

compound in an almost pure form. It was further purified by repetition of the column chromatography followed by crystallisation. It had an m.p. 180–82°, $[\alpha]_D - 105.4^\circ$ and it analysed for $C_{20}H_{30}O_2$ and had $M^+ 302$. Its i.r. spectrum (nujol) had the carbonyl frequency at 1695 cm^{-1} attributable to the presence of a carboxyl group as the compound was also soluble in NaHCO_3 . Its reaction with CH_2N_2 to form the ester provided further confirmation. This accounted for both the oxygen atoms in the compound.

The presence of unsaturation was shown by i.r. absorptions at 1655 and 875 cm^{-1} . The compound also gave a positive TNM test. A quantitative catalytic hydrogenation agreed with the presence of only one double bond in the compound. Therefore, it was considered to be a tetracyclic diterpene acid.

The n.m.r. spectrum of this acid (δ values) showed two tertiary methyls at 0.98 and 1.27 and a broad signal centered at 4.8 integrating to 2 protons assigned to a terminal methylene group. When the acid was converted into the methyl ester (m.p. 84–86° C., $[\alpha]_D - 106^\circ$), the two tertiary methyls now appeared at 0.84 and 1.18. This methyl ester on LAH reduction gave the corresponding alcohol (m.p. 142–3° C., $[\alpha]_D - 80.5^\circ$) which was converted into its acetate (m.p. 112–13°, $[\alpha]_D - 67^\circ$). The n.m.r. spectrum of this acetate showed an AB quartet centered at 3.95 assigned to a grouping of the $-\text{C}-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_3$ type with the axial configuration.² In addition, a broad signal centered at 4.7 was also shown attributable again to the terminal methylene group. Reduction of the original acid (Pd/C) gave a saturated compound (m.p. 209–12°, $[\alpha]_D - 67^\circ$) which did not answer the TNM test and whose n.m.r. spectrum showed an extra methyl group and the absence of unsaturation.

All the above-mentioned data agree with the structure of (–) kaurenoic acid with the carboxyl group at the 19 position and the double bond in the 16 position. An acid of this constitution was earlier isolated by Henrick and Jefferies³ from *Ricinocarpus stylosus* (family: Euphorbiaceae) and the properties reported by them are as follows: (–) kaur-16-en-19-oic acid, m.p. 179–81°, $[\alpha]_D - 110^\circ$; methyl ester, m.p. 88–89°, $[\alpha]_D - 107^\circ$; (–) kaur-16-en-19-ol, m.p. 141–42°, $[\alpha] - 75^\circ$; its acetate, m.p. 117–18°, $[\alpha]_D - 74^\circ$; 16 β (–) kauran-19-oic acid, m.p. 210–14°, $[\alpha]_D - 68^\circ$. These data agree closely with the

series of corresponding compounds obtained from *Enhydra fluctuans*. Direct comparison of the sample of acid of Jefferies with our sample using co-TLC, m.m.p. and co-i.r. showed complete identity. This diterpene acid has also been isolated by Shibata *et al.*⁴ from the roots of *Aralia cordata* (family: Araliaceae). The present report is the first on its occurrence in the Compositae.

Our thanks are due to Professor Jefferies for the kind supply of an authentic sample.

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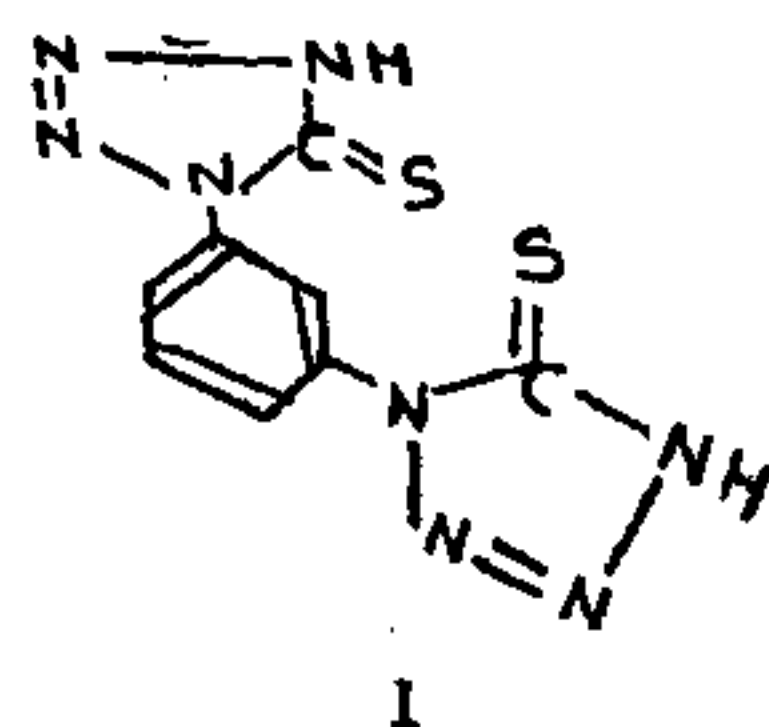
September 2, 1969.

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GRAVIMETRIC DETERMINATION OF COPPER, SILVER AND CADMIUM WITH *m*-PHENYLENE-DI-(1-TETRAZOLINE-5-THIONE) (MDT-5)

m-PHENYLENE-DI-(1-tetrazoline-5-thione) (MDT-5) (I), PDT-5, and some other 1-substituted tetrazoline-5-thiones have recently been used in the detection and determination of certain metals.¹⁻³ The purpose of the present communication is to investigate further uses of MDT-5 for analytical problems. Studies have indicated that MDT-5 reacts quantitatively with Cu^{2+} , Ag^+ and Cd^{2+} ions, at pH range of 5.5–7.0, giving precipitates of insoluble metal complexes. The silver and cadmium complexes are white, whereas that of copper is dark green. The results of elemental analysis show that the mole ratio of 'metal to ligand' is 2 : 1 in the silver complex, and 1 : 1 in copper and cadmium complexes. A method is also described for the determination of cadmium in presence of copper.



All the reagents used were of AnalaR grade. The ligand MDT-5 was prepared by the reaction of sodium azide⁴ on *m*-phenylene diisothiocyanate.⁵ The following stock solutions were prepared:

- (A) MDT-5 0.5 g. in 100 ml. of warm acetone.
 (B) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 2 g./l. (standardization of the solution by the usual methods⁶ showed that it contained 0.5 mg. Cu^{2+} ion/ml.).
 (C) AgNO_3 (dried at 120°).... 1.6 g./l. (this solution was found to contain 1 mg. Ag^+ ions/ml.).
 (D) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 2.8 g./l. (this solution was found to contain 1.001 mg. Cd^{2+} ions/ml.).

Determination of Copper.—A known volume (1 to 25 ml.) of B was taken and diluted to about 50 ml. (the amount of Cu did not exceed 30 mg.). The solution was acidified with a few drops of conc. HCl or H_2SO_4 , and a freshly filtered A was added. A greenish precipitate of copper complex that formed, was made to flocculate by digesting on the water-bath for 5 minutes, and filtered through a medium porosity sintered glass crucible. It was washed first with 100 ml. of water, then with 25 ml. of acetone, dried at 110 – 120° to a constant weight (~ 45 minutes), and finally weighed as $\text{Cu}(\text{C}_8\text{H}_4\text{N}_8\text{S}_2)$. The gravimetric factor for copper is 0.18701.

Determination of Silver.—The procedure was the same as reported previously¹ for a similar determination with PDT-5. The precipitate was dried in a vacuum desiccator, and weighed as $\text{Ag}_2(\text{C}_8\text{H}_4\text{N}_8\text{S}_2)$. The gravimetric factor is 0.4386.

Determination of Cadmium.—The procedure was the same as described above for copper. The precipitate was dried at 110 – 150° , and weighed as $\text{Cd}(\text{C}_8\text{H}_4\text{N}_8\text{S}_2)$. The gravimetric factor for cadmium is 0.2892.

Concentrated solutions metal ions (containing 5–50 mg. Cu^{2+} , Ag^+ , or Cd^{2+} ions/ml.) were also prepared and analysed. A summary of combined results of Cu, Ag and Cd determination are given in Table I.

TABLE I

Determination of copper, silver and cadmium with MDT-5

Metal ion analysed	Mg. metal taken	Mg. metal recovered	Error %
Copper ..	0.50 25.00	0.70 ₁ 24.91 ₀	0.2 0.3
Silver ..	1.00 50.00	1.00 ₀ 49.89 ₁	... 0.2
Cadmium	1.00 25.00	1.00 ₈ 24.89 ₈	0.3 0.4

Determination of Cadmium in Presence of Copper.—The mixed copper-cadmium solution (containing 5–20-folds of Cu^{2+} ions) was treated at $\text{PH} \simeq 7$ with a requisite amount of a 5% aq. solution of EDTA. The solution was stirred and allowed to stand for 5–10 minutes. Only copper was masked by EDTA at this pH. A freshly filtered solution A was then added, when a white precipitate of cadmium complex was formed. The precipitate was further treated as described above.

Coprecipitation studies were also made with Cr and Mn, since these metals are often found present in cadmium alloys and certain corrosion-resistant coatings along with cadmium. The results indicated negligible or practically nil coprecipitation.

The analytical data in Table I, and results of coprecipitation studies indicate that the ligand MDT-5 can act, like PDT-5, as a promising analytical reagent to give new weighing forms for copper, silver and cadmium. The amount of metal down to 0.5 mg., and a maximum of 50 mg. may be determined rapidly. Solutions containing > 50 mg. of metal ions are difficultly determined since the precipitates of these metals with MDT-5 are very voluminous and a little slimy, thus becoming hard to filter. Out of 50 cations tested,² only Pb, Hg, Pd, Au, Tl, Ru, Ir, Bi and Pt interfered. With the exception of CN^- , no other common anion caused any interference. The precision of all the determinations was fair, and accuracy within the permissible limits. The high insolubility in water and organic solvents of the precipitates gave an appreciable increase in the sensitivity. A single determination with MDT-5 took > 90 minutes; the error was generally 0.5%.

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