CLVI. NEUTRAL SALT ADDITION COMPOUNDS OF ALKALINE EARTH GLUTAMATES AND ASPARTATES.

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It was shown a few years ago by King and Palmer [1920] that glycine could form a series of addition compounds with alkali halides and alkaline earth halides under experimental conditions free from dubiety, thus extending and confirming the earlier work of Pfeiffer and his co-workers. About the same time Hugounenq and Florence [1920], by the action of calcium carbonate upon glutamic acid hydrochloride, obtained an addition compound which they represented by either of the formulae

but they were unable to isolate analogous compounds using barium or other metallic oxides. A year later [1921] the same observers prepared from the reaction product of aspartic acid hydrochloride and chalk, by alcoholic precipitation, a calcium chloride addition compound analogous to that from glutamic acid.

As no further work has appeared on these interesting products, which are essentially glycine derivatives with the added complication of an extra carboxyl group in salt formation, the subject has been examined more closely in the hope of deciding between the formulae advanced by Hugounenq and Florence and of arriving at some conclusion as to the mode of attachment of these inorganic addenda.

d-Glutamic acid was chosen as starting material since it is optically active and can be readily obtained in large quantities. In the experimental portion a process is described whereby 30.5 g. of pure *d*-glutamic acid hydrochloride may be obtained from 100 g. of gluten flour avoiding alcohol as a precipitant and also the laborious process of saturation with hydrogen chloride gas. In addition an effective modification of Hugounenq and Florence's method for preparing glutamic acid from the hydrochloride is described.

When glutamic acid hydrochloride, hydrobromide or hydriodide is boiled in aqueous solution with freshly precipitated calcium or barium carbonate or with the corresponding hydroxide followed by saturation with carbon

dioxide, the filtrates, on concentration, readily deposit well-formed crystals of the new addition compound of the type

where M may be calcium or barium and A may be chlorine, bromine, or iodine.

In the case of strontium, the first crystalline crop was invariably strontium glutamate, so for purposes of comparison calcium and barium glutamates were prepared from free glutamic acid and found to be much more soluble than strontium glutamate. The exceptional behaviour of the strontium solutions is thus due to the solubility product of strontium glutamate being reached before that of the addition compounds. In confirmation of this it was found that if solutions of strontium glutamate were allowed to crystallise in presence of excess of strontium chloride, bromide or iodide, then addition compounds of the same type as those formed with calcium and barium halides were readily obtained.

In a similar manner aspartic acid hydrochloride and strontium carbonate gave the addition compound

without the need for excess of strontium chloride, and definite evidence was also obtained for the formation of an addition compound between barium chloride and barium aspartate, but only in the presence of large excess of barium chloride. The calcium analogue obtained by Hugounenq and Florence by precipitation with alcohol could not be obtained by us, using aqueous media alone.

The chief interest of these compounds apart from their possible physiological significance lies in their constitution. The starting materials are optically active and a determination of the variation of specific rotation with concentration over a wide range of concentrations might be expected to cast some light upon their constitution. The results of such an experiment are shown graphically in Fig. 1, where a number of addition compounds are compared with the corresponding alkaline earth glutamates and alkali glutamates. The general trend of the curves is similar, from a region of positive rotation at high concentrations to a region of negative rotation at low concentrations, the whole corresponding to a change of molecular rotating species with dilution. At high dilutions, 1–2 %, the curves show a tendency to flatten out, and it is of interest that if the ionic value for the negative glutamate ion be calculated from these curves at a concentration in the region of 2.5 % then the ionic values show a measure of agreement.

Salt	$[\alpha]_{5461}$ for ion	Salt	$[\alpha]_{5461}$ for ion
$(\text{C}_5\text{H}_8\text{O}_4\text{N})_2 \text{Ca} \cdot \text{H}_2\text{O}$	– 6.3°	$(\text{C}_5\text{H}_8\text{O}_4\text{N})_2 \text{Ca} \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	– 5.8°
$(\text{C}_5\text{H}_8\text{O}_4\text{N})_2 \text{Ba} \cdot 5\frac{1}{2}\text{H}_2\text{O}$	– 5.8°	$(\text{C}_5\text{H}_8\text{O}_4\text{N})_2 \text{Ca} \cdot \text{CaBr}_2 \cdot 2\text{H}_2\text{O}$	– 5.8°
$(\text{C}_5\text{H}_8\text{O}_4\text{N})_2 \text{Sr} \cdot 4\text{H}_2\text{O}$	– 6.1°	$(\text{C}_5\text{H}_8\text{O}_4\text{N})_2 \text{Ba} \cdot \text{BaCl}_2 \cdot 6\text{H}_2\text{O}$	– 6.3°
$\text{C}_5\text{H}_8\text{O}_4\text{N} \text{Li}$	– 5.9°	$(\text{C}_5\text{H}_8\text{O}_4\text{N})_2 \text{Ba} \cdot \text{BaBr}_2$	– 6.2°
$\text{C}_5\text{H}_8\text{O}_4\text{N} \text{Na}$	– 5.5°	Mean	– 6.0°

It seems justifiable to conclude that at high concentrations comparable indeed with saturated solutions, the non-ionised alkaline earth glutamates

where the calcium has, progressively, co-ordination numbers of 2, 4 and 6 [cf. Pfeiffer, 1922]. If the chlorine atoms in the last of these were united by a co-valency, calcium would have the unlikely co-ordination number of eight.

Sugden [1927] has recently discussed molecular compounds in terms of singlet linkages but his views do not appear to present any advantage over the preceding.

EXPERIMENTAL.

Preparation of glutamic acid. Gluten flour¹ (100 g.) was added to warm concentrated HCl (300 cc., d. 1.16) and the mixture boiled for 6 hours. After treatment with charcoal and filtration the solution was kept below 0° for 12 hours and deposited 28.9 g. of crude glutamic acid hydrochloride. This crop was recrystallised from 50 cc. of boiling 20 % HCl and gave 23.7 g. of hydrochloride, which was dissolved in 20 cc. boiling water and treated with charcoal; it was then filtered and 33 cc. HCl (d. 1.16) were added. 21.6 g. of pure glutamic acid hydrochloride were obtained. By concentration of the original mother-liquors under reduced pressure further crops of crude glutamic acid hydrochloride mixed with ammonium chloride were obtained, and these recrystallised from the mother-liquors of the first crop gave finally a further 8.9 g. of pure glutamic acid hydrochloride. The total yield was therefore 30.5 g. from 100 g. of gluten. (Found: Cl, 19.3; N, 7.8. Theory: Cl, 19.3; N, 7.6%.) The rotation of the pure hydrochloride was determined at different concentrations with the following results:

c	10.0	7.5	5.0	2.5	1.25	0.6	0.5	0.25
$[\alpha]_{5461}$	+28.63°	+28.25°	+27.45°	+26.85°	+26.28°	+23.54°	+22.87°	+20.59°

The hydrochloride (36.7 g.) was dissolved in 200 cc. of water and heated on the water-bath. Aniline (18.6 g. = 1 mol.) was added and to the clear solution 200 cc. of 95 % alcohol. On cooling 27.55 g. of glutamic acid separated. It was recrystallised from the minimum volume (250 cc.) of boiling water and gave 24.1 g. of pure glutamic acid crystallising in hexagonal plates. From the mother-liquors a further 1.8 g. was obtained. (Found: N, 9.4. Theory: N, 9.5 %.)

Salts of glutamic acid. The hydrobromide, described by Hlasiwetz and Habermann [1873] as crystalline conglomerates, separates in large hexagonal tablets on treatment of glutamic acid with slight excess of 48 % HBr. Like the hydrochloride it melts at 214°, but this depends on the rate of heating. (Found: Br, 35.1. Theory: Br, 35.0 %.) The rotation was determined at different concentrations in water.

c	10.0	7.5	5.0	3.0	2.0	1.0	0.5
$[\alpha]_{5461}$	+23.09°	+23.30°	+23.13°	+22.50°	+22.0°	+20.57°	+18.70°

The hydriodide crystallises similarly on dissolving glutamic acid in slight excess of constant boiling HI freshly distilled over red phosphorus. It melts

¹ Purchasable from Messrs Bishop and Brooke, 21 Cock Lane, Snowhill, E.C.

with effervescence at 180–185°. (Found: I, 45.7; N, 5.1. Theory: I, 46.1; N, 5.1 %.) The only reference to this salt appears to be a crystallographic one by Kaplanova [1917].

The rotations of the salt were determined at various concentrations.

<i>c</i>	10.0	7.5	5.0	3.0	2.0	1.0	0.5
$[\alpha]_{5461}$	+18.64°	+18.39°	+18.35°	+18.14°	+17.59°	+15.79°	+11.57°

If the effect of variation of the concentration of the three halogen acid salts be plotted against specific rotation the curves shown in Fig. 2 are obtained.

There is a rapid falling off of specific rotation in solutions below 3 % due to hydrolysis of the salts, the values for dissociated salt approaching that of glutamic acid. Exact confirmation of this is found in the work of Wood [1914] who observed a similar phenomenon for several amino-acids when specific rotation was plotted against the ratio of the number of molecules of hydrochloric acid to molecules of amino-acid. If the specific rotation of the glutammonium ion be calculated from each salt at a dilution where hydrolysis is negligible there is substantial agreement between the observations.

Fig. 2

Calcium glutamate. Prepared from pure glutamic acid and calcium carbonate, this salt crystallises slowly from syrupy solutions in small hexagonal plates which are readily soluble in water.

0.2000 g. dried at 160° lost 0.0073 g. $H_2O = 3.7\%$.
 0.2052 g. dried at 160° lost 0.0087 g. $H_2O = 4.2\%$.
 0.1927 g. dry; $NH_3 = 12.01$ cc. $N/10$ acid. $N = 8.7\%$.
 0.1783 g. dry; 0.0751 g. $CaSO_4$. $Ca = 12.4\%$.

Calc. for $(C_5H_8O_4N)_2 Ca \cdot H_2O$; $H_2O = 5.1\%$; for $(C_5H_8O_4N)_2 Ca$; $Ca = 12.1\%$; $N = 8.4\%$.

The rotations were determined over a wide range of concentrations.

<i>c</i>	30.0	25.0	20.0	15.0	10.0	5.0	2.5
$[\alpha]_{5461}$	+0.81°	-0.34°	-1.71°	-2.62°	-3.84°	-5.05°	-5.22°

Strontium glutamate. This salt crystallises very readily from concentrated solutions and separates in hexagonal plates.

0.2105 g. dried at 95° lost 0.0353 g. $H_2O = 16.8\%$.

0.2945 g.; 0.1152 g. $SrSO_4$. $Sr = 18.7\%$.

0.1752 g. dry; $NH_3 = 8.85$ cc. $N/10$ acid. $N = 7.1\%$.

Calc. for $(C_5H_8O_4N)_2 Sr \cdot 4H_2O$; $Sr = 19.3\%$; $H_2O = 16.0\%$; for $(C_5H_8O_4N)_2 Sr$; $N = 7.4\%$.

It gave the following specific rotations:

c	10.0	5.0	2.5
$[\alpha]_{5461}$	-2.96°	-3.59°	-3.95°

Barium glutamate. This salt crystallises in irregular hexagonal plates from concentrated solutions.

0.2093 g. dried at 160° lost 0.0376 g. $H_2O = 18.0\%$.

0.2040 g.; $NH_3 = 7.87$ cc. $N/10$ acid. $N = 5.4\%$.

0.1975 g.; 0.0881 g. $BaSO_4$. $Ba = 26.2\%$.

Calc. for $(C_5H_8O_4N)_2 Ba \cdot 5\frac{1}{2}H_2O$; $H_2O = 18.0\%$; $N = 5.3\%$; $Ba = 26.2\%$.

The following specific rotations were obtained:

c	10.0	5.0	2.5
$[\alpha]_{5461}$	-2.44°	-2.94°	-3.22°

Lithium glutamate. This salt crystallises in irregular hexagonal plates which are anhydrous.

0.1959 g.; $NH_3 = 12.43$ cc. $N/10$ acid. $N = 8.9\%$.

Calc. for $C_5H_8O_4N Li$. $N = 9.2\%$.

The specific rotations of this salt were as follows:

c	10.0	5.0	2.5	1.25
$[\alpha]_{5461}$	-3.01°	-4.52°	-5.19°	-5.68°

Sodium glutamate. A standard solution was made up from a known weight of pure glutamic acid and standard alkali. The specific rotations were determined at a variety of concentrations.

c	15.0	10.0	5.0	2.5	1.25
$[\alpha]_{5461}$	-2.57°	-3.57°	-4.30°	-4.67°	-4.75°

Addition compounds of alkaline earth glutamates.

Calcium glutamate calcium chloride. Glutamic acid hydrochloride (9.2 g.) was boiled with 50 cc. water and excess of calcium carbonate; the solution was filtered and concentrated. On keeping, the dihydrate of calcium glutamate calcium chloride (5.8 g.) separated in hexagonal plates. It also crystallises in needles. To avoid the known decomposing action of water on certain addition compounds, the crystalline crops were in every case filtered on hardened paper without washing and then rubbed dry on porous plate before analysis.

0.1138 g. dried at 160° lost 0.0086 g. $H_2O = 7.6\%$.

0.2046 g.; 0.1211 g. $AgCl$. $Cl = 14.7\%$.

0.2062 g.; $NH_3 = 8.7$ cc. $N/10$ acid. $N = 6.0\%$.

Calc. for $(C_5H_8O_4N)_2 Ca \cdot CaCl_2 \cdot 2H_2O$; $Cl = 14.8\%$; $N = 5.8\%$; $H_2O = 7.5\%$.

It was unchanged by recrystallisation from water in which it is readily soluble (1 in 2.5 parts).

0.2024 g.; 0.1191 g. $AgCl$. $Cl = 14.6\%$.

On recrystallisation from solutions containing 2 or 5 molecules excess of calcium chloride, the same compound was obtained in each case.

2 molecules excess—0.1886 g. (anhydrous); 0.1265 g. AgCl. Cl=16.6 %.
5 molecules excess—0.1746 g. (anhydrous); 0.1206 g. AgCl. Cl=17.1 %.

Calc. for $(C_5H_8O_4N)_2 \text{ Ca} \cdot \text{CaCl}_2$; Cl=16.0 %.

The specific rotations of solutions of the addition compound at a variety of concentrations were determined with the following results:

c	33.8	26.9	21.0	14.9	10.0	5.0	3.0	2.0	1.3
$[\alpha]_{5461}$	+0.9°	-0.18°	-1.13°	-2.02°	-2.7°	-3.40°	-3.50°	3.38°	-3.56°

Calcium glutamate calcium bromide. Glutamic acid hydrobromide (11.4 g.) was boiled with excess of calcium carbonate in 50 cc. water; the solution was filtered and concentrated. The addition compound separated on keeping in hexagonal plates (6.9 g.).

0.2060 g. dried at 160° lost 0.0145 g. H_2O =7.0 %.

0.1917 g.; 0.1255 g. AgBr. Br=27.9 %.

0.1927 g.; NH_3 =7.06 cc. $N/10$ acid. N=5.1 %.

Calc. for $(C_5H_8O_4N)_2 \text{ Ca} \cdot \text{CaBr}_2 \cdot 2H_2O$; Br=28.0 %; N=4.9 %; H_2O =6.3 %.

The addition compound gave the following specific rotations:

c	15.0	10.0	5.0	3.75	1.9
$[\alpha]_{5461}$	-2.07°	-2.45°	-2.95°	-3.0°	-3.0°

Calcium glutamate calcium iodide. Prepared similarly to the preceding, this addition compound crystallised in irregular hexagonal plates.

0.1997 g. dried at 160° lost 0.0140 g. H_2O =7.0 %.

0.1997 g.; 0.1380 g. AgI. I=37.8 %.

Calc. for $(C_5H_8O_4N)_2 \text{ Ca} \cdot \text{CaI}_2 \cdot 2\frac{1}{2}H_2O$; I=37.8 %; H_2O =6.7 %.

Barium glutamate barium chloride. Glutamic acid hydrochloride (9.2 g.) was dissolved in water, made alkaline with baryta and the boiling solution was saturated with carbon dioxide. On filtration and concentration the addition compound (11.3 g.) separated in irregular hexagonal plates.

0.2020 g. dried at 160° lost 0.0299 g. H_2O =14.8 %.

0.1721 g. (anhydrous); 0.0794 g. AgCl. Cl=11.4 %.

0.1712 g. (anhydrous); NH_3 =5.91 cc. $N/10$ acid. N=4.8 %.

Calc. for $(C_5H_8O_4N)_2 \text{ Ba} \cdot \text{BaCl}_2$; Cl=11.1 %; N=4.4 %: for $(C_5H_8O_4N)_2 \text{ Ba} \cdot \text{BaCl}_2 \cdot 6H_2O$; H_2O =14.5 %.

The following specific rotations were obtained at various concentrations:

c	18.0	15.0	10.0	5.0	4.0	3.0	2.0
$[\alpha]_{5461}$	-1.38°	-1.62°	-1.90°	-2.45°	-2.49°	-2.25°	-2.47°

Barium glutamate barium bromide. Prepared similarly to the above, glutamic acid hydrobromide (11.4 g.) gave 8.4 g. of the addition compound crystallising in minute hexagonal plates which were *anhydrous*.

0.1896 g.; 0.0963 g. AgBr. Br=21.6 %.

0.2018 g.; NH_3 =5.9 cc. $N/10$ acid. N=4.1 %.

Calc. for $(C_5H_8O_4N)_2 \text{ Ba} \cdot \text{BaBr}_2$; Br=22.0 %; N=3.9 %.

On recrystallisation from water a *tetrahydrate* was obtained.

0.2040 g. dried at 160° lost 0.0191 g. H_2O =9.4 %.

0.1894 g. (anhydrous); 0.0942 g. AgBr. Br=21.7 %.

Calc. for $(C_5H_8O_4N)_2 \text{ Ba} \cdot \text{BaBr}_2 \cdot 4H_2O$; H_2O =9.0 %.

The specific rotations of the anhydrous salt at various concentrations were as follows:

c	20.0	15.0	10.0	5.0	4.0	3.0
$[\alpha]_{5461}$	-1.41°	-1.74°	-2.03°	-2.38°	-2.34°	-2.49°

Barium glutamate barium iodide. Prepared similarly to the preceding, this addition compound separated in irregularly shaped crystals.

0.1938 g. dried at 120° lost 0.0252 g. $H_2O = 11.4\%$.

0.1686 g. (anhydrous); 0.0977 g. AgI. $I = 31.3\%$.

Calc. for $(C_5H_8O_4N)_2 Ba \cdot BaI_2$; $I = 30.9\%$; for $(C_5H_8O_4N)_2 Ba \cdot BaI_2 \cdot 6H_2O$; $H_2O = 11.6\%$.

Strontium glutamate strontium chloride. Glutamic acid hydrochloride (9.2 g.) was boiled in 50 cc. water with excess of strontium carbonate; the solution was filtered and concentrated. On keeping, a large crop (6.9 g.) separated of homogeneous appearance and consisting of microscopic narrow leaflets. It proved on analysis to be mainly strontium glutamate. (Found: $Cl = 1.2\%$.) The mother-liquors on concentration deposited tablets (1.8 g.) which were evidently crude addition compound ($Cl = 9.6$; $N = 3.6\%$, whence $Cl : N = 1.07 : 1$). On further concentration the liquors gave crude strontium chloride (1.7 g.) crystallising in long needles. (Found: $Cl = 36.6\%$.)

The first crop on recrystallisation from 12 cc. of boiling water gave pure strontium glutamate crystallising in rectangular plates.

0.2042 g. dried at 95° lost 0.0350 g. $H_2O = 17.1\%$.

0.1692 g. (anhydrous); NH_3 equivalent to 8.84 cc. $N/10$ acid. $N = 7.3\%$.

Calc. for $(C_5H_8O_4N)_2 Sr$; $N = 7.4\%$; for $(C_5H_8O_4N)_2 Sr \cdot 4\frac{1}{2}H_2O$; $H_2O = 17.1\%$.

The pure addition compound was obtained as follows. Glutamic acid hydrochloride (4.6 g.) was treated with 50 cc. N hydrochloric acid, made alkaline by addition of strontia and the boiling solution was saturated with carbon dioxide. On filtration and concentration the addition compound separated in bold tablets. Preliminary essays showed that even with this excess of strontium chloride, strontium glutamate tended to separate first.

0.2047 g. dried at 160° lost 0.0642 g. $H_2O = 31.4\%$.

0.2047 g.; 0.0802 g. AgCl. $Cl = 9.7\%$.

0.2102 g.; $NH_3 = 5.84$ cc. $N/10$ acid. $N = 3.9\%$.

0.1965 g.; 0.0980 g. $SrSO_4$. $Sr = 23.8\%$.

Calc. for $(C_5H_8O_4N)_2 Sr \cdot SrCl_2 \cdot 12H_2O$; $Cl = 9.4\%$; $N = 3.7\%$; $Sr = 23.2\%$; $H_2O = 28.7\%$.

Strontium glutamate strontium bromide. Glutamic acid hydrobromide (2.8 g.) was treated in aqueous solution with excess of strontia and the boiling solution saturated with carbon dioxide. On filtration and concentration microscopic needles (2.1 g.) of crude strontium glutamate (found: $N, 5.5\%$; $Br, 3.3\%$) separated. The mother-liquors, now relatively richer in strontium bromide, deposited on concentration a homogeneous crop of needles, quite different in appearance from the first crop, which proved to be the required addition compound.

0.2020 g.; 0.0919 g. AgBr. $Br = 19.4\%$.

0.2123 g.; $NH_3 = 4.7$ cc. $N/10$ acid. $N = 3.1\%$.

Calc. for $(C_5H_8O_4N)_2 Sr \cdot SrBr_2 \cdot 11H_2O$; $Br = 19.4\%$; $N = 3.4\%$.

Strontium glutamate strontium iodide. A solution made up in the usual way from 3.4 g. glutamic acid hydriodide deposited 2.35 g. crude strontium

glutamate (found: I = 3.9 %; N = 5.5 %). The mother-liquors, now relatively richer in strontium iodide deposited on further concentration well-formed hexagonal plates (0.55 g.) of the required addition compound.

0.1560 g.; 0.0863 g. AgI. I = 29.9 %.
0.2215 g.; NH₃ = 5.00 cc. N/10 acid. N = 3.2 %.

Calc. for (C₅H₈O₄N)₂ Sr.SrI₂.7H₂O; I = 29.9 %; N = 3.3 %.

Lithium glutamate and lithium halides. From solutions of glutamic acid hydrochloride, hydrobromide or hydriodide and lithium carbonate only crude lithium glutamate was isolated (found in the three cases respectively: Cl = 1.2 %; Br = 1.9 %; I = 3.9 %).

Calcium chloride and glutamic acid hydrochloride. Solutions of glutamic acid hydrochloride containing 2 or 5 molecular proportions of calcium chloride deposited crude glutamic acid hydrochloride. (Found: Cl = 22.0 %; 23.9 % respectively.)

Calcium chloride and glutamic acid. When glutamic acid was crystallised from a solution containing two molecular proportions of calcium chloride it was recovered contaminated with a small proportion of chloride. (Found: Cl = 2.0 %.)

Addition compounds of alkaline earth aspartates.

Strontium aspartate strontium chloride. Aspartic acid (2.66 g.), prepared from asparagine, was dissolved in 20 cc. hot N hydrochloric acid (1 mol.) and boiled gently with excess of strontium carbonate. On filtration and slight concentration the solute crystallised readily as a micro-crystalline powder (1.85 g.).

0.2110 g. dried at 160° lost 0.0128 g. H₂O = 6.1 %.
0.1990 g.; 0.1346 g. SrSO₄. Sr = 32.3 %.
0.2011 g.; 0.0975 g. AgCl. Cl = 12.3 %.
0.1937 g.; NH₃ = 6.84 cc. N/10 acid. N = 4.9 %.

Calc. for (C₄H₆O₄N)₂ Sr.SrCl₂.2H₂O; Sr = 32.1 %; Cl = 13.0 %; N = 5.1 %; H₂O = 6.6 %.

On concentration the mother-liquors deposited the same addition compound (1.25 g.).

Barium aspartate and barium chloride. Aspartic acid (1.33 g.) was treated with 100 cc. 0.1 N hydrochloric acid (1 mol.), made alkaline with baryta and then carbon dioxide was passed into the boiling solution in excess. The filtered solution was concentrated to about 10 cc. and the compound crystallised in microscopic narrow leaflets of homogeneous appearance, yield 1.7 g. On analysis it gave Ba = 35.8 %, Cl = 5.0 %; N = 5.2 %, corresponding to a mixed crystal containing barium chloride and barium aspartate in the ratio 1:2.6 respectively.

When a similar quantity of aspartic acid was subjected to the same series of operations but using three molecular proportions of hydrochloric acid, the crystalline product consisted of microscopic rhomb-shaped plates, yield 1.7 g. On analysis it gave Ba = 39.6 %, Cl = 7.6 %, N = 5.2 %, corresponding to

a mixed crystal, this time relatively richer in barium chloride, containing barium chloride and barium aspartate in the ratio 1:1.7 respectively.

Calcium aspartate and calcium chloride. No crystalline product could be obtained from equimolecular proportions of these compounds in water.

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