by the same enzyme and whether O-glucosides are normal metabolites of the corresponding hydroxyamino acids. These questions are being studied further.

Acknowledgement We are grateful to Prof. L. Fowden, Department of Botany and Microbiology, University College London, for his encouragement during the course of this work and for his critical review of the manuscript. We also are indebted to Prof. P.O. Larsen, Department of Organic Chemistry, Royal Veterinary and Agricultural College, Copenhagen, Denmark, for an authentic sample of L-tyrosine-O-β-D-glucoside.

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Received October 30, 1971

[Chem. Pharm. Bull. 20(4) 857—859 (1972)]

UDC 547.896.057

Syntheses of New 6,9,6 Ring System, 5H-Dibenz[*b.g*]azonine Derivatives

Most psychotropic drugs have tricyclic dibenzo ring system.

Major parts of them have concerned with 6,6,6 ring system (*e.g.* phenothiazine or acridane) or 6,7,6 ring system (*e.g.* dibenzocycloheptane or dibenzazepine). Although as a part of 6,8,6 ring system, many dibenz[*b.f*]azocines have been synthesized,[1] their homologue, 5H-dibenz[*b.g*]azonines have not yet been reported. We report herein the first syntheses of 6,11,12,13-tetrahydro-5H-dibenz[*b.g*]azonines having unknown ring system.

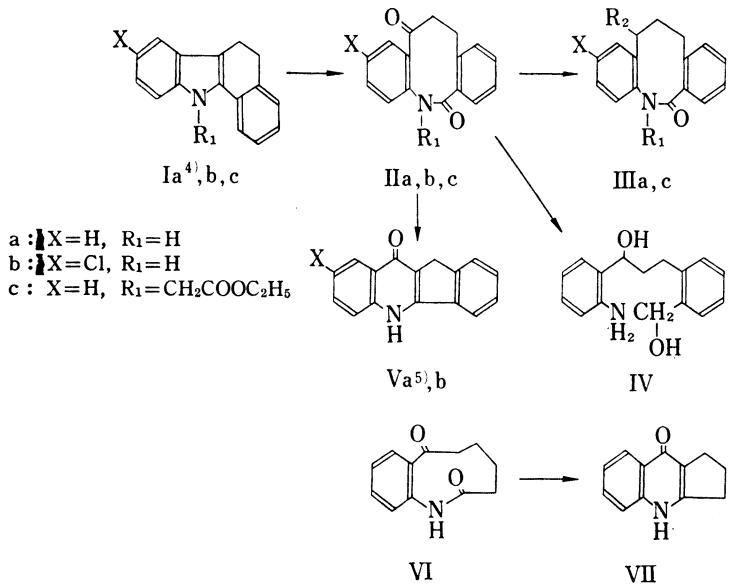

Chart 1

1) *e.g.* F. Sowinski and H.L. Yale, *Arz. Forsch.*, **14**, 117 (1964); O. Schindler, R. Blaser, and F. Hungiker, *Helv. Chim. Acta*, **49**, 985 (1966).

5,6-Dihydro-11H-benzo[*a*]carbazoles (I a,b,c) prepared from phenylhydrazines and 1-tetralone, were oxidized with ozone[2] in chloroform or with sodium periodate[3] in water-ethyl acetate to afford 6,11,12,13-tetrahydro-5H-dibenz[*b.g*]azonin-6,13-diones (II a,b,c).

IIa $C_{16}H_{13}O_2N$. M^+ 251. mp 169—172°. IR cm^{-1}: 1670 (KBr), 1645 (KBr)·NMR[6] (DMSO-d_6): 2.6—3.7 $C_{16}H_{12}O_2NCl$ (4H, complex signals).

IIb $C_{16}H_{12}O_2NCl$. M^+ 285. mp 160—162°. IR cm^{-1}: 1680 (KBr), 1630 (KBr)·NMR (DMSO-d_6): 2.4—3.7 (4H, complex signals).

IIc $C_{20}H_{19}O_4N$. M^+ 337. mp 129—131°. IR cm^{-1}: 1730 (KBr), 1650 (KBr)·NMR (DMSO-d_6): 2.4—3.4 (4H, complex signals), 4.18 and 4.80 (2H, AB quartet, J=17.5 Hz).

IIa,c were treated with $NaBH_4$ in ethanol for 2—3 hr to give lactam alcohols (IIIa,c R_2=OH). IIIa (R_2=OH) $C_{16}H_{15}O_2N$. M^+ 253. mp 185—188°. IR cm^{-1}: 1640 (KBr). IIIc (R_2=OH) $C_{20}H_{21}O_4N$. M^+ 339. mp 132—135°. IR cm^{-1}: 1730 (KBr), 1630 (KBr).

When IIa was treated with $NaBH_4$ in ethanol for two days at room temperature, not only ketone but also lactam was unexpectedly reduced and amino alcohol (IV) was obtained. IV $C_{16}H_{19}O_2N$. mp 104—105°. Infrared (IR) spectrum showed no absorption assigned to carbonyl. Chlorination of IIIa (R_2=OH) with thionyl chloride in chloroform gave the corresponding chloride (IIIa R_2=Cl).

Refluxing in toluene with amine such as morpholine, N-methylpiperazine or N-phenylpiperazine, the chloride gave amino lactams (IIIa R_2=morpholino, R_2=N-methylpiperazino and R_2=N-phenylpiperazino respectively).

IIIa (R_2=morpholino) $C_{20}H_{22}O_2N_2 \cdot 1/5\ H_2O$. M^+ 322. mp 236—239°. IR cm^{-1}: 1660 (KBr).

IIIa (R_2=N-methylpiperazino) $C_{21}H_{25}ON_3$. mp 233—236°. IR cm^{-1}: 1660 (KBr).

IIIa (R_2=N-phenylpiperazino, hydrochloride) $C_{26}H_{27}ON_3 \cdot HCl$. mp 265—270°. IR cm^{-1}: 1670 (KBr).

Indenoquinolinones (Va, b) were obtained by heating of IIa, b at 180°, and these results are analogous to the transformation of VI to VII reported by Witkop.[7]

IVa $C_{16}H_{11}ON$. mp above 300°. IR cm^{-1}: 1620 (KBr).

IVb $C_{16}H_{10}ONCl$. M^+ 267. mp above 300°. IR cm^{-1}: 1620 (KBr).

Although the structures of IIa,b,c were suggested from their physical data, furhter supports were obtained from mass spectrometry.[8] The mass spectra of IIa,b had the following peaks.

IIa *m/e* 251 (M^+ 23%), 234 (15%), 131 (8%), 120 (100%), 119 (17%), 103 (11%), 92 (20%), 77 (11%).

IIb *m/e* 287 (10%), 285 (M^+ 25%), 270 (11%), 268 (27%), 156 (35%), 154 (100%), 131 (19%), 126 (17%), 103 (20%), 90 (11%), 77 (17%).

The following fragmentations (Fig. 1) were assumed and most fragment peaks had corresponding metastable peaks.

These results were quite different from that of 5,6,11,12-tetrahydrodibenz[*b.f*]azocin-6,11-dione (VIII[9]) which was synthesized by oxidative cleavage of 5,10-dihydroindeno[1,2-*b*]indole. VIII $C_{15}H_{11}NO_2$·mp 280—282°. IR cm^{-1}: 1660 (KBr). NMR (DMSO-d_6): 3.88 and 4.48 (2H, AB quartet, J=15 Hz).

2) Y. Ban and Y. Sato, *Chem. Pharm. Bull.* (Tokyo), **13**, 1073 (1965).
3) L.J. Dolby and D.L. Booth, *J. Am. Chem. Soc.*, **88**, 1049 (1966).
4) J. Hausmann, *Chem. Ber.*, **22**, 2019 (1889).
5) B.K. Blaut, W.H. Perkin, Jr., and S.G.P. Plant, *J. Chem. Soc.*, **1927**, 1978.
6) Nuclear magnetic resonance (NMR) spectra were measured on Varian A-60 Spectrometer with tetramethylsilane as internal standard and chemical shifts were given in ppm.
7) B. Witkop, J.B. Patrick and, M. Rosenblum, *J. Am. Chem. Soc.*, **60**, 2641 (1951).
8) Mass spectra were taken on Hitachi Mass Spectrometer Model RMU-6L.
9) The derivatives of this compound were appeared on Japan Patent 23395 (1971), T. Okamoto, T. Kobayashi, and H. Yamamoto.

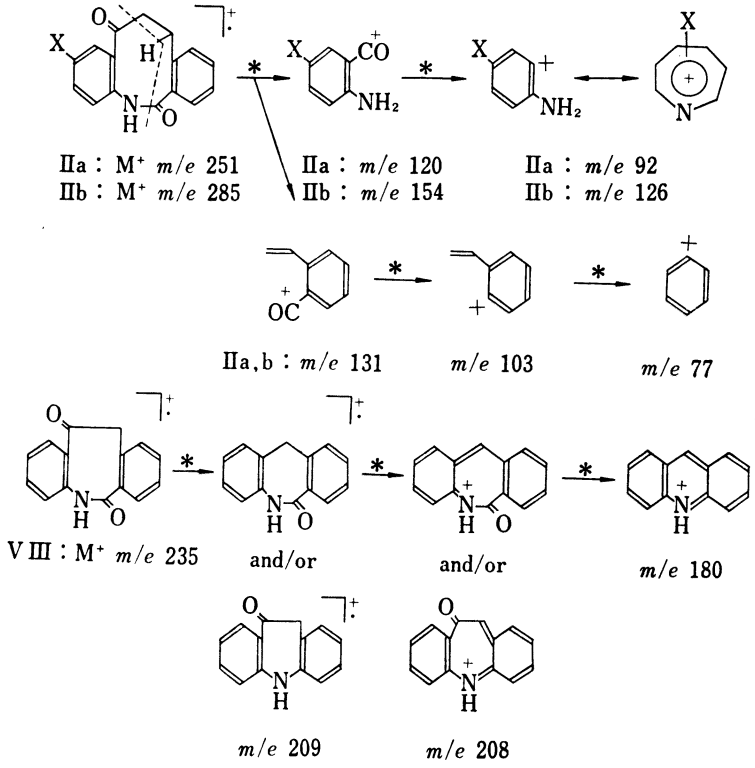

Fig. 1

On the mass spectrum of VIII the following peaks were observed and their peaks were assinged as Fig. 1. VIII *m/e* 237 (M^+ 100%), 209 (58%), 208 (35%), 181 (11%), 180 (43%), 119 (13%), 118 (15%), 90 (49%), 89 (28%), 64 (12%), 63 (16%).

Acknowledgement The authors wish to thank Drs. T. Mizuma, H. Takamatsu, S. Minami, S. Umemoto and H. Nishimura for their encouragement throughout this work, Mr. A. Itokawa for NMR measurements and Mr. K. Yoshida for Mass measurements.

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Received November 27, 1971