TABLE I

SYNTHESIS OF NICOTINIC ACID BY RESTING CELLS OF *E. coli*

The reaction mixture contained per 2 ml.: 20 mg. of cells (dry weight); 125 μM. phosphate buffer, *p*H 6.0; 75 μM. NH_4Cl; 20 μM. D-ribose; 10 μM. adenine; and 20 μM. of each of the different substrates. Incubation was for 3.5 hours at 37° (aerobically). After hydrolysis by heating at 120° for 30 min. in 1 *N* H_2SO_4, the nicotinic acid content of each reaction mixture was determined by microbiological assay with *Lactobacillus arabinosus* 17-5.[3]

Substrate added	Nicotinic acid content, mμg./mg. cells
None	222
None, acidified at 0 time	240
Succinate	362
Glycerol	396
Tryptophane	261
Succinate + glycerol	464
Succinate + glycerol (omit adenine)	231
Succinate + glycerol (omit ribose)	216
Succinate + glycerol (omit adenine and ribose	216

1,3-C^{14} and pyruvic acid-2-C^{14}. After incubation and hydrolysis with sulfuric acid an aliquot was removed from each vessel to determine the amount of nicotinic acid synthesized. Twenty mg. of carrier nicotinic acid then was added to the remainder of each reaction mixture. The nicotinic acid was isolated by passage through Dowex-50 and IRA-400 ion exchange resins and finally crystallized, as the picrate, and recrystallized to a constant melting point (210–215°) and constant specific radioactivity. Radioactive succinate and radioactive glycerol were both incorporated into nicotinic acid (Table II). The incorporation of C^{14}-

TABLE II

INCORPORATION OF C^{14} COMPOUNDS INTO NICOTINIC ACID

The reaction mixture and incubation conditions were as given in Table I

Substrate added	Specific activity of picrate of nicotinic acid c.p.m./μM.	Moles substrate incorporated per mole nicotinic acid synthesized
Glycerol-1,3-C^{14}	76	2.0
Succinate-2,3-C^{14} + pyruvate	44	1.0
Pyruvate-2-C^{14} + succinate	2	0
Glycerol-1,3-C^{14} + succinate + pyruvate	23	0.5

pyruvate was negligible. When C^{14}-glycerol was used as the only precursor, two moles of glycerol was incorporated per mole of nicotinic acid synthesized. This suggests that glycerol is capable of supplying all of the carbon atoms of nicotinic acid.

(3) E. E. Snell and L. D. Wright, *J. Biol. Chem.*, **139**, 675 (1941).

(4) Supported by a Karl T. Compton fellowship from the Nutrition Foundation (1956–1958) and the Banco de México, S.A.

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STABLE MERCUROUS COMPLEXES

Sir:

When a complexing ligand is added to a mercurous solution, the usual reaction that occurs is disproportionation of the mercurous ion to give elementary mercury and a complexed mercuric ion. In fact, several well-known textbooks assert that there are no known complexes of mercurous ion. It has been suggested recently that Hg_2^{++} does exhibit weak ion pair association with ClO_4^- and NO_3^- with formation constants of 0.9 M^{-1} and 2.5 M^{-1}.[1] Some time ago, Stromeyer[2] reported that when sodium pyrophosphate solution is added to a mercurous solution, a white precipitate forms and then redissolves in excess of the reagent, which suggests the formation of a strong, stable complex.

We have now found that the mercurous ion forms stable soluble complexes with pyrophosphate, oxalate, succinate, and tripolyphosphate. The results with pyrophosphate will be described in detail. There is no doubt that mercury of oxidation state (I) is still present in the clear solution of mercurous nitrate in excess sodium pyrophosphate, since Hg_2Cl_2 can be precipitated by addition of NaCl solution. The mercurous solutions are also formed by reaction of Hg(II) pyrophosphate complexes with elementary mercury, so the complex is stable to disproportionation. A potentiometric study indicates that the predominant species are $Hg_2Py_2^{-6}$, and $Hg_2Py(OH)^{-3}$ (where $Py = P_2O_7^{-4}$).

The potential of a Hg,Hg(I) electrode in solutions at *p*H's 7–10, $\mu = 0.75$ *M* ($NaNO_3$), ($Hg_2(I)$) = 5×10^{-5} to 2×10^{-3} *F*, (Na_4Py) = 0.004–0.05 *F*, *T* = 27.5°, can be interpreted in terms of the two equilibria (*M* = mole liter^{-1})

$$Hg_2^{++} + 2\ Py^{-4} \rightleftarrows (Hg_2Py_2)^{-6} \qquad K_2 = 2.4\ (\pm 0.6) \times 10^{12}\ M^{-2}$$

$$Hg_2^{++} + OH^- + Py^{-4} \rightleftarrows (Hg_2Py(OH))^{-3} \qquad K_1 = 1.3\ (\pm 0.2) \times 10^{16}\ M^{-2}$$

The predicted equation for the potential considering the above equilibria, is E(mv.) = E^0 + 29.7 [log (ΣHg_2^{++}) − log (1 + K_1(OH)(Py) + K_2(Py)^2)], with E^0 *vs.* SCE = 539 mv. Representative data are displayed in Table I. Roughly speaking, $(Hg_2Py_2)^{-6}$ is the main species at Σ(Py) = 0.02 *F* for *p*H's between 7 and 8.5; Hg_2Py-

TABLE I

POTENTIAL MEASUREMENTS

*p*H	(ΣHg_2^{++}) $\times 10^5$ / *F*	(ΣPy) $\times 10^{22}$ / *F*	*E* (*vs.* S.C.E.) mv.	*E* (calcd.)
9.10	7.55	0.484	151.34	153.5
	6.71	2.571	124.10	126.0
	6.25	3.723	118.70	119.2
8.39	7.57	0.484	177.29	174.7
	7.01	1.877	150.10	151.3
	3.83	4.90	121.72	122.5
	5.71	4.90	127.16	127.1
	7.51	4.90	131.22	130.6

[a] We measure the effective *pK* of HPy^{-3} in this medium as 8.00; *cf.* Lambert and Watters.[3]

(1) S. Hietanen and L. G. Sillén, *Arkiv Kemi*, **10**, 103 (1956).

(2) F. Stromeyer, *Schweigger's Journal*, **58**, 130 (1830); as reported in J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Company, London, 1923; Vol. IV, p. 1003.

(3) S. M. Lambert and J. I. Watters, THIS JOURNAL, **79**, 4262 (1957).

$(OH)^{-3}$ is predominant in the pH range 9 to 10. In strongly alkaline solutions, a mixture of mercury and mercuric oxide precipitates. Below about pH 6.5, insoluble mercurous pyrophosphate salts precipitate.

The Hg–Hg distance increases in the series Hg_2F_2,[a] Hg_2Cl_2, Hg_2Br_2, Hg_2I_2; 2.43, 2.53, 2.58, 2.69 Å.[4] This plus the fact that complexing ligands such as NH_3 or CN^- cause disproportionation to Hg(II) and the metal suggest that the formation of a covalent bond between such a ligand and Hg_2^{++} diminishes the amount of s character in the Hg–Hg bond and thus weakens it. We then expect stable mercurous complexes only with strong "ionic" ligands, such as $P_2O_7^{-4}$, $C_2H_4(CO_2)_2^{--}$, etc., in accordance with our observations. Preliminary studies indicate that oxalate forms $Hg_2(C_2O_4)_2^{--}$ and $Hg_2(C_2O_4)(OH)^-$; this work is continuing.

(4) G. Grdenic, *J. Chem. Soc.*, 1312, 1316 (1956).

(5) This research has been supported by the AEC, Contract AT(11-1)-188; TY wishes to acknowledge gratefully the support of the Brazilian government via a CAPES fellowship.

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PARTIAL MOLAL VOLUMES OF HYDROGEN AND DEUTERIUM

Sir:

In 1958 Jolley and Hildebrand published a paper[1] on Solubility, Entropy, and Partial Molal Volumes of Gases in Non-polar Solvents which included figures indicating that the partial molal volume of hydrogen is larger than that of deuterium in the same solvent. This is so interesting that we undertook the more careful determinations herein described.

The main improvement in technique, other than extreme care in all controls, has been to reduce the pressure in one of the two capillaries of the Horiuti dilatometer so as to keep the mercury in the other, open capillary always at the same level, thus avoiding an "apparent compressibility" correction for the increased head of mercury. There were no significant changes in barometric pressure during a run.

At least four additions of gas were made for each determination. In the absence of leaks or other errors, a plot of ΔV *vs.* moles of gas added gave points falling accurately on a straight line. Partial molal volumes, $\bar{v}$, were calculated from the slopes of these lines. These solutions were all so dilute that $\bar{v}$'s so determined are essentially the limiting values for infinite dilution.

Results are given in the table. The approximately 10% excess of $\bar{v}$ for hydrogen in benzene and toluene is very striking. We think the explanation lies in difference in zero-point energy. Although the temperature is far above 0°K., the potential "boxes" are very small. A quantitative treatment of the problem by John Walkley and Berni J. Alder is in preparation.

(1) J. E. Jolley and J. H. Hildebrand, THIS JOURNAL, **80**, 1050 (1958).

PARTIAL MOLAL VOLUMES OF HYDROGEN AND DEUTERIUM AT 25° AND 1 ATMOSPHERE

		Hydrogen	Deuterium
Benzene		35.1	32.7
		35.5	32.5
		35.4	32.7
	Av.	35.3	32.7
Toluene		35.7	32.3
		35.7	32.4
			32.4
	Av.	35.7	32.4
f-Heptane		54.5	52.9
		54.3	(53.4)
		54.3	52.9
	Av.	54.4	52.9

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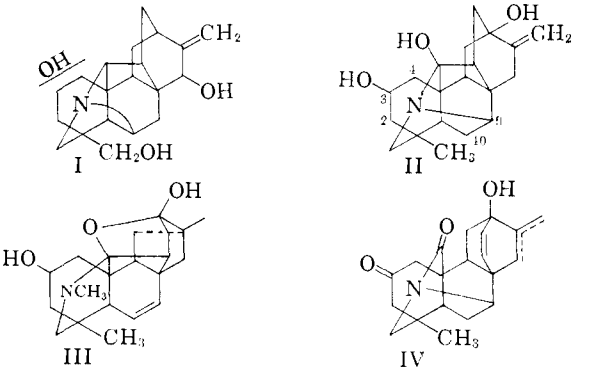
THE ACONITE ALKALOIDS. THE STRUCTURE OF HETISINE

Sir:

On the basis of Jacobs' data[1,2] and certain new considerations, Wiesner has proposed the hypognavine-like[3] structure I for hetisine.[4] In refutation of I and in support of structure II, we submit these data.



The presence of an exocyclic methylene group in hetisine is shown by bands at 6.04 and 11.10 μ (KBr) which do not appear in the spectrum of dihydrohetisine, and is confirmed by the isolation of formaldehyde upon ozonolysis of hetisine. C-Methyl determinations (0.57 C-Me/mole)[5] and infrared studies indicate the existence of one C-methyl group in hetisine.

Jacobs' Hofmann data[2] appear to require rearrangement of an allylic alcohol.[4] The presence of a secondary allylic alcohol, as proposed by Wiesner[4] in I, is untenable. Such systems are oxidized easily

(1) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **143**, 605 (1942).
(2) W. A. Jacobs and C. F. Huebner, *ibid.*, **170**, 189 (1947).
(3) S. Sakai, *Chem. and Pharm. Bull. (Japan)*, **6**, 448 (1958).
(4) K. Wiesner and Z. Valenta, *Fortsch. der Chemie*, **16**, 27 (1958).
(5) Atisine and isoatisine also average 0.5 C-Me/mole by this method.