spectrometer.[11] It is clear from Table I that reaction 1 is the dominant means of production of $C_7H_{11}O^+$.[12]

$$C_3H_7^+ + C_4H_4O \longrightarrow C_7H_{11}O^+ \quad (1)$$

Since the propyl ion is clearly established as the major primary ion in reaction 1, we undertook a study of this ion prepared from various sources. A study of the various 1- and 2-halopropanes is illustrated in Figure 1. Instead of finding a common reactivity for all propyl ions, the ion from 2-halopropanes is clearly more reactive than that from 1-halopropanes, and that from 1-chloropropane is even less reactive, since no product $C_7H_{11}O^+$ ion could be detected under the conditions of the study.

A second study was conducted at higher partial pressures of C_3H_7X in order to examine the whole spectrum of propyl ion reactivities (Figure 2). The propyl ions group themselves into three reactivity classes. Class I (greatest reactivity) includes the 2-halopropanes and propane, class II (intermediate reactivity) includes 1-bromo- and 1-iodopropane and various hexane, heptane, and octane isomers; and class III (lowest reactivity) includes 1-chloropropane and various pentane and hexane isomers. The reactivity of the propyl ion from propane is not surprising since it is known that a secondary hydrogen is lost in its production.[13] The reactivity exhibited by the propyl ion from isopentane and 2,3-dimethylbutane is indeed surprising, however, since *a priori* one would predict this ion to resemble those produced in class I.

In all cases, the relative abundance of the complex at *m/e* 111 increased as the ionizing energy decreased. This is not unexpected, since the complex surely possesses less vibrational excitation at lower electron energies and is, therefore, more stable. This effect has been observed in other ion–molecule reactions which presumably occur *via* an intermediate complex.[14]

To be certain that the reactivity differences observed at high ionizing energy are not due to internal energies only, measurements were made between 0.3 and 0.8 eV above the appearance potentials[15] of the propyl ions from 1- and 2-iodopropane. In both cases, the relative abundance of *m/e* 111 leveled off at *ca.* 0.5 eV above threshold, yet the ratio of the relative abundance of *m/e* 111 was identical with that found at 20 eV.[16]

A number of explanations are possible for these observations. For example, each classification could implicate a different propyl ion structure or a different mixture of structures, whose composition remains constant with electron energy. Class I and class III propyl ions could possess a unique structure, and class II ions a mixture of these structures or the structure of class III ions with lower vibrational excitation. A third explanation is based on internal energy differences only.[17] If a 1-propyl ion rearranges during or after formation to a 2-propyl ion, 16 kcal/mol of internal excitation is released[6] which would lower the overall rate of complex formation with furan. In fact, the near-threshold reactivity of the class II ion is equal to that of class I ions at $V - E$ greater than 5 eV (Figure 2), suggesting that the class II ion possesses a vibrationally excited class I (isopropyl) structure. However, this interpretation is less probable since an additional increase in the internal excitation of the class II ion (accomplished by increasing the ionizing energy) should produce essentially no change in the rate of formation of the complex (as is observed for class I at $(V - E) > 5$ eV). Instead a drastic decrease in reactivity is observed. Therefore, we feel that the results indicate that *two*, and perhaps three, propyl ions are produced in mass spectral fragmentations.[18]

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(11) This study was made with the tandem mass spectrometer at the Aerospace Research Laboratory, Wright-Patterson Air Force Base, Ohio. We are deeply indebted to Dr. Thomas O. Tiernan and his group for making these measurements.

(12) Reaction 1 may well be the gas-phase analogy of the Friedel–Crafts alkylation reaction. Studies are underway to test this possibility.

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(15) The appearance potential was arbitrarily taken to be that electron energy at which *m/e* 43 abundance was 0.05% of that at 30 eV.

(16) Unfortunately the class I propyl ions were of insufficient abundance for a similar measurement to be made.

(17) We thank Professor F. W. McLafferty and one of the referees for making this suggestion.

(18) Many of the complications in this study can be eliminated if more selective ion–molecule reactions of $C_3H_7^+$ can be found. A search for such reactions is presently underway.

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Studies on Indole Alkaloid Biosynthesis. VI.[1] The Eburnamine–Vincamine Alkaloids

Sir:

The eburnamine–vincamine group of alkaloids[2] is an interesting family which has received considerable attention from both the structural and synthetic point of view but no results are as yet available concerning the biosynthetic pathway. Structural analysis of the various members reveals that these alkaloids may be related biosynthetically to the Aspidosperma family for which a considerable body of experimental evidence is now available.[3] If this was the case some very interesting rearrangements of the fundamental indole template must prevail and these would be rather different than the ones presently considered in the other indole alkaloid areas.[3] In this regard, Wenkert[4] has put forth a postulate which considers the implication of the Aspidosperma intermediate **1** and its rearrangement *via* **2**, **3**, and **4** to the system necessary for this family as shown by the alkaloid vincamine (**5**) (Scheme

(1) Part V: J. P. Kutney, J. F. Beck, V. R. Nelson, K. L. Stuart, and A. K. Bose, *J. Amer. Chem. Soc.*, 92, 2174 (1970).

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(3) For a recent review and collection of references, see A. I. Scott, *Accounts Chem. Res.*, 3, 151 (1970).

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Table I. Results of Incorporation of Various Intermediates into *V. minor* L.

Expt	Compound fed	Feeding time, hr	Activity fed, dpm	% Incorporation	
				Vincamine	Minovine
1	(ar-^{3}H) Tryptophan	24	7.4×10^7	0.089	0.080
2	(ar-^{3}H) Geissoschizine (**6**)	24	3.9×10^7	0.005	<0.001
3	(ar-^{3}H) Stemmadenine (**7**)	24	4.2×10^7	0.076	0.001
4	(ar-^{3}H) Tabersonine (**10**)	24	1.6×10^7	0.070	0.002
5	(ar-^{3}H) 16,17-Dihydrosecodin-17-ol[a] (**9**)	24	1.9×10^7	≤0.001	<0.001
6	(ar-^{3}H) 16,17-Dihydrosecodin-17-ol	96	2.4×10^7	≤0.002	0.001
7	(ar-^{3}H) Secodine[b] (**8**)	24	3.4×10^8	<0.001	<0.001
8	(ar-^{3}H) Secodine	96	2.6×10^8	0.001	0.001[c]

[a] Synthesized in our laboratory by a route other than that published.[10] Full experimental details will be published later. [b] Blank experiments revealed that after the *maximum* period required for the plant to absorb a solution of this labeled compound, 61% remained as the monomer while 32% had been converted to the dimers, the presecamines.[8] [c] In a separate series of experiments in *Vinca rosea* L. to be reported later, secodine has been incorporated into the related Aspidosperma alkaloid vindoline to the extent of 0.02%.

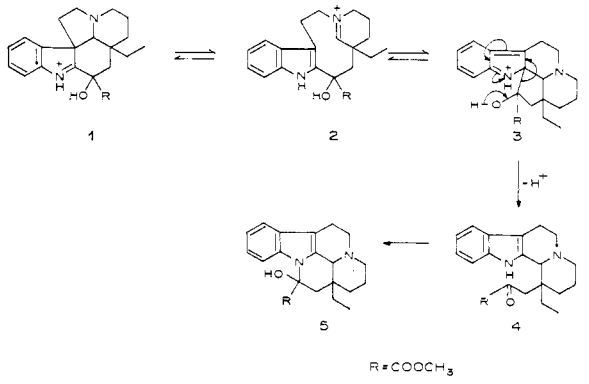
Table II. Specific Activities Resulting on Incorporation of Secodine to *V. minor* L.

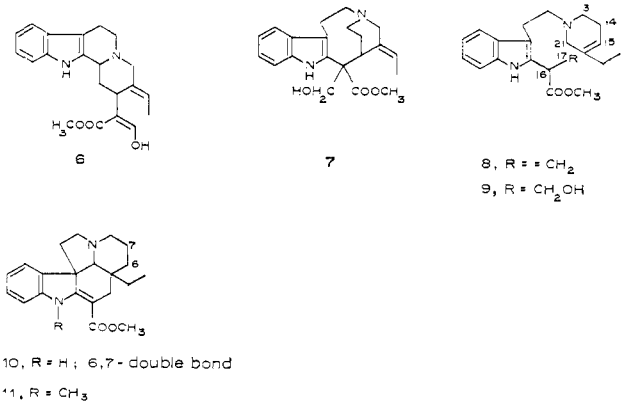
Expt	Feeding, time, hr	Feeding method	Specific activity fed, dpm/mmol	Specific activity isolated, dpm/mmol	
				Vincamine	Minovine
1	24	Hydroponic[a]	2.83×10^{10}	4.67×10^4	2.76×10^5
2	96	Hydroponic[a]	2.83×10^{10}	9.49×10^4	2.03×10^5
3	96	Hydroponic[a]	2.83×10^{10}	9.88×10^4	1.84×10^5
4	96	Hydroponic[b]	2.83×10^{10}	5.31×10^4	2.00×10^5

[a] Compound fed as the acetate salt. [b] Compound fed as a Tween 20 suspension.

I). The involvement of such intermediates would in view of previous results link the biosynthetic pathway to the corynantheinoid (geissoschizine (**6**)),[5] strychnos (stemmadenine (**7**)),[6,7] and secodine systems (**8**).[8-10] We wish to report some of our results which provide some information in this direction.

Scheme I





Our previous experience with *Vinca minor* L.[11] provided the ideal opportunity to evaluate the possible intermediacy of the above-mentioned precursors in the alkaloid vincamine (**5**) and, for comparison, the co-occurring alkaloid minovine (**11**). Consequently the appropriate precursors were administered *via* the hydroponic technique to young plant cuttings of *Vinca minor* L. After a 24–96-hr exposure period, the cuttings were harvested and processed for alkaloids. The results of the various experiments are presented in Table I.

As anticipated, tryptophan is readily incorporated into vincamine and minovine. Furthermore the results in Table I suggest but *do not prove* that the eburnamine–vincamine group of alkaloids may be derived from the corynantheinoid family *via* the strychnos and Aspidosperma bases as outlined in Scheme I.

The feedings utilizing 16,17-dihydrosecodin-17-ol and secodine (**8**) provided some encouraging results. The former substance was not incorporated into the alkaloids in spite of repeated attempts and in fact appeared to be a toxic component with marked deterioration of the plant occurring within 24 hr. On the other hand, secodine showed a low but definite incorporation into both alkaloids in the various experiments completed (Table II) and only slight plant deterioration was observed.

In summation, the above experiments provide the first series of results on the possible relationships between the above-mentioned group of alkaloids and the more heavily studied Aspidosperma bases. Further information must await results from considerably more

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sophisticated experiments with doubly labeled precursors and dilution experiments to isolate the postulated intermediates, etc.

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Spectrum and Lifetime of the Acoustically and Chemically Induced Emission of Light from Luminol

Sir:

The emission of light from an acoustically cavitated alkaline solution of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione)[1,2] and the luminescence from the chemically induced oxidation of similar solutions[3-5] have been studied. We have investigated the mechanism of the light emission from an acoustically cavitated luminol solution by comparing its spectrum with that of its chemically induced luminescence and by measuring the lifetime of the excited species.

A scanning spectrophotometer as previously described[6] was used to obtain the spectra. A steady luminescence was produced by a solution of 300 mg of luminol and 20 g of sodium carbonate in 100 ml of 3% hydrogen peroxide contained in a quartz cell fitted at the entrance to the spectrometer. In the acoustic case a solution of 100 mg of luminol in 1 l. of 2 *N* sodium carbonate was circulated from a reservoir through a heat exchanger and either a 14-kHz tubular piezoelectric transducer or a 500-kHz cylindrical segment transducer attached to the entrance of the spectrometer. Each of these transducers produced a sound pressure of 2 atm rms at the focus, corresponding to an acoustic power in the cavitation region of about 3×10^4 W m^{-2}. Circulation of the sample solution without cavitation produced no light, and sonoluminescence from the cavitation of the sodium carbonate solution without luminol made a negligible contribution to the spectrum.

The spectra of the light emitted with the two sound frequencies and with the chemical oxidation were identical, and this spectrum is shown in Figure 1.

The excited species is clearly the same in each case, and it is probable that it is produced by the same chemical reactions, since it has been shown[2] that the acoustically induced light emission from neutral solutions is very feeble (evidently insufficient OH radicals are formed by the cavitation to produce the dinegative luminol ion), and the formation of hydrogen peroxide in cavitated water has often been observed. The spectrum has the same form as spectra previously reported for the chemical oxidation of luminol,[4,7,8] and its

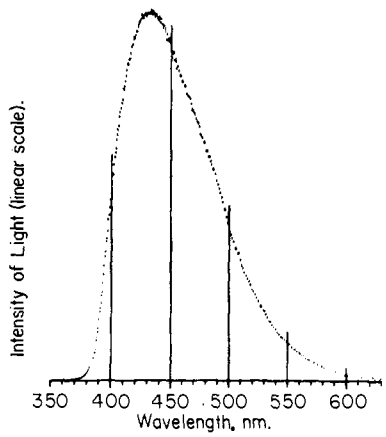

Figure 1. Spectrum of the acoustically or chemically induced light emission from luminol.

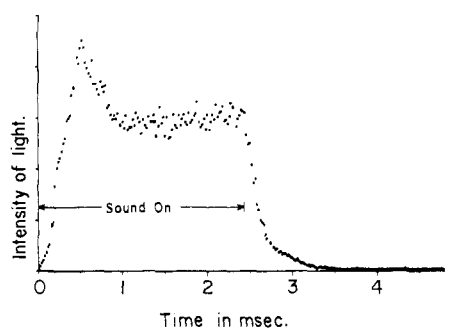

Figure 2. Intensity of light emission during and immediately after a sound pulse of 2.45-msec duration and of frequency 14 kHz.

maximum energy occurs at a wavelength of 4330 ± 40 Å. The wavelength calibration has an accuracy of ±10 Å, and the resolution is better than 15 Å: by using different slit widths it was shown that the shape of the continuum was not limited by the resolution of the spectrophotometer. Furthermore, the spectra were found to be unaltered by substantial variations in the concentrations of the reactants.

A modification to the spectrometer arrangement made it possible to plot the light intensity as a function of time at any wavelength, and this was used to measure the lifetime of the light emission. The 14-kHz oscillator used to produce the cavitation was gated to produce pulses of sound of 2.45-msec duration. The intensity of luminescence during and immediately after the pulse is shown in Figure 2. The intensity increases steadily to its maximum over the first eight sound cycles and then declines to an equilibrium level. At the end of the pulse it takes only 140 μsec for the light intensity to fall to half its equilibrium value, and the shape of the curve during the decline is roughly exponential. The distribution was the same for all wavelengths.

This result contradicts Negishi's report[2] of a lifetime of the order 50 msec, and so we verified our result of 140 μsec by looking for a modulation in the light intensity of luminol cavitated at 14 kHz. Figure 3 shows that this intensity is modulated with peaks corresponding to excited species produced at those two phases of each sound cycle when the main and secondary flashes of sonoluminescence occur (these are attributed

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