chloride was passed in rapidly until the solution became saturated (one and one-half hours) and then more slowly for two hours longer.[14] The milky solution gradually cleared and then an orange solid slowly separated. The ether was decanted, and after washing the solid with fresh ether it was warmed with water (50–100 cc.) until all the imide hydrochloride decomposed. The mixture was cooled and the aldehyde was removed and crystallized from 50% acetic acid, dilute alcohol or chloroform–petroleum ether. The yield was 5.6 g. (64%) and the melting point was 158–160°. The chief impurity in the crude aldehyde was a black substance (quinhydrone?). Steam distillation of the aldehyde gave only quinone in the distillate and a residue of red oil which solidified on cooling; vacuum distillation was also unsatisfactory as a method of purification. The aldehyde could not be converted into an oxime, but with aniline it gave a precipitate of beautiful red needles.

Condensation with Malonic Ester.—To the aldehyde (1.44 g.) in alcohol (2 cc.) there was added piperidine (0.76 g.) and ethyl malonate (2 cc.). The mixture was warmed on the steam-bath until a clear solution resulted, then set aside for a day. The product which had crystallized from the solution was allowed to stand with hydrochloric acid for fifteen to twenty minutes, filtered and washed with cold alcohol and ether. Crystallized from alcohol, the product weighed 0.43 g. and melted at 209–211°; the mixed melting point with a specimen of III (m. p. 208–209°) was 208–209°. Acetylation of this product gave the same acetyl derivative (IV) as was obtained from the ester III; m. p. and mixed m. p. 193–195°.

Condensation of the aldehyde (1 g.) with malonic ester (2 cc.) in acetic acid (2 cc.) led to a solid (0.05 g.) which was chiefly the acetyl derivative VIII. It melted at 248–253°; the mixed m. p. with VIII (m. p. 258°) was 246–250°.

Condensation with Malonic Acid.—To the aldehyde (1.4 g., crude) and malonic acid (0.7 g.) in dry methanol (7 cc.) was added one drop of piperidine and the solution was refluxed on the steam-bath for eighteen hours. A small amount of chloroform was added and the solution was filtered. The chloroform was evaporated from the filtrate, a little methanol was added and the yellow solid was filtered and washed with water and dilute hydrochloric acid. The solid melted at 273–275°; the mixed melting point with a specimen of the acid VII (m. p. 273–275°) was also 273–275° (copper block).

(14) Adams and Levine, THIS JOURNAL, **45**, 2373 (1923).

Summary

1. Sodium malonic ester reacts with 2,3-dimethylnaphthoquinone to give a purple sodium derivative which when treated with acid gives 5-methyl - 6 - hydroxy - 3 - carbethoxy - α - naphthocoumarin.

2. The physical and chemical properties of this coumarin and a number of its derivatives have been described, and the structure of the coumarin was proved by an independent synthesis from 1,4-dihydroxy-3-methyl-2-naphthaldehyde.

3. The course of the reaction between the methylated naphthoquinone and sodium malonic ester is entirely analogous to that between duroquinone and sodium malonic ester, but the hetero ring in the naphthocoumarin is much more resistant to opening by alkaline reagents.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 8, 1937

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Quinones and Sodium Enolates. VI. Duroquinone and Sodium Acetoacetic Ester[1]

BY LEE IRVIN SMITH AND DAVID TENENBAUM[2]

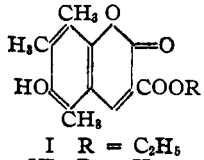
In the first paper of this series[3] it was shown that the fully methylated quinone, duroquinone, reacted with sodium malonic ester to give a coumarin derivative (I). In a later paper, Smith and MacMullen[4] showed that trimethylquinone, with one unsubstituted position in the ring, reacted with malonic ester and with acetoacetic ester to give benzofuran derivatives, malonic ester giving only one product (Ia), while acetoacetic ester gave two products (Ia and Ib). These products were the result of an initial 1,4-addition of the reagent to the quinone conjugated system which terminated in the free position, but this reaction was not accompanied by the oxidative step which occurred when the coumarin was formed from duroquinone. The fact that acetoacetic ester gave two products suggested a study of the reaction between this reagent and duroquinone. If the reaction followed the same course as that of malonic ester, the product would be the acetylcoumarin II; but there was also the possibility that the intermediate addition product (IIa) would be oxidized to a form which could undergo self-condensation leading to the *amphi*-naphthoquinone derivative IIb. These products would themselves be of interest,

(1) Paper V, THIS JOURNAL, **59**, 662 (1937).

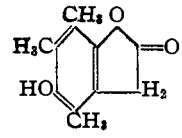
(2) Abstracted from a thesis by David Tenenbaum, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1936.

(3) Smith and Dobrovolny, THIS JOURNAL, **48**, 1693 (1926).

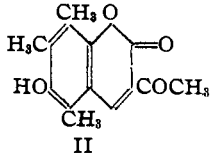
(4) Smith and MacMullen, *ibid.*, **58**, 629 (1936).



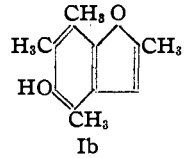
I R = C_2H_5
VI R = H



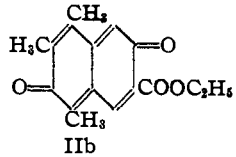
Ia



II



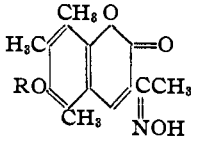
Ib



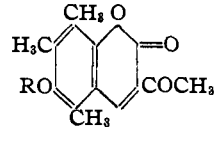
IIb

for few representatives of either acetylcoumarins or *amphi*-naphthoquinones are known; but, in addition, if the naphthoquinone derivative were formed, it might be possible, by a detailed study of the reaction, to gain some information as to the oxidative step in the process.

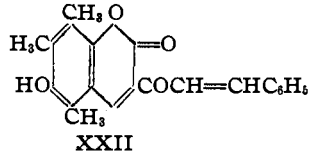
When duroquinone and acetoacetic ester were condensed according to the method of Smith and Dobrovolny[3] there resulted a *purple* sodium compound (IIa). The reaction mixture poured into iced hydrochloric acid gave a solid which crystallized from acetic acid in the form of tan needles melting at 222–226°. The wide melting point range of this substance and the failure to obtain concordant analyses led to the discovery that the substance held duroquinone tenaciously. When this was removed by treatment of the acetic acid solution with charcoal, a bright yellow substance (II), melting at 227–228°, was obtained. The substance had the composition $C_{14}H_{14}O_4$ corresponding to the acetylcoumarin II; it could be readily converted into a yellow oxime (III), a *colorless* acetyl derivative (IV), and a benzal derivative XXII.



III R = H
VIII R = CH_3



IV R = Ac
V R = Na
VII R = CH_3
XXI R = C_6H_5CO



XXII

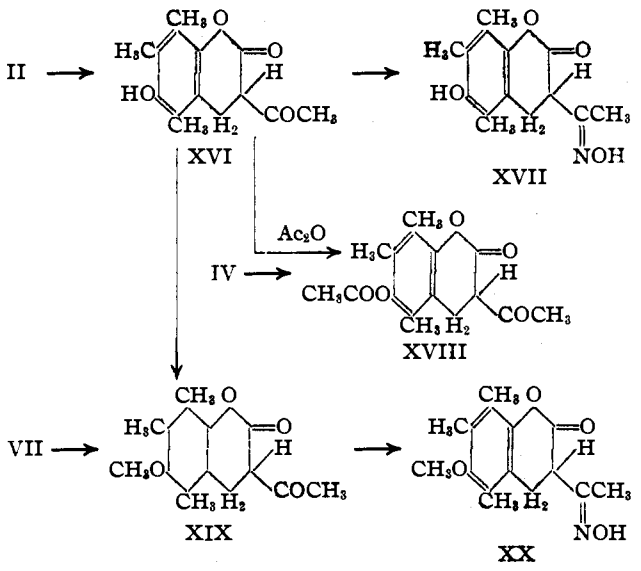
It was not possible to obtain anything but high melting, amorphous products when the coumarin II was subjected to the action of methyl sulfate and potassium hydroxide in methanol, but aqueous sodium hydroxide (10%) converted the coumarin into a *red* sodium derivative, represented as V, and when methyl iodide, or better methyl sulfate, was added to this sodium derivative suspended in methanol, the methoxy compound VII separated in the form of pale *yellow* needles. The red sodium compound V, refluxed with a solution of benzoyl chloride in benzene, gave the benzoate XXI.

Catalytic reduction of the coumarin II led to a dihydro compound (XVI) which formed an oxime (XVII), as well as an acetyl derivative (XVIII), and could be methylated with methyl sulfate and potassium hydroxide to give the methyl ether XIX. Reduction of the acetyl derivative IV also gave XVIII, and similarly reduction of the methyl ether VII gave XIX—that is, the same methyl or acetyl derivative resulted regardless of whether reduction preceded or followed methylation or acetylation. These reactions proved the presence of a double bond in the coumarin II and also proved conclusively that reduction of the acetylcoumarin involved only the double bond. The methyl derivative XIX gave an oxime (XX), but the acetyl derivative XVIII gave the hydroxy oxime XVII, the acetyl group being removed during the reaction between XVIII and hydroxylamine.

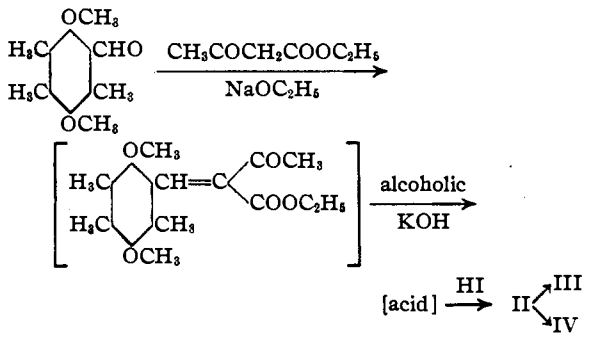
Numerous attempts were made to oxidize the acetylcoumarin II by hypohalites, and thus convert it into the carboxycoumarin VI, a known substance prepared several years ago by Smith and Dobrovolny.[3] But the acid VI was itself attacked by hypohalites, and in only one case, by action of sodium hypobromite on the red sodium compound V, was it possible to isolate the acid VI in quantity sufficient for identification.

The reactions given so far indicated quite clearly the structure of the product from the reaction between duroquinone and sodium acetoacetic ester, but the final proof of this structure was furnished by an independent synthesis of the acetylcoumarin II. Dimethoxydurylic aldehyde[5] was condensed with acetoacetic ester. Unfortunately neither the benzalacetoacetic ester nor the acid obtained from it by hydrolysis could be made to crystallize. Nevertheless, when the resulting oil

(5) Smith, THIS JOURNAL, **56**, 472 (1934).



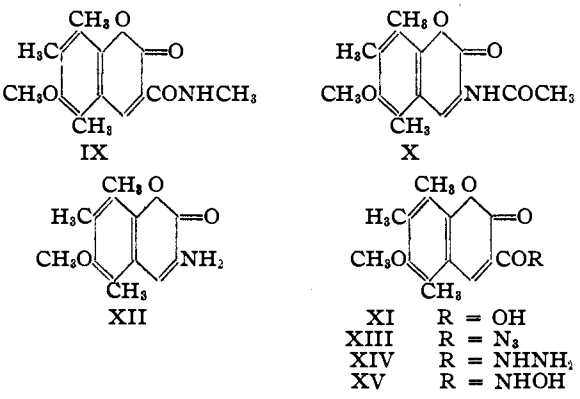
was boiled with hydriodic acid, it gave the acetylcoumarin II, and the synthesized coumarin gave the same oxime and acetyl derivative as those given by the coumarin obtained from duroquinone and sodium acetoacetic ester.



Hence the reaction between duroquinone and sodium acetoacetic ester follows the same course as that taken by this quinone and sodium malonic ester. The product is 5,7,8-trimethyl-3-acetyl-6-hydroxycoumarin and half of the quinone is converted to the hydroquinone. The failure to obtain any *amphi*-naphthoquinone derivative (IIb) from the reaction shows that the oxidation is confined to the side chain (or coumarin ring) of the product.

Since the oximes III and VIII were obtained readily, considerable study was devoted to their behavior in the Beckmann rearrangement. The oxime III did not react with sulfuric acid below 100°; above that temperature complete decomposition resulted. Both phosphorus pentachloride and benzene sulfonyl chloride reacted, but the resulting product was a mixture from which no pure compounds could be separated. The methoxy oxime VIII was more tractable, and when it was treated with benzene sulfonyl chloride and pyridine, an isomer resulted. Depending upon the configuration of the oxime VIII, structures IX or X were possible for this product.

Since the quantity of material was small, no attempt was made to hydrolyze this product until after the methyl amide IX was synthesized from the acid XI[3] via the acid chloride. The methyl amide IX so obtained was different from the rearrangement product of the oxime VIII. The structure of the latter was therefore strongly indicated to be X, a result in agreement with the work of Linch[6] who found that the oximes of 3-acetylcoumarin and 6-bromo-3-acetylcoumarin, when rearranged, gave the corresponding acetylaminocoumarins rather than the methyl amides of the coumarin acids. When hydrolyzed, the rearrangement product gave a crystalline compound containing nitrogen, the analysis of which corresponded to that required by formula XII, 3-amino-6-methoxy-5,7,8-trimethylcoumarin. Attempts were made to convert the acid XI into XII and so prove the structure X. The hydrazide (XIV) and the hydroxamic acid (XV) of XI were prepared, but these could not be rearranged. Attempts to prepare XII via the azide (XIII) of XI were also made, but neither the procedure of Newman[7] nor that of Nelles[8] was successful. The only product isolated was a non-basic substance containing nitrogen (XIII?) which melted at 210° with violent decomposition.



In spite of failure to synthesize the amine XII, it is felt that the non-identity of the rearranged

(6) Linch, *J. Chem. Soc.*, **101**, 1761 (1912).
(7) Newman, THIS JOURNAL, **57**, 732 (1935).
(8) Nelles, *Ber.*, **65**, 1345 (1932).

product with IX, together with its reactions, point fairly conclusively to structure X. If then the Beckmann rearrangement of the oxime VIII is a *trans* migration, it follows that the configuration of the oxime is as represented in formula VIII with the hydroxyl group *anti* to the coumarin ring.

Experimental Part

The Addition Reaction: 3-Acetyl-6-hydroxy-5,7,8-trimethylcoumarin, (II).—Acetoacetic ester (80 g.) was added in small portions to a suspension of powdered sodium (13 g.) in boiling benzene (1000 cc.). The addition of the ester required forty-five minutes, after which the mixture was refluxed, with frequent shaking, for two hours. Duroquinone (35 g.) dissolved in dry benzene (400 cc.) was added and the mixture refluxed for eight days. The color of the solution changed from yellow through brown to reddish-brown, and a purple solid (IIa) precipitated. The entire reaction mixture was poured into hydrochloric acid (500 cc.) and ice (500 g.). The tan solid was removed, washed twice with benzene and dried *in vacuo*. It was crystallized twice from acetic acid using Norite, which removed unchanged duroquinone. The product crystallized in bright yellow needles melting at 227–228°. It was insoluble in petroleum ether, benzene or methanol; difficultly soluble in boiling ethanol, chloroform or cold acetic acid. The yield of tan solid was 20 g.; that of the purified product was 12 g.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.29; H, 5.69. Found: C, 68.05, 67.97; H, 5.61, 5.88.

3 - Acetyl - 6 - acetoxy - 5,7,8 - trimethylcoumarin (IV) resulted when the coumarin II (1 g.) was warmed with acetic anhydride (10 cc.) and a drop of sulfuric acid. Crystallized from acetic acid (with charcoal to remove the dark color) the product formed pale yellow needles melting at 201–202.5°. The yield was 0.8 g.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.64; H, 5.60. Found: C, 67.00; H, 5.70.

3 - Acetyl - 6 - benzoyl - 5,7,8 - trimethylcoumarin, (XXI).—The purple sodium compound IIa from the reaction between duroquinone and acetoacetic ester was filtered and triturated twice with benzene. The salt (0.5 g.) was suspended in a solution of benzoyl chloride (2 cc.) in benzene (10 cc.) and the mixture refluxed for three hours. Unchanged salt (0.25 g.) was filtered off and the filtrate was stirred vigorously into water. Ether was added and the layers were separated. Evaporation of the organic layer left an oily residue containing benzoyl chloride, which was decomposed by adding alcohol and allowing to stand for five hours. The white solid was removed and crystallized from alcohol (using Norite). It weighed 0.12 g. and melted at 162–163°.

Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.97; H, 5.18. Found: C, 71.45; H, 5.49.

The oxime III resulted when the coumarin II (0.2 g.) was suspended in water (2 cc.) and ethanol (5 cc.) containing hydroxylamine hydrochloride (0.5 g.) and sodium hydroxide (2 cc., 10%) and the mixture warmed on the steam-bath for ten minutes. The oxime formed long, pale yellow needles melting at 258–260° (dec.). The yield was 0.2 g. The same oxime III resulted when the acetyl derivative IV reacted with hydroxylamine.

Anal. Calcd. for $C_{14}H_{15}O_4N$: C, 64.34; H, 5.79. Found: C, 63.92; H, 6.18.

The oxime III could not be made to undergo the Beckmann rearrangement. Benzene sulfonyl chloride in pyridine, as well as phosphorus pentachloride in ether, gave only impure amorphous products; sulfuric acid, at room temperature or at 100°, was without action.

Synthesis of II.—To the solution obtained by dissolving sodium (0.1 g.) in methanol (15 cc.) were added acetoacetic ester (1 cc.) and dimethoxydurylic aldehyde (0.5 g.). The mixture was warmed until the aldehyde dissolved and then allowed to stand at room temperature for three days. Water was added and the mixture was steam distilled. Dimethoxydurylic aldehyde (0.2 g.) was recovered from the distillate. The residual alkaline solution was acidified, extracted with ether (three times) and the ether was evaporated. As the oily residue could not be made to crystallize it was dissolved in ethanol (5 cc.) and boiled for ten minutes with potassium hydroxide (1 g.) in ethanol (10 cc.).

The solution was diluted with water, acidified, extracted with ether and the ether evaporated. The product was again an oil, which was warmed for an hour with constant boiling hydriodic acid (2 cc.). The solution was poured into ice water, and the precipitate was removed and crystallized from acetic acid with the aid of a little Norite. The product (0.2 g.) formed bright yellow needles melting at 226–227°; when mixed with the coumarin II from duroquinone, the melting point was 226–227°. The oxime melted at 257–260° (dec.), and when mixed with the oxime III the melting point was 257–260° (dec.).

Oxidation of II to VI.—To a solution of sodium hydroxide (3.4 g.) in water (30 cc.) was added the coumarin II (1 g.). The red sodium salt (V) precipitated. Bromine (1.8 cc.) was dropped slowly into the cold, stirred suspension of the sodium salt. Bromoform was removed by extracting with ether, and bisulfite was added to remove the excess hypobromite. The solution was acidified, extracted three times with ether and the ether evaporated. The residue was an orange oil which slowly deposited a small amount of solid. Washing with ethanol removed the oil, and the residual solid was crystallized from acetic acid. The product weighed 0.05 g., and the melting point was 260° (dec.). The mixed melting point with a specimen of 3-carboxy-6-hydroxy-5,7,8-trimethylcoumarin (VI) (m. p. 256–257°, dec.) was 257–260° (dec.). No other solid could be isolated; the low yield was due to the fact that VI was itself oxidized by hypobromite, giving only oils and bromoform (odor).

3 - Acetyl - 6 - methoxy - 5,7,8 - trimethylcoumarin, (VII).—The usual procedures for methylation with methyl sulfate and alkali failed when applied to the coumarin II but the methyl derivative VII was obtained as follows: the sodium salt V was precipitated by suspending the coumarin II (0.64 g.) in sodium hydroxide (20 cc., 10%). The salt V was filtered, washed several times with cold acetone and suspended in methanol (50 cc.). Methyl sulfate (3 cc.) was added with shaking. In about three minutes the red color changed to yellow and the methoxy compound began to crystallize. The product was filtered,

suspended in ether and extracted several times with sodium hydroxide (2%) to remove unchanged II. From the ether solution was obtained 0.41 g. of the methoxy compound VII melting at 158.5–159.5° and crystallizing in long, pale yellow needles.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.23; H, 6.15. Found: C, 69.26; H, 6.30.

Oxidation of the methyl derivative VII by hypoiodite or by hypobromite gave iodoform (or carbon tetrabromide) and either unchanged VII or else only oily tars.

3 - Benzalacetyl - 6 - methoxy - 5,7,8 - trimethylcoumarin, (XXII).—To the methoxycoumarin VII (0.56 g.) and benzaldehyde (5 cc.) in methanol (30 cc.) was added dilute sodium hydroxide (5 cc.) and the mixture was refluxed for three hours. The product was obtained by acidifying with acetic acid (3%), diluting with water and cooling. Crystallized from methanol, it melted at 187–189° and weighed 0.28 g.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.83; H, 5.79. Found: C, 75.45; H, 6.12.

Treatment of the benzal derivative with chromic acid in acetic acid in the cold gave unchanged material as the only isolable product; when the reaction mixture was warmed, the substance was oxidized completely.

The oxime VIII resulted when the methoxycoumarin (VII) (0.2 g.) was warmed for ten minutes with hydroxylamine hydrochloride (0.5 g.), water (1.5 cc.), sodium hydroxide (1.5 cc., 10%) and methanol (5 cc.). Crystallized from toluene, it weighed 0.18 g., and formed white needles melting at 225–227° (dec.).

Anal. Calcd. for $C_{15}H_{17}O_4N$: C, 65.42; H, 6.23. Found: C, 65.34; H, 6.68.

Beckmann Rearrangement: 3-Acetylamino-6-methoxy-5,7,8-trimethylcoumarin, (X).—To a solution of the oxime VIII (0.175 g.) in dry pyridine (2 cc.) was added benzene sulfonyl chloride (2 cc.). A dark brown color developed at once. After standing at room temperature (26°) for three hours, the solution was poured into ice (5 g.) and hydrochloric acid (5 g.). The mixture was extracted with ether and the ether, as well as the suspended solid, washed with water. Both the ether and the water were filtered and the solids were combined and crystallized from methanol. A second crop was obtained by concentrating the ether solution. The product weighed 0.075 g., melted at 237–238°, and formed long white needles. The mixed melting point with the oxime VIII (m. p. 225–227°, dec.) was 190–195°.

Anal. Calcd. for $C_{15}H_{17}O_4N$: C, 65.42; H, 6.23. Found: C, 65.74; H, 6.60.

3 - Amino - 6 - methoxy - 5,7,8 - trimethylcoumarin, (XII).—The acetylaminocoumarin X (0.04 g.) was refluxed with hydrochloric acid (6 *N*, 15 cc.) for fifteen minutes. The cooled solution was neutralized with sodium carbonate and the precipitate taken up in ether. The ether was evaporated and the residue crystallized from aqueous methanol. The product weighed 0.02 g., and melted at 150–151°.

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.92; H, 6.49; N, 6.00. Found: C, 66.62; H, 6.70; N, 6.40.

Methylamide of 3-Carboxy-6-methoxy-5,7,8-trimethylcoumarin, (IX).—The methoxy acid[8] (p. 1706) (1 g.) was warmed with thionyl chloride (5 cc.) and the thionyl chloride was then removed under reduced pressure, leaving a pale yellow solid. This was dissolved in dry benzene (5 cc.) and methylamine was passed into the solution. The yellow color disappeared and a white solid precipitated. The solvent was evaporated and the product crystallized from dilute acetic acid. It weighed 0.85 g., and melted at 214–215°. The mixed melting point with X (m. p. 237–238°) was 205–207°.

Anal. Calcd. for $C_{15}H_{17}O_4N$: C, 65.42; H, 6.23. Found: C, 65.28; H, 6.23.

Attempts to Prepare the Aminocoumarin, XII.—A chloroform solution of hydrazoic acid was prepared[7] using technical sodium azide (0.15 g.) and sulfuric acid (0.6 cc.). This solution was added dropwise, with stirring, to a solution of the methoxy acid XI (0.56 g.) in sulfuric acid (5 cc.) at a temperature of 40°. No gas was liberated; after standing for thirty minutes the mixture was poured onto ice. The only product was unchanged acid XI.

The methoxy acid XI (0.5 g.) was refluxed for one hour with thionyl chloride (5 cc.) and the excess thionyl chloride then removed under reduced pressure. The acid chloride was taken up in dry benzene and stirred for two hours with activated sodium azide.[8] No gas was evolved. Hydrochloric acid (10 cc.) was then added and the mixture was refluxed for an hour. Evaporation of the solvents left an oily material from which no pure product could be isolated. Repetition of the experiment, heating the acid chloride with sodium azide at 50°, gave a small amount (0.12 g.) of white solid which could not be purified. It melted at about 210° with violent decomposition, and was unaffected by boiling with hydrochloric acid in acetone.

The methoxy acid XI (0.5 g.), sodium azide (1 g.) and sulfuric acid (5 cc.) were sealed in a Carius tube and heated at 150° for an hour. The material was recovered unchanged.

Hydrazide of 3-Carboxy-6-methoxy-5,7,8-trimethylcoumarin, (XIV).—To a suspension of the methoxy acid XI (0.5 g.) in alcohol (10 cc.) was added with shaking, a few drops of hydrazine hydrate solution (40%). The white solid, crystallized from alcohol, weighed 0.5 g. and melted at 184–185° with violent decomposition.

Anal. Calcd. for $C_{14}H_{16}O_4N_2$: C, 60.84; H, 5.84. Found: C, 60.48; H, 6.10.

The hydrazide (0.25 g.) in ether was stirred with a solution of sodium nitrite (0.5 g.) in water (10 cc.). To the mixture, at 5°, was added slowly hydrochloric acid (6 *N*, 2 cc.). No product, other than a small amount of unchanged hydrazide, could be isolated and the same result was obtained when the experiment was repeated substituting acetic acid for the ether.

Hydroxamic Acid of 3-Carboxy-6-methoxy-5,7,8-trimethylcoumarin, (XV).—The acid XI (0.25 g.) was suspended in alcohol and hydroxylamine hydrochloride (0.5 g.) was added. Sodium hydroxide (3%) was dropped in slowly and with shaking, until a faint alkaline reaction resulted. The solution was acidified with dilute acetic acid (5%), an equal volume of water was added and the mixture was allowed to stand for several hours. The product, crystallized from aqueous alcohol, was pale yellow, melted at 236–237° and weighed 0.15 g.

Anal. Calcd. for $C_{14}H_{15}O_5N$: C, 60.62; H, 5.46. Found: C, 60.39; H, 5.70.

The hydroxamic acid was recovered unchanged after boiling in acetone and acetic anhydride.

3 - Acetyl - 6 - hydroxy - 5,7,8 - trimethyl - 3,4 - dihydrocoumarin (XVI).—The coumarin II (0.5 g.) and a palladium catalyst (0.5 g.)[9] were suspended in alcohol (100 cc.) and the solution was subjected to the action of hydrogen under 45 pounds (3.0 atm.) pressure. Reduction was complete in forty-five minutes. The solution was decanted from the catalyst and diluted to three times its volume with water. The product, crystallized from petroleum ether–benzene, weighed 0.45 g. and formed white needles melting at 164–165°.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.71; H, 6.50. Found: C, 67.36; H, 6.85.

Methylation.—A solution of potassium hydroxide (5 g.) in methanol (25 cc.) was added dropwise to the boiling solution of the reduced coumarin XVI (0.2 g.) in methanol (10 cc.) and methyl sulfate (5 cc.). The reaction was stopped as soon as the red color remained permanent for about ten seconds. Most of the methanol was evaporated, water was added and the solution was extracted with ether. Evaporation of the ether left an oily solid which was digested with dilute ammonium hydroxide (3%) to remove excess methyl sulfate. The solid, crystallized from aqueous alcohol, weighed 0.05 g. and melted at 111–113°. It was identical (m. p. and mixed m. p.) with the product XIX obtained by reduction of VII.

Acetylation.—The dihydrocoumarin XVI (0.25 g.) was warmed for thirty minutes with acetic anhydride (5 cc.) and sulfuric acid (2 drops). The reaction mixture was poured into ice water and the product was crystallized from aqueous alcohol. It weighed 0.15 g., and melted at 123–125°. It was identical (m. p. and mixed m. p.) with the product XVIII obtained by reduction of the acetyl derivative IV.

The oxime XVII resulted when the hydrocoumarin XVI (0.2 g.) followed by sodium hydroxide (1 cc., 10%) was added to a suspension of hydroxylamine hydrochloride (0.5 g.) in alcohol (10 cc.). After warming on the water-bath the solution was filtered and the filtrate concentrated to half its volume. Water (10 cc.) was added and the solution was cooled. The product (0.2 g.) crystallized from aqueous alcohol, formed long white needles melting at 179–180° (dec.).

Anal. Calcd. for $C_{14}H_{17}O_4N$: C, 63.85; H, 6.51. Found: C, 63.47; H, 6.81.

3 - Acetyl - 6 - methoxy - 5,7,8 - trimethyl - 3,4 - dihydrocoumarin, (XIX).—Catalytic reduction of the methoxycoumarin VII (0.5 g.) by the method described above gave 0.5 g. of the dihydro compound XIX. Crystallized from aqueous alcohol, the substance melted at 112–113.5°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.67; H, 6.92. Found: C, 68.39; H, 7.23.

The oxime XX, prepared in the same manner as XVII, crystallized from aqueous methanol in colorless needles melting at 156–157° (dec.).

3 - Acetyl - 6 - acetoxy - 5,7,8 - trimethyl - 3,4 - dihydrocoumarin, (XVIII).—Catalytic reduction of the acetyl derivative IV (0.25 g.) in ethanol (75 cc.) by the method described above gave 0.24 g. of the dihydro compound XVIII. Crystallized from aqueous alcohol, it melted at 124–125°.

Anal. Calcd. for $C_{16}H_{18}O_5$: C, 66.17; H, 6.25. Found: C, 65.93; H, 6.25.

Summary

1. Sodium acetoacetic ester has been added to duroquinone. The reaction follows the same course as that of the reaction between this quinone and malonic ester, and involves one of the methyl groups of the quinone.

2. The product is a methylated 3-acetyl-6-hydroxycoumarin; no evidence of any naphthoquinone derivative was obtained. The structure of the coumarin was proved by an independent synthesis.

3. Several reactions of the coumarin and its derivatives were investigated, particularly the Beckmann rearrangement of the oxime of the methoxycoumarin, which led to an aminocoumarin, indicating that the hydroxyl group was *anti* to the coumarin ring in this oxime.

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(9) Busch and Stöve, *Ber.*, **49**, 1064 (1916).