methanol-chloroform (3 : 17). All the compounds were identified by co-TLC, IR, UV, NMR and ms spectral data and preparation of derivatives.

Compound A, $C_{38}H_{50}O_6$, Yellow needles, m.p. 122–24°, $[\alpha]_D^{26}$ + 130°. Rf 0·4 (benzene-methanol, 1 : 1), M^+ 602. It was identified as xanthochymol.

Compound B, $C_{38}H_{50}O_6$, pale yellow needles, m.p. 218–20°, Rf 0·88 (methanol-chloroform, 3 : 17) was identified as isoxanthochymol.

Compound C, $C_{30}H_{20}O_{10}$, yellow crystals, m.p. 250°, Rf 0·82 (methanol-chloroform, 3 : 17), hexa methyl ether, m.p. 258–60°, Rf. 0·5 (Benzene-pyridine-formic acid, 36 : 9 : 5). It was identified as Volkensiflavone.

Compound D, $C_{30}H_{20}O_{11}$, yellow granules, m.p. 301–2°, $[\alpha]_D^{26}$ 0°, Rf 0·71 (methanol-chloroform, 3 : 17), acetate, m.p. 210–2°, methyl ether, m.p. 210°, Rf. 0·94 (benzene-pyridine-formic acid, 36 : 9 : 5), identified as morelloflavone.

Compound E, $C_{13}H_8O_4$, yellow solid, m.p. 266–68°, Rf 0·80 (ethyl acetate chloroform, 1 : 9) and was identified as 1,5-dihydroxyxanthone.

Compound F, $C_{30}H_{22}O_{10}$, yellow crystals, m.p. 210°, $[\alpha]_D^{26}$ -9° 16′, Rf 0·63 (methanol-chloroform, 3 : 17), hexa methyl ether, m.p. 132–3°. It was identified as GB–1*a*.

Compound G, $C_{13}H_{10}O_6$, yellow needles, m.p. 220–22°, Rf 0·66 (benzene-ethyl acetate, 14 : 6), methyl derivative, yellow crystals, m.p. 164–5°. The compound was identified as maclurin.

Compound H, $C_{13}H_8O_4$, yellow solid, m.p. 237–40°, Rf 0·68 (ethyl acetate-toluene, 15 : 85) and was identified as 1,7-dihydroxyxanthone.

Compound I, $C_{30}H_{22}O_{11}$, amorphous powder, m.p. 202–4°, Rf 0·50 (methanol-chloroform, 3 : 17), hepta methyl ether, m.p. 126–7°. It was identified as GB–1.

The presence of 1,5-dihydroxyxanthone; 1,7-dihydroxyxanthone, maclurin and GB–1 reported for the first time in this species.

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SPECTROPHOTOMETRIC METHOD FOR THE DIRECT DETERMINATION OF CYSTEINE IN THE PRESENCE OF OTHER NATURALLY OCCURRING AMINO ACIDS

Sulphur containing amino acids are of great importance in biochemical processes of animals. A number of spectrophotometric procedures have been developed for the determination of cysteine and none of them are specific. We have observed that cysteine out of more than 20 other amino acids tested found to form red coloured ternary complex at pH 3·5 (λ_{max} : 510 nm). The maximum intensity of the colour is developed in about 160 minutes and is stable for several hours. The concentration of the product formed is directly proportional to cysteine initially taken. Based on this, a simple and specific method is developed for the determination of cysteine and cystine.

Experimental

Procedure for cysteine : To amounts of cysteine varying from 0·001 to 0·0075 millimoles in 4 ml solution, 15 ml of potassium biphthalate-hydrochloric acid buffer (pH 3·3), 2 ml of 0·2% metol solution and 3 ml of 0·01 M potassium dichromate solution were added successively. It was diluted to 25 ml with distilled water in a calibrated volumetric flask and the absorbance was measured at 510 nm after 160 minutes against a corresponding reagent blank prepared in the same manner. The cysteine content was computed from an appropriate calibration curve.

Procedure for cystine : 10 ml of cystine solution containing between 0·00065 and 0·0075 millimoles of cystine per ml was treated with requisite quantity of 1·0 N potassium hydroxide to maintain the pH 9·20. After adding 10 ml of 2% sodium borohydride solution, the resulting mixture was warmed on a water-bath which was preheated to 50° for 30 minutes. Then the excess sodium borohydride was destroyed by dropwise addition of 10 ml of 10% acetic acid. Finally, the solution was diluted to 50 ml after the pH of the solution was brought to 5·0. 4 ml of this solution were taken and completed the determination as given for cysteine.

Procedure for groundnut protein: 1 g of groundnut protein was hydrolysed as reported earlier[1] by refluxing with 15 ml of 16% hydrochloric acid for 24 h.

After removing the excess hydrochloric acid under vacuum, the residue which contained cystine was dissolved in warm water and filtered. The filtrate was diluted to 50 ml, from which 25 ml solution was taken and followed the procedure as outlined for cystine.

Results and Discussion

The results obtained in the analysis of cysteine are accurate within 0·8%. The comparison of the results obtained in the proposed method and paper chromatography procedure[2] showed that they agree within 2% error. Beer's law is found to be valid over the concentration range 0·001 to 0·0075 millimoles of cysteine per 25 ml with molar absorptivity value $1·73 \times 10^3$ l. mole^{-1} cm^{-1}.

There is no interference from alanine, glycine, valine, leucine, lysine, tryptophan, serine, threonine, isoleucine, glutamic acid, aspartic acid, arginine, tyrosine, phenylalanine, methionine, cystine, glucose, lactose, sucrose, purines and pyrimidines upto 2 millimoles but histidine, proline and hydroxyproline interfere when present in concentrations more than one millimole. However, glutathione interferes. The method is found to be unsuitable in presence of ascorbic acid, epinephrine and heavy metals such as mercury and lead. Hence, the reaction appears to be highly specific for cysteine and has the advantage that cysteine need not be separated from the amino acid mixtures or from the remaining amino acids which are present in protein hydrolysates.

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CATIONS OF TETRAPHENOXY NIOBIUM(V) AND TANTALUM(V) CHLORIDES

Niobium(V), tantalum(V) and antimony(V) chlorides act predominently as chloride ion acceptors[1–3]. The spectra of addition compounds of tetrachlorides of sulphur, selenium and tellurium with niobium(V) and tantalum(V) chlorides show the presence of pyramidal MCl_3^+ and weakly perturbed octahedral $NbCl_6^-$ and $TaCl_6^-$ ions in the crystal[4]. Raman spectra of solidified $SbCl_5$–$NbCl_5$ mixtures have been explained on the basis of a dimer $SbNbCl_{10}$.[5] Cationic complexes of the type T_4Nb^+ and T_4Ta^+ where T is the tropolone cation have been stabilized by large symmetrical anions.[6–8] An attempt has therefore been made to explore the possibility of the formation of ions of the type $M(OC_6H_5)_4^+$ from these phenoxides.

Tetraphenoxy niobium(V) and tantalum(V) chlorides were prepared by the methods as described in literature[9,10]. Compounds of composition $MSb(OC_6H_5)_4Cl_6$ were prepared by mixing the two components in 1 : 1 molar ratio in dichloromethane. The resulting solutions were refluxed for one hour, when reactants went into solution. The compounds were isolated by the addition of inert solvents like petroleum ether. They were filtered in dry atmosphere and finally dried under vacuum.

Stoichiometric composition of these compounds has been established by carrying out conductometric titrations of tetraphenoxy niobium(V) and tantalum(V) chlorides *versus* antimony(V) chloride; in nitrobenzene at 25 ± 0·1° C. The conductance – Composition curve (Fig. 1) reveal sharp breaks at 1 : 1 molar ratio suggesting that the resulting compound has 1 : 1 stoichiometry. The continuous increase in conductance of the solution has been attributed to the formation of ions in solution, thus excluding the possibility of the formation of non conducting compounds of the type $SbNbCl_6(OC_6H_5)_4$. These compounds are crystalline solids and have high melting points. They are insoluble in nitromethane, acetonitrile but fairly soluble in nitrobenzene. Molar conductance values of millimolar solutions of these compounds in nitrobenzene suggest their ionic character.

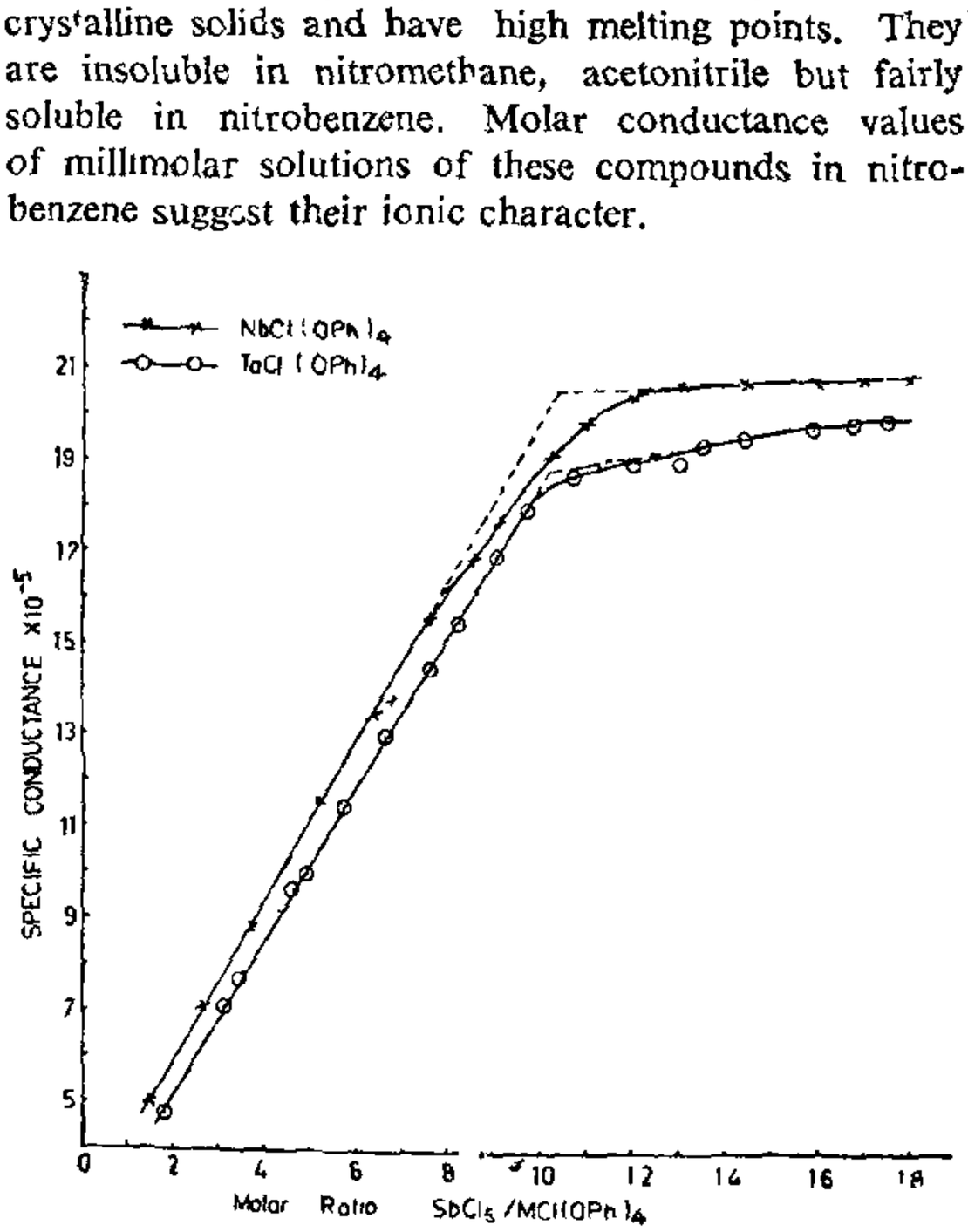

FIG. 1. Conductometric titrations of tetraphenoxy M(V) chloride against $SbCl_5$ in nitrobenzene at 25 ± 0·1° C.