in pseudoecgonine the hydroxyl is *cis* to the nitrogen, as in pseudotropine,[7] and that the carboxyl is *trans* to both the nitrogen and the hydroxyl group (IV).[6] Therefore also, the carboxyl group of ecgonine itself is *cis* to these two functions. Ecgonine may accordingly be called, the nitrogen atom being used as the point of reference, 2-*cis*-carboxy-3-*cis*-hydroxytropane (I).

The failure of N-acetylnorecgonine ethyl ester to rearrange to the O-acetyl isomer was considered by Fodor to favor Willstätter's opinion. This failure is, however, negative evidence, and it has been found here that O-benzoylnorecgonine [*Anal.* Calcd. for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.24; N, 5.09. Found: C, 65.30; H, 6.24; N, 5.20], m.p. 250° (hydrochloride, m p. 219–221°[8]) rearranges in dilute aqueous potassium carbonate to N-benzoylnorecgonine [*Anal.* Calcd. for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.24; N, 5.09. Found: C, 65.67; H, 6.19; N, 4.87], m.p. 163.5°. The neutral O-benzoyl isomer (Nujol mull) has broad weak absorption from *ca.* 3.65 to 5.5 μ attributable to NH_2^+ of a zwitterion[9] and maxima at 5.80 μ and 6.45 μ ascribable to benzoate and carboxylate ion,[9] respectively. The acidic N-benzoyl isomer (Nujol mull) has absorption maxima at 3.12 and 5.76 μ assignable to bonded hydroxyl and the carboxyl group, respectively, and a double maximum at 6.21 and 6.26 μ attributable to the disubstituted amide linkage.

Ecgonine methyl ester, cocaine, pseudoecgonine methyl ester, and pseudococaine are, in view of the foregoing considerations, to be represented by II, III, V and VI. I shall present a more detailed account of this investigation in the near future.

(8) A. Einhorn, *Ber.*, **21**, 3029 (1888).
(9) L. Larsson, *Acta Chem. Scand.*, **4**, 27 (1950).

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OXIDATION-REDUCTION POTENTIALS OF HORSERADISH PEROXIDASE

Sir:

A systematic, potentiometric study of horseradish peroxidase (HRP), organized as a joint project of the Department of Biochemistry, Medical Nobel Institute, and the Department of Physiological Chemistry, The Johns Hopkins University School of Medicine, has now been carried to a first point of general interest.

Our studies to date indicate that the oxidation–reduction potentials of the ferri HRP/ferro HRP system are much more negative than the corresponding potentials that have been determined for other hemoproteins. Detailed data over a large range of *p*H are not yet available, but measurements made between *p*H 6 and 8 indicate that here the values of E_0' are more negative even than those reported for free iron protoporphyrin IX. The contrasts are shown in the table.

System	Temp., °C.	*p*H	E_0', volt	Ref.
ferri HRP/ferro HRP	30	6.1	−0.21	
		7.3	−0.27	
ferri protoporphyrin IX/ ferro protoporphyrin IX	30	7.0	−0.14[a]	1
metmyoglobin/myoglobin	30	7.0	+0.05	2
methemoglobin/hemoglobin	30	7.0	+0.14	3
ferri cytochrome c/ ferro cytochrome c	30	7.0	+0.25	4, 5

[a] Value found by extrapolation of experimental data on the basis of an estimated pK_a' value.

It would appear that the different ferri hemoprotein/ferro hemoprotein systems range from among the most positive biological oxidation–reduction systems known to among the most negative systems known. It seems reasonable to ask now whether the well-known resistance to reduction displayed by free catalase might not be at least in part the result of a very negative oxidation–reduction potential for the ferri catalase/ferro catalase system.

The author wishes to acknowledge the great aid of Dr. Hugo Theorell and Dr. Karl-Gustav Paul, who directed the preparation of HRP in crystalline form. Dr. W. Mansfield Clark has lent invaluable advice, and has supplied the equipment for the potentiometric measurements.

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(4) F. L. Rodkey and E. G. Ball, *ibid.*, **182**, 17 (1950).
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(6) Public Health Service Research Fellow of the National Institutes of Health, 1951–1953. These studies supported in part by a grant from Eli Lilly and Company.

MAGNAMYCIN.[1] II. MYCAROSE, AN UNUSUAL BRANCHED-CHAIN DESOXYSUGAR FROM MAGNAMYCIN

Sir:

Methanolysis of the antibiotic Magnamycin[2,3] by 1 *N* methanolic hydrochloric acid yields a crystalline *base* of the formula $C_{29-30}H_{47-49}NO_{12}$ and an oily *neutral substance*, $C_{13}H_{24}O_5$ [b.p. 116° (1.1 mm.), $n^{25}D$ 1.4493, $[\alpha]^{25}D$ − 10.7° (*c* 9, $CHCl_3$), *Anal.* Calcd. for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29; OCH_3, 11.90; mol. wt., 260. Found: C, 60.04; H, 9.40; OCH_3, 11.70; sap. eq., 263]. We wish to record evidence which proves that the neutral substance is the 4-isovaleryl methyl glycoside (I)[4] of a new sugar, *mycarose*, of the structure (II).[4]

(1) Magnamycin is the registered trade name of Chas. Pfizer and Company for the antibiotic carbomycin.
(2) F. W. Tanner, A. R. English, T. M. Lees and J. B. Routien, *Antibiotics and Chemotherapy*, **2**, 441 (1952).
(3) R. L. Wagner, F. A. Hochstein, K. Murai, H. Messina and P. P. Regna, THIS JOURNAL, in press.
(4) These formulas should be regarded as devoid of configurational implications. The stereochemistry of mycarose is now under investigation.