produce xylulose, in confirmation of conclusions reached from substrate specificity tests.

TABLE I

ANALYSES OF THE XYLITOL DEHYDROGENASE REACTIONS

Reaction[a]	Coenzyme reduced (μM)[b]	Ketose formed (μM)[c]	Red. coenz: ketose	Orcinol test (O.D.)[d] 540/670	435/670
TPN-Xylitol	1.176	1.253	1:1.07	0.38	0.53
DPN-Xylitol	0.947	0.817	1:0.86	.40	.59

[a] Flask contents: 78.8 μM. xylitol, 29.6 μM. coenzyme, and 0.5 ml. of enzyme (1.0 ml. of enzyme extract is derived from the mitochondria of 1.3 g. of liver) in 1.5 ml. of solution 0.05 *M* to "tris" buffer (*p*H 9.0) and 0.008 *M* to $MgCl_2$; reaction time, 180 min. at 36°. [b] Determined by measuring increase in 340 mμ absorption in the Beckman Model DU spectrophotometer. [c] Based on the cysteine–carbazole method[12] (after Ba–Zn deproteinization), with xylulose as standard. The rate of color formation was typical of xylulose. [d] Method of Mejbaum,[13] with 40 min. heating period (Ba–Zn filtrate treated with charcoal to remove DPN). Authentic xylulose: 540/670,0.41; 435/670,0.55; ribulose, 0.75 and 0.66, respectively.

In contrast to particulate preparations, the solubilized enzymes are stable for many weeks at 0°. Both of the xylitol dehydrogenases are completely inhibited by 0.005 *M* iodoacetate. The substrate requirements as well as the cellular location of the DPN-dependent D-xylulose-enzyme clearly differentiate it from the liver polyol dehydrogenase of Blakley.[14] The enzymes probably provide a bridge between glucuronic acid metabolism and the 6-phosphogluconate pathway, since D-glucuronolactone enhances L-xylulose excretion in mammals.[2,3] The D-xylulose formed from L-xylulose probably would have to be phosphorylated before it could be acted upon by TK, since liver TK[15] has no, and yeast TK[6] only limited, activity on the free ketopentose. The existence of a bacterial kinase which converts D-xylulose to its 5-phosphate derivative[16] opens the possibility for a similar enzyme in mammalian tissues.

(12) Z. Dische and E. Borenfreund, *J. Biol. Chem.*, **192**, 583 (1951).
(13) W. Mejbaum, *Z. physiol. Chem.*, **258**, 117 (1939).
(14) (a) R. L. Blakley, *Biochem. J.*, **49**, 257 (1951); (b) J. McCorkindale and N. L. Edson, *ibid.*, **57**, 518 (1954).
(15) P. Z. Smyrniotis and B. L. Horecker, *J. Biol. Chem.*, **218**, 745 (1956).
(16) P. K. Stumpf and B. L. Horecker, *ibid.*, **218**, 753 (1956).
(17) University of Göttingen School of Medicine, Göttingen, Germany. Fulbright Scholar, 1955–6; aided by a grant from the United States Department of State.

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THE PARAMAGNETIC RESONANCE SPECTRA OF COPPER PORPHIN DERIVATIVES

Sir:

We recently have investigated the paramagnetic resonance absorption spectra of the copper complexes of α,β,γ,δ-tetraphenylporphin and its *p*-chloro derivative, prepared by the methods of Rothemund and Menotti.[1]

Dipole–dipole interaction between neighboring copper atoms in such large molecules is so reduced, even in the concentrated crystal, that the separate hyperfine components of the spectrum can be clearly resolved without resorting to dilution with an isomorphous diamagnetic compound. The hyperfine structure of the unchlorinated derivative consists of four equally-spaced components as in most copper compounds (see Fig. 1A), and the spin Hamiltonian coefficients are

$A = 0.025\,\text{cm.}^{-1}$ $B \approx 0.003\,\text{cm.}^{-1}$ $g_{\parallel} = 2.17$ $g_{\perp} = 2.05$

These values are very close to those obtained for copper phthalocyanine,[2] and A is again considerably greater than that of the octahedral complexes.[3]

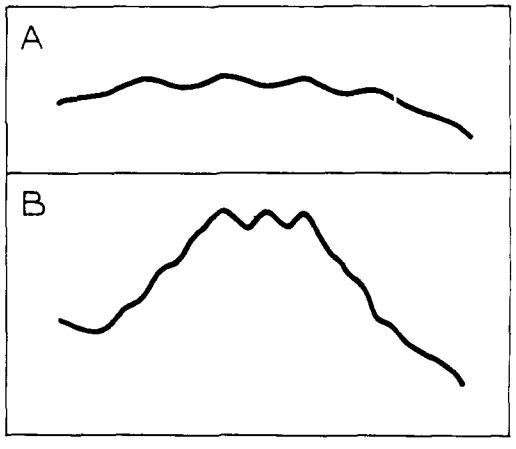

Fig. 1.—Spectra corresponding to the "parallel direction" of A, copper tetraphenylporphin, and B, its *p*-chloro derivative, from measurements at 20°K. and 36,000 mc./sec. with the same magnetic sweep scale.

However the hyperfine pattern of the chloro derivative no longer consists of four equally-spaced lines but exhibits the standard "christmas tree effect"[4,5] (see Fig. 1B), which shows that there is considerable interaction with the chlorine nuclei causing a further splitting of each hyperfine component. The spectrum has exactly the same general appearance as that first observed with ammonium chloriridate.[4]

Since the splitting is so large, about 100 gauss, it implies that the magnetic electron is associated with the chlorines for an appreciable time. If the chloro derivative crystallizes in such a way that the copper atom of one molecule is close to the chlorine of another, then it is possible that the nuclear interaction is with chlorines of adjacent molecules. But it seems highly unlikely that an electron could be shared between different molecules, because there would be a profound change in *g*-values from those obtained with copper phthalocyanine if this were so. Hence the results indicate an intramolecular movement of the magnetic electron to peripheral Cl-atoms via the π-orbitals of the conjugated ring system.

The interatomic Cu---Cl distance in this particular molecule can be estimated as about 9–10 Å., and although such a long-range interaction is well known for free radicals[6] where the unpaired

(1) P. Rothemund and A. R. Menotti, THIS JOURNAL, **63**, 268 (1941); **70**, 1809 (1948).
(2) J. E. Bennett and D. J. E. Ingram, *Nature*, **175**, 130 (1955).
(3) B. Bleaney, K. D. Bowers and D. J. E. Ingram, *Proc. Phys. Society (London)*, **A64**, 758 (1951); and *Proc. Roy. Soc. (London)*, **A228**, 147 (1955).
(4) J. Owen and K. W. H. Stevens, *Nature*, **171**, 836 (1953).
(5) J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc.*, **A226**, 96 (1954).
(6) H. S. Jarret and G. J. Sloan, *J. Chem. Phys.*, **22**, 1783 (1954).

electron would be expected to move in a non-localized orbital, it does not appear to have been previously observed for the case of magnetic electrons associated with a normal paramagnetic atom.

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THE STRONG ACID BEHAVIOR OF DECABORANE

Sir:

Decaborane, in sharp contrast to the lower boranes, dissolves in alcohols, water–alcohol, water–dioxane and other protolytic solvents without rapid hydrolysis[1]; further, the rate of hydrogen evolution as observed by H. C. Beachell and W. A. Mosher[2] for the alcoholysis of decaborane exhibits a marked induction period. These observations suggest that a reasonable stable intermediate, a precursor to the hydrogen-producing reactions, is formed.

Consistent with these observations we have noted that the solution of decaborane in these solvents produces a strong monoprotic acid without the evolution of hydrogen and that decaborane is recoverable in part from such solutions. Typically, the titration of 122 mg. (1.00 millimole) of decaborane (approx. 95% pure) dissolved in 75% ethyl alcohol–water with 0.10 *N* sodium hydroxide was followed potentiometrically. The titration curve so obtained was characteristic of a strong monoprotic acid, the end-point being observed after the addition of 0.96 milliequivalent of base. Back titration with aqueous hydrochloric acid reproduced the same titration curve. That the decaborane structure is probably not destroyed in the formation of the strong acid is demonstrated by the recovery of decaborane (identified by melting point and mixed melting point, 97–98°) from alkaline water or alcohol–water solution in 35% yield by acidification. A large fraction of the decaborane apparently is lost through hydrolysis or alcoholysis as indicated by vigorous evolution of gas.

The formation of the strong acid is sufficiently slow so that its rate of growth can be followed potentiometrically, spectrophotometrically or conductimetrically. The last method, in 75% water–dioxane, yielded results sufficiently satisfactory for kinetic treatment. The rate ($-\log k_{9.4} = 3.16$; $-\log k_{15.2} = 3.00$; $-\log k_{21.5} = 2.71$; $-\log k_{25.5} = 2.57$) is first order in decaborane and independent of hydrogen ion. From the data is derived $\Delta H^{\pm} = 14.2$ kcal. mole^{-1}.

It is proposed that the hydrogen ion originates either by reaction between decaborane and the solvent

$$B_{10}H_{14}(\text{soln.}) + H_2O = [B_{10}H_{14}OH]^-(\text{soln.}) + H^+(\text{soln.})$$

or by loss of a proton from the decaborane

$$B_{10}H_{14}(\text{soln.}) = [B_{10}H_{13}]^-(\text{soln.}) + H^+(\text{soln.}).$$

Either process would fit the observed kinetics. Deuterium exchange and kinetic experiments which should help to distinguish between them are now in progress.

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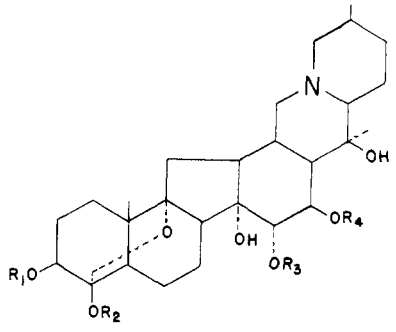
(1) W. H. Hill and M. S. Johnson, *Anal. Chem.*, **27**, 1300 (1955); H. C. Beachell and T. R. Meeker, THIS JOURNAL, **78**, 1796 (1956).

(2) H. C. Beachell and W. A. Mosher, private communication.

ZYGADENUS ALKALOIDS. VII. ON THE STRUCTURE OF ZYGADENINE

Sir:

The alkamine zygadenine[1] ($C_{27}H_{43}O_7N$) and its ester alkaloid derivatives have been shown to occur, alongside germine and its esters, in several species of *Zygadenus*[1–4] and *Veratrum*.[5,6] I wish to report evidence for structure I for zygadenine.



I, $R_1 = R_2 = R_3 = R_4 = H$
II, $R_1 = R_3 = R_4 = Ac$; $R_2 = H$
III, $R_1 = R_2 = R_3 = R_4 = Ac$
V, $R_1 = R_4 = Ac$; $R_2 = R_3 = H$
VI, $R_1 = Ac$; $R_2 = R_3 = R_4 = H$

The order of stability of the zygadenine isomers [zygadenine (3-β-hydroxy-4,9-hemiketal)<isozygadenine[7] (3-β-hydroxy-4-keto-9-α-hydroxy-A/B *trans*)<pseudozygadenine (3-α-hydroxy-4,9-hemiketal)][2] parallels that of the veracevine isomers and differs from that of the germine series.[8] Zygadenine forms a triacetate (II) upon acetylation with acetic anhydride alone; acetylation with acetic anhydride–pyridine affords a tetraacetate (III).[3] Acetylation of zygacine acetonide[3] (zygadenine-14,15-acetonide-3-acetate) with acetic anhydride yields zygadenine-14,15-acetonide-3,16-diacetate (IV), m.p. 271–272° dec., $[\alpha]^{23}D$ − 29° (py.). Found: C, 66.33; H, 8.35; acetyl, 13.61. Hydrolysis of IV with dilute mineral acid affords zygadenine-3,16-diacetate (V), m.p. 255–257° dec., $[\alpha]^{23}D$ − 50° (py.). Found: C, 64.69; H, 8.17; acetyl, 14.83; equiv. wt., 582. Periodate titrations indicate the following uptakes: zygadenine (I), 3 mole; zygacine[3,4] (VI), 2 mole; zygadenine diacetate (V), 1 mole; zygadenine triacetate (II), 0 mole; zygacine acetonide, 0 mole. Formulation I for zygadenine was first conceived as a reasonable rationalization of the above facts.

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(2) S. M. Kupchan and C. V. Deliwala, *ibid.*, **75**, 1025 (1953).

(3) S. M. Kupchan, D. Lavie and R. D. Zonis, *ibid.*, **77**, 689 (1955).

(4) S. M. Kupchan, C. V. Deliwala and R. D. Zonis, *ibid.*, **77**, 755 (1955).

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(6) M. W. Klohs, M. D. Draper, F. Keller, S. Koster, W. Malesh and F. J. Petracek, THIS JOURNAL, **75**, 4925 (1953).

(7) I propose the name isozygadenine for the amorphous carbonyl-containing isomer of zygadenine described in reference 2.

(8) S. M. Kupchan and C. R. Narayanan, *Chemistry and Industry*, in press.