaction of platinum chloride with potassium bromide and to which he ascribed the formula $K_2PtCl_4Br_2$. It has been stated, however (Herty, *J. Am. Chem. Soc.*, 1896, **18**, 130), that this salt is not a true chemical compound, but an isomorphous mixture of two parts of potassium platinumchloride, K_2PtCl_6 , and one part of the platinumbromide, K_2PtBr_6 ; this question, however, cannot be regarded as definitely settled (Miolati, *Zeit. anorg. Chem.*, 1897, **14**, 237).

If this view be extended to the gold salts described above, they would have to be regarded as a mixture of three parts of the aurichloride with one part of the auribromide. On investigating the matter, however, it appears that these gold salts must be regarded as true chemical compounds and not as simple mixtures.

This conclusion is based on the following results :

1. The percentage of gold in the salt was not altered by recrystallisation.
2. The substance obtained on mixing 3 parts of the aurichloride and 1 of auribromide was quite unlike the gold salt, $B, HBr, AuCl_3$, both in colour and in general appearance.
3. When precipitated in three fractions, each appeared to have the same colour.
4. In the case of the atropine and hyoscyamine salts, the melting points are sharp and *above* those of the corresponding aurichlorides and auribromides.
5. After the gold had been precipitated with hydrogen sulphide, the salt recovered from the filtrate contained no chlorine, and on the addition of auric chloride yielded a red precipitate identical with the original salt.
6. The red salt is obtained when the solutions used are so dilute that it remains a solution, instead of being precipitated. The same result is obtained in the presence of a large or small excess of hydrochloric acid.

The formation of these salts is very interesting from a theoretical point of view, particularly that of the auribromide by the mass action of the hydrobromic acid and the failure of the hydrochloric acid to bring about the formation of the aurichloride.

They are also important as adding to the list of easily formed and well defined alkaloidal salts, which may be of use for purposes of identification. In this respect, it must be noted that the statement of the United States Pharmacopœia, that "hyoscyamine hydrobromide with gold chloride test solution yields a precipitate which, when recrystallised from a small quantity of boiling water acidulated with hydrochloric acid, is deposited on cooling in minute, lustrous, golden-yellow scales," requires modification. In conclusion, it seems very probable that most of the vegetable alkaloids would, under similar conditions, afford compounds of this, or analogous types; the author, however, does not intend to pursue the investigation further, the object of the present note being to draw attention to this new class of alkaloidal gold salts.

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