SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM(IV) AFTER EXTRACTION OF ITS PHENANTHRENEQUINONE MONOTHIOSEMICARBAZONE COMPLEX INTO MOLTEN NAPHTHALENE

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PLATINUM(IV) reacts with most of the organic reagents[1-6] only on heating. The ordinary liquid-liquid extraction cannot be applied directly for the extraction of the metal chelates into low boiling solvents. In this work, phenanthrenequinone monothiosemicarbazone has been used for the extraction and spectrophotometric determination of Pt(IV) by the technique of solid-liquid separation after liquid-liquid extraction[7,8].

The absorption spectra of the reagent and its Pt-complex were taken in naphthalene-chloroform solution against water and the reagent blank respectively. The complex absorbed strongly and showed λ_{max} at 486–495 nm where the absorption by the reagent was negligible. The characteristics of the spectral curves remained the same at various pH values showing the formation of only one complex. The absorbances of the extracts were constant at pH 0.8–4.4. The system obeyed Beer's law from 7.5 to 150 μg Pt(IV) per 10 ml of the final solution. The molar absorptivity and Sandell's sensitivity were calculated to be 1.630 $\times 10^4$ l.mol^{-1}.cm^{-1} and 0.0119 μg/cm^2 respectively. Ten replicate determinations containing 45 μg Pt gave mean absorbance of 0.376 with standard deviation of 0.0035 and relative standard deviation of 0.93%. Application of the methods of continuous variations and mole ratio indicated the formation of a 1:2 Pt-ligand complex. In the determination of 45 μg Pt in 10 ml of the solution, the following species (in mg) could be tolerated: F^-, Cl^-, Br^-, NO_3^- (10); I^-, SO_4^{2-}, $C_2O_4^{2-}$, tartrate, PO_4^{3-}, citrate (5); TeO_3^{2-}, MoO_4^{2-}, AsO_3^{3-}, VO_4^{3-}, EDTA, Ag^+, Sn^{2+}, Pb^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, ZrO^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, In^{3+}, Bi^{3+}, Fe^{3+}, Au^{3+}, OsO_4 (2); WO_4^{2-}, Cr^{3+}, tartar emetic (1); Ru^{3+}, Rh^{3+} and Ir^{3+} (0.5). The method is applied to determine Pt(IV) in synthetic mixtures containing the other Pt-group metals, Ag^+, Ni^{2+}, Cu^{2+} and Au^{3+} (maximum error 1.1%).

Reagents

Standard Pt(IV) solution was prepared by dissolving platinum chloride (1 g ampule) in 100 ml of 6 M HCl and diluting to 1 litre. It was standardized by the usual method[9]. Phenanthrenequinone monothiosemicarbazone, after purification[10], was dissolved in ethanol to get 1×10^{-3} M solution.

Procedure

To a suitable aliquot of Pt(IV) solution, 2 ml of the reagent solution (10^{-3} M) were added and the volume was made to about 30 ml. The pH was adjusted between 0.8–4.4 with an acetate buffer and the solution transferred to a 100 ml round-bottom stoppered flask. Naphthalene (2 g) was added to it and the mixture was stirred for 30 min on a hot plate at 90° for complete extraction. The flask was removed from the hot plate and allowed to stand for few min. The solidified naphthalene containing platinum-complex was separated by filtration, dried on a filter paper and dissolved in chloroform. The chloroform solution was dried with anhydrous Na_2SO_4, made up to 10 ml with the solvent and its absorbance was measured at 495 nm against a reagent blank.

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CHEMICAL INVESTIGATION OF *PSIDIUM GUAJAVA* ROOTS

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PSIDIUM GUAJAVA is an economically important plant of medicinal value. Flavonoids, gallic acid and tannins are invariably present in all the parts of the plant *viz.* fruits[1], leaves[2,3], stembark[4], heart-wood[5]. In this investigation roots have been investigated and found to contain β-sitosterol, quercetin, leucocyanidin, gallic acid, 2,3,4-trigalloyl 6-(m-trigalloyl) glucose.

The powdered roots were extracted by the following three different procedures.

i) *Extraction with boiling ethanol*: The extract concentrated and fractionated into light petrol, ether, ethyl acetate and acetone soluble fractions. Petroleum ether fraction gave β-sitosterol, ether fraction gave quercetin, gallic acid and ethyl gallate, while ethyl acetate fraction showed the presence of leucocyanin; from acetone fraction tannin was isolated.

ii) *Extraction with bioling acetone*: The extract concentrated and fractionated into light petrol, benzene, chloroform and acetone soluble fractions respectively. Light petrol gave β-sitosterol, benzene fraction gave quercetin. Chloroform gave leucocyanidin and tannin II was isolated from the acetone soluble fraction of the extract.

Extraction with water was carried out at room temperature and the extract after deionisation over cation and anion exchange resin was concentrated and then fractionated using light petrol ether, ethyl acetate and acetone respectively. Light petrol fraction did not give anything significant, ether and ethyl acetate fractions gave quercetin and leuco-cyanidin respectively and from acetone fraction a tannin was isolated and found to be identical with tannin II.

β-sitosterol, quercetin, leucocyanidin, ethyl gallate and gallic acid were identified by comparison with respective authentic samples.

Tannin I – It was isolated as buff-coloured chromatographically homogeneous semicrystalline compound and analysed for $C_{34}H_{28}O_{22}4H_2O$. It gave blue precipitate with ferric chloride[2] and positive Molisch test showing it to be a polyphenol glycoside. However, positive test with AHP reagent indicated the presence of a potential aldehyde group. Acid as well as alkaline hydrolysis of the compound gave gallic acid and glucose. Therefore, it could be a galloyl ester of glucose. Quantitative estimation of glucose and gallic acid in the hydrolysate showed the presence of four units of gallic acid per mole of glucose. Quantitative estimation of glucose and gallic acid in the hydrolysate showed the presence of four units of gallic acid per mole of glucose. As the reducing group of the sugar is free, it could be characterised as tetragalloyl glucose, with four galloyl units attached at 2,3,4 and 6 positions of glucose assuming the sugar to be in pyranose form.

The isolation of ethyl gallate from the ethanolic extract of roots was rather suggestive that depside linkages if present in the genuine tannin might have got ethanolysed during extraction with ethanol, resulting in the formation of ethyl gallate and tetra galloyl glucose. This has been reported in the past by Haworth *et al*[6].

Tannin II – It was a microcrystalline compound, chromatographically homogeneous and analysed for $C_{48}H_{36}O_{33}.4H_2O$. It gave all the characteristic tests of tannins[6] similar to tannin I. On acid as well as alkaline hydrolysis it gave glucose and gallic acid. Quantitative hydrolysis showed the presence of six moles of gallic acid per mole of glucose.

In order to get more information about the structure, it was methylated with diazomethane and subsequently hydrolysed when 3,4,5-tri-O-methyl and 3,4-di-O-methyl gallic acids were obtained which were identified by mmp and co-chromatography with authentic samples. The detection of 3,4-di-O-methyl gallic acid in the hydrolysate was indication of the presence of depside links in the molecule. Intensity of the two spots of 3,4,5-tri-O-methyl gallic acid and 3,4-di-O-methyl gallic acid was compared with the intensity of the spots obtained by running the artificially prepared mixtures of these acids in different molecular proportions on descending strip chromatogram. The 2:1 proportion of 3,4,5-tri-O-methyl and 3,4-di-O-methyl gallic acid respectively, agreed with that of the hydrolysate, which supported the conclusion that four ester and two depside links are present in the molecule.