and Mr. D. Y. Yee formerly of New York University for determining the mass spectrum of the nitrogen trifluoride sample. This work was supported by the Air Force under Contract No. AF33(616)-5222, Mr. Forrest Forbes, Project Engineer.

REACTION MOTORS DIVISION
THIOKOL CHEMICAL CORPORATION
DENVILLE, NEW JERSEY
SCOTT I. MORROW
DONALD D. PERRY
MURRAY S. COHEN

RECEIVED SEPTEMBER 21, 1959

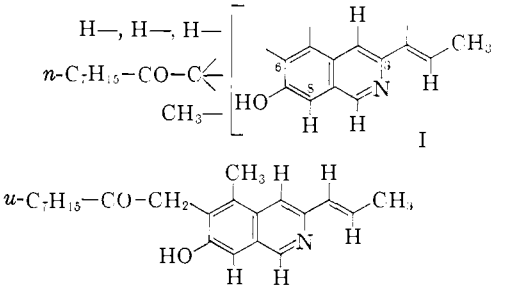
MONASCORUBRIN. I. "MONASCAMINONE," A DEGRADATION PRODUCT

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).



I

(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).

(4) G. B. Jackman, A Robertson, R. B. Travers and W. B. Whalley, *J. Chem. Soc.*, 1825 (1958).

(5) Analyses of monascorubrin and derivatives also agree with the $C_{22}H_{24}O_5$ 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).

CHEMICAL INSTITUTE
NAGOYA UNIVERSITY
CHIKUSA, NAGOYA
MAMORU OHASHI
SHO-ICHIRO KUMASAKI
SHOSUKI YAMAMURA

DEPARTMENT OF CHEMISTRY
TOKYO KYOIKU UNIVERSITY
OTSUKA, BUNKYO, TOKYO
(INQUIRIES TO)
KOJI NAKANISHI

PHARMACY DEPARTMENT
NAGOYA CITY UNIVERSITY
MIZUHO, NAGOYA
HISASHI KOIKE

RECEIVED SEPTEMBER 9, 1959

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

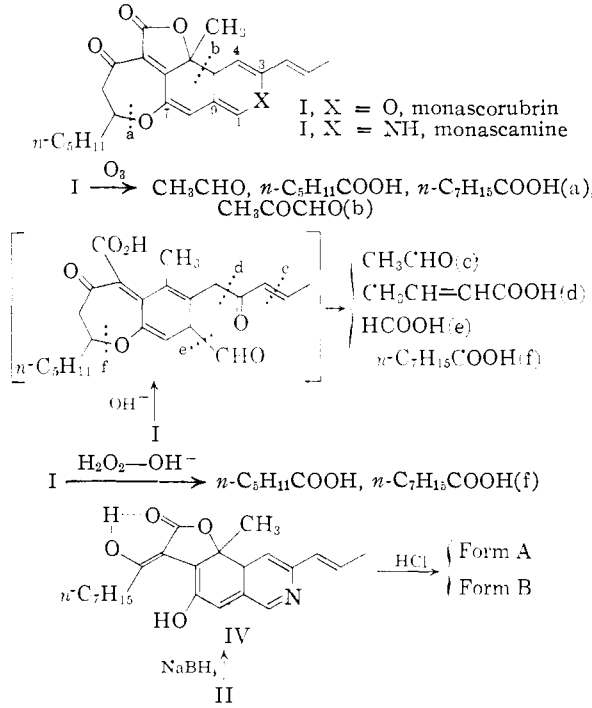
(1) Paper I, preceding communication.

(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.

tonic group are conjugated with the annular heteroatom X since the shift of the infrared bands to lower wave numbers in the conversion of I to II is not due to a C=O· · ·H–N hydrogen bonding as evidenced by the band positions of N-methylmonascamine, m.p. 105°. The assumption also is supported by the hypsochromic shifts in infrared peaks of II–HCl, m.p. 198–202°, and accordingly the n-C_7H_{15}-CO-C- side-chain in III can only be attached to C-6.

SCHEME I

(parenthesized letters show position of cleavage)



Production of acetaldehyde from I and butyric acid from dihydromonascorubrin, m.p. 119–121°, upon ozonolysis requires attachment of a propenyl group at C-3 and a double bond at C_3-C_4. The C_1-C_9 double bond accounts for the production of formic acid with alkali.[3] Secomonascamine (IV), m.p. 218–220°, $C_{23}H_{29}O_4N$ (C, 72.1; H, 7.71; N, 3.74), positive enol tests, showed only a single carbonyl absorption, and this suggested the two carbonyl functions to be located in positions capable of conjugate chelation. Secomonascamine hydrochloride, m.p. 125°, was obtained in two modifications, the unstable A and stable B. Form A presumably results from simple N-protonation of structure IV (hypsochromic shift of infrared peak, 1703→1715 cm.$^{-1}$; also presence of immonium band besides ammonium band), whereas Form B corresponds to the N-protonated form of II cleaved at dotted line (a) (infrared peaks compare well with those of monascamine hydrochloride). Structures I and II are consistent with current biogenetic considerations.[4]

(3) *E.g.*, D. H. Johnson, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 2971 (1950); J. C. Roberts and C. W. H. Warren, *ibid.*, 2992 (1955); N. B. Graham, H. Page, A. Robertson, R. B. Travers, K. Turner and W. B. Whalley, *ibid.*, 4924 (1957).

(4) A. J. Birch, P. Fitton, E. Pride, A. J. Ryan, H. Smith and W. B. Whalley, *ibid.*, 4576 (1958).

The authors wish to thank Professor H. Nishikawa, formerly of Nagoya University, for an abundant supply of starting material and suggestions, and Professor Y. Hirata, Nagoya University, for encouragements.

DEPARTMENT OF CHEMISTRY
TOKYO KYOIKU UNIVERSITY
OTSUKA, BUNKYO, TOKYO
CHEMICAL INST.
NAGOYA UNIV.
CHIKUSA, NAGOYA

(INQUIRIES TO)
KOJI NAKANISHI
MAMORU OHASHI
SHO-ICHIRO KUMASAKI
SHOSUKE YAMAMURA

RECEIVED SEPTEMBER 9, 1959

TWO NEW SYNTHESES OF NITRILES FROM ALDEHYDES, USING O,N-BIS-(TRIFLUOROACETYL)-HYDROXYLAMINE OR TRIFLUOROACETOHYDROXAMIC ACID

Sir:

There are a number of methods of preparing nitriles from the corresponding aldehydes,[1] most of which require vigorous reaction conditions or involve several steps. We have found that O,N-bis-(trifluoroacetyl)-hydroxylamine (I) reacts with aldehydes in a one-step reaction to give the corresponding nitriles. Yields are mostly between 70–90% (Table I). Reaction conditions are mild: a solution of I, the aldehyde, and pyridine (molar ratio 1:1:2) in benzene is heated to reflux for 1–2 hours; the reaction also proceeds smoothly at room temperature, but more slowly.

TABLE I

SYNTHESES OF NITRILES FROM ALDEHYDES AND BIS-(TRIFLUOROACETYL)-HYDROXYLAMINE

Aldehyde	Nitrile	Yield, %
Heptanal	Heptanenitrile	71.5
Veratraldehyde	Veratronitrile	86.6
Salicylaldehyde	Salicylonitrile	53.6
Anisaldehyde	Anisonitrile	73.7
Cinnamaldehyde	Cinnamonitrile	87.6
3-Indolecarboxaldehyde	3-Indolecarbonitrile	82.0
m-Nitrobenzaldehyde	*m*-Nitrobenzonitrile	78.9

O,N-Bis-(trifluoroacetyl)-hydroxylamine is prepared readily by refluxing 3.2 moles of trifluoroacetic anhydride with 1 mole of hydroxylamine hydrochloride for 1.5 hours. After removal of trifluoroacetic acid and trifluoroacetyl chloride under vacuum, the residue is recrystallized from dichloromethane. The product is an 80% yield of hygroscopic and easily volatile needles of O,N-bis-(trifluoroacetyl)-hydroxylamine; 50° (transition), m.p. 62° (with sublimation, in a sealed capillary, Kofler hot stage). (*Anal.* Calcd. for $C_4HF_6NO_3$: C, 21.35; H, 0.45; N, 6.22; neut. eq., 112.5. Found: C, 21.73; H, 0.78; N, 6.45; neut. eq., 112.8.)

It also has been found that trifluoroacetohydroxamic acid ($CF_3CONHOH$) reacts with aldehydes to give nitriles, although more slowly and in a lower yield under similar conditions. Trifluoroacetohydroxamic acid was prepared in 74% yield by the reaction of 2.1 moles of trifluoroacetic anhydride with hydroxylamine hydrochloride, and then re-

(1) *Cf.* reviews by V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publ. Corp., New York, N. Y., 1947, p. 2; D. T. Mowry, *Chem. Rev.*, **42**, 189 (1948); P. Kurtz in "Methoden der Organischen Chemie (Houben-Weyl)," Georg Thieme Verlag, Stuttgart, 1952, Vol. VIII, pt. 3, p. 265.