Qualitative Observations on Cyanoplatinate(II)-Compounds

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It is the purpose of the present note to point out that simple, qualitative experiments indicate the existence of a number of hitherto unreported cyanoplatinate(II) compounds, and that the methods implied most likely would be of help in a more systematic search for new materials of this type. The technique makes use of the fluorescence excited in the crystals by ultraviolet radiation, through the fact that the color of the fluorescence usually is characteristic of the species under study.

The formation of salt hydrates of a single cyanoplatinate(II) salt can be observed in the following way. A dilute solution of the salt is placed in a thin layer on the surface of a porous porcelain plate. After a gentle drying the centre of the plate is heated with a micro-burner. Under an ultraviolet lamp the colors corresponding to different salt hydrates can now be observed as rings going out from the centre. The color changes can be reversed when water vapor is admitted to the plate. It is in this way seen that the cyanoplatinate(II) salts in general form several salt hydrates. Only in very few cases are detailed investigations [1] available for comparison.

Evidence for the formation of double salts comes from small scale crystallization experiments. Solutions of two salts are mixed on a watch glass and allowed to crystallize. Double salt formation can now be deduced from the appearance of fluorescence colors not belonging to the constituents. Many such cases were observed.

A search for new cyanoplatinate(II) materials should be of special interest since it has recently been shown [2], in a study involving 11 salts, that a number of these show promise for scintillation counting. Thus, $Cs_2Pt(CN)_4 \cdot H_2O$ has a light yield of 70 % relative to NaI(Tl) and a decay time of 0.47 μsec, and must be regarded as having certain advantages in experimental nuclear physics and other fields where radiation detection is involved. It would indeed be very valuable if a reinvestigation of the cyanoplatinate(II) salts should result in a scintillator providing better energy resolution than NaI(Tl). However, even without the stimulus of practical and experimental applications a study of the chemistry and luminescence properties might well be rewarding.

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On the Labelling of Sulphur-contaning Amino Acids and γ-Glutamylpeptides after Injection of Labelled Sulphate into Onion (*Allium cepa*)

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In order to establish the utilization of sulphate in the biosynthesis of the numerous sulphur-containing amino acids and peptides in the onion, sulphate labelled with ^{35}S was injected into onions in dilute NaCl solution. 0.2 ml of a solution containing 0.5 mC of ^{35}S was injected into the onion in five different places. The onion sets were placed for six days in moist sand before the injection. Subsequently, the enzymic reactions were inhibited by placing the onions in ethanol after certain intervals: the first onion 7 days after the injection, the second after 24 days, the third after 46 days, when some roots had been formed, and the last after 85 days, when the onion had green leaves. The experiment was started in September 1961, onions harvested in August being used as onion sets. Growth was extremely slow, as is revealed by the fact

Table 1. The radioactivities of the different fractions of onion injected with $^{35}SO_4^{2-}$. The onions were planted on September 9, 1961, $^{35}SO_4^{2-}$ was injected on September 15, 1961.

Dry weight of the onion g	Reaction time of $^{35}SO_4^{2-}$ days	Radioactivity of the amino acid fraction c/min *	Radioactivity of the water fraction c/min *
77	7	14 636 000	26 071 000
100	24	21 713 000	15 375 000
72	46	17 100 000	19 728 000
7 green leaves	85	759 000	1 367 000
95 bulb		10 400 000	16 550 000

* Countings uncorr.

that the first roots only began to appear after a month, and the green leaves only after two months.

The onions were chilled with solid carbon dioxide in ethanol, and then homogenized in cold ethanol. The ethanol content was

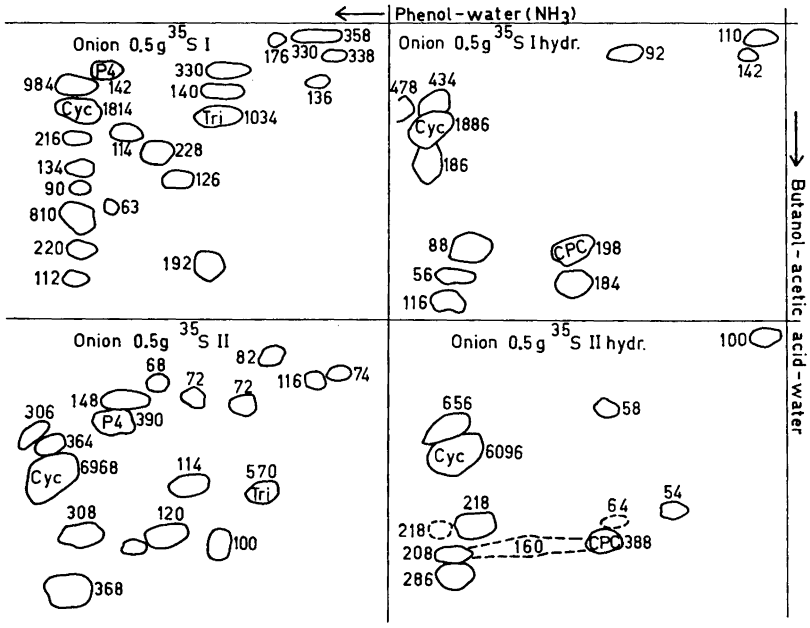

Fig. 1. Two-dimensional chromatograms of ^{35}S-containing amino acids and γ-glutamyl peptides in onion. Onions were placed for 6 days in moist sand and then injected with labelled sulphate. The upper chromatograms were developed 7, and the lower ones 46 days after the injection of labelled sulphate. The chromatograms to the left were developed before, and those to the right after hydrolysis. The spots were drawn on the basis of radiation measurements, and the numbers give the counts/min. Cyc = cycloalliin, P 4 = γ-L-glutamyl-(+)-S-(prop-1-enyl)-L-cysteine, Tri = γ-L-glutamyl-S-(β-carboxy-propyl)-L-cysteinyl-glycine, CPC = (−)-S-(β-carboxy-propyl)-L-cysteine.

70 % (= ethanol + the water which the onions contained). The homogenate was allowed to stand for 24 h, after which it was filtered and the precipitate washed with 70 % ethanol. The filtrates were combined, and the amino acids and acidic peptides (γ-glutamyl peptides) separated on an Amberlite IR-120 (H-form) column. 20 ml of resin and 300 ml of water were used for the separation, and 200 ml of 1 N ammonia for the elution of the amino acids and peptides.

In order to determine the radioactivity, the following samples were taken: (1) of the ethanol extract, (2) of the aqueous solution which had passed through the resin, (3) of the amino acid fraction eluted from the resin with ammonia. The radioactivity of the whole onion was calculated from that of the samples. A two-dimensional chromatogram (BuOH-AcOH-H_2O; 630—100—270; water-saturated phenol-NH_3) was prepared from the amino acid fraction. Radioautograms were made from the chromatograms obtained for the location of the active spots. The intensity of the radiation was then measured on the paper, and the paper chromatograms were sprayed with 0.25 % ninhydrin. The spots could partly be identified by comparison with chromatograms run on known amino acids and γ-glutamyl peptides.

Table 1 shows the radioactivity (c/min) of the amino acid fraction and the water fraction of the whole onion at different stages of growth.

The first radioautogram, made from the paper chromatogram of the amino acid fraction isolated, was prepared 7 days after the injection and showed 21 spots labelled with ^{35}S. When the amino acid fraction was hydrolyzed with 1 N HCl for 3 h at 100°C, only 12 radioactive spots could be seen on the paper chromatogram [1] (Fig. 1).

The decrease in the number of spots is partly due to the hydrolysis of γ-glutamyl peptides, partly to the decomposition of sulphur-containing amino acids (*e.g.* S-(prop-1-enyl)-cysteine sulpoxide). Some spots present on the chromatogram 7 days after the injection could not be seen on the paper chromatograms prepared from onions 46 days after the injection. On the other hand, new spots had now appeared (Fig. 1).

Among the spots occurring on the radioautograms cycloalliin [2] and γ-glutamyl-S-(β-carboxy-propyl)-L-cysteinyl-glycine [3] could be identified by comparison with the amino acids and γ-glutamyl peptides previously isolated in this laboratory, and after hydrolysis the corresponding S-(β-carboxy-propyl)-L-cysteine [3]. Methionine, glutathione and γ-glutamyl-S-(prop-1-enyl)-cysteine sulphoxide [4] probably also occurred on the chromatograms. The highest labelling was found in cycloalliin, which is the most abundant amino acid in the onion. The labelling of cycloalliin increased throughout the growing season (Table 2).

Table 2. The radioactivity of the cycloalliin spot on the paper chromatogram in different periods after the injection of $^{35}SO_4^{2-}$.

7	days	1814 c/min/0.5 g *	
24	,,	6064 ,,	
46	,,	6968 ,,	
85	,,	3540 ,,	green leaves
		4172	bulb

* Countings uncorr.

The spot (192 c/min) seen on the upper chromatogram (Fig. 1), which travels rapidly in butanol-acetic acid-water and with average speed in phenol-water, and which does not disappear on hydrolysis (184 c/min), is obviously a hitherto unknown S-containing amino acid.

Suzuki and his collaborators [5] have recently started to study the peptides in garlic, using sulphate labelled with ^{35}S during cultivation. After 24 h feeding, some of the γ-glutamylpeptides isolated in this laboratory from onion and chemically characterized, were labelled.

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