TABLE I

Reactants: X (NO₂)	Amine	Product: Y (NO₂)	Yield, %	Empirical formula	Analyses,[a] % As Calcd.	As Found	N Calcd.	N Found
—OCH_2COOCH_3	Alcoholic NH_3	—OCH_2CONH_2	72	$C_8H_9AsN_2O_7$	23.40	23.36	8.75	8.76
—OCH_2COOCH_3	Aqueous NH_3	—OCH_2CONH_2	61			23.30		8.70
—OCH_2COOCH_3	$H_2NCH_2CH_2OH$	—$NHCH_2CH_2OH$	76	$C_8H_{11}AsN_2O_6$	24.47	24.50	9.15	9.06
—OCH_2COOH	$H_2NCH_2CH_2OH$	—$NHCH_2CH_2OH$	56			24.42		8.96
—OCH_2CH_2OH	$H_2NCH_2CH_2OH$	—$NHCH_2CH_2OH$	42			24.60		9.10
—OCH_3	$H_2NCH_2CH_2OH$	—$NHCH_2CH_2OH$	67			24.50		...
—OH	$H_2NCH_2CH_2OH$	—$NHCH_2CH_2OH$	24			24.37		...
—OCH_2COOCH_3	$H_2NCH_2CH_2NH_2$ (excess)	—$NHCH_2CH_2NH_2$	37	$C_8H_{12}AsN_3O_5$	24.55	24.59	13.73	13.95
—OCH_2COOCH_3	$HN(CH_2CH_2OH)_2$	—$N(CH_2CH_2OH)_2$	55	$C_{10}H_{15}AsN_2O_7$	21.39	21.15		
—OCH_2COOCH_3	HNC_4H_8O	—NC_4H_8O	46	$C_{10}H_{13}AsN_2O_6$	22.55	22.50		

[a] The authors wish to thank A. W. Spang and C. S. Chamberlain (dec.) for the analytical determinations.

ether added slowly. The amine salts of the arsonic acids crystallized and were filtered off, dissolved in water, and the free acids caused to crystallize by acidification to congo red paper.

Summary

1. 2-Nitro-4-arsonophenyl ethers reacted with aliphatic primary and secondary amines to yield 2-nitro-4-arsonoanilines.

2. Methyl 2-nitro-4-arsonophenoxyacetate reacted with ammonia to yield the corresponding acetamide.

3. Reduction of 2-nitro-4-arsonophenoxyacetamide with hydrogen, using Raney catalyst, in neutral solution resulted in elimination of the amide and formation of 6-arsono-3-hydroxy-1,4,2-benzoxazine.

DETROIT, MICH. RECEIVED MAY 15, 1947

[CONTRIBUTION FROM NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Some Naphthalene Analogs of Desoxycorticosterone

BY CHARLES C. PRICE,[1] HERMAN I. ENOS, JR.,[2] AND WILLIAM KAPLAN[3]

The object of the present investigation was the preparation of simple naphthalene analogs of desoxycorticosterone, especially by conversion of 6-methoxy-1-naphthoic acid, available by condensation of anisole with furoic acid,[4] into hydroxymethyl ketone derivatives.

Spurred by the discovery of the high estrogenic activity of synthetic analogs of estradiol and estrone, such as diethylstilbestrol and hexestrol, a number of investigators have explored the synthesis and testing of analogs of cortical hormones. Linnell and Roushdi[5] reported slight activity for hydroxymethyl phenyl ketone and appreciable activity for 3-(4′-hydroxyphenyl)-4-(3′-hydroxyacetylphenyl)-3-hexene. A number of other hydroxyacetyl compounds were devoid of activity.[5,6,7,8] These have included 1-hydroxyacetylnaphthalene,[5] 1-hydroxyacetyldecahydronaphthalene[8] and 7-methoxy-1-hydroxyacetylnaphthalene.[7]

We have prepared 4- and 6-acetoxy-1-acetoxyacetylnaphthalene (X and VI) and they showed no significant activity.[9] 6-Methoxy-1-acetoxyacetyl-1,2,3,4-tetrahydronaphthalene (III) was prepared and characterized but found too unstable for physiological testing.

The procedures used for the preparation of these compounds are outlined below.

Long and Burger[8] had previously reported experiments on the hydrogenation of I and IV. In every instance, any conditions which lead to hydrogenation also lead to simultaneous removal of the oxygen function at carbon 6. We had hoped the primary chemical reduction of the ring holding the carboxyl group might permit reduction of the other ring without removal of the oxygen. Unfortunately, this hope was not realized. Hydrogenation of IV, either at low temperature and pressure with Adams platinum oxide catalyst or at higher temperatures and pressure with Raney nickel, yielded only the desoxy acid VIII. Attempts to hydrogenate the methoxy acid II with either of these catalysts were entirely unsuccessful; starting material was recovered unchanged.

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(4) Price, Chapin, Krebs, Goldman and Schaeffer, THIS JOURNAL, **63**, 1857 (1941).

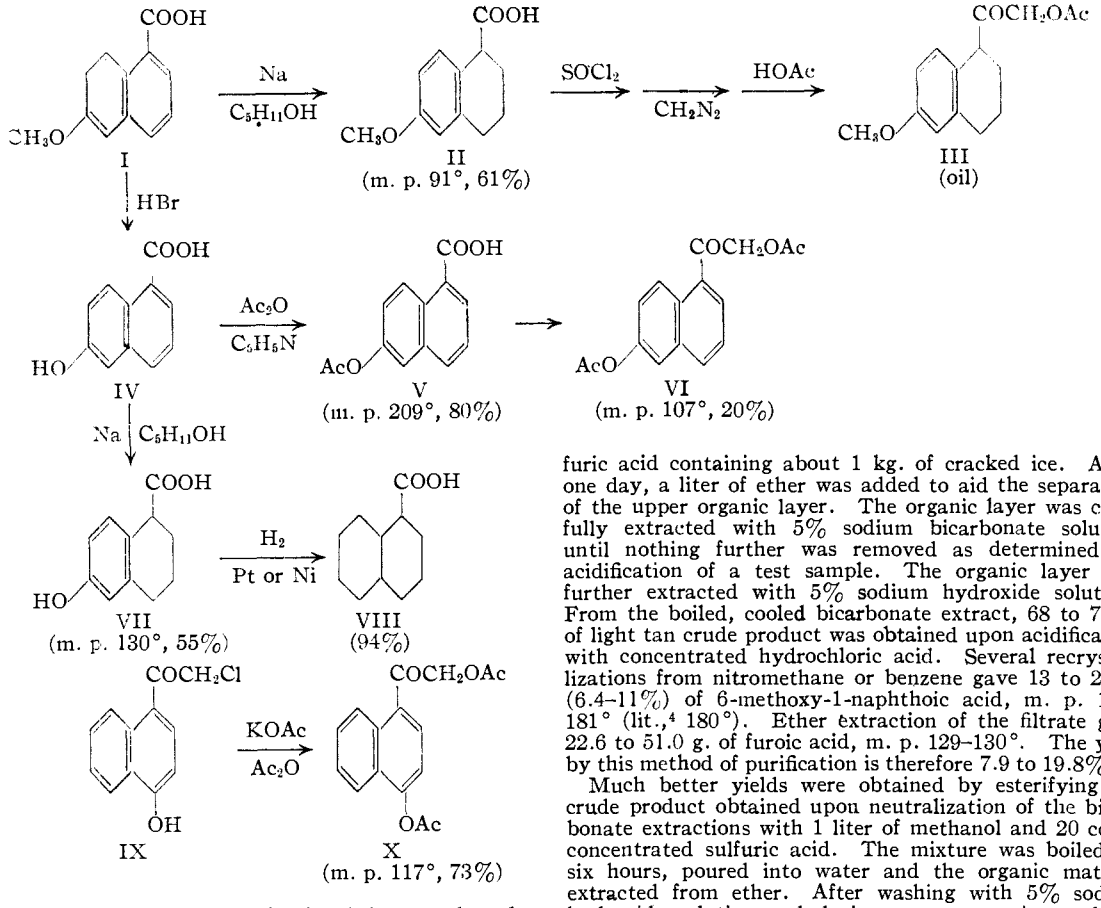
(5) Linnell and Roushdi, *Quart. J. Pharm. Pharmacol.*, **14**, 270 (1941).

(6) Walker, *J. Chem. Soc.*, 347 (1942).

(7) Ross, *ibid.*, 538 (1945).

(8) Long and Burger, *J. Org. Chem.*, **6**, 852 (1941).

(9) These compounds were tested in adrenalectomized rats through the courtesy of Eli Lilly and Company. Daily doses of 0.25 mg. subcutaneously failed to prolong survival significantly.



Although II could be obtained from I by the method of Birch[10] using sodium and methanol in liquid ammonia–ether solution, its sodium salt was so insoluble in the mixture that no further reduction occurred.

The 4-acetoxy ketone (X) was prepared from starting material obtained from Brown, Bryan and Enos.[11]

Experimental[12]

6-Methoxy-1-naphthoic Acid (I).—After a long series of experiments, the most satisfactory conditions were found to be the following. A suspension of 120 g. (1 mole) of pure furoic acid in 1 kg. of anisole in a 2-liter, round-bottomed, three-necked flask provided with an efficient Hershberg stirrer through a mercury seal, a short reflux condenser connected to a gas absorption trap and a 125-cc. addition appendix was placed in a thermostatically controlled heating-bath. Three hundred grams (2.3 moles) of J. T. Baker technical aluminum chloride was added as rapidly as possible, taking care that the temperature did not rise above 60–70°. This required about three-fourths of an hour. The temperature was then adjusted to 65–67°. Heating and stirring were continued until evolution of hydrogen chloride had almost ceased (ten hours). Then an additional 66 g. (0.5 mole) of aluminum chloride was added rapidly in three portions. Stirring and heating were continued overnight. The warm mixture was hydrolyzed by pouring into 2 liters of 10% sulfuric acid containing about 1 kg. of cracked ice. After one day, a liter of ether was added to aid the separation of the upper organic layer. The organic layer was carefully extracted with 5% sodium bicarbonate solution until nothing further was removed as determined by acidification of a test sample. The organic layer was further extracted with 5% sodium hydroxide solution. From the boiled, cooled bicarbonate extract, 68 to 78 g. of light tan crude product was obtained upon acidification with concentrated hydrochloric acid. Several recrystallizations from nitromethane or benzene gave 13 to 23 g. (6.4–11%) of 6-methoxy-1-naphthoic acid, m. p. 178–181° (lit.,[4] 180°). Ether extraction of the filtrate gave 22.6 to 51.0 g. of furoic acid, m. p. 129–130°. The yield by this method of purification is therefore 7.9 to 19.8%.

Much better yields were obtained by esterifying the crude product obtained upon neutralization of the bicarbonate extractions with 1 liter of methanol and 20 cc. of concentrated sulfuric acid. The mixture was boiled for six hours, poured into water and the organic material extracted from ether. After washing with 5% sodium hydroxide solution and drying over magnesium sulfate, the ether was removed by distillation and the residue distilled to yield 32.1 to 59.0 g., b. p. 138–144° (2 mm.). The ester solidified on cooling. Recrystallization from alcohol gave short white needles, m. p. 44–45°. Boiling the recrystallized ester with 200 cc. of 10% sodium hydroxide until complete solution was effected, cooling to room temperature and acidification with concentrated hydrochloric acid gave 27.6 to 53.8 g. of 6-methoxy-1-naphthoic acid, m. p. 181.5–182.5° (13.6 to 26.6% conversion; 16.8 to 46.4% yield).

Between 500 to 600 g. of anisole, suitable for re-use in the reaction, can be recovered by distillation of the dried ether solution.

6-Hydroxy-1-naphthoic Acid (IV).—A solution of 6.40 g. of 6-methoxy-1-naphthoic acid in 130 cc. of glacial acetic acid and 130 cc. of 42% hydrobromic acid was refluxed for five and one-fourth hours. After cooling overnight, 1.5 g. of a brown powder was separated by filtration. Recrystallization from water gave 1.14 g. of matted white needles, m. p. 210.5–211.5° (lit.,[8] 212–212.5°). From the mother liquor was obtained 2.54 g. of white needles, m. p. 210–211°. The yield was 3.66 g., or 61% of the theoretical amount.

Repetition with 27 g. of 6-methoxy-1-naphthoic acid gave 19.6 g. of 6-hydroxy-1-naphthoic acid, m. p. 208–210° (77.8%).

6-Hydroxy-1,2,3,4-tetrahydro-1-naphthoic Acid (VII).—To a boiling solution of 1.83 g. (0.01 mole) of 6-hydroxy-1-naphthoic acid in 50 cc. of *n*-amyl alcohol, 4.7 g. (0.21 mole) of sodium was added rapidly in small pieces during twenty minutes. An oily yellow deposit formed in the flask after the first sodium was added. The mixture was treated with 100 cc. of water, and the layers separated. After washing the lower basic layer twice with ether it was boiled, cooled, and acidified with concentrated hydro-

(10) Birch, *J. Chem. Soc.*, 430 (1944).

(11) Brown, Bryan and Enos, *J. Org. Chem.*, **11**, 384 (1946).

(12) Microanalyses by Miss Theta Spoor and Miss Lillian Hruda. All melting points are corrected.

chloric acid. The precipitated acid was dried and recrystallized from high-boiling petroleum ether. The yield was 1.03 g. (55.4%) of colorless short prisms, m. p. 128.5–130°.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.86; H, 6.48.

This preparation was repeated twice with the following results. From 13.5 g. and 22.4 g. of 6-hydroxy-1-naphthoic acid, 8.0 g. (58%) and 19.6 g. (85.7%), respectively, of 6-hydroxy-1,2,3,4-tetrahydro-1-naphthoic acid were obtained.

Methyl 6-Hydroxy-1,2,3,4-tetrahydro-1-naphthoate.—The crude reduction product of 8.59 g. of 6-hydroxy-1-naphthoic acid was dissolved in 75 cc. of methanol and boiled under reflux for three and one-half hours with 7 cc. of concentrated sulfuric acid. The excess methanol was distilled and the residue extracted with ether. After washing with water and 5% sodium bicarbonate solution and drying, the ether was removed by distillation from a water-bath. The residue was fractionated at 3 mm.: fraction I, 3.74 g., b. p. 164–167°; fraction II, 3.9 g., b. p. 167–180°.

Fraction I solidified on standing to a colorless solid, m. p. 74–80°. It was recrystallized from toluene and then several times from benzene, m. p. 96–97°, after sintering at 93°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.78. Found: C, 69.86; H, 6.74.

Fraction II was not further investigated.

6-Methoxy-1,2,3,4-tetrahydro-1-naphthoic Acid (II).—A solution of 16.5 g. (0.082 mole) of 6-methoxy-1-naphthoic acid in 350 cc. of isoamyl alcohol was boiled under reflux on a hot-plate while 15.9 g. (0.69 mole) of sodium was added in small pieces as rapidly as possible. When the sodium had completely dissolved, the mixture was poured into an equal volume of water. The alkaline layer was extracted with ether, boiled with Darco S-51, filtered and acidified with concentrated hydrochloric acid. The crude product was separated by filtration, dried and suspended in hot high-boiling petroleum ether and brought into solution by the addition of ethyl acetate. The product crystallized as stubby white needles, m. p. 87–89°. The yield of 6-methoxy-1,2,3,4-tetrahydro-1-naphthoic acid was 10.4 g. (61.5%).

When the preparation was repeated using 10.0 g. of 6-methoxy-1-naphthoic acid, 5.4 g. (53%) of 6-methoxy-1,2,3,4-tetrahydro-1-naphthoic acid was obtained. A sample prepared for analysis melted at 90–91°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.78. Found: C, 69.58, 69.63; H, 6.84, 7.08.

A sample of the methyl ester was prepared, b. p. 141–143° (2 mm.), $n^{20}D$ 1.5392.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.05; H, 7.46.

Reduction of 6-Hydroxy-1,2,3,4-tetrahydro-1-naphthoic Acid with Platinum Oxide Catalyst.—A solution of 0.500 g. (0.0026 mole) of 6-hydroxy-1,2,3,4-tetrahydro-1-naphthoic acid in 50 cc. of absolute alcohol was placed in the reaction flask of the special Adams hydrogenation apparatus with 23 mg. of platinum oxide and three drops of alcoholic hydrogen chloride. Shaking at atmospheric pressure was continued until 184.3 cc. (0.0082 mole) of hydrogen was absorbed. This required seventy-three hours. The catalyst was removed by filtration and the alcohol was removed by evaporation in a stream of air. After drying, the product weighed 0.480 g. and melted at 95–111°. A sample of 85 mg. was removed and dissolved in 3 cc. of pyridine and 0.5 cc. of acetic anhydride. The mixture was heated several hours and was allowed to stand overnight, but no acetate was obtained.

Extraction of the remainder of the product with high-boiling petroleum ether left a residue of 90 mg. Evaporation of the petroleum ether left 285 mg. of decahydro-1-naphthoic acid, m. p. 101–107.5° (lit.,[8] m. p. 112–118°). Another sample melted at 115–117°.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.60, 72.54; H, 9.80, 9.96.

The yield of 285 mg. of decahydro-1-naphthoic acid from 395 mg. of the crude reduction product represents 94%.

6-Methoxy-1-naphthoyl Chloride.—A mixture of 1.93 g. of 6-methoxy-1-naphthoic acid, 3.5 cc. of thionyl chloride, 8 cc. of dry benzene and a drop of pyridine was allowed to stand at room temperature for six hours. The solvent and excess thionyl chloride was removed by distillation at reduced pressure. The solid acid chloride was suspended in low-boiling petroleum ether and washed twice by decantation.

A small sample recrystallized from low-boiling petroleum ether melted at 70–72°.

6-Methoxy-1-(ω-acetoxyacetyl)-naphthalene.—The acid chloride from the previous preparation was dissolved in 200 cc. of dry benzene and added slowly to an ice-cold solution of diazomethane in dry ether prepared from 7 g. of nitrosomethylurea.[13] An amorphous solid was deposited almost immediately. After one hour of standing at room temperature, the solvent and excess reagent were removed *in vacuo*. The crude diazoketone was dissolved in 5 cc. of acetic acid and the solution was allowed to stand overnight. Ether was added and the solution was extracted with several portions of water. The organic layer was dried over magnesium sulfate and the solvent removed by evaporation. An oil was obtained which did not crystallize on standing. The addition of ethanol converted it to an amorphous solid. Repeated attempts to crystallize this material in ethanol and chloroform were unsuccessful.

6-Acetoxy-1-naphthoic Acid (V).—Five grams (0.027 mole) of 6-hydroxy-1-naphthoic acid was dissolved in 50 cc. of pyridine and 5.5 cc. of acetic anhydride at room temperature. The mixture was allowed to stand for twenty-one hours. It was poured into 300 cc. of water and the resulting solution was evaporated to a volume of 100 cc. The precipitate, separated by filtration, weighed 4.9 g. (80%). It was recrystallized from an isopropyl alcohol-high-boiling petroleum ether mixture as white needles, m. p. 208–209°.

6-Acetoxy-1-naphthoyl Chloride.—A suspension of 3.45 g. (0.015 mole) of 6-acetoxy-1-naphthoic acid in 14 cc. of dry benzene and 6 cc. of thionyl chloride was allowed to stand six hours at room temperature and then heated for four hours at 60°. All of the acid had dissolved and the evolution of hydrogen chloride had ceased. The solvent was evaporated *in vacuo*. The solid that remained was redissolved in 24 cc. of warm benzene and the benzene again removed *in vacuo*. In this way most of the excess thionyl chloride was removed. The solid acid chloride was only very slightly soluble in low-boiling petroleum ether. It was recrystallized from 1 liter of high-boiling petroleum ether to yield 2.20 g. of colorless needles, m. p. 84–86°.

6-Acetoxy-1-(ω-acetoxyacetyl)-naphthalene (VI).—A solution of diazomethane in ether was prepared from 7.5 g. of nitrosomethylurea as previously described and dried for three hours with potassium hydroxide pellets. The acid chloride (2.2 g.) was suspended in 30 cc. of benzene and 10 cc. of ether and added in portions to the cold diazomethane solution. The mixture was allowed to stand for one and one-half hours in an ice-bath and then for one-half hour at room temperature. The amorphous diazoketone was obtained by removal of the solvent and excess reagent *in vacuo*. It was dissolved in 5 cc. of acetic acid and heated on the steam-bath for one-half hour. After standing overnight, most of the acetic acid was removed *in vacuo* and the product was obtained by adding water. The crude product was recrystallized from dilute acetic acid, 1.82 g. of golden brown plates, m. p. 92–98°. Several recrystallizations from 95% ethanol gave 0.520 g. of golden brown plates, m. p. 106–107° after sintering at 103°.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.33; H, 4.94.

(13) Arndt, "Organic Syntheses," 1st ed., Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 166.

6-Methoxy-1,2,3,4-tetrahydro-1-(ω-acetoxyacetyl)-naphthalene (III).—To 17 cc. of dry benzene containing 7.5 cc. of thionyl chloride and two drops of pyridine, 4.7 g. of 6-methoxy-1,2,3,4-tetrahydro-1-naphthoic acid was added. The mixture was allowed to stand for three hours and was warmed to 60° for two hours, until no further evolution of hydrogen chloride could be detected. The solvent and the excess thionyl chloride were removed *in vacuo*, and the crude acid chloride was distilled, b. p. 118–121.5° (2 mm.). The yield was 3.5 g. (68.4%).

A few drops of the acid chloride was washed from the side-arm of the distilling flask with a little dry benzene. Three drops of aniline was added and the solution was filtered from the aniline hydrochloride which precipitated. The benzene was evaporated and the residue was recrystallized from dilute alcohol, m. p. 127–129°. After several recrystallizations from aqueous ethanol, the **anilide** was obtained as a fine powder, m. p. 130.5–132°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.84; H, 6.81. Found: C, 76.60; H, 6.94.

The purified acid chloride was dissolved in 10 cc. of dry benzene and added dropwise during ten minutes to an ice-cold dry ether solution of diazomethane prepared from 14 g. of nitrosomethylurea. The mixture was allowed to stand for one-half hour in an ice-bath and for one-half hour at room temperature, after which the solvent was removed *in vacuo*. The amorphous residue was dissolved in 7.5 cc. of acetic acid and heated for one-half hour on the steam-cone and allowed to stand overnight. The mixture was dissolved in 50 cc. of ether and was extracted with water and with 5% sodium bicarbonate until all of the acidic material was removed. After drying, the ether was removed *in vacuo* and the residue was distilled using a mercury vapor pump. A clear amber-colored oil, b. p. 142–142.5° (0.1 mm.), $n^{20}D$ 1.5519, was obtained. The material darkened rapidly, even though it was sealed in a glass vial. The analysis was conducted four days after the distillation.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.55. Found: C, 69.62; H, 6.98.

A semicarbazone was prepared in the usual manner for water-insoluble compounds. Several recrystallizations from 50% ethanol gave fine colorless needles, m. p. 158–159°.

Anal. Calcd. for $C_{16}H_{21}O_4N_3$: C, 60.17; H, 6.63; N, 13.16. Found[14]: C, 60.73, 60.54; H, 6.61, 6.74; N, 13.14.

(14) This analysis was conducted by Mr. Howard Clark of the Illinois State Geological Survey.

4-Acetoxy-1-(ω-acetoxyacetyl)-naphthalene (X). (a) From **4-Hydroxy-1-(ω-chloroacetyl)-naphthalene (IX).**—A solution of 1.63 g. of 4-hydroxy-1-(ω-chloroacetyl)-naphthalene and 2.4 g. of freshly-fused potassium acetate in 15 cc. of acetic acid and 20 cc. of acetic anhydride was boiled under reflux for five hours. The warm mixture was diluted with 50 cc. of water and the solvents were partly removed in a stream of air. The solid which separated was removed by filtration and recrystallized from dilute acetic acid, m. p. 114.5–115.5°. It weighed 1.55 g. (73%). Further recrystallization from dilute acetic acid or dilute ethanol gave colorless plates, m. p. 116–117°.

(b) From **4-Acetoxy-1-(ω-bromoacetylnaphthalene**[11]). —A solution of 0.46 g. of 4-acetoxy-1-(ω-bromoacetyl)-naphthalene and 0.5 g. of freshly-fused potassium acetate in 10 cc. of acetic acid and 10 cc. of acetic anhydride was diluted with 20 cc. of water and the mixture was allowed to stand overnight, after which it was concentrated by evaporation. There was obtained 0.35 g. (81%) of colorless plates, m. p. 116–117°. Recrystallization from dilute acetic acid did not raise the melting point.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.33; H, 5.04.

Summary

The preparation of 4- and 6-acetoxy-1-acetoxyacetylnaphthalene has been reported. Neither compound showed any significant activity in prolonging survival of adrenalectomized rats.

6-Methoxy-1-acetoxyacetyl-1,2,3,4-tetrahydronaphthalene was prepared but proved to be an unstable oil.

6-Methoxy-1,2,3,4-tetrahydro-1-naphthoic acid was resistant to catalytic hydrogenation with nickel or platinum catalysis and to reduction by sodium amalgam and methanol in liquid ammonia–ether. The corresponding 6-hydroxy acid suffered loss of the hydroxyl group to yield decahydro-1-naphthoic acid on catalytic hydrogenation with nickel or platinum.

NOTRE DAME, INDIANA RECEIVED APRIL 9, 1947

[CONTRIBUTION FROM THE WOOD CONVERSION LABORATORY OF THE UNIVERSITY OF IDAHO]

The Constitution of Mesquite Gum. III. Hexamethyl-3-glucuronosido-methyl-galactoside Methyl Ester[1]

BY E. V. WHITE

The structural arrangement of the sugar anhydride units in the simple polysaccharides is determined generally without difficulty since only one monosaccharide type is present and this is united with neighboring units by a repetitive type of glycosidic linkage. On the other hand, the polymolecularity of the complex polysaccharides may present a very difficult problem in structural analysis. These macromolecules often contain uronic acid residues in addition to both pentose and hexose sugars of different ring structure and configuration. The individual units are united with each other by various methods of glycosidic linkage and three dimensional systems are a common occurrence. In general, the problem of structural representation in such instances is greatly simplified by isolation of disaccharide fragments through partial hydrolysis since these can be studied separately and their characteristics determined. The identification of such units always provides positive information as to a substantial portion of the repeating unit and correspondingly reduces the possibility for error in its representation.

The current investigation of mesquite gum from *Prosopis juliflora*[2a,b,c] has shown[3] that arabi-

(1) Presented at the regional meeting of the American Chemical Society, Washington–Idaho Border Section, Moscow–Pullman, May 2–3, 1947.

(2) (a) Proctor, *Am. J. Pharm.*, **27**, 224 and 542 (1855); (b) Morfit, *Am. J. Sci.*, **19**, 264 (1855); (c) Forbes, *Arizona Expt. Station Bull.*, **13** (1895).

(3) White, THIS JOURNAL, **68**, 272 (1946).