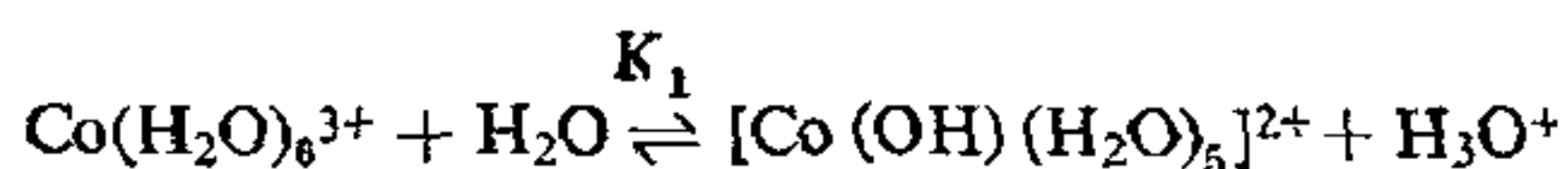


TABLE I
Oxidations by bonded mechanism with $\text{Co}(\text{H}_2\text{O})_6^{3+}$
as the active species

Substrate	Medium	K	Refer- ence
Propionic acid	HClO_4 (39% CH_3CN) (15° C)	0.72	6
Phenylacetic acid	HClO_4 (39% CH_3CN) (15° C)	27.7	6
$\text{Ph}(\text{CH}_2)_3\text{COOH}$	HClO_4 (50% CH_3CN) (20° C)	4.7	7
$\text{Ph}(\text{CH}_2)_4\text{COOH}$	HClO_4 (50% CH_3CN) (20° C)	17.0	7
$\text{Ph}(\text{CH}_2)_5\text{COOH}$	HClO_4 (60% CH_3CN) (20° C)	14.0	7
Glutaric acid	HClO_4 (15° C)	12.37	2
Glutaric acid	H_2SO_4 (15° C)	1.65	2
4-Hydroxy-4-methylpentan-2-one	HClO_4 (20° C)	7.8	8

has not been realized in any of the oxidations by $\text{Co}(\text{III})$ where K_1 is the hydrolytic equilibrium constant,



The general characteristic of all the oxidations by $\text{Co}(\text{III})$ occurring *via* bonded mechanism with $\text{Co}(\text{H}_2\text{O})_6^{3+}$ as the active oxidant cannot be a mere coincidence of the experimental facts. This may point to a common reason as to why the hexa-aquo cobaltic ion is the active species in oxidations proceeding *via* complex formation between $\text{Co}(\text{III})$ and substrate. Probably, in reactions occurring *via* inner sphere oxidative path or bonded mechanism, the deciding factor is the lability of the active species of $\text{Co}(\text{III})$. The change in spin multiplicity of $\text{Co}(\text{III})$ is inevitable whether the oxidation occurs by bonded or non-bonded mechanism. But the ruling factor in oxidations by bonded mechanism appears to be the lability of the cobaltic species. Since $\text{Co}(\text{H}_2\text{O})_6^{3+}$ is more labile than $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ the former is found to be the active species in all the oxidations proceeding *via* complex formation.

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SIMPLE PHOTOMETRIC ESTIMATION OF METHYLDOPA

METHYLDOPA, L-3-(3,4-Dihydroxyphenyl)-2-methylalanine is a widely used antihypertensive agent. The reported methods of micro estimation of methyldopa include colour formation with iron salts^{1,2}, complex formation with molybdenum³, colour formation with *p*-dimethylaminobenzaldehyde⁴ and with thiosemicarbazide⁵. The methods are either not specific or they require long time and critical reaction conditions.

In the present paper a simple and quick photometric estimation of methyldopa has been described with: (i) *p*-phenylenediamine dihydrochloride (PPDA), (ii) aqueous ammonia, (iii) *p*-aminophenol (PAP) and (iv) resorcinol.

A comparative data of estimation of methyldopa with the four reagents are given in Table I.

Experimental

Methyldopa standard was prepared in 0.1 M HCl. All the reagents used were of analytical grade.

Assay Procedures

(i) By PPDA—Aliquots of standard and samples containing 100 μg were mixed with 1 ml of reagent and 2 ml of NaOH and diluted to mark (10 ml) with water. The absorbance of the colour at 494 nm against a reagent blank was measured after 5 minutes.

(ii) By NH_4OH —In 10 ml graduated test tubes, aliquots containing 200 μg of standard and sample

TABLE I

Reagent	Reagent concentration	Concentration of alkali	Colour stability minutes	λ_{\max} nm	Beer's law obeyed in the range $\mu\text{g/ml}$	Extinction coefficient of the coloured species $\times 10^{-3}$
PPDA	1 ml of 0.5% (Aqueous)	2 ml of 1 M NaOH	120	494	3 to 20	5
Ammonia	..	2 ml of 10 M NH_4OH	7	418	5 to 35	2.2
PAP	1 ml of 0.04% (Alcoholic)	1.5 ml of 10 M NH_4OH	5	588	5 to 20	4.8
Resorcinol	1.5 ml of 0.1% (Aqueous)	4 ml of 1 M NH_4OH	30	416	1.5 to 12	19.5

TABLE II

Preparation	Methyldopa present (mg)	Methyldopa found (mg)				Methyldopa found by official method ¹
		PPDA	Ammonia	PAP	Resorcinol	
Tablet (A)	250	250.3	250.6	249.3	249.8	250.1
Tablet (B)	250	249.8	250.2
Tablet (C)	250	250.1	249.4	249.3	249.9	249.8
Tablet (D)*	250	250.2	250.4	250.3	250.5	250.1
Tablet (E)*	250	249.6	250.1	250.1	249.5	249.8

* These tablets contain 15 mg of hydrochlorothiazide.

were mixed with 2 ml of ammonia and diluted to 10 ml with water. The absorbance was measured at 418 nm against water blank, within 7 minutes.

(iii) By PAP—The aliquots of standard and sample containing 100 μg were mixed with 1 ml reagent and 1.5 ml of ammonia, in 10 ml graduated test tubes. Volume was made by water. The absorbance was measured against a reagent blank within 5 minutes.

(iv) By Resorcinol—20 μg of each standard and sample were mixed with 1.5 ml reagent and 4 ml ammonia in 10 ml. test tubes, then diluted with water and absorbance was measured at 416 nm against a reagent blank.

$$\text{mg of methyldopa} = \frac{A_t \times S \times D}{A_s \times 1000}$$

A_t = Absorbance of sample.

A_s = Absorbance of standard.
 S = μg of standard/ml.
 D = Dilution factor.

Table II gives the application of the method for analysis of methyldopa in marketed samples.

Discussion

The proposed photometric estimation of methyldopa is much quicker than that with the reported methods of its analysis. The estimation with resorcinol is extremely sensitive and methyldopa can be successfully estimated in blood samples employing resorcinol as the colour developing agent. The method is therefore important from forensic science point of view.

It was observed that the excipients added to methyldopa such as starch and tale do not interfere.

It is clear from the data given in Table II that the results obtained by the present method compare satisfactorily with those of the official method.

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CONE-IN-CONE STRUCTURE FROM UPPER CRETACEOUS ROCKS OF TIRUCHIRAPALLI, TAMIL NADU, SOUTH INDIA

A DETAILED study of the Upper Cretaceous rocks of Tiruchirapalli area by the author (1969-75) has revealed the presence of many sedimentary structures associated with the arenites and argillites of Utattur, Trichinopoly, Ariyalur and Niniyur groups.

In this paper only the cone-in-cone structure is reported. Occurrence of the cone-in-cone structure in the area investigated is confined to the thin bands of poorly fossiliferous argillite members of Utattur group which are gypseous and also commonly associated with concretions. Blanford¹ has referred these argillites as zig-zag shales. The rocks of this group have regular bedding and generally dip south-east at low angles. The specimens are collected from about a kilometer away from Periyakurke-Agaram village along N.NE. direction and from the *nalas* almost east of Utattur village.

Cone-in-Cone structures are mostly found in clusters. Individual cones are normally circular, with a series of cones one in the other. The sides of the cones are always transversely ribbed or fluted. The ribs are sharp and leave deep impressions of ridges and annular depressions on the inner surface of the enclosing cone (Fig. 1). The ribs or ridges are discontinuous, but are parallel to the bases. This feature is more pronounced near the base of the cone and fades towards the apex. The number of cone layers in each cone-in-cone structure varies very much (Fig. 2).

The height of the present cone-in-cone structures varies from 2.5 to 20 cm, width (base) is 10-12.5 cm, and the apex 2.5 cm. The width of the base

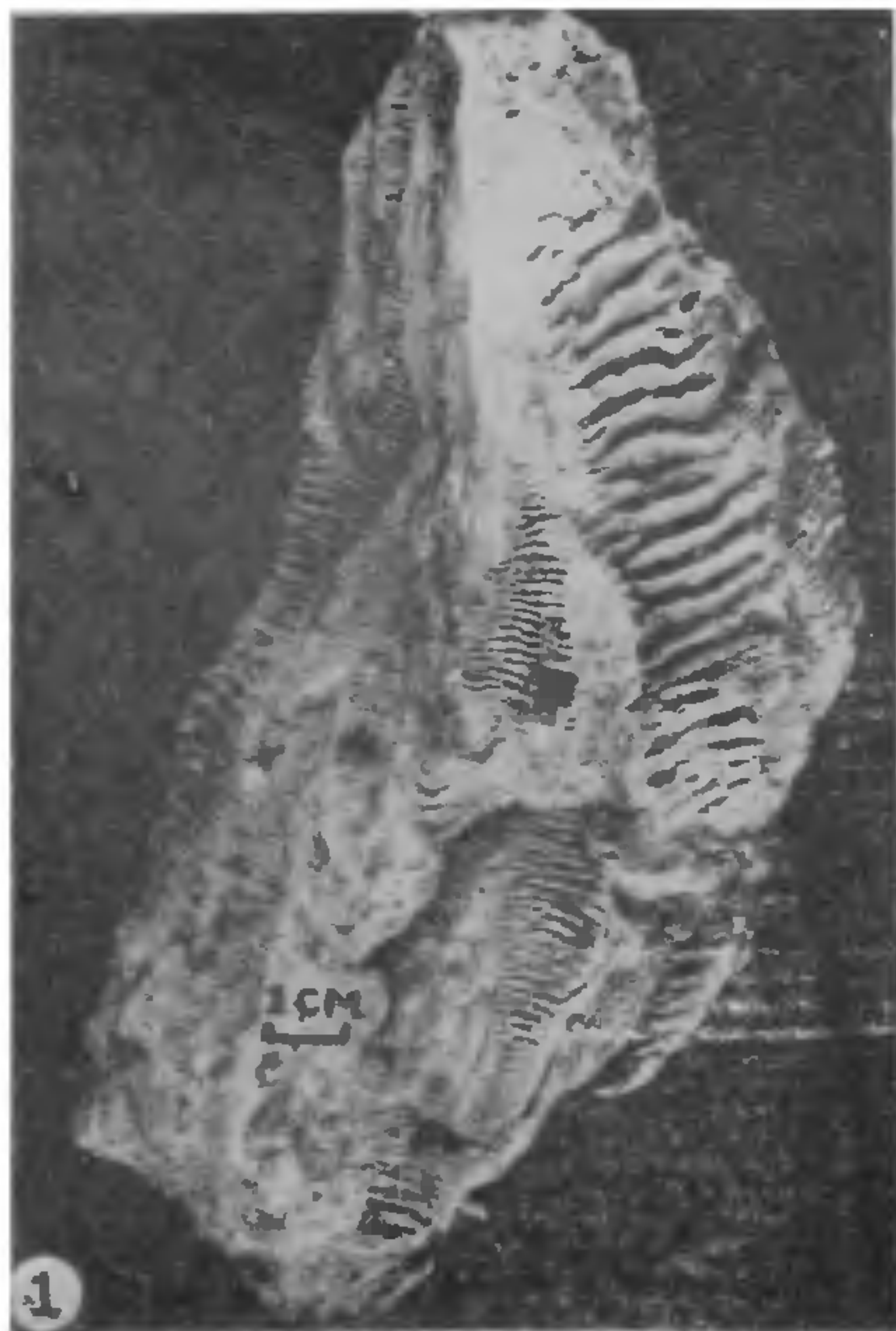


FIG. 1



FIG. 2