

SHORT COMMUNICATIONS

WEAK GAMMA TRANSITION OF 0.89 MeV OF ^{207}Pb

R. K. MISHRA

Department of Physics, AL-Fateh University,
Tripoli, Libya.

THE ^{207}Bi isotope decays through electron capture to ^{207}Pb which further de-excites to ground state with the emission of gamma rays. Many workers have studied the decay of ^{207}Pb by using coincidence techniques. Besides the well-established gammas of ^{207}Pb , controversial reports appear in literature about some of its weak gamma transitions^{1,2}. Recent studies have reported³ the weak gamma transitions of 1.440 MeV and 1.460 MeV. However, they failed to detect the 0.8978 MeV gamma transition as reported earlier^{1,2}. This communication describes the attempts to detect the weak gammas by analysing the single conversion electron spectrum with a surface barrier Si-detector.

We have used an old and chemically pure ^{207}Bi source of about $1\mu\text{Ci}$ which was obtained from Amersham (U.K.). An old source was preferred to ensure its purity. The conversion electron spectrum was measured with an Ortec surface barrier Si-detector. The system resolution was 18 keV (FWHM) at 0.978 MeV. The energies of the conversion lines were determined by the internal calibration of the Ortec multichannel analyser using the conversion electrons in the decay of ^{207}Bi . As the source was very weak it was placed very close (about 1 cm) to the detectors. The method of least square fit was applied to draw the calibration curve.

Figure 1 shows the single conversion electron spectrum measured with surface barrier Si-detector. A weak K0.8978 conversion electron line can be observed. The 0.8978 MeV transition is a weakly converted gamma ray, as 99% of this transition goes to ground level with multipole mixture of M1 (0.8%) and

E2 (0.14%). The upper limit of the intensity of this line is of the order of 10^{-2} compared to that of the K1.06 conversion electron line. The line intensity of the conversion electron was calculated by determining the area of the line and allowing subtraction of the beta background. The gamma energies used here were from Jardine⁴.

Thanks are due to Dr. Anwar Zaki, Chairman of Physics Department of AL-Fateh University, for encouragement.

1 December 1982

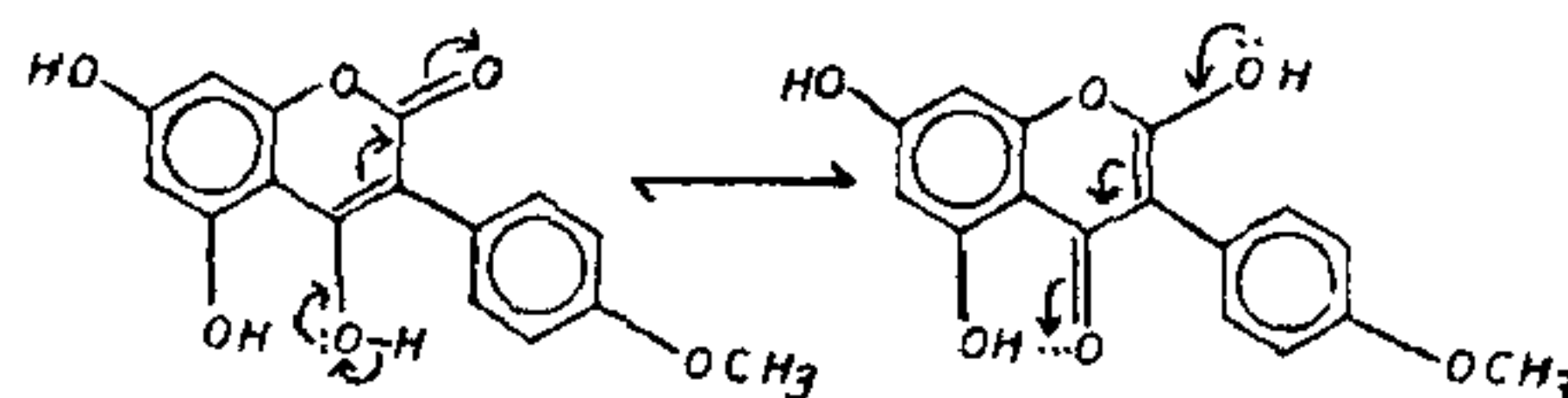
1. Prescott, J. R., *Proc. Phys. Soc.*, 1954, **A67**, 540.
2. Alburger, D. E. and Sunyar, A. W., *Phys. Rev.*, 1955, 695.
3. Singh, G. P., Mishra, R. K., Singh, A. K. and Kumar, A., *Czech. J. Phys.*, 1979, **B29**, 8, 853.
4. Jardine, L. J., *Phys. Rev.*, 1975, **C11**, 1385.

SPECTROPHOTOMETRIC STUDIES OF IRON (III) AND URANIUM (VI) COMPLEXES WITH 4,5,7-TRIHYDROXY-3-(p-METHOXYPHENYL) COUMARIN

M. L. DHAR AND KULDEEP PANDITA

Department of Chemistry, University of Jammu,
Jammu 180 001, India.

4,5,7-Trihydroxy-3-(p-methoxyphenyl) coumarin (scheme 1) has been reported by Dhar *et al.*¹ as a useful chromatographic spray reagent for the detection of metal ions in micro and macro quantities. Its colour reactions with V(V), Fe(II), Fe(III), Cu(II), Ce(III) and $\text{UO}_2(\text{II})$ are especially sensitive. In the present communication the use of the coumarin derivative for the spectrophotometric determination of Fe(III) and $\text{UO}_2(\text{II})$ ions is reported.



The reagent m.p. 308°C (Lit. $308^\circ\text{-}310^\circ\text{C}$) was synthesised². Metal ion solutions were prepared from AnalaR (BDH) grade FeCl_3 and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salts. Stock solutions $1 \times 10^{-3}\text{M}$ of the reagent in pure methanol and of the metal ions in methanol (80%) were prepared. The optical density was measured using a Pye Unicam SP8-100 spectrophotometer. The pH was measured using Elico digital pH meter, model LI-120 employing sodium acetate-acetic acid buffer mixture. Mostly sodium, potassium, ammonium

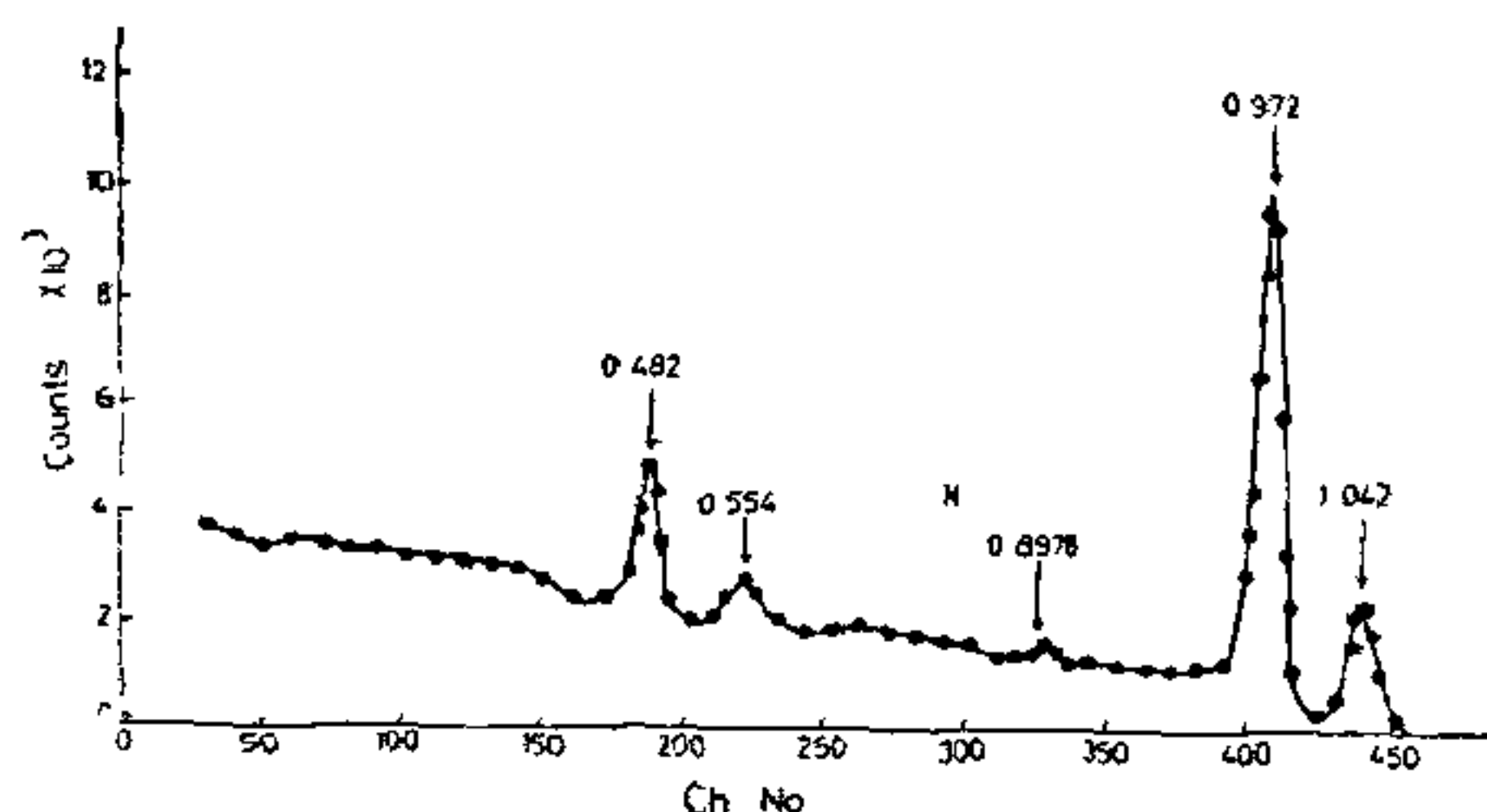


Figure 1. Conversion electron spectrum of ^{207}Bi measured with surface barrier Si-detector. (Electron energies are given in MeV).

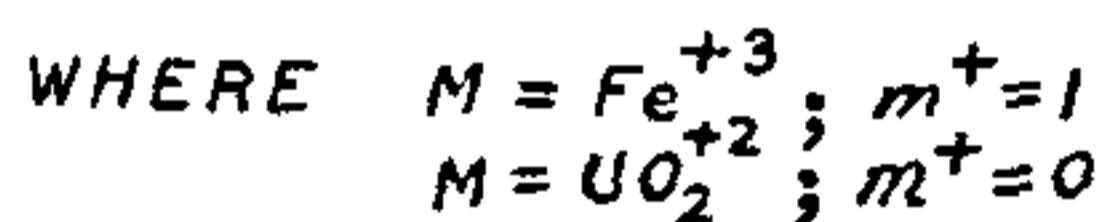
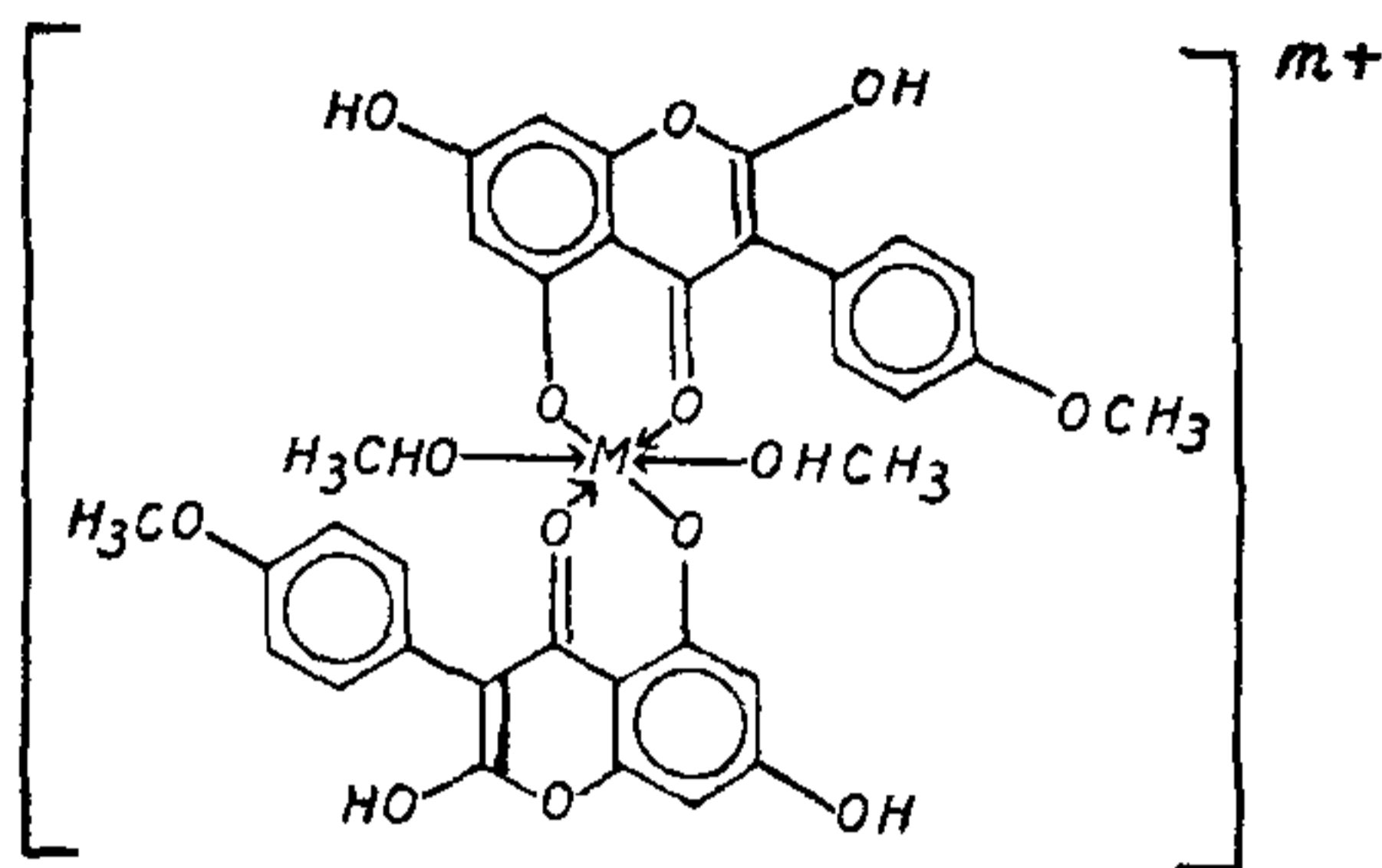
salts for anions and chloride, nitrate salts for cations were used for preparing the solutions of the diverse ions in double-distilled water or dilute hydrochloric acid wherever necessary. The working solution for the optical density measurements was prepared by mixing the respective metal ion and the reagent solutions, adjusting to the required pH and making up the final volume in such a way as to keep the methanol concentration above 75% to prevent precipitation of the reagent or the complex formed. The stoichiometries of the complexes in solution were determined by the mole ratio³, continuous variations^{4,5} and slope ratio methods⁶.

The blue-grey Fe(III) complex showed absorption maxima (λ_{\max}) values at 390 and 590 nm while the orange-red $\text{UO}_2(\text{II})$ complex showed these bands at 390 and 510 nm respectively. The reagent showed absorption maxima at wavelengths not corresponding to the maxima of either of the complexes and as such in all subsequent studies the colour measurements were made at λ_{\max} values of the respective complexes. The solution ($1 \times 10^{-3} \text{ M}$) of the metal ions and the reagent was used to study the effect of pH on the absorption of the complexes. The optical density reached a maximum at pH values 4 and 5 for the Fe(III) and $\text{UO}_2(\text{II})$ complexes respectively. At higher pH values the absorbance dropped considerably probably due to the decomposition of the complexes.

The colour attainment was instantaneous and showed no change up to 48 hr at room temperature. However, all absorbance was measured after 12 hr of mixing to ensure complete equilibrium. On plotting absorbance values of a series of solutions of the reagent and the respective metal ions in the molar ratios of 0.5:1 to 9:1, a straight line was obtained upto 5:1 in Fe(III) complex and 6:1 in $\text{UO}_2(\text{II})$ complex. However in all subsequent studies a ratio in excess of 9:1 (reagent:metal) was maintained.

The Fe(III) and $\text{UO}_2(\text{II})$ complexes obey the Beer's law in the concentration ranges 0.5-20 ppm and 0.4-20 ppm of Fe^{3+} and UO_2^{2+} respectively. The interference caused and tolerance limits (ppm) for various diverse ions were: (i) For Fe(III); Th^{4+} , UO_2^{2+} (60), Zr^{4+} , Ti^{4+} , VO^{2+} (100), Cu^{2+} , Cd^{2+} , Al^{3+} , Ni^{2+} , Co^{2+} , Mo^{6+} (200), Au^{3+} , Mg^{2+} , Sb^{3+} (300), Na^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ , SO_4^{2-} , CH_3COO^- , SO_3^{2-} , Cl^- , F^- did not interfere while PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, citrate, tartrate caused serious interference, and (ii) For $\text{UO}_2(\text{II})$; Ti^{4+} , VO^{2+} , Zr^{4+} (100), Co^{2+} , Ni^{2+} , Zn^{2+} (200), Ca^{2+} , Mg^{2+} , Au^{3+} , Cd^{2+} , Bi^{3+} , Al^{3+} , Sb^{3+} (300). Fe^{2+} , Fe^{3+} , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, BO_3^{3-} , succinate, malonate, ferrocyanide interfered seriously while Na^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ , NO_3^- , Cl^- , I^- , SO_3^{2-} and CH_3COO^- caused no interference.

The stoichiometry of the complexes in solution was determined employing $1 \times 10^{-3} \text{ M}$ solutions. Both Fe^{3+} and UO_2^{2+} ions gave 1:2 (metal:reagent) complexes. The complex species in solution could therefore be represented as: $[\text{Fe}(\text{C}_{16}\text{H}_{11}\text{O}_6)_2 (\text{CH}_3\text{OH})_2]^+$ and $[\text{UO}_2(\text{C}_{16}\text{H}_{11}\text{O}_6)_2 (\text{CH}_3\text{OH})_2]$ and tentatively the structures of these species can be shown as in scheme 2.



To determine iron (III) the reagent compares favourably in terms of sensitivity with the known reagents, tartaric acid⁷; 1,10-phenanthroline⁸; phenyl-2-pyridylketoxime⁸ and 2,2',2''-terpyridine⁸. For uranium(VI) the reagent appears to be better and more sensitive than the already existing reagents arsenazo III⁷, dibenzoylmethane⁷, mercaptoacetic acid⁷ and ammonium thiocyanate⁷ cited in literature. The reagent is nearly as sensitive as acetylacetone⁷, 8-hydroxyquinoline⁷ and sodium diethyldithiocarbamate⁷. The selectivity of the reagent is Fe^{3+} and UO_2^{2+} ions can be determined fairly well even in the presence of a number of other ions.

The procedure recommended for the determination using this reagent is: To 4.0-20 ppm of the metal ion in about 5 ml of methanolic solution (80%) the reagent is added in excess. The pH is adjusted to the required value after making up the volume with methanol (80%) and then the absorbance of the resulting solution measured after nearly 12 hr against the reagent blank.

28 June 1982; Revised 7 December 1982

1. Dhar, M. L., Pandita, K. and Jain, A. C., *Chromatographia*, 1979, 12, 299.
2. Gilbert, A. H., McGookin, A. and Robertson, A., *J. Chem. Soc.*, 1957, 3740.
3. Yoe, J. H. and Jones, A. L., *Ind. Eng. Chem., Anal. Ed.*, 1944, 16, 111.

4. Job, P., *Ann. Chim. (France)*, 1928, 9, 113.
5. Vosburgh, W. C. and Cooper, G. R., *J. Am. Chem. Soc.*, 1941, 63, 437.
6. Harvey, A. E. and Manning, D. L., *J. Am. Chem. Soc.*, 1950, 72, 4488.
7. Burger, K., *Organic reagents in metal analysis.*, Pergamon Press I ed. 1973, p. 72.
8. Meites, L., *Handbook of Analytical Chemistry*, McGraw-Hill, New York, I edn. 1963.

A NEW ONE STEP PREPARATION OF PICROPODOPHYLLONE FROM PODOPHYLLOTOXIN

C. ANJANA MURTHY AND K. M. LOKANATHA RAI
Department of Chemistry, University of Mysore,
Manasa Gangotri, Mysore 570 006 India.

DURING our studies on the synthesis of analogues of podophyllotoxin (I), a lignan antitumor^{1,2} and cytotoxic spindle poison³, we required picropodophyllone (II), a cis ketolactone, an isomer of the trans ketolactone, podophyllotoxone (III). The known method of preparing picropodophyllone (II) is a two-step process, the first by isomerizing podophyllotoxin I by bases to the picropodophyllin⁴ (IV) and then oxidiz-

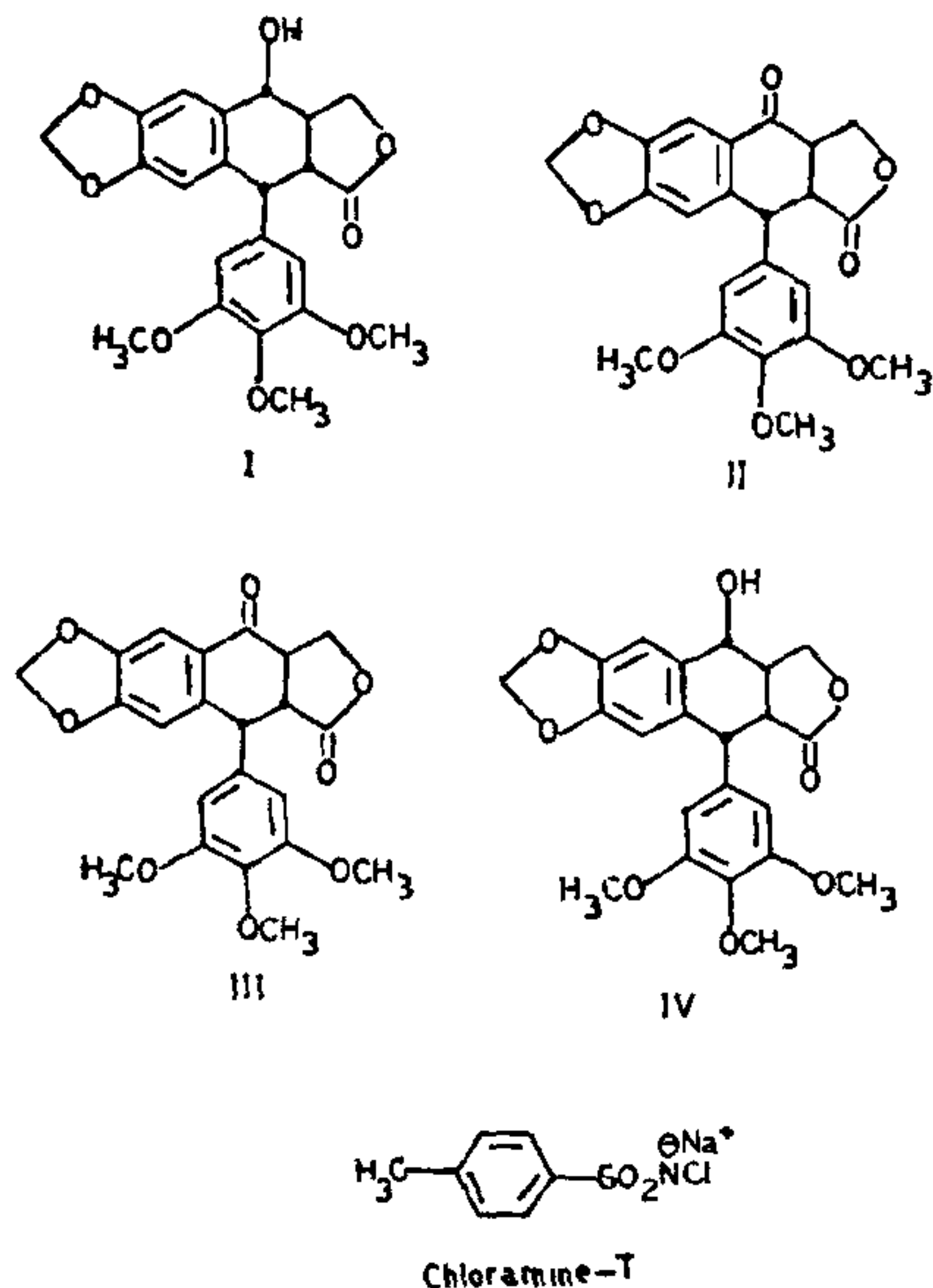
ing the hydroxy lactone (IV) to the ketolactone (II) by manganese dioxide⁵. Though the yield in first step is very good, it was very low in the second step.

We had earlier⁶ used successfully, chloramine-T (trihydrate) in nonaqueous medium such as dimethyl sulphoxide and dioxan to oxidize some benzylic alcohols such as benzyl alcohol, benzoin, and furoin and therefore we considered utilizing both the base properties and the oxidizing ability of chloramine-T, to convert the podophyllotoxin (I) to picropodophyllone (II). We report here the successful conversion of podophyllotoxin to picropodophyllone with a very much improved yield of the desired product in a single step, using DMSO as nonaqueous medium.

The product obtained in the above reaction was identical with the product obtained by the two-step synthesis in mp⁵; COTLC in 5 different solvent systems and products showed no change in mixed m.p.

In a typical experiment a mixture of podophyllotoxin (I) (0.5 g) and chloramine-T trihydrate (1 g) was kept stirred in dry DMSO (50 ml) at 60-65°C for 30 hr. The reaction mixture was diluted with water (Ca 100 ml) and then with 10% NaOH (Ca 50 ml) and stirred well and extracted into ether. The ether layer was successively washed with water and dried over sodium sulphate. The solid residue obtained after evaporation of ether was purified by column chromatography using chloroform: acetone (7:1) yield of the product: (0.27, 54%); mp 151-152°C (lit⁵ mp 153-154°C).

9 June 1982



1. Smissman, E. E., Murray, R. J., McChesney, J. D., Houston, L. L. and Pazdernik, T. L., *J. Med. Chem.*, 1976 19, 148.
2. Hartwell, J. L., and Schracker, A. W., *Fortsch. Chem. Org. Naturstoffe.*, 1958, 15, 93.
3. Wilson, L., *Ann. N. Y. Acad. Sci.*, 1975, 253, 213.
4. Gensler, W. J., and Gastonis, C. D., *J. Org. Chem.*, 1966, 31, 3224.
5. Gensler, W. J., and Francis Johnson, *J. Am. Chem. Soc.*, 1955, 77, 3674.
6. Anjanamurthy, C. and Lokanath Rai, K. M., *Mysore Univ. J.*, 1983, (under press).