Experimental Section[12]

5-(Palmitoxymethyl)-2,2,8-trimethyl-4H-*m*-dioxino[4,5-*c*]pyridine (Isopropylidenepyridoxol 5′-Palmitate) (2a).—Isopropylidenepyridoxol (1,[13] 1.68 g) was dissolved in 100 ml of anhydrous pyridine, and 3 ml of palmitoyl chloride was added quickly. The mixture was stirred at room temperature overnight, at which time 100 ml of petroleum ether (bp 30–60°) was added. This solution was washed twice with 0.1 *N* aqueous hydrochloric acid, with 1.0 *M* aqueous potassium carbonate until no further interfacial emulsion was formed (about ten times), dried over sodium sulfate, and evaporated to dryness at room temperature. The resulting white residue of isopropylidenepyridoxol 5′-palmitate weighed 2.34 g (65%, mp 45–48°). Recrystallization from methanol raised the melting point to 50–51° (lit.[14] mp 43–44°).

2-Methyl-3-hydroxy-4-hydroxymethyl-5-palmitoxymethylpyridene (Pyridoxol 5′-Palmitate) (3a).—This compound was prepared by the method of Korytnyk and Paul[14] except that the product was crystallized from methanol–water and then acetone–petroleum ether: mp 104–105° (lit.[7,14] mp 72–76 and 99–100°).

2-Methyl-3-hydroxy-4-formyl-5-palmitoxymethylpyridine (Pyridoxal 5′-Palmitate) (6a) and 2-Methyl-3-hydroxy-4-formyl-5-benzoxymethylpyridine (Pyridoxal 5′-Benzoate) (6b).—Pyridoxol 5′-palmitate (**3a**) or -benzoate[15] (**3b**, 0.25 g) was dissolved in 20 ml of chloroform or anhydrous methanol, respectively. Manganese dioxide "B" [16] (1 g) was added, and the suspension was stirred 36 hr at room temperature. Most of the manganese dioxide was removed by filtering the mixture through a fine paper filter. The solvent was evaporated to a volume of about 1 ml and applied to a 2 in. × 1 in. silicic acid chromatographic column. The pyridoxal 5′-palmitate or -benzoate was eluted with chloroform. The elution could be monitored visually owing to the yellow color of the product. As the desired products passed through the column, the manganese dioxide remained on top. The chloroform eluate was evaporated at room temperature, and the residue was taken up in acetone. The products were precipitated with water, filtered, and dried. The yield of the palmitate was 0.18 g (72%) with mp 66–68°, which was raised to 68–70° by recrystallization from methanol. A yield of 0.77 g (77%) was obtained with the benzoate. Its melting point was 95–106°, which was raised to 106–108° with recrystallization from methanol.

Anal. Calcd for $C_{24}H_{39}NO_4$: C, 71.07; H, 9.69; N, 3.45. Found: C, 71.27; H, 9.63; N, 3.64. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.13. Found: C, 66.10; H, 4.92; N, 5.14.

2-Methyl-3-acetoxy-4-formyl-5-palmitoxymethylpyridine (Pyridoxal 3-Acetate 5′-Palmitate) (5c), 2-Methyl-3-acetoxy-4-formyl-5-benzoxymethylpyridine (Pyridoxal 3-Acetate 5′-Benzoate) (5d), and 2-Methyl-3-palmitoxy-4-formyl-5-palmitoxymethylpyridine (Pyridoxal 3,5′-Dipalmitate) (5e).—To a solution of 0.25 g of pyridoxal 5′-palmitate or benzoate in 20 ml of dry pyridine was added 1.2 equiv of acetic anhydride or palmitoyl chloride. The solution was allowed to stand 3–4 hr at room temperature. The solvent was removed under reduced pressure, and the residue was taken up in dry acetonitrile. Upon refrigeration for several hours, 0.21 g (77%, mp 63–65°), 0.22 g (77%, mp 98–100°), 0.36 g (90%, mp 64–69°), respectively, of pyridoxal 3-acetate 5′-palmitate, pyridoxal 3-acetate 5′-benzoate, and pyridoxal 3,5′-dipalmitate were obtained. The melting points were raised to 65–67°, 108–109°, and 68–69° with two recrys tallizations from dry acetonitrile.

Anal. Calcd for $C_{26}H_{41}NO_5$: C, 69.77; H, 9.23; N, 3.13. Found: C, 69.73; H, 9.37; N, 3.41. Calcd for $C_{17}H_{15}NO_5$: C, 65.17; H, 4.83; N, 4.47. Found: C, 64.73; H, 4.99; N, 4.69. Calcd for $C_{40}H_{69}NO_5$: C, 74.60; H, 10.80; N, 2.17. Found: C, 74.61; H, 10.84; N, 1.89.

(12) Ultraviolet spectra were determined with a Cary recording spectrometer, Model 11M. Nuclear magnetic resonance spectra were obtained using a Varian A-60A instrument at 60 Mcps. Compounds were used as 30% solutions in deuterated chloroform. Results are expressed in parts per million (δ) units from tetramethylsilane as internal standard. Infrared spectra were recorded with a Beckman IR-7 spectrometer, with samples used as potassium bromide pellets or 10% solutions in carbon tetrachloride. Microanalyses were performed by the Clark Microanalytical Laboratories, Urbana, Ill. All melting points are corrected.

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Registry No.—**2a**, 14320-27-5; **2b**, 17288-58-3; **3a**, 14210-75-4; **3b**, 17288-60-7; **5c**, 17288-61-8; **5d**, 17288-62-9; **5e**, 1961-81-5; **6a**, 17288-64-1; **6b**, 17288-65-2.

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A Synthesis of Sempervirine[1]

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Sempervirine, an interesting indole alkaloid obtained from *Gelsemium sempervirens*, Ait.,[2,3] has been the subject of several communications relating to its synthesis.[4–7] We now wish to report a very convenient route to sempervirine that should be capable of extension to related ring systems.

Condensation of α-picolinium salts having an active methylene group as part of the substituent on the nitrogen atom, as, *e.g.*, in 2-methyl-1-ethoxycarbonylmethylpyridinium halides, with suitable α diketones has been shown[8] to be a very effective route to quinolizinium salts. In most instances, spontaneous hydrolysis and decarboxylation of the original ester function occurred but under certain conditions,[8] the ester group could be retained in the resulting quinolizinium salt. As sempervirine contains the quinolizinium nucleus, this procedure should provide a simple route for its synthesis and this expectation was borne out as described below.

Quaternization of harman with ethyl bromoacetate occurred in excellent yield, either at the reflux temperature in benzene, or at room temperature in ethanol. Similarly, reaction of harman with methyl iodide was found to give the corresponding methiodide in good yield. That reaction had occurred at N-2 in both cases was indicated by the analytical data and also by the visible and ultraviolet absorption spectral characteristics of these salts. The development of anhydro-

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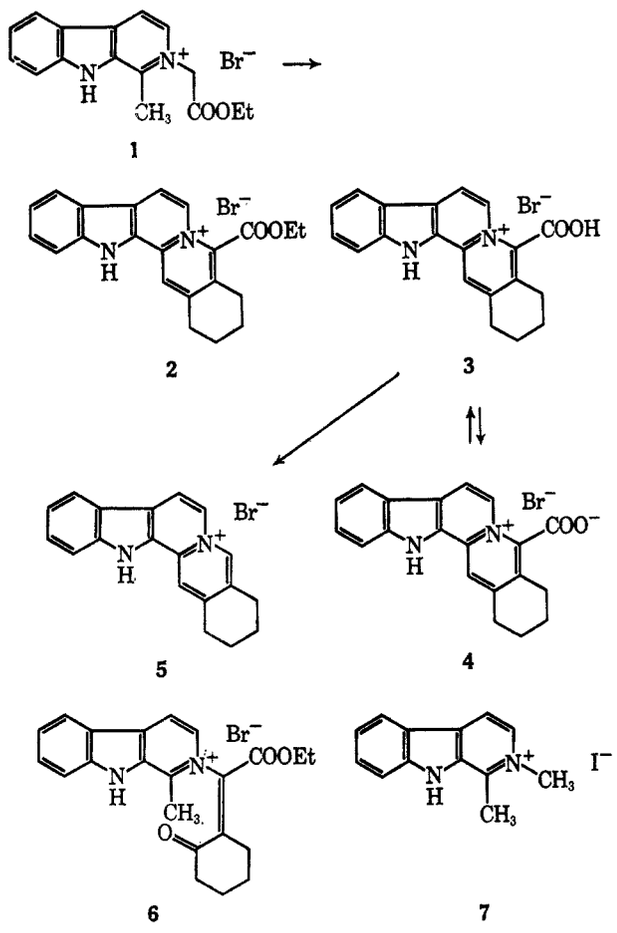
nium bases[9] in the β-carboline series on treatment of the pyridine quaternary compounds with base is now a well-documented phenomenon, and the spectral characteristics of these bases in acid and neutral alcoholic solutions are identical, with maxima at about 390, 315, and 255 mμ. In weakly alkaline media, a characteristic shift of the absorption to longer wavelengths with maxima at about 425, 330, and 285 mμ is observed. These data agree well with that of the above harman salts reported in the Experimental Section.

Reaction of the harman quaternary salt **1** with 1,2-cyclohexanedione in refluxing ethanol over a 2-hr period gave a 48% yield of crude 5-ethoxycarbonyl-1,-2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium bromide (**2**). These optimum conditions for condensation were determined by removing aliquots from the reaction system and determining the amount of condensation from the characteristic ultraviolet absorption spectrum of the sempervirine system.[5,6] Analytical and spectral data (see Experimental Section) were in agreement with structure **2** for this product. Final confirmation was obtained by its conversion into sempervirine by hydrolysis and subsequent decarboxylation of the resulting acid **3**. This hydrolysis was effected under basic conditions, the ester being relatively stable to acid, and it is interesting to note that the acid **3** was stable to refluxing 48% hydrobromic acid over 48 hr. Ultraviolet absorption data for the acid are reported in the Experimental Section.



Repeated efforts to recrystallize the acid **3** resulted in material that exhibited a range in melting point far below that of the pure acid and, after two recrystallizations from methanol, a pale yellow crystalline solid was obtained. Elemental analysis of this material indicated that the acid had lost HBr and established an empirical formula of $C_{20}H_{16}N_2O_2$, consistent with structure **4**. The infrared spectra of the acid **3** showed absorption at 1720 cm^{-1}, indicative of an unionized carboxyl group, whereas the betaine **4** was devoid of absorption in the 1750–1650-cm^{-1} region and showed new absorption at 1625 cm^{-1} which can be attributed to an ionized carboxyl group. Such a shift in carbonyl absorption upon ionization is well known.[10] Confirmation of this structure was obtained by the ready conversion of the betaine **4** into the acid **3** with ethanolic hydrobromic acid.

The betaine **4** was also obtained when the reaction mixture from the saponification of the ester **2** in hot 0.5 *N* sodium hydroxide solution (15 min), followed by acidification with 25% hydrobromic acid solution, was allowed to stand for several days.

Decarboxylation of the acid **3** occurred readily on heating *in vacuo* at 250° and 1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium bromide (**5**) (sempervirine bromide) was obtained in 84% yield. The identity of the synthetic material was readily established by superimposition of its infrared spectrum with that of authentic material and by identical R_f values in two solvent systems.

In several preparations of **2**, it was observed that a deep red solution was rapidly obtained when the reaction mixture was brought quickly to vigorous reflux. However, when a similar reaction was heated at a temperature not exceeding 70° for 2 hr, reaction work-up as before gave a red solid. Treatment with a methanol–ether solution left a yellow crystalline material of empirical formula $C_{22}H_{23}BrN_2O_3$, in agreement with structure **6** proposed for this product. Spectral data gave additional support for structure **6**; the infrared spectrum showed absorption bands at 3400 cm^{-1}, indicative of an associated NH group, and two intense carbonyl bands at 1735 and 1720 cm^{-1}, indicative of ketonic and ester carbonyl absorptions. The ultraviolet absorption spectrum of **6** showed an absorption pattern strikingly similar to the spectrum of 1-methyl-2-ethoxycarbonylmethyl-9H-pyrido[3,4-*b*]-indolium bromide (**1**), except that the additional conjugation present in the molecule resulted in a bathochromic shift of all absorption maxima to 395, 312, and 258 mμ.

As concomitant hydrolysis and decarboxylation of the ester function in **2** did not occur in this present quinolizinium synthesis, a more direct route would be the condensation of 1,2-dimethyl-9H-pyrido[3,4-*b*]indolium iodide (**7**) with 1,2-cyclohexanedione. However, crude products isolated from several attempted condensations using different reaction conditions indicated that no sempervirine chromophore was present.

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Experimental Section[11]

1-Methyl-2-ethoxycarbonylmethyl-9H-pyrido[3,4-*b*]indolium Bromide (1). Method A.—Harman[12] (4.0 g, 0.022 mol) and ethyl bromoacetate (12.0 g) were refluxed in dry benzene (1200 ml) for 72 hr. There resulted a quantitative yield of **1**, mp 230–233° dec. Crystallization from methanol gave brilliant yellow cubes: mp 235–237° dec; ir, 3450 (indole N–H) and 1740 cm^{-1} (C=O); $\lambda_{max}^{95\%\ EtOH}$ mμ (ϵ), pH 1 or 6, 375 (8870), 309 (39,870), 254 (55,820), pH 12, 410 (29,000), 329 (52,850), 281 (127,500).

Anal. Calcd for $C_{16}H_{17}Br_2O_2$: C, 55.0; H, 4.9; N, 8.0. Found: C, 54.9; H, 5.0; N, 7.9.

Using lesser amounts of ethyl bromoacetate and/or shorter reflux time in the above preparation resulted in somewhat lower yields.

Method B.—Harman (40 mg, 0.22 mmol) and ethyl bromoacetate (1.0 g) in absolute ethanol (3 ml), after standing at room temperature for 4 days, gave 1-methyl-2-ethoxycarbonylmethyl-9H-pyrido[3,4-*b*]indolium bromide as yellow cubes: 53 mg (69%); mp 235–237° dec. The product was identical with the material obtained above.

In a similar manner, 1,2-dimethyl-9H-pyrido[3,4-*b*]indolium iodide (**7**) was obtained in 88% yield from harman and methyl iodide. It separated from ethanol as pale yellow needles: mp 295–297° (lit.[13] mp 275°); ir, 3100, 1640, 1580, 1530, 1500, 1450, 1380, 1340, 1301, 1228, 1129, 1006, 808, 775, 759, and 738 cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$, m$\mu$ (ϵ), pH 1 or 6, 370 (7840), 306 (39,200), 251 (55,520); pH 12, 415 (10,230), 325 (23,390), 280 (79,530).

Anal. Calcd for $C_{13}H_{13}IN_2$: C, 48.2; H, 4.1; N, 8.6. Found: C, 48.0; H, 4.0; N, 8.5.

Condensation of 1-Methyl-2-ethoxycarbonylmethyl-9H-pyrido[3,4-*b*]indolium Bromide with 1,2-Cyclohexandione in Absolute Ethanol. A. Isolation of 5-Ethoxycarbonyl-1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium Bromide (2).—1-Methyl-2-ethoxycarbonylmethyl-9H-pyrido[3,4-*b*]indolium bromide (**1**) (2.00 g, 4.7 mmol), 1,2-cyclohexanedione (1.12 g, 10 mmol), and dibutylamine (1.00 g, 7.7 mmol) were dissolved in absolute ethanol (300 ml) and refluxed for 2 hr under nitrogen. The red solid obtained on evaporation of the solvent was refluxed with ether for 1 hr and the ether discarded. The product was then dissolved in methanol and treated with charcoal; the addition of ether caused an oily product to separate. This sequence was repeated and a large volume of ether was added. Over several days at 0°, a solid product together with some oily material was deposited. Addition of acetone dissolved the oil and the solid was collected and dried. There was obtained 1.2 g (48%) of 5-ethoxycarbonyl-1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium bromide, mp 176–180°. Recrystallization from methanol-1,2-dimethoxyethane gave orange-yellow needles: 0.76 g (30%); mp 186–188° dec; ir, 3400 (indole N—H) and 1730 cm^{-1} (C=O).

Anal. Calcd for $C_{22}H_{21}BrN_2O_2 \cdot H_2O$: C, 59.6; H, 5.2; N, 6.3. Found: C, 59.9; H, 5.4; N, 6.1.

B. Isolation of 1-Methyl-2-[1-(2-oxocyclohexylidene)ethoxycarboxylmethyl]-9H-pyrido[3,4-*b*]indolium Bromide (6).—1-Methyl-2-ethoxycarbonylmethyl-9H-pyrido[3,4-*b*]indolium bromide (3.00 g, 8.6 mmol), 1,2-cyclohexanedione (1.55 g, 13.8 mmol) and dibutylamine (1.55 g, 12 mmol) were dissolved in absolute ethanol (400 ml) and heated gently for 2 hr, keeping the temperature below 70°. Work-up as described above gave 3.9 g of red solid product. A portion of the product (0.5 g) was treated with 15 ml of methanol–ether (2:1) solution, whereupon yellow crystalline 1-methyl-2-[1-(2-oxocyclohexylidene)ethoxycarbonylmethyl]-9H-pyrido[3,4-*b*]indolium bromide (**6**), 40 mg, remained undissolved. It separated from absolute ethanol as yellow needles: mp 206–208°; ir, 3400, 1740, 1720 cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$, m$\mu$ (ϵ), 395 (7840), 312 (29,950), 258 (43,510).

Anal. Calcd for $C_{22}H_{23}BrN_2O_3$: C, 59.6; H, 5.2. Found: C, 59.5; H, 5.4.

5-Carboxy-1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium Bromide (3). A.—5-Ethoxycarbonyl-1,2,3,4-tetrahydro-13H-benz[g]indolo[2,3-*a*]quinolizinium bromide (50 mg, 0.11 mmol), ethanol (30 ml) and 0.5 *N* sodium hydroxide solution (20 ml) were refluxed for 15 min and, after the addition of 25% HBr solution (20 ml), reflux was continued for a further 2 hr. After standing for 48 hr, 5-carboxy-1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium bromide deposited from the solution as orange needles: 45 mg (93%); mp 322–324°; ir, 3400 (–NH–) and 1720 cm^{-1} (C=O); $\lambda_{max}^{95\%\ EtOH}$, m$\mu$ (ϵ), pH 1, 389 (23,330), 350 (23,200), 299 (20,760), 243 (50,630), pH 6, 389 (30,630), 369 (23,710), 351 (22,360), 296 (22,030), 242 (53,590), pH 12, 430 (10,550), 357 (30,550), 321 (21,520), 288 (35,570), 242 (46,120).

Two recrystallizations of **3** from methanol gave 5-carboxy-1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium hydroxide inner salt (**4**) as yellow needles: mp 217–220°; ir, 3400 (indole N—H), 2925, 1625 (–COO^-), 1520, 1470, 1410, 1395, 1310, 1237, 1216, 1195, 1165, 1092, 771, 748, and 736 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}N_2O_2 \cdot CH_3OH$: C, 72.4; H, 5.8. Found: C, 72.5; H, 5.6.

B.—5-Ethoxycarbonyl-1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium bromide (60 mg, 0.14 mmol), 95% ethanol (25 ml) and 0.5 *N* sodium hydroxide solution (15 ml) were refluxed for 15 min. The solution was cooled to room temperature and 25% hydrobromic acid solution (15 ml) was added. Removal of portion of the solvent gave 37 mg of the inner salt **4** which crystallized from methanol as yellow needles, mp 217–220°.

Conversion of the Inner Salt 4 into the Acid 3.—The inner salt **4** (50 mg) was dissolved in 95% ethanol (30 ml) containing 0.5 *N* sodium hydroxide solution (2 ml). To the resulting solution was added a 25% HBr solution (20 ml) and after refluxing for 2 hr, the solution was allowed to stand for 48 hr during which time it deposited 5-carboxy-1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium bromide (**3**), 40 mg, as red needles, mp 318–322° dec. The infrared spectrum was identical with that of **3** obtained above.

Decarboxylation of 5-Carboxy-1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium Bromide (3) to Sempervirine Bromide (5).—The bromide (50 mg, 0.12 mmol) was heated in a sublimation apparatus to 250°. The product that was obtained crystallized from ethanol–ether upon the addition of HBr solution (10 drops) and 1,2,3,4-tetrahydro-13H-benz[*g*]indolo[2,3-*a*]quinolizinium bromide (**5**); 36 mg (85%) separated as yellow microcrystals: mp 323–325° dec (the melting point on admixture with an authentic sample of sempervirine bromide was 322–324° dec and their infrared spectra were superimposable: ir, 3400, 1647, 1630, 1402, 1218, 1193, and 741 cm^{-1}); $\lambda_{max}^{95\%\ EtOH}$, m$\mu$ (ϵ), pH 1 or 6, synthetic product, 385 (26,470), 342 (27,550), 294 (24,550), 249 (57,070), 242 (59,280), authentic material, 385 (25,940), 342 (26,670), 295 (23,330), 249 (55,280), 242 (58,330), pH 12, synthetic product, 435 (10,780), 360 (32,930), 320 (23,350), 288 (46,700), 243 (47,190), authentic material, 435 (10,280), 360 (32,450), 320 (23,310), 288 (46,120), 242 (46,390); tlc (silica gel) ethyl acetate, R_f 0.08, 95% ethanol, R_f 0.12.

Attempted Condensation of 1,2-Dimethyl-9H-pyrido[3,4-*b*]indolium Iodide (7) with 1,2-Cyclohexanedione.—The following experiment illustrates the results obtained. 1,2-Dimethyl-9H-pyrido[3,4-*b*]indolium iodide (500 mg, 1.5 mmol), 1,2-cyclohexanedione (300 mg, 2.7 mmol), and freshly distilled dibutylamine (300 mg, 2.3 mmol) in absolute ethanol (150 ml) were refluxed for 2 hr under nitrogen. The dark solution was then evaporated to a volume of 30 ml and stored overnight at 0° whereupon it deposited a green crystalline material (320 mg). Evaporation of the filtrate gave a dark oil which could not be further purified. A portion of the green crystalline solid (200 mg) was recrystallized from ethanol–ether giving a gray material, mp 285–290° dec, whose infrared and ultraviolet spectra were nearly superimposable on the spectra of the starting iodide.

Registry No.—**1**, 17350-51-5; **2**, 17350-52-6; **3**, 17350-53-7; **4**, 17350-54-8; **5**, 17350-55-9; **6**, 17366-27-7; **7**, 17350-56-0; sempervirine, 6882-99-1.

Acknowledgment.—The authors wish to express their appreciation to Dr. J. Wong for many helpful and stimulating discussions during this work.

(11) All evaporations were done under reduced pressure using a rotatory evaporator and melting points were determined in capillaries, using an electrically heated block. Ir spectra were determined in KBr on a Perkin-Elmer Model 421 spectrophotometer and uv spectra were determined on a Cary Model 14 spectrophotometer. Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

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