was heated at reflux under a nitrogen atmosphere for 24 hr. After cooling, the resin was filtered off and washed with ether until the filtrates were clear. The filtrates and washings were combined and neutralized with 40% aqueous sodium hydroxide solution and then washed with water. The ethereal solution was dried and the solvent was removed to give 0.42 g. (85%) of pale yellow mobile oil which showed strong infrared absorption at 6.02 and 6.2 and very weak absorption at 2.85 and 3.00 μ. After chromatography on Merck alumina, using a mixture of 30% benzene–70% hexane as eluent, a clear colorless oil was obtained: $[\alpha]^{22}D$ −14.3° (*c* 0.0388, $CHCl_3$), λ_{max} 240 mμ (log ϵ 4.01).

Anal. Calcd. for $C_{18}H_{24}O$: C, 85.03; H, 9.01. Found: C, 84.83; H, 8.86.

B.—A mixture of 0.5 g. of the ethynylcarbinol and 8 ml. of 98% formic acid was heated under reflux for 2.5 hr. The dark brown solution was cooled to room temperature, neutralized with saturated aqueous sodium bicarbonate solution, and extracted with ether. The ether extracts were washed several times with water, dried, concentrated, and chromatographed on Bio-Rad AG-7 neutral alumina with benzene as eluent. Upon removing the benzene under vacuum, there was obtained 0.38 g. (75%) of a pale yellow oil showing strong infrared absorption at 6.02 and 6.2 μ, identical with that obtained in method A.

***cis*-1a-Methyl-3-acetyl-7-isopropyl-1,1a,2,3,3a,4,5-hexahydrocyclopenta[*a*]naphthalene.**—To a well-stirred mixture of prereduced 10% palladium on carbon in ethyl acetate, 200 mg. of the above α,β-unsaturated ketone in 8 ml. of ethyl acetate was added. After 2.5 hr., 27.0 ml. of hydrogen at atmospheric pressure and room temperature was absorbed. The mixture was filtered, and upon evaporation of solvent 150 mg. of an almost colorless oil was obtained. This material showed strong infrared absorption at 5.86 μ. The compound was chromatographed on Merck alumina using benzene as solvent and as eluent: $[\alpha]^{22}D$ −5.04° (*c* 0.0250, $CHCl_3$).

Anal. Calcd. for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.16; H, 9.69.

***cis*-1a-Methyl-3-acetyl-3-hydroxy-7-isopropyl-1,1a,2,3,3a,4,5-hexahydrocyclopenta[*a*]naphthalene.**—A mixture of 0.5 g. of the ethynylcarbinol, 1 g. of Dowex 50W-X12, 1 g. of Dowex 50W-X12 which had been preactivated with mercuric acetate, and 40 ml. of aqueous ethyl ether was stirred for 50 hr. at room temperature. The resin was filtered off and washed with ethyl ether until the filtrate was clear. The filtrate and washings were combined, dried, and concentrated to give 0.49 g. (92%) of a pale yellow viscous oil. This oil showed strong infrared absorption at 2.81 and 5.90 and weak absorption at 3.00 μ. Chromatography on Florosil and elution with benzene gave a colorless oil. The analytical sample was a colorless oil prepared by rechromatography of the once-chromatographed material: $[\alpha]^{23}D$ −4.6° (*c* 0.0860, $CHCl_3$).

Anal. Calcd. for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.61; H, 9.20.

Oxidation of *cis*-1a-Methyl-3-acetyl-7-isopropyl-1,1a,2,3,3a,4,5-hexahydrocyclopenta[*a*]naphthalene.—In 4 ml. of 95% ethanol, 15 mg. of the hydroxy ketone and 30 mg. of periodic acid were stirred overnight at room temperature. Dilute aqueous sodium bicarbonate was added to the reaction mixture which was extracted several times with ether. After washing well with water, drying, and concentrating the ether extracts, 9 mg. of yellow oil was obtained. The infrared absorption spectrum of this material was identical with that of original five-membered ketone.

Acknowledgment.—This work was supported by Grant GM-07817 from the Division of General Medical Sciences of the National Institutes of Health. The authors would like to thank the Hercules Powder Company for generous gifts of dehydroabietonitrile.

1,8-Naphthyridines. I. Derivatives of 2- and 4-Methyl-1,8-naphthyridines

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Received December 17, 1964

2-Methyl-1,8-naphthyridine has been prepared by a series of reactions starting with 2-methyl-5-hydroxy-1,8-naphthyridine-6-carboxylic acid and compared with the known 4-methyl-1,8-naphthyridine. The compound previously thought to be 2-methyl-4-hydroxy-7-amino-1,8-naphthyridine has been shown to be 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine by conversion to 4-methyl-1,8-naphthyridine. A new ring closure has furnished 2-methyl-7-amino-1,8-naphthyridine and, in addition, 2-amino-5-methyl-1,8-naphthyridine and 2-methyl-5-amino-1,8-naphthyridine have been prepared by other means.

Our interest in naphthyridines arose from their gross similarity to quinolines and our desire to prepare azo compounds in this series to compare with the quinoline azo compounds which have such interesting variations in carcinogenic activity.[1,2] In the course of syntheses leading to the requisite amines, a number of interesting naphthyridines have been prepared (Scheme I).

In our first series we used as the starting material 2-methyl-5-hydroxy-6-carbethoxy-1,8-naphthyridine which was prepared by Lappin from 6-methyl-2-aminopyridine (I) and ethyl ethoxymethylenemalonate.[3] The same author also hydrolyzed the ester to the corresponding acid II. We have decarboxylated the acid in mineral oil at 300° to obtain 2-methyl-5-hydroxy-1,8-naphthyridine (III). Refluxing with $POCl_3$ gave the chloro compound IV. The chloro group could either be replaced by amino, hydrazino, or hydrogen. In the latter case, the new 2-methyl-1,8-naphthyridine (V) was produced. The hydrazine could also be converted to 2-methyl-1,8-naphthyridine by oxidation with copper sulfate.

For comparison, the known 4-methyl-1,8-naphthyridine was prepared. The usual starting material for this synthesis is 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine (XI) which has been prepared by heating ethyl acetoacetate and 2,6-diaminopyridine[4] to 145–150°. We have found that about the same yield of a nearly white product can be obtained by heating the reactants at 90–100° in phosphoric acid. This result was somewhat surprising because Hauser[5a] had claimed that these reactants in the presence of a few drops of concentrated HCl standing 30 days at room temperature produced an 8% yield of 2-methyl-4-hydroxy-7-amino-1,8-naphthyridine. We next heated the reactants at 80–90° for 1 hr. in the presence of concentrated

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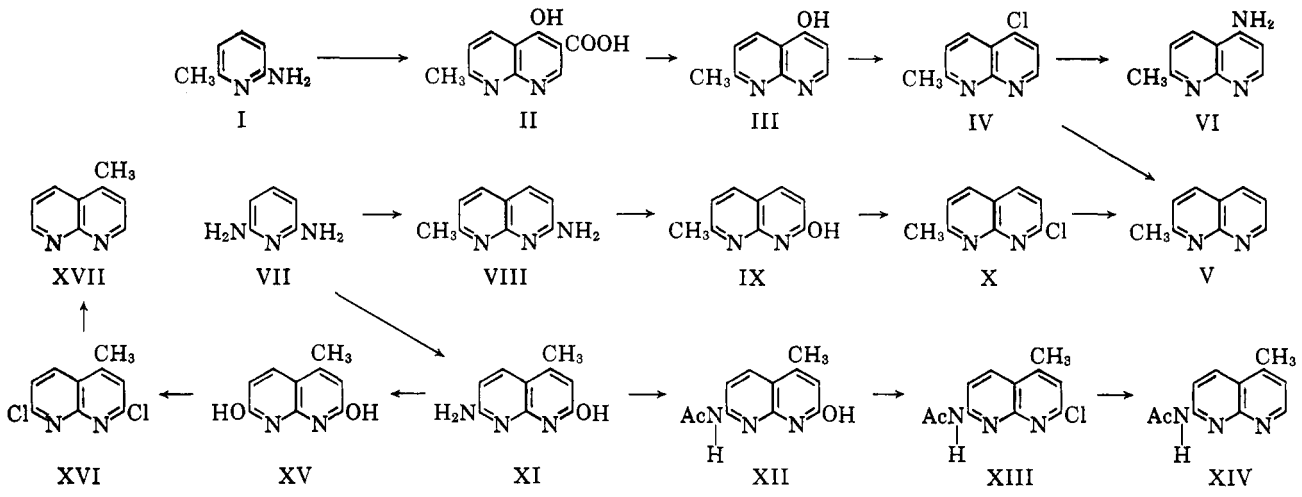
(2) E. V. Brown, R. M. Novack, and A. A. Hamdan, *J. Natl. Cancer Inst.*, **26**, 1461 (1961).

(3) G. R. Lappin, *J. Am. Chem. Soc.*, **70**, 3348 (1948).

(4) O. Seide, *Ber.*, **59**, 2465 (1926).

(5) (a) C. R. Hauser and M. J. Weiss, *J. Org. Chem.*, **14**, 453 (1949); (b) S. Carboni, A. DaSettimo, and G. Pirisino, *Ann. Chim.* (Rome), [7] **54**, 677 (1964).

SCHEME I



HCl, and we have found that the product yield varies with temperature and amount of HCl used but that the product is 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine (XI). Identification of these products is somewhat difficult and unsatisfactory because they melt over 300° and are quite insoluble in spectrographic solvents. Identification was made by mixture melting point determinations of a number of transformation products starting with both the product of Seide[4] and the acid-produced material, *i.e.*, 2-chloro-4-methyl-7-acetylamino-1,8-naphthyridine (XII), 2-acetylamino-5-methyl-1,8-naphthryidine (XVI), and 2-amino-5-methyl-1,8-naphthyridine. Melting point, mixture melting point and infrared spectra comparisons of these last three products and the product of Hauser and Weiss[5] confirmed their identity. After this work had been completed, a paper by Carboni, DaSettimo, and Pirisino[5b] came to our attention indicating that Hauser's interpretation was incorrect. Their method involved preparing a ditetrazole from the 2,7-dihydrazino-4-methyl-1,8-naphthyridine.

Starting with the 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine, it was possible to obtain 4-methyl-1,8-naphthyridine (XVII) by the method previously described.[4,6] This liquid compound was converted to a solid derivative by heating with chloral in pyridine. This was compared with the same derivative of 2-methyl-1,8-naphthyridine.

A novel ring closure also led to the preparation of 2-methyl-1,8-naphthyridine. 3-Ketobutanal dimethyl acetal[7] was added to a solution of 2,6-diaminopyridine in phosphoric acid and heated to 95° for 3 hr. to produce 2-methyl-7-amino-1,8-naphthyridine (VIII). This, in turn, was converted to the 2-methyl-7-hydroxy-1,8-naphthyridine (IX) by nitrous acid. Treatment of this compound with $POCl_3$ at the reflux furnished 2-methyl-7-chloro-1,8-naphthyridine. The chloro group could be replaced by hydrogen to give the 2-methyl-1,8-naphthyridine as shown by melting point and mixture melting point determinations. This reaction along with others[3,4,5b] would indicate an order of attack on the 2-amino group as CHOEt > COOEt > C=O > $CH(OMe)_2$.

(6) E. Ochai and K. Miyaki, *Ber.*, **74**, 1115 (1941).

(7) We are grateful to Henley and Co., New York, N. Y., for a generous sample of this material.

Experimental

2-Methyl-5-hydroxy-1,8-naphthyridine-6-carboxylic Acid (II).—The procedure of Lappin[3] was followed and from 125 g. of diethyl ethoxymethylenemalonate and 65 g. of 6-methyl-2-aminopyridine was obtained 157 g. of crude ethyl 6-methyl-2-pyridylaminomethylenemalonate which was recrystallized from ethanol to give 140 g., m.p. 103–104°. This was cyclized in 25-g. portions using 150 ml. of refluxing diphenyl ether for 45 min. After cooling, 300 ml. of hexane was added and the product was filtered, washed with hexane, and dried to give 14–18 g. of the naphthyridine ester. This was then saponified by refluxing in 250 ml. of 10% NaOH for 2 hr., filtering, and precipitating the acid with a slight excess of HCl giving 11–15 g. of crude acid.[3]

2-Methyl-5-hydroxy-1,8-naphthyridine (III).—To 150 ml. of stirred mineral oil at 300° was added 10 g. of the above crude acid portionwise over a period of 5–10 min. The mineral oil solution of the hydroxy compound was then decanted without cooling from a black tarry residue, and crystallization occurred during cooling. Two volumes of hexane was added and the crude hydroxy compound was filtered. There was obtained 5 g. (64% of the theoretical amount) melting 236–238°. This crude material was recrystallized from 100 ml. of water and the product was dehydrated in boiling xylene to give 4 g. of 2-methyl-5-hydroxy-1,8-naphthyridine, m.p. 238–240°.

Anal. Calcd. for $C_9H_8N_2O$: C, 67.50; H, 5.04. Found: C, 67.15; H, 5.06.

2-Methyl-5-chloro-1,8-naphthyridine (IV).—The anhydrous hydroxy compound (5 g.) was refluxed for 1 hr. with 50 ml. of $POCl_3$. After cooling, the mixture was poured onto ice, neutralized with ammonium hydroxide, and extracted three times into chloroform. Evaporation gave 4.5 g. of crude chloro compound, m.p. 119–122°; recrystallization from methylcyclohexane gave 2-methyl-5-chloro-1,8-naphthyridine, m.p. 121–122°.

Anal. Calcd. for $C_9H_7ClN_2$: C, 60.50; H, 3.92. Found: C, 60.72; H, 3.90.

2-Methyl-1,8-naphthyridine (V).—The chloro compound (10 g.) was treated with 5 g. of 5% Pd–$CaCO_3$, a trace of 5% Pd–C, and 300 ml. of 2.5% KOH–methanol and hydrogenated in a Parr apparatus at 40 p.s.i. of hydrogen for 1 hr. The catalyst was removed by filtration, the solution was evaporated to near dryness, 50 ml. of water was added, and the mixture was extracted with chloroform. Evaporation of the chloroform afforded 7 g. of crude material, m.p. 110–115° (87% of the theoretical amount). Recrystallization from methylcyclohexane gave 2-methyl-1,8-naphthyridine, m.p. 114–115°.

Anal. Calcd. for $C_9H_8N_2$: C, 75.00; H, 5.55. Found: C, 75.36; H, 5.71.

2-Methyl-5-hydrazino-1,8-naphthyridine.—2-Methyl-5-chloro-1,8-naphthyridine (4 g.) was refluxed 3 hr. with 15 ml. of 85% hydrazine hydrate and 25 ml. of absolute ethanol. The mixture was evaporated to dryness and the crude hydrazine derivative was recrystallized from absolute ethanol to give 3 g. of 2-methyl-5-hydrazino-1,8-naphthyridine, m.p. 208–210°.

Anal. Calcd. for $C_9H_{10}N_4$: C, 62.07; H, 5.75. Found: C, 61.72; H, 5.74.

This substituted hydrazine (2 g.) was put into 75 ml. of water, brought to boiling, added to a boiling solution of 10 g. of $CuSO_4$ in 50 ml. of water, refluxed 15 min., made alkaline with sodium hydroxide, and extracted with methylene chloride. Evaporation of the solvent left 0.8 g. of product, m.p. 92–100°. Recrystallization from methylcyclohexane gave 2-methyl-1,8-naphthyridine, m.p. 114–115°, which did not depress the melting point of the material obtained from the 5-chloro compound by reduction.

2-Hydroxy-4-methyl-7-amino-1,8-naphthyridine (XI). Method A.—This compound was obtained in the amount of 27 g. (33% of the theoretical amount) by the method of Seide[4] from 50 g. of 2,6-diaminopyridine and 70 g. of ethyl acetoacetate heated at 150° for 4 hr. (Seide[4] obtained a yield of 56%).

Method B.—2,6-Diaminopyridine (25 g.) and ethyl acetoacetate (30 g.) were heated in 100 ml. of H_3PO_4 on the steam bath for 3 hr., cooled, mixed with ice and water, and neutralized with NH_4OH. The white product was filtered, washed, and dried to give 25 g. of 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine (61% of the theoretical amount). The heating time could be reduced to 1 hr. without change in yield.

Method C.—2,6-Diaminopyridine (25 g.) was treated according to Hauser.[5a] There was obtained 3–8 g. of product/run in a number of such runs. This material was shown to be 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine and not 2-methyl-4-hydroxy-7-amino-1,8-naphthyridine as indicated by Hauser[5a] by comparison with the product of Seide's[4] reaction in three subsequent reactions (see below).

Method D.—2,6-Diaminopyridine (50 g.), 56 g. of ethyl acetoacetate, and 16 drops of concentrated HCl were heated to 80° for 1 hr. The mixture was cooled, filtered, and washed with water and ether to give 0.8 g. of 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine. The run was repeated with 5, 10, and 20 ml. of concentrated HCl and the yields of product were 18.5, 26, and 24.5 g., respectively.

2-Chloro-4-methyl-7-acetylamino-1,8-naphthyridine (XII).—2-Hydroxy-4-methyl-7-amino-1,8-naphthyridine (20 g.) from method A was acetylated to give 22 g. of acetylated amine. This product was treated[8] to give 12 g. of crude chloro compound, m.p. 232–240°. After recrystallization from toluene the 2-chloro-4-methyl-7-acetylamino-1,8-naphthyridine[8] melted at 245–247° (lit.[8] m.p. 240°). The chloro compound made in the identical manner from the hydroxy compound made by method C[5a] above melted at 230–245° and after recrystallization from toluene melted at 246–248°. The mixture of these two materials melted at 247–248° and their infrared spectra from Nujol mulls and chloroform solutions were identical.

2-Acetylamino-5-methyl-1,8-naphthyridine (XIV).—Five grams of the above chloro compound (from Seide product above) with 3 g. of 5% Pd–$CaCO_3$ plus a trace of 5% Pd–C and 200 ml. of 2.5% KOH–methanol was treated with hydrogen in a Parr apparatus at 40 p.s.i. pressure for 2 hr. The catalyst was filtered, the methanol was evaporated, and water was added to precipitate 3 g. of 2-acetylamino-5-methyl-1,8-naphthyridine, m.p. 197–200°. Recrystallization from butanol gave a product melting at 202°.

Anal. Calcd. for $C_{11}H_{11}N_3O$: C, 65.67; H, 5.48. Found: C, 65.55; H, 5.50.

In a similar manner the chloro compound from the Hauser[5a] hydroxy compound was prepared and reduced. The product showed no depression in melting point when mixed with the above acetylamino compound and their infrared spectra in both Nujol mulls and chloroform solutions were identical.

The acetylamino compound was hydrolyzed by refluxing 3 g. with 30 ml. of 50 vol. % sulfuric acid for 2 hr. and neutralizing with NH_4OH. There was obtained a quantitative amount of 2-amino-5-methyl-1,8-naphthyridine, m.p. 196–198. Recrystallization from butanol gave a product melting at 198–200°.

Anal. Calcd. for $C_9H_9N_3$: C, 68.09; H, 5.66. Found: C, 68.18; H, 5.60.

Again products originating from the Seide[4] or Hauser[5a] hydroxy compound showed no depression in melting when mixed and had identical infrared spectra in Nujol mulls and chloroform solutions.

4-Methyl-1,8-naphthyridine (XVII).—This compound has been prepared[4,6] from 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine through the 2,7-dihydroxy (XV) and the 2,7-dichloro (XVI) compounds followed by reduction. Repetition of these steps afforded the known 4-methyl-1,8-naphthyridine as a liquid boiling at 131–135° at 0.35 mm. (lit.[6] b.p. 147–148° at 0.05 mm.) and giving a picrate melting at 204–205° (lit.[6] m.p. 204–205°).

1-[4-(1,8-Naphthyridyl)]-3,3,3-trichloropropanol-2.—4-Methyl-1,8-naphthyridine (12 g.) was warmed to 90° for 2 hr. with 12 ml. of chloral and 25 ml. of pyridine. The mixture was poured onto ice and water, filtered, and dried to give 21 g. of crude product, m.p. 183–190°. Recrystallization from ethanol gave 1-[4-(1,8-naphthyridyl)]-3,3,3-trichloropropanol-2, m.p. 197–198°.

Anal. Calcd. for $C_{11}H_9Cl_3N_2O$: C, 45.30; H, 3.09. Found: C, 45.17; H, 3.13.

1-[2-(1,8-Naphthyridyl)]-3,3,3-trichloropropanol-2.—2-Methyl-1,8-naphthyridine (1.5 g.), 4 ml. of pyridine, and 2 ml. of chloral were warmed to 90° for 2 hr., poured onto ice and water, filtered, and dried to give 2.75 g. of product, m.p. 192–195°. Recrystallization from ethanol gave 1-[2-(1,8-naphthyridyl)]-3,3,3-trichloropropanol-2, m.p. 199–200°.

Anal. Calcd. for $C_{11}H_9Cl_3N_2O$: C, 45.30; H, 3.09. Found: C, 45.38; H, 3.18.

When the 2- and the 4-isomer were mixed the melting range was reduced to 182–189°.

2-Methyl-7-amino-1,8-naphthyridine (VIII).—2,6-Diaminopyridine (11 g.), 13 g. of 3-ketobutanal dimethyl acetal, and 100 ml. of H_3PO_4 were held at 90° for 3 hr., neutralized, and extracted five times with chloroform. After evaporation of the chloroform there was obtained 14 g. (90% of the theoretical amount) of crude 2-methyl-7-amino-1,8-naphthyridine, m.p. 175–185°, which was chromatographed on alumina and recrystallized from toluene giving m.p. 217–218°.

Anal. Calcd. for $C_9H_9N_3$: C, 68.09; H, 5.66. Found: C, 68.28; H, 5.56.

The infrared spectra of this amine both in Nujol mull and chloroform was quite different from the 2-amino-5-methyl-1,8-naphthyridine prepared above. Also a mixture of these amines melted at 165–180°. The acetylated amine melted at 279–281°.

Anal. Calcd. for $C_{11}H_{11}N_3O$: C, 65.67; H, 5.48. Found: C, 65.59; H, 5.42.

2-Methyl-7-hydroxy-1,8-naphthyridine (IX).—The above amine (3 g.) was dissolved in 25 ml. of 40% H_2SO_4 and treated with 2 g. of $NaNO_2$ at −5°. After warming to 80°, then cooling, neutralizing, extracting five times with chloroform, and evaporating the chloroform, there was obtained 2.5 g. of 2-methyl-7-hydroxy-1,8-naphthyridine, m.p. 176–177°.

Anal. Calcd. for $C_9H_8N_2O$: C, 67.50; H, 5.00. Found: C, 67.42; H, 5.06.

2-Methyl-7-chloro-1,8-naphthyridine (X).—The above hydroxy compound (4.5 g.) was refluxed with 50 ml. of $POCl_3$ for 1 hr., cooled, neutralized with NH_4OH, and extracted into chloroform. Evaporation of the chloroform extract gave 5 g. of crude product which was recrystallized from toluene giving 2.5 g. of 2-methyl-7-chloro-1,8-naphthyridine, m.p. 215–216°.

Anal. Calcd. for $C_9H_7ClN_2$: C, 60.50; H, 3.92. Found: C, 60.58; H, 4.01.

This compound, when reduced in the manner detailed above with Pd–$CaCO_3$ catalyst, gave 2-methyl-1,8-naphthyridine identical in all respects with that obtained with the series of reactions starting with 6-methyl-2-aminopyridine.

2-Methyl-5-amino-1,8-naphthyridine (VI).—2-Methyl-5-chloro-1,8-naphthyridine (IV, 6 g.), 12 g. of phenol, and 8 g. of acetamide were heated to 160° and ammonia gas was bubbled in for 1 hr. The solid was filtered, washed with ether, and dissolved in water. Treatment with sodium hydroxide solution precipitated 4.5 g. of crude amine, m.p. 209–211°. Recrystallization from water gave the 2-methyl-5-amino-1,8-naphthyridine, m.p. 211–212°.

Anal. Calcd. for $C_9H_9N_3$: C, 68.09; H, 5.66. Found: C, 68.20; H, 5.72.

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Acknowledgment.—The author wishes to thank the Kentucky Research Foundation for a sabbatical leave grant. He is also deeply grateful for the hospitality of Professor Jaques Metzger of the Faculty of Sciences, Aix-Marseille, in whose laboratory part of this work was done.

On the Isolation of the Allergenically Active Components of the Toxic Principle of Poison Ivy

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Received June 29, 1964

The olefinic components of the poison ivy principle have been separated for the first time from natural sources in their allergenically active (free phenolic) form by a process involving benzylation, chromatography, and debenzylation. The composition of poison ivy "urushiol" has been estimated. A method is described for the cleavage of benzyl ethers in molecules containing multiple olefinic bonds, each separated by only one methylene group. The procedure results in debenzylation without alteration in the position or geometrical configuration of the olefinic bonds.

Poison ivy "urushiol" is made up of four components having the carbon skeleton of 3-pentadecylcatechol, and differing from each other only in the degree of unsaturation in the 15-carbon side chain.[2,3] The saturated and minor component, 3-pentadecylcatechol (Hydrourushiol), is a stable and colorless crystalline solid that has been available synthetically for some time[4] and has been extensively used in clinical studies.[5-10] The three olefinic components (mono-, di-, and triolefin), which make up approximately 95–97% of the urushiol principle, are labile oily substances that show marked sensitivity to air oxidation and polymerization. Except for the monoolefin, a very small amount of which was made available by synthesis several years ago,[11] the olefinic components of urushiol have not been available in pure form for clinical study. They were isolated from the natural principle, and their structures were determined, in the form of their dimethyl ether derivatives, which are not allergenically active.[2] It has not been possible to convert these methyl ethers back to the free and active catechols because the acid condition required for the hydrolysis causes rapid and extensive polymerization of such alkenyl phenols.

The synthesis of the monoolefinic component in the free phenolic (allergenically active) form was achieved *via* a dibenzyl ether intermediate which was subsequently debenzylated under conditions which did not structurally alter the olefinic side chain.[11] The present investigation was undertaken to explore the possibility that a similar procedure of benzylation and debenzylation might be employed as part of a chromatographic method for isolating, from the plant extract, each of the olefinic components of urushiol in allergenically active form.

Preliminary experiments on the benzylation and chromatography of cardanol[12,13] gave promising results. Consequently, crude poison ivy "urushiol" was treated with benzyl bromide following the procedure previously described[14] and was separated into its components by repeated column chromatography on grade I alumina.[15] The components were hydrogenated, and their unsaturation values were plotted against their respective refractive indices, showing a linear relationship.[15] Chromatographically pure samples of the dibenzyl ethers of the monoolefinic (II), the diolefinic (III), and the triolefinic components (IV) were obtained, and their relative concentrations were determined to be: monoolefin (and saturated component), about 12%; diolefin, about 64%; and triolefin, about 23% (Table I).

TABLE I

HYDROGENATION OF THE CHROMATOGRAPHICALLY SEPARATED DIBENZYL ETHER COMPONENTS OF BENZYLATED "URUSHIOL"[a]

Component	n^{25}D, deg.	Estd. amt., %	Moles of H_2 —absorbed— Total	Olefinic	Unsaturation value[b]
Saturated	1.5315[c]	2	2.00[d]	...	...
Monoolefin	1.5362	10	2.91	0.91	0.09
Diolefin	1.5455	64	4.06	2.06	1.32
Triolefin	1.5551	23	4.86	2.86	0.66

[a] Original n^{25}D 1.5460, d.b.v. 1.92 ± 0.05. [b] Contribution to the approximate d.b.v. of 2 of the original benzylated "urushiol" sample as calculated on the basis of amounts of each component estimated from the chromatogram. [c] Since dibenzylhydrourushiol is a solid at room temperature (m.p. 58–59°), its refractive index at 25° was obtained by extrapolating values obtained using molten and supercooled material between 40 and 70°. [d] For the debenzylation reaction 2.00 moles of H_2 is theoretically required.

Because of its very low concentration in the "urushiol" mixture, it was not convenient to obtain a chromatographic fraction corresponding to the saturated

(1) (a) This paper is based on a portion of the thesis submitted by Kenneth H. Markiewitz to Columbia University in partial fulfillment of the requirements for the Ph.D. degree in chemistry. (b) To whom inquiries should be made.

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