rectangular barrier of width 0.5 Å and height 700 cm^{-1}—540 cm^{-1} above the zero-point level of the ν_{25} carbonyl wagging mode—we find a tunneling rate of 5×10^3 sec^{-1} for a particle of mass 16 amu. Thermal hopping over the barrier would become competitive with tunneling at temperatures above 40°K and would attain rates as high as 2×10^7 sec^{-1} at 77°K. The multiplicity of epr triads and the distinct emission spectra (Figure 1) indicate that the potential wells separated by the barrier(s) are not symmetrically disposed with respect to one another.

While these estimates are in encouragingly good accord with our experimental findings, the lack of vibronic structure in the emission spectra suggest that electronic and nuclear motion are strongly coupled in the cyclopentanone triplet. Our picture of nuclei tunneling through a stationary electronic potential barrier must therefore be taken as tentative.

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Structures of the Lythraceae Alkaloids Lythrumine and Acetyllythrumine[1]

Sir:

Five new alkaloids have been isolated from the aerial portions of the Lythraceae plant *Lythrum lanceolatum* obtained near St. Marks, Fla. The structures, absolute configurations, and biosynthesis of two of these alkaloids, lythrumine and monoacetyllythrumine, are reported here. This structural investigation makes it possible to directly correlate the Lythraceae alkaloids of North America with those from Japan and it suggests that the three structural types elaborated by this plant family have a common biosynthesis.

Lythrumine (1), $C_{26}H_{31}NO_4$,[2] mp 214–216°, $[\alpha]^{26}D$ $-8.0°$ (MeOH), shows hydroxyl (3550, 3500 cm^{-1}) and a carbonyl (1700 cm^{-1}), λ max 294 nm (ϵ 6790), in base λ max 296 nm (ϵ 5290).

Monacetyllythrumine (2), $C_{28}H_{33}NO_5$, mp 184–185°, $[\alpha]^{26}D$ $-34°$, ν max 3400, 1740, 1705 cm^{-1}, λ max 292.5 nm (ϵ 8030), δ 1.9 (s, 3 H), 3.9 (s, 3 H), 6.8–7.3 (m, 6 H) ppm, yielded the same diacetate (3) obtained from lythrumine as shown by identical ir spectra, melting points, and an undepressed mixture melting point.

Crystals of lythrumine hydrobromide were grown by slow evaporation of a methanol solution. Preliminary X-ray photographs displayed $2/m$ Laue symmetry and the systematic absence for hkl (absent if $h + k = 2n + 1$). Diffractometer measured cell constants are $a = 36.62$ (1), $b = 10.294$ (5), $c = 12.618$ (5) Å, and $\beta = 83.40$ (4)°. A calculated density of 1.34 g/cm³ was interpreted to mean $Z = 8$ or two molecules per asymmetric unit in the monoclinic space group C_2. A total of 3481 reflections were measured and 3115 were judged to be observed after standard corrections for Lorentz and polarization effects.

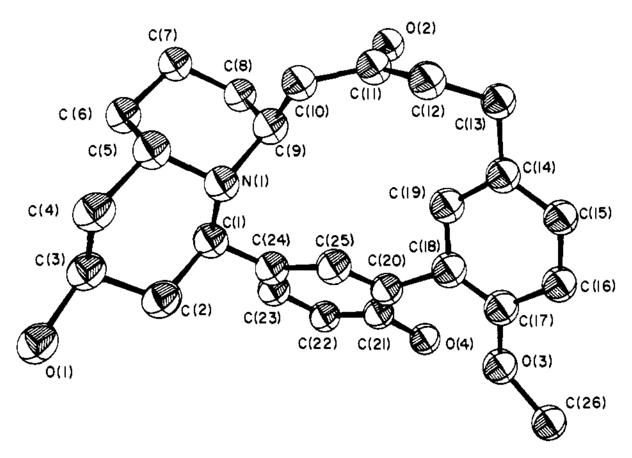
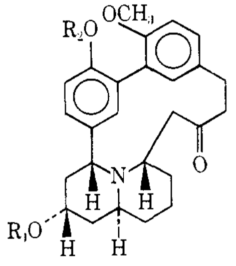
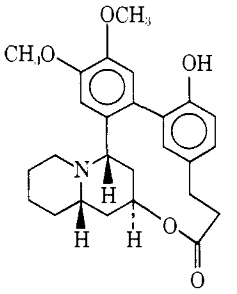


Figure 1.



1, $R_1 = R_2 = H$
2, $R_1 = COCH_3$; $R_2 = H$
3, $R_1 = R_2 = COCH_3$



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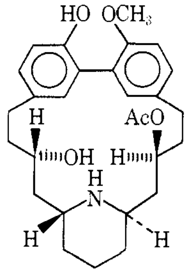

4

A sharpened three-dimensional Patterson synthesis was computed.[3] A satisfactory deconvolution of the Patterson was discovered with three independent bromines rather than the anticipated two. One full bromine was in a general position and two half-bromines were on the twofold axes at $(0,y,0)$ and $(0,y,\frac{1}{2})$. The remaining 62 nonhydrogen atoms were revealed on successive three-dimensional electron density syntheses. Full-matrix least-squares refinements with anisotropic temperature factors for all nonhydrogen atoms lowered the discrepancy index to 0.093.[4] The mirror image was fully refined to a discrepancy index of 0.096 indicating that the correct enantiomer of the molecule had been chosen at the start.[5] Both molecules in the asymmetric unit have the same configuration and conformation and the final X-ray model for one is shown in Fig-

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(1) Lythraceae Alkaloids. XI. For the previous paper in this series see J. P. Ferris, C. B. Boyce, R. C. Briner, U. Weiss, I. H. Qureshi, and N. E. Sharpless, *J. Amer. Chem. Soc.*, **93**, 2963 (1971).

(2) The details of the isolation and purification of these alkaloids will be presented later. Elemental analyses and mass spectra were obtained in agreement with the elemental composition shown.

(3) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and Programs ALFF, ALFFDP, ALFFPROJ, ALEFT, and FRIEDEL," U. S. Atomic Energy Commission Report IS-2625, Iowa State University, Ames Institute for Atomic Research, 1971.

(4) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965. See paragraph at end of paper regarding supplementary material.

(5) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

ure 1.[6] All bond distances and angles agree well, within experimental error (0.02 Å and 2°), with generally accepted values.[7] There were no abnormally short intermolecular contracts.

The unusual Lythrumine skeleton has recently been identified in *Lythrum anceps*, a member of the Lythraceae family which is native to Japan.[8] Another structural type with a piperidine ring (**4**) in place of the quinolizidine ring has also been isolated from *L. anceps*.

We isolated a third structural varient from *L. lanceolatum*, the lactone alkaloid decinine (**5**), which was found previously in the Lythraceae plants *Decodon verticillatus*,[9] *Heimia* species[10] (as the dehydro derivatives, lythrine), and *Lagerstroemia indica*.[11] This is the first observation of the lactone structural type in a *Lythrum* species. This observation supports the taxonomical grouping of *Lythrum* together with *Decodon*, *Heimia*, and *Lagerstroemia* in the Lythraceae plant family. Furthermore, this finding suggests that all three structural types of Lythraceae alkaloid (**1**, **4**, and **5**) have a common biosynthesis.[12,13]

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Supplementary Material Available. A listing of fractional coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6467.

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(13) The biosynthesis proposed for **5**[12] can be readily accommodated to account for the formation of the *Lythrum* alkaloids. Oxidation of the proposed isopelletierine intermediate and condensation of the resulting enamine with acetoacetate gives 2,6-diacetonylpiperideine. The subsequent condensation of this piperidine derivative with *p*-oxygenated benzaldehydes and oxidative phenyl coupling follows familiar routes to **1** and **4**.

(14) Camille and Henry Drefus Foundation Awardee, 1972–1977. Fellow of the Alfred P. Sloan Foundation, 1973–1975.

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Tetramethyl-1,2-dioxetane. Simple Procedures for Chemiexcitation or Photoexcitation of Acetone Phosphorescence in Fluid Solution[1]

Sir:

In spite of the tremendous amount of published work[2] concerned with the photochemistry of alkanones in fluid solution, attempts to observe phosphorescence from simple alkanones[3] by conventional spectrophotoluminescence techniques have apparently been unsuccessful.[4,5] For example, it has been reported that no phosphorescence could be detected from either acetone or acetone-d_6 in degassed solvents at room temperature or even in solutions at Dry Ice temperature.[4] Furthermore, it has been reported that the photoluminescence of acetone is unaffected by the presence of dissolved oxygen.[4,6] In view of these reported observations, we,[7] and apparently other workers,[6,8,9] have assumed that the photoluminescence observed when acetone is excited in fluid solution is pure fluorescence and that the phosphorescence of acetone is difficult or impossible to observe by conventional photoluminescence techniques.[10] In spite of the above experimental reports, acetone phosphorescence has been detected by time-resolved flash photolysis[5] and by time-correlated single-photon counting.[11,12] Each

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(3) Studies of the phosphorescence of organic molecules in fluid solution have been very intense recently because of the theoretical implications and practical importance of such research: C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **65**, 2823 (1969); *Chem. Commun.*, 749 (1968); J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970); W. D. K. Clark, A. D. Litt, and C. Steel, *ibid.*, **91**, 5413 (1969); *Chem. Commun.*, 1087 (1969); A. F. Vando and D. M. Hercules, *J. Amer. Chem. Soc.*, **92**, 3573 (1970); C. A. Parker and A. Hatchard, *J. Phys. Chem.*, **66**, 2506 (1962); M. A. Slifkin and R. H. Walmsley, *Photochem. Photobiol.*, **13**, 57 (1971); (i) J. Langelaar, R. P. H. Rettschnick, and G. J. Hoijtink, *J. Chem. Phys.*, **54**, 1 (1971); S. C. Tsai and G. W. Robinson, *ibid.*, **49**, 3184 (1968); C. A. Parker, *Ber. Bunsenges. Phys. Chem.*, **74**, 764 (1970); M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, **68**, 539 (1972); R. W. Yip, R. O. Loutfy, Y. L. Chow, and L. K. Magdzinski, *Can. J. Chem.*, **50**, 3426 (1972); D. I. Schuster, T. M. Weil, and A. M. Halpern, *J. Amer. Chem. Soc.*, **94**, 8248 (1972).

(4) (a) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966); (b) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(5) The only report of phosphorescence of triplet acetone in fluid solution required a flash experiment in which the emission intensity after a 30 μsec delay of a 5 J photoflash was measured point-by-point: G. Porter, R. W. Yip, J. M. Dunston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, **67**, 3149 (1971). This method of obtaining a phosphorescence spectrum is quite elaborate and unconventional and might be taken to imply that the authors were unsuccessful in obtaining acetone phosphorescence by conventional spectrophotoluminescence techniques. See also R. W. Yip, R. O. Loutfy, Y. L. Chow, and L. K. Magdzinski, *Can. J. Chem.*, **50**, 3426 (1972).

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(7) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

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(12) We thank Professer A. Halpern of New York University for verifying these phosphorescence results on his single-photon counting apparatus.