

Phosphorescence Lifetimes. The triplet state lifetime τ_p of benzophenone in liquid hydrocarbon solvents can generally be related to the rate constant for photoreduction.^{6,7} In benzene, however, τ_p is anomalously short (5.4 μ sec at 304°C).⁶ This anomalous solvent effect has been attributed to (1) diffusion-controlled quenching by photochemically generated transient impurities,⁸ (2) a rapid reversible photoreduction,⁷ and (3) the reversible formation of an adduct diradical.^{1,9} By using a matrix such as III that has phenyl rings that presumably can interact with the benzophenone solute in the same manner that benzene does, yet prevents molecular diffusion over a wide temperature range, it should be possible to evaluate the above mechanisms.

We observe a relatively long lifetime (1.0 msec) for the phosphorescence of benzophenone in III at 300°K, which by itself suggests that the first mechanism above is important in fluid benzene. In addition, we find that τ_p for benzophenone in benzene increases significantly upon cooling the solvent below its melting point. However, we also observe relatively large values of τ_p at 300°K for benzophenone in I (1.0 msec),¹⁰ II (0.7 msec), and IV (0.65 msec), even though these polymers have alkyl hydrogen atoms available for abstraction from the polymer chain. Apparently, there is a steric requirement for the hydrogen abstraction that is restricted by the polymer matrix. Melhuish has shown directly, using flash spectroscopy, that I hinders the photoreduction of benzophenone.¹¹ Thus, our data indicate that if the second or third mechanism listed above is important there must be a strong steric requirement for the interaction between the carbonyl group and the benzene ring that is hindered in rigid polymer matrices but not in fluid benzene.

Acknowledgment. The authors are grateful to Dr. G. F. L. Ehlers, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, for kindly providing the poly(α,β,β -trifluorostyrene). This work was supported by the U. S. Air Force under Contract No. F04701-69-C-0066.

(7) C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **65**, 2823 (1969).

(8) P. J. Wagner, *Mol. Photochem.*, **1**, 71 (1969).

(9) G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970).

(10) P. F. Jones and S. Siegel in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, pp 15-19.

(11) W. H. Melhuish, *Trans. Faraday Soc.*, **62**, 3384 (1966).

Peter F. Jones, A. R. Calloway
The Aerospace Corporation
El Segundo, California 90245
Received June 8, 1970

The Structure of Concentrine: A Novel Dimeric Benzyloquinoline Alkaloid

Sir:

We report here the structure of concentrine (F_{22}), the yellow alkaloid of *Dicentra canadensis* (Goldie) Walp.^{1,2} The composition of concentrine, **1**, its *O*-methyl ether, **2** (from **1** by the Rodionov method³), and its *O*-acetate, **3**, were established by high-resolution mass spectrometry.⁴ The following physical properties

(1) R. H. F. Manske, *Can. J. Res., Sect. B*, **7**, 258 (1932).

(2) R. H. F. Manske, *ibid.*, *Sect. B*, **16**, 81 (1938).

(3) W. Rodionov, *Bull. Soc. Chim. Fr.*, **39**, 305 (1926).

were recorded: **1**, mp 238°; $\nu_{\max}^{\text{CHCl}_3}$ 3450 and 1665 cm^{-1} hydroxyl and carbonyl, respectively; $\lambda_{\max}^{\text{EtOH}}$ 213, 230 (sh), 268, 291 (sh), 330 (sh), and 435 μ ; log ϵ_{\max} 4.80, 4.63, 4.32, 4.22, 3.62, and 3.82, respectively. The 100-MHz pmr spectrum of concentrine has signals corresponding to three aromatic methoxyl groups and one *N*-methyl group but no *C*-methyl or methylenedioxy groups. The presence of one basic and one nonbasic nitrogen in concentrine was deduced from the analysis of its hydrochloride and from paper electrophoresis and the presence of one phenolic hydroxyl group from an examination and comparison of the ir, uv, and pmr spectra of **1**, **2**, and **3**. The *N*-methyl group was shown to be both the basic center of the alkaloid and part of a modified morphine⁵ unit by means of physical and chemical methods.

Concentrine methiodide undergoes Hofmann degradation to the methine **4**⁴ (mp 230°; $\nu_{\max}^{\text{CHCl}_3}$ 3450 and 1660 cm^{-1} ; $\lambda_{\max}^{\text{EtOH}}$ 227, 270, and 435 μ ; log ϵ_{\max} 4.61, 4.38, and 3.75, respectively), which upon hydrogenation (H_2 -Pt) and methylation (diazomethane) gave the dihydromethine-*O*-methyl ether **5**⁴ (mp 189°; $\nu_{\max}^{\text{CHCl}_3}$ 1660 cm^{-1} ; $\lambda_{\max}^{\text{EtOH}}$ 208, 230 (sh), 270, 330 (sh), and 433 μ ; log ϵ_{\max} 4.57, 4.37, 4.28, 3.61, and 3.77, respectively). The hydrobromide of **5** forms golden yellow orthorhombic crystals from methanol and these were used for an X-ray single-crystal structure analysis.⁶

There were four molecules per unit cell (space group $P2_1 2_1 2_1$) with dimensions of $a = 10.639$ (2), $b = 12.036$ (4), and $c = 26.979$ (7) Å. The observed density was 1.366 g/cm^3 and the calculated value 1.379 g/cm^3 . The reflections with $2\theta > 135^\circ$ for Cu $K\alpha$ radiation were measured using the stationary-crystal-stationary-counter method. The 2475 reflections with I (counts) $> B$ (background counts) $+ 3\sqrt{B}$ were considered observed and used in the analysis. The 1034 reflections below the above level were considered unobserved.

The structure was solved by locating the Br-Br vectors in the sharpened Patterson function and the light atoms in successive Fourier syntheses. The structure was refined by least-squares methods to an R , the usual residual, of 0.13 using individual isotropic thermal parameters, and to an R of 0.072 using anisotropic thermal parameters. No attempt was made to locate the hydrogen atoms, nor is the absolute configuration implied in structure **5**.

The three C-N bonds about nitrogen in the *N,N*-dimethyl group average 1.502 ± 0.010 Å which is close to the value for a C-N single bond. However the N-C₂₅ distance of 1.346 ± 0.011 Å is significantly shorter than a single bond and indicates definite double bond character. The bonds N-C₂₅-C₂₄-C₇-O all have distances consistent with a conjugated system (*cis-trans*- β -amino enone), which, being part of a dibenzoxapine, is believed to be responsible for the long-wavelength absorption in the visible region⁷ observed in the alkaloid and its derivatives.

(4) **1** Calcd for $\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}_7$: 606.2365. Found: 606.2397. **2** Calcd for $\text{C}_{37}\text{H}_{36}\text{N}_2\text{O}_7$: 620.2522. Found: 620.2526. **3** Calcd for $\text{C}_{38}\text{H}_{38}\text{N}_2\text{O}_8$: 648.2471. Found: 648.2427. **4** Calcd for $\text{C}_{37}\text{H}_{36}\text{N}_2\text{O}_7$: 620.2522. Found: 620.2545. **5** Calcd for $\text{C}_{38}\text{H}_{40}\text{N}_2\text{O}_7$: 636.2835. Found: 636.2888. Satisfactory elemental analyses were obtained for the compounds **1**, **2**, **4**, and **5** and the hydrochloride of **1**.

(5) G. Stork, *Alkaloids*, **6**, 219 (1960).

(6) Several other crystalline derivatives of concentrine were found to be unsuitable for various reasons.

(7) C. Kashima, M. Yamamoto, and N. Sugiyama, *J. Chem. Soc. C*, **111** (1970).

To deduce the structure of concentrine from **5** it is necessary (a) to show that the transformation **1** \rightarrow **5** involves only the opening of the nitrogen containing bridge and (b) to locate the nitrogen terminus of the bridge and the OH function of **1**.

Compounds **1**, **2**, **3**, **4**, and **5** are all bright yellow with very similar uv spectra and in every case an ir band at $\nu_{\text{max}}^{\text{CHCl}_3}$ $1665 \pm 5 \text{ cm}^{-1}$. All pmr spectra have a sharp singlet at $\delta 5.0 \pm 0.2$ attributed to $\text{C}_5\text{-H}$ and three AB quartets accounting for six aromatic protons. An additional AB quartet (vinylic, $\text{H}_9\text{-H}_{10}$) is present in the spectrum of **4**. Thus, it is clear that in the conversion **1** \rightarrow **4** \rightarrow **5** only the simple expected changes have taken place.

The terminus of the bridge was established through pmr examination of **1** and comparison of its spectrum with that of codeine, **6**.⁸ The splitting patterns and the chemical shifts of the protons $\text{C}_9\text{-C}_{10}$ in the two systems are very similar. Thus $\text{H}_{10\beta}$ ($\delta 3.18$) in **1** is coupled to $\text{H}_{10\alpha}$ ($\delta 2.43$) ($J_{10\alpha,10\beta} = 18.5 \text{ Hz}$) but is only weakly

coupled to H_9 ($\delta 3.43$; $J_{\text{H}_{10\beta},\text{H}_9} = 1.0 \text{ Hz}$). In the spectrum of concentrine, $\text{H}_{10\alpha}$ is partially obscured although it has been observed in the morphine systems,⁸ while H_9 appears as a multiplet in both coupled as it is to $\text{H}_{10\alpha}$, $\text{H}_{10\beta}$, and H_{14} with coupling constants in **1** of $J_{\text{H}_9,\text{H}_{10\alpha}} = 6.0 \text{ Hz}$, $J_{\text{H}_9,\text{H}_{10\beta}} = 1.0 \text{ Hz}$, and $J_{\text{H}_9,\text{H}_{14}} = \text{ca. } 1.5 \text{ Hz}$. The couplings for codeine are virtually identical⁸ suggesting the same steric arrangement in the two systems as shown in the structures. A spectrum completely different from that of codeine would have resulted for the protons at C_9 and C_{10} in concentrine had the nitrogen been joined to C_{14} as in hasubanone,⁹ or to C_{10} , which is biogenetically unlikely.

The site of the acetoxy group in **3** and, therefore, of the OH group in **1** has been established by pmr examination of **1** and **3**. The aromatic protons appear as three AB quartets with one proton at lower field than the rest. This proton is centered at $\delta 7.51$ and 7.88 in **1** and **3**, respectively. A shift of this order upon acetylation is characteristic of a proton para to a phenolic OH group.¹⁰ This places the OH group of **1** and the acetoxy group of **3** at C_{20} in agreement with observed nuclear Overhauser effects¹¹ of 25, 25, and 24% in the aromatic signals at $\delta 6.83$, 6.68 , and 6.98 when the methoxyl signals at $\delta 3.91$, 3.76 , and 3.85 , respectively, in **1** were irradiated—a result only possible if the phenolic OH group in **1** is located at C_{20} where it is not vicinal to any aromatic protons.

Thus, concentrine is the first member of a new class of dimeric benzyloquinoline alkaloids, unique both in the nature of the individual benzyloquinoline units (morphine and cularine¹²), and in the manner of their linkage. Three more alkaloids of the concentrine family have been isolated from the same source. Their structures will be the subject of a subsequent publication.

Acknowledgments. This investigation was supported by grants from the National Research Council of Canada.

(9) M. Tomita, T. Ibuka, Y. Inubushi, Y. Watanabe, and M. Matsui, *Chem. Pharm. Bull. (Tokyo)*, **13**, 538 (1965).

(10) R. J. Highet and P. F. Highet, *J. Org. Chem.*, **30**, 902 (1965).

(11) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

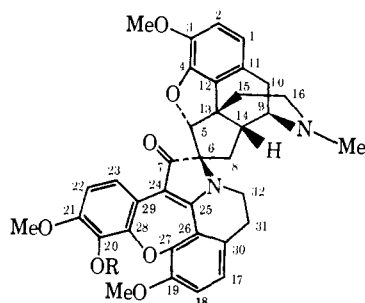
(12) R. H. F. Manske, *Alkaloids*, **4**, 249 (1954).

* To whom correspondence should be addressed.

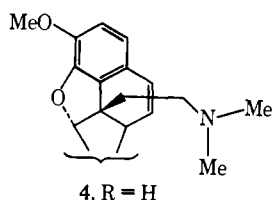
G. R. Clark, R. H. Manske,* G. J. Palenik, R. Rodrigo
Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada

D. B. MacLean, L. Baczynskyj, D. E. F. Gracey, J. K. Saunders
Department of Chemistry, McMaster University
Hamilton, Ontario, Canada

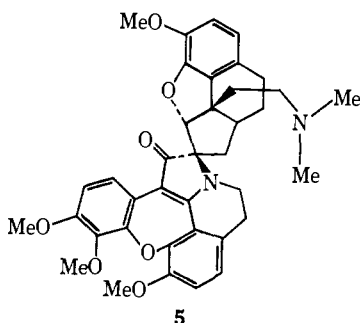
Received May 4, 1970



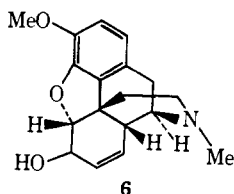
1, R = H
2, R = Me
3, R = COMe



4, R = H



5



6

(8) (a) T. Rüll, *Bull. Soc. Chim. Fr.*, 568 (1963); (b) T. Rüll and D. Gaznaire, *ibid.*, 2189 (1963); (c) S. Okuda, S. Yamaguchi, Y. Kawazoe, and K. Tsuda, *Chem. Pharm. Bull. (Tokyo)*, **12**, 104 (1964); (d) T. J. Batterham, K. H. Bell, and U. Weiss *Aust. J. Chem.*, **18**, 1799 (1965).

Reactions of the Nitrosonium Ion. I. The Reaction of Alkyl Azides with Nitrosonium Salts. A New Method for the Production of Carbonium Ions

Sir:

Interest in the reaction between azides and various sources of the nitrosonium ion has existed since Curtius attempted to produce hydrogen azide from hydrazine and nitrous acid.¹ Only recently, however, has the reaction between the azide ion and nitrous acid been

(1) T. Curtius, *Ber.*, **26**, 1263 (1893).