Photochemical Reaction of (-)-Quebrachamine. Unusual Photoformation of an Ibogamine-like Ring System†

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Irradiation of (-)-quebrachamine, a C_4N–C_5N–C_6–C_8N four-ring system, gives a 16-hydroxy derivative of a C_4N–C_5N–C_6–C_6–C_6N five-ring system (a 16-hydroxy derivative of an ibogamine-like ring system). Some aspects of the photohydroxy cyclization reaction are discussed.

As part of an ongoing program that is involved with the photochemical behavior of nitrogen organic compounds (amines[1] and alkaloids[2]), we have examined the photoreaction of (-)-quebrachamine in different solvents.

The photochemistry of alkaloids is intriguing because of the wide array of new chemical reactions that are now on record in this group of biologically active compounds[3a] and because of the isolation of oxoalkaloids raises the question whether these compounds are genuine natural products or photochemical products.[3b]

As it is known,[4] quebrachamine is biosynthetic precursor of the aspidospermine skeleton presumably by C_7–C_{21} ring closure and the interconversion of *Corynanthe*, *Aspidosperma* and *Iboga* alkaloids has been postulated by Scott.[5] Recently, a synthetic road to the forest of *Strychnos*, *Aspidosperma*, *Schizozygane*, *Iboga*, and *Eburnamine* alkaloids by way of the photoisomerization of 1-acylindoles have been described.[6-9]

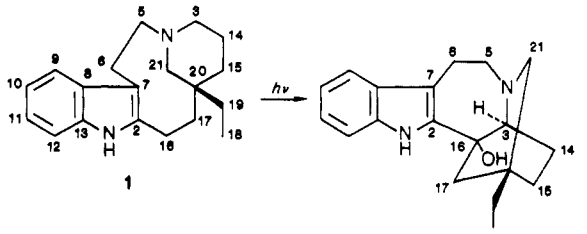
We think that the photochemical results obtained in the present study could be of use to understand the precise sequence of biosynthetic events and the reaction pathways at the enzymatic level of the indole alkaloid formation.

Results and Discussion

In our hands, irradiation of (-)-quebrachamine (**1**) in hexane for 1 h gave **2** [mp 165–167 °C; M^+ *m/e* 296 ($C_{19}H_{24}N_2O$)], as a white precipitate in 85% yield (Φ_2 = 0.26) (Scheme I). Compound **2** has peaks at *m/e* 296 (M^+, 50), 295 ($M^+ - H$, 59), and 278 ($M^+ - H_2O$, 51). The mass spectrum (MS) of **2** was compared with those of quebrachamine,[10] rhazidigenine,[11] and their oxo and hydroxy derivatives[12,13] and those of aspidospermidine.[10,14] The IR spectrum of **2** has a broad band at 3525 cm^{-1} (OH). In the ^1H NMR spectrum of **2**, the value of the ratio between the area of aromatic protons and the area of the aliphatic protons (4:20, $DCCl_3$) was different from that of **1** (4:22, $DCCl_3$) and from that of **2** after treatment with deuterium oxide (4:18, $DCCl_3$–D_2O). The ^{13}C NMR spectrum of **2** has a signal at 89.3 ppm. In the ^{13}C NMR spectrum of **2** the signals of C-14 and C-16, which appear at 22.5 and 22.2 ppm in ^{13}C NMR spectrum of **1**, are not observed in this spectral region (only one signal appears at 21.1 ppm in **2**), and new signals are found at δ values between 51.6 and 61.5 ppm and at δ values between 32.6 and 38.3 ppm. The ^{13}C NMR spectrum of **1** has been previously described by Wenkert et al.[15] The chemical shifts of the carbons were assigned by comparison with the chemical shifts of indole compounds[16] and other indole alkaloids.[17]

These spectral data suggest introduction of a hydroxyl group at C-16 and a C_3–C_{16} new bond for **2**. The simultaneous replacement of two hydrogen atoms at C-16 of **1** by a hydroxyl group and an alkyl group (**1** → **2**) causes shift

Scheme I



1 **2**

changes at α (C-16), β (C-3 and C-17), and γ (C-14 and C-20) positions. Similar chemical shift changes were observed for dihydrocleavamine and its 20-hydroxy derivative (velbanamine).[15] When the acetylation of the hydroxyl group of **2** was achieved (**3**) a signal at *m/e* $M^+ - CH_3COOH$ (278, 100), which is due to an spatial interaction of the CH_3COO group at C-16 and hydrogen atoms[18] at C-14, C-15, and C-17 (Scheme I, compound **2**, axial–axial 1–2,

† Dedicated to the memory of Prof. Dr. Venancio Deulofeu.

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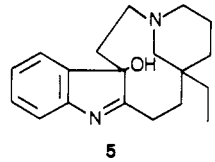
1–3, and 1–4 interaction in the cyclohexane boat ring[19]), was observed. A similar spatial interaction allows us to explain the very important peak observed at m/e M − 18 ($M^+ - H_2O$) in the MS and the broad signal at 3525 cm^{-1} (H···O) in the IR spectrum of **2**.

As the ordinary oxidation product of indole compounds is a 3-hydroxyindolenine[20,21] derivative, we isolated rhazingenine (**5**) as a byproduct in the recrystallization of quebrachamine from hot hexane to compare its MS,[11] and ^1H and ^{13}C NMR spectra with those of **2**. As it can be seen in Experimental Section a 3-hydroxyindolenine moiety is not present in the structure of **2**.

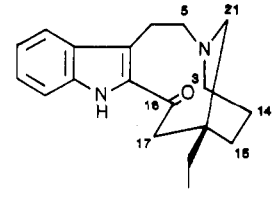
When the irradiation was preformed in CCl_4 solution compound **2** was also isolated in very high yield (84%, Φ_2 = 0.22).

The absorption spectra data of **1** in hexane and in CCl_4 show that these absorption spectra are very similar. When the irradiation of **1** was performed in CCl_4 solution, chloride anion ($AgNO_3/HNO_3$ test) was not detected. Both results allow us to discard a charge transfer complex (CTC) formation in the ground state of **1** (**1**···CCl_4),[22] as well as an excited charge-transfer complex (exciplex)[1a-d,2b,22] (**1***···CCl_4) and a single electron transfer mechanism ($1^{\bullet+}$ + Cl^- + $^\bullet CCl_3$).[1a-d,22]

As is known[23,24] the photooxidation of 2,3-dialkylindole derivatives involves the alkyl substituent attached to the 2-position preferentially. Thus, from the electronic excited (−)-quebrachamine a C-16 carbonylic intermediate could be formed (formula a). From a Dreiding model of a it can be seen that the carbonyl group at C-16 is located sufficiently close to H-3 to strip the latter off in an intramolecular Norrish type II reaction[25] and produce the C_4N–C_5N–C_6–C_6–C_6N five ring system (**2**).



5



formula a

This hypothesis is supported by the fact that: (i) Irradiation of **1** in polar solvents such as EtOH and AcOH do not lead to the photoformation of the compound **2**. In both examples nonconverted alkaloid **1** (conversion <10%, Φ_1 < 0.03), mixtures of mono-, di-, tri-, and tetraoxo derivatives of **1** [GC/MS analysis show molecular ion peaks at m/e 296, 298, 314, 328, and 344, respectively] in poor yield (mixture yield ≤5%, $\Phi_{mixture} \leq 0.02$), and brown polymeric mixtures (yield 5–8%, Φ_{pol} = 0.02–0.03) are obtained. (ii) When the irradiation of **1** in hexane solution is performed bubbling HBr, the quantum yield of **2** is appreciably reduced ($\Phi_{2(HBr)} < 0.01$). As it is known,[22,26a-b] HBr(g) is a very efficient quenching agent for the Norrish type II reaction. Features to note are as follows: as (−)-quebrachamine is a basic alkaloid, the study of the HBr(g) quenching approaches limiting experimental conditions because the corresponding hydrobromide (−)-quebrachamine salt precipitates at high HBr concentration.

The nonconverted alkaloid (**1**) and compound **2** were characterized by comparison with authentic samples (TLC, GC, and GC/MS analyses). Unfortunately, we have been unable to identify the other components of the reaction mixture of the HBr trapping reaction.

Experimental Section

General information concerning instrumentation and materials was described previously.[1,2,16,27,28] GC analyses were carried out on PORAPAK Q, Downfax 9N9 and Chromosorb W (N°C-8264; acid washed) columns. Light sources external to the reaction vessel were used: a low-pressure mercury lamp (Hanau Quartz-lampen GmBH 5631; 0.13 A), a high-pressure mercury lamp (Hanau Quartz-lampen GmBH-TQ 150), and a tungsten lamp (Sylvania, 400 W). Quantum yields were determined by using acetanilide as the actinometer.[29a,b] The conversion of the (−)-quebrachamine (Φ_1) and the formation of **2** (Φ_2) were monitored by GC analysis and by gravimetric analysis.

(−)-Quebrachamine (1). This compound was obtained according to the method described in literature.[30] Its authenticity was confirmed by comparison of melting point,[30] $[\alpha]^{25}_D$, UV, IR, ^1H NMR, ^{13}C NMR,[15] mass spectrum,[10b] and TLC analyses with those of a genuine sample.

Rhazidigenin (5). This compound was obtained according to the method described in literature.[11,30,31] Its authenticity was confirmed by comparison of melting point,[11] UV,[11] IR,[11] ^1H NMR, ^{13}C NMR, mass spectrum,[10b,11] and TLC analyses with those of a genuine sample: ^{13}C NMR ($DOCD_3$) 170.8, 129.9, 123.3, 119.8, 117.0, 110.4, 87.9, 59.9, 56.6, 55.6, 37.4, 35.5, 34.1, 32.7, 23.2, 21.9, 7.5 ppm.

Irradiation of 1 in Hexane, CCl_4, and EtOH. A solution of the alkaloid **1** (10 mg, 0.355×10^{-4} mol) in hexane solution (1000 mL) was placed in quartz Erlenmeyer flasks and irradiated with stirring for 1 h. The light source (low-pressure mercury lamp) was placed 10 cm from the flasks. The progress of the reaction was followed by GC, GC/MS, and TLC (neutral alumina; hexane–MeOH and MeOH–CH_3COOH (drops); the spots on the plates were made visible with I_2).

In all cases, the crystalline precipitate formed and the mother liquors were analyzed by TLC, GC, and GC/MS. The analysis of the mother liquors showed the nonconverted starting alkaloid, which was isolated by evaporation of the solvent (1.2 mg, conversion 88%) and identified from its R_f, retention time, melting point, and MS (EI), Φ_1 = 0.27.

When the irradiation was stopped, the white crystalline precipitate that formed was filtered off, washed with cold hexane, and recrystallized (compound **2**, 8.9 mg, 85%, Φ_2 = 0.26). Recrystallization of this material from hexane afforded pure **2** as a colorless microcrystalline solid: mp 165–167 °C; $[\alpha]^{25}_D$ −371° (MeOH, c 0.21); IR (Nujol) 3525 cm^{-1} (broad, OH and NH); electronic spectra, UV absorption λ_{max} (lg ϵ) (MeOH) 202 (2.02), 220 (2.11), 224 (2.11), 230 (2.11), 244 (2.13), 282 nm (1.83); emission spectra (λ_{exc}) λ_{max} (relative intensity) (hexane) (290 nm) 333 (4), 573 (3), 657 (0.7); ^1H NMR ($DOCD_3$) 7.40–7.00 (m, 4 H), 3.05–1.00 (m, 17 H), 0.98 ppm (t, J = 6.0 Hz, CH_3); ^{13}C NMR ($DOCD_3$) 134.1 (C-13), 131.1 and 130.9 (C-2 and C-11), 125.2 (C-10), 124.5 (C-9),

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123.6 (C-8), 117.8 (C-12), 114.4 (C-7), 89.3 (C-16), 61.5 (C-3), 58.2 and 57.3 (C-5 and C-21), 38.3 (C-17), 35.6 (C-20), 34.3 (C-15), 32.6 (C-19), 28.2 (C-14), 21.2 (C-6), 7.64 ppm (CH_3); MS (EI) m/e (relative intensity) 296 (50), 295 (59), 282 (13), 278 (51), 250 (13), 249 (100), 221 (13), 210 (13), 167 (21), 156 (10), 152 (20), 150 (38), 149 (50), 136 (13), 124 (16), 122 (18), 110 (16), 97 (54), 96 (13), 95 (13), 84 (12), 83 (15), 77 (15), 71 (30), 70 (21). Anal. Calcd for $C_{19}H_{24}N_2O$: C, 76.99; H, 8.16; N, 9.45; O, 5.40. Found: C, 76.95; H, 8.19; N, 9.46; O, 5.40.

Irradiations in CCl_4 and in EtOH were performed in a similar manner. When CCl_4 was used as solvent, chloride anion formation was not detected ($AgNO_3/HNO_3$ test).

The conversion of 1 was poor (conversion 10%; 2 yield 9%) when it was irradiated in hexane with an external high-pressure mercury lamp in a Pyrex container (higher energy cutoff 290 nm). No phototransformation was detected when 1 (in hexane and in CCl_4 solution) was irradiated with a tungsten lamp.

Compound 2 was not detected as a photoproduct when a solution of 1 in hexane (quartz container, external low-pressure mercury lamp, irradiation time 1 h) was irradiated under N_2 atmosphere.

Irradiation of 1 in the Presence of HBr. The alkaloid 1 (10 mg, 0.355×10^{-4} mol) was dissolved in hexane (1000 mL), and the solution was placed in a quartz Erlenmeyer flask and in a Pyrex Erlenmeyer flask. Then, HBr(g) was slowly bubbled ($\leq$0.05 mL/min) in both solutions.

Method A. The solution contained in the Pyrex Erlenmeyer flask (A solution) was kept in the dark while that contained in the quartz Erlenmeyer flask (B solution) was irradiated according to the above described method, with the low-pressure mercury lamp. HBr(g) was bubbled in both solutions simultaneously. The irradiation was stopped when a light yellow precipitate (A precipitate) was observed in the A solution. The crystalline A precipitate that formed was filtered off and then characterized as the monohydrobromide (-)-quebrachamine salt by the $AgNO_3/HNO_3$ test and by the Volhard method. The HBr concentration in the mother A liquors was determined by the Volhard method and the alcaloid 1 concentration by GC analysis.

The precipitate formed in the irradiated B solution (B precipitate) was collected by vacuum filtration and analyzed by TLC, GC, GC/MS, and by Volhard method. Then, B precipitate was dissolved in CH_2Cl_2 and extracted with H_2O, dried over anhydrous Na_2SO_4, and evaporated. The residue obtained was worked up as usual. The mother B liquors were analyzed as usual.

Method B. Both solutions, A and B, were kept in the dark while HBr(g) was bubbled in both containers. The HBr bubbling in the A solution was initiated 0.5 s before than the bubbling in the B solution. The HBr bubbling was stopped when a light turbidity was shown by A solution. In that moment, the irradiation of the B solution, with the low-pressure mercury lamp, was started while A solution was kept in the dark. After 1 h of irradiation, the usual workup and GC analysis of both solutions gave the 1 conversion, 2 yield, and 2 quantum yield values mentioned in the text.

Irradiation of 1 in AcOH. A solution (0.355×10^{-4} M) of (-)-quebrachamine in AcOH (glacial) was irradiated with the low-pressure mercury lamp, contained in a quartz Erlenmeyer flask. After 1 h of irradiation the light brown solution was diluted with H_2O: (i) First, the acidic aqueous solution was extracted with benzene and then with CH_2Cl_2, (ii) then, the aqueous solution was neutralized with NaOH(aq) and extracted with benzene and then with CH_2Cl_2. The organic layers were separated and washed with H_2O and then with $NaHCO_3$(aq). The residues obtained by evaporation of the solvent were analyzed by TLC, GC, and GC/MS.

Photosensitized Irradiation of 1. The photosensitized reactions of 1 (10 mg) were performed by employing Rose Bengal (RB) and Hematoporphirine (HP) (0.6 mg) dissolved in EtOH (RB) and in CCl_4 (HP) (1000 mL). The solutions were irradiated with a tungsten lamp for 18 h. The progress of the reaction was followed as usual, and 2 was not detected as product of the dye photosensitized reaction of (-)-quebrachamine (1).

Acetylation of 2. The monoacetyl derivative (3) was obtained from 2 as an oily compound from hexane: MS (EI) m/e (relative intensity) 338 (0.7), 279 (54), 278 (100), 263 (5), 250 (46), 249 (81), 236 (50), 235 (49), 222 (9), 221 (65), 207 (23), 181 (44), 167 (22), 118 (6), 110 (5). Anal. Calcd for $C_{21}H_{26}N_2O_2$: C, 74.52; H, 7.74; N, 8.28; O, 9.46. Found: C, 74.50; H, 7.75; N, 8.29; O, 9.46.

The diacetyl derivative 4 was obtained, in very poor yield, as impurity of 3, and it was characterized by GC/MS: MS (EI) m/e (relative intensity) 380 (0.5), 321 (23), 320 (100), 277 (18), 263 (10), 250 (27), 249 (78), 236 (47), 235 (23), 222 (8), 221 (63), 207 (15), 181 (32), 167 (18), 118 (5), 110 (7).

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Registry No. 1, 4850-21-9; 2, 120411-05-4; 3, 120385-95-7; 4, 120416-95-7; 5, 3384-38-1.

Photochemistry of 4,4-Dimethyl-1-phenyl-2-pentyn-1-one[1]

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The photochemistry of 4,4-dimethyl-1-phenyl-2-pentyn-1-one has been examined by a combination of laser flash photolysis experiments and product studies. The triplet ketone is relatively long-lived in inert solvents such as acetonitrile but reacts readily with hydrogen donors via hydrogen abstraction to give the corresponding ketyl radical and with substituted aromatics via charge-transfer quenching. For example, rate constants for quenching by cyclohexane and anisole are 2.9×10^7 and 2.8×10^8 M^{-1} s^{-1}, respectively, in acetonitrile. The ketone undergoes efficient photodecomposition in cyclohexane ($\Phi = 0.86$) to give the expected radical coupling products but is unreactive in benzene. The ketone radical anion (λ_{max} = 510 nm in acetonitrile) is formed directly by quenching the triplet with 1,4-diazabicyclo[2.2.2]octane. It may also be generated indirectly in the reaction with triethylamine by reduction of the parent ketone by the amine-derived radical produced by hydrogen abstraction by the triplet ketone.

Despite the wide amount of attention that α,β-enone systems have received,[3] there have been relatively few investigations of the analogous α,β-acetylenic ketones.[4-14] Most of the available examples indicate that these com-

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