

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XVI.—*On some Saline Compounds of Cane-Sugar.*

By C. HAUGHTON GILL.

PELIGOT has described* a compound of cane-sugar and salt, to which he ascribed the formula $C_{24}H_{42}O_{21}NaCl$ ($C = 6$ $H = \cdot 5$ $O = 8$), which requires 14·92 per cent. of sodic chloride; this indicates the replacement of 9 parts of water by 58·5 parts of sodic chloride. Blondeau de Carrolles subsequently examined a similar compound, to which he ascribed the formula $C_{21}H_{20}O_{20}, NaCl, 3HO$; this includes water of crystallisation, of which Peligot makes no mention. Subsequently Mitscherlich denied the existence of the body, and Hochstetter mentioned that other chemists had failed to obtain it. Others in France and Germany having incidentally thrown doubts on the existence of any saline compounds of cane-sugar, it became of interest to me, for technical reasons, to examine into the question, and to ascertain whether Peligot's statements were really unfounded.

Having obtained some positive results, I beg to lay them before the Society, for though of little interest in themselves, their publication may prevent the necessity of some other worker wasting so much time on an ungrateful subject.

Being at first unsuccessful in preparing Peligot's compound by the method which he describes, I boiled a solution of sugar with an excess of salt for some time, filtered, and set aside the apparently uncrystallisable syrup, while other experiments were undertaken. At the end of some months, a few small, not very transparent, but individually distinct crystals, had formed. They were drained, rinsed, and pressed.

·5744 grm. lost ·045 grm. water by drying for 74 hours at 60° — 120° C., and when ignited with hydric sulphate left ·1304 grm. sodic sulphate.

These numbers lead to the formula $2C_{12}H_{22}O_{11}, 3NaCl, 4H_2O$.

	Calculated.	Found.
$C_{12}H_{22}O_{11}$ (by difference) ..	73·43	73·47
NaCl	18·84	18·70
H_2O	7·73	7·83
	100·00	100·00

This compound, of an unexpected composition, having been obtained,

* Ann. Ch. Pharm. xxx, 71.

a number of solutions of sugar with various proportions of different salts, were made up and set aside to crystallise spontaneously in a dry air-space, or in the gentle and regular warmth of a sugar-house working floor. Where crystals were not obtained by these means, a more rapid evaporation was tried, or an alcoholic solution was slowly evaporated, and in many cases these and other methods were tried with liquids, neutral, alkaline, and faintly acid. The salts employed were, the chlorides of potassium, sodium, lithium, and ammonium, the bromides of potassium, and sodium, and the iodides of potassium, sodium, lithium and ammonium. In each case, four solutions were prepared, having one, two, three, and four molecules of the salt to the double molecule of sugar $2C_{12}H_{22}O_{11}$.

None of the potassium salts gave compounds of a definite composition. The mixture containing the chloride in the smallest proportion, gave crystals of pure sugar; those containing the two largest proportions gave a crop of pure potassic chloride. From the solution containing $2KCl$ to $2C_{12}H_{22}O_{11}$, *anhydrous* crystals containing from 1·3 per cent. to 19·6 per cent. of potassic chloride, slowly separated, leaving behind a mother liquor of the consistency of treacle.

The solutions containing potassic bromide behaved in a very similar manner, giving crystals often very clear and sharp, and sometimes five or six mm. in extreme dimensions, but always *anhydrous* and of irregular composition. Different specimens contained such proportions of potassic bromide as 24·8, 19·15, 16·17, 12·0, 7·56, 28·15 and 22·3 per cent. In appearance the crystals could not be distinguished from those of pure sugar. The solutions containing potassic iodide evaporated to very thick sticky masses, sometimes containing a number of minute crystals which could not be separated from the mother liquor.

The sodium salts gave more definite results. In the case of the chloride, the solution containing least salt first gave crystals of pure sugar, and then, on further concentration, deposited crystals which are doubtless the same as those of the compound examined by Peligot, and are identical with those obtained from the liquid containing the next higher proportion of salt, viz., $NaCl$ to $C_{12}H_{22}O_{11}$.

This compound crystallises in prisms terminated by pyramids; it deliquesces only in very moist air—loses no water in a dry vacuum at ordinary temperatures, but gives off the whole of its water of crystallisation, amounting to 8·25 per cent. by long exposure to a temperature of 60° — 70° C. It is very soluble in water, less so in spirit. From its solution in hot spirit of 85 per cent., *anhydrous* crystals containing from 5 to 10 per cent. of sodic chloride are deposited on cooling or slow evaporation, and these, on being again crystallised from spirit, give a crop of pure sugar. When ether is added to its solution in spirit of not more than 75 per cent., an oily layer is formed

at the bottom of the vessel, and in this crystals form, and continue to grow for eight or ten months; these are hydrated and definite in composition. They are thin, hard, and transparent, and of exactly the same composition as those obtained by recrystallisation of the original crop from water or, what is better, spirit of 10 per cent.

1·4011 grm. ether deposited compound lost ·1157 water by drying for 152 hours at 65° C., and gave ·2277 grm. sodic sulphate.

1·0121 grm. which had been recrystallised from water lost ·083 grm. water, and gave ·1641 grm. sodic sulphate.

	Calculated.	Ether deposited crystals.	Re-crystallised from water.
$C_{12}H_{22}O_{11}$ (by difference) ..	—	—	—
NaCl.....	13·4	13·39	13·36
H ₂ O.....	8·25	8·26	8·20

These numbers agree closely with those required by the formula $C_{12}H_{22}O_{11} \cdot NaCl \cdot 2H_2O$.

Many different preparations of this compound were analysed, some of which were deposited from solutions containing sugar or salt in excess. The crystals were pressed and dried, but not recrystallised.

Found	{ NaCl ..	13·48	13·5	13·5	13·6	13·35
	{ H ₂ O ..	—	—	—	8·0	—

The solutions containing three and four molecules of sodic chloride to the double molecule of sugar, for the most part, first deposited crystals of salt, and then those of the above-described compound; and hitherto I have been unable to satisfactorily determine the conditions necessary for the production of the body described at the beginning of this paper. I have only once succeeded in preparing that compound since the first lot of accidentally formed crystals, and on this solitary occasion there had been a continuance of very cold weather during the whole period of crystallisation. This second lot of crystals gave the following numbers on analysis:—

1·3005 grm. lost ·1004 water, and gave ·2927 grm. sodic sulphate, or 7·72 per cent. water, and 18·55 per cent. sodic chloride, which numbers show it to be the same body as that previously analysed.

The solutions containing sodic bromide can hardly be made to crystallise at all. A small quantity of minute confused crystals were deposited after some months from the solution containing $3NaBr$ to $2C_{12}H_{22}O_{11}$; these, when pressed and dried over oil of vitriol, gave numbers which would point to a formula $NaBr \cdot C_{12}H_{22}O_{11} \cdot 1\frac{1}{2}H_2O$, but it is more probable that when pure it is similar in composition to the analogous compound of sodic chloride: unless, like the iodine compound next to be described, it differs from the corresponding chlorine compound in respect to water of crystallisation.

	Calculated for $C_{12}H_{22}O_{11}.NaBr.2H_2O.$	Found.	Calculated for $2C_{12}H_{22}O_{11}.2NaBr.3H_2O.$
$C_{12}H_{12}O_{11}..$	—	—	—
NaBr	21.4	22.07	21.82
H ₂ O	7.48	5.49	5.72

The solutions containing sodic iodide give crystals of definite and constant composition with remarkable ease. These crystals always have the same composition whatever the proportions of the constituents in the mixture, unless one be in such large excess that it can in part crystallise out before the liquid becomes saturated with the compound. The solutions containing a moderate excess of sodic iodide yield the best crystals and quickest growth. They can be recrystallised as often as desired from water or dilute spirit, without suffering decomposition, forming large transparent crystals even from small quantities of solution—70 c.c. of the saturated solution when allowed to evaporate spontaneously over oil of vitriol often giving crystals more than an inch long and half an inch thick, resembling Rochelle salt in general appearance.

For the following analysis a portion, which had been three times crystallised from water, was used:—

(a.) .7949 grm. crushed and dried over oil of vitriol gave .472 grm. silver iodide.

(b.) 1.5307 grm. lost .0683 by drying 64 hrs. at 60°—100° C., and gave .275 grm. sodic sulphate.

These numbers agree with the formula $2C_{12}H_{22}O_{11}.3NaI.3H_2O.$

	Calculated.	Found.	
		a.	b.
NaI	37.88	37.9	37.87
H ₂ O	4.54	—	4.46

Other crystals from solutions containing either a large excess of sugar, or of sodic iodide, or which had been crystallised from spirit, gave the following numbers, which show that this body forms under very various conditions:

NaI ..	37.85	37.76	38.3	38.4	37.71	37.9
H ₂ O ..	—	—	—	4.35	—	4.67

When powdered, the crystals lose no water in a dry vacuum, but they lose all at 60° C. without melting, and the dry mass will then bear a temperature of about 120° C. without decomposition. Fresh crystals melt at about 90° C., and cannot afterwards be dried. They are slightly deliquescent in very moist air, soluble in 1.5 times their weight of water at ordinary temperatures, and in an indefinitely small quantity at 100° C. They are soluble in spirit to a less extent, nearly absolute

alcohol causes a separation of sugar. 20 grms. of crystals crushed between paper, but not otherwise dried, dissolved up to 100 c.c., gave a liquid which in a column of 200 mm., rotated a ray of polarised light $\frac{6.9}{100}$ as much as a plate of right-handed quartz 1 mm. in thickness, while the sugar contained in it (reckoned as pure) would, if brought to the same volume, have caused a rotation of $\frac{7.04}{100}$, from which it appears that the rotatory power of sugar is not altered by combining with sodic iodide.

The specific gravity of the crystals themselves is 1.854.

Professor W. H. Miller has been so kind as to examine these and some other crystals for me. His measurements and other observations here quoted. I take this opportunity of expressing my thanks and obligations for Professor Miller's most valuable help.

"Compound of cane-sugar and sodic iodide.

"*Oblique*.—Simple forms, a 1 0 0, c 0 0 1, v 1 0 1, t 1 0 $\bar{1}$, m 1 1 0, s 1 1 1, r 3 3 2.

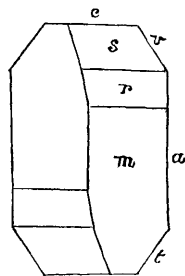
"Angles, measured by the angles between normals to the faces—

$c a$	85°	20'
$c v$	54	26
$c t$	118	53
$a m$	63	46
$c m$	87	56
$c r$	77	29
$c s$	72	30
$v s$	58	52

"Cleavage, c perfect, a less distinct. The forms to which the faces r , s , v , t , belong occur but seldom, and the values of the angles they make with c , and with one another, are liable to considerable uncertainty.

"*Twins*.—Twin-face a . $c\bar{v} = 9^\circ 20'$.*

"The optic axes are in a plane normal to the plane of symmetry. When seen through the face a and the opposite parallel face, in oil, they make with each other an angle of between 114° and 115° . A line bisecting this angle lies between normals to c and a , making with the latter an angle of about 12° . When the crystal is immersed in oil, so that light is refracted through the faces c , a , in a plane normal to the edge ca , the most refracted ray is found to be polarized in the plane of refraction."



* The $c\bar{v}$ is the letter c and a letter v turned upside down—a notation that I have found very convenient in expressing the angle between the faces of two crystals constituting a twin crystal.

None of the mixtures containing lithium gave any crystals other than those of sugar; those containing a large proportion of the salt simply dried up to a gummy mass.

The mixtures containing ammoniac salts gave no definite compounds. The chloride, when in small quantity, allowed sugar to crystallise out freely; when in large quantity, it hindered crystallisation, but in time allowed the liquids to deposit well formed, isolated, anhydrous crystals, generally opaque, but having the appearance of a definite body. These crystals in fact contained most variable proportions of ammoniac chloride, *e.g.*, 7·2, 6·76, 6·7, 0·78, 0·85, and 4·9 per cent.

No results were obtained from the solutions containing ammoniac iodide.

These crystals of sugar, containing ammoniac chloride, and the equally distinct, though generally smaller ones, containing potassic bromide, and those deposited from a hot alcoholic solution of the lower salt compound, must, I imagine, be built up by an *anhydrous* compound of the salt and sugar, isomorphous with sugar itself, crystallising out, together with an excess of the latter.

Professor Miller has examined some of the crystals containing ammoniac chloride, and reports as follows:—

“The crystals of the compound of cane sugar and ammoniac chloride are not distinguishable in form from those of pure sugar. In consequence probably of the difficulty of removing the syrup from the faces of the crystals, the measurements made by Rammelsberg, Hankel, and Wolff, differ considerably from one another (Rammelsberg, *Handbuch der krystallographischen Chemie*, S. 397), and from measurements made by myself some time ago (Cambridge Philosophical Transactions, vol. vii, p. 209).

“The crystals of sugar and ammoniac chloride belong to the oblique system. The simple forms are:—

$$c \ 0 \ 0 \ 1, \ a \ 1 \ 0 \ 0, \ e \ 0 \ 1 \ 1, \ r \ 1 \ 0 \ 1, \ s \ \bar{1} \ 0 \ 1, \ m \ 1 \ 1 \ 0, \ o \ 1 \ 1 \ 1.$$

“As in crystals of pure sugar, the forms to which the faces *e*, *o* belong appear to be hemihedral, those faces only being found which are on one side (not always the same) of the plane of symmetry.

“Taking the angle between normals to two faces of a crystal drawn towards the faces from a point in the interior, for the measure of the dihedral angle made by the faces, Wolff’s observations give:—

<i>c a</i>	=	76°	30'
<i>a r</i>	=	46	15
<i>a s</i>	=	115	30
<i>c e</i>	=	40	30
<i>a m</i>	=	50	46

$r o$	$=$	32°	$24'$
$c m$	$=$	81	30
$c o$	$=$	43	10
$c e$	$=$	40	30
$m r$	$=$	64	4
$m s$	$=$	105	48
$a e$	$=$	79	46
$m o$	$=$	38	20
$a o$	$=$	54	16

“The differences between these angles and those of the crystals of sugar containing ammoniac chloride, are not larger than the differences between the angles obtained for pure sugar by the observers mentioned above.”

That the crystals are not simply sugar with adhering ammoniac chloride is, I think, shown by their individual perfection, and by the fact that they are deliquescent, whereas neither constituent is so.

The solutions of all the bodies described in this paper, especially those of the lower salt compound, exhibit persistent supersaturation in a remarkable degree. A saturated warm solution, when cooled and shut up in an air-tight vessel with several crystals of the solid body, continues to deposit more of the compound for several months.

It is to be remarked that the sodium salts which give definite compounds are known to crystallise with two molecules of water, when deposited at low temperatures, and that the iodide does so at all temperatures up to 20° C., whereas the corresponding potassium salts are anhydrous, at whatever attainable temperature they may be crystallised.

The composition of the sodic iodide compound makes it seem probable that the true molecular weight of cane sugar should be represented by $C_{24}H_{44}O_{22}$.

I have endeavoured to prepare compounds of sugar with sodic acetate, nitrate, iodate, and rhombic phosphate, but in no case did I get any but anhydrous bodies of indefinite composition.

These experiments were made in Messrs. Martineau's refining laboratory.

