∂c_1), evaluated at $c_1 = 0$)

$$\lim_{c_1 \to 0} s_1 = \frac{M_1(1 - \bar{v}_1\rho)D_{11}}{RT} \left\{ 1 + c_2 \left[\frac{M_2(1 - \bar{v}_2\rho)}{M_1(1 - \bar{v}_1\rho)} \right] \times \left[\frac{\frac{1}{D_{11}} \left(\frac{\partial D_{12}}{\partial c_1} \right)_{c_2,T,P} - \left(\frac{\partial \ln y_1}{\partial c_2} \right)_{c_1,T,P}}{1 + c_2 \left(\frac{\partial \ln y_2}{\partial c_2} \right)_{c_1,T,P}} \right] \right\} \quad (7)$$

where y_1 is the activity coefficient of solute 1.

In this form, the result bears a striking resemblance to Svedberg's equation.[8] Measurement of the required quantities presents no unusual difficulty. Provided that $s_1 >> s_2$, the determination of s_1 is straightforward. The Gouy diffusiometer has been used to determine the four diffusion coefficients of several three-component systems.[2,5,6,7] Certain other methods for determining the molecular weight of a solute in a three-component system contain terms of the form $c_2(\partial \ln y_1/\partial c_2)$: for example, light-scattering[12] and sedimentation equilibrium.[13]

I am much indebted to Dr. L. J. Gosting for helpful suggestions and advice.

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THE STRUCTURAL RELATIONSHIP OF DELTALINE, DELPHELINE AND LYCOCTONINE[1]

Sir:

The alkaloid deltaline has been chemically transformed into delpheline and the latter into desoxylycoctonine, a known degradation product of lycoctonine. These interconversions prove that lycoctonine, delpheline, and deltaline possess the same skeleton structure, and establish the functional relationship of these three important *Delphinium* alkaloids, thus unifying much hitherto unrelated structural evidence. Moreover, we have found that all three alkaloids occur together in *Delphinium barbeyi* Huth, along with traces of several other closely related bases.

Deltaline was isolated as the major base of *D. barbeyi* and *D. occidentale*. It melts at 193.5–194° (evac. cap.; cor.), $[\alpha]^{33}\text{D}$ −28.5° (CH_3OH). *Anal.* Calcd. for $C_{27}H_{41}NO_8$: C, 63.88; H, 8.14; N, 2.76; O, 25.22; CH_3 on carbon (3) 8.86; active H (1), 0.20; CH_3O (3), 18.34. Found: C, 63.83; H, 8.21; N, 2.79; O (Unterzaucher), 25.32; CH_3 on carbon (Kuhn–Roth), 7.49; active H (Zerewitinoff), 0.20; CH_3O (Zeisel), 18.75, 18.13. Deltaline was first isolated from *D. occidentale* by Couch.[2] An examination of specimens of deltaline given to one of us (M. C.) by Couch revealed the invariable presence of another alkaloid, delphoccine, not previously reported and not readily separable from deltaline except by chromatography. The presence of delphoccine (whose properties we shall describe elsewhere) in Couch's material accounts for the fact that Couch's formula and constants differ from ours. The functionality of deltaline is $C_{17}H_{18}(\text{-OCOCH}_3)(\text{-OCH}_2\text{O-})(\text{-OCH}_3)_3(>\text{NCH}_2\text{CH}_3)(>\text{C-CH}_3)(\text{OH})$.[3,4]

Replacement of the hydroxyl group of deltaline with hydrogen and conversion of the acetoxyl group to hydroxyl produces delpheline.[5,6] Treatment of deltaline with highly purified thionyl chloride at room temperature yielded *chloroacetyldelpheline*, m.p. 173.3–173.5° (evac. cap.; cor.), $[\alpha]^{26}\text{D}$ −40.7° ($CHCl_3$). *Anal.* Calcd. for $C_{27}H_{40}ClNO_7$: C, 61.64; H, 7.66; Cl, 6.74; N, 2.66; O, 21.29. Found: C, 61.54; H, 7.66; Cl, 6.69; N, 2.65; O (Unterzaucher), 21.09. The reaction of chloroacetyldelpheline with $LiAlH_4$ in refluxing ethyl ether gave an excellent yield of delpheline, identical in m.p., mixed m.p., infrared spectrum, R_f value, and optical rotation with specimens isolated by us from *D. occidentale* and *D. barbeyi* and with a specimen kindly supplied by Dr. R. C. Cookson.

The chromic acid oxidation[7] of lycoctonine $[(C_{17}H_{19}(\text{-OH HO-})(\text{-OCH}_3)_4(>\text{NCH}_2\text{CH}_3)(>\text{CCH}_2\text{OH})]$ yields the aldehyde, lycoctonal,[7] reducible to the base, desoxylycoctonine, containing two C-methyl groups.

We have synthesized desoxylycoctonine from delpheline in two steps. The secondary hydroxyl group of delpheline, corresponding to the acetoxyl group in deltaline, was methylated by means of sodium hydride and methyl iodide. The resulting *O-methyldelpheline* melts at 102.5–103° (evac. cap.; cor.); $[\alpha]^{24}\text{D}$ −6.3° ($CHCl_3$). *Anal.* Calcd. for $C_{26}H_{41}NO_6$: C, 67.37; H, 8.92; N, 3.02; CH_3O (4), 26.78. Found: C, 67.44; H, 9.07; N, 3.19; CH_3O (Zeisel), 24.6. Hydrolysis of the acetal function of O-methyldelpheline with hot 10% sulfuric acid yielded desoxylycoctonine, identical in m.p., mixed m.p., infrared spectrum, and R_f value with the product prepared from lycoctonine by the procedure of Edwards and Marion.[7]

(1) Presented before the Section of Pharmaceutical Chemistry and Biochemistry at the Fourth Pan-American Congress of Pharmacy and Biochemistry in Washington, D. C., November 7, 1957.

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COMPOSITION AND ENZYMATIC SYNTHESIS OF N-ACETYLNEURAMINIC ACID (SIALIC ACID)

Sir:

Previous reports[1,2,3] indicated N-acetylneuraminic acid (NANA) to be an 11 carbon keto acid.

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