5°, 3.8 g. of crystalline hydrobromide was obtained. Recrystallization from methanol gave crystals with the following analysis after drying at 100° in high vacuum over phosphorus pentoxide.

Calcd. for $C_{21}H_{39}N_7O_{12}\cdot 3HBr$: C, 30.59; H, 5.14; N, 10.68; Br, 29.08. Found: C, 30.97; H, 5.53; N, 11.07; Br, 28.70. $[\alpha]^{26}D$ −72.2 (*c* 1% in water). Activity *vs. K. Pneumoniae* = 797 μg./mg.

Preparation of Crystalline Streptomycin Nitrate.—Ten grams of crystalline streptomycin tergitate was dissolved in 50 ml. of methanol. Thirty-five ml. of 10% methanolic calcium nitrate was added followed by 0.3 ml. of concd. HNO_3. The cloudy solution was allowed to stand in the cold room 4 hours and filtered. Recrystallization from methanol gave crystals with the following analysis (dried in high vacuum over phosphorus pentoxide at 56°):

Calcd. for $C_{21}H_{39}N_7O_{12}\cdot 3HNO_3$: C, 32.73; H, 5.49; N, 18.18. Found: C, 33.11; H, 5.53; N, 17.91. $[\alpha]^{26}D$ −82.3° (*c* 1% in water). Activity *vs. K. Pneumoniae* = 733 μg./mg.

Preparation of Crystalline Streptomycin Sulfate.—Twenty grams of crude streptomycin tergitate was dissolved in 100 ml. of butanol and filtered. The rich solvent was added slowly with agitation to 100 ml. of 5% aqueous guanidine sulfate solution which had been adjusted to *p*H 3.0 with dilute sulfuric acid. The crystals were allowed to remain overnight at 5° and then filtered and dried. The yield was 5.3 g. Recrystallization from warm 5% aqueous guanidine sulfate solution yielded crystals with the following analysis after drying in high vacuum phosphorus pentoxide at 100°.

Calcd. for $C_{21}H_{39}N_7O_{12}\cdot 3/2H_2SO_4$: C, 34.61; H, 5.81; N, 13.45; S, 6.60. Found: (1) C, 34.85; H, 5.77; N, 14.43; S, 6.65. (2) C, 34.83; H, 5.84; N, 13.46; S, 6.82. $[\alpha]^{26}D$ −83.2 (*c* 1% in water). Activity *vs. K. Pneumoniae* = 843 μg./mg.

Preparation of Crystalline Streptomycin Phosphate.—Five grams of crystalline streptomycin hydrochloride was dissolved in 10 ml. of water and 40 ml. of 5% aqueous guanidine phosphate solution, acidified to *p*H 2.5 with phosphoric acid, was added. Methanol was added until the solution became turbid and the solution allowed to stand overnight at 5°. After filtration and drying, 0.81 g. crystalline streptomycin phosphate was obtained. Recrystallization from 2.5% phosphoric acid in methanol solution gave crystals with the following analysis after drying in high vacuum phosphorus pentoxide at 100°.

Calcd. for $C_{21}H_{39}N_7O_{12}\cdot 3/2H_3PO_4$: C, 34.62; H, 6.02; N, 13.45; P, 6.39. Found: C, 34.31; H, 6.30; N, 13.35; P, 6.58. $[\alpha]^{26}D$ −77.2° (*c* 1% in water). Activity *vs. K. Pneumoniae* = 770 μg./mg.

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF CHAS. PFIZER & CO., INC.]

Terramycin.[1] IX. The Synthesis of Indanone Degradation Products of Terramycin[2]

BY L. H. CONOVER

RECEIVED APRIL 25, 1953

Decarboxyterracinoic acid and isodecarboxyterracinoic acid, degradation products of Terramycin, have been synthesized confirming the structures assigned these compounds. The synthesis of decarboxyterracinoic acid provides additional proof of structure of terracinoic acid since the relationship between these two products has already been established. Terracinoic acid has also been converted to 5-methoxy-2,3-dimethylindanone which has been synthesized.

Included among the alkaline degradation products of Terramycin are terracinoic acid (I) and isodecarboxyterracinoic acid (II). The structure of terracinoic acid has been shown[3] to be 4-carboxy-5-hydroxy-3-methylindanone-2-acetic acid. Isodecarboxyterracinoic acid, the "bicarbonate soluble fraction"[4] which was obtained from the alkaline degradation of Terramycin, has been identified[5] as 7-hydroxy-3-methylindanone-2-acetic acid.[6] The present work was undertaken to provide synthetic confirmation of the structures of these important Terramycin degradation products.

Proof of the structure of decarboxyterracinoic acid (III) through synthesis would also constitute confirmation of the structure of terracinoic acid. This follows from previous studies which have established the position of the aromatic carboxyl function which is eliminated when terracinoic acid is decarboxylated.[3]

The preparation of decarboxyterracinoic acid (III) was accomplished through introduction of an acetic acid side chain at the 2-position of 5-hydroxy-3-methylindanone (IV) by a modification of the method employed by Knott[7] for the conversion of substituted acetophenones, acetonaphthones, etc., to the corresponding aroylpropionitriles and propionic acids. This useful procedure consists of the formation of an N,N-dialkyl ketonic Mannich base, followed by treatment of the Mannich base with aqueous alkali cyanide to form the nitrile, which may be hydrolyzed to the corresponding carboxylic acid.[8] Knott concluded that the method failed in the case of cyclic ketones and propiophenones; however, in the present case 5-methoxy-3-methylindanone (V) was converted to 5-methoxy-3-methylindanone-2-acetonitrile (VI), which on hydrolysis and demethylation yielded 5-hydroxy-3-methylindanone-2-acetic acid (III). The latter was shown to be identical with decarboxyterracinoic acid obtained by degradation of Terramycin.

The indanone (IV) was prepared in two ways. The preferred method involved treatment of phenyl α-bromobutyrate with aluminum chloride at 145°. This synthesis was suggested by the previously reported[9] conversion of phenyl α-bro-

(1) Terramycin is the registered trademark of Chas. Pfizer & Co., Inc. for oxytetracycline.

(2) Part of this work was presented before the Division of Organic Chemistry at the 121st National Meeting of the American Chemical Society, Buffalo, N. Y., March 25, 1952.

(3) Paper III of this series, R. Pasternack, L. H. Conover, A. Bavley, F. A. Hochstein, G. B. Hess and K. J. Brunings, THIS JOURNAL, **74**, 1928 (1952).

(4) Paper II of this series, R. Pasternack, A. Bavley, R. L. Wagner, F. A. Hochstein, P. P. Regna and K. J. Brunings, *ibid.*, **74**, 1926 (1952).

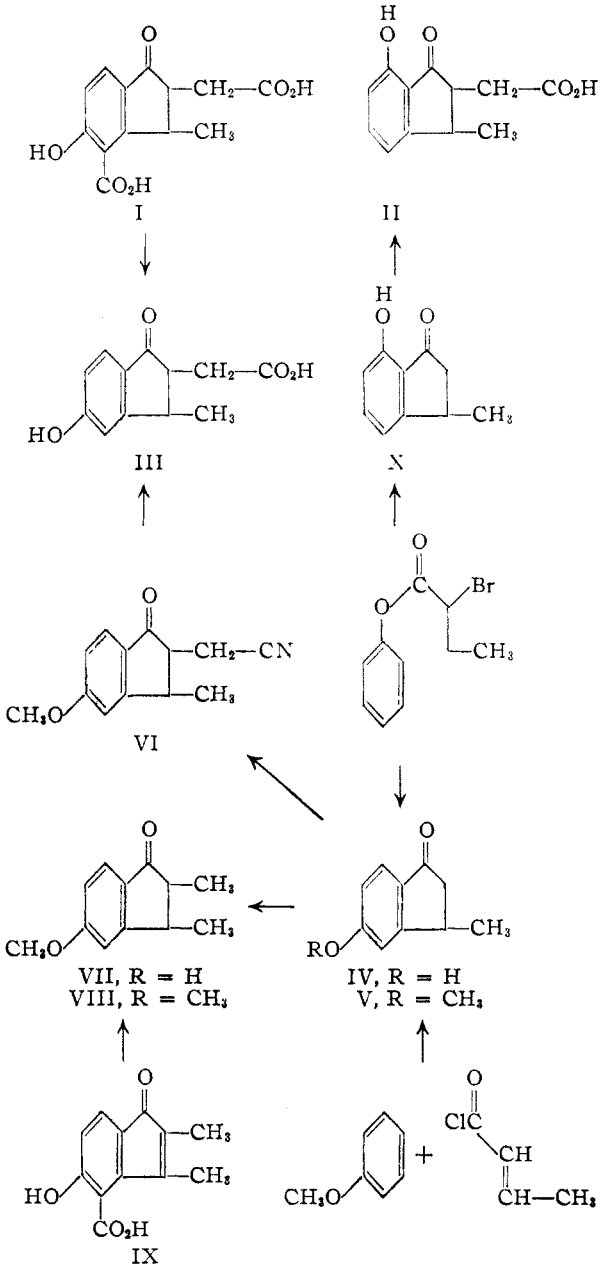
(5) Paper VII of this series, F. A. Hochstein, C. R. Stephens, L. H. Conover, P. P. Regna, R. Pasternack, K. J. Brunings and R. B. Woodward, *ibid.*, **74**, 3708 (1952).

(6) The structure proof of isodecarboxyterracinoic acid is to be published by F. A. Hochstein, *et al.*

(7) E. B. Knott, *J. Chem. Soc.*, 1190 (1947).

(8) An analogous reaction has been used to convert other types of Mannich bases to substituted acetic acids. *Cf.* H. R. Snyder and F. J. Pilgrim, THIS JOURNAL, **70**, 3770 (1948), and E. L. Eliel, *ibid.*, **73**, 43 (1951).

(9) K. v. Auwers and E. Hilliger, *Ber.*, **49**, 2410 (1916).



mopropionate to 5-hydroxyindanone. The reaction of crotonyl chloride and anisole under the influence of aluminum chloride (patterned after Kohler's synthesis of indanone[10]) gave under forcing conditions a low yield of IV. The formation of the methyl ether (V) was effected using either diazomethane or methyl iodide and potassium carbonate.

Further confirmation of the structure of I was obtained by converting terracinoic acid to the completely decarboxylated compound, 5-hydroxy-2,3-dimethylindanone (VII) and proving the structure of VII through synthesis of the methyl ether (VIII). The conversion of I to VIII proceeded as follows. 4-Carboxy-5-hydroxy-2,3-dimethylindenone (IX) (obtained[3] from 2-bromoterracinoic acid by the action of hot alkali) was selectively hydrogenated at low pressure over palladized charcoal or Adams catalyst to yield 4-carboxy-5-hydroxy-2,3-dimethylindanone. This compound was decarboxylated in hot 85% phosphoric acid yielding 5-hydroxy-2,3-dimethylindanone (VII), which was in turn converted to the methyl ether (VIII).

The synthesis of VIII was accomplished by alkylation of V with methyl iodide in the presence of potassium *t*-butoxide. This reaction gave a mixture of products which proved difficult to separate. It was found possible to isolate VIII as its semicarbazone since as would be expected this derivative formed much more slowly than the semicarbazone of V.

Isodecarboxyterracinoic acid (II) was synthesized by methods analogous to those used for the preparation of decarboxyterracinoic acid (III). 7-Hydroxy-3-methylindanone (X), which was obtained as a second product of the aluminum chloride treatment of phenyl α-bromobutyrate,[11] was converted to its methyl ether. From the latter was obtained 7-hydroxy-3-methylindanone-2-acetic acid which was proved to be identical with the Terramycin degradation product (II).

Experimental[12]

Phenyl α-bromobutyrate was prepared by the method of Bischoff[13] except that α-bromobutyryl chloride was used in place of the corresponding acid bromide and no solvent was employed. The yield was 66% of material of b.p. 100–108° (3 mm.) and d^{20}_4 1.363.

5-Hydroxy-3-methylindanone (IV). Method A.—Phenyl α-bromobutyrate (99 g.) was vigorously stirred under a nitrogen atmosphere while 200 g. of aluminum chloride was added over a period of 30 minutes. The reaction vessel was then placed in an oil-bath and heated judiciously until the temperature reached 145°. After five hours at this temperature, stirring was discontinued and the oil-bath replaced by an ice-bath. The dark red cake was treated slowly with 600 g. of cracked ice and 50 cc. of concd. hydrochloric acid and the mixture allowed to stand overnight. Extraction with ether[14] gave a dark oil which deposited crystalline material when cooled. The oil was subjected to an exhaustive steam distillation to remove all steam volatile material, the oily residue in the distillation flask was taken up in ether and the ether evaporated to yield 24 g. of crude 5-hydroxy-3-methylindanone. After decolorization with activated charcoal and recrystallization from water the white crystals (13.7 g., 21%) melted at 149–150°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.97; H, 6.29.

5-Hydroxy-3-methylindanone (IV). Method B.—Aluminum chloride (45 g.) followed by anisole (36 g.) was added gradually at 0° to a stirred solution of crotonyl chloride (38 g.). After one hour the temperature was raised to 150° where it was maintained for 14 hours. The cooled reaction mixture was hydrolyzed (100 g. of ice, 10 cc. of concd. hydrochloric acid) and extracted with ether. The product was refluxed with 200 cc. of 48% hydrobromic acid and 50 cc. of glacial acetic acid for 24 hours; the reaction mixture was diluted with an equal volume of water and extracted with ether. The product was sublimed (140°, 0.05 mm.) yielding 0.47 g. of white crystals. On recrystallization from water, these melted 146–147°, and did not depress the m.p. of the product of method A.

5-Methoxy-3-methylindanone (V). Method A.—To a solution of 7.1 g. of 5-hydroxy-3-methylindanone in 50 cc. of dry dioxane there was added 5.2 g. of diazomethane in 300

(10) E. P. Kohler, *Am. Chem. J.*, **42**, 376 (1909).

(11) *Cf.* ref. 9 in which 7-hydroxyindanone was obtained from phenyl α-bromopropionate.

(12) All melting points are corrected, boiling points uncorrected.

(13) C. A. Bischoff, *Ber.*, **39**, 3830 (1906).

(14) In all cases, unless further details are furnished, "extraction with ether" signifies that five extractions were made, each with a volume of ether equal to about one-fourth the volume of aqueous solution and that the combined ether extracts were dried over "Drierite" and the product obtained by removal of the ether by distillation.

cc. of ether. The reaction mixture stood 60 hours at room temperature, then the excess diazomethane was distilled off and the solvents removed *in vacuo*. The oily product was distilled (108°, 0.5 mm.) to yield 5.4 g. (70%) of a liquid which was induced to crystallize by cooling in a Dry Ice and acetone bath. After recrystallization from petroleum ether–ether the white crystals of 5-methoxy-3-methylindanone melted at 50–51°.

5-Methoxy-3-methylindanone (V). Method B.—5-Hydroxy-3-methylindanone (5.0 g.) was dissolved in 1000 cc. of reagent grade acetone and to this solution 30 g. of anhydrous potassium carbonate and 15 cc. of methyl iodide were added. Sufficient heat was applied to cause vigorous refluxing with bumping. After 18 hours an additional 10 g. of potassium carbonate and 10 cc. of methyl iodide were added. Refluxing was continued for six additional hours, then the hot solution was filtered and the solid potassium salts were collected. These were dissolved in water, the aqueous solution was extracted with ether and the dried ether solution combined with the original acetone filtrate. Evaporation yielded an oil which crystallized when seeded with the product of method A. After washing with petroleum ether, the dried white crystals weighed 3.4 g. (62% yield), m.p. 49–50°. Recrystallization from pentane–ether raised the m.p. to 50–51°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.08; H, 6.94.

5-Methoxy-3-methylindanone semicarbazone was prepared in the usual manner.[15] It melted at (dec.) 213–214°.

Anal. Calcd. for $C_{12}H_{15}N_3O_2$: C, 61.78; H, 6.48. Found: C, 61.80; H, 6.48.

5-Methoxy-3-methylindanone-2-acetonitrile (VI).—5-Methoxy-3-methylindanone (12.5 g.) dissolved in 50 cc. of ethanol was added to a mixture of 3.8 g. of paraformaldehyde, 6.3 g. of dimethylamine hydrochloride, 25 cc. of ethanol and 0.3 cc. of concd. hydrochloric acid. Heat was applied and a reflux temperature maintained for 12 hours under a nitrogen atmosphere. The ethanol was removed from the pale yellow solution *in vacuo* and the residual oil (presumably the Mannich base hydrochloride) was added to 250 cc. of water containing 6.2 g. of sodium cyanide; this mixture was heated at reflux under nitrogen for three hours, acidified with 50% sulfuric acid and extracted with ether. The yield of crystalline material, m.p. 84–89°, was 6.5 g. Recrystallization from ethanol raised the m.p. to 94–95°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.35; H, 6.11; N, 6.32.

5-Hydroxy-3-methylindanone-2-acetic Acid (III).—5-Methoxy-3-methylindanone-2-acetonitrile (3.3 g.) was refluxed for 12 hours under nitrogen with 30 cc. of glacial acetic acid and 150 cc. of 48% hydrobromic acid. The mixture was cooled, diluted with an equal volume of water and extracted with ether. The product was refluxed overnight with 100 cc. of 10% sodium hydroxide (to assure isolation of the correct diastereoisomer), the solution cooled, acidified (5% sulfuric acid) and extracted with ether. The combined ether extracts were back extracted with saturated sodium bicarbonate solution and the bicarbonate extracts acidified and extracted with ether to give an oil which crystallized when seeded with an authentic sample of III. Sublimation at 140° and 0.1 mm. removed a volatile by-product (which was shown to be IV—evidently carried into the bicarbonate extracts by virtue of its water solubility) and on raising the sublimation temperature to 210°, 1.2 g, (35%) of white crystalline material was obtained, m.p. 165–166°. Recrystallization from water or ethyl acetate raised the m.p. to 169–170°. The m.p. of this product was not changed on admixture with an authentic sample of decarboxyterracinoic acid. Comparison of ultraviolet and infrared absorption curves also confirmed the identity of the product with decarboxyterracinoic acid (III). (See ref. 3 for information on the ultraviolet and infrared absorption of III.)

4-Carboxy-5-hydroxy-2,3-dimethylindanone.—4-Carboxy-5-hydroxy-2,3-dimethylindenone[3] (IX) (10.3 g.) in 120 cc. of ethanol with 1 g. of 5% palladized charcoal was shaken under 25 pounds of (initial) hydrogen pressure at room temperature until the pressure drop corresponded to a one-mole uptake. The catalyst was removed by filtration and the solvent evaporated *in vacuo* leaving 7.5 g. (72%) of crystalline product. After one recrystallization from acetone–ethyl acetate the white crystals melted at 230–230.5°. (A mixture of the starting material, which melts at 230.5-231°, and the product had a m.p. of 210–214°.)

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.28; H, 5.40.

The same product was isolated[16] when platinum oxide catalyst was employed.

5-Hydroxy-2,3-dimethylindanone.—4-Carboxy-5-hydroxy-2,3-dimethylindanone (0.3 g.) was heated in 50 g. of 85% phosphoric acid under a nitrogen atmosphere for three hours at 150°. (During this time 78% of the theoretical evolution of carbon dioxide was isolated as barium carbonate.) The cooled reaction mixture was diluted with 50 cc. of water and extracted with ether. The product obtained was sublimed (150°, 0.05 mm.) to yield 0.11 g. (46%) of crystalline 5-hydroxy-2,3-dimethylindanone (VII). This, after recrystallization from water and ether, and resublimation, melted at 128–129°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.87; H, 6.76.

5-Methoxy-2,3-dimethylindanone (VIII).—5-Hydroxy-2,3-dimethylindanone (2.5 g.) was dissolved in 500 cc. of reagent grade acetone; 50 g. of anhydrous potassium carbonate and 10 g. of methyl iodide were added. The mixture was refluxed for 24 hours, then 10 g. of additional methyl iodide was put in and refluxing continued for two days. The potassium salts were filtered from the hot solution and washed with boiling acetone. The acetone was distilled from the combined filtrate and washings and the residual oil evaporatively distilled (110°, 0.05 mm.) yielding 1.3 g. of 5-methoxy-2,3-dimethylindanone (VIII).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.38; H, 7.44.

5-Methoxy-2,3-dimethylindanone semicarbazone was prepared from VIII in the conventional manner[15] except that the reaction was heated for 24 hours. The semicarbazone, after recrystallization from ethanol, melted at 248–249°.

Anal. Calcd. for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93. Found: C, 63.25; H, 6.91.

5-Methoxy-2,3-dimethylindanone Semicarbazone (Synthetic).—5-Methoxy-3-methylindanone (5.0 g.) was dissolved in 25 cc. of dry *t*-butyl alcohol and to this solution there was added under nitrogen a solution prepared from 1.1 g. of potassium and 25 cc. of *t*-butyl alcohol. To the stirred mixture a solution of 4.0 g. of methyl iodide in 100 cc. of *t*-butyl alcohol was added over a period of one hour; stirring was continued for five hours. Ether was added and 3.7 g. of potassium iodide filtered off. The filtrate was evaporated and the residual oil shaken with water; the oil layer was taken up in ether, the ether removed and the residual liquid distilled (97–99°, 0.07 mm.) yielding 1.8 g. of a liquid. One gram of this liquid was treated in the manner conventionally used for semicarbazone formation.[15] After 30 minutes at 100° the reaction mixture had deposited 0.5 g. of 5-methoxy-3-methylindanone semicarbazone (identified by infrared absorption and mixed melting point). Heating was continued for 24 hours, during which time additional crystalline material separated. After recrystallization of the latter product from ethanol there was obtained 0.045 g. of 5-methoxy-2,3-dimethylindanone semicarbazone, m.p. 247–248°. This m.p. was not depressed on admixture of the product with the semicarbazone obtained from the Terramycin degradation product. Comparison of the infrared absorption curves of the two products in Nujol mull also proved their identity.

7-Hydroxy-3-methylindanone (X).—The distillate from the steam distillation described above in connection with the preparation of 5-hydroxy-3-methylindanone (IV) was extracted with ether. The liquid product was fractionally distilled *in vacuo*, yielding 29 g. (44%) of colorless liquid; b.p. 63°, 0.07 mm., $n^{20}D$ 1.5685.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.07; H, 6.22. Found: C, 73.98; H, 6.40.

7-Methoxy-3-methylindanone.—7-Hydroxy-3-methylindanone (29 g.) was heated at reflux with 100 cc. of 2.5%

(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170, procedure 13-B.

(16) Observation by Dr. F. A. Hochstein.

sodium hydroxide while 28 g. of dimethyl sulfate was added dropwise. When the *p*H reached 2, sufficient 10% sodium hydroxide was added to bring the *p*H to 10. The mixture was then refluxed for 12 hours. Twenty-five cc. of methyl sulfate was then added and after the *p*H had again reached 2 (1.5 hours), 10% sodium hydroxide was added to return the *p*H to 10. Heating was continued for an additional two hours. (The insoluble sodium salt of the hydroxy indanone reacted slowly with dimethyl sulfate. Thus, this somewhat cumbersome procedure was adopted in order to obtain complete reaction.) The cooled alkaline solution was extracted with ether and the product was distilled (104°, 0.1 mm.) to yield 22 g. (71%) of a liquid which crystallized on standing (m.p. 55–57°).

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.25; H, 7.15.

7-Hydroxy-3-methylindanone-2-acetic Acid (II).—A mixture consisting of 21.3 g. of 7-methoxy-3-methylindanone, 10.7 g. of dimethylamine hydrochloride, 6.5 g. of paraformaldehyde, 0.5 cc. of concd. hydrochloric acid, and 100 cc. of ethanol was refluxed for six hours, then allowed to stand for two days at room temperature. The solvents were removed *in vacuo* without warming, 100 cc. of water was added, and the mixture was extracted with ether. The combined ether extracts gave 11.4 g. of unreacted 7-methoxy-3-methylindanone. The raffinate was heated at reflux with 10.8 g. of sodium cyanide for five hours, during which time an oil layer separated. The mixture, which stood overnight at room temperature, was extracted with ether to yield 9.0 g. of an oil. (This was presumably crude 7-methoxy-3-methylindanone-2-acetonitrile.) This was heated at reflux for 24 hours with 250 cc. of 10% methanolic sodium hydroxide and the acid isolated as an oil by acidification and extraction with ether. This oil was then heated in a refluxing mixture of 100 cc. of 48% hydrobromic acid and 25 cc. of glacial acetic acid for 18 hours. The solution was cooled, diluted with an equal volume of water and extracted with ether. The product was redissolved in ether and the ether extracted with saturated sodium bicarbonate. Acidification of the bicarbonate solution and extraction with ether gave 3.63 g. of an oil which crystallized immediately when seeded with crystals of isodecarboxyterracinoic acid (II). The m.p. of the crude material (96–105°) was raised by recrystallization from benzene–ethyl acetate to 109.5–110.5°. There was no depression of the m.p. when the sample was mixed with an authentic sample of II. Comparison of the ultraviolet and infrared absorption curves of the two samples confirmed their identity. (The ultraviolet and infrared absorption characteristics of II will be published by Hochstein, *et al.*)

Acknowledgments.—The author gratefully acknowledges the helpful suggestions offered in the course of this work by K. J. Brunings, P. N. Gordon, F. J. Pilgrim, C. R. Stephens and R. B. Woodward. He is indebted to G. B. Hess, J. A. Means and T. J. Toolan for microanalyses and physical measurements. Special thanks are due to F. A. Brastow, A. T. Gilman and R. J. Grabowski for valuable technical assistance.

GROTON, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

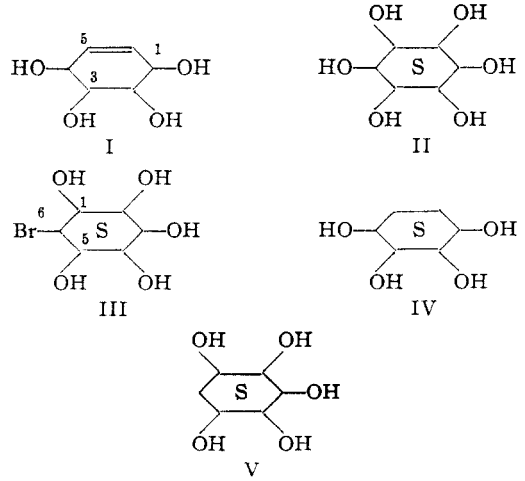
Debromination of Inositol Bromohydrins.* Synthesis of "Conduritol-*B*," *scyllo*Quercitol, and D,L-*vibo*Quercitol[1,2]

BY G. E. MCCASLAND AND E. CLYDE HORSWILL[3]

RECEIVED MARCH 30, 1953

A new cyclohexenetetrol, "conduritol-*B*," has been prepared and shown to have the configuration IX. Dihydroconduritol-*B* is identical with the cyclohexanetetrol m.p. 188° prepared from cyclohexadiene-1,3 by Bedos and Ruyer in 1933. Bedos and Ruyer's other tetrol, m.p. 209°, must then be identical with the dihydro derivative of Kubler's conduritol (conduritol-*A*). Conduritol-*B* tetraacetate is obtained by treating the bromoquercitol pentaacetate of m.p. 240° with zinc–acetic acid. The corresponding free bromoquercitol is 6-bromo*scyllo*quercitol (XI), since it gives *scyllo*quercitol on catalytic debromination. From *myo*inositol another bromoquercitol, m.p. 171°, can be obtained, and it must be 6-bromo*vibo*quercitol (XV), since it gives D,L-*vibo*quercitol on catalytic debromination. The tetraacetate of XV reacts with zinc to give conduritol-*B* identical with the above. The mechanisms of formation and configurations of the known bromoquercitols are discussed.

In 1908 Kubler[4] isolated from the bark of the vine *Marsdenia condurango* the first known cyclohexenetetrol (I), m.p. 143°, which he named *conduritol*.[5] The configuration *meso*-XX for Kubler's conduritol was later established by Dangschat and Fischer.[6] Five other diastereomers of this structure are possible. To avoid ambiguity, the diastereomer XX will be called conduritol-*A* in the remainder of this article.



* Presented before the Organic Division at the Windsor Meeting of the Chemical Institute of Canada, June, 1953.

(1) For related publications on cyclitol chemistry see: (a) G. E. McCasland, THIS JOURNAL, **73**, 2295 (1951); (b) G. E. McCasland and S. Boutsicaris, *ibid.*, **75**, 3845 (1953); (c) H. E. Carter, R. K. Clark, Jr., Betty Lytle and G. E. McCasland, *J. Biol. Chem.*, **175**, 683 (1948); (d) H. E. Carter, C. Belinskey, R. K. Clark, Jr., E. H. Flynn, B. Lytle, G. E. McCasland and Mary Robbins, *ibid.*, **174**, 415 (1948).

(2) From the Ph.D. Thesis of E. Clyde Horswill, 1953.

(3) Fellow of the National Research Council, 1952–1953.

(4) K. Kubler, *Arch. Pharm.*, **246**, 620 (1908).

(5) We use *conduritol* in the generic sense to designate any of the six diastereomers of 5-cyclohexenetetrol-1,2,3,4—also specifically to designate Kubler's conduritol. (*Cf.* usage of *inositol.*) To be fully explicit, Kubler's diastereomer (first one discovered) may be called "conduritol-*A*," and the diastereomer reported by us "conduritol-*B*."

(6) G. Dangschat and H. O. L. Fischer, *Naturwissenschaften*, **27**, 756 (1939).