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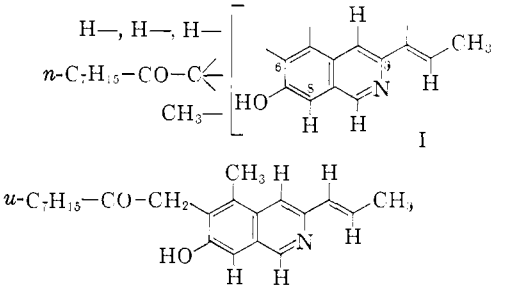
MONASCORUBRIN. I. "MONASCAMINONE," A DEGRADATION PRODUCT

Sir:

Monascorubrin, first isolated by Nishikawa[1] from *Monascus purpureus* Wentii, belongs to the group of azaphilones[2] such as sclerotiorin[3] and rotiorin.[4] Monascorubrin, m.p. 134–136°, $C_{23}H_{26}O_5$[5] (C, 72.2; H, 6.66), $[\alpha]^{16}_{700}$ −1500° (*c* 0.1% in EtOH), C—CH_3 2.5, reacts with ammonia[6] to give monascamine,[7] m.p. 192°, $C_{23}H_{27}O_4N$ (C, 72.2; H, 6.93; N, 4.10), $[\alpha]^{16}_{700}$ −2600° (*c* 0.125% in $CHCl_3$), which when treated with zinc in various media is converted into monascaminone (I),[8] m.p. 186°, $C_{22}H_{29}O_2N$ (C, 77.8; H, 8.50; N, 4.08), $[\alpha]_D$ 0°, λ^{EtOH}_{max} in mμ 253 (4.73), 302 (3.95) and 352 (3.78), ν^{KBr}_{max} in cm.$^{-1}$ 1710 (C=O).

Hydrogenation of I furnished dihydromonascaminone (II), m.p. 97–98°, λ^{EtOH}_{max} in mλ 239 (4.69), 288 (3.53) and 343 (3.69), ν^{KBr}_{max} 1717 cm.$^{-1}$ (C=O), and octahydromonascaminone (III), m.p. 181°, λ^{EtOH}_{max} in mμ 226 (3.90) and 282 (3.11). Thorough spectroscopic comparisons of II and derivatives with synthetic hydroxyisoquinolines established the nucleus to be 7-hydroxyisoquinoline.[9]

Beckmann rearrangement of monascaminone oxime, m.p. 211°, gave *n*-heptylamine. Treatment of I with sodium borohydride afforded monascaminol (IV), m.p. 196–197°, $C_{22}H_{31}O_2N$ (C, 77.1; H, 9.10; N, 4.31), λ^{MeOH}_{max} in mμ 256 (4.80), 307 (3.88) and 352 (3.77), which when heated in polyphosphoric acid at 150° gave dehydromonascaminol (V), m. 192–3°, $C_{22}H_{29}ON$ (C, 81.3; H, 9.34), λ^{EtOH}_{max} in mμ 225 (4.33), 262 (4.59), 318 (3.75) and 352 (3.69). The infrared peak at 1710 cm.$^{-1}$ in I, and comparisons of the ultraviolet peaks of IV and V with I demonstrate that the *n*-heptoyl chain must be attached to the aromatic nucleus through one saturated carbon atom. Permanganate oxidation of I afforded pyridine-1,3-4-tricarboxylic acid. Ozonolysis of O-acetylmonascaminone, m.p. 76–79°, gave acetaldehyde, and subsequent hydrogen peroxide oxidation of the nonvolatile ozonolysis product furnished an acid, m.p. 240°, $C_{22}H_{27}O_5N$ (C, 68.1; H, 7.06; N, 3.20), which gave an intense orange color with ferrous sulfate.[10] Accordingly, a propenyl group is attached to C-3. The C-8 position should be vacant because of the positive diazo coupling reactions of I and derivatives. Taking into account the presence of three C–CH_3 groups in monascaminone, these results can be expressed by the partial structure I, and evidence to extend this to VI was provided by structure considerations of monascorubrin (following communication).



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(1) H. Nishikawa, *J. Agr. Chem. Soc Japan*, **5**, 1007 (1932).

(2) A. D. G. Powell, A. Robertson and W. B. Whalley, *Chem. Soc.*, Special Publ., No. 5, 27 (1956).

(3) G. B. Jackman, A. Robertson, R. B. Travers and W. B. Whalley, *J. Chem. Soc.*, 1814 (1958); J. H. Birkinshaw and P. Chaplen, *Biochem. J.*, **69**, 505 (1958); H. Watanabe, *J. Pharm. Soc. Japan*, **72**, 807 (1952); Y. Yamamoto and N. Nishikawa, *ibid.*, **79**, 297 (1959).

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(5) Analyses of monascorubrin and derivatives also agree with the $C_{23}H_{24}O_5$ formula adopted by Nishikawa[1] and Powell, *et al.*[2]

(6) Hence the name azaphilones.

(7) Also a fungal metabolite; described as monascorubramine in reference 2.

(8) Described as dideoxymonascorubramine in reference 2.

(9) These results will be reported elsewhere in detail.

(10) H. Ley, Chr. Schwarte and O. Münnich, *Ber.*, **57**, 349 (1924).

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MONASCORUBRIN. II.[1] STRUCTURES OF MONASCORUBRIN AND MONASCAMINE

Sir:

Probable structures I and II are assigned to monascorubrin and monascamine, respectively, and the partial structure of monascaminone (III)[1] is completed. Comparisons of the ultraviolet and infrared (1600–1500 cm.$^{-1}$ skeletal stretching region) of I and II and their dihydro derivatives suggested that the conversion involved was merely an exchange of –O– for –NH–. Furthermore, production of III under various conditions indicated the absence of skeletal rearrangements, and thus the framework of III is retained in I and II. The five-membered lactone[2] and ke-

TABLE I

INFRARED CARBONYL BANDS, CM.$^{-1}$

Monascorubrin (I) (CCl_4)	1759	1729
Monascamine (II) (CCl_4)	1734	1705
Monascamine-HCl (KBr)	1745	1718
N-Methylmonascamine (CCl_4)	1733	1712
Tetrabromomonascamine[2] (KBr)	1796	1742
Secomonascamine (IV) (KBr)	1703	
Tetrabromosecomonascamine[2] (KBr)	1795	1742
Secomonascamine-HCl, Form A (Nujol)	1715	
Form B (KBr)	1745	1725

(1) Paper I, preceding communication.

(2) Though definite structures cannot yet be assigned to tetrabromomonascamine, m.p. 88–91°, $C_{23}H_{25}O_4NBr_4$, and tetrabromosecomonascamine, m.p. 138–140°, $C_{23}H_{27}O_4NBr_4$, their infrared spectra serve to demonstrate the presence of an α-bromo-γ-lactone. The lactone is lost as carbon dioxide during the conversion of II to III.