55 mg. of ammonium acetate to a solution of 155 mg. of the anhydride in 5 cc. of ethyl acetate and 1 cc. of acetic acid. After standing overnight the solution was diluted with ligroin and chilled, when 80 mg. of the amide No. 8a separated, m. p. 160.6–162.4°. Crystallization from dilute alcohol gave a yellow powder that gave no depression when mixed with material prepared as described above (No. 8).

For conjugation with **sulfanilamide,** a solution of 302 mg. of the anhydride and 172 mg. of the amine in acetone was allowed to stand for one hour, concentrated, and the yellow solid that separated crystallized from alcohol–water; 370 mg., m. p. 185.6–188.2°. The substance (No. 12) forms small yellow crystals; it is soluble in alcohol, acetone, and dilute sodium bicarbonate solution. The reaction with **sulfaguanidine** was conducted similarly in acetone and the product precipitated by saturating the solution with ether (m. p. 197–198.5°); recrystallization from methyl cellosolve–water gave a yellow microcrystalline powder. The conjugate is soluble also in ethylene glycol and in dilute sodium carbonate solution and somewhat soluble in alcohol and in acetone. Treatment with sodium nitrite and acetic acid at 0°, followed by the addition of alkaline β-naphthol solution, resulted in no coloration, whereas sulfaguanidine on similar treatment gave a brilliant purple solution. The amide from **sulfadiazine** was obtained in the same way and purified by dissolving it in a mixture of hot ethylene glycol (readily soluble) and methyl cellosolve (to moderate the temperature) and adding water; the substance is practically insoluble in most solvents. The amide from **sulfapyridine,** prepared in acetone at 25°, is moderately soluble in dioxane or methyl cellosolve and was crystallized from the latter solvent diluted with water. The reaction of the anhydride (400 mg.) with **sulfathiazole** (340 mg.) was conducted in boiling acetone and the product that separated was recrystallized from ethyleneglycol–methyl cellosolve–water; like the related amides, the substance was obtained as an orange microcrystalline powder.

Summary

Several 2,3-disubstituted naphthoquinones of types thought to possess potentialities for biological activity were prepared by the addition of mercaptans to 2-methyl-1,4-naphthoquinone. The quinone obtained from thiomalic acid was conjugated through the anhydride with several amines.

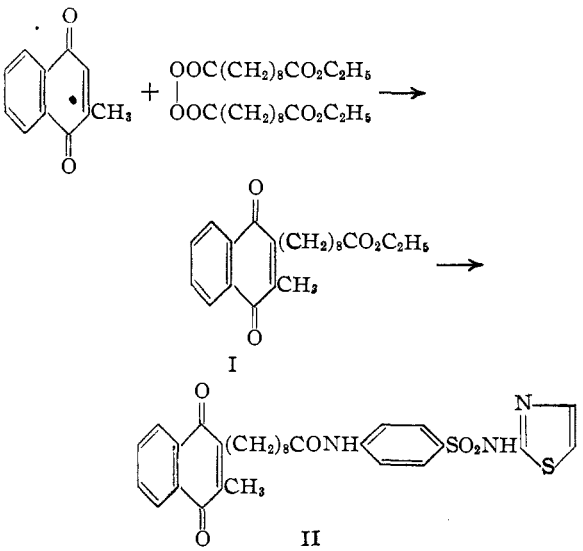
CONVERSE MEMORIAL LABORATORY
CAMBRIDGE 38, MASSACHUSETTS RECEIVED APRIL 23, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Naphthoquinone Acids and Ketols[1]

BY LOUIS F. FIESER AND RICHARD B. TURNER

For an extension of the project outlined in the preceding paper[2] a satisfactory route was sought to 1,4-naphthoquinones with an acidic side chain in the 2-position and a protective methyl group at position 3. Fieser, Gates and Kilmer[3] obtained γ-(1,4-naphthoquinonyl-3)-butyric acid by a rather lengthy synthesis but found that the reaction with lead tetraacetate[4] afforded the methyl-substituted derivative in only 3.8% yield. C-Methylation of the same acid with diazomethane[5] was tried in the present work and found to give no better results. The introduction of the acid side chain by the reaction of the half ester of a dibasic acid with methylnaphthoquinone and red lead according to one of the procedures of Fieser and Chang[4] also proved unsatisfactory (5.6% yield). When, however, the procedure for effecting alkylation with a diacyl peroxide was discovered,[6] this method was tried and found to be well adapted to the problem at hand. Disuccinoyl and diglutaroyl peroxide, obtainable from the anhydrides and alkaline hydrogen peroxide, react with methylnaphthoquinone in hot acetic acid to give methylnaphthoquinonylpropionic and butyric acids in yields up to 40%. The peroxide obtained from ethyl hydrogen sebacate through the acid chloride affords the pelargonic ester I in 41% yield. The one-step synthesis thus provides an easy route to naphthoquinone acids of the type sought.



The acid derived from I was conjugated through the acid chloride with each of four sulfonamide drugs to products exemplified by II. In another series of reactions the acid chloride III was converted through the diazoketone to the ketol IV and its acetate. 2-Hydroxy-1,4-naphthoquinone was similarly alkylated with disebacoyl peroxide

(1) From the doctoral dissertation of Richard B. Turner, May 1, 1942. The research was assisted by a fellowship from the Allied Chemical and Dyestuff Corporation in 1941–1942.

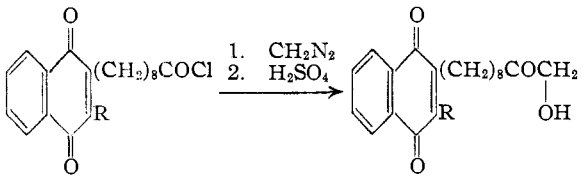
(2) Fieser and Turner, THIS JOURNAL, **69**, 2335 (1947).

(3) Fieser, Gates and Kilmer, *ibid.*, **62**, 2966 (1940).

(4) Fieser and Chang, *ibid.*, **64**, 2043 (1942).

(5) Fieser and Peters, *ibid.*, **53**, 4080 (1931); Fieser and Hartwell, *ibid.*, **57**, 1479 (1935); Bergmann and Bergmann, *J. Org. Chem.*, **3**, 128 (1938).

(6) Fieser and Oxford, THIS JOURNAL, **64**, 2060 (1942).



III, R = CH_3
V, R = OAc

IV, R = CH_3
V, R = OAc

diethyl ester and the product converted by hydrolysis and acetylation into a derivative (V) that could be employed for the synthesis of a second ketol, VI. Ketols IV and VI are yellow substances that reduce Fehling solution, and the absorption spectra conform to the pattern of model 2,3-disubstituted naphthoquinones (*e. g.*, phthiocol acetate). In the first attempt to prepare the ketol VI the diazomethane solution used contained water and methanol and the reaction afforded an anomalous colorless product isomeric with the true diazoketone. The white substance yielded a supposed ketol and ketol acetate, but these were both colorless and the former had no reducing properties. The nature of the compounds was not elucidated, but it was found that the reaction can be caused to proceed normally by the use of absolute, alcohol-free diazomethane solution.

The ketols IV and VI contain two centers capable of participating in oxido-reduction reactions, the quinone group and the ketol group. They also bear a superficial structural relationship to the cortical hormones. Thus IV, like corticosterone, is a C_{21} compound with a ketol grouping in one part of the structure and an α,β-unsaturated ketonic group in another and possessing one additional carbonyl group. Ketol VI, like Kendall's Compound E, contains also a hydroxyl group (acetylated).

Another point of interest is a possible relationship to luciferin, which has been regarded as a hydroquinone, possibly of the naphthalene series, having the $-COCH_2OH$ side chain.[7] Drs. E. Newton Harvey and Frank H. Johnson of Princeton University kindly tested the ketol IV (as hydroquinone) for luminescence on the addition of luciferase, the enzyme involved in light production on oxidation of luciferin of luminous animals. No light was emitted from the reduced naphthoquinone–luciferase mixture, and the naphthoquinone present did not inhibit luminescence on addition of luciferin.

Experimental[8]

γ-2-(Methyl-1,4-naphthoquinonyl-3)-butyric Acid.—(a) A benzene solution of 540 mg. of γ-(1,4-naphthoquinonyl-3)-butyric acid[3] was treated with an ethereal solution of diazomethane from 3 cc. of nitrosomethylurethan and after three hours the solvent was evaporated and the residual red oil heated to 130° (gas evolution). The residue was refluxed under nitrogen with alkaline hydrosulfite, the solution was acidified with acetic acid and extracted with ether, and the extract dried, shaken with silver oxide and magnesium sulfate, and the resulting yellow product crystallized four times from benzene–ligroin. The yield of granular yellow quinone (m. p. 141–142°; identical with that below) was only 23 mg. (3.9%).

(b) Digluteroyl peroxide[9] (4.45 g.) was added in small portions to a solution of 2.92 g. of methylnaphthoquinone in 5 cc. of acetic acid at a temperature just below the boiling point (vigorous gas evolution after each addition). The solution was then diluted with water and neutralized with 10% sodium carbonate containing enough hydrosulfite to convert the quinone to the alkali-stable hydroquinone. The alkaline liquor was washed with ether to remove neutral starting material, made acid with acetic acid, and extracted with ether. The ethereal extract was dried, shaken with 3 g. of silver oxide and 4 g. of magnesium sulfate, treated with Norit, filtered and evaporated. The residual yellow solid on crystallization from benzene–ligroin gave 1.75 g. (40%) of acid, m. p. 138–141°. A recrystallized sample consisted of granular yellow crystals, m. p. 143.3–144.1°.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46. Found: C, 69.91; H, 5.62.

β-(2-Methyl-1,4-naphthoquinonyl-3)-propionic Acid.—(a) The reaction of methylnaphthoquinone (3 g.), methyl hydrogen succinate (30.5 g.), ethyl acetoacetate (3 g.) and red lead (48 g.) was conducted at 120–130° essentially according to Fieser and Chang.[4] The reaction mixture was submitted to hydrolysis under reducing conditions and the product extracted as the hydroquinone as in (a) and oxidized with silver oxide. The yield of once crystallized quinone, m. p. 139–142.5°, was 240 mg. (5.6%); a purified sample was identical with that of (b).

(b) Alkylation of 2.24 g. of methylnaphthoquinone with 3.04 g. of disuccinoylperoxide[5] by the procedure described above yielded 640 mg. (20%) of once crystallized product, m. p. 142–144°. Four recrystallizations from benzene–ligroin gave clusters of microprisms, m. p. 145.9–146.5°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.84; H, 5.13.

9-(2-Methyl-1,4-naphthoquinonyl-3)-pelargonic Acid and Derivatives (*see Table I*).—Disebacoyl peroxide diethyl ester was best prepared by warming ethyl hydrogen sebacate with phosphorus trichloride decanting the upper layer, and shaking the crude acid chloride (14.6 g.) in petroleum ether (100 cc.) with water (25 cc.), ice (30 g.), and sodium peroxide (8 g.), added in small portions at 0°. The peroxide partly separated and was redissolved by the addition of ether and isolated by evaporation of the dried organic phase; yield 7.5 g. (59%), m. p. 33.5–35°.

Alkylation was conducted by warming a solution of 2.74 g. of methylnaphthoquinone and 7.3 g. of peroxide in 20 cc. of acetic acid to 85°, when reaction set in and continued without further application of heat. The reaction mixture was collected in ether and the well washed solution shaken with 2% potassium hydroxide containing hydrosulfite; the ethereal solution of substituted and unsubstituted hydroquinones was extracted with alkaline hydrosulfite as long as the extract was colored yellow with methylnaphthohydroquinone, and the ether phase was then dried and oxidized with silver oxide. One crystallization of the quinone acid from ligroin gave 2.31 g. (41%) of product, m. p. 64–65°. The analytical sample of the ethyl ester (No. 2 in Table) formed light yellow microprisms.

For hydrolysis to the *acid* (No. 1), 2 g. of the ester in a small volume of alcohol was reduced with aqueous hydrosulfate and the solution was treated with 30 cc. of 30% potassium hydroxide (and more hydrosulfite, as required) and refluxed for two hours. A white precipitate separated on neutralization with acetic acid and was taken up in ether and the solution shaken with silver oxide and magnesium sulfate. The quinone, once crystallized from ligroin, amounted to 1.58 g. (86%); m. p. 88–90°. Fur-

(7) Chakravorty and Ballentine, THIS JOURNAL, **63**, 2030 (1941).

(8) All melting points are corrected.

(9) Clover and Houghton, *Am. Chem. J.*, **32**, 60 (1904).

TABLE I

9-(2-METHYL-1,4-NAPHTHOQUINONYL-3)-PELARGONIC ACID AND DERIVED COMPOUNDS

No.	Side chain	M. p., °C.	Solvent	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	$-(CH_2)_8CO_2H$	91.4- 91.8	C_6H_5–Lig.	$C_{20}H_{24}O_4$	73.15	7.37	73.00	7.32
2	$-(CH_2)_8CO_2C_2H_5$ (I)	68.2- 69.4	Lig.	$C_{22}H_{28}O_4$	74.13	7.92	74.13	8.18
3	$-(CH_2)_8CO-N^4$—sulfanilamide	192.4–193.1	Alc.	$C_{26}H_{30}O_5N_2S$	64.70	6.27	64.52	6.37
4	$-(CH_2)_8CO-N^4$—sulfapyridine	175.5–175.9	Methcel.[a]	$C_{31}H_{33}O_5N_3S$	66.52	5.94	66.20	5.99
5	$-(CH_2)_8CO-N^4$—sulfadiazine	204.3–204.5	Methcel.[a]	$C_{30}H_{32}O_5N_4S$	64.27	5.75	64.01	5.81
6	$-(CH_2)_8Co-N_4$—sulfathiazole (II)	212.3–213.4	Methcel.[a]	$C_{29}H_{31}O_5N_3S_2$	61.57	5.52	61.35	5.76
7	$-(CH_2)_8COCHN_2$	121.8–122.2 dec.	C_6H_6–Lig.	$C_{21}H_{24}O_3N_2$	71.57	6.86	71.36	6.95
8	$-(CH_2)_8COCH_2OH$ (IV)	105–106.3	C_6H_6–Lig.	$C_{21}H_{26}O_4$	73.66	7.65	73.59	7.63
9	$-(CH_2)_8COCH_2OCOCH_3$	88.6- 89.4	C_6H_6–Lig.	$C_{23}H_{28}O_5$	71.85	7.34	71.90	7.26

[a] Methocellosolve-water.

TABLE II

9-(2-HYDROXY-1,4-NAPHTHOQUINONYL-3)-PELARGONIC ACID AND DERIVED COMPOUNDS

No.	Side chain	M. p., °C.	Solvent	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
10	$-(CH_2)_8CO_2H$	125 -125.8	C_6H_6–Lig.	$C_{19}H_{22}O_5$	69.07	6.71	68.90	6.69
11	Ethyl ester	69.9–71.0	Lig.	$C_{21}H_{26}O_5$	70.37	7.31	70.18	7.11
12	Acetate (V)	90.4–91.2	C_6H_6–Lig.	$C_{21}H_{24}O_6$	67.73	6.50	67.56	6.41
13	Hydroquinone triacetate	121.2–122	Dil. alc.	$C_{25}H_{30}O_8$	65.49	6.60	65.43	6.73
	Derivatives of 9-(2-Acetoxy-1,4-naphthoquinonyl-3)-pelargonic Acid							
14	$-(CH_2)_8COCHN_2$	81.6–82.4	C_6H_6–Lig.	$C_{22}H_{24}O_5N_2$	66.65	6.10	66.45	6.24
15	$-(CH_2)_8COCH_2OH$	58.8–60.6	C_6H_6–Lig.	$C_{22}H_{26}O_6$	68.38	6.78	68.33[a]	6.33[a]
16	$-(CH_2)_8COCH_2OCOCH_3$	84.0–84.8	C_6H_6–Lig.	$C_{24}H_{28}O_7$	67.27	6.59	67.29	6.57
	Anomalous products							
17	Isomer of No. 14	122.6–123.6	C_6H_6–Lig.	$C_{22}H_{24}O_5N_2$	66.65	6.10	66.96[a]	6.26[a]
18	Isomer of No. 15	111.6–112.2	C_6H_6–Lig.	$C_{22}H_{26}O_6$	68.38	6.78	68.30	6.81
19	Isomer of No. 16	116.4–117.0	C_6H_6–Lig.	$C_{24}H_{28}O_7$	67.27	6.59	67.36	6.53

[a] Microanalysis by E. Werble.

ther purification from benzene–ligroin gave rosets of pale yellow needles.

The crude **acid chloride** was obtained by heating 3.5 g. of the acid with 5 cc. of purified thionyl chloride at 60° for one hour, removing the excess reagent at the water pump, and flushing the residue twice with dry ether.

The preparation of the **sulfonamide derivatives** 3–6 is illustrated as follows. The acid chloride from 300 mg. of acid was dissolved in acetone and a hot acetone solution of 228 mg. of sulfapyridine was added. After one-half hour the solution was concentrated and diluted with ether, when 358 mg. (70%) of light yellow microscopic blades of the conjugate separated, m. p. 169.6–172.6°.

For conversion to the **diazoketone** (No. 7), a solution of the acid chloride from 3.5 g. of acid in 10 cc. of dry ether was chilled to −10° and treated with a similarly chilled ethereal solution of diazomethane from 7.5 cc. of nitrosomethylmethane. Nitrogen evolution proceeded vigorously for about five minutes and a large crop of yellow needles separated. After one-half hour at −10°, the mixture was allowed to come to room temperature and after eighteen hours ligroin was added and the product collected; yield 3.3 g. (88%), m. p. 116–118°, dec. The purified diazoketone formed clusters of pale yellow needles.

The **ketol IV** (No. 8) was obtained by treating 1 g. of the diazoketone in 30 cc. of dioxane with 9 cc. of 2 *N* sulfuric acid. Nitrogen was evolved at once and after ten minutes the solution was warmed to 40° to complete the reaction. The product was isolated by dilution with water and extraction with ether; the dried extract was concentrated and saturated with petroleum ether, when the ketol separated in yield of 561 mg. (58%), m. p. 105–106.3°. The substance reduced Fehling solution and afforded the acetate No. 9 when heated on the steam-bath for one hour with acetic anhydride and sodium acetate.

For preparation of the **ketol acetate** (No. 9) 352 mg. of the diazoketone was heated in 3 cc. of acetic acid for one-half hour on the steam-bath and the product extracted with benzene and ether. The washed and dried extract when concentrated and chilled deposited 218 mg. (57%) of yellow needles, m. p. 87.8–88.6°.

9-(2-Hydroxy-1,4-naphthoquinonyl-3)-pelargonic Acid and Derivatives (*see Table II*).—The alkylation of 2-hydroxy-1,4-naphthoquinone (12.2 g.) with disebacoyl peroxide diethyl ester (32 g.) was conducted as above in 125 cc. of acetic acid at 90°. After the initial reaction had subsided the solution was heated to boiling for a few minutes and then cooled in ice and filtered from 2.16 g. of hydroxynaphthoquinone. A washed ethereal extract of the residual mixture was then extracted exhaustively with 10% potassium bicarbonate solution to remove all traces of hydroxynaphthoquinone and then dried and evaporated. The residual oil when triturated with a small amount of ligroin and chilled afforded 12.0 g. (49%) of the **ethyl ester** (No. 11) as a bright yellow solid, m. p. 65.2–68.9°.

Hydrolysis to the **acid** was accomplished best through the hydroquinone. A mixture of 10 g. of the ester, 100 cc. of 30% potassium hydroxide and 10 g. of sodium hydrosulfite was refluxed gently for one hour and the solution was cooled, acidified with acetic acid, and extracted with ether. The extract was washed free of acetic acid and alcohol and shaken with silver oxide, magnesium sulfate and Norit, filtered and evaporated at reduced pressure. One crystallization of the residual yellow solid from benzene–ligroin afforded 7.51 g. (81%) of prisms, m. p. 123–125°.

For **acetylation**, 6.1 g. of the acid was dissolved in 15 g. of acetic anhydride containing 3 g. of fused sodium acetate and the mixture was heated on the steam-bath for

two hours, when the initial blood-red color had changed to orange-yellow. On hydrolysis of the excess anhydride the acetate separated as a solid and was crystallized from benzene–ligroin; yield 5.12 g. (74%), m. p. 86.4–88.4°. The analytical sample (No. 12) consisted of pale yellow microprisms.

Reductive acetylation (No. 13) was accomplished by heating 1 g. of the acid with 6 cc. of acetic anhydride and 0.2 g. of fused sodium acetate for one hour on the steam-bath and treating the cooled solution with 1 g. of zinc dust. The yellow color was discharged in a few minutes and the mixture was then boiled briefly, diluted with acetic acid, filtered and treated with water. The product was caused to solidify by cooling and scratching, and initial crystallization from benzene containing a little ether gave 1.14 g. (82%) of product melting at 115–118°. Recrystallization from dilute alcohol afforded white microprisms.

From preparation of the **diazoketone** (No. 14), 4.78 g. of 9-(2-acetoxy-1,4-naphthoquinonyl-3)-pelargonic acid (No. 12) was converted to the acid chloride with 5 cc. of thionyl chloride at 60° as above and a solution of the chloride in dry ether was chilled to −10° and treated with a similarly chilled ethereal solution of 0.0256 mole of diazomethane prepared according to Arndt[10] and dried over solid potassium hydroxide and then sodium wire. Gas was evolved vigorously and after one-half hour at −10° the mixture was allowed to stand at room temperature for one-half hour, when the gas evolution had ceased and considerable yellow solid had separated. The mixture was concentrated at 0°, ligroin was added, and the oily yellow solid collected and triturated with 5 cc. of cold ether. The residual solid was suitable for use and melted at 74–78°; yield 2.92 g. (52%). A sample recrystallized five times from benzene–ligroin formed small yellow needles; it melted at 81.6–82.4° and began to decompose at 118–128°.

The **ketol VI** (No. 15) was prepared as above; yield from 500 mg. of diazoketone, 286 mg. (60%), m. p. 53–55°. The analytical sample formed rosets of tiny bright yellow needles (strong positive Fehling test). The yield of the corresponding **ketol acetate** (no. 16) from 148 mg. of diazoketone was 129 mg. (81%), m. p. 84–85.4° (light yellow rectangular plates).

Anomalous Products.—The anomalous substance No. 17 was prepared in the same way as the true diazoketone No. 14 except for the use of an alcohol- and water-containing diazoethane solution prepared in the usual manner from nitrosomethylurethan. The yield from 5.3 g. of acid was only 650 mg. The purified substance consisted of cream-colored granules. The non-reducing supposed ketol No. 18 likewise formed cream-colored granules; on acetylation it afforded a substance identical with the acetate, No. 19, resulting from the action of acetic acid on No. 17 (131 mg. from 221 mg.); the acetate formed rosets of cream-colored blades. A Rast molecular weight determination (E. Werble) gave the value 448 (calcd. 428). In absorption spectra the substances 18 and 19 are very similar to one another and show some similarity to the true ketols in the region 240–280 mμ but absorb more intensely in the region 330 mμ. Maxima were observed for No. 18 at the following wave lengths (and log E values): 240 (4.4), 260 (4.15), 268 (4.1), 330 (3.9).

(10) Arndt, "Organic Syntheses," Coll. Vol. II, 165 (1943).

Summary

A carboxylated side chain is easily introduced at the free position of 2-methyl-1,4-naphthoquinone by alkylation with the peroxide derived from the half ester of a dibasic acid. Such naphthoquinonyl acids have been conjugated with sulfanilamides and also converted through diazoketones to naphthoquinonyl ketols possessing at least superficial structural relationships to cortical hormones and possibly to luciferin.

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CAMBRIDGE 38, MASSACHUSETTS RECEIVED APRIL 23, 1947

[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Aminoalkanol Derivatives of Benzo(f)chroman[1,2]

BY G. BRYANT BACHMAN AND HAROLD A. LEVINE

The antimalarial activity of compounds of the type RCHOH—$(CH_2)_nNR'_2$ (R = aryl, R′ = alkyl) suggested the preparation of related compounds in which the alcohol grouping is part of a ring system. Compounds of the 1-(α-naphthyl)-alkanolamine structure (X, XII, Fig. 1) in which the side-chain is linked to the beta position of the naphthalene nucleus by an oxygen atom, derivatives of benzo(f)chroman, seemed desirable compounds to prepare for comparison in view of the known high activity of the corresponding naphthalene derivatives.[3]

The synthetic methods usually employed in preparing compounds of the desired type start with a ketone which is brominated to form the alpha-bromoketone and then condensed with a secondary amine. The resulting α-dialkylaminoketone is reduced to the corresponding aminoalcohol. Alternatively the bromoketone may be converted to the corresponding bromohydrin by aluminum isopropoxide reduction and then condensed with a secondary amine.[4]

The parent ketone of this series, 1-benzo(f)-chromanone (I), has been prepared previously by the action of phosphorus pentoxide on β-(2-naphthoxy)-propionic acid.[5] A more convenient preparation was developed in this investigation. β-(2-Naphthoxy)-propionitrile,[6] from β-naphthol and acrylonitrile in the presence of Triton B,[6a] was cyclized by 85% sulfuric acid to give I in excellent yields. The same procedure applied to β-

(1) Based on the Ph.D. thesis of H. A. Levine, February, 1947.

(2) Read before the Medicinal Division of the American Chemical Society at the Atlantic City Meeting, April, 1947.

(3) Jacobs, Winstein, Ralls, Robson, Henderson, Akawie, Florsheim, Seymour and Seil, *J. Org. Chem.*, **11**, 21 (1946).

(4) Winstein, Jacobs, Henderson and Florsheim, *ibid.*, **11**, 150 (1946).

(5) Chakravarti and Dutta, *J. Indian Chem. Soc.*, **16**, 639 (1939).

(6) This compound is claimed in French Patent 833,734 (1938), and Ufer, German Patent 670,357 (1939), but its physical constants are not reported.

(6a) Benzyltrimethylammonium hydroxide obtained from Rohm and Haas Company, Philadelphia. Other strong bases also function as catalyst for this addition.