minutes. After cooling somewhat, alcohol was added and the solution was allowed to stand until crystallization had taken place. After 2 recrystallizations the constant melting point of 110° to 111° was obtained. It was observed that Strache and Iritzer,[1] who previously described this compound, gave the melting point 105° to 107°. When crystallized from alcohol it crystallized in well defined small, thin, rectangular prisms. It is readily soluble in hot alcohol, but sparingly soluble in cold alcohol. 100 cc. of 95% alcohol at 29° dissolved 0.076 g. A yield of 18% of the pure derivative was obtained.

Subs., 0.1315; CO_2, 0.3706; H_2O, 0.1298.
Calc. for $C_{24}H_{41}N_2O$: C, 76.93; H, 11.04. Found: C, 76.71; H, 11.05.

Arachidic Phenylhydrazid, $C_{20}H_{39}O.HNNHC_6H_5$ was obtained in the same manner as the stearyl derivative starting with 2 g. of arachidic acid and 1.5 cc. of phenylhydrazine. The highest melting point obtained by recrystallization from alcohol was 108 to 109°. From alcohol it crystallizes in small illy defined thin prisms. It was found that 100 cc. of 95% alcohol at 27° dissolved 0.050 g. while at 40° 0.0530 g. was dissolved. A yield of 29% of the pure derivative was obtained.

Subs., 0.1384; CO_2, 0.3924; H_2O, 0.1409.
Calc. for $C_{26}H_{46}N_2O$: C, 77.54; H, 11.52. Found: C, 77.33; H, 11.39.

Summary.

The menthyl esters of lauric, myristic, palmitic, stearic, and arachidic acids have been prepared and their optical rotations have been determined.

Also the phenylhydrazine derivatives of palmitic, stearic, and arachidic acids have been made and studied.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

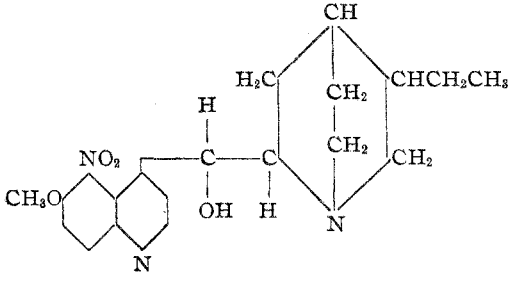
SYNTHESES IN THE CINCHONA SERIES.

IV.[2] NITRO- AND AMINO-DERIVATIVES OF THE DIHYDRO ALKALOIDS.

BY WALTER A. JACOBS AND MICHAEL HEIDELBERGER.

Received May 4, 1920.

In the preparation of 5-nitro-dihydro-quinine



[1] *Loc. cit.*

[2] Cf. THIS JOURNAL, 41, 817, 2090, 2131 (1919).

and 5-amino-dihydro-quinine according to German patent No. 283,537, difficulties were encountered which had to be overcome before the amino compound could be obtained readily enough to serve as a starting point for certain synthetic work which we had contemplated. In the first place, nitro-dihydro-quinine is described as resulting from the nitration of dihydro-quinine sulfate by the use of a nitric-sulfuric acid mixture, with no reference to the exact proportions employed. A study of the reaction showed that the formation of nitro-dihydro-quinine was complicated by the production of a nitro-dihydro-quinine sulfonic acid. Although this did not occur when the sulfate was added to a mixture of equal volumes of nitric and sulfuric acids, the tendency toward sulfonation increased as the proportion of sulfuric acid to nitric acid was increased, with consequent diminution of the yield of nitro-dihydro-quinine. It was then found that a quantitative conversion of dihydro-quinine into the nitro base could easily be realized with fuming nitric acid, and this was finally adopted as the most satisfactory reagent since it is less viscous and dissolves the alkaloid more rapidly than the mixture of equal parts of sulfuric and nitric acids, and also yields a less highly colored product.

Experiments with nitro-dihydro-quinine sulfonic acid explained its occurrence, since it was shown that this substance is formed both by nitration of dihydro-quinine sulfonic acid and by sulfonation of nitro-dihydro-quinine. In the latter case, it is sufficient to allow a solution of the nitro base in conc. sulfuric acid to stand at room temperature, a result in no way surprising, since the dihydro alkaloids have been found to yield sulfonic acids readily under the same conditions.[1] Since the nitro acid may be obtained from dihydro-quinine sulfonic acid, the sulfonic acid group occupies the same position in both of these acids, but according to Schmid's[2] experiments with cinchotine sulfonic acid, it is not situated in the quinoline nucleus. The lability of the sulfonic acid group toward boiling hydrochloric acid and its stability in boiling alkaline solution as demonstrated by Schmid for dihydro-quinine sulfonic acid, are properties retained by the nitro acid.

By following the method for the reduction of nitro-dihydro-quinine given in the patent we obtained but poor yields of the amino alkaloid, and it was necessary to modify the method considerably before a smooth conversion of the nitro alkaloid into the amino compound was afforded. In extending the work, the methods outlined were successfully applied to ethyl-dihydro-cupreine (optochin), dihydro-quinidine, ethyl-dihydro-cupreidine,[3] and dihydro-quinane,[4] resulting in the synthesis of the corre-

[1] Hesse, *Ann.*, **241**, 283 (1887); Skraup, *Monatsh.*, **18**, 414 (1897).

[2] Schmid, *ibid.*, **22**, 803 (1901).

[3] THIS JOURNAL, **41**, 830 (1919).

[4] See following paper.

sponding nitro and amino derivatives. Like 5-amino-quinoline, the amino alkaloids form orange-red, non-fluorescent solutions in dilute acids and in addition give the thalleoquinine reaction. This reaction is not given by the nitro compounds.

Experimental Part.

5-Nitro-dihydro-quinine.—Although this substance was prepared by the use of a nitration mixture consisting of equal parts of conc. nitric and sulfuric acids as in the preparation of dinitro-quinine by Rennie,[1] fuming nitric acid was found to give the most satisfactory results with dihydro-quinine and was, therefore, employed in the other cases described below.

Fifty g. of anhydrous dihydro-quinine sulfate were added in small portions to 200 cc. of fuming nitric acid (sp. gr. 1.52), with turbining, and keeping the temperature at 0°. The salt dissolved rapidly, and after addition of the full amount the clear solution was allowed to stand for 15 minutes at 0° and then poured on to ice. After dilution to about 4 liters the solution was treated with 25% aqueous sodium hydroxide until most of the nitric acid was neutralized and the alkaloid still remained dissolved as the nitrate. The solution was then vigorously stirred and the base quickly precipitated by the rapid addition of ammonia in excess. If the precipitation is too slow, or if the solution is not sufficiently dilute, a gummy mass of what is presumably the mono nitrate separates and is difficult to transform into an easily filterable form. The pale yellow, partially crystalline precipitate is filtered off, washed well with water, and dissolved in dil. hydrochloric acid. After adding an equal volume of alcohol, warming, and making alkaline with ammonia, the nitro-dihydro-quinine separates rapidly as lustrous yellow plates. After washing with 50% alcohol the yield is 90%.

For final purification the base was dissolved in 50% alcohol by the addition of sufficient acetic acid, and, after warming again, precipitated with ammonia, forming lustrous, pale yellow, hexagonal scales which decompose at 220–2° with preliminary darkening and softening, and not at 209–12° as given in the patent. The nitro compound is appreciably soluble in methyl or ethyl alcohol, acetone or benzene, more readily so in the hot solvents. It is easily soluble in chloroform and dil. acids and very sparingly in ether. It does not give the thalleoquinine test, and on exposure to sunlight turns a purplish brown. $[\alpha]_D^{25°} = -200.0°$ in chloroform; $c = 1.350$.

Subs., 0.1293: 12.91 cc. N (25.0°, 760 mm.).
Calc. for $C_{20}H_{25}O_4N_3$: N, 11.32. Found: 11.42.

5-Nitro-dihydro-quinine Sulfonic Acid.—(*A*). From nitro-dihydro-quinine. This substance was obtained as the main product of the reaction when the nitration of dihydro-quinine was attempted with a mixture

[1] Rennie, *J. Chem. Soc.*, **39**, 470 (1881).

of sulfuric acid and the theoretical amount of conc. nitric acid. It was then found that the compound results either from the nitration of dihydro-quinine sulfonic acid, or by allowing a solution of nitro-dihydro-quinine in conc. sulfuric acid to stand at ordinary temperature, just as in the formation of dihydro-quinine sulfonic acid.

Five g. of nitro-dihydro-quinine were dissolved in 25 cc. of conc. sulfuric acid and allowed to stand for 24 hours. After pouring on to ice and diluting, the greenish yellow solution was partly neutralized with sodium hydroxide and finally made neutral to Congo red with sodium acetate solution. On rubbing the acid separates as yellow needles which were washed with water. It was recrystallized by dissolving in dil. alkali, warming, and reacidifying with acetic acid, a transitory turbidity appearing at the neutral point. The acid separates as flat, glistening, yellow needles which rapidly turn green on exposure to sunlight. It chars when heated above 260° but does not melt below 285°, and is practically insoluble in the usual solvents except boiling 50% alcohol. It dissolves in dil. hydrochloric and nitric acids but less readily in dilute sulfuric acid. The addition of strong sodium hydroxide or sodium chloride solution to the solution of the acid in dil. sodium hydroxide salts out the sodium salt as a gummy precipitate. Like dihydro-quinine sulfonic acid, the nitro acid is relatively stable in alkaline solution but on boiling with 20% hydrochloric acid the sulfonic group is quantitatively eliminated with the formation of nitro-dihydro-quinine. This property was, therefore, employed for the sulfur determination. The position occupied by the sulfonic acid group was not determined, although it was shown to be the same as that occupied by the sulfo group in dihydro-quinine sulfonic acid, since this yielded the same nitro compound. $[\alpha]_D^{25°} = -133.0°$ in 0.5 N NaOH; $c = 1.000$.

Subs., 0.1240: 10.6 cc. N (28.0°, 759 mm.). Subs., 0.1509: $BaSO_4$, 0.0751.
Calc. for $C_{20}H_{25}O_7N_3S$: N, 9.31; S, 7.10. Found: N, 9.69; S, 6.84.

(B). From dihydro-quinine sulfonic acid. Dihydro-quinine sulfonic acid was obtained by allowing a solution of 10 g. of anhydrous dihydro-quinine sulfate in 50 cc. of conc. sulfuric acid to stand for 24 hours. After dilution with water and partial neutralization with sodium hydroxide solution, the mixture was neutralized to Congo red with sodium acetate, causing the separation of 8.7 g. of the sulfonic acid as lustrous, colorless rhombs, often grouped as serrated aggregates. This was added in small portions to 30 cc. of fuming nitric acid (sp. gr. 1.52) kept at 0°. After 15 minutes' standing at 0°, the mixture was poured on to ice and the acid isolated as previously described. After recrystallization 8.7 g. of slightly greenish yellow, flat, glistening needles were obtained, identical in all respects with the acid obtained from nitro-dihydro-quinine. $[\alpha]_D^{27°} = -129.6°$ in 0.5 N NaOH; $c = 1.012$.

Subs., 0.1201: 10.0 cc. N (23.5°, 759 mm.). Subs., 0.2005: $BaSO_4$, 0.1052.
Calc. for $C_{20}H_{25}O_7N_3S$: N, 9.31; S, 7.10. Found: N, 9.58; S, 7.21.

Hydrolysis of Nitro-dihydro-quinine Sulfonic Acid to Nitro-dihydro-quinine.—2 g. of the sulfonic acid dissolved in 25 cc. of 1 : 1 hydrochloric acid were boiled for one hour. An equal volume of alcohol was added and the solution made alkaline with ammonia. The crystalline precipitate was recrystallized as previously described, forming lustrous, pale yellow, hexagonal scales which decomposed at 220–2° and proved identical with the 5-nitro-dihydro-quinine prepared by the direct method.

Subs., 0.1312: 13.2 cc. N (24.0°, 758 mm.).
Calc., N, 11.32. Found: 11.54.

5-Amino-dihydro-quinine.—On repeating the directions given in German patent 283,537 for the reduction of nitro-dihydro-quinine, it was found that when the reaction mixture was made alkaline before extracting the amino compound with ether, it rapidly turned deep green owing to oxidation, showing that decomposition had occurred. In consequence, the yield of amino-dihydro-quinine was poor, only 5.8 g. being recovered from 18 g. of the nitro compound. A number of experiments finally led to the following satisfactory method, which was then applied to the reduction of the other nitro cinchona derivatives described below.

18.5 g. of nitro-dihydro-quinine were dissolved in 185 cc. of conc. hydrochloric acid with chilling and stirring, the alkaloid being slowly added in order to diminish the tendency to form a gum. After chilling the solution to 0°, 45 g. of stannous chloride were added. On removing the beaker from the freezing mixture and stirring, the temperature rose as the reaction proceeded, but was not allowed to exceed 35°. A thick, partially crystalline, yellow paste of the tin salt separated, and after standing for 15 minutes, the mass was dissolved in water and ice added. The deep orange-red solution was then treated with an excess of 25% sodium hydroxide solution, no trace of green coloration being evident. The amorphous amino compound was shaken out with about one liter of ether, the yellow solution depositing most of the substance as yellow needles on standing. On concentration the mother liquor yielded the remainder, the total being 15 g. Recrystallized from hot benzene, in which it is fairly easily soluble at the boiling point, it separates as rosets of thickly matted, minute, yellow, microscopic needles which melt at 220–1° with slight preliminary softening. Giemsa and Halberkann[1] give 217–8° as the melting point, while in German patent 283,537 it is given as 208–12°. The base is very readily soluble in chloroform, quite easily in methyl or ethyl alcohol, less so in acetone, and very sparingly in ether or cold benzene. It gradually turns a brownish purple on exposure to sunlight. It dissolves in dilute acids with an orange-red color

[1] *Ber.*, **52**, 922 (1919).

and gives the thalleoquinine reaction, and, as we shall describe more fully in a subsequent communication, it couples smoothly with diazo compounds to form well defined amino-azo dyes. $[\alpha]_D^{21^\circ} = -17.7^\circ$ in absolute alcohol; $c = 1.020$.

Subs., 0.1187: 12.85 cc. N (20.0°, 749 mm.).
Calc. for $C_{20}H_{27}O_2N_3$: N, 12.31. Found: 12.44.

5-Nitro-ethyl-dihydro-cupreine (5-Nitro-optochin).—20 g. of anhydrous ethyl-dihydro-cupreine sulfate (from a solution of the chloride with ammonium sulfate) were nitrated as in the case of dihydro-quinine sulfate. The base, precipitated from the diluted reaction mixture with ammonia, first separated amorphous and then partly crystallized. It was recrystallized by dissolving in 50% alcohol with the aid of acetic acid and reprecipitated by the addition of ammonia to the warm solution. The base separated in excellent yield as lustrous, pale yellow, hexagonal platelets which melted and decomposed at 225–6° with preliminary darkening and softening after another recrystallization from toluene. It is rather difficultly soluble in cold alcohol or acetone but readily on boiling, and is more easily soluble in cold methyl alcohol or chloroform. A concentrated neutralized solution of the nitro alkaloid in hydrochloric acid deposits pale yellow, delicate needles of the hydrochloride. $[\alpha]_D^{22.5^\circ} = -198.2^\circ$ in chloroform; $c = 0.515$.

Subs., 0.1267: 12.15 cc. N (23.5°, 760 mm.).
Calc. for $C_{21}H_{27}O_4N_3$: N, 10.91. Found: 11.04.

5-Amino-ethyl-dihydro-cupreine (5-Amino-optochin).—18.5 g. of the nitro compound, treated as in the case of nitro-dihydro-quinine, yielded 14 g. of the amino alkaloid after recrystallizing from dil. alcohol with the aid of boneblack. Recrystallized from 85% alcohol, the base separates as minute, lemon-yellow platelets which melt with slow decomposition at 214–5° with slight preliminary softening and darkening. It is very readily soluble in chloroform, quite easily in methyl and ethyl alcohols and less readily in acetone, forming yellow solutions. It dissolves in hot benzene, separating in gelatinous form on cooling. The solution in dil. hydrochloric acid is orange in color, and gives the thalleoquinine reaction. $[\alpha]_D^{24.5^\circ}$ is -15.9° in absolute alcohol, $c = 1.034$, while Giemsa and Halberkann[1] give $[\alpha]_D^{20} = -13.2^\circ$ and the melting point as 211–2°.

Subs., 0.1225: 12.55 cc. N (23.0°, 770 mm.).
Calc. for $C_{21}H_{29}O_2N_3$: N, 11.83. Found: 11.97.

5a-Nitro-dihydro-quinidine.—46.5 g. of anhydrous dihydro-quinidine sulfate were nitrated as in the previous cases, the final precipitation of the free base being carried out rapidly with ammonia from the highly diluted reaction mixture. If the precipitation is too slow, or if the solution is too concentrated the substance separates largely as a gum consisting of the

[1] *Loc. cit.*, pp. 922–3.

nitrate of the base. It is advisable even when precipitation is properly accomplished to grind the filtered and washed base with dil. ammonia and to filter and wash again. The yield of amorphous base was 43 g. and was sufficiently pure for reduction to the amino alkaloid.

On dissolving the dried base in hot ethyl acetate and allowing to cool rapidly it separates as a jelly, but when the concentrated solution is kept warm and rubbed, the nitro compound separates slowly as yellow rhombs. The same phenomena occur in 50% alcohol, since crystallization is slow, and in order to avoid contamination with amorphous material the solutions must be kept warm. The crystalline base is readily soluble in alcohol, chloroform, acetone and ethyl acetate, less easily in benzene and very sparingly in ether. It melts and decomposes at about 208–9° with preliminary darkening and softening, and does not give the thalleoquinine test. $[\alpha]_D^{23} = +326.5°$ in absolute alcohol; $c = 0.668$.

Subs., 0.1082: CO_2, 0.2579; H_2O, 0.0647. Subs., 0.1307: N, 13.2 cc. (23.0°, 765 mm.).

Calc. for $C_{20}H_{25}O_4N_3$: C, 64.65; H, 6.79; N, 11.32. Found: C, 65.00; H, 6.69; N, 11.72.

The Nitrate.—This salt was obtained in one experiment in which the insufficiently diluted reaction mixture from the nitration of dihydroquinidine sulfate had been precipitated with ammonia, the precipitate consisting mostly of the nitrate. Although flocculent at first, it sintered to a gum which prevented filtration, but was collected and dissolved in 95% alcohol, the salt separating as pale yellow rhombs, which were again crystallized from alcohol. The air-dry salt contains solvent approximately equivalent to 2 molecules of water of crystallization, and like the anhydrous salt intumesces at 142–5°. It is slowly but fairly readily soluble in water with a bright yellow color and dissolves readily in methyl and ethyl alcohols, acetone and chloroform, and only sparingly in hot benzene. $]\alpha[_D^{22}$ of the anhydrous salt is +232.8° in water; $c = 0.896$.

Air-dry: Subs., 0.6727: loss, 0.0570, *in vacuo* at 80° over H_2SO_4.
Calc. for $C_{20}H_{25}O_4N_3.HNO_3.2H_2O$: H_2O, 7.66. Found: 8.47.
Anhydrous: Subs., 0.1112: N, 12.0 cc. (22.0°, 763 mm.).
Calc. for $C_{20}H_{25}O_4N_3.HNO_3$: N, 12.90. Found: 12.54.

5-Amino-dihydro-quinidine.—18.5 g. of the dried, amorphous nitro alkaloid yielded 11.5 g. of the amino compound. The substance separates slowly from the ethereal extract as olive-yellow rhombs. Recrystallized from 95% alcohol, it forms minute, rhombic platelets which, when rapidly heated to 235°, then slowly, darken and decompose at 238–42°. The base is somewhat less soluble in cold alcohol than in methyl alcohol, forming yellow solutions, and is more easily soluble in hot chloroform than in hot acetone. It gives the thalleoquinine reaction and dissolves in dil. hydrochloric acid with an orange-red color which appears orange-brown in thin layers. $[\alpha]_D^{20}$ is +115.5° in absolute alcohol; $c = 0.870$.

Subs., 0.1230: N, 13.05 cc. (24.5°, 768 mm.).
Calc. for $C_{20}H_{27}O_2N_3$: N, 12.31. Found: 12.30.

5-Nitro-ethyl-dihydro-cupreidine.—5 g. of ethyl-dihydro-cupreidine[1] were slowly added to 25 cc. of fuming nitric acid (sp. gr. 1.52), keeping the temperature below 0°. Five cc. of conc. sulfuric acid were then added, and after standing for 20 minutes in the cold the mixture was poured into 1500 cc. of water. The nitro base was precipitated with ammonia and shaken out with ether, which, on concentration, yielded 4–5 g. of the crystalline nitro compound. Recrystallized as in previous examples from 50% alcohol, it separates as rosets and plumes of minute, narrow, pale yellow, glistening platelets which melt and decompose at 220–1° with preliminary darkening and softening. It is quite soluble in alcohol, acetone, benzene, and ether, and very readily so in chloroform. $[\alpha]_D^{22}$ is +322.4° in absolute alcohol; c = 0.951.

Subs., 0.1082: CO_2, 0.2593; H_2O, 0.0688. Subs., 0.1194: 11.3 cc. N (22.0°, 758 mm.).

Calc. for $C_{21}H_{27}O_4N_3$: C, 65.41; H, 7.07; N, 10.91. Found: C, 65.36; H, 7.12; N, 10.92.

5-Amino-ethyl-dihydro-cupreidine.—The nitro compound was reduced as in previous examples, but an entirely pure product was not obtained. The ethereal solution of the amino alkaloid left a crystalline residue on evaporation, which was recrystallized first from 85% alcohol, then from not too little toluene, separating on cooling as rosets of minute, lemon-yellow needles which melt at 216–7° with slight preliminary darkening and show $[\alpha]_D^{26.5}$ = —69.4° in dry chloroform; c = 1.017, $[\alpha]_D^{26.5}$ = +91.6° in absolute alcohol, c = 0.524. The base is rather difficultly soluble in alcohol, more easily in methyl alcohol, and fairly readily in dry chloroform, especially on warming. It is sparingly soluble in cold toluene, readily at the boiling point, separating in gelatinous form on cooling unless the solution is seeded and permitted to crystallize while still warm. It gives the thalleo-quinine reaction.

Subs., 0.1166: CO_2. 0.3007; H_2O, 0.0834. Subs., 0.1309: 14.0 cc. N (23.5°, 770 mm.).

Calc. for $C_{21}H_{29}O_2N_3$: C, 70.93; H, 8.23; N, 11.83. Found: C, 70.33; H, 8.00; N, 12.48.

5-Nitro-dihydro-quinane.—Dihydro-quinane trihydrate[2] was nitrated in the same way as was ethyl-dihydro-cupreidine. The partially crystalline nitro compound was shaken out with ether, which was dried and the solution then concentrated. The residue was taken up in 85% alcohol and diluted with water until the initial turbidity just redissolved. On rubbing and cautiously adding further small amounts of water, the hydrated nitro compound separated in a yield equal to that of the dihydro-quinane used. Recrystallized from 50% alcohol it forms radia-

[1] THIS JOURNAL, 41, 830 (1919).

[2] See following paper.

ting masses of pale yellow, delicate needles which retain 3.5 molecules of water of crystallization when dried to constant weight in a desiccator over water. When dried in the air, water is lost and the substance sinters to a gum. The hydrate begins to soften above 60° and melts to a turbid liquid at 67.5–9°. It dissolves readily in alcohol, acetone, or chloroform, and rather less easily in ether. It does not give the thalleoquinine test. $[\alpha]_D^{22}$ is +80.2° in 95% alcohol; c = 1.059.

Air-dry: Subs., 0.4842: loss, 0.0717 *in vacuo* at 80° over H_2SO_4. Subs., 0.1218: 10.8 cc. N (23.5°, 757 mm.).

Calc. for $C_{20}H_{26}O_3N_2.3.5H_2O$: H_2O, 15.07; N, 10.04. Found: H_2O, 14.80; N, 10.17.

An attempt to reduce this substance failed owing to the insolubility of its tin double salt.

Summary.

Improved methods are given for the preparation of 5-nitro- and 5-amino-dihydro-quinine, and it is shown that under the usual conditions of nitration with nitric and sulfuric acids sulfonation also occurs, and 5-nitro-dihydro-quinine sulfonic acid is formed as a by-product. The extension of the methods of nitration and reduction to ethyl-dihydro-cupreine (optochin), dihydro-quinidine and ethyl-dihydro-cupreidine led to the formation of the nitro and amino derivatives of these alkaloids, and descriptions of these new substances are given. 5-Nitro-dihydro-quinane (see next paper) is also described.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

SYNTHESES IN THE CINCHONA SERIES. V. DIHYDRO-DESOXY-QUININE AND DIHYDRO-DESOXY-QUINIDINE AND THEIR DERIVATIVES.

BY MICHAEL HEIDELBERGER AND WALTER A. JACOBS.

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As a part of our studies on the cinchona alkaloids it became of interest to examine the biological properties of the so-called "desoxy" compounds, in which the secondary alcoholic group of the parent bases