charcoal) and evaporated. The residue was taken up in a minimum amount of 95% ethanol and cooled. The crystalline product was collected and recrystallized repeatedly until only a single radioactive spot could be seen after radioscanning a tlc strip.

TABLE III

Isomer	Amt used, mg	Reaction time, hr	% recovery	% exchange	Spec act., μcuries/mg
IIa	450	12	51	50.9	9.95
IIb	450	15	42	52.4	9.13
IIc	500	9.5	63	26.7	4.98

Acknowledgment.—The authors are grateful to Dr. William H. Beierwaltes for his interest and encouragement during the course of this work. Support for this investigation was provided by Grants CA-08349-01 from the National Cancer Institute, U. S. Public Health Service, Bethesda, Md., and PRA-18 from the American Cancer Society, New York, N. Y. Grants from the Horace H. Rackham School of Graduate studies and the Cancer Research Institute of the University of Michigan contributed to the initiation of this study.

Tumor Inhibitors. XXV. The Synthesis and Evaluation of 9-Nitro-1,2,3,4-tetrahydrophenanthrene-8-carboxylic Acid[1]

S. MORRIS KUPCHAN AND MICHAEL MOKOTOFF[2]

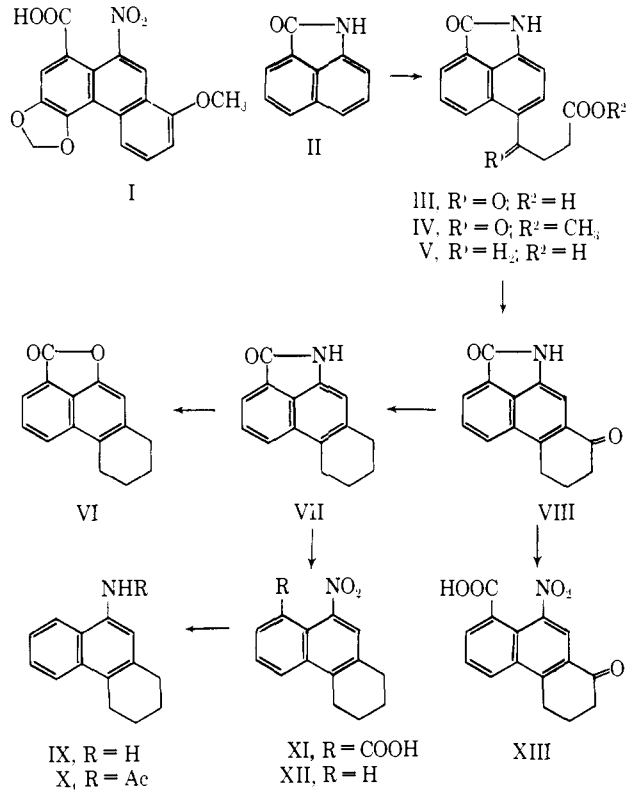
Department of Pharmaceutical Chemistry, University of Wisconsin, Madison, Wisconsin

Received April 7, 1967

In the course of a continuing search for tumor inhibitors of plant origin, aristolochic acid (I) was characterized as a tumor (Adenocarcinoma 755)-inhibitory principle from *Aristolochia indica* L.[3] A subsequent report described a synthetic approach to aristolochic acid and related phenanthrene carboxylic acids.[4] We report herewith the synthesis and evaluation of an aristolochic acid analog without oxygen ether functions and with a saturated ring, namely 9-nitro-1,2,3,4-tetrahydrophenanthrene-8-carboxylic acid (XI).

Naphthostyril (8-amino-1-naphthoic acid lactam, II) proved to be a useful starting material for a Haworth synthesis of XI (see Scheme I). In accord with expectation based upon analogy to similar acylations of acetyl derivatives of aniline[5] and 1-aminonaphthalene,[6] succinoylation of naphthostyril afforded III, with the acyl group *para* to the amido nitrogen. Attempts at Clemmensen reduction of III or its methyl ester (IV) were unsuccessful. However, Wolff–Kishner reduction under the conditions of Huang-Minlon[7] gave γ-(5-naphthostyril)butyric acid (V). Cyclization of V with polyphosphoric acid[8] proceeded smoothly to yield 1-keto-9-amino-1,2,3,4-tetrahydrophenanthrene-8-carboxylic lactam (VIII). Huang-Minlon reduction of VIII gave VII. Lactam VII was hydrolyzed with NaOH in refluxing aqueous dioxane, and the liberated amino acid was directly converted, *via* a Sandmeyer reaction,[9,10] to 9-nitro-1,2,3,4-tetrahydrophenanthrene-8-carboxylic acid (XI) in 37% yield. The Sandmeyer reaction was markedly pH dependent, and a satisfactory yield was obtained only at about pH 6.5. Under more strongly acidic conditions the yield of desired product decreased, and the principal isolable product was 9-hydroxy-1,2,3,4-tetrahydrophenanthrene-8-carboxylic acid lactone (VI). An alternative projected route to XI was VIII → XIII → XI. However, the poor yield in the Sandmeyer-type conversion of VIII to 1-keto-9-nitro-1,2,3,4-tetrahydrophenanthrene-8-carboxylic acid (XIII) made this approach less practical.

SCHEME I



The structure of XI was proven by decarboxylation to 9-nitro-1,2,3,4-tetrahydrophenanthrene (XII), and this was characterized by conversion to the known 9-amino-1,2,3,4-tetrahydrophenanthrene (IX)[11] and 9-acetylamino-1,2,3,4-tetrahydrophenanthrene (X).[11]

Compounds VII and XI were evaluated for tumor-inhibitory activity against Adenocarcinoma 755 in mice and against human carcinoma of the nasopharynx carried in cell culture (KB).[12] No significant inhibitory

(1) (a) Part XXIV: S. M. Kupchan, T.-H. Yang, G. S. Vasilikiotis, M. H. Barnes, and M. L. King, *J. Am. Chem. Soc.*, **89**, 3075 (1967). (b) This investigation was supported by research grants from the National Cancer Institute (CA-04500) and the American Cancer Society (T-275).

(2) American Foundation for Pharmaceutical Education Fellow, 1963–1965.

(3) S. M. Kupchan and R. W. Doskotch, *J. Med. Pharm. Chem.*, **5**, 657 (1962).

(4) S. M. Kupchan and H. C. Wormser, *J. Org. Chem.*, **30**, 3792 (1965).

(5) J. P. English, R. C. Clapp, Q. P. Cole, and J. Krapcho, *J. Am. Chem. Soc.*, **67**, 2263 (1945).

(6) N. J. Leonard and A. M. Hyson, *ibid.*, **71**, 1392 (1949).

(7) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(8) F. Uhlig and H. R. Snyder, *Advan. Org. Chem.*, **1**, 35 (1960).

(9) H. Goldstein and P. Francey, *Helv. Chim. Acta*, **15**, 1362 (1932).

(10) E. R. Ward, C. D. Johnson, and J. G. Hawkins, *J. Chem. Soc.*, 894 (1960).

(11) W. E. Bachmann and M. W. Cronyn, *J. Org. Chem.*, **8**, 456 (1943).

(12) Cytotoxicity and *in vivo* inhibitory activity were assayed under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health. The procedures were those described in *Cancer Chemotherapy Rept.*, **25**, 1 (1962).

activity was observed for either of the compounds tested.

Experimental Section[13]

γ-(5-Naphthostyril)-γ-ketobutyric Acid (III).—A suspension of 4.0 g (24 mmoles) of naphthostyril and 4.8 g (48 mmoles) of finely powdered *succinic* anhydride in *sym*-tetrachloroethane was cooled in ice and stirred vigorously. Anhydrous powdered $AlCl_3$ (26.0 g, 196 mmoles) was added over a 2-hr period. The ice bath was removed and the stirring was continued for approximately 72 hr. When the initial yellow suspension became green (about 1 hr after the addition of the $AlCl_3$) the reaction mixture thickened. The mixture was treated (while cooling in ice) with 100 ml of 10% HCl and steam distilled until no more tetrachloroethane came over; the hot yellow mixture was immediately filtered. This yielded a brown precipitate (A) and yellow filtrate (B). Precipitate A was suspended in aqueous Na_2CO_3, stirred for 1 hr, and filtered, and the brown filtrate was cautiously acidified with HCl to yield 3.1 g of crude product (III), mp >275° dec. Filtrate B, upon cooling, deposited a precipitate which was shown to be mainly crude naphthostyril. Treating the recovered crude naphthostyril with Na_2CO_3 solution and acidifying the filtrate yielded 0.2 g of III. Recovered naphthostyril weighed 1.3 g. Both crops of III were combined and recrystallized from boiling acetic acid with Norit to yield 2.8 g (42%) of light mint colored fine needles, mp ~278° dec. Repeated crystallizations yielded fine yellow needles: mp ~278° dec; λ_{max} 5.80–5.98 μ (s); λ_{max} 237 mμ (ε 16,000), 252.5 (14,000), 326 (52200). The yield of III, based on unrecovered naphthostyril, was 63%.

Anal. Calcd for $C_{15}H_{11}NO_3$: C, 66.91; H, 4.12; N, 5.20; neut equiv, 269. Found: C, 66.72; H, 4.31; N, 5.17; neut equiv, 266.

The methyl ester IV was prepared by CH_2N_2 methylation of the acid III. Recrystallizations from toluene gave yellow needles: mp 181.5–183°; λ_{max} 5.76, 5.80–5.98 μ.

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 67.84; H, 4.63; N, 4.95. Found: C, 67.57; H, 4.91; N, 4.75.

γ-(5-Naphthostyril)butyric Acid (V). A mixture of ketone III (3.50 g, 13 mmoles), KOH (3.70 g, 66 mmoles), and 85% hydrazine hydrate (3.8 ml) in diethylene glycol (35 ml) was treated by the procedure of Huang-Minlon.[7] The cooled dark brown solution was poured into 150 ml of water to form a clear solution, which yielded a precipitate when poured into 70 ml of cold 6 *N* HCl. The yield of crude green precipitate V was 2.8 g. The crude precipitate V was dissolved in aqueous Na_2CO_3 solution and filtered free of nonacidic substances and the filtrate was acidified to yield 2.1 g of green precipitate, mp 200–220°. A portion of the product (0.23 g) was further purified by adsorbing onto 1.0 g of silicic acid, which was added as a dry powder to 6.0 g of silicic acid packed in benzene. The desired product V was eluted with 10% MeOH in $CHCl_3$ (0.19 g), mp 220–225°. Repeated crystallizations from tetrahydrofuran (THF) gave an analytical sample of V: mp 225–227°; λ_{max} 340 mμ (ε 4100), 324 (7750), 256.5 (22,200), 213 (34,400).

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.67; H, 5.25; N, 5.61.

Lactam of 1-Keto-9-amino-1,2,3,4-tetrahydrophenanthrene-8-carboxylic Acid (VIII). Polyphosphoric acid (25 g) was weighed directly into a tared 150-ml beaker and heated to about 80°. While stirring, the acid V (2.5 g, 10 mmoles) was added, and gradually the suspension became a dark brown-red solution. The reaction proceeded for 30 min and then was stopped by pouring the solution into cold water, to yield a yellow-green precipitate. This precipitate was suspended in Na_2CO_3 solution to remove unreacted acid. The nonacidic product was sublimed at 210° (0.3 mm) to yield yellow crystalline product VIII, 1.8 g (74%). The melting point was indefinite; the compound sublimed and decomposed above 270°. One resublimation gave an analytical sample: λ_{max} 5.90 (s) (lactam carbonyl), 6.01 μ (s) (ketone); λ_{max} 237 mμ (ε 27,000), 271 (32,500), 273 (33,000), 348 (3200).

Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.99; H, 4.81; N, 5.88.

The **2,4-dinitrophenylhydrazone** was recrystallized from dimethylformamide to give rust-colored needles, mp >290° dec.

Anal. Calcd for $C_{21}H_{15}N_5O_5$: C, 60.43; H, 3.62; N, 16.78. Found: C, 60.44; H, 3.71; N, 16.55.

Lactam of 9-Amino-1,2,3,4-tetrahydrophenanthrene-8-carboxylic Acid (VII). To a solution of KOH (1.00 g, 18 mmoles) in 12 ml of diethylene glycol, were added ketone VIII (0.90 g, 3.8 mmoles) and 1.0 ml of 85% hydrazine hydrate. The procedure and work-up were identical with those for the reduction of ketone III. After acidification, a greenish precipitate (0.76 g) was obtained, mp 210–240°. This was dissolved in THF and adsorbed onto 1.0 g of Merck alumina by gradual evaporation of the solvent. This dry mixture was added to 21 g of the same adsorbent in benzene. Compound VII was eluted with $CHCl_3$; yield 0.64 g (76%), mp 225–230°. Repeated crystallizations from acetone–water, followed by sublimation at 150° (0.1 mm), yielded an analytical sample of VII: mp 238–239°; λ_{max} 5.93 μ (lactam carbonyl); λ_{max} 261 mμ (ε 27,000), 325 (33,000), 341 (43,000).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.35; H, 6.04; N, 6.29.

9-Nitro-1,2,3,4-tetrahydrophenanthrene-8-carboxylic Acid (XI). To a solution of NaOH (0.57 g, 14 meqniv) in hot water (10 ml) was added a solution of the lactam V (0.45 g, 0.7 mmole) in dioxane (6 ml), and the mixture was refluxed for 17 hr. The resulting orange solution was cooled in ice and $NaNO_2$ (0.40 g, 5.8 mmoles) was added. The solution was added dropwise to an ice-cooled solution of 5.0 ml (60 meqniv) of HCl and 10 ml of water (positive β-naphthol test). The resulting orange suspension was added with cooling to a suspension of $NaNO_2$ (4.5 g, 65 mmoles), $NaHCO_3$ (3.5 g), $CuSO_4 \cdot H_2O$ (0.8 g), and Cu_2O (0.5 g) in 50 ml of water. The resulting foam was broken with a few milliliters of ether. The solution was stirred for 2 hr and allowed to stand overnight. The suspension was filtered and the filtrate (pH ~6.5) was acidified (HCl) to yield a light buff colored precipitate of XI, 0.068 g (37%), mp 245–260°. Repeated crystallizations from acetone–water, with Norit, gave an analytical sample of XI as light yellow crystals: mp 262–265° dec; λ_{max} 5.94, 6.59, 7.43 μ; λ_{max} 232 mμ (ε 43,000).

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.91; H, 4.69; N, 5.3.

Lactone of 9-Hydroxy-1,2,3,4-tetrahydrophenanthrene-8-carboxylic Acid (VI). A mixture of lactam VII (0.50 g, 2.2 mmoles), NaOH (2.0 g, 50 meqniv), dioxane (21 ml), and water (38 ml) was refluxed for 24 hr. Sodium nitrite (1.25 g, 18 mmoles) was added and the solution was added dropwise to a solution of concentrated HCl (18 ml, 216 meqniv) and water (32 ml). The resulting orange suspension of the diazonium salt was added to $NaNO_2$ (15.0 g), $CuSO_4 \cdot H_2O$ (2.5 g), $NaHCO_3$ (5.0 g), and Cu_2O (2.0 g) in water. The mixture showed evolution of brown NO_2 and a decidedly acid reaction to pH paper. The suspension was filtered and the precipitate was extracted with acetone, to yield lactone VI. Recrystallization from acetone–water afforded yellow needles (0.18 g, 36%), mp 164.5–166°. Recrystallization twice more from acetone gave yellow prisms, mp 168–168.5°; λ_{max} 5.64 μ (γ-lactone).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.37; H, 5.44.

1-Keto-9-nitro-1,2,3,4-tetrahydrophenanthrene-8-carboxylic Acid (XIII). The procedure described for the synthesis of XI was followed, using 0.40 g (1.7 mmoles) of keto lactam VIII. Upon acidification of the filtrate, a pinkish tan precipitate (0.16 g) was obtained. This precipitate was collected and dissolved in a small amount of methanol and adsorbed onto 0.4 g of Davison silica gel by evaporation of the solvent. The dry orange powder was added to 7.1 g of the same adsorbent packed in benzene. The fractions eluted with 10% ether in benzene were combined (0.10 g, 21%), mp 230–235°. The combined material was rechromatographed in the same way on 4.8 g of silica gel, and again the fractions eluted with 10% ether in benzene were combined (0.077 g). Repeated crystallizations from methanol–water gave an analytical sample of XIII: mp 239–241°; λ_{max} 6.58, 7.44 μ (nitro group); λ_{max} 257 mμ (ε 40,100), 310 (5330).

Anal. Calcd for $C_{15}H_{11}NO_4$: C, 63.16; H, 3.89; N, 4.91. Found: C, 63.58, 63.44; H, 3.39, 3.97; N, 5.04.

(13) Melting points were determined on a Fisher-Johns melting point stage which had been calibrated with standard samples; melting points above 250° are uncorrected. Ultraviolet absorption spectra were determined in 95% ethanol on a Beckman (Model DK2A) recording spectrophotometer and a Cary (Model 11-MS) recording spectrophotometer. Infrared absorption spectra were recorded in KBr as microdisks (magnified with a Beckman beam condenser) on a Beckman (Model 5A) double-beam infrared recording spectrophotometer. Microanalyses were performed by Mr. J. F. Alicino, Metuchen, N. J. Skellysolve B refers to petroleum ether fraction boiling at 60–68°. The naphthostyril was obtained from K and K Laboratories and recrystallized from benzene with Norit treatment.

9-Nitro-1,2,3,4-tetrahydrophenanthrene (XII).—A mixture of XI (0.05 g, 0.18 mmole), copper (0.075 g, electrolytic metal, Fisher), and quinoline (8 ml) was heated for 15 min at reflux temperature. The dark brown solution was cooled, dissolved in $CHCl_3$, and filtered free of copper. The $CHCl_3$ solution was extracted four times with 10% HCl, twice with saturated $NaHCO_3$, twice with water, and dried (Na_2SO_4). The $CHCl_3$ was evaporated under reduced pressure to leave a brown oily residue (0.046 g) which was dissolved in a minimum amount of Skellysolve B and chromatographed on 1.5 g of Merck alumina in Skellysolve B. The second 10-ml fraction eluted with Skellysolve B yielded 0.024 g (61%) of yellow crystalline material (XII), mp 75.5–76.5°, $\lambda_{max}^{CHCl_3}$ 6.63 and 7.46 μ, which was used as such for reduction.

9-Acetylamino-1,2,3,4-tetrahydrophenanthrene (X).—A mixture of 0.027 g (0.12 mmole) of XII, 0.080 g (1.2 g-atoms) of zinc dust, and acetic acid (3.5 ml) was refluxed for 1.5 hr. The suspension was filtered hot, and the resulting yellow filtrate was diluted with water and the solution was evaporated to dryness under reduced pressure. The residue (0.023 g) was taken up in $CHCl_3$ and dried (Na_2SO_4). Evaporation of the $CHCl_3$ under reduced pressure left a semisolid brown residue which was dissolved in a minimum amount of benzene and chromatographed on 1.0 g of Merck alumina in benzene. Fractions (10 ml) were collected, and fractions 3, 4, and 5, eluted with 5% ether in benzene, yielded light yellow material. These fractions were combined, dissolved in benzene, and rechromatographed on 1.0 g of Davison silica gel in benzene. The fractions eluted with 10% ether in benzene yielded crystalline residues; these were combined and recrystallized from ethanol–water with Norit to afford colorless fine needles (2 mg): mp 192.5–193°; λ_{max} 3.04 (s), 3.26 (w) (NH of amide), 6.05 μ (s) ("amide-I band"). The latter physical data supported characterization of the material as X (lit.[11] mp 191–192° from ethanol).

9-Amino-1,2,3,4-tetrahydrophenanthrene (IX).—The nitro compound XII was reduced catalytically with Pt and hydrogen. Recrystallization of the product from Skellysolve B gave light tan crystals: mp 76–77°; λ_{max} 2.89 (s), 2.96 (w) (free NH_2 stretching), 6.18 μ (w) (NH bending). The literature[11] reports mp 76.5–77° for IX from ethanol–methanol.

New Compounds

A Direct Synthesis of 1-β-D-Arabinofuranosyl-5-fluorocytosine[1]

F. KELLER, J. E BUNKER, AND A. R. TYRRILL

Medicinal Chemistry Section, Research Division, Riker Laboratories, Division of Rexall Drug and Chemical Company, Northridge, California 91326

Received March 15, 1967

The interesting cancer chemotherapeutic agent, 1-β-D-arabinofuranosyl-5-fluorocytosine (1), has recently been synthesized[2] by an application of the Fischer-Helferich procedure[3] in a seven-step sequence. The Hilbert-Johnson[4] method when applied to the synthesis of this compound has resulted in a more direct synthesis of 1 and 1-β-D-arabinofuranosyl-5-fluorouracil (**2**).[2,3,5,6]

An unusual feature of the nmr spectra of the nucleosides in the 5-fluoropyrimidine series was the appearance of a pair of doublets for the anomeric hydrogen rather than the expected doublet which is attributed to an apparent long-range coupling effect of the 5-fluoro group on the C_1' proton[7] (see Table I). The effect is also evident in the very recently published nmr spectra of α- and β-5-fluoro-2-deoxyuridine,[8] wherein the pattern for the anomeric proton appears as a split triplet (multiplet of six) and a split pair of doublets (multiplet of eight) in the β and α anomers, respectively, rather than the normal patterns consisting of a triplet (pseudo-triplet) or a pair of doublets (multiplet of four) expected in the nonfluorinated compounds.[9,10]

TABLE I

60-MC NMR SPECTRA OF $C_1'H$ IN 1-β-D-ARABINOFURANOSYLPYRIMIDINES

Base	τ[d]	Description	J, cps
5-Fluorouracil (**2**)	4.02[a]	Pair of doub	4, 2
2',3',5'-Tri-O-acetate of **2**	3.72[b]	Pair of doub	4.5, 2
5-Fluorocytosine (1)	3.98[a]	Pair of doub	4, 2
5-Fluoro-4-methoxy-1H-pyrimidin-2-one (**3**)	3.99[a]	Pair of doub	4, 2
4-Methoxy-5-methyl-1H-pyrimidin-2-one	3.94[a]	Doub	4
Cytosine	3.88[c]	Doub	4.5
Uracil 2',3',5'-tri-O-acetate	3.64[b]	Doub	4
Thiouracil 2',3',5'-tri-O-acetate	3.66[b]	Doub	4

[a] In DMSO-d_6. [b] In $CDCl_3$. [c] In D_2O. [d] Relative to TMS internal standard for organic solvents and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for D_2O.

Experimental Section

1-(β-D-Arabinofuranosyl)-5-fluoro-4-methoxy-1H-pyrimidin-2-one (3).—2',3',5'-Tri-O-benzyl-1-(*p*-nitrobenzoyl)-D-arabinofuranose[11] (28.5 g, 0.05 mole) was added to dry methylene chloride (350 ml) which had been saturated with HCl at 0°. The solution was allowed to stand at 0° for 2 hr while bubbling in a slow stream of anhydrous HCl. The *p*-nitrobenzoic acid which had separated in nearly quantitative yield was removed by rapid filtration through a sintered-glass funnel. The filtrate was concentrated to dryness *in vacuo* (bath 40°) and evacuated (0.1 mm) for 16 hr (25°). The residual chloro sugar was dissolved in dry CH_2Cl_2 (320 ml) and 2,4-dimethoxy-5-fluoropyrimidine[12] (7.9 g, 0.05 mole) in CH_2Cl_2 (80 ml) was added along with molecular sieves[13] (20 g). The mixture was stirred for 3 days at ambient temperature protected by a drying tube. The mixture was filtered (Celite) and the filtrate and a CH_2Cl_2 wash were combined and concentrated *in vacuo* to a pale yellow syrup (29.2 g). The syrup was dissolved in dry CH_3OH (400 ml) and hydrogenated in two batches each using freshly prereduced $PdCl_2$ (3 g) and an initial hydrogen pressure of 3 atm. Reduction was complete in 15 min and the systems were bled free of hydrogen and flushed with N_2 and the mixtures were filtered from the catalyst. The catalyst was washed with CH_3OH and the filtrates and washes were neutralized by stirring with Dowex

(1) This work was carried out under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, Public Health Service, Contracts No. SA-43-ph-3764 and PH43-66-904. The opinions expressed in this paper are those of the authors and not necessarily those of the Cancer Chemotherapy National Service Center.

(2) J. J. Fox, N. Miller, and I. Wempen, *J. Med. Chem.*, **9**, 101 (1966).

(3) N. C. Yung, J. H. Burchenal, R. Fecher, R. Duschinsky, and J. J. Fox, *J. Am. Chem. Soc.*, **83**, 4060 (1961).

(4) T. Y. Shen, H. M. Lewis, and W. V. Ruyle, *J. Org. Chem.*, **30**, 835 (1965); F. Keller, and A. R. Tyrrill, *ibid.*, **31**, 1289 (1966).

(5) E. J. Reist, J. H. Osiecki, L. Goodman, and B. R. Baker, *J. Am. Chem. Soc.*, **83**, 2208 (1961).

(6) F. Keller, N. Sugisaka, A. Tyrrill, L. H. Brown, J. E. Bunker, and I. J. Botvinick, *J. Org. Chem.*, **31**, 3842 (1966).

(7) We wish to thank Dr. E. J. Reist, Stanford Research Institute, Menlo Park, Calif., for confirming the presence of this spectral feature in anomerically pure **2** prepared by another method.[5]

(8) A. Dipple and C. Heidelberger, *J. Med. Chem.*, **9**, 715 (1966).

(9) M. J. Robins and R. K. Robins, *J. Am. Chem. Soc.*, **87**, 4934 (1965).

(10) R. U. Lemieux and M. Hoffer, *Can. J. Chem.*, **39**, 110 (1961).

(11) R. Barker and H. G. Fletcher, Jr., *J. Org. Chem.*, **26**, 4605 (1961).

(12) M. Prystas and F. Sorm, *Collection Czech. Chem. Commun.*, **30**, 1900 (1965).

(13) Linde Molecular Sieves Type 4A, 1/16-in. pellets, Linde Division, Union Carbide Corp.