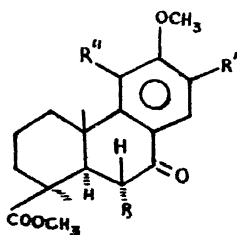


spectra and elemental analysis. Chlorination of acetophenone under the similar conditions gives ω -chloro acetophenone in 84% yield. Authenticity of the compound was confirmed by the mixed m.p. with an authentic sample. 7-Oxomethyl-O-methyl podocarpate also provided a good yield of the 6-chloro derivative, which showed characteristic doublets as in I_a & I_b with a coupling constant of 7 cps.

- I_a R = R' = H, R'' = NO₂
 I_b R = R' = H, R'' = NO₂
 I_c R'' = H, R = Cl, R' = NO₂
 I_d R' = H, R = Cl, R'' = NO₂
 I_e R = R'' = H, R' = NH₂
 I_f R = R' = H, R'' = NH₂
 I_g R' = R'' = H, R = Cl.



Experimental

1. 6-Chloro-7-oxo-11-nitro methyl-o-methyl podocarpate :

Compound I_b (1 gm) was dissolved in acetic acid (30 ml), H₂O₂ (5 ml) and conc. HCl (5 ml) were added into the solution and the mixture was kept at 5°-10° for the whole night. The mixture was then poured over ice and triturated. White solid obtained was filtered off, washed with water, dried and crystallized from methanol, m.p. 171°. Yield 880 mg (80%). (Found : C, 57.22; H, 5.62; N, 3.30; Cl, 9.10. C₁₉H₂₂NCLO₈ requires C, 57.65; H, 5.56; N, 3.54; Cl, 8.98%.)

2. 6-Chloro-7-oxo-13-nitro-methyl-o-methyl podocarpate :

Compound, I_a (1 gm) was dissolved in acetic acid (150 ml). H₂O₂ (10 ml) and HCl (10 ml) were added into the solution and the mixture was kept at 5°-10° for the whole night. The mixture was then poured over ice and triturated. White solid obtained was filtered off, washed with water, dried and extracted with solvent ether. The undissolved product was filtered off, washed with ether and dried, m.p. 242°-43° (500 mg). Mixed m.p. with the starting compound showed no depression.

Ether extract was dried completely and the solid obtained was crystallized from methanol. White needles m.p. 186°. Yield 350 mg (65%). (Found : Cl, 8.80; C₁₉H₂₂NCLO₆ requires Cl, 8.98%.)

3. 6-Chloro-7-oxo-methyl-o-methyl podocarpate :

Keto ester, I_g (1 gm) was dissolved in dichloromethane (4 ml) and methanol (2 ml). The reaction mixture was treated with H₂O₂ (5 ml) and conc. HCl (1 ml) and was kept at the room temperature overnight. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with water, dried over magnesium sulphate and ether was evaporated completely to give 0.92 g of yellow oily product which was crystallized from methanol to give a colourless crystalline product, m.p. 119°. Yield 0.750 g (68%). (Found : Cl, 9.60; C₁₉H₂₃ClO₄ requires Cl, 10.01%.)

4. ω -Chloro Acetophenone :

Acetophenone (10.20 g) was dissolved in acetic acid (25 ml). H₂O₂ (5 ml) and conc. HCl (5 ml) were added into the solution and the mixture was kept at 5°-10° for the whole night. The mixture was then poured over ice and the white solid obtained was washed with water, dried and crystallized from petroleum ether, m.p. 54°. Yield 11.0 g (84%).

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Physicochemical Studies of the Co(II) and Ni(II) Chelates of Sodio Benzene-sulphonate Azo *P*-Cresol

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THE azedye-sodio benzene sulphonate-azo-*p*-cresol has been synthesized by the authors. The stoichiometry of the complexes of Co(II) and Ni(II) has been investigated. The chelate contains metal and metal ligand in the ratio of 1 : 1. The stability constants of the cobalt and nickel complexes are found as 8.237×10^8 and 1.139×10^8 respectively.

Experimental and Discussion

Cobalt chloride and nickel chloride used were of B.D.H. A.R. specifications. All other chemicals and reagent used were of A.R. specifications and chemically pure. The spectrophotometric measurements were carried out with a quartz spectrophotometer, Beckmann model D.U. and the *pH* of the solutions were measured with Philips *pH* meter. P.R. 9400. All the solutions were kept in a thermostat bath and the measurements were carried out at $28^{\circ} \pm 1^{\circ}$.

Synthesis of the Azo-dye: The above azo-dye have been synthesized by diazotising sulphanilic acid and then coupling the diazotised product with *p*-cresol. The dye was isolated as barium salt and the above dye was obtained by treating the barium salt with sodium sulphate solution. The azo dye was recrystallised with ethanol and its purity was tested by percentage estimation of carbon, hydrogen, nitrogen and sulphur.

Stoichiometry of the Chelates: Vosburgh and Cooper method¹, Job's method of continuous variation² and mole ratio method³ were used to determine the stoichiometry of the chelates with the help of spectrophotometer at *pH* range 6.5 to 7.0 maintained with the help of 0.1*M* HCl. The data have been shown in Figures 1 to 4. Figures clearly indicate that in the chelates the ratio of metal and ligand is 1 : 1.

Stability Constants of the Chelates: Stability constants of the chelates have been calculated using Job's method with non-equimolar solutions and the values obtained are 8.237×10^2 and 1.139×10^3 for cobalt and nickel chelate respectively. The above values are confirmed by the mole ration method⁴ also.

The above low stability constant values of cobalt than nickel are in natural order of stability *i.e.*, the stability constant values vary in the order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$. This order is relatively consistent with the charge to radius concept, since the radii of the ions vary in the order $Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+}$.

Discussion and Formula: The 1 : 1 complex clearly indicates that the ligand is bidentate and the OH group ortho to azo group is holding the metal ion. The metal is coordinated with two molecules of water also. Thus the possible formula is $(ML_2 \cdot 2H_2O) Na$, where M stands for metal, cobalt and nickel and L is the ligand under study.

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Studies on N-Substituted Salicylhydroxamic Acids as Metal Complexing Ligands. Part VII. $UO_2(II)$ Chelates of N-Methyl Salicylhydroxamic Acid

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N-METHYLSALICYLHYDROXAMIC acid (RH_2) gives different coloured solutions with $UO_2(II)$ with changes in *pH* values indicating the existence of a number of $UO_2(II)$ complexes in solution. Therefore in order to find out the composition of various $UO_2(II)$ complexes present in the solution, Job's method of continuous variation¹ has been undertaken employing colour as the index property.

Experimental

In the preparation of the solutions, double-distilled water was used. N-Methyl salicylhydroxamic acid was prepared in the laboratory and purified by recrystallisation². All other reagents used were either of A.R. quality or properly purified. Optical densities were measured with a Spectrophotometer (Hilger's UVISPEK) using 1 cm quartz cell against water. A Cambridge portable type *pH*-meter was employed for adjusting *pH* values.

In studying the formation of complexes by Job's method of continuous variation, all solutions were prepared in 1 : 1 aqueous ethanol. First spectral curves were drawn for complexes formed at three different *pH* values. From the curves wavelengths 540 nm and 480 nm were selected for studying the formation of complexes by Job's method at three different *pH* values ≈ 2.0 , ≈ 4.5 and $\approx 5.8-6.0$. The differences of optical densities between the observed values and the calculated values were plotted against the corresponding composition. From the curves the existence of (1 : 1) complexes in solution has been observed at three different *pH* values.

Results and Discussion

By Job's method of continuous variation, two different complexes of $UO_2(II)$ with RH_2 are indicated. The reddish-brown complex at *pH* ≈ 2.0 and the yellow one at *pH* $\approx 5.8-6.0$, both have the same composition (1 : 1). It is known that diuranates are formed at *pH* ≈ 6.0 , therefore it may be suggested that the yellow complex at *pH* $\approx 5.8-6.0$, is a binuclear diuranate type compound—composition being (2 : 2). The composition of this complex by means of the method of proportional absorptivities³ has also been studied. The proportion of absorptivities A_2/A_1 can be determined at various *pH*-values, where A_2 and A_1 are the optical densities of the stronger and weaker solutions respectively at the