was poured into a dilute solution of ammonium hydroxide and allowed to stand. The crude solid was purified by further treatment with ammonium hydroxide and with decolorizing charcoal, and recrystallized from ligroin; m. p. 50–52°[4]; yield, 18.2 g.

α^2-Isodurylamine Hydrochloride

A. From Mesitonitrile.—A mixture of 10 g. of the nitrile, 130 cc. of absolute alcohol and 2 g. of Raney nickel was treated with hydrogen for about two hours at 150° and 2200 lb. pressure. After removal of the catalyst by filtration the solution was concentrated to a small volume and hydrochloric acid added. The amine hydrochloride crystallized from water in the form of long, white needles melting at 315°, with decomposition. The yield was nearly quantitative.

Anal. Calcd. for $C_{10}H_{16}NCl$: N, 7.54; Cl, 19.12. Found: N, 7.47; Cl, 19.21.

B. From Potassium Phthalimide and α^2-Chloroisodurene.—A mixture of 20 g. of the chloride and 33 g. of the potassium salt was heated for four hours at 170–180°. The solid product was digested with dilute sodium hydroxide, collected on a filter and washed with water until the wash water was no longer basic to litmus. The N-α^2-isodurylphthalimide was crystallized from glacial acetic acid and then from alcohol. It formed small white needles melting at 209.5–210°. The yield of once recrystallized material was 21 g.

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.14; N, 5.02. Found: C, 77.56; H, 6.41; N, 5.06.

Hydrolysis.—A mixture of 7.0 g. of N-α^2-isodurylphthalimide, 50 cc. of hydrobromic acid (sp. gr., 1.36), 40 cc. of glacial acetic acid and 10 cc. of acetic anhydride was heated under reflux for sixteen hours. The solid from the reaction mixture was collected on a filter and the filtrate was evaporated to a small volume. The solid which formed in the latter was combined with the main product and the resulting mixture was thoroughly washed with warm water. The solid residue was discarded and the aqueous solution was evaporated to a small volume. The α^2-isodurylamine hydrobromide separated from the aqueous solution in white needles; yield, 2.8 g. Benzoylation of this solid gave a compound causing no depression in the melting point of an authentic sample of N-α^2-isodurylbenzamide.

Summary

An attempt to prepare mesitaldehyde from α^2-chloroisodurene and hexamethylenetetramine by the method of Sommelet led to anomalous results. The product has been shown to be N,N′-di-α^2-isodurylmethanediamine ($C_9H_{11}CH_2NHCH_2NHCH_2C_9H_{11}$).

URBANA, ILLINOIS RECEIVED DECEMBER 13, 1940

---

[4] Küster and Stallberg, *Ann.*, **278**, 207 (1893).

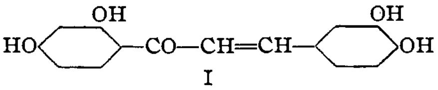
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Anthochlor Pigments. The Pigment of *Coreopsis Douglasii*

BY T. A. GEISSMAN

Certain yellow flowers, notably in the *Compositae*, are characterized by the fact that upon treatment with alkali (for example, by exposure to ammonia vapor) they turn red. The majority of yellow flowers are pigmented by carotenoids or flavone derivatives or mixtures of these[1] and give color changes with alkali which are generally no more than a deepening of the normal shade of yellow. The color change to red is characteristic of a class of pigments which has been termed "anthochlor"[1] and whose existence in a number of species of *Compositae* has been demonstrated by Gertz.[2] While information concerning the chemical constitution of the anthochlor pigments would be of great interest in connection with studies on the phytosynthetic and genetic relationships between the coloring matters of flowers, very little is known about them.

The yellow *Dahlia variabilis* is among the species shown by Gertz to contain anthochlor. Recently Price,[3] following the work of Schmid and his collaborators[4] who isolated apigenin from this flower, has shown that *Dahlia* contains the chalcone butein (I), possibly as a glycoside.[5]



I

Butein was first obtained by Perkin and Hummel[6] in the course of isolating butin (the isomeric flavanone) from the flowers of *Butea frondosa.*

---

[1] Klein, *Sitzb. Akad. Wiss., Wien*, **129**, 341 (1920); **130**, 247 (1921).

[2] Gertz, *Kgl. Physiograf. Sällskap. Lund, Förh.*, **8**, 62, 71, 215 (1938); *C. A.*, **34**, 473 (1940).

[3] Price, *J. Chem. Soc.*, 1018 (1939).

[4] Schmid and Waschkan, *Monatsh.*, **49**, 83 (1928); Schmid and Seebald, *ibid.*, **60**, 32 (1932); Schmid and Hacheck, *ibid.*, **62**, 317 (1932).

[5] Klein ("Handbuch der Pflanzenanalyse," Julius Springer, Vienna, 1932, Bd. III/2; p. 858) designates apigenin as the anthochlor of *Dahlia*. Since apigenin is a typical flavone which in the free or glycosidic condition gives only yellow salts with alkalies and since butein gives a deep red coloration with alkalies such as is shown by the flowers themselves, it is clear that butein is the true anthochlor, as this term is used.

[6] A. G. Perkin and Hummel, *J. Chem. Soc.*, **85**, 1459 (1904).

Price has suggested[3] that the butein may have arisen from the isomerization of the butin in the isolation process, since it is reported[6] on the basis of dyeing experiments that butein probably does not occur as such in the flowers of *Butea frondosa.* An alternative suggestion is that butein may be present in this flower in glycosidic combination, in which case the fresh blossoms would probably give a red coloration on treatment with alkali, a reaction not shown by butin.[6] Perkin and Hummel do not state, however, that this test was performed and consequently Price's suggestion and his statement that *Dahlia* is the first example of the occurrence of butein in nature cannot be accepted.

Butein has now been found to be present in *Coreopsis Douglasii,* a golden-yellow composite found in Southern California. The identity of the pigment was established by comparison of its properties and those of its tetraacetate with those of the synthetic compounds. Butein is accompanied in the flower by a carotenoid pigment which was not identified but which is assumed to be largely carotene on the basis of its distribution between ligroin and 90% methyl alcohol (before and after treatment with alcoholic alkali) and its bright blue color reaction with concentrated sulfuric acid.

The possibility that *C. Douglasii* contains no butein but butin, which was isomerized in the process of isolation, can be discarded on several grounds. The flowers instantly give a brilliant red color on treatment with cold, dilute alkali, and at no point in the process of isolation was the butein treated with strong or hot alkaline solutions nor allowed to remain in alkaline solution longer than was necessary. Although Perkin and Hummel[6] reported that butin dissolves in cold alkali to give a pale orange-red solution (which darkens on heating) it seems probable that this coloration was due to the presence of some butein present as an impurity in their sample of butin. This conclusion is based upon the experience gained in this Laboratory on the behavior of other closely related flavanones toward alkali. For example, eriodictyol dissolves in cold, dilute alkali to give a colorless solution which upon heating acquires a deep red color qualitatively indistinguishable from that of alkaline solutions of butein. The color thus appears to be a property of the salt of the chalcone and the fact that the fresh flowers of the anthochlor-pigmented species give immediate, intense colorations with dilute alkali points strongly to the probability that they contain the free polyhydroxychalcones or these pigments combined with sugars by some linkage which does not prevent the highly colored anion from being formed readily.

The method used in the isolation of butein from *Coreopsis Douglasii* was such as to indicate that at least some of the pigment occurs as the free (nonglycosidic) substance in this plant. There is no doubt, however, that only a portion of the total content occurs in this form since aqueous extracts of the ether-extracted flowers contained copious amounts of a substance giving an intense red coloration with alkali.

In confirmation of Klein's[1] observation that anthochlor occurs not only in the flowers but in other parts of the plant, qualitative tests on *C. Douglasii* showed that the leaves and stems contain a substance which turns red on exposure to ammonia vapor.

It is probable that the anthochlor pigments are all polyhydroxychalcones, possibly containing the 2,4-dihydroxybenzoyl nucleus in all cases. Shinoda and Sato[7] have pointed out that chalcones containing the 2,4,6-trihydroxybenzoyl nucleus isomerize readily to the corresponding flavanones while those containing the 2,4-dihydroxybenzoyl grouping are relatively more stable in the chalcone form. The widespread occurrence in nature of flavanones containing the phloroglucinol nucleus supports this view. That all the anthochlor pigments are not butein is indicated by recent results obtained in this Laboratory on the pigment of *Coreopsis grandiflora,* which is probably a pentahydroxychalcone. The identity of this pigment is still uncertain, however, and will be reported on in a later communication.

Experimental

Isolation.—The flowers were collected on the Mojave desert near Mojave, California. The rays were separated from the disk florets, dried (15 g.) and examined separately. No crystalline material could be obtained from this portion of the flower but a preliminary extraction with ligroin removed a yellow pigment which by the usual methods of examination by distribution between solvents[8] and by its intense blue coloration when the ligroin solution was stratified with concentrated sulfuric acid, was provisionally assumed to be carotene. The partially dried florets were extracted continuously with ether in a Soxhlet extractor until fresh portions of solvent were no longer colored.

---

[7] Shinoda and Sato, *J. Pharm. Soc. Japan,* **48,** 791 (1928).

[8] Kuhn and Brockmann, *Z. physiol. Chem.,* **206,** 41 (1932).

The ether was evaporated under reduced pressure and the sirupy residue taken up in alcohol. A small amount of amorphous solid separated and was removed by filtration. The alcoholic solution was poured into ether and the resulting solution washed thoroughly with water and then extracted with 5% sodium carbonate solution. The intensely red aqueous layer was separated and acidified and extracted with ether. The ether layer was washed with several portions of dilute ammonium carbonate solution, dried over sodium sulfate and evaporated to dryness. The yellow-brown, solid residue was extracted with 25 cc. of boiling xylene in several portions. The filtered xylene solution was allowed to stand for several days and slowly deposited a mixture of an amorphous yellow powder (40 mg.) and hard brown-yellow nodules (190 mg.). The nodules were partially purified by solution in cold, dilute aqueous–alcoholic sodium hydroxide followed immediately by precipitation with dilute hydrochloric acid. The pigment was thus obtained as brownish-yellow needles. After several recrystallizations from dilute alcohol it formed golden-yellow needles, m. p. 214–215° (dec.); reported for butein, 211–213°,[3] 212–213°,[9] 214–215°.[6] *Anal.* Calcd. for $C_{15}H_{12}O_5$: C, 66.20; H, 4.41. Found: C, 65.88; H, 4.84. The substance gives a yellow color in concentrated sulfuric acid, a brown color with ferric chloride and a deep red solution in aqueous sodium hydroxide.

The melting point was not depressed upon admixture with a synthetic sample of butein, m. p. 213–214° (preparation described below).

Butein Tetraacetate.—A solution of 10 mg. of the natural pigment and 20 mg. of anhydrous sodium acetate in 0.6 cc. of acetic anhydride was heated to boiling and allowed to stand at room temperature overnight. The excess acetic anhydride was decomposed with ice; the acetate (15 mg.) separated in crystalline form, m. p. 125–127°. After two recrystallizations from dilute alcohol it formed nearly colorless needles, m. p. 129–130°; reported for butein tetraacetate, 129–131°,[6] 128–129°.[9]

A sample of butein tetraacetate prepared from synthetic butein by the above method melted at 129.5–130°. A mixture of this material with the acetate of the natural pigment melted at 129–130°.

Synthesis of Butein.—The following procedure is essentially that used by Nadkarni and Wheeler[10] for the condensation of *p*-hydroxybenzaldehyde with resacetophenone.

Nitrogen was bubbled through an ice-cooled suspension of 5 g. of protocatechualdehyde and 5.5 g. of resacetophenone in 10 cc. of alcohol, a solution of 50 g. of potassium hydroxide in 35 cc. of water was added, with shaking, and the resulting mixture allowed to stand under nitrogen for five days at room temperature. The deep red mixture was poured onto enough ice to dilute it to twice the original volume and acidified with 6 *N* hydrochloric acid. The precipitate was collected, washed with water and recrystallized from 50% alcohol. There was obtained 2.4 g. of golden-yellow needles, m. p. 213–214°.

Summary

Butein (2′,4′,3,4-tetrahydroxychalcone) has been shown to be the anthochlor pigment of *Coreopsis Douglasii.*

LOS ANGELES, CALIFORNIA

RECEIVED SEPTEMBER 30, 1940

---

[9] Saiyad, Nadkarni and Wheeler, *J. Chem. Soc.*, 1737 (1937).

[10] Nadkarni and Wheeler, *J. Chem. Soc.*, 1320 (1938).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Use of Bunte Salts in Synthesis. I. The Preparation of Mercaptals

BY HARRY E. WESTLAKE, JR., AND GREGG DOUGHERTY

Bunte salts, esters of sodium thiosulfuric acid, undergo acid hydrolysis as follows

$$(1)\quad R—S—SO_2—O—Na + HOH \xrightarrow{\text{acid}} R—S—H + NaHSO_4$$

It was of interest therefore to determine whether acid solutions of Bunte salts could be used to carry out mercaptan reactions without the necessity of isolating the latter.

The literature revealed only two cases in which Bunte salts were used in reactions with compounds containing the carbonyl group. A patent was issued to Baeyer and Company for the preparation of acetone ethyl and methyl mercaptols by heating the Bunte salts with acetone and hydrochloric acid.[1] Also Gibson prepared the cyclic compound, ethylene mercaptal or dithiolane, from formaldehyde and the reaction product of sodium thiosulfate and ethylene chloride.[2] No references were found in the literature to the use of Bunte salts in the synthesis of normal, open chain mercaptals.

It has now been found that this method is generally applicable to mercaptal formation and the following have been prepared: formaldehyde dibenzyl mercaptal, benzaldehyde dibenzyl mercaptal, formaldehyde bis-β-oxyethyl mercaptal, formaldehyde dibutyl mercaptal, acetaldehyde dibutyl mercaptal, formaldehyde diethyl mercaptal. The obvious course of the reaction is a hydrolysis as in equation (1) followed by

---

[1] German Patent, *Ber.*, **22**, 115 (1889).

[2] Gibson, *J. Chem. Soc.*, 12 (1930).