4.49, 4.63, and 3.92); $\lambda_{max}^{MeOH-0.01NNaOH}$ 232, 266, 340, and 418 mμ (log ε 4.45, 4.53, 3.77, and 4.08).

Unusual features of the tautomerism of II and the stability of III have been discussed previously.[4]

(4) L. H. Conover, Special Publication No. 5, The Chemical Society, London, 1956, p. 48.

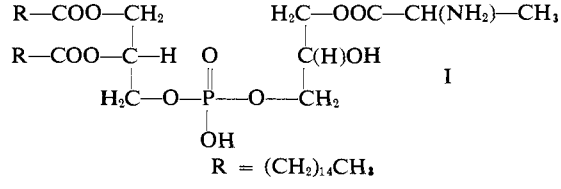
M. Schach von Wittenau, Robert K. Blackwood, L. H. Conover
Medical Research Laboratories
Chas. Pfizer & Co., Inc., Groton, Connecticut 06340

R. H. Glauert, R. B. Woodward
Converse Memorial Laboratory
Harvard University, Cambridge, Massachusetts 02138
Received November 19, 1964

Synthesis of Amino Acid-Esters of Phosphatidylglycerols

Sir:

Various investigators have reported the formation of lipoamino acid complexes in tissue preparations and in microorganisms.[1-7] Apart from the fact that these complexes were usually found in the phospholipid fractions, little was known regarding their chemical structure. Recently, MacFarlane reported[8] that the phospholipid fraction in a batch of *Clostridium welchii* was bound almost entirely to amino acids, and she presented experimental evidence which suggests strongly that the lipoamino acid complexes are amino acid esters of phosphatidylglycerol. The phosphatidyl moiety of the lipoamino acid complexes is presumed to have the same structure and configuration as in phosphatidylglycerol. The amino acids, which were found to consist of alanine, glutamic acid, aspartic acid, lysine, and possibly arginine and histidine, were arbitrarily assigned the terminal position in the fatty-acid-free glycerol moiety. Further evidence, supporting the structure proposed by MacFarlane, was reported by Sinha, Fogel, and Gaby[9] and Vorbeck and Marinetti.[10] However, without definite knowledge of the position of the amino acids in these complexes proof of the structure cannot be considered complete. For this reason, we have synthesized an alanine ester of α-(L-α-phosphatidyl)glycerol having the structure proposed by MacFarlane for the lipoamino acid complexes.[8] In it the amino acid is attached to the terminal hydroxyl of the fatty-acid-free glycerol moiety (formula I). The compound was obtained *via* the following



I

(1) R. W. Hendler, *Science*, **128**, 143 (1958).
(2) R. W. Hendler, *J. Biol. Chem.*, **234**, 1473 (1959).
(3) W. L. Gaby, R. N. Naughten, and C. Logan, *Arch. Biochem. Biophys.*, **82**, 38 (1959).
(4) W. L. Gaby, H. L. Wolin, and I. Zajac, *Cancer Res.*, **20**, 1508 (1960).
(5) W. L. Gaby and R. Silberman, *Arch. Biochem. Biophys.*, **87**, 188 (1960).
(6) G. D. Hunter and R. A. Goodsall, *Biochem. J.*, **74**, 34P (1960).
(7) G. D. Hunter and R. A. Goodsall, *ibid.*, **78**, 564 (1961).
(8) M. G. MacFarlane, *Nature*, **196**, 136 (1962).
(9) D. B. Sinha, S. Fogel, and W. L. Gaby, *Federation Proc.*, **23**, 221 (1964).
(10) M. L. Vorbeck and G. V. Marinetti, *ibid.*, **23**, 375 (1964).

series of intermediates: α,γ-benzylideneglycerol → α,γ-benzylidene-β-benzylglycerol → β-benzylglycerol → α-azidopropionyl-β-benzylglycerol [$n^{26}D$ 1.5147, d^{25}_4 1.180. *Anal.* Calcd. for $C_{13}H_{17}O_4N_3$: C, 55.90; H, 6.13; N (Kjeldahl), 5.02; N (Dumas), 15.04. Found: C, 56.10; H, 6.06; N (Kjeldahl), 4.60; N (Dumas), 14.05] → α-(dipalmitoyl-L-α-glycerylphosphoryl)-β-benzyl-α′-(2-azidopropionyl)glycerol [m.p. 27.5–28.5°, $[\alpha]^{23}D$ +2.9° (c 10, chloroform). *Anal.* Calcd. for $C_{54}H_{88}O_{11}N_3P$: C, 65.76; H, 8.99, P, 3.14, N (Kjeldahl), 1.42; N (Dumas), 4.26. Found: C, 65.41; H, 8.81; P, 3.06; N (Kjeldahl), 1.37; N (Dumas), 4.63] → α-(dipalmitoyl-L-α-glycerylphosphoryl)-α′-(2-aminopropionyl)glycerol [m.p. 164–165°, meniscus formation, $[\alpha]^{23}D$ +6.6° (*c* 10, chloroform). *Anal.* Calcd. for $C_{41}H_{80}O_{11}NP$: C, 62.01; H, 10.16; N (Kjeldahl), 1.76; N (Dumas), 1.76; P, 3.90. Found: C, 62.16; H, 9.98; N (Kjeldahl), 1.73; N (Dumas), 1.86; P, 3.81].

The synthesis of the corresponding glycine ester of L-α-phosphatidyl-α-glycerol is in progress in this laboratory.

Acknowledgment. The support of this work by grants from the Multiple Sclerosis Society of Canada and the Medical Research Council (Canada), Grant MT 684, is gratefully acknowledged.

Erich Baer, K. V. Jagannadha Rao
Subdepartment of Synthetic Chemistry in Relation to Medical Research, Banting and Best Department of Medical Research, University of Toronto, Toronto, Canada
Received November 14, 1964

Conjecture on the Composition of Dilute Alkali Metal–Ammonia Solutions

Sir:

There is evidence from calculated values of the electron affinities of the alkali metals[1] that their anions should be stable in the gas phase. This stability should be enhanced in polar solvents as the result of ionic solvation.[2] For this reason, we conjecture that such solvated anionic species are constituents of solutions of the alkali metals in liquid ammonia. We propose that these species are involved in an oxidation–reduction equilibrium (eq. 1) involving solvated metal

$$M^+ + 2S^- \rightleftharpoons M^- + 2S \qquad (1)$$

cations and solvent where all species are assumed to be solvated, M^+ is the metal cation, S is the solvent, M^- is the metal anion, and S^- is a solvent anion, *i.e.*, solvated electron. In addition, we propose that ion pairing occurs according to

$$M^+ + A^- \rightleftharpoons M^- \cdot A^- \qquad (2)$$

where A^- is either S^- or M^-. For dilute solutions, to which we restrict ourselves, the presence of higher ionic multiples may be disregarded.[3]

By assuming that ion pairing is nonspecific, that the related equilibrium constant K_2 is given by Fuoss'

(1) E. Clementi, *Phys. Rev.*, 133, A1274 (1964).
(2) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).
(3) Estimates of ion triples by the Bjerrum-Kraus-Fuoss theory (R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933)) would indicate that these species are relatively unimportant for concentrations of total metal less than *ca.* 0.1 *M*.