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**Chemical Investigation of the Dry Fruits of  
*Schrebera swietenoides***

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**SCHREBERA swietenoides** Roxb. (Oleaceae) is a plant of average height (2-3 m) occurring in the tropics of Telangana and yields fruits in summer. The roots of this plant are reported to be used in the treatment of leprosy<sup>1</sup>. In this communication we report the isolation of two known triterpene acids from the fruits of *S. swietenoides* which has not been previously investigated chemically.

**Experimental**

**Plant material** : The plant material was collected from Mananoor forest, 150 km south-east of Hyderabad.

**Extraction and isolation of the constituents** : The ground dry fruits of *S. swietenoides* were extracted with methanol by percolation. The extract on concentration and cooling furnished a solid residue. Silica gel chromatography of the solid resulted in the isolation of oleanolic acid and that of the mother liquor furnished betulinic acid.

The isolated compounds were identified by spectral data<sup>2,3</sup> and comparison with authentic samples (superimposable ir, co-tlc). Derivatives of the isolated compounds, prepared to aid the

identification of the structures, included oleanolic acid acetate, methyl ester of oleanolic acid acetate, betulinic acid acetate and its methyl ester. Full details of the isolation and identification of the compounds are available on request.

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**Extractive Spectrophotometric Determination of Trace  
Amounts of Tin(IV) with Diphenylcarbazone**

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**N**UMEROUS reagents have been proposed for spectrophotometric determination of tin but a few are suitable for common use. A simple, sensitive and selective extraction-photometric method for the determination of tin with diphenylcarbazone is described in this paper. The use of diphenylcarbazone as an analytical reagent has long been known. It forms chelate complexes with many heavy metals<sup>1-4</sup>. Balt and Dalen<sup>4</sup> found that Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup> and Sn<sup>2+</sup> form 1 : 2 complexes with diphenylcarbazone while Cu<sup>+</sup> forms 1 : 1 and Fe<sup>2+</sup> 1 : 3 complexes. In the present investigation, it is found that tin(IV) reacts with diphenylcarbazone in 1 N hydrochloric acid medium forming a rose-red coloured complex which is extractable into isobutyl methyl ketone. This forms the basis of the method.

**Experimental**

Absorbance measurements were made with a Beckmann DK-2 spectrophotometer in matched quartz cells of 1.0 cm optical path.

A stock solution was prepared by dissolving 2.995 g stannic chloride pentahydrate (B.D.H.) in 1 litre 1 : 1 hydrochloric acid. The amount of tin was estimated gravimetrically by the N-benzoyl-phenylhydroxylamine method<sup>5</sup>. The solutions of lower concentrations were prepared by dilution of the stock solution and were made 1N with respect

## NOTES

to hydrochloric acid. A 0.1% solution of diphenylcarbazone (B.D.H.) in isobutyl methyl ketone was employed as the reagent. Solutions of diverse ions were prepared from the metal salts or from the sodium, potassium or ammonium salts of anions and estimated according to standard methods.

**Extraction procedure :** An aliquot of the standard solution containing 5 to 55  $\mu\text{g}$  tin was made upto 5 ml with 1*N* hydrochloric acid. This was shaken for 3 min with 10 ml of 0.1% solution of diphenylcarbazone in isobutyl methyl ketone and the rose-red coloured organic layer was transferred to a 25 ml volumetric flask. The aqueous phase was again shaken for 3 min with 10 ml of the reagent and the two extracts were mixed together. Volume of the combined extract was made upto the mark with isobutyl methyl ketone. The absorbance of this solution was measured at 525 nm against a reagent blank prepared in a similar way. The amounts of tin in unknown solutions were calculated from the standard calibration curve. The results showed good recovery of tin with an error within 4%. In the concentration range, 15 to 50  $\mu\text{g}$  tin per 25 ml extract, the error is less than 2%.

**Interference of foreign ions :** The standard tin solution containing 30  $\mu\text{g}$  tin in each case was mixed with an aqueous solution of one of the foreign ions iron(II and III), cobalt, nickel, palladium, platinum(IV), copper(II), gold(III), zinc, cadmium, mercury(II), chromium(III and VI), molybdenum(VI), vanadium(V), arsenic(III), antimony(III), bismuth(III), fluoride, bromide, iodide, cyanide, thiocyanate, sulphate, sulphite, nitrate, nitrite, phosphate, oxalate and acetate in amounts almost equal to and five times that of tin. The volume of the solution in each case was made upto 5 ml and the solution made 1*N* with respect to hydrochloric acid. The estimation of tin was completed as described before. It was found that chromium(VI) and molybdenum(VI) interfered seriously.

Interference due to chromium can be removed by reducing chromium(VI) to chromium(III) with sodium sulphite solution and that due to molybdenum(VI) can be removed by using hydrogen peroxide as a masking agent.

## Results and Discussion

Diphenylcarbazone reacts with tin(IV) in acidic solution forming a rose-red coloured complex which is extractable into isobutyl methyl ketone. The complex has an absorption maximum at 525 nm and obeys Beer's law over the concentration range of 5 to 55  $\mu\text{g}$  tin per 25 ml extract. The sensitivity is 0.04  $\mu\text{g}/\text{cm}^2$ .

Although extraction of tin is possible from dilute hydrochloric acid (0.4 to 1.5 *N*), the absorbance values of the extracts decrease with increase in acidity beyond 1.5 *N*. Maximum absorbance for the extract is obtained when the acid strength of the aqueous phase is  $1 \pm 0.2$  *N*. The acid concentration of the aqueous phase is therefore maintained at 1 *N*,

The effect of varying reagent concentration on the extraction of tin was studied. 0.1% solution of diphenylcarbazone in isobutyl methyl ketone was found to be the most suited for quantitative extraction. When the tin solution is  $1 \pm 0.2$  *N* with respect to hydrochloric acid and 10 ml of 0.1% solution of diphenylcarbazone in isobutyl methyl ketone is used, only 94% of tin can be extracted by a single extraction. It is, therefore, necessary to carry out a second extraction for complete extraction of tin.

The absorbance of the extract was measured at elapsed intervals of 5, 10, 30, 60, 80, 120, 150, 180, 200, 240, 300 and 360 min after extraction. The absorbance value was stable for upto 180 min and then decreased very slowly. The absorbance of the extract is independent of temperature in the range 20-35°.

A standard solution containing 30  $\mu\text{g}$  of tin was estimated 10 times by the standard procedure. The average absorbance was 0.385 with a standard deviation of 0.005 absorbance unit and a relative error of  $\pm 1.2\%$ .

**Effect of diverse ions :** An examination of the effect of foreign ions revealed that equal amount of chromium(VI) and molybdenum(VI) and five fold excess of iron(II and III) and vanadium(V) interfered. But five fold excess of cobalt, nickel, palladium, platinum(IV), copper, gold, zinc, cadmium, mercury, arsenic, antimony, bismuth, chromium(III) and common anions like fluoride, bromide, iodide, cyanide, thiocyanate, nitrate, nitrite, sulphate, sulphite, phosphate, acetate and oxalate did not interfere. Interference due to chromium(VI) and molybdenum(VI) could be easily removed and a good recovery of tin (within 5% error) was achieved.

Thus, the method proved to be a simple, rapid and sensitive one providing a good recovery of tin in trace concentrations in presence of the common ions. The results obtained by this method are accurate and compare well with those of the standard method using toluene-3,4-dithiol°. The present method is superior to the dithiol method because of its simplicity, rapidity and selectivity. In the standard method using toluene-3,4-dithiol, a large number of common ions interfere; specially in the determination of tin in canned foods, copper interferes and must be removed. The present method is more advantageous in determining tin in canned foods, even in presence of copper which does not interfere. The present method is also applicable to ores containing tin in trace amounts.

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### Extractive Spectrophotometric Determination of Ruthenium(III) with 3-Chloro-1-nitroso-2-naphthol

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**I**SONITROSO derivatives of acetylacetone<sup>1</sup>, benzoylacetone<sup>2</sup>, dibenzoylmethane<sup>3</sup> and ethylbenzoylacetate<sup>4</sup> have been used in this laboratory for the extractive spectrophotometric determination of ruthenium(III). In the present communication, we propose a new chromogenic agent, 3-chloro-1-nitroso-2-naphthol for spectrophotometric determination of ruthenium. The proposed method has proved to be more selective and specific.

#### Experimental

A stock solution of ruthenium(III) ( $1.95 \times 10^{-3} M$ ) was prepared by dissolving ruthenium trichloride (Johnson Mathey, London) in dil. hydrochloric acid and standardized by known method<sup>5</sup>. Test solutions of lower concentration were prepared by appropriate dilution of the stock.

3-Chloro-1-nitroso-2-naphthol was synthesized by reported method<sup>6</sup> and its 0.1% (w/v) ethanolic solution was used for the estimation of ruthenium. Diverse ion solutions were prepared from analytical grade salts.

**Working procedure:** An aliquot (25 ml) of aqueous solution containing 10 to 100  $\mu\text{g}$  ruthenium(III), 1 ml 0.1% reagent solution and acetic acid (4.5M in 25 ml total volume) was heated for 30 min in a boiling water bath. After cooling, the solution was extracted in a separatory funnel for 15 sec with 10 ml MIBK (methyl isobutyl ketone). The organic phase was dried with anhydrous sodium sulphate and absorbance of the yellow-green complex was measured at 595 nm against the reagent blank. The ruthenium contents were computed from the earlier drawn calibration curve.

#### Results and Discussion

The yellow-green ruthenium complex of 3-chloro-1-nitroso-2-naphthol extracted into MIBK from acetic acid solution (4-5 M) absorbs at 595 nm. The ligand shows negligible absorbance at this wave length. The colour system conforms to Beer's

law over the concentration range of 10 to 100  $\mu\text{g}$  of ruthenium(III) per 10 ml of organic phase. The quantitative extraction of the ruthenium complex occurs from 4.5 to 5 M acetic acid solution. Hydrochloric acid, sulphuric acid and nitric acid are unsuitable for the extraction. 1 ml 0.1% ethanolic solution of the ligand and 15 sec shaking period is adequate for complete extraction of the complex. The colour of the complex is stable for more than 4 days. Carbontetrachloride, chloroform, benzene, toluene, xylene, amyl alcohol and MIBK were tested as solvent for the extraction, but MIBK was found to be the only effective solvent. Job's variation method and mole ratio method indicate the formation of 1:3 (metal to reagent) complex. The tolerance limit of the various cations and anions are shown in Table 1. The ions showing strong interference in ruthenium estimation

TABLE 1—EFFECT OF DIVERSE IONS  
Ru(III) = 30  $\mu\text{g}$

Tolerance limit	Ions
mg	
0.1	La(III), Ce(IV).
0.2	Au(III), Pt(IV).
0.3	EDTA, SCN <sup>-</sup> .
0.4	Cd(II).
0.5	Th(IV), Zr(IV), Mo(VI), PO <sub>4</sub> <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , tartrate.
1.0	Co(II), Cr(III), Ir(III).
2.0	Te(IV), citrate, F <sup>-</sup> .
3.0	Ni(II), Se(IV), U(VI).
5.0	Zn(II), Mn(II), Hg(II), W(VI), SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> .
Interfering ions	Pd(II), Fe(II), Rh(III), Os(VIII), ascorbate and thiourea.

by the proposed method are Pd, Fe(III), Rh(III), Os(VIII), ascorbate and thiourea. Interference due to iron(III) is removed by its prior extraction with mesityl oxide<sup>7</sup>. Palladium(II) is separated from ruthenium(III) by its extraction into MIBK from cold aqueous solution containing 4.5 M acetic acid and 5 ml 0.1% ligand solution and finally estimated in the organic phase; the aqueous phase is evaporated to dryness and the residue is taken up in water for estimation of ruthenium by the proposed method.

The standard deviation and coefficient of variation of the absorbance was found to be 0.004 and 1.02%, respectively for 50  $\mu\text{g}$  ruthenium.

A comparison of the proposed method with some of the earlier tried ligands (Table 2) showed

TABLE 2—COMPARISON OF THE PROPOSED METHOD

Ligand	Sandell's sensitivity $\mu\text{g}/\text{cm}^2$	Molar absorptivity 1 mole <sup>-1</sup> cm <sup>-1</sup>	Colour stability hr
Isonitrosoacetylacetone	0.022	$4.5 \times 10^4$	36
Isonitrosobenzoylacetone	0.018	$5.4 \times 10^4$	6
Isonitrosodibenzoylmethane	0.024	$4.1 \times 10^4$	48
Isonitrosoethylbenzoylacetate	0.041	$2.4 \times 10^4$	24
3-Chloro-1-nitroso-2-naphthol	0.011	$8.6 \times 10^4$	>96