

This mechanism would perforce generate an electronically excited PO* in the close proximity of a ground state PO, an ideal situation for excimer formation. (2) The overall spectral characteristics—a discreet band juxtaposed to a broad diffuse band on the longer wavelength side—are strongly indicative of excimer formation. Since an excimer has a bound excited electronic state and a dissociative ground state, the excimer emission is diffuse and red shifted from the monomer emission. (3) In the chemiluminescent reaction we observe an isotope effect on the kinetics of the luminescence reactions, in which emission from PO γ falls to 84% of its original value, and the intensity of the continuum decreases to 70%. The kinetic dependence is currently under investigation.

The discrete visible bands show the most marked deuterium effect. The few weak bands seen with H₂O are increased in intensity by a factor of 5 in D₂O and a number of new bands are seen. Unlike the PO bands which do not exhibit frequency shift, the most intense band at 525.5 nm (19,030 cm⁻¹) is shifted to 523.5 nm (19,100 cm⁻¹) and other bands are similarly shifted to the blue (see Table I). The characteristic frequency

Table I

	HPO ($\nu_1'\nu_2'\nu_3'$) → ($\nu_1''\nu_2''\nu_3''$)	DPO ($\nu_1'\nu_2'\nu_3'$) → ($\nu_1''\nu_2''\nu_3''$)
Lam Thanh and Peyron ^{4,5}	(000) → (010) 17,860 cm ⁻¹ (559.91 nm)	(000) → (010) 17,931 cm ⁻¹ (557.69 nm)
This work	17,850 cm ⁻¹ (560.2 nm)	17,930 cm ⁻¹ (557.8 nm)
Most intense transition Lam Thanh and Peyron ^{4,5}	(000) → (000) 19,047 cm ⁻¹ (525.01 nm)	(000) → (000) 19,116 cm ⁻¹ (523.12 nm)
This work	19,030 cm ⁻¹ (525.5 nm)	19,100 cm ⁻¹ (523.5 nm)

shift due to isotopic substitution indicates the species has H covalently bound (d). In an electric discharge investigation of the Ludlam⁸ bands associated with the burning of phosphorus in hydrogen, Lam Thanh and Peyron⁴ attributed similar bands to HPO and DPO (d). The increase in the emission intensity of DPO compared to HPO can be understood in terms of decrease in the Franck-Condon factors in substituting D₂O for H₂O and the consequent decrease in the radiationless transitions.⁹ An interpretation of this phenomenon would possibly be similar to the case of pre-dissociative HNO.¹⁰

Currently we are investigating kinetic aspects of the excimer emission and are attempting to clarify the assignments associated with some weak lines in the ultraviolet. Since the essential features of the emitting species have now been established, it should be possible to understand the detailed nature of the oldest known chemiluminescence system.

(8) E. B. Ludlam, *J. Chem. Phys.*, **3**, 617 (1935).(9) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **38**, 1187 (1963).(10) M. J. Y. Clement and D. A. Ramsay, *Can. J. Phys.*, **39**, 205 (1961).

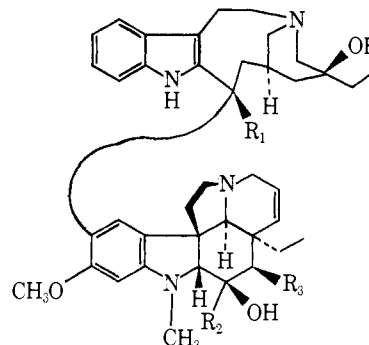
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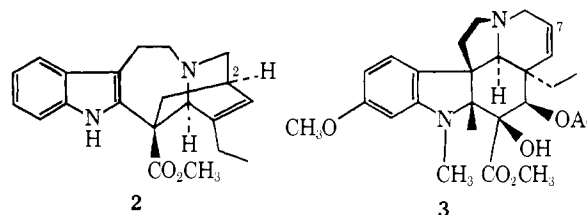
Biosynthesis of the Dimeric Indole Alkaloids. Vincaleukoblastine¹

Sir:

Although the biosynthetic pathway(s) for the three main structural variants of the indole alkaloids found in *Vinca rosea* L. (*Catharanthus roseus* G. Don) is rather well understood,² the details of the bioorganic chemistry leading to vincaleukoblastine (VLB), **1a**, and other



1a, R₁ = COOCH₃; R₂ = COOCH₃; R₃ = OAc
1b, R₁ = H; R₂ = CONHNH₂; R₃ = OH



dimeric alkaloids found in this plant² are only presumptive. Because of the obvious structural similarity between catharanthine (**2**), vindoline (**3**), and VLB, the biogenesis of **1a** can be assumed to occur *via* a direct dimerization of **2** and **3**, or closely related alkaloids. Experimental corroboration of such a hypothesis has never been reported in the literature, although suitable experiments have been carried out in other laboratories.³ We now report experimental results that can be viewed as a substantiation of a dimerization hypothesis, although nothing can be said from consideration of them about the precise bioorganic details of VLB's biosynthesis.

The report of Scott, *et al.*,⁴ describing results from feeding experiments with (5R)-[5-³H₂]- and (5S)-[5-³H₁]mevalonic acid, and the preliminary data of Battersby, *et al.*,⁵ derived from feeding experiments with [3,6-³H₃;CH₃O-¹⁴C]loganin (**4**), both are in accord with an *apparently* stereospecific tritium retention in the biosynthesis of **2** and **3**.⁶ For these reasons, the doubly

(1) Supported in part by a grant from the National Institutes of Health (CA 13616).

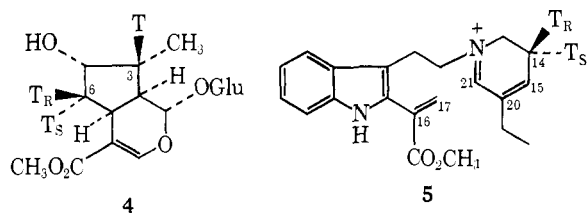
(2) R. J. Parry in "The *Catharanthus* Alkaloids: Botany, Chemistry, and Pharmacology," W. I. Taylor and N. R. Farnsworth, Ed., Marcel Dekker, New York, N. Y., in press.

(3) (a) Professor E. Leete, personal communication; (b) Professor A. I. Scott, Dr. J. D. Michael, and Dr. C. L. Yeh, personal communication.

(4) A. I. Scott, P. B. Reichardt, M. B. Slaytor, and J. G. Sweeny, *Recent Advan. Phytochem.* **6**, 138 (1973).

(5) A. R. Battersby, C. R. Hutchinson, N. D. Westcott, and R. A. Larson, manuscript in preparation. Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., 1972, Abstracts ORGN 11.

(6) The stereospecific retention of the 5S tritium of mevalonate and the 6 *pro R* tritium of **4** on their incorporation into **2** and the 6 *pro S* tritium of **4** on its incorporation into **3** *must* be viewed only as the most likely of several alternatives,⁴ due to the lack of or as yet incomplete chemical degradation of the resulting radioactive **2** and **3** obtained by these investigators.



labeled **4** was chosen to be tested as a precursor of **1a**. Its synthesis was carried out as described by Battersby, *et al.*,⁵ wherein the distribution of tritium labeling in **4** was shown to be 44% at C-3, 44% at C-6 *pro R*, and 11% at C-6 *pro S*. A sample of this compound in admixture with [CH₃O-¹⁴C]-**4** was wick-fed to 6 month old plants, which were growing in a growth chamber.⁷ After 20 days the alkaloids **1a**, **2**, and **3**, were isolated without dilution by standard procedures and crystallized to constant specific activity and ³H:¹⁴C ratio. The radioactive VLB was diluted with radioinactive VLB and converted to its monohydrazone (**1b**).⁸ The resulting **1b** contained no observable ¹⁴C radioactivity and had the same ³H specific radioactivity as **1a**, indicative of a site-specific incorporation of **4** into **1a** as anticipated.

The experimental results (Table I) can be interpreted

Table I. Biosynthetic Data of the Incorporation of **4**^a into **1a**, **2**, and **3**

Alkaloid	Amount isolated, ^b mg (mmol)	% of specific incorp ^c	³ H: ¹⁴ C ratio
1a	5.4 (0.007)	0.069	7.5
2	95.0 (0.28)	0.39	8.7 ^d
3	135.0 (0.30)	0.26	6.0 ^d

^a ³H:¹⁴C ratio of the administered **4** = 8.2; 58 mg was administered by a cotton wick to each of two plants, whose total fresh weight was 215 g (tops). ^b By preparative layer chromatography. ^c Dpm/mmol isolated divided by dpm/mmol fed × 100. ^d See ref 5 for the explanation of these ratios' significance.

as strong, circumstantial evidence that the biosynthesis of VLB involves the dimerization of compounds closely related to **2** and **3**. The ratio of the specific incorporation of ³H radioactivity from **4** into **2** and **3** (1.50) mirrors the inverse molar ratio of their pool sizes (1.04), if the relative molar amount of tritium at C-2 of **2** and C-7 of **3** is taken into consideration.⁵ Hence, a steady-state situation apparently was operating whereby the relative rate of formation of **2** and **3** *via* **4** was the same over the metabolism period. If it also could be expected that the relative rates of the biosynthesis of **1a** from any intermediate of the pathway between the putative dihydropyridinium acrylic ester (**5**)^{4,9} and **2** or **3**, or **2** and **3** themselves, were also the same over this period, the ³H:¹⁴C ratio of **1a** would be anticipated to fall midway between that of **2** and **3**. This is what is shown by our results, for the ³H:¹⁴C ratio of VLB (7.5) is essentially identical with the averaged ³H:¹⁴C ratio of **2** and **3** (7.4). Thus the data indicate pre-

(7) Lab-Line Biotronette Mark III equipped with Westinghouse Plant Gro F40 lamps.

(8) N. Neuss, M. Gorman, W. Hargrove, N. J. Cone, K. Beimmann, G. Buchi, and R. E. Manuing, *J. Amer. Chem. Soc.*, **86**, 1440 (1964); K. Beimmann and M. Friedmann-Spiteller, *ibid.*, **83**, 4805 (1961).

(9) J. P. Kutney, J. F. Beck, N. J. Eggers, H. W. Hanssen, R. S. Sood, and N. D. Westcott, *J. Amer. Chem. Soc.*, **93**, 7322 (1971); A. I. Scott and C. C. Wei, *ibid.*, **94**, 8263, 8264, 8266 (1972).

sumptively that **1a** is formed from intermediates following **5**, although without any direct evidence as to how.¹⁰

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(10) An attractive mechanistic hypothesis is that the velbanamine⁹ half of **1a** is formed *in vivo* directly from **5** by bond formation between C-17 and C-14, reduction at C-21, and stereospecific hydroxylation at C-20,¹¹ although not necessarily in that order. This *may* be the reason for the repeated failures to obtain a significant incorporation of radioactivity from **2** and related alkaloids into **1a** at Yale.^{3b}

(11) Analogous to the synthetic route to velbanamine described by J. P. Kutney and F. Bylsma, *J. Amer. Chem. Soc.*, **92**, 6090 (1970).

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Type II and Homo-Type II Photoprocesses. Specific Reactivity of Upper and Lower Excited States of Aralkyl Thiones^{1,2}

Sir:

The study, deriving originally from the work of Norrish,³ of the intramolecular photochemical reactions of carbonyl compounds having a chain possessing a γ -hydrogen, has been pursued intensively up to the present time. In particular, extended investigations by several groups have established that, with phenyl alkyl ketones, reaction proceeds, *via* the ³(n, π^*) state, to a 1,4-biradical which subsequently undergoes β cleavage, cyclization (Norrish type II processes⁴), or disproportionation.⁵ The same photochemical processes are observed in solution independently of the original excitation wavelength, since the photophysical processes leading to population of the lowest (n, π^*) triplet state are faster than alternative chemical pathways that may be available.

We wish to report that, in contrast, aralkyl thiones show photochemical behavior which is *dependent* on the excitation wavelength and to describe new photocyclizations leading to the formation of five- (and six-) membered rings.

The only relevant thiocarbonyl work available at the outset of our studies was the report that *O*-1-alkyl-2-phenylethyl thiobenzoates, in which the γ -hydrogen was activated, undergo cleavage and cyclization of Type II process nature. The reactive state was shown

(1) Photochemical Synthesis, Part 57. This is the sixteenth of a series on thione photochemistry.

(2) Publication No. 108 from the Photochemistry Unit, University of Western Ontario, London, Canada.

(3) R. G. W. Norrish, *Trans. Faraday Soc.*, **33**, 1521 (1937).

(4) For a review and leading references see P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971); P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7480 (1972).

(5) The cyclization to cyclobutanols was first reported by Yang: N. C. Yang and D. H. Yang, *J. Amer. Chem. Soc.*, **80**, 2913 (1958).