



Scheme 2

units while the peaks at  $m/e$  591 and 560 obtained due to the loss of 31 mass units (scheme 2).

From the foregoing spectral and chemical evidences, the assignment of structure (VI) for the biflavone SA4 is taken as supporting evidence for the structure of semecarpufflavanone (V).

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## RAPID SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF THORIUM (IV)

K. N. THIMMAIAH, G. T. CHANDRAPPA and A. THIMME GOWDA

Department of Post-Graduate Studies & Research in Chemistry, University of Mysore, Manasagangothri, Mysore 570 006, India.

MOST of the proposed methods for the spectrophotometric determination of thorium (IV) suffer from disadvantages like extraction, low sensitivity<sup>1</sup> or allowing the solution to stand for a long time for maximum colour development<sup>2</sup>. Sodium 5-(4-diethyl-amino-2-hydroxy phenylazo) 1,2,4-triazole-3-carboxylate (SATC) was synthesised<sup>3</sup> and proposed for the spectrophotometric determination of cobalt present in natural and geological materials<sup>4</sup> and in uranium (VI)<sup>5</sup>. The present investigation deals with the study of the colour reaction of SATC with thorium (IV) for the rapid spectrophotometric determination of traces of thorium.

A stock solution of thorium (IV) was prepared from AR grade thorium (IV) nitrate and standardised<sup>6</sup>. A 0.02% solution of SATC was prepared in doubly-distilled water. Walpole buffer solutions<sup>7</sup> of pH values from 3.72–5.80 were prepared by mixing 0.2 N acetic acid and 0.2 N sodium acetate solutions. The absorbance was measured with a spectrophotometer (Beckman model DB).

An aliquot of the stock solution containing 1.5–142.5  $\mu\text{g}$  of thorium, 5 ml of a buffer (pH 4.27) and 6 ml of 0.02% SATC solution was made up to 25 ml in a volumetric flask and its absorbance was measured at 535 nm against a corresponding reagent blank. The thorium (IV) content in the sample solution was then deduced from the standard calibration curve.

SATC reacts with thorium (IV) instantaneously to form a reddish pink complex at room temperature (27°C) in hydrochloric, sulphuric, phosphoric or acetic acid or acetic acid-sodium acetate buffer medium. The study of the Th (IV)-SATC complex in hydrochloric, sulphuric, phosphoric or acetic acid medium is not recommended because of lower stability (< 2 min), least sensitivity and interference of foreign ions at low concentrations. Acetic acid-sodium acetate buffer medium was therefore selected for further studies because of the greater stability of the complex and higher tolerance limits of the diverse ions in this medium. The effective pH range is 3.75–5.1. A buffer of pH 4.5 was therefore selected. A 3-fold molar excess of the reagent over thorium (IV) was necessary for full

development of the colour intensity. The thorium (IV)-SATC complex is stable for 30 min in the buffer medium. The order of addition of reagents is not critical. The absorbance values are not affected in the temperature range 7–70 °C. At higher temperature the absorbance gradually decreases.

The reddish pink thorium (IV)-SATC complex exhibits maximum absorption at 530–540 nm where thorium (IV) and the reagent blank solutions show very little absorption. All the present studies were made at 535 nm. The thorium (IV)-SATC complex obeys Beer's law over the concentration range 0.06–5.7 ppm. The optimum concentration range as evaluated by Ringbom's curve<sup>8,9</sup> is 0.16–5.1 ppm. The sensitivity of the reaction is  $7.3 \mu\text{g cm}^{-2}$  with a molar absorptivity of  $3.2 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 535 nm. The accuracy of the method is  $\pm 2\%$ .

Job's method of continuous variation<sup>10,11</sup> and molar ratio<sup>12</sup> methods indicated the formation of 1:1 complex and the apparent stability constant ( $\log K$ ) as calculated from molar ratio and Asmus<sup>13</sup> methods is found to be  $6.3 \pm 0.1$ . The complex is cationic in nature.

In order to assess the possible analytical applications of the method, the effects of some ions which often accompany thorium were studied with 3 ppm of thorium(IV) and their tolerance limits in ppm are given in brackets: nitrate (6000); Mg (II), Mn (II), chloride (2400); Sr (II), Cd (II), bromide (1200), iodide (850), Yb (II), Ca (II), Zn (II), sulphate (500); Al (III), phosphate (250); Sn (II), EDTA (100); W (VI), fluoride (50); Cr (III), Ru (III), Ir (III), Mo (VI), Rh (III), Ti (IV), Ce (IV), La (III), Er (III), Gd (III), Sm (III), Pr (III), Ho (III), Y (III), oxalate, citrate, tartarate (20); Zr (IV), Fe (III), Pt (IV), Os (VIII), Nd (III) (15); Ni (II), Pd (II), V (V), Au (III), Dy (III) (10), Co (II), U (VI) (5).

A comparison of the present reagent with the literature reagents for the estimation of thorium reveals the following advantages: water solubility, simplicity, good sensitivity, stability, elimination of extraction, insensitivity to temperature in the range 7–70 °C. Further the order of addition of reactants is not critical.

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## A NEW DITERPENE, DIPOLOIC ACID FROM THE STEM OF *DILLENIA PENTAGYNA*

SANTOSH K. SRIVASTAVA and SAVITRI D. SRIVASTAVA

Department of Chemistry, University of Saugar,  
Sagar 470 003, India.

THE earlier work on the stem of the plant *Dillenia pentagyna* (N. O. Dilleniaceae) was reported by Tiwari *et al.*<sup>1,2</sup>. In this paper the authors report the isolation and characterization of a new diterpene, dipoloic acid [7-hydroxy-pimara-(15:16)-ene-19-oic acid] (I) by physico-chemical techniques.

Dipoloic acid (I), crystallized from MeOH as white needles, m.p. 150–52° (d), analysed for  $\text{C}_{20}\text{H}_{32}\text{O}_3$  ( $M^+$  320) and had no UV absorption above 218 nm. IR ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ) showed the presence of hydroxyl (3400  $\text{br}$ ), carboxyl (1690), tert methyl (1380, 1360, 1210 and 1200) and vinylic group (1635, 1410, 980 and 940). Its  $^1\text{H}$  NMR spectrum ( $\delta$ , TMS) exhibited signals for tert methyl (0.94, 1.05 and 1.35) assignable to 20, 17 and 18 groups respectively. The hydroxyl proton appeared as a broad signal at 4.40 ( $W^{1/2}$  5 Hz) which disappeared on  $\text{D}_2\text{O}$  shaking. The methylene protons showed as a pair doublets at 2.45 and 3.20 ( $J = 17 \text{ Hz}$ ) and ABC pattern for the signal of vinylic protons at 5.45, 5.40 and 4.80 ( $J_{AB} \approx 10.00$ ;  $J_{AC} = 17.00$ ;  $J_{BC} = 15 \text{ Hz}$ ) which suggested that dipoloic acid possessed