that was recrystallized from water. Analytical data indicated that the compound was 2,5-thiophenedicarboxylic acid. The melting point was above 260°.[16]

Anal. Calcd. for $C_6H_4O_4S$: C, 41.86; H, 2.34; neut. eq., 86.07. Found: C, 42.46; H, 2.57; neut. eq., 86.05.

Oximes of 5-Acetyl-2-thiopheneacetic Acid.—Ten grams of methyl 5-acetyl-2-thiopheneacetate was stirred rapidly with a solution of 6.0 g. of sodium hydroxide in 100 ml. of water until a clear solution was obtained. After fifteen minutes, 10.0 g. of hydroxylamine hydrochloride was added (*p*H about 7) and the solution was heated on the steam-bath for thirty minutes, cooled, and acidified to *p*H 2 with concentrated hydrochloric acid. After standing in the refrigerator, the product was filtered and recrystallized from 500 ml. of hot water, using decolorizing carbon; yield 5.5 g., m. p. 159–160° (dec.). An additional 2.1 g., m. p. 156–157°, was obtained by concentration of the filtrate. One gram of the oxime was heated on the steam-bath with 2 ml. of 96% sulfuric acid for fifteen minutes, cooled, and poured into 20 g. of finely chopped ice. The solid which separated was recrystallized four times from hot water; m. p. 172–173° (dec.).

Anal. Calcd. for $C_8H_9NO_3S$: C, 48.23; H, 4.55. Found (m. p. 159–160°): C, 48.42; H, 4.53. Found (m. p. 172–173°): C, 48.10; H, 4.40.

The infrared spectra of the oximes which melted at 159–160° and 172–173° were very similar. The lower melting form contained all the bands of the higher melting form as well as some additional ones in the long wave length region and was probably a mixture of the *syn* and *anti* forms of the oxime. The higher melting form was believed to be predominately a single isomer.

Oximes of Methyl 5-Acetyl-2-thiopheneacetate.—A solution of 10.0 g. of methyl 5-acetyl-2-thiopheneacetate and 10.0 g. of hydroxylamine hydrochloride in 25 ml. of pyridine and 25 ml. of methanol was boiled under reflux for two hours and then concentrated to a sirup under reduced pressure on the steam-bath. About 100 ml. of water was added and the mixture was adjusted to *p*H 2 with hydrochloric acid and then extracted twice with 100-ml. portions of benzene. The benzene extracts were evaporated from the frozen state and recrystallized from 25 ml. of carbon tetrachloride. The resulting white crystals melted at 57–59°; yield, 8.8 g. (82%).

One gram of the above described oxime of the methyl ester was dissolved in 10 ml. of 96% sulfuric acid and heated on the steam-bath for two minutes, cooled and poured into 80 g. of finely chopped ice. The solid which separated melted at 63–65°. Recrystallization from hot water raised the melting point to 68–69° and a recrystallization from carbon tetrachloride raised the melting point to 72–73°.

A solution of 1.0 g. of the 57–59° oxime in 2 ml. of 96% sulfuric acid was heated on the steam-bath for thirty minutes, cooled and poured into a mixture of ice and water which contained 7 g. of sodium acetate. The resulting solution was dried from the frozen state.' The residual solids were extracted twice with 25-ml. portions of boiling chloroform. A crystalline residue was obtained upon removal of the chloroform; yield, 0.24 g. After two recrystallizations from benzene it melted at 126–127°.

Anal. Calcd. for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20. Found (m. p. 57–59°): C, 50.74; H, 4.93. Found (m. p. 72–73°): C, 50.64; H, 5.04. Found (m. p. 126–127°): C, 50.99; H, 4.89.

Summary

A series of 5-substituted 2-thiopheneacetic acids has been prepared and the compounds tested and evaluated as regards their utilization as penicillin precursors by molds.

KALAMAZOO, MICHIGAN RECEIVED JULY 14, 1949

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[16] Messinger, *Ber.* **18**, 563 (1885), reported the melting point of 2,5-thiophenedicarboxylic acid to be above 350°.

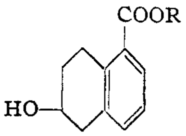
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MISSOURI]

The Hydrogenation of Some Substituted β-Naphthols[1]

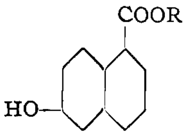
BY HERBERT E. UNGNADE[2] AND FRANCIS V. MORRISS[3]

Various reported attempts to prepare hydroxy acids derived from decalin by catalytic hydrogenation of naphthalene derivatives have met with failure due to the tendency of these compounds or perhaps their starting materials to undergo hydrogenolysis of the hydroxyl group.[4,5] Inasmuch as the hydrogenolysis reaction in the hydroxybenzoic acids can be prevented by reducing their esters with Raney nickel in the presence of small amounts of the corresponding sodium salts,[6] it appeared feasible that it could be repressed similarly in the naphthalene series. The reduction method has now been used successfully for the reduction of two hydroxynaphthoic esters and of 6-methoxy-2-naphthol without appreciable hydrogenolysis.[7]

Ethyl 6-hydroxy-1-naphthoate can be reduced partially by this method to give a tetrahydro ester (I) or a mixture (II) with analytical values corresponding to ethyl 6-hydroxyoctahydro-1-naphthoate, or perhydrogenated to give (III) depending on the activity of the catalyst.



I, R = Et
IV, R = H



III, R = Et
V, VI, VIII, R = H

Fresh W-4 Raney nickel catalyst gives an excellent yield (100%) of (III) while aged W-4 catalyst yields (I) or (II) and a little phenolic material which has not been further investigated.

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[1] From the Ph.D. thesis of F. V. Morriss.

[2] Present address: Chemistry Department, New Mexico Highlands University, Las Vegas, New Mexico.

[3] Shell Fellow, 1948–1949.

[4] Price, Enos and Kaplan, THIS JOURNAL, **69**, 2261 (1947).

[5] Long and Burger, *J. Org. Chem.*, **6**, 852 (1941).

[6] Ungnade and Morriss, THIS JOURNAL, **70**, 1898 (1948).

[7] An independent investigation of the hydrogenation of the two hydroxynaphthoic acids came to our attention at the conclusion of this work. Dauben, Hiskey and Markhart (abstract of a paper presented before the Division of Organic Chemistry of the American Chemical Society at San Francisco, March, 1949, page 44L) have disclosed a successful method for the hydrogenation of the free hydroxynaphthoic acids in alkaline solution which enables them to prepare either tetrahydro or perhydro acids.

Hydrolysis of (I) yields 44%[8] of a pure hydroxy acid (IV), m. p. 157.5–158.5°.[7] The hydrolysis of the liquid saturated ester (III) gives a mixture of isomers from which two pure acids (V), m. p. 220.5–221.5° and (VI), m. p. 219–220° have been isolated in yields of 18 and 0.29%.[8,9] The acid (IV) shows the characteristic absorption spectrum of an aromatic acid. The structures of (V) and (VI) follow from acetylation, oxidation and general weak absorption of the compounds over the range of 200–300 mμ (Fig. 1).

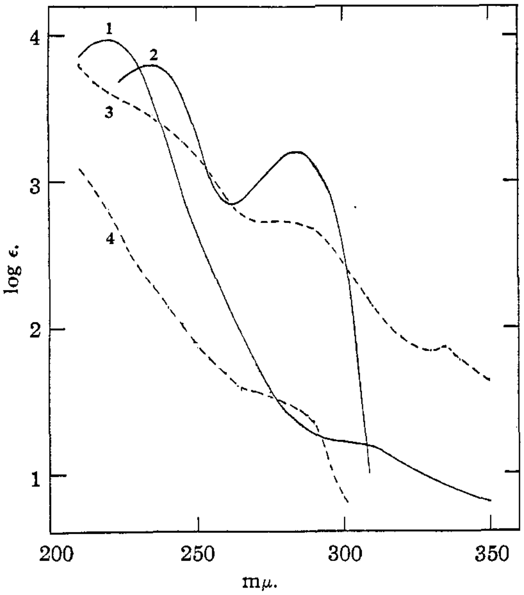
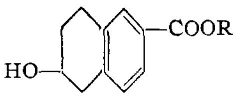


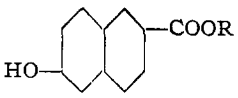
Fig. 1.—Absorption spectra: 1, octahydro-1-naphthoic acid (VIII); 2, 6-hydroxy-5,6,7,8-tetrahydro-1-naphthoic acid (IV); 3, mixture of acids (IIa); 4, ethyl 6-hydroxydecahydro-1-naphthoate (III).

The ester (II) and the corresponding acid (IIa) are regarded as mixtures of approximately equal amounts of tetrahydro and decahydro compounds although they could not be separated by the usual methods. Such an assumption is in accord with the spectral evidence. The possibility that these substances represent octahydro compounds[10] appears unlikely since the ultraviolet absorption spectrum of (IIa) differs from the absorption curves for (III) and a synthetic octahydro acid (VIII)[11] (Fig. 1).

In the beta series perhydrogenation occurs with fresh catalyst (yield 88.8%) while aged nickel yields a mixture of approximately 50% of ethyl 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoate (IX) and somewhat less ethyl 6-hydroxydecahydro-2-naphthoate (X).



IX, R = Et
XI, R = H



X, R = Et
XII, R = H

A pure tetrahydro acid (XI), m. p. 178.5–179°, has been isolated from the hydrolysis products of (IX). This substance is probably identical with the tetrahydro acid of Dauben and co-workers[7] melting at 180–181°. Its ultraviolet spectrum shows strong bands at 240 and 280 mμ which are characteristic for aromatic acids (Fig. 2).

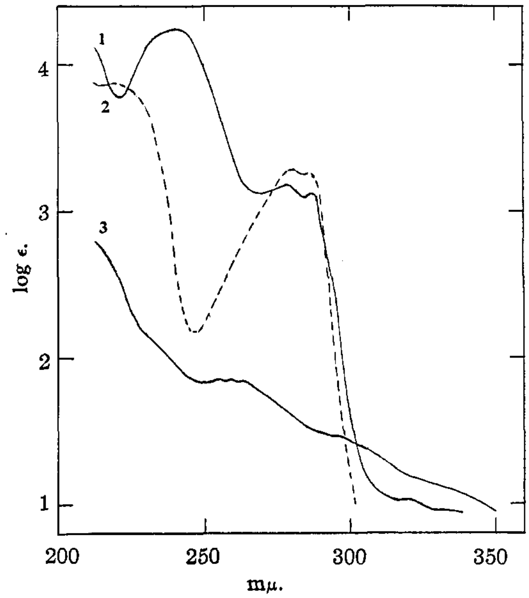
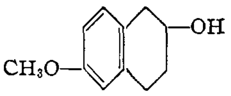


Fig. 2.—Absorption spectra: 1, 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid (XI); 2, 6-methoxy-1,2,3,4-tetrahydro-2-naphthol (XIV); 3, ethyl 6-hydroxydecahydro-2-naphthoate (X).

The perhydro ester (X) has been converted to an acetate and maleate. Hydrolysis of (X) gives a mixture of hydroxy acids (XII) from which a pure acid (XIII), m. p. 198–200°, has been separated in small yield (17%). The ultraviolet absorption spectrum of the ester (X) shows weak absorption similar to that of the isomer (III) (Fig. 2).

Application of the reduction method to 6-methoxy-2-naphthol has given an 80% yield of a single pure product (XIV), 6-methoxy-2-tetralol,



XIV

m. p. 52.8–53.5°. The marked effect of the alkali in promoting hydrogenation of the phenolic ring

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[8] Yield on the basis of hydroxynaphthoic ester.

[9] No attempt has been made to effect a complete separation of the mixture of isomeric acids.

[10] Difficulties in the reduction of a double bond common to two rings have been reported some time ago (Hückel, Daneel, Schwartz and Gercke, *Ann.*, 474, 121 (1929); v. Braun, *Ber.*, **65**, 883 (1932)).

[11] A single unsaturated acid has been obtained by H. V. Z. bromination and dehydrobromination of all-*cis*-1-decahydronaphthoic acid. This acid shows an absorption maximum at 220 mμ (log ε 3.97). The acids RCH═CHCOOH absorb at 210 mμ (log ε 4.3) (Lauer, Gensler and Miller, THIS JOURNAL, **63**, 1153 (1941)).

in these compounds is in agreement with previous work.[12]

Experimental[13]

Hydrogenation of Ethyl 6-Hydroxy-1-naphthoate

A. Products of Partial Hydrogenation.—Ethyl 6-hydroxy-1-naphthoate (5 g., m. p. 107–108°[5]) was dissolved in 100 cc. of ethanolic sodium ethoxide solution containing 0.02 g. of sodium. The solution was hydrogenated immediately for five hours with 3 g. of W-4 Raney nickel (age six months). The initial hydrogen pressure was 2000 lb. and the maximum temperature was 62°. After removal of catalyst and solvent, the product was taken up in benzene and washed with 10% aqueous sodium hydroxide. Distillation of the benzene left 2.3 g. of colorless liquid residue (I). This oil was refluxed for three hours with 20% aqueous sodium hydroxide. A solid acid (IV) precipitated after acidification of the hydrolysate. It was filtered with suction, washed and dried; yield 1.9 g. (42.7%),[8] m. p. 153–155°. One crystallization from benzene raised the melting point to 157.5–158.5°.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.65; H, 6.40.

A similar reduction of ethyl 6-hydroxy-1-naphthoate with aged nickel (eleven months old) at 160° gave 65% of non-phenolic liquid ester (II). The hydrolysis product from this ester was a gummy solid mixture (IIa) which could not be separated by the usual methods.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.20. Found: C, 67.65, 67.23; H, 8.28, 8.20.

B. 6-Hydroxydecahydro-1-naphthoic Acid (V).—The perhydrogenation of ethyl 6-hydroxy-1-naphthoate (15 g.) was carried out under essentially the same conditions with freshly prepared W-4 Raney nickel. The reaction took place at 60–80°. The product, washed free from alkali-soluble material, dried by distillation with benzene and evaporated, proved to be pure perhydro ester (III), a colorless oil, yield 100%.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.98; H, 9.81. Found: C, 68.79; H, 9.56.

The ester (15.7 g.) was refluxed for three hours with a mixture of 10% aqueous sodium hydroxide (80 cc.) and 20 cc. of ethanol. The basic solution was washed with ether. Acidification of the aqueous solution with hydrochloric acid yielded 2 g. (14.5%) of crystalline acid which was decanted with the aqueous solution from the oily main product and filtered. Crystallization of the solid substance from aqueous alcohol gave colorless needles of (V) melting at 220.5–221.5°.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.65; H, 9.17. Found: C, 66.55; H, 9.17.

Acetate.—Acetylation of this acid (50 mg.) with 10 cc. of acetyl chloride furnished 42 mg. (69%) of acetate melting at 125.5–127° (from benzene–Skellysolve A).

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.39. Found: C, 64.64; H, 8.73.

The oily mixture of acids (above) was taken up in ether and dried. The solvent-free product weighed 9.35 g. (67.5%).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.65; H, 9.17. Found: C, 66.77; H, 8.74.

The oil crystallized partially on standing. Extraction of this mixture with a small amount of ether left 540 mg. of insoluble crystalline solid which melted at 195–205°. Fractional crystallization of this material from aqueous alcohol gave largely the perhydro acid (V) and 40 mg. of a second pure acid (VI), m. p. 219–220°, which depressed the melting point of the isomer (V).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.65; H, 9.17. Found: C, 66.48; H, 9.11.

Acetylation of the remaining oily mixture of isomers (VII) (0.25 g.) yielded 93% of oily acetate.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.39. Found: C, 64.78; H, 8.73.

6-Ketodecahydro-1-naphthoic Acid.—The ester (III) was hydrolyzed as above. The oxidation of the resultant mixture of isomeric acids (6.85 g.) with 3.7 g. of chromic oxide, 2 cc. of water and 300 cc. of acetic acid took place in the cold. The temperature of the mixture was allowed to rise exothermically to 30°. It was allowed to stand for forty-eight hours at room temperature. The solvent was removed under reduced pressure at 30°. The residue was taken up in benzene and the solution was washed with water. Removal of the benzene left 3.05 g. (45%) of colorless oil which partially crystallized on standing. The isomers (1.42 g.) were separated by extraction with ether in which the oil dissolves. The solid residue (520 mg. (36%), m. p. 138.5–140°) was crystallized from *p*-xylene. It melted at 141–142°.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.20. Found: C, 67.32; H, 8.25.

Ethyl Ester.—Oxidation of ethyl 6-hydroxydecahydro-1-naphthoate (2.0 g.) in precisely the same manner gave the crude keto ester which was adsorbed on alumina from Skellysolve B solution. Elution with the same solvent yielded a colorless liquid (1.0 g., 50.5%).

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.97. Found: C, 69.21; H, 9.14.

Decahydro-1-naphthoic Acid.—1-Naphthoic acid (12 g.) on reduction with sodium (16 g.) and 250 cc. of isoamyl alcohol gave a 52% yield of crude 1,2,3,4-tetrahydro-1-naphthoic acid, m. p. 68–75°. This product (2.0 g.) was hydrogenated with 200 mg. of Adams catalyst in 50 cc. of glacial acetic acid. After removal of the catalyst, water was added to the solution. The crystalline acid was filtered and dried. It melted at 121–122.5°, yield 1.6 g. (77.6%). One crystallization from Skellysolve A raised the melting point to 124–125° (lit., m. p. 112–118°[5] and m. p. 125–126°[14]).

1-Bromodecahydro-1-naphthoic Acid.—Decahydro-1-naphthoic acid (1.0 g.) was heated for five hours with 0.91 g. of dry bromine and 4 drops of phosphorus trichloride. The temperature was maintained at 60–70° for the first three hours and then raised to 100°. The excess bromine was distilled off under reduced pressure. The residue was poured into 10% aqueous sodium hydroxide solution. The mixture was allowed to stand for three days. Acidification with concentrated hydrochloric acid precipitated 250 mg. of colorless crystals which were identical with the starting material. The bromo acid was extracted from the aqueous solution with benzene. The crude product (850 mg., 79%) crystallized only partially. It was used without further purification.

Anal. Calcd. for $C_{11}H_{17}O_2Br$: C, 50.58; H, 6.56. Found: C, 49.96; H, 6.68.

Octahydro-1-naphthoic Acid (VIII).—The crude bromodecahydronaphthoic acid (500 mg.) was refluxed with 25 cc. of dry pyridine. Water was added and the solution was acidified with concentrated hydrochloric acid. The solution was extracted with benzene and the benzene extract was washed with dilute hydrochloric acid and then with water. The solvent was distilled off leaving 240 mg. of solid which melted at 110–130° after sublimation under reduced pressure. Two crystallizations from aqueous ethanol gave 25 mg. (7.2%) of colorless acid, m. p. 158.5–160°.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.31; H, 8.95. Found: C, 73.32; H, 9.05.

6-Hydroxy-2-naphthoic Acid.—6-Bromo-2-methoxynaphthalene[15] (34.5 g., m. p. 101–102°) was converted to the cyano compound through the Rosenmund–v.

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(12) Ungnade and McLaren, THIS JOURNAL, **66**, 119 (1944); Stork, *ibid.*, **69**, 577 (1947).

(13) All temperatures uncorrected. Analyses by K. Zilch, R. A. Carpenter and F. V. Morriss.

(14) Ranedo and Leon, *Ann. soc. espan. fis. quim.*, **25**, 421 (1927).

(15) French and Sears, THIS JOURNAL, **70**, 1279 (1948).

Braun synthesis.[16] The crude product (25.5 g., 94.5%) melted at 97–103° (lit., 103°[17]). Hydrolysis of this nitrile with sodium hydroxide in *n*-propyl alcohol (forty-eight hours) gave an 88% yield of crude methoxy acid, m. p. 190–205° (lit., m. p. 209°,[18] m. p. 200–203°[19]). Demethylation of this acid according to Miller and Morello[19] afforded 6-hydroxy-2-naphthoic acid in 79% yield. It melted at 240–241° (from water).

Ethyl Ester.—The esterification of this acid (23 g.) was carried out by refluxing with absolute ethyl alcohol (280 cc.) saturated with hydrogen chloride. The mixture was diluted with water and extracted with ether. The extract was washed with aqueous bicarbonate. The solvent was displaced with benzene which in turn was distilled off. The brown solid residue was sublimed at 0.0001 mm.[20] The colorless crystalline sublimate (18 g.) (66%) melted at 107–110°. Two crystallizations from glacial acetic acid raised the melting point to 114–116.5° (remelt 115–115.5°, lit., 111–112°[21]).

6-Hydroxy-5,6,7,8-tetrahydro-2-naphthoic Acid (XI).—Ethyl 6-hydroxy-2-naphthoate (12 g.) was dissolved in 150 cc. of sodium ethoxide solution containing 0.03 g. of sodium. The mixture was hydrogenated with 3 g. of W-4 Raney nickel (eleven months old) at 115° under an initial pressure of 2400 lb. The reaction product, isolated as usual, was taken up in benzene. The solution was washed with 10% aqueous sodium hydroxide solution and with water and was distilled to remove the solvent. The residual oil (IX) (11.2 g., 88.8%) was hydrolyzed by refluxing with 80 cc. of 10% aqueous sodium hydroxide and 20 cc. of ethyl alcohol. The solution was acidified with concentrated hydrochloric acid and extracted with ether. The dry residue from the extract (8.7 g., 80%)[8] was shaken with benzene. The insoluble solid material was crystallized twice from aqueous alcohol. The pure tetrahydro acid (XI) (2.0 g.) melted at 178.5–179°.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.78; H, 6.63.

The remaining partially crystalline material (6.7 g.) was identified as a mixture of approximately equal amounts of tetrahydro and perhydro acids by its ultraviolet absorption spectrum and analysis. The total yield of tetrahydro acids amounts to approximately 50%.

Anal. Found: C, 67.58; H, 8.01.

Ethyl 6-Hydroxydecahydro-2-naphthoate (X).—The hydrogenation of ethyl 6-hydroxy-2-naphthoate (9.2 g.) was carried out as described above with fresh W-4 Raney nickel catalyst (3 g.) at 180–185°. The non-phenolic product (8.24 g., 85.6%) was a nearly colorless oil (X).

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.98; H, 9.81. Found: C, 69.16; H, 9.84.

While the substance was analytically pure, the ultraviolet spectrum of this ester showed slight contamination with the tetrahydro ester. A spectroscopically pure sample was obtained by reducing at 200°.

Acetate.—The acetate obtained by acetylation of the ester (0.50 g.) with acetyl chloride (10 cc.) in the cold was adsorbed on aluminum oxide from Skellysolve B solution. The benzene eluate of the chromatogram gave 0.50 g. (84%) of colorless oil.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 67.38; H, 8.84.

Maleate.—Heating of the ester (X) (1.0 g.) with 0.234 g. of maleic anhydride for six hours at 180° gave 0.58 g. of starting material and 0.59 g. (100%) of liquid maleate which was separated through its sodium salt.

Anal. Calcd. for $C_{17}H_{24}O_6$: C, 62.94; H, 7.40. Found: C, 63.03; H, 6.79.

Hydrolysis of this material with aqueous alkali gave 0.3 g. (80%) of liquid hydroxy acid (XII).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.65; H, 9.17. Found: C, 66.88; H, 9.12.

6-Hydroxydecahydro-2-naphthoic Acid (XIII).—Pure ethyl 6-hydroxydecahydro-2-naphthoate (X) (1.8 g.) was hydrolyzed by refluxing for four hours with 20% aqueous sodium hydroxide solution. The reaction mixture was acidified with concentrated hydrochloric acid and extracted with benzene. The extract was washed and distilled leaving 1.57 g. (100%) of residual oil. Part of this material dissolved on shaking with ether, the remainder precipitated. A solid acid (XIII) was removed by filtration and recrystallized from aqueous alcohol. It melted at 198–200°; yield 80 mg.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.65; H, 9.17. Found: C, 66.62; H, 9.05.

A second crop (200 mg.) melted at 120–145°. The remaining mixture was a liquid.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.65; H, 9.17. Found: C, 66.55; H, 9.05.

6-Methoxy-1,2,3,4-tetrahydro-2-naphthol (XIV).—6-Methoxy-2-naphthol[15] (11 g.) was reduced as described previously at 125°. The benzene solution of the product was washed with 10% aqueous sodium hydroxide solution and water and was distilled. The liquid product boiled at 160–165° (1 mm.). The distillate (9 g., 80%) crystallized on cooling. Recrystallization from benzene–Skellysolve B gave a product melting at 52.8–53.5°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.14; H, 7.92. Found: C, 74.20; H, 7.82.

The phenylurethan was prepared by heating 0.5 g. of the reduction product with 0.5 cc. of phenyl isocyanate at 100° for one-half hour. The product was crystallized twice from ethyl alcohol.

Anal. Calcd. for $C_{18}H_{19}O_3N$: C, 72.70; H, 6.45. Found: C, 73.06, 72.91; H, 6.88, 6.77.

Ultraviolet Absorption Spectra.—The absorption spectra of the compounds were determined in 95% alcohol in 0.001 molar solutions with a Beckman spectrophotometer.[22]

Summary

Three substituted β-naphthols have been successfully hydrogenated over Raney nickel catalyst by reduction in the presence of small amounts of their sodium salts.

Columbia, Missouri

Received May 13, 1949

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(16) Koelsch and Whitney, *J. Org. Chem.*, **6**, 795 (1941).

(17) Horeau and Jacques, *Compt. rend.*, **222**, 1113 (1946).

(18) Fries and Schimmelschmidt, *Ber.*, **58**, 2840 (1925).

(19) Miller and Morello, This Journal, **70**, 1900 (1948).

(20) Attempts to purify the ester through its sodium salt resulted only in complete hydrolysis even at 0°.

(21) Butler and Royal, *J. Chem. Soc.*, **123**, 1653 (1923).

(22) Absorption spectra by Dr. E. E. Pickett, University of Missouri.