[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, M. R. SCIENCE INSTITUTE, GUJARAT COLLEGE]

Studies in Chalcones and Related Compounds Derived from 2-Hydroxy-5-acetaminoacetophenone: Part I. Synthesis of 2-Hydroxy-5'-acetaminochalcones and 6-Aminoflavanones

A. A. RAVAL AND N. M. SHAH*

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The condensation of 2-hydroxy-5-acetaminoacetophenone with various aldehydes has been studied and various acetamino chalcones have been obtained. Deacetylation of the above chalcones was attempted so as to get aminochalcones; it was found that they were converted into the corresponding 6-aminoflavanones, except in the cases of 2',3-dihydroxy-5'-acetaminochalcone and 2',4-dihydroxy-5'-acetamino-3-carboxychalcone; in the former case, 2',3-dihydroxy-5'-aminochalcone was obtained; in the latter case the original acetaminochalcone was recovered unchanged.

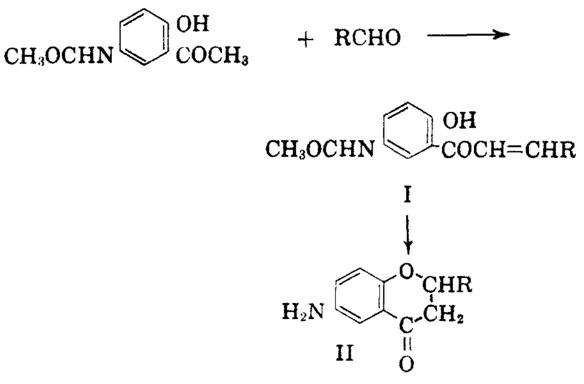
The reactivity of some of the chalcones has been investigated with bromine, ethyl acetoacetate, and phenylhydrazine; the corresponding dibromides, cyclohexenone derivatives, and pyrazoline derivatives were obtained.

A considerable amount of work has been done on chalcones containing hydroxy and methoxy groups. But very little work has been reported on the chalcones derived from amino ketones. To avoid complications due to the free amino group, Kunckell and co-workers[1] condensed 2-hydroxy-5-acetaminoacetophenone with benzaldehyde and salicylaldehyde and reported the formation of 2'-hydroxy-5'-acetaminochalcone (m.p. 190°) and 2',2-dihydroxy-5'-acetaminochalcone (m.p. 134°) respectively: while Scholtz and Huber[2] condensed *p*-aminoacetophenone directly and obtained benzylidene aminochalcones. Recently Marrian, Russell, and Todd[3] reported the synthesis of 4,4'-diaminochalcone with a view to studying its bacteriostatic action. The present work was undertaken with a view to exploring the probability of synthesizing amino chalcones and studying the effect of acetamino group on the chalcone formation.

On carrying out the condensation of 2-hydroxy-5-acetaminoacetophenone with benzaldehyde, 2'-hydroxy-5'-acetaminochalcone was obtained, identical with that of Kunckell and co-workers.[1] But in the case of the chalcone obtained by similar condensation with salicylaldehyde, the product obtained melted at 158°, and not at 134° as stated by them.[1] On repeating the condensation with phosphorus oxychloride as the condensing agent,[4] two substances, m.p. 158° and m.p. 134°, were isolated. The product, m.p. 134°, is insoluble in dilute sodium hydroxide, does not give a color with alcoholic ferric chloride and gives negative results with Wilson's boric acid reagent; it also was found to be soluble in diltute hydrochloric acid. Hence it was inferred to be 6-amino-2'-hydroxyflavanone [II, R = $-C_6H_4(OH)$-*o*], confirmed by a mixture melting point with an authentic sample. It is thus clear that the chalcone structure assigned by Kunckell and co-workers to the product melting at 134° is erroneous. The product, m.p. 158°, has been found to be a chalcone [I, R = $-C_6H_4(OH)$-*o*] as it responds to all the tests characteristic of a chalcone and gives on cyclization the flavanone, m.p. 134°.

2-Hydroxy-5-acetaminoacetophenone then was condensed with (1) anisaldehyde, (2) piperonal, (3) *m*-hydroxybenzaldehyde, and (4) 5-aldehydosalicylic acid. In the first three cases, the chalcones were obtained in good yields with 20 per cent alcoholic potassium hydroxide as the condensing agent. Increase in the strength of alkali decreased the yields of the chalcones in all the three cases. In the last case, the chalcone was obtained in good yield when hydrogen chloride gas in dry ethyl acetate was used as the condensing agent.

All the chalcones were subjected to ring closure with alcoholic hydrochloric acid or sulfuric acid or both, the corresponding 6-aminoflavanones being obtained, except in the case of the last two chalcones.



R = $-C_6H_5$; $-C_6H_4(OH)$—*o*;
$-C_6H_4(OMe)$—*p*;
$-C_6H_3(CH_2O_2)$—*3,4*;
$-C_6H_4(OH)$—*m*; $-C_6H_3(OH)(COOH)$—*o*.

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* Present address: Department of Chemistry, St. Xavier's College, Ahmedabad 6, India.

(1) Kunckell and co-workers, *Ber.*, **37**, 2826 (1904); **46**, 2678 (1913).

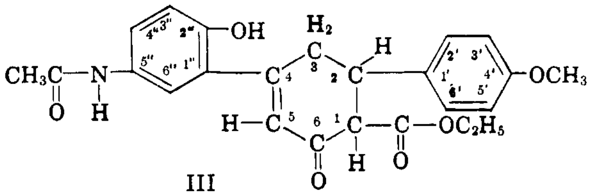
(2) Scholtz and Huber, *Ber.*, **37**, 390 (1904).

(3) Marrian, Russell, and Todd, *J. Chem. Soc.*, 1419 (1947).

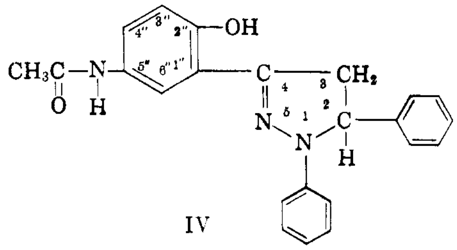
(4) Vyas and Shah, *Current Science* (*India*), **18**, 134 (1949).

On submitting the above chalcones to deacetylation with a view to prepare the corresponding amino chalcones, it was found that deacetylation was accompanied by ring closure, 6-aminoflavanones being obtained. However in the case of 2′,3-dihydroxy-5′-acetaminochalcone only deacetylation took place, 2′,3-dihydroxy-5′-aminochalcone being obtained.

The above chalcones on treatment with bromine gave the dibromides which were debrominated with KI in acetone; and some of them on treatment with ethyl acetoacetate and phenylhydrazine yielded the corresponding cyclohexenone derivatives (III) and pyrazoline derivatives (IV).



III



IV

EXPERIMENTAL

2-Hydroxy-5-acetaminoacetophenone required for this investigation was prepared by Fries rearrangement of *p*-aminophenol diacetate.[5]

2-Hydroxy-5-aminoacetophenone hydrochloride, which separated as a silvery-white solid, crystallized from ethanol in colorless shining plates, m.p. 231°. Kunckell[6] reports m.p. 155°.

Anal. Calc'd for $C_8H_9NO_2{\cdot}HCl$: C, 51.2; H. 5.3; Neut. equiv., 187.5. Found: C, 51.0; H, 5.4; Neut. equiv., 189.8 (Ag salt method).

The above hydrochloride, on treatment with ammonia, gave the keto-base; it crystallized from dilute ethanol as reddish-brown plates, m.p. 118°. Kunckell[6] records a melting point of 110° for it.

Anal. Calc'd for $C_8H_9NO_2$: N, 9.27. Found: N, 9.00.

Further, the hydrochloride was diazotized and the aqueous solution was heated slowly, when nitrogen was given off and quinacetophenone was obtained.

2′-Hydroxy-5′-acetaminochalcone. To a hot solution of 2-hydroxy-5-acetaminoacetophenone (2 g., 1 mole) and benzaldehyde (1 g., 1 mole) in ethanol (25 ml.), a sodium or potassium hydroxide solution (30%, 25 ml.) was added gradually with shaking. The reaction mixture was shaken for 10–15 minutes and then was diluted with ice-cold acidulated water. An orange solid separated; it was collected, washed with sodium bicarbonate solution, and then with water: it crystallized from ethanol as saffron-colored needles. m.p. 190°. Yield, 1.2 g. Kunckell and co-workers[1] report the same melting point.

Anal. Calc'd for $C_{17}H_{15}NO_3$: C, 72.59; H, 5.33; N, 4.98. Found: C, 72.38; H, 5.12; N, 4.70.

If the condensation is left overnight, the yield of chalcone decreases considerably.

The *acetoxy* derivative, prepared by the sodium acetate-acetic anhydride method, crystallized from ethanol as colorless shining needles, m.p. 147°. Kunckell and co-workers[1] give the same melting point.

6-Aminoflavanone hydrochloride. To a solution of 2′-hydroxy-5′-acetaminochalcone (0.5 g.) in ethanol (20 ml.), dilute hydrochloric acid (10%, 20 ml.) was slowly added until a slight turbidity was formed, which was dissolved by adding more ethanol (20 ml.) and the clear solution was refluxed on water-bath for 24 hours. On removal of the ethanol, the remaining solution on cooling deposited a pale yellow solid, which crystallized from hot water in pale yellow needles, m.p. 206°. Yield, 0.2 g.

Anal. Calc'd for $C_{15}H_{13}NO_2{\cdot}HCl$: C, 65.3; H, 5.1; Neut. equiv., 275.5. Found: C, 65.2; H, 5.0; Neut. equiv., 276.9 (Ag salt method).

6-Aminoflavanone sulphate. The chalcone (0.2 g.) in ethanol (15 ml.) was treated with dilute sulfuric acid (10%, 12.5 ml.) as above, and then was refluxed on the water-bath for six hours. On removal of the ethanol, a pale yellow solid separated; it crystallized from hot water as pale yellow needles, m.p. 200°.

Anal. Calc'd for $C_{15}H_{13}NO_2{\cdot}{}^1/_2H_2SO_4$: Neut. equiv., 289.0. Found: Neut. equiv., 291.0 (Ba salt method).

6-Aminoflavanone. An aqueous solution of 6-aminoflavanone hydrochloride or sulfate, on treatment with ammonia, gave a dark-brown solid; it was collected, washed and then crystallized from ethanol as yellowish-red plates, m.p. 141–142°.

Anal. Calc'd for $C_{15}H_{13}NO_2$: N, 5.85. Found: N, 5.46.

It is soluble in ethanol, acetic acid, chloroform, and acetone. It is insoluble in dilute alkali, but soluble in dilute mineral acids. It gives neither an alcoholic ferric chloride nor a Wilson's boric acid color tests.

2′-Hydroxy-5′-acetaminochalcone dibromide. To an ice-cold solution of 2′-hydroxy-5′-acetaminochalcone (0.5 g., 1 mole) in chloroform (40 ml.), bromine in the same solvent (50%; 0.6 ml., 1.1 moles) was added gradually with constant stirring. The reaction mixture then was kept in an ice-bath for four hours. On removal of chloroform, a deep yellow solid was obtained; it was washed with sodium thiosulfate solution and was crystallized from ethanol as yellowish-brown needles, m.p. 170° (decomp.). Yield, 0.2 g.

Anal. Calc'd for $C_{17}H_{15}Br_2NO_3$: Br, 36.28. Found: Br, 36.16.

On refluxing it with KI in acetone solution, it gave 2′-hydroxy-5′-acetaminochalcone, m.p. and mixture m.p. 190°.

4-(2″-Hydroxy-5″-acetaminophenyl)-1,2-diphenyl-Δ^4-pyrazoline (IV). Phenylhydrazine (0.5 ml.) was added to 2′-hydroxy-5′-acetaminochalcone (0.5 g.) in acetic acid (15 ml.) and the mixture was heated on wire gauze for ten minutes. It then was diluted with ice-cold acidulated water. The solid was collected, washed with water, and crystallized from ethanol as pale yellow plates, m.p. 225°. Yield, 0.2 g.

Anal. Calc'd for $C_{23}H_{21}N_3O_2$: N, 11.32. Found: N, 10.91.

It gives green coloration with bromine vapor and also gives Knorr's pyrazoline test.

2′,2-Dihydroxy-5′-acetaminochalcone. (i). 2-Hydroxy-5-acetaminoacetophenone (2 g., 1 mole) and salicylaldehyde (1.3 g., 1 mole) in ethanol (25 ml.) were treated with potassium hydroxide solution (30%, 25 ml.) gradually with shaking. The clear solution was refluxed on water-bath for 30 minutes and then was kept at room temperature for 24 hours. On working up as before, a yellowish-brown solid separated, which was washed with hot water and crystallized from ethyl acetate as yellow plates, m.p. 158°. Yield, 0.5 g. Kunckell and co-workers[1] have recorded the melting point 134°.

Anal. Calc'd for $C_{17}H_{15}NO_4$: N, 4.71. Found: N, 4.45.

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[5] Julia and Baillarge, *Bull. soc. chim. France*, 639 (1952); *Chem. Abstr.*, 47, 3815 (1953).

[6] Kunckell, *Ber.*, 34, 125 (1901).

It is soluble in ethanol, ethyl acetate, acetic acid, chloroform, acetone, and benzene. It dissolves with an orange color in caustic alkali and with a deep red color in concentrated sulfuric acid. It is insoluble in dilute hydrochloric acid. It gives positive color test with alcoholic ferric chloride as well as with Wilson's boric acid reagent.

(ii). 2-Hydroxy-5-acetaminoacetophenone (2 g., 1 mole), salicylaldehyde (1.3 g., 1 mole), and phosphorus oxychloride (0.5 ml.) were mixed and heated on water-bath for five minutes, when the mixture became pasty homogeneous mass. It was left overnight at room temperature and then was treated with an ice-cold saturated solution of sodium bicarbonate (25 ml.). The solid that separated was dissolved in dilute sodium hydroxide solution (5%, 25 ml.) and the solution was filtered. A part that remained as an insoluble residue was crystallized from ethanol as yellowish needles, m.p. 134° (Yield, 0.2 g.) identical with 6-amino-2'-hydroxyflavanone which is described later.

The filtrate, on acidification with cold hydrochloric acid gave the chalcone; it crystallized from ethyl acetate as yellow plates, m.p. and mixture m.p. 158°. Yield, 0.5 g.

(iii). Dry hydrogen chloride gas was passed through an ice-cold solution of 2-hydroxy-5-acetaminoacetophenone (2.0 g., 1 mole) and salicylaldehyde (1.3 g., 1 mole) in ethyl acetate (25 ml.) at 0–5° for 24 hours. On removal of ethyl acetate, a brown solid separated, which, on crystallization from ethyl acetate, gave yellow plates, m.p. 158° (Yield, 1.5 g.); a mixture m.p. with the chalcone obtained alone was undepressed.

The *benzoyl* derivative crystallized from ethanol as pale brown needles, m.p. 155°.

Anal. Calc'd for $C_{31}H_{23}NO_6$: N, 2.77. Found: N, 2.48.

6-Amino-2'-hydroxyflavanone. The chalcone (0.5 g.) in ethanol (25 ml.) was treated with dilute HCl (10%, 15 ml.) as before, and was refluxed on water-bath for 24 hours. On working up as before, the hydrochloride did not separate. The clear solution therefore was treated with ammonia. The solid was collected, washed, and crystallized from ethanol as yellowish needles, m.p. 134°. Yield, 0.2 g.

Anal. Calc'd for $C_{15}H_{13}NO_3$: N, 5.49. Found: N, 5.05.

The chalcone was similarly treated with dilute H_2SO_4. The soluble sulfate did not separate. It was therefore basified: the flavanone crystallized from ethanol as yellowish needles, m.p. 134°, the mixture melting point with the flavanone described above remaining undepressed.

2'-Hydroxyacetamino-4-methoxychalcone. To a cold solution of 2-hydroxy-5-acetaminoacetophenone (2 g., 1 mole) and anisaldehyde (1.5 g., 1 mole) in ethanol (25 ml.), a potassium hydroxide solution (20%, 25 ml.) was added gradually with shaking and the whole was kept at room temperature for 24 hours. On decomposing as before, an orange solid separated; it was washed with sodium bicarbonate solution (or with hot water) and was crystallized from ethyl acetate as brownish-yellow needles, m.p. 172–173°. Yield, 1.1 g.

Anal. Calc'd for $C_{18}H_{17}NO_4$: C, 69.45; H, 5.46; N, 4.50. Found: C, 69.17; H, 5.20; N, 4.35.

It gives all the characteristic tests of a chalcone. It is soluble in ethanol, ethyl acetate, acetic acid, acetone, and nitrobenzene and less soluble in chloroform, benzene, and petroleum ether.

The *benzoyl* derivative, prepared by the benzoyl chloride-pyridine method, crystallized from acetic acid as white needles, m.p. 191°.

Anal. Calc'd for $C_{25}H_{21}NO_5$: N, 3.37. Found: N, 3.03.

6-Amino-4'-methoxyflavanone hydrochloride. An ethanolic solution of 2'-hydroxy-5'-acetamino-4-methoxychalcone (0.5 g.) was treated with dilute hydrochloric acid (10%, 15 ml.) as before and was refluxed on a water-bath for 24 hours. On removal of ethanol, a brown solid separated; it was crystallized from water as pale yellow needles, m.p. 202°. Yield, 0.2 g.

Anal. Calc'd for $C_{16}H_{15}NO_3 \cdot HCl$: Neut. equiv., 305.5. Found: Neut. equiv., 308.2 (Ag salt method).

6-Amino-4'-methoxyflavanone sulfate was similarly obtained, using dilute sulfuric acid (10%, 12.5 ml.). A light yellow solid was obtained which crystallized from hot water as pale yellow needles, m.p. 198°.

Anal. Calc'd for $C_{16}H_{15}NO_3 \cdot {}^1/_2H_2SO_4$: Neut. equiv., 319.0. Found: Neut. equiv., 314.1. (Ba salt method).

6-Amino-4'-methoxyflavanone. An aqueous solution of 6-amino-4'-methoxyflavanone hydrochloride or sulfate, on treatment with ammonia, yielded a brown solid. It was washed with water and was crystallized from ethanol as light orange needles, m.p. 149°.

Anal. Calc'd for $C_{16}H_{15}NO_3$: N, 5.20. Found: N, 4.85.

It is soluble in ethanol, acetic acid, chloroform, and acetone. It is insoluble in dilute alkali, but is soluble in dilute mineral acids. It gives neither alcoholic ferric chloride nor Wilson's boric acid color test.

2'-Hydroxy-5'-acetamino-4-methoxychalcone dibromide. 2'-Hydroxy-5'-acetamino-4-methoxychalcone (0.5 g., 1 mole) in acetic acid (20 ml.) was treated with bromine in acetic acid (50%; 0.5 ml., 1.1 moles) and left for four hours at room temperature. On diluting with cold water, a yellow solid separated; it crystallized from ethanol as small yellow needles, m.p. 160° (decomp.). Yield, 0.25 g.

Anal. Calc'd for $C_{18}H_{17}Br_2NO_4$: Br, 33.97. Found: Br, 33.67.

On refluxing with KI in acetone solution, it yields 2'-hydroxy-5'-acetamino-4-methoxychalcone, m.p. and mixture m.p. 172–173°.

Ethyl 2-(4'-methoxyphenyl)-4-(2''-hydroxy-5''-acetaminophenyl)-Δ^4-cyclohexene-6-one-1-carboxylate (III). 2'-Hydroxy-5'-acetamino-4-methoxychalcone (0.5 g.) was added to a solution of sodium (0.2 g.) in ethanol (10 ml.), followed by ethyl acetoacetate (0.5 g.) and more ethanol (25 ml.). It was refluxed on a water-bath at 90° for 3 hours and then was diluted with ice-cold acidulated water, when a pale yellow solid separated. This solid was crystallized from an acetone-chloroform mixture as yellow plates, m.p. 160° Yield, 0.15 g.

Anal. Calc'd for $C_{24}H_{25}NO_6$: C, 68.1: H, 5.9; N, 3.31. Found: C, 67.9; H, 6.0; N, 2.92.

It is soluble in ethanol, acetic acid, and acetone, but less soluble in chloroform and petroleum ether.

2'-Hydroxy-5'-acetamino-3,4-methylenedioxychalcone. To a cold solution of 2-hydroxy-5-acetaminoacetophenone (2 g., 1 mole) and piperonal (1.6 g., 1 mole) in ethanol (25 ml.), potassium hydroxide solution (20%, 25 ml.) was added gradually with shaking, and then the whole kept at room temperature for 24 hours. On working up as before, an orange solid separated; it was collected, washed, and crystallized from ethanol as brown needles, m.p. 197–198°. Yield, 1.2 g.

Anal. Calc'd for $C_{18}H_{15}NO_5$: N, 4.30. Found: N, 4.04.

It is soluble in ethanol, ethyl acetate, acetic acid, chloroform, and acetone, and less soluble in benzene. It dissolves in dilute alkali with an orange-red color, but is insoluble in dilute mineral acids. It gives positive color test with an alcoholic ferric chloride and Wilson's boric acid reagent.

The *benzoyl* derivative, prepared by the benzoyl chloride-pyridine method, crystallized from acetic acid as brownish-yellow needles, m.p. 183°.

Anal. Calc'd for $C_{25}H_{19}NO_6$: N, 3.26. Found: N, 2.98.

6-Amino-3',4'-methylenedioxyflavanone hydrochloride. 2'-Hydroxy-5'-acetamino-3,4-methylenedioxychalcone (0.5 g.) in ethanol (25 ml.) was treated with dilute hydrochloric acid (10%, 15 ml.) as before, and was refluxed on the water-bath for 24 hours. On removal of alcohol, the remaining solution deposited a pale yellow solid on cooling; it crystallized from water as pale yellow needles, m.p. 205°. Yield, 0.20 g.

Anal. Calc'd for $C_{16}H_{13}NO_4 \cdot HCl$: Neut. equiv., 319.5. Found: Neut. equiv., 323.8 (Ag salt method).

6-Amino-3',4'-methylenedioxyflavanone sulfate was similarly prepared using dilute sulfuric acid (10%, 12.5 ml.).

The product crystallized from hot water as light yellowish needles, m.p. 196°.

Anal. Calc'd for $C_{16}H_{13}NO_4{}^1/_2\cdot H_2SO_4$: Neut. equiv., 333.0. Found: Neut. equiv., 335.4 (Ba salt method).

6-Amino-3′,4′-methylenedioxyflavanone. An aqueous solution of 6-amino-3′,4′-methylenedioxyflavanone hydrochloride or sulfate was treated with ammonia and the product was crystallized from ethanol as pale orange needles, m.p. 170°.

Anal. Calc'd for $C_{16}H_{13}NO_4$: N, 4.94. Found: N, 4.50.

It is soluble in ethanol, acetic acid, and chloroform. It is insoluble in dilute alkali, but dissolves readily in dilute mineral acids. It gives neither an alcoholic ferric chloride color test nor a Wilson's boric acid test.

2′-Hydroxy-5′-acetamino-3,4-methylenedioxychalcone dibromide. The chalcone (0.5 g., 1 mole) in chloroform (75 ml.) was treated with bromine in chloroform (50%; 0.6 ml., 1.1 moles) as before and then was left in an ice-bath for four hours. On working up as before, the product which was obtained was crystallized from ethanol as brown needles, m.p. 210°. Yield, 0.12 g.

Anal. Calc'd for $C_{18}H_{15}Br_2NO_5$: Br, 32.99. Found: Br, 32.64.

On treatment with KI in acetone solution, it gave 2′-hydroxy-5′-acetamino-3,4-methylenedioxychalcone, m.p. and mixture m.p. 197–198°.

2′,3-Dihydroxy-5′-acetaminochalcone. To a cold solution of 2-hydroxy-5-acetaminoacetophenone (2 g., 1 mole) and *m*-hydroxybenzaldehyde (1.3 g., 1 mole) in ethanol (25 ml.) a potassium hydroxide solution (20%, 25 ml.) was added with shaking. The red solution was kept at room temperature for 24 hours. On working up as before, the orange solid that separated was washed with hot water and was crystallized from ethanol as orange needles, m.p. 210°. Yield, 1.1 g.

Anal. Calc'd for $C_{17}H_{15}NO_4$: N, 4.71. Found: N, 4.34.

It is soluble in dilute alkali with a red color. It gives an alcoholic ferric chloride as well as a Wilson's boric acid color test. It is soluble in ethanol, acetic acid, ethyl acetate, chloroform, and acetone.

The *benzoyl* derivative, prepared by the Schotten-Bauman method, crystallized from dilute acetic acid as small colorless granules, m.p. 195°.

Anal. Calc'd for $C_{31}H_{23}NO_6$: N, 2.77. Found: N, 2.50.

2′,3-Dihydroxy-5′-aminochalcone. The ethanolic solution of the above chalcone (0.5 g. in 20 ml.) was treated with dilute hydrochloric acid (10%, 20 ml.) or dilute sulfuric acid (5%, 12 ml.) as before. On removal of ethanol, the residue on treatment with ammonia, gave a brown solid. It crystallized from ethanol, as reddish-brown needles, m.p. 135°. Yield, 0.25 g.

Anal. Calc'd for $C_{15}H_{13}NO_3$: N, 5.49. Found: N, 5.00.

It is soluble in ethanol, ethyl acetate, acetic acid, chloroform, and acetone. It is soluble in dilute alkali with a deep red color. It also dissolves in dilute mineral acids. It gives an alcoholic ferric chloride as well as a Wilson's boric acid color test.

The *dibromide* of the acetamino-chalcone (0.5 g. in 15 ml. of acetic acid) was prepared by treating it with bromine in acetic acid (50%; 0.6 ml., 1.1 moles) as before. On working up as before, the product obtained was crystallized from dilute acetic acid as yellow granules, m.p. 155°. Yield, 0.2 g.

Anal. Calc'd for $C_{17}H_{15}Br_2NO_4$: Br, 35.01. Found: Br, 34.51.

It is soluble in ethanol, ethyl acetate, acetic acid, chloroform, and acetone. On debromination with KI in acetone solution, it yielded 2′,3-dihydroxy-5′-acetaminochalcone, m.p. and mixture m.p. 210°.

Ethyl 2-(3′-hydroxyphenyl)-4-(2″-hydroxy-5″-acetaminophenyl)-Δ⁴-cyclohexene-6-one-1-carboxylate. The chalcone (0.5 g.) was added to a solution of sodium (0.2 g.) in ethanol (10 ml.), followed by ethyl acetoacetate (1.5 ml.). Then more alcohol (10 ml.) was added and the mixture was refluxed on a water-bath at 90° for four hours. On dilution and acidification in the cold a pale yellow solid separated. This was crystallized from dilute acetic acid as pale yellow needles, m.p. 150° (decomp.).

Anal. Calc'd for $C_{23}H_{23}NO_6$: N, 3.42. Found: N, 3.03.

It is soluble in ethanol, acetic acid, ethyl acetate, and acetone. It is also soluble in dilute alkali but insoluble in dilute mineral acids.

2′,4-Dihydroxy-5′-acetamino-3-carboxychalcone. Dry hydrogen chloride gas was passed through a solution of 2-hydroxy-5-acetaminoacetophenone (2 g., 1 mole) and 5-aldehydosalicylic acid (0.85 g., 1 mole) in dry ethyl acetate (25 ml.) kept in ice-bath for 24 hours. On removal of the solvent, the orange crystals which were obtained were recrystallized from ethyl acetate to give orange plates, m.p. 155°. Yield, 1.1 g.

Anal. Calc'd for $C_{18}H_{15}NO_6$: N, 4.10. Found: N, 3.77.

The chalcone is soluble in ethanol, ethyl acetate, acetic acid, chloroform, acetone, and benzene. It dissolves in dilute alkali with an orange color, but is insoluble in dilute mineral acids. It gives orange color with conc'd H_2SO_4 and a deep red-brown color with alcoholic ferric chloride.

The *dibenzoyl* derivative, prepared by the benzoyl chloride-pyridine method, crystallized from alcohol as colorless plates, m.p. 150°.

Anal. Calc'd for $C_{32}H_{23}NO_8$: N, 2.55. Found: N, 2.26.

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