described above, 6 g. (94%) of XLVIII was obtained. This compound appeared as a colorless liquid, b.p. 224° (18 mm.), n_D, 1.5410 (23°).

Anal. Calcd. for $C_{20}H_{26}O$: C, 85.10; H, 9.21. Found: C, 84.80; H, 9.34.

Demethylation of XLVIII.—A mixture of 6.5 g. of XLVIII and 13 g. of pyridinium chloride was heated for 1.5 hr. then poured into dilute hydrochloric acid and extracted with benzene. The treatment of the organic layer gave 3 g. (48%) of *4-hydroxy-4′-(3-hexyl)diphenylmethane* (IL): amber liquid, b.p. 236° (17 mm.), n_D, 1.5530 (25°).

Anal. Calcd. for $C_{19}H_{24}O$: C, 85.07; H, 8.95. Found: C, 84.50; H, 92.0.

***p*-Nitrobenzoate of IL** was obtained as colorless pearly leaflets, m.p. 52.5°.

Anal. Calcd. for $C_{26}H_{27}O_4N$: C, 74.82; H, 6.47; N, 3.35. Found: C, 74.90; H, 7.00; N, 3.36.

4-Methoxy-3′-(3-hexyl)diphenylmethane (L).—The reduction of 6 g. of XLIII was carried out by heating it for 1.5 hr. with 1.5 g. of hydrazine hydrate, and 1.4 g. of potassium hydroxide in 100 ml. of diethylene glycol. This gave 3.2 g. of a resinous red compound [b.p. 288–295° (25 mm.)] which was directly desulfurized by refluxing for 45 min. in the presence of 65 g. of Raney nickel in 180 ml. of ethanol. Compound L is an amber liquid, b.p. 225° (20 mm.), n_D, 1.5380 (26°).

Anal. Calcd. for $C_{20}H_{26}O$: C, 85.10; H, 9.21. Found: C, 84.72; H, 9.51.

Infrared spectra were recorded on a Perkin Elmer double beam spectrophotometer n° 21, fitted with a sodium chloride prism. The samples examined were placed between two rock-salt plates.

Acknowledgment.—The authors wish to acknowledge the technical assistance of Miss M. L. Desvoyes.

The Unexpected Fate of an Attempted Steroid Synthesis

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Received May 18, 1962

In an attempted synthesis of equilenin, 2-propionyl-6-methoxynaphthalene (I) was converted, *via* the hydroxymethylene derivative II and the isoxazole III, into the cyano ketone IV which, as its sodio derivative, was alkylated with ethyl bromoacetate. The product proved to be a mixture of C- and O-alkylated derivatives. On base-catalyzed condensation with succinate, the former substance (V) failed to give the desired product (VI); hence the synthetic objective could not be realized. The O-alkylation product VII gave a crystalline condensation product which proved to be the furano compound VIII as shown by spectroscopy studies of VIII and its reaction products X, XI, and XII.

Some years ago[1] we planned a total synthesis of the female sex hormone equilenin by an approach which obviated the use of 1,6-disubstituted naphthalene derivatives,[2] employing instead the more accessible 2,6-disubstituted derivative, namely, 2-propionyl-6-methoxynaphthalene (I).[3] Thus it was proposed to convert this ketone by a known sequence of steps,[2b] *via* II and III, into the cyano ketone IV which in turn was to be alkylated with ethyl bromoacetate. Condensation of the resulting keto ester nitrile V with succinic ester was envisaged for the completion of ring D,[2b] to give VI, and finally the acetic acid side chain was to serve for completion of ring C by cyclization into the 1-position in the naphthalene nucleus.

The early steps of the synthesis proceeded as planned, but we first met with difficulty in the reaction of the cyano ketone IV with ethyl bromoacetate, which proceeded to give a mixture of C- and O-alkylated material (V and VII). On treatment of this mixture with succinic ester under conditions for the Stobbe reaction, the only condensation product that could be isolated eventually proved to be derived from the O-alkylated material. The C-alkylated material, unfortunately, gave none of the desired keto ester VI; hence the original objective could not be realized.[4]

In an effort to ascertain the structure of the crystalline condensation product, a number of its reactions were studied which, until recently, we had not been able to interpret to our satisfaction. The present report constitutes an account of our experiments with an interpretation which has now been made possible through the use of infrared and n.m.r. spectroscopy.

The hydroxymethylene derivative of 6-methoxy-2-propionylnaphthalene II, m.p. 152.1–153.7°, was obtained in 92% yield by the treatment of this ethyl ketone with ethyl formate in the presence of sodium methoxide. The crude hydroxymethylene derivative II was treated with hydroxylamine hydrochloride in glacial acetic acid to give in 98% yield the isoxazole III, m.p. 122–123.2°, conversion of which into the alkali-soluble cyano ketone IV was effected by treatment with sodium alkoxide. In this way it was possible to isolate, in 96% yield, α-(6-methoxy-2-naphthoyl)-propionitrile (IV), which has the potential carbon atoms 13, 14, and 17 and also the methyl group at carbon 13 of the equilenin structure.

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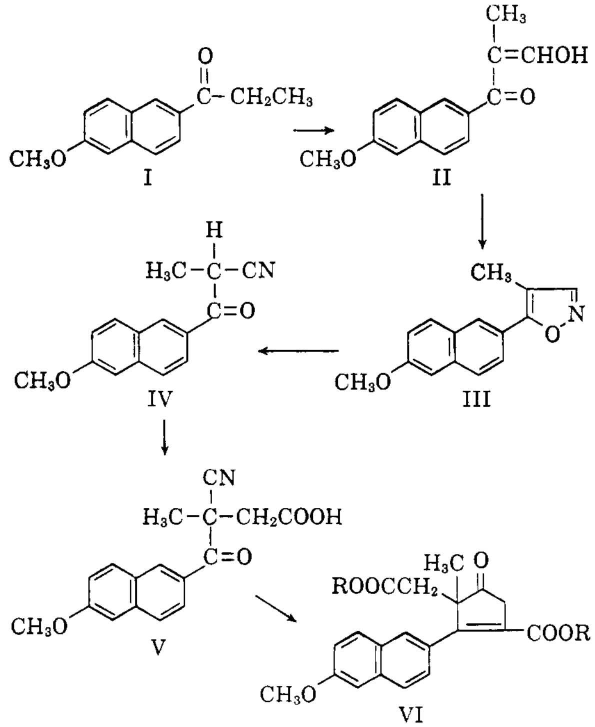
(1) Richard T. Rapala, Ph.D. thesis, University of Wisconsin, 1949.

(2) *Cf.*(a) W. E. Bachmann, W. Cole, and A. L. Wilds, *J. Am. Chem. Soc.*, **62**, 824 (1940). (b) W. S. Johnson, J. W. Petersen, and C. D. Gutsche, *ibid.*, **67**, 2274 (1945).

(3) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 864 (1934).

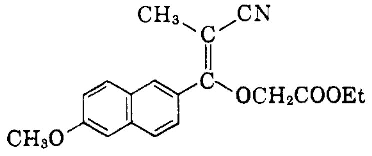
(4) Much of the work described below was performed before the "useless" nature of the products was appreciated. While this study is of interest in its own right, it serves to emphasize the not uncommon fate of many well laid synthetic plans.



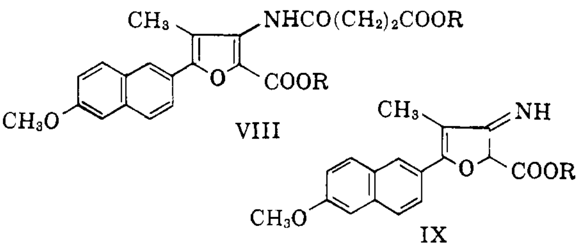
When the cyano ketone IV was treated with ethyl bromoacetate in the presence of sodium hydride, a yellow-red oily mixture of products (V and VII) of C- and O-alkylation was obtained in 62% yield. Initially it was assumed that the product was mainly the desired cyano ketone V; however, after considerable study of the reaction with succinate esters, it was realized that the condensation products were derived solely from O-alkylated material. The proof of structure of the O- and C-alkylation products is considered in the experimental part.

Condensation of the mixture of alkylation products V and VII with dimethyl succinate led to the isolation of a crystalline neutral compound, $C_{23}H_{23}O_7N$, m.p. 166–167°. The yield of the crude material was 12%, but when the condensation was carried out on a fraction which was enriched in O-alkylated material by chromatography, the yield was raised to 31%. The 167° compound did not form ketonic derivatives, and the infrared spectrum showed bands at 3.0, 6.0, and 6.4 μ attributable to a secondary amide. No absorption was found at 4.5 μ, indicating the absence of a nitrile function. Bands at 5.75 and 5.85 μ were suggestive of normal and conjugated ester groups, respectively. The n.m.r. spectrum indicated the presence of six aromatic and one N—H proton. Three protons assignable to an aromatic methyl group were present, as well as three assignable to an aromatic methyl ether. Six additional protons could be assigned to methyl esters and four more to a —CH_2CH_2— grouping.

The furano structure VIII (R = CH_3) appears to be consistent with all of the spectral data as well as with the chemical evidence (see below), and its



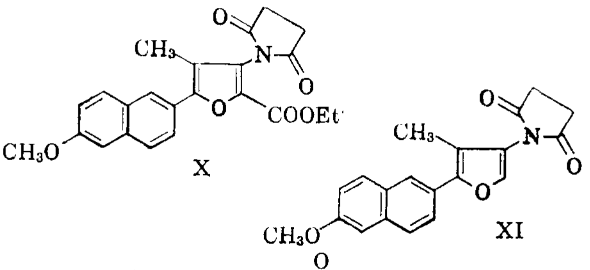
VII

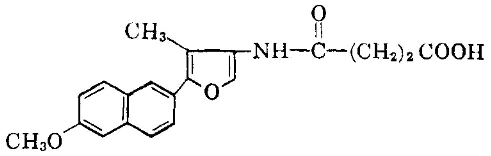


formation is explicable by an intramolecular Thorpe cyclization to the imino ester IX followed by isomerization to the amino furan, then acylation (of the amino group) with succinate. At some stage during this sequence the carboethoxy group attached to the furan nucleus must have undergone methoxide-catalyzed ester exchange to produce the methyl ester.

Saponification of the 167° substance with barium hydroxide yielded an immediate precipitate which upon acidification with hydrochloric acid gave a dibasic acid VIII (R = H), $C_{21}H_{19}O_7N$, m.p. 194–196°, treatment of which with diazomethane regenerated the ester VIII (R = CH_3).

Condensation of the original yellow-red oil with diethyl succinate led to the homologous diethyl ester VIII (R = C_2H_5), $C_{25}H_{27}O_7N$, m.p. 158–159.5°. The infrared spectrum was very similar to that of VIII (R = CH_3), and saponification with barium hydroxide furnished the same diacid VIII (R = H). The infrared spectrum of this diacid showed bands at 3.0, 6.0, and 6.45 μ characteristic of a secondary amide as well as evidence of hydrogen bonding in the 3.0–4.0-μ region typical of an acid group, plus absorption at 5.8 μ indicative of a carboxyl group.





XII

Pyrolysis of the diethyl ester VIII (R = C_2H_5) with potassium acid sulfate under diminished pressure gave a neutral solid product, $C_{23}H_{21}O_6N$, m.p. 252.5–253°, in 91% yield. The infrared spectrum indicated the absence of amide N—H (no absorption at 3.0 μ) while the carbonyl region showed two bands, at 5.6 and 5.9 μ, assignable to an imide structure, plus absorption at 5.8 μ attributable to a conjugated ester. This evidence is consistent with the imide structure X for the 253° compound. Confirmation of this structure was afforded by alkaline hydrolysis which regenerated the diacid VIII (R = H).

Upon melting, the diacid VIII (R = H) decomposed to give a gas which was shown to be carbon dioxide, and a neutral, colorless compound, $C_{20}H_{13}O_4N$, m.p. 228.5–230°, isolated in 62% yield. This substance failed to form ketonic derivatives, and the infrared spectrum showed no evidence of amide structure (lack of absorption at 3.0 μ), but instead exhibited bands at 5.6 and 5.85 μ characteristic of an imide structure. The furan nucleus is not easily detectable by infrared spectroscopy; however, the n.m.r. absorption of a proton attached to a furan nucleus is characteristic.[5,6] The n.m.r. spectrum of the 230° compound indicated the presence of seven aromatic protons, six of which are assignable to the naphthalene nucleus and one to the furan nucleus. In addition there was absorption characteristic of three protons of an aromatic methyl group, three of an aromatic methyl ether and four indicating a $—CH_2CH_2—$ grouping. The furano imide structure XI is compatible with all of the above data.

The substance XI was insoluble in dilute potassium hydroxide solution but dissolved readily upon warming, and upon acidification afforded, in 57% yield, a monobasic acid (XII), $C_{20}H_{19}O_5N$, m.p. 184–186°, which upon sublimation reformed the imide XI.

When the imide XI was boiled with 10% potassium hydroxide solution for four days, ammonia was evolved, and a neutral solid, shown to be 6-methoxy-2-propionylnaphthalene (I) was isolated in 30% yield. From the acidic fraction there was isolated, in 17% yield, material identified as 6-methoxy-2-naphthoic acid.

Experimental[7]

6-Methoxy-2-propionylnaphthalene (I).—This compound was prepared by a slight modification of the reported procedure.[3] Thus, from 224 g. of anhydrous aluminum chloride, 1300 ml. of dry nitrobenzene, 212 g. of 2-methoxynaphthalene, and 143 g. of propionyl chloride there was obtained after steam distillation of the entire mixture, followed by distillation and recrystallization from ethanol, 182 g. (64%) of colorless ketone, m.p. 111.5–113.5, reported[2] 109°. However, when only the nitrobenzene layer was steam-distilled,[2] the yield of ketone, m.p. 105–108°, was 43%.

The **2,4-dinitrophenylhydrazone** was prepared in ethanol and hydrochloric acid and recrystallized from chloroform as tiny red rods, m.p. 238.0–239.8°.

Anal. Calcd. for $C_{20}H_{18}O_5N_4$: C, 60.91; H, 4.60. Found: C, 61.1; H, 4.7.

6-Methoxy-2-(α-methyl)hydroxymethyleneacetylnaphthalene (II).—According to a general procedure,[8] 80.8 g. of 6-methoxy-2-propionylnaphthalene, m.p. 111–112°, was treated with 56.0 g. of ethyl formate, 43.2 g. of commercial sodium methoxide (Mathieson Alkali Works), and 600 ml. of benzene. After 96 hr. at room temperature, the product was isolated as previously described,[3] and the yield of material, m.p. 151–152.5°, was 92%.

When the reaction period was 5 or 86 hr., the yield of hydroxymethylene compound, m.p. 150–153°, was 37% and 89%, respectively. This product was crystallized twice from absolute ethanol and once from a mixture of ethyl acetate and petroleum ether (b.p. 60–68°), giving yellow crystals, m.p. 152.1–153.7°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.2; H, 6.1.

4-Methyl-5-(6-methoxy-2-naphthyl)isoxazole (III).—According to a general procedure,[2b] a mixture of 73.0 g. of 6-methoxy-2-(α-methyl)hydroxymethyleneacetylnaphthalene, 31.2 g. of hydroxylamine hydrochloride, and 1500 ml. of glacial acetic acid was refluxed for 10 min. Upon dilution with water and cooling, 69.0 g. (96%) of light brown-colored crystal plates, m.p. 118–120°, was obtained. Colorless plates were obtained after several recrystallizations from petroleum ether (60–68°), m.p. 122–123.2°.

Anal. Calcd. for $C_{15}H_{13}O_2N$: C, 75.29; H, 5.47. Found: C, 75.3; H, 5.5.

α-(6-Methoxy-2-naphthoyl)propionitrile (IV).—A previously described procedure[2b] was slightly modified. To a stirred solution of 43.5 g. of the aforementioned isoxazole, m.p. 119–121°, in 1240 ml. of dry benzene was added 21.6 g. of sodium hydride followed by 11.6 ml. of absolute ethanol. The resulting mixture was stirred at 23° for 64 hr., then diluted with water. Ether was added, and the organic layer was washed thoroughly with 5% potassium hydroxide. The combined aqueous layers were washed with ether and acidified with cold hydrochloric acid to give 39.7 g. (91.5% yield) of the light tan cyano ketone, m.p. 108–110°. Recrystallization of a small sample four times from benzene and petroleum ether (b.p. 90–100°) gave colorless leaflets, m.p. 108.4–109.2°.

Anal. Calcd. for $C_{15}H_{13}O_2N$: C, 75.29; H, 5.47. Found: C, 75.1; H, 5.5.

The **2,4-dinitrophenylhydrazone** was obtained from ethyl acetate as yellow needles, m.p. 220.0–221.5°.

Anal. Calcd. for $C_{21}H_{17}O_5N_5$: C, 60.14; H, 4.09. Found: C, 60.19; H, 3.99.

Alkylation of the Cyano Ketone IV with Ethyl Bromoacetate.—A solution of 10.0 g. of the cyano ketone, m.p. 105–107°, in 240 ml. of dry benzene was treated with 0.96 g. of sodium hydride to form the sodio derivative of the cyano ketone. Reaction was complete in about 5 min., then 4.40 ml. of ethyl bromoacetate was added and the mixture refluxed for 3 hr. Water was added and the organic layer extracted thoroughly with dilute potassium hydroxide solution. The combined aqueous layers were acidified and the product that separated was taken up in ether and washed with saturated sodium bicarbonate solution. Acidification of these bicarbonate extracts afforded 0.7 g. of 6-methoxy-2-naphthoic acid, m.p. 194–198°. The ether solution was dried over anhydrous sodium sulfate and evaporated to give 1.9 g. of recovered cyano ketone, m.p. 100–105°. The original benzene solution was dried over anhydrous magnesium sulfate and evaporated. The residue was distilled to give 8.1 g. of a yellow-red viscous oil, b.p. 210–230° (0.03–0.1 mm.), the major portion of which boiled at 230° (0.1 mm.).

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(5) E. J. Corey, G. Slomp, S. Dev, and S. Tobinaga, *J. Am. Chem. Soc.*, **80**, 1204 (1958).

(6) L. H. Briggs and L. D. Colebrock, *J. Chem. Soc.*, **2458** (1960).

(7) All melting points are corrected unless otherwise noted. N.m.r. spectra were determined at 60 Mc. Deuteriochloroform was employed as solvent and tetramethylsilane as an internal standard. Data are expressed as δ-value in parts per million from tetramethylsilane.

(8) W. S. Johnson, J. M. Anderson, and W. E. Shelberg, *J. Am. Chem. Soc.*, **66**, 218 (1944).

Anal. Calcd. for $C_{19}H_{19}O_4N$: C, 70.14; H, 5.88. Found: C, 70.6; H, 6.05.

A solution of 6 g. of the alkylation product described above in 8 ml. of benzene was adsorbed on a column of 120 g. of acid-washed alumina. The column was eluted with 480 ml. of benzene, 500 ml. of 25% ether-in-benzene, and finally with 475 ml. of 50% ether-in-benzene. Evaporation of the benzene eluate yielded 2.5 g. of pale yellow oil A. The remaining two eluates were combined and evaporated to give 1.9 g. of yellow oil B.

Fraction A was shown to consist mainly of C-alkylated material by virtue of its alkaline hydrolysis in high yield to 6-methoxy-2-naphthoic acid. Thus a solution of 0.26 g. of 85% potassium hydroxide in 3 ml. of water was added to a solution of 0.146 g. of the oil A in 15 ml. of 95% ethanol. After refluxing for 2 hr., the mixture was allowed to stand at room temperature for 22 hr. The solvent was removed by distillation and the residue dissolved in benzene and extracted with dilute potassium hydroxide solution. Acidification of the basic extracts followed by recrystallization from 95% ethanol afforded 0.084 g. (92% yield) of 6-methoxy-2-naphthoic acid, m.p. 199–201°, undepressed on admixture with authentic material. Fraction B, on the other hand, appeared to have been enriched in the O-alkylated material since on alkaline hydrolysis as described above 0.102 g. of this material afforded only 0.025 g. of 6-methoxy-2-naphthoic acid. Further evidence for the constitution of these fractions A and B was provided by the condensations with succinic ester described below.

Succinic Ester Condensation. (a) With the Mixture of C- and O-Alkylation Products.—To a stirred mixture of 0.49 g. of the oily alkylation product and 1.9 ml. of dimethyl succinate, maintained at a temperature of 31–33°, was added dropwise a solution of 0.435 g. of potassium in 9 ml. of anhydrous *t*-butyl alcohol. After addition was complete (5 hr.), the dark red mixture was treated with cold dilute hydrochloric acid and extracted with benzene. The organic layer was washed with dilute hydrochloric acid, dilute sodium hydroxide, water, and finally dried over Drierite. The residue obtained on evaporation of the solvent was freed of traces of *t*-butyl alcohol by co-evaporation with small portions of benzene. The yellow semisolid residue (0.36 g.) was chromatographed on 12 g. of acid-washed alumina. Elution with 80 ml. of 50:50 benzene–petroleum ether (b.p. 40–60°) yielded 0.15 g. (45% yield) of methyl 6-methoxy-2-naphthoate, m.p. 126–128°, undepressed on admixture with authentic material (see below). Further elution of the column with 80 ml. of benzene gave 0.037 g. of oily material; then elution with 50 ml. of 2% ethanol in benzene afforded, from a 15-ml. center fraction which washed off a brown-yellow band from the column, **methyl 3-N-(β-carbomethoxyethylcarbamido)-4-methyl-5-(6-methoxy-2-naphthyl)furan-2-carboxylate (VIII. R = CH_3)**. Recrystallization from methanol gave 0.076 g. (12% yield) of almost colorless material, m.p. 153–159°. Repeated recrystallization from methanol gave small colorless needles, m.p. 166–167°, $\lambda_{\max}^{\text{KBr}}$ 3.0 μ (N—H); 5.75 (COOR); 5.85 (conj. COOR); 6.0, 6.4 (RCONHR). The n.m.r. spectrum showed absorption for one proton at 8.25 p.p.m. (N—H), six "aromatic" protons at 7.0–8.1, three protons at 3.89 and three at 3.87 ($COOCH_3$ at C-2 and $ArOCH_3$), three protons at 3.68 (succinate $COOCH_3$), four protons as a singlet at 2.74 ($-CH_2CH_2-$), and three protons at 2.23 (CH_3 at C-4).

Anal. Calcd. for $C_{23}H_{23}O_7N$: C, 64.93; H, 5.45; N, 3.29. Found: C, 65.3; H, 5.3; N, 3.6.

When an equivalent amount of diethyl succinate was substituted for dimethyl succinate in the condensation, there was secured 0.476 g. of neutral product. From this semisolid material by chromatography on 15 g. of acid washed alumina there was isolated 0.116 g. (33% yield) of ethyl 6-methoxy-2-naphthoate, m.p. 90–92°, undepressed on admixture with authentic material (see below), and 0.110 g. (16% yield) of slightly yellow-colored **ethyl 3-N-(β-carboethoxyethylcarbamido)-4-methyl-5-(6-methoxy-2-naphthyl)furan-2-carboxylate (VIII. R = C_2H_5)**, m.p. 150–153°. Repeated recrystallization from dilute (85%) ethanol gave colorless fibers, m.p. 165–166°, $\lambda_{\max}^{\text{KBr}}$ 3.0 μ (N—H); 5.75 (COOR); 5.82 (conj. COOR); 6.0, 6.4 (RCOHNR).

Anal. Calcd. for $C_{25}H_{27}O_7N$: C, 66.21; H, 6.02. Found: C, 66.3; H, 6.0.

(b) With the Fraction A (Rich in the C-Alkylated Product V).—To a stirred mixture of 2.85 g. of the oily fraction A (see above) and 12.8 ml. of diethyl succinate, maintained at a temperature of 31–33°, there was slowly added over a period of 5 hr. a solution of 2.5 g. of potassium in 54 ml. of dry *t*-butyl alcohol. The mixture was then treated as described above, giving 1.55 g. of neutral material which was chromatographed on 31 g. of acid-washed alumina. There were thus obtained three distinct fractions: 0.638 g. (31% yield) of almost colorless ethyl 6-methoxy-2-naphthoate, m.p. 78–84°; 0.71 g. of oily material; and 0.030 g. (0.75% yield) of the diethyl ester VIII (R = C_2H_5), m.p. 157–160°.

(c) With the Fraction B (Rich in the O-Alkylated Product VII).—A stirred mixture of 2.10 g. of the oily fraction B (see above) was treated just as described above with a solution of 1.03 g. of potassium in 24 ml. of *t*-butyl alcohol. Chromatography of the neutral product (2.5 g.) gave the following fractions: 0.41 g. (28% yield) of ethyl 6-methoxy-2-naphthoate, 0.250 g. of oily material, and 0.90 g. (31% yield) of slightly yellow diethyl ester VIII (R = C_2H_5), m.p. 159–161°.

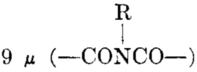
3-N-(β-Carboxyethylcarbamido)-4-methyl-5-(6-methoxy-2-naphthyl)furan-2-carboxylic Acid (VIII. R = H).—The saponification of 0.40 g. of the dimethyl ester VIII (R = CH_3), m.p. 156–159°, was effected with a solution of 1.48 g. of barium hydroxide octahydrate in 65 ml. of dilute (75%) ethanol. After refluxing the mixture for 2 hr. in an atmosphere of nitrogen, the precipitated solid was collected by filtration and washed with 10 ml. of dilute (75%) ethanol. This product was then warmed with dilute hydrochloric acid on the steam bath for 1 hr. The yellow-green precipitate that remained amounted to 0.30 g. (80% yield), m.p. 183–189° (dec.). Repeated recrystallization from 95% ethanol gave tan-colored flakes, m.p. 194–196° (dec.), $\lambda_{\max}^{\text{KBr}}$ 3.0 μ (N—H); 3.0–4.0, 5.8 (COOH); 6.0, 6.45 (RCONHR).

Anal. Calcd. for $C_{21}H_{19}O_7N$: C, 63.47; H, 4.82; N, 3.52; neut. equiv., 198.6. Found: C, 63.2; H, 4.8; N, 3.2; neut. equiv., 198.

When a sample of this acid in anhydrous ether was treated with an excess of diazomethane, there was obtained, upon evaporation of the solvent, light yellow fibers, m.p. 165–167°, undepressed on admixture with a pure sample of the dimethyl ester VIII (R = CH_3).

Saponification of the diethyl ester VIII (R = C_2H_5) similarly gave the crude diacid VIII (R = H), m.p. 180–185° (dec.), in 81% yield. Recrystallization from ethanol raised the m.p. to 193.5–196°. Admixture of this material with the analytical sample (see above) gave no depression of the melting point.

Ethyl 3-N-Succinimido-4-methyl-5-(6-methoxy-2-naphthyl)furan-2-carboxylate (X).—A mixture of 0.10 g. of the diethyl ester VIII (R = C_2H_5) and 0.35 g. of potassium acid sulfate was heated for 1 hr. at diminished pressure. The fraction that evaporatively distilled at 240–270° (0.2 mm.) was collected. The yield of light yellow oil, that solidified on cooling, was 0.08 g. (90%), m.p. 246–249°, with slight previous softening. Repeated recrystallization from ethyllene glycol dimethyl ether gave colorless prisms, m.p. 252.5–253° (turning red), $\lambda_{\max}^{\text{KBr}}$ 5.6, 5.9 μ ($-CO\overset{\overset{R}{|}}{N}CO-$); 5.8 (conj. COOR).



$-CO\overset{\overset{R}{|}}{N}CO-$

Anal. Calcd. for $C_{23}H_{21}O_6N$: C, 67.80; H, 5.20; N, 3.44. Found: C, 67.9; H, 5.3; N, 3.6.

When 10 mg. of this compound was saponified with 20 ml. of 8% potassium hydroxide solution, there was obtained on acidification a gray solid acid, m.p. 173–177°, which after two recrystallizations from dilute ethanol melted at 185–187°, undepressed on admixture with the diacid VIII (R = H).

3-N-Succinimido-4-methyl-5-(6-methoxy-2-naphthyl)furan (XI).—A 0.87-g. sample of dibasic acid VIII (R = H), m.p. 184–186°, was decomposed by heating at 180–215° (10 mm.) for 20 min. and the resulting material was evaporatively distilled at 220–260° (0.4 mm.). The light yellow-colored solid that collected in the upper end of the sublimation tube amounted to 0.498 g. (67% yield) and upon recrystallization from benzene afforded 0.461 g., m.p. 227–229.5°. Repeated recrystallization from a mixture of benzene and petroleum ether (60–68°) gave colorless rods, m.p. 228.5–230°, $\lambda_{\max}^{\text{KBr}}$ 5.6, 5.85 μ ($\text{—CO}\overset{\overset{\text{R}}{|}}{\text{N}}\text{CO—}$). The n.m.r., spectrum showed absorption for seven protons at 7.2–8.25 p.p.m. (including six "aromatic" protons and one furano proton at 7.83), three protons at 3.88 ($ArOCH_3$), four protons as a singlet at 2.88 (—CH_2CH_2—), and three protons at 2.14 (CH_3 at C-4).

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.9; H, 5.15; N, 4.4.

3-N-(β-Carboxyethylcarbamido)-4-methyl-5-(6-methoxy-2-naphthyl)furan (XII).—To 0.100 g. of the aforementioned imide XI was added 200 ml. of 5% potassium hydroxide solution and the mixture was heated on a steam bath for 90 min. The bright green solution that developed was filtered, cooled in an ice bath, and slowly added to ice-cold dilute hydrochloric acid. The acidic solution was kept at ice bath temperature for 10 hr., and then extracted twice with a mixture of ethyl acetate and ether. The organic layer, after washing once with water and drying over anhydrous sodium sulfate followed by evaporation at room temperature under a stream of air, afforded 0.058 g. (55% yield) of a brown-yellow solid, m.p. 180–188° (dec.). Recrystallization from dilute alcohol gave an amorphous powder, m.p. 185–187° (dec.), $\lambda_{\max}^{\text{KBr}}$ 3.0 μ (N—H); 3–4, 5.8–5.9 (COOH); 6.0, 6.4 (RCO-NHR).

Anal. Calcd. for $C_{20}H_{19}O_5N$: C, 67.98; H, 5.42. Found: C, 68.5; H, 5.5.

A sample of this monobasic acid when sublimed at 220–260° (0.1 mm.) yielded an almost colorless solid which upon recrystallization from benzene melted at 227–229°. These crystalline rods were insoluble in dilute alkali and gave no depression in melting point upon admixture with a sample of the imide XI described above.

Exhaustive Saponification of the Imide XI.—The imide XII (0.190 g.) was added to 170 ml. of 8% potassium hydroxide solution, the mixture heated to effect solution, poured into a stainless steel flask, and refluxed for 99 hr. Ammonia was detected at the mouth of the condenser within a few hours, and after 5 hr. a solid collected above the refluxing liquid in the tube of the condenser. At the end of the heating period, the accumulated slightly yellow solid was washed out of the condenser with water and dried, yielding 0.016 g., m.p. 103–105°. Recrystallization three times from petroleum ether (b.p. 60–68°) gave colorless flakes, m.p. 115.2–116.4°, undepressed on admixture with an authentic sample of 6-methoxy-2-propionylnaphthalene. The melting point of the 2,4-dinitrophenylhydrazone of this hydrolytic product, alone or on admixture with the 2,4-dinitrophenylhydrazone of 6-methoxy-2-propionylnaphthalene, was 238–239.8°.

The alkaline solution was cooled and extracted with a mixture of benzene and chloroform. These organic extracts were dried over anhydrous sodium sulfate and evaporated to give 0.094 g. of dark brown solid. Trituration with petroleum ether (b.p. 60–68°) gave an additional 0.020 g. of 6-methoxy-2-propionylnaphthalene, m.p. 110–115°, bringing the total yield to 30%.

The basic solution upon cooling and acidification yielded 0.033 g. (17% yield) of pale yellow acid, m.p. 202–204°. The infrared spectrum was identical with that of 6-methoxy-2-naphthoic acid. The methyl ester, prepared with diazomethane, was obtained after crystallization from methanol as buff-colored plates, m.p. 131.2–132.9°, undepressed on admixture with an authentic sample of methyl 6-methoxy-2-naphthoate. The infrared spectra of the two samples were identical.

Methyl 6-methoxy-2-naphthoate was prepared by direct esterification of the acid. It crystallized from petroleum ether (b.p. 60–68°) as colorless needles, m.p. 129–130.2°, reported[9] 126°.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.60. Found: C, 72.4; H, 5.6.

Ethyl 6-methoxy-2-naphthoate, which was similarly prepared, crystallized from petroleum ether (b.p. 60–68°) as colorless needles, m.p. 102–103.8°, reported[10] 96°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.0; H, 6.2.

***t*-Butyl 6-methoxy-2-naphthoate** was prepared in 84% yield by the reaction of the acid with isobutylene.[11] It crystallized from petroleum ether (b.p. 60–68°) as colorless plates, m.p. 89.5–91°.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 73.9; H, 7.2.

Acknowledgment.—This work was supported in part by grants from the National Science Foundation and the U. S. Public Health Service. We are grateful to Dr. L. J. Durham for assistance in performing and interpreting the n.m.r. spectra.

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