

The sterile discs (6 mm in diameter) prepared from the discs of very pure and highly absorbant paper for the assay of penicillin and other substances⁵ have been used. The discs dipped in the essential oil were placed over the seeded medium and incubated for 36 hours in the case of bacteria and 72 hours in the case of fungi. The experiment was performed in duplicate and the average zones of inhibition have been recorded. The activity of the oil was also tested in different concentrations. The dilutions of the oil were prepared in ethylene glycol, which has no antimicrobial property. The experiment was also performed with standard antibacterial and antifungal substances, i.e., 0.5% actidione and 0.5% hamycin respectively. The activities of the oil are compared with standard substances.

The results show that the oil is more active than the corresponding reference in controlling the growth of *B. subtilis*, *P. aeruginosa*, *S. newport*, *S. richmond*, *A. niger* and *C. albicans* and similar activity against *S. pullorum* and *Fusarium* sp. The oil has almost the same activity as that of the reference in inhibiting the growth of *B. anthracis*, *E. coli*, *S. typhimurium*, *A. flavus* and *P. digitatum*. The oil has not shown any activity in controlling the growth of *C. pyogenes* and *Pasteurella* sp. Against the rest of the organisms the oil has shown some activity but less than the references. The results also show that the oil is active even at a concentration of 1% against some organisms.

Thanks are due to Prof. S. P. Saxena, Head, Department of Microbiology, College of Veterinary Science and Animal Husbandry, Jabalpur, for providing organisms and suggestions. Thanks are also due to C.S.J.R., New Delhi, for the award of Fellowship to one of us (G. S. Grover).

November 5, 1980.

1. Krishna and Badhawar, "Aromatic plants of India", Pt. I, *J. Sci. and Ind. Res. (India)*, 1947, 11 (2), 62.
2. Nadkarni, R. A., *Indian Materia Medica*, Popular Book Depot. and Dhoot Papeswar Prakashan, Bombay, 1954, 1, 1265.
3. Kirtikar, K. R. and Basu, B. D., *Indian Medicinal Plants*, Lalit Mohan Basu, 49, Leader Road, Allahabad. 1933, 1, 292.
4. Maruzzella, J. C. and Henry, P. A., *J. Am. Pharm. Assoc.*, 1958, 47, 471.
5. Vincent and Vincent, *Proc. Soc. Exp. Biol. Med.*, 1944, 55, No. 3.

BIDENTATE-BRIDGED HEXAMETHYLENE-TETRAMINE COMPLEXES WITH MERCURY(II) CHLORIDE, BROMIDE AND CYANIDE

I. S. ARUJA, RAGHUVIR SINGH* AND C. L. YADAVA
Chemistry Department, Banaras Hindu University
Varanasi 221 005, India

HEXAMETHYLENETETRAMINE (Hmta), a heterocyclic system having three fused rings in the chair configuration with four-bridge-head nitrogen atoms, is known to form complexes with metal salts¹⁻³ as well as with halogens^{4,5}. However, there is no report on the complexes of mercury(II) salts with this ligand. The present study on the preparation and i.r. spectral features down to 200 cm⁻¹ on the coordination compounds formed by the interaction of mercury(II) chloride, bromide and cyanide with Hmta has been undertaken to elucidate the mode of bonding of Hmta, of the halogen/cyanide groups and the tentative stereochemistries of the complexes.

Mercury(II) chloride, bromide and cyanide complexes of Hmta were prepared by mixing together the respective mercury(II) salts and an excess of Hmta solution in ethanol. The complexes precipitated or crystallized immediately were suction-filtered, washed with ethanol and dried. Stoichiometries of the complexes isolated were established by standard analytical methods and satisfactory analytical data were obtained.

Hg(Hmta) Cl₂ : m.p. 212° C; Hg(Hmta) Br₂ : m.p. 200° C; Hg(Hmta) (CN)₂ : m.p. 205° C.

Conductivity measurements were made on freshly prepared ~ 10⁻³ M solutions in DMF at 25° C using a Philips conductivity bridge Model PR 9500. I.r. spectra of Hmta and its complexes were recorded as nujol mulls on a Perkin-Elmer 621 spectrophotometer.

Hmta formed 1 : 1 complexes with all the mercury (II) salts. The complexes investigated are insoluble in methanol and ethanol but soluble in DMF. Molar conductances of ~ 10⁻² M solutions in DMF indicate that they behave as non-electrolytes ($\Lambda \approx \sim 2-7$ ohms⁻¹ cm² mole⁻¹). Insolubility of these complexes in molten camphor precluded molecular weight measurements. No absorption bands were observed which could be attributed to water or ethanol in any of these spectra thus establishing that these complexes were free from coordinated or lattice water/ethanol.

Hmta is a potentially tetradentate ligand and the chemical and steric equivalence of the four nitrogen atoms has been demonstrated by various physico-chemical methods^{6,7}. It may thus act as a mono-, bi-, tri- or tetra-dentate ligand. Molecular models

* School of Chemistry, University of Hyderabad, Hyderabad 500 001.

show that it is more likely to bond to different metal ions and thus act as a bridging rather than a chelating ligand. 1300–200 cm^{-1} region i.r. spectrum of the uncoordinated Hmta shows absorption bands at 1225s, 1180w, 1040m, 1006s, 823w, 803s, 714w, 664s, 610m and 508s. Of these, the two strong bands at 1225 and 1000 cm^{-1} are assigned to νCN modes⁹. Both these bands are split up into doublets in complexes in which Hmta acts as a bidentate bridging ligand⁶ but they suffer only a very minor splitting forming closely spaced doublets or triplets in complexes where Hmta molecule(s) act as monodentate ligand(s). Apart from some intensity changes and the splitting of νCN bands the i.r. spectra due to coordinated Hmta in the mercury(II) complexes studied here are almost superimposable on the spectrum of the uncoordinated ligand. This may be attributed to the fact that the chair configuration of the uncoordinated Hmta¹⁰ is retained in all the mercury(II) complexes. Although a potentially tetradentate ligand stereochemically Hmta seems to act only as a bidentate ligand bridging between two metal atoms retaining the chair configuration in all the mercury(II) complexes.

Mercury(II) being a d^{10} system does not exhibit $d-d$ transitions and, therefore, magnetic susceptibility and electronic spectral measurements do not yield information on the structure of its complexes. Information on the tentative stereochemistry of the complexes in the present study has been derived from a comparison of the metal–ligand stretching modes with those of similar modes in compounds of proven structures.

The low frequency i.r. spectra of the 1 : 1 mercury(II) chloride and bromide complexes with Hmta show strong absorption bands at 312 and 260 cm^{-1} , respectively. The frequency of these bands is halogen-dependent and in fair agreement with terminal mercury–halogen bands in tetrahedral mercury(II) chloride and bromide complexes¹¹. With bidentate bridging Hmta molecules retaining the chair configuration (*vide infra*) and the Hg–X stretching modes consistent with terminal Hg–X bonds in tetrahedral structures these 1 : 1 mercury(II) chloride and bromide complexes with Hmta are tentatively assigned to have polymeric chain structures with tetrahedral environments of two nitrogen atoms of bidentate bridging Hmta molecules and two terminally bonded halogens around the mercury atoms in the solid state.

In addition to the bands due to bridging Hmta molecules i.r. spectrum of the 1 : 1 mercury(II) cyanide–Hmta complex shows absorption bands at 2178, 410 and 315 cm^{-1} due to νCN , $\nu\text{Hg-C}$ and $\delta\text{Hg CN}$ modes, respectively. The frequencies of these modes strongly suggest the presence of terminally bonded CN groups¹² in the complex. From a consideration of the bidentate bridging nature of Hmta

(*vide supra*) and terminal cyano groups this complex is tentatively assigned to have a polymeric chain structure with tetrahedral environment of two nitrogen atoms of the bridging Hmta molecules and two carbon atoms of the terminally bonded cyano groups around the mercury atoms in the solid state. One could postulate polymeric chain octahedral structures with bridging Hmta molecules as well as bridging Cl, Br and CN groups for these 1 : 1 mercury(II) chloride, bromide and cyanide complexes with Hmta. However, such structures are ruled out as the $\nu\text{Hg-Cl}$, $\nu\text{Hg-Br}$ and $\nu\text{Hg-C}$ modes in the present study are consistent with the presence of terminal Hg–Cl, Hg–Br and Hg–C bonds in tetrahedral structures. $\nu\text{Hg-Cl}$ and $\nu\text{Hg-Br}$ modes in polymeric chain octahedral structures with bridging Hg–Cl and Hg–Br bonds would be expected to absorb¹² much below 200 cm^{-1} . The bridging νCN , $\nu\text{Hg C}$ and $\delta\text{Hg CN}$ bonds, however, absorb at higher energies than the terminal bonds¹⁴. The frequency of meta'-halogen vibrations is dependent on the coordination arrangement about the metal atom¹³, occurring at higher values in the spectra of tetrahedral and tetragonal complexes than in the octahedral ones. Moreover, the terminal $\nu\text{M-halogen}$ modes in monomeric octahedral structures absorb at higher energies than the $\nu\text{M-halogen}$ mode in polymeric halogen-bridged octahedral structures.

The authors thank Professor B. M. Shukla, Head of the Chemistry Department, B.H.U., for providing facilities.

November 17, 1980.

1. Barbieri, G. A. and Calzolari, F., *Atti. Accad. Lincei*, 1911, 19, 594;
Scagliarini, G. and Tartarini, G., *Ibid.*, 1926, 4, 287;
— and Brasi, E., *Ibid.*, 1928, 7, 509;
— and Cesari, C. C., *Gazz. Chim. Ital.*, 1934, 64, 742;
Watt, G. W. and Machel, A. R., *J. Am. Chem. Soc.*, 1950, 72, 2861.
2. Gyunter, E. A. and Mel'nichenko, L. M., *Z. Neorg. Khim.*, 1966, 11, 429; De-Santis, P., Kovacs, A. L., Liquori, A. M. and Mazzarella, L., *J. Am. Chem. Soc.*, 1965, 87, 4965.
3. Allan, J. R., Brown, D. H. and Lapping, M., *J. Inorg. Nucl. Chem.*, 1970, 32, 2287.
4. Marsoochi, M. and Ferroni, E., *Gazz. Chim. Ital.*, 1961, 91, 1200, 1216.
5. Negita, H., Nishi, Y. and Koga, K., *Spectrochim. Acta*, 1965, 21, 2144.
6. Andersen, A. F., *Acta Cryst.*, 1957, 10, 107.
7. Becka, L. N. and Cruickshank, D. W. J., *Ibid.*, 1961, 14, 1092.

8. Mecke, R. and Spiecke, H., *Ber.*, 1955, 88, 1997.
9. Ahuja, I. S., Singh, Raghu/ir and Yadava, C. L., *Spectrochim. Acta* (in press).
10. Finar, I. L., *Organic Chemistry*, Longmans, London, 1973, Vol. I.
11. Deacon, G. B., Green, J. H. S. and Harrison, D. J., *Spectrochim. Acta*, 1968, 24A, 1921.
12. Jain, S. C. and Rivest, R., *Inorg. Chim. Acta*, 1970, 4, 291.
13. Clark, R. J. H. and Williams, C. S., *Inorg. Chem.*, 1965, 4, 350.
14. Dows, D. A., Haim, A. and Wilmarth, W. K., *J. Inorg. Nucl. Chem.*, 1961, 21, 33.

TEPHRINONE—A NEW FLAVANONE FROM *TEPHROSIA VILLOSA*

P. PULLA RAO AND G. SRIMANNARAYANA

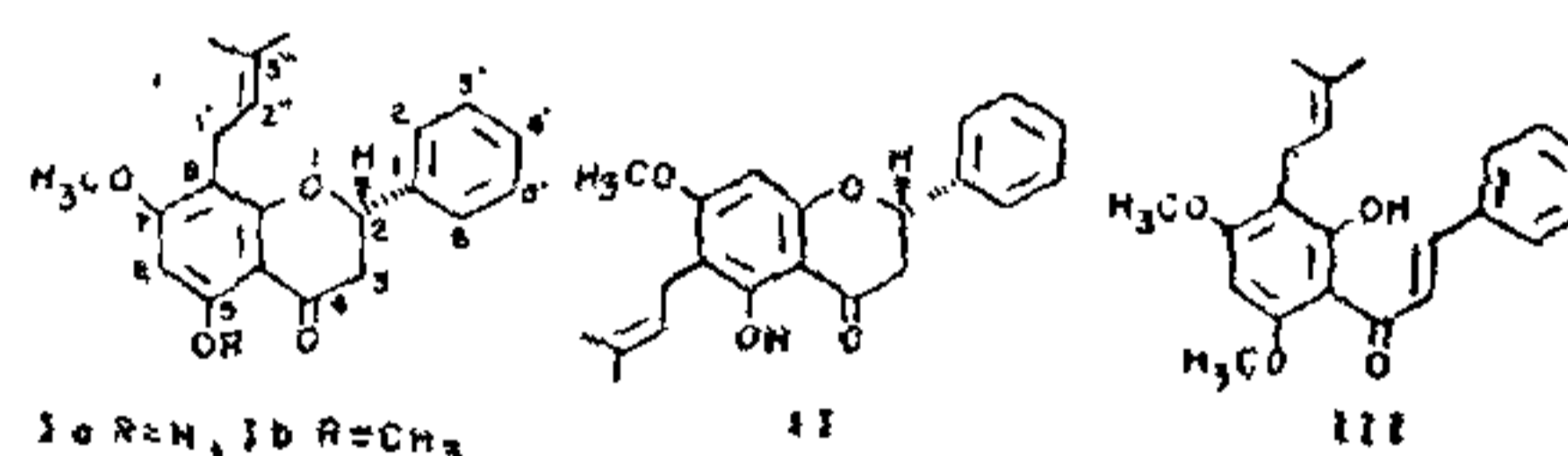
Department of Chemistry, Osmania University
Hyderabad 500 007 India

The structure and absolute configuration of tephri-
none (Ia), an extractive of the roots of *Tephrosia*
villosa, was established as (2S)-5-hydroxy-7-methoxy-8-
(3"-methylbut-2"-enyl) flavanone on the basis of
physical and chemical evidence.

The past work of *Tephrosia villosa* reveals the
presence of isoflavones¹, rotenoids^{2, 3} and coumenstone⁴
in it. The petroleum ether extract of the roots of
Tephrosia villosa on column chromatography furnished
a new flavanone designated as tephri-
none (yield 0.01%). We present evidence here to show the structure of
tephri-
none as (2S)-5-hydroxy-7-methoxy-8-(3"-methyl-
but-2"-enyl) flavanone (Ia).

Tephri-
none, m.p. 128°, C₂₁H₂₂O₄, M⁺ 338 gave
positive Shinoda test⁵, indicating its flavanoid nature.
The ir spectrum (CHCl₃) of tephri-
none showed a phenolic hydroxyl at 3375 cm⁻¹ and a chelated carbonyl^{6a}
at 1630 cm⁻¹. Strong violet colour with alcoholic
ferric chloride confirmed chelated hydroxyl group.
The uv absorption maxima (MeOH, λ nm) 285 (log ε
4.26) and 345 (3.44) and a bathochromic shift of
30 nm of 285 nm in presence of AlCl₃-HCl is charac-
teristic feature of 5-hydroxy flavanone^{6b}. The nmr
spectrum (CDCl₃) of tephri-
none showed a double
doublet at 5.4 δ (1H, J_{2,3ax} = 11 Hz and J_{2,3eq} = 6 Hz)
and a multiplet in the region 2.81-3.1 δ (2H) are
assignable to C₂ and C₃ protons, respectively, of
flavanone⁷. A set of peaks appeared at 1.63 δ [6H,
broad singlet, =C(CH₃)₂], 3.24 δ (2H, d, J = 6 Hz,
-CH₂-) and 5.16 δ (1H, t, J = 6 Hz, -CH=) are
characteristic of a C-3-methylbut-2-enyl group⁸.
The absorption due to a methoxyl group, 3.85 δ
(3H, S), a D₂O exchangeable chelated phenolic

hydroxyl group, 11.0 δ (1H, S, 5-OH), a phenyl
group, 7.45 δ (5H, broad singlet) and a up field proton,
6.12 δ (1H, S, C₆H or C₈H) are also observed. Tephri-
none gave a monomethyl ether (Ib) (dimethylsulphate-
K₂CO₃ in acetone, 6 hr.), C₂₂H₂₄O₄, m.p. 97°, M⁺ 352.
Tephri-
none on oxidation with alkaline hydrogen
peroxide and subsequent methylation with diazomethane
gave methyl benzoate, identified by GLC with
authentic sample, indicating the presence of unsubsti-
tuted phenyl group in tephri-
none. Methoxyl group
was placed at 7-position on biogenetic grounds.
Tephri-
none failed to give positive Gibbs test⁹ or a
cyclised product with formic acid containing a drop
of sulphuric acid¹⁰ or dichlorodicyanobenzoquinone
(DDQ)¹¹. Therefore 3-methylbut-2-enyl group was
placed at 8-position rather than at 6-position of
flavanone skeleton. Further direct comparison of
tephri-
none with isomeric and naturally occurring
flavanone, 5-hydroxy-7-methoxy-6-(3"-methylbut-2"-enyl)
flavanone(II)^{10, 12} revealed that they are not identical.
5-Hydroxy flavanones on prolonged refluxion (40 hr)
with dimethylsulphate in acetone-potassium carbonate
medium are known to undergo ring opening and methy-
lation to give chalcone methyl ethers¹³. When this
reaction applied to tephri-
none a chalcone methyl ether
(III) (m.p. 122°, C₂₂H₂₄O₄, ir νC=O 1630 cm⁻¹, uv
λ_{max} 340 nm) was obtained whose properties are
similar to that of ovalichalcone(III)¹⁴. However direct
comparison could not be made due to the lack of
authentic sample III.



The C.D. spectrum of tephri-
none [310 (ΔE + 4.4),
285 (ΔE - 13.4) nm] (CHCl₃) showed a positive cotton
effect due to π → π* transition in the region (310-
330 nm) and a negative cotton effect due to π-π*
transition in the region (270-290 nm), which is charac-
teristic of 2S-flavanones¹⁵. The large coupling constant
between C₂H and C₃H protons (J_{2,3ax} = 11 Hz)
suggest that the 2-phenyl ring exists in the equatorial
position¹⁶. Elementary analysis of Ia, Ib and III
gave satisfactory values.

Authors thank Prof. R. N. Khanna for sending
authentic sample of II. One of the authors (P. P. R.)
thanks the CSIR, India, for providing fellowship.

December 31, 1980.

1. Rangaswamy, S. and Sastey, B. V. R., *Indian J. Pharma*, 1956, 18, 43.