after about four minutes the alkaline color of phenolphthalein faded. Two additional drops (0.1 cc.) of base were required for complete neutralization (total 4.8 cc.). A further 0.2 cc. of alkali was added followed by the addition of an equivalent volume (5.00 cc.) of 0.5007 *N* hydrochloric acid. The solution was quickly made up to 15.00 cc. and the polarimetric reading taken (initial reading, three minutes); spec. rot. +20.1° (23°, *c* 3.1). Thereafter there was no observable mutarotation over a period of eighty hours.

We acknowledge the general assistance of Messrs. Percy McWain (N.Y.A. Project O.S.U. 170) and Clarence M. Clevenger.

Summary

1. 1-Diazo-1-desoxy-*keto*-*d*-fructose tetraacetate has been synthesized by the action of diazomethane upon *d*-arabonyl chloride tetraacetate.

2. The 1-chloro and the 1-bromo derivatives of the *keto*-forms of *d*-fructose and of *d*-glucoheptulose acetates have been synthesized by the action of the hydrogen halides upon the corresponding diazomethyl ketone acetates (II).

3. 1-Diazo-1-desoxy-*keto*-*d*-glucoheptulose pentaacetate (II) underwent the Wolff rearrangement to produce a lactone form of 2-desoxyglucoheptonic acid tetraacetate, from which 2-desoxyglucoheptonolactone was obtained by saponification.

4. The above 2-desoxyaldonolactone and its acetate exhibited anomalous properties.

5. The above reactions represent transformations from the aldose series to (*a*) the ketose series and to (*b*) the 2-desoxyaldonic acid series.

COLUMBUS, OHIO RECEIVED MAY 2, 1942

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

Anthochlor Pigments. III. The Pigments of *Cosmos Sulphureus*

BY T. A. GEISSMAN

Previous studies on the sap-soluble flower pigments of certain species of *Compositae* have shown that the petals of these species contain substances which form intensely red salts with alkalies. For convenience these pigments have been described by the term "anthochlor." The tetrahydroxychalcone butein (I) has been identified as one member of this class of pigments and has been isolated from *Dahlia variabilis*[1] and from two species of *Coreopsis*.[2]

It was noted in the paper describing the studies on *Coreopsis gigantea*[2b] that in this flower a second substance accompanies butein, and it was suggested on the basis of the analytical figures for its crystalline acetate that this substance was a pentahydroxychalcone hexoside. This compound has now been isolated from the ray florets of *Cosmos sulphureus* ("Orange Flare"). *C. sulphureus* is a garden annual whose bright orange rays and yellow disk florets give the anthochlor reaction with alkali. Ether extraction of the dried, powdered rays yielded the glycoside as a yellow amorphous powder which separated from the ether during the extraction. Further treatment of the ether-extracted rays by a somewhat more lengthy procedure yielded an additional amount of the pigment. It formed a white crystalline acetate identical with that of the pigment previously isolated from *Coreopsis gigantea*. It is proposed to call this pigment "coreopsin."

The previously reported analytical figures on the basis of which coreopsin was assumed to be a pentahydroxychalcone hexoside were somewhat in error since it has been found that the aglycone of the pigment is butein. Hydrolysis of coreopsin acetate (the acetate was chosen since it is readily crystallized while the pigment itself has been obtained only in an amorphous, although apparently homogeneous, condition), followed by acetylation of the ether-extractable products, yielded the triacetate of butin (II), the flavanone isomeric with butein. The formation of butin in the hydrolysis is undoubtedly due to the isomerization of the butein first produced from the glycoside. The isomerization of *o*-hydroxychalcones to the corresponding flavanones under these conditions is a well-known reaction[3] and the sample of butin triacetate used for purposes of comparison was synthesized by treating a sample of synthetic butein under conditions identical with those used for the hydrolysis of the glycoside. That coreopsin is a glycoside of butein and not of butin

(1) Price, *J. Chem. Soc.*, 1018 (1939).

(2) (a) Geissman, THIS JOURNAL, **63**, 656 (1941); (b) **63**, 2689 (1941).

(3) (a) Perkin and Hummel, *J. Chem. Soc.*, **85**, 1462 (1904); (b) Göschke and Tambor, *Ber.*, **45**, 186 (1912). These describe the preparation of butin.

is indicated by a number of considerations. The pigment is a bright yellow in color, while the corresponding flavanone and glycosides of similar flavanones are colorless substances; it dissolves instantly in cold, dilute aqueous alkali with the formation of a red color; it gives no color when reduced with magnesium and hydrochloric acid.

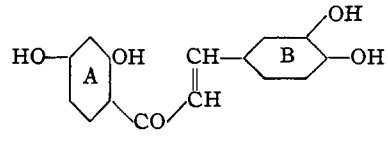
The aqueous solution from the hydrolysis of coreopsin acetate, after removal of the coloring matter, was found to reduce Fehling solution, but positive identification of the sugar has not yet been accomplished. On the basis of the analytical figures for coreopsin acetate it is probably a hexose. The position of attachment of the sugar has not yet been established, but it is very probable that it is attached to either the 2′ or 4′ position. The red color of alkaline solutions of coreopsin is similar to that shown by other chalcones hydroxylated in the 3,4-positions and is deeper than the colors of alkaline solutions of 4-hydroxy- or 4-hydroxy-3-methoxychalcones. Further, no naturally-occurring member of the large class of substances having the C_6–C_3–C_6 structure found in butein carries a sugar residue in the phenyl ring corresponding to the catechol nucleus of butein.

The study of the flowers of *Cosmos sulphureus* has been extended to include the remainder of the flower-head, consisting of the yellow disk-florets and the scarious involucral bracts. From this material there have been isolated a glycoside of quercetin, probably isoquercitrin, and (as the acetate)[4] luteolin (IV). Quercetin (III) was obtained in calculated amount from the hydrolysis of a weighed amount of the glycoside and identified by conversion to its acetate and comparison of this with an authentic sample. Although the disk-florets as well as the rays show the anthochlor reaction when touched with alkali, no pigment of this class was isolated from them except as a probable component of a crystalline acetate mixture which developed an intensely red solution when hydrolyzed with alcoholic alkali but which melted over a broad range.

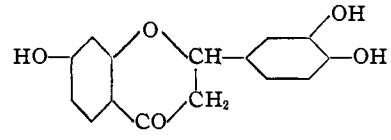
It appears likely that luteolin occurs as the free flavone since it was extracted from the flowers with ether and isolated without the use of any hydrolytic step.

(4) Since several thousand flower-heads yield an amount of dried material of the order of only a hundred grams, relatively small amounts of isolated substances have been available. For this reason it has proved convenient and often necessary to work up crude pigment fractions by acetylation, followed by purification of the readily crystallizable acetates. The pigments themselves are difficult to purify from the crude condition without considerable loss.

A comparison of the structures of the substances present in the flowers of *C. sulphureus* (I, III, and IV) adds an interesting example of a biogenetically and chemically related group of compounds to a number already recorded from studies on other plants.



I



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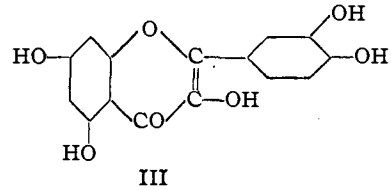
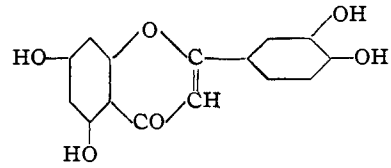


III



IV

All of these compounds have the $C_{6(A)}$–C_3–$C_{6(B)}$ carbon skeleton (*cf.* (I)) which is widespread in the plant kingdom and all of them contain the catechol nucleus as the $C_{6(B)}$ part of the molecule. They differ in the degree of oxidation in the $C_{6(A)}$–C_3 part of the molecule and in this respect bear to each other the same kind of relationship that exists between such related pairs of substances as pelargonidin and apigenin or pelargonidin and kampferol.

In view of the fact that all of the flowers so far known to belong to the anthochlor group, with the single recorded exception of the legume, *Butea frondosa*, are closely related taxonomically[5] a detailed study of their flower pigments should furnish a basis for evaluating in terms of the results obtained certain of the proposals that have been made concerning the biogenesis of plant materials, particularly those of the "flavone" (C_6–C_3–C_6) type.

(5) This close relationship is indicated by the fact that they have sometimes been classified as a sub-tribe *Coreopsidinae* of the tribe *Helianthеae*.

Experimental

All melting points are uncorrected.

Cosmos sulphureus was grown from commercially available seed. The flowers were collected at intervals, the rays separated immediately, and the rays and disk florets (with the involucral bracts) air-dried, ground to a powder and stored in stoppered containers.

Ray Flowers: Coreopsin.—Sixty grams of the dried, ground rays was extracted (Soxhlet) with petroleum ether (30–60°) until fresh portions of the solvent were no longer colored. The solution contained carotenoid pigments but no pigments of the anthochlor type. The powder was freed of petroleum ether and extracted with ether. The ether extract was greenish-yellow in color and contained a small amount of suspended solid. This was removed and dried. It weighed 0.130 g. It was a bright yellow substance, insoluble in ether, soluble in hot methanol, slightly soluble in hot water and gave an intense crimson solution in cold, dilute sodium hydroxide. Upon acidification of its alkaline solution, it separated as spherical globules of a glassy nature. The behavior of the crude material on melting indicated that it was not crystalline: it sintered at about 150° and decomposed at 190–195°.

Anal. Calcd. for $C_{21}H_{22}O_{10}\cdot 1.5H_2O$: C, 54.40; H, 5.39. Found: C, 54.50; H, 5.25.

From the ether solution was isolated by extraction with sodium carbonate solution, acidification and extraction with ether 40 mg. of a yellow-brown amorphous substance which could not be crystallized or converted into a crystalline acetate.

The ether-extracted petal-meal was dried and extracted with methanol. The filtered extract was evaporated, the sirupy residue dissolved in water and the solution washed with ether and clarified by filtration through Hyflo Supercel. To the deep red filtrate saturated lead acetate solution was added until no further precipitate was formed. The brick-red precipitate was removed and suspended in methanol and hydrogen sulfide passed into the suspension. The precipitated lead sulfide was removed and the deep orange-red solution evaporated under reduced pressure. The red-brown tar thus obtained was acetylated with acetic anhydride–sodium acetate and the tarry acetylation product separated into ether-soluble and ether-insoluble fractions by dissolving it in alcohol, adding ether and washing the resulting solution with water. The process was repeated with the tar which separated during the water washing. The nearly colorless ether solution finally resulting was evaporated and the gummy residue allowed to stand overnight with 20 ml. of 10% sodium hydroxide solution. The deep red alkaline solution resulting was decanted from some unchanged tarry material, washed with ether, acidified and the acidified solution saturated with ammonium sulfate. A yellow powdery solid separated on standing. It weighed 0.280 g. and was shown to be coreopsin by conversion into its crystalline acetate.

Coreopsin Acetate.—A portion of the pigment was acetylated with sodium acetate–acetic anhydride. The acetate formed soft, white needles; m. p. 171–172° after one recrystallization from alcohol. Mixed with a sample of the acetate, m. p. 171–2.5°, from *Coreopsis gigantea* no depression in melting point was observed. The two acetates gave identical colors when heated with alcoholic sodium hydroxide.

Anal. Calcd. for $C_{35}H_{36}O_{17}$: C, 57.67; H, 4.98. Found: C, 57.27, 57.22; H, 4.88, 4.79.

Hydrolysis of Coreopsin Acetate.—A suspension of 0.265 g. of coreopsin acetate (m. p. 171–172°) in a mixture of 50 ml. of 2% hydrochloric acid and 10 ml. of methanol was refluxed for four hours. The solid dissolved after about one hour and a pale yellow solution resulted. The solution was cooled and extracted with ether and the ether extract was dried and evaporated, leaving a red-yellow gum. This was acetylated by boiling it for about a minute with 2 ml. of acetic anhydride and 0.2 g. of sodium acetate. A nearly colorless solution resulted. After several hours ice and water and a few ml. of ether were added and upon standing colorless crystals (70 mg.) formed in the ether layer. After two recrystallizations from alcohol this material formed shining white leaflets, m. p. 120.5–121°. It was found to be butin triacetate by comparison with a sample prepared from synthetic butein by a procedure identical with that described above for the hydrolysis of coreopsin acetate. The melting points of both products and of a mixture of the two were identical, as were the colors produced by the magnesium and hydrochloric acid reduction test.

The behavior of butin triacetate when reduced with magnesium and hydrochloric acid in alcohol is noteworthy. The color produced is an intense red-violet to blue-violet (depending upon the concentration), and is markedly bluer than the colors shown by flavanones hydroxylated in the 5,7-positions, such as naringenin, eriodictyol and homoeriodictyol. This color test is the subject of another investigation now being carried on in this Laboratory. Butin triacetate has been previously reported to have a melting point of 123–125°[3a] and 123°.[3b] The sample from the hydrolysis of coreopsin acetate was analyzed.

Anal. Calcd. for $C_{21}H_{18}O_8$: C, 63.28; H, 4.57. Found: C, 63.01; H, 4.92.

The aqueous solution from which the butin had been removed was treated with lead carbonate and the lead removed with hydrogen sulfide. The solution reduced Fehling solution but no crystalline derivative of the sugar could be isolated in amount sufficient for identification.

Disk-florets and Involucral Bracts.—After a preliminary treatment with petroleum ether the powdered material was extracted with ether. The ether solution was washed with sodium carbonate solution and the deep red extract acidified and extracted with ether. The ether extract was dried and evaporated, leaving a brown, tarry residue which was induced to crystallize partially by adding small amounts of ether and allowing evaporation to proceed slowly between fresh additions. There was finally obtained 50 mg. of a yellow, powdery solid. An attempt to recrystallize this resulted in a product which did not melt below 250° but darkened from about 230°, and was obviously still impure. It was finally acetylated and yielded a white, crystalline acetate which after two recrystallizations from alcohol melted at 217–219°. It was similar in melting point and behavior to luteolin tetraacetate which has been reported by various investigators to melt at 213–

215°,[6] 223–226°,[7] 222–224°.[8] A sample of luteolin tetraacetate was synthesized according to the method of Kostanecki, Rozycki and Tambor,[8] starting with methyl veratrate and trimethoxyacetophenone. The synthetic material melted at 221–222° and a mixture of this and that from the natural source melted at 219–221°. In a repetition of the isolation from the florets and bracts there was obtained a product melting at 220–222°. The natural and synthetic samples gave identical red-orange colors when to their solutions in alcohol were added a fragment of magnesium and a drop of concentrated hydrochloric acid, and both samples dissolved in hot alcoholic sodium hydroxide to form yellow solutions. Unfortunately too little of the material from the natural source was obtained for satisfactory analytical figures. Each of the two samples described was analyzed.

Anal. Calcd. for $C_{23}H_{18}O_{10}$: C, 60.78; H, 4.00. Found: C, 61.74, 60.15, 60.29; H, 4.27, 4.04, 3.80.

It is felt, however, that the information from the melting point and color-test observations, coupled with the approximate agreement in the analyses is sufficient to establish the identity of the compound isolated.

From the oily mother liquor from which the crude luteolin separated was obtained a crystalline mixture of acetates; m. p. 130–190°. It formed a deep red solution in hot alcoholic alkali. Too little of it was obtained to permit of its separation into its components.

Isoquercitrin.—The alcohol extract of the ether-extracted meal (disk-florets and bracts) was diluted with water and concentrated to remove most of the alcohol. Saturated lead acetate was added in small portions and the brown precipitates which first appeared were discarded. The bright orange-yellow precipitate which then formed was removed, suspended in hot water and decomposed with hydrogen sulfide. The filtered solution was saturated with salt and extracted with ethyl acetate. Removal of the ethyl acetate left a yellow gum which on standing in alcohol–water solution deposited 60 mg. of a yellow powder. This crystallized from dilute alcohol as lemon-yellow needles; m. p. 217–219° after shrinking at about 115° (loss of water of hydration). It dissolved in alkali to a deep yellow solution, gave a deep olive-green color with aqueous-alcoholic ferric chloride and a rose-red solution when reduced in alcoholic solution with magnesium-hydrochloric acid. These observations are in agreement with those recorded for isoquercitrin (quercetin-3-glucoside); m. p. reported as 217–219°,[9] 218–220°,[10] 219°.[11]

Hydrolysis of 24.0 mg. of the glycoside with 6 ml. of 1 *N* sulfuric acid yielded 14.1 mg. of quercetin; calcd. for isoquercitrin, 14.4 mg. The product of the hydrolysis was converted into its acetate, m. p. 192–193°; no depression on mixing with an authentic sample, m. p. 193–194°, of quercetin pentaacetate.

Anal. Calcd. for quercetin pentaacetate, $C_{25}H_{20}O_{12}$: C, 58.58; H, 3.94. Found: C, 58.66; H, 3.99.

Summary

1. The flowers of *Cosmos sulphureus* ("Orange Flare") contain coreopsin (rays), luteolin and a quercetin glycoside which is probably isoquercitrin (disk-florets and involucral bracts).

2. Coreopsin has been found to be a butein glycoside. The nature and position of the sugar residue are as yet undetermined.

(6) Perkin, *J. Chem. Soc.*, **69**, 206 (1896).
(7) Herzig, *Ber.*, **29**, 1013 (1896).
(8) Kostanecki, Rozycki and Tambor, *ibid.*, **33**, 3416 (1900).
(9) Perkin, *J. Chem. Soc.*, **95**, 2190 (1909).
(10) Sando and Bartlett, *J. Biol. Chem.*, **54**, 640 (1922).
(11) Viehover, Chernoff and Johns, *J. Agr. Research*, **13**, 348 (1918).

LOS ANGELES, CALIFORNIA RECEIVED APRIL 22, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Catalysis of the Thermal Decomposition of Acetaldehyde by Hydrogen Sulfide

BY WALTER L. ROTH AND G. K. ROLLEFSON

In some previous work it has been shown that the acceleration of the rate of the thermal decomposition of acetaldehyde when iodine is added is due to a series of reactions in which the iodine reacts with the aldehyde and then is regenerated by reactions between the products of the first reaction.[1] In this paper we are presenting the results of some investigations of the nature of the action of hydrogen sulfide which has also been reported to accelerate the decomposition of acetaldehyde.[2]

Fromherz reported that the rate of the decomposition in the presence of hydrogen sulfide is dependent only on the pressure of the catalyst. In accordance with this statement the rate was constant throughout a considerable portion of any given run and the ratio of the time required for three-fourths completion to that required for half completion was approximately 1.5 as it should be if the rate were independent of the aldehyde pressure. On the other hand, if we utilize this linear character of the pressure–time curves to calculate the initial rates, we find continuous variation of the rate constants calculated on the assumption of independence of the aldehyde according to the

(1) Faull and Rollefson, THIS JOURNAL, **59**, 625 (1937).
(2) Fromherz, *Z. physik. Chem.*, **B25**, 301 (1934).