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Institute of History of Medicine and Medical Research, Tughlaqabad, New Delhi 110062, and Department of Chemistry, Aligarh Muslim University, Aligarh,
December 7, 1977.

M. S. Y. KHAN.
I. KUMAR.
NIZAM U. KHAN.
M. ILYAS.

1. Kirtikar, K. R. and Basu, B. D., *Indian Medicinal Plants*, Published by Lalit Mohan Basu, M. B., 49, Leader Road, Allahabad, India, Second edition 1933, **1**, 269.
2. Chopra, R. N., Nayar, S. L. and Chopra, I. C., *Glossary of Indian Medicinal Plants*, C.S.I.R., New Delhi, 1956, p. 178.
3. Afaq, S. H. and Rizwan, M., *Ind. J. Pharm.*, 1971, **33**, 20.
4. Naqvi, S. A. H., Vohora, S. B. and Khan, M. S. Y., *Planta Medica*, 1976, **29**, 98.
5. Koeppen, B. H. and Roux, D. G., *Biochem., J.*, 1965, **97**, 444.

ASCORBATE-M(II) SYSTEMS—EQUILIBRIUM STUDIES

L-ASCORBIC ACID (Vitamin C) solution in water readily undergoes aereal oxidation in presence of traces of some transitional metal ions[1] especially under alkaline conditions. The reversible oxidation-reduction of L-ascorbic acid in biological systems is probably influenced by the thermodynamic and kinetic stabilities of ascorbic acid-transitional metal complexes. The stabilities of a number of metal ions determined by physicochemical techniques are reported in literature[2–4]. These studies are scanty specially with the biologically active metal ions and they do not throw any light on the role of metal ions on ascorbic acid oxidation. We have now determined the step stability constants of ascorbic acid complexes with bivalent metal ions namely, Fe(II) Mn(II), Co(II), Ni(II), Be(II) and Pb(II) using *Bjerrum-Calvin pH titration technique*[5–6] in aqueous solutions of ionic strength 0·05 M (KNO_3) at 25° C. During the pH titration reaction mixtures were kept saturated with N_2 gas to avoid aereal oxidation of L-ascorbic acid.

Materials and Methods

Solutions of Analar grade reagents of BDH (India) were prepared in redistilled water. The metal ion solutions were standardized by *conventional* techniques. L-ascorbic acid (BDH) was used as such. Potassium nitrate solution was employed to maintain constant ionic strength. Philips pH meter (PR 9405) was used to record the changes in pH during titration.

Following sets of reaction mixtures were prepared for studying each of the complexes :

Total volume	KNO_3 (1 M)	HNO_3 (0·10 M)	Water	Metal ions (0·01 M)
100·0 ml Solution A	5·0 ml	10·0 ml	85·0	..
95·0 ml* Solution B	do.	do.	80·0	..
95·0 ml* Solution C	do.	do.	75·0	5·0 ml

* 0·0440 g of ascorbic acid was transferred with 5 ml of water ($TCL_0 = 2·5 \times 10^{-3}$ M).

The solutions were titrated by standard KOH solution in an air-tight bottle in which N_2 was constantly bubbled and change in pH measured. After the titration the analysis[8] of ascorbic acid showed that it remained unoxidised during titration. In the titration of *metal-ligand systems turbidity was observed* at pH 9·0 for Mn(II), Fe(II), Ni(II) and Co(II) as pH 7·0 for Pb(II). For Be(II) no turbidity appeared.

On the basis of above data, the titration curves were prepared from which $\bar{n}$, $n\bar{H}$ and pL were calculated by Irving and Rossotti method[9] and finally pk_n and $\log k_n$ were evaluated from formation curves by Bjerrum half $\bar{n}$ method. The nature of formation curves indicates that only Be(II) forms stable 1:2 complexes whereas others form only 1:1 complex which probably hydrolyse at higher pH. The relevant stability constants are given in Table I.

TABLE I

Stability constants of ascorbic acid-metal complexes at ionic strength of 0·06 *M* (KNO_3 0·05M + HNO_3 0·01M) T 25° C

Cation	log K_1	log K_2
Be^{2+}	9·0 (8·84)	7·9 (8·08)
Pb^{2+}	8·2	..
Mn^{2+}	5·2	..
Fe^{2+}	6·9	..
Co^{2+}	5·6	..
Ni^{2+}	5·6	..

The values given in parentheses are calculated by least square method.

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Department of Chemistry, The University of Kashmir, Srinagar 190 006 (India).
KESHAVA P. DUBEY.
(Miss) SHAMAH PARVEEN.

November 16, 1977.

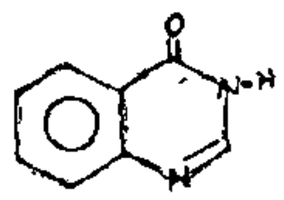
1. Bell, H. G. and Davidson, J. N. *et al.*, *Text Book of Physiology and Biochemistry* (E and S Livingstone Ltd., London, 4th Ed., 1959, p. 135.
2. Stolyarov, K. P. and Amantova, I. A., *Talanta*, 1967, **14** (2), 1237.
3. Umlognen, P. and Wahlberg, O., *Acta Chem. Scand*, 1971, **25** (3), 1064, 1000, 1079, 1045.
4. Yoshio, O. and Yoshio, K., *Tetrahedron*, 1970, 26 (20), 4711.
5. Bjerrum, J., *Metal Ammine Formation in Aqueous Solution* (P. Haase and Sons), Copenhagen, 1941.
6. Calvin, M. C. and Wilson, K. W., *J. Am. Chem. Soc.*, 1945, 67, 2003.
7. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis* (Longman Green, London), 1968.
8. Sant, B. R., *Chemist-Analyst*, 1958, 47, 65.
9. Irving, H. M. and Rossotti, H. S., *J. Chem. Soc.*, 1954, p. 2904.

SYNTHESIS OF QUINAZOLINONE-4-N-MANNICH BASES

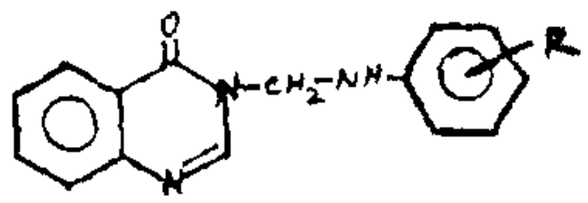
A SERIES of quinazolinone–4–N–Mannich bases have been synthesised from quinzolinone–4 and various primary aromatic amines in the presence of formaldehyde.

Compounds having an active hydrogen atom on nitrogen such as salicylamide[1], succinimide[2,3], phthalimide[4-6], 4-nitrophthalimide[7], isatins[8] and quinazolinones[9] have been reported to undergo ready Mannich condensations furnishing N–Mannich bases in good yields. Quinazolinone–4(I) may be considered a cyclic amide and as such the hydrogen atom attached at position 3 to nitrogen should be appreciably labile to participate in the Mannich condensation. It was therefore considered of interest to treat I with a few primary aromatic amines to furnish N–Mannich bases (II).

Fusion of anthranilic acid with formamide yielded I, which was then treated with formalin and primary amines in equimolar proportions. II thus obtained were characterised by means of elemental analyses and I.R. spectral data. As is evident from Table I this condensation reaction is possible with aromatic amines having electron donating as well as electron withdrawing substituents. That the Mannich reaction occurs at N–3 has already been established[9].



I



II

TABLE I

Quinazolinone-4-N-Mannich Bases(II)

Sl. No.	R	M.P. °C	Yield %	Molecular formula
1.	H	152	60	$C_{15}H_{13}N_3O$
2.	4–Me	135–36	55	$C_{16}H_{15}N_3O$
3.	4–OMe	160–61	65	$C_{16}H_{15}N_3O_2$
4.	4–Cl	186–87	55	$C_{15}H_{12}ClN_3O$
5.	3–Cl	166–67	50	$C_{15}H_{12}ClN_2O$
6.	2-OEt	148	55	$C_{17}H_{17}N_3O_2$
7.	4–Ph	174	60	$C_{21}H_{17}N_3O$
8.	4–COOH	215–17	60	$C_{16}H_{13}N_3O_3$
9.	4–COOMe	204	55	$C_{17}H_{15}N_3O_3$
10.	3–COOH	198–99	50	$C_{16}H_{13}N_3O_3$
11.	2–COOH	184–85	45	$C_{16}H_{13}N_3O_3$

All compounds gave satisfactory nitrogen analyses
I.R. (cm^{-1}) : 6 = 1675 (C = O), 3380 (NH), 1605 (C=N).
8 = 1678 (C=O, ring), 1700 (C=O, carboxylic), 3000 (OH, carboxylic), 3345 (NH), 1602 (C=N).

Experimental

Quinazolinone–4 was prepared according to published method[10,11].

Quinazolinone–4–N–Mannich bases(II) (*Table* I)

An intimate mixture of I (1·46 g; 0·01 mode), formalin (1·5 ml) and aniline (0·93 g.) in 20 ml of ethanol was warmed on a waterbath with stirring for 10 min and thereafter it was allowed to remain at room temp. overnight. The solid product thus separated was filtered and rectystallised from ethanol.

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Chemistry Department,
Lucknow University,
Lucknow 226 007,
RAJENDRA S. VARMA.

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