rated with sodium bromide profoundly modifies the addition of bromine to the unsaturated hydrocarbons styrene and indene.

2. The method appears to be quantitative for the formation of the respective dibromides when based on the total bromine consumed.
3. The anomalous feature is that approximately one-half of the total bromine consumed is present in the reaction flask as hydrobromic acid in solution.
4. An equation is suggested in an effort to explain the final mixture reached when titrating styrene.

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

Anthochlor Pigments. II. The Pigments of *Coreopsis gigantea*[1,2]

BY T. A. GEISSMAN

Coreopsis gigantea (Compositae) is a perennial common to the coastal areas of California. It blooms during March or April, bearing showy flowers consisting of deep yellow disk-florets and golden-yellow rays. Both the ray- and disk-flowers, as well as the involucral bracts, show the color reaction described by Gertz[3] as being characteristic of a class of pigments known as "anthochlor" pigments,[1,3] one member of which has been shown to be butein (2′,4′,3,4-tetrahydroxychalcone), which has been isolated from *Coreopsis Douglasii*,[2] *Dahlia variabilis*[4] and from *Butea frondosa*[5] (Leguminosae).

Butein is also present in *Coreopsis gigantea*. It was isolated from the ether extract of the dried whole flowers (including the involucral bracts) and was characterized by comparison with a synthetic sample and by conversion into its acetate. The whole flower heads were used because of the difficulty of securing more than a small quantity of material during the flowering season of the present year, and consequently it cannot be stated with certainty whether butein is present in all parts of the flower-head or is localized in the ray- or disk-flowers or the involucral bracts. The qualitative observation of the appearance of a red coloration when a part of the plant is treated with alkali cannot be taken as evidence for the presence of butein since a second substance which could be responsible for this reaction has also been isolated.

This substance, for which no name will be proposed for the present, was isolated from the methanol extract of the dried flowers after exhaustive extraction with ether. It has not yet been obtained in the crystalline state but was converted into a white, crystalline acetate, m. p. 172.5–3°. The amorphous material was in the form of a brown-yellow powder which microscopic examination disclosed to be composed of minute spherical globules of a glassy nature, deep yellow in color. The substance dissolves in aqueous alkali to give an intensely red solution. It is insoluble in ether and somewhat soluble in water, from which butyl alcohol extracts it readily. Its acetate is insoluble in cold, dilute alkali but on warming with alcoholic alkali it dissolves to form an intensely red solution such as is produced when the amorphous pigment dissolves in alkali. The quantity of this material (as acetate) so far available has been small and at present little is known concerning its constitution.

In the preceding paper[2] the remark was made that aqueous extracts of the ether-extracted flowers of *C. Douglasii* contained some water-soluble pigment which gave a red color with alkali. It is therefore probable, in view of the present results, that a second pigment is also present in that flower.

Work on these pigments and on those present in certain other members of the Compositae is being continued.

Experimental

The flowers were collected near the Coast Highway north of Malibu, California, during April. The whole flower

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(1) The use of the term "anthochlor" to describe those pigments whose presence causes certain yellow flowers to turn red when exposed to alkali is to a certain extent undesirable since the term has been used with more than one connotation in the literature. However, since work in progress in this Laboratory on certain Compositae showing this color reaction has so far not given assurance that all the substances responsible belong to a single class of compounds, the use of the term will be continued until a more uniquely descriptive one is found.

(2) First paper of this series, THIS JOURNAL, **63**, 656 (1941).

(3) Gertz, *Kgl. Physiograf. Sällskap, Lund, Förh.*, **8**, 62, 71, 251 (1938).

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

(5) Perkin and Hummel, *ibid.*, **85**, 1459 (1904).

heads were used, and these were dried at 40° and ground to a powder in a Wiley Mill. A total of 252 g. of the dried material was obtained. This was worked up in two portions, an exploratory 50 g. run and the 202 g. remaining.

Method of Isolation of Pigments.—(1) The powdered material (202 g.) was extracted continuously in a Soxhlet extractor with petroleum ether (b. p. 30–60°), then with ether. The petroleum ether contained chlorophyll and carotenoid pigment but none of the "anthochlor." The ether extract was washed with sodium acetate solution (A) and then extracted with 3% sodium carbonate solution in small portions until a fresh portion was no longer colored The intensely red extract was washed once with fresh ether and acidified with dilute sulfuric acid. The resulting deep brown-yellow solution was extracted with numerous small portions of ether, the aqueous solution being saved (B). The ether solution was washed with sodium acetate solution and dried over anhydrous sodium sulfate. The ether was evaporated until the volume was reduced to about 5 ml. and 15 ml. of benzene was added. On standing a yellow, crystalline precipitate separated. It weighed 0.73 g. From the 50 g. of material worked up in a similar way only 0.11 g. was obtained but in this case a further amount was isolated as the acetate by acetylation of the tarry residues. The 0.73 g. obtained from the larger batch represents practically all of the material obtainable since no more could be recovered by acetylation of the residues.

The compound was recrystallized twice from dilute alcohol and formed bright yellow needles, m. p. 212–214° dec. Mixed with a sample of synthetic butein (m. p. 213–214° dec.) the m. p. was not depressed. The compound is identical with synthetic butein in appearance and color reactions (alkali, ferric chloride, concentrated sulfuric acid).

A sample of the natural butein was acetylated in the usual way. The acetate thus obtained melted at 128–130° after two recrystallizations and its m. p. was not depressed upon admixture with a sample of the acetate of the synthetic material (m. p. 129–130°).

(2) The material from the ether extraction was freed of ether and extracted (Soxhlet) with methanol until fresh portions of solvent were no longer colored. The methanol was removed under reduced pressure and to the sirupy residue was added water and ether and the ether layer separated. The aqueous layer was further extracted with several portions of ether, then saturated with sodium sulfate and extracted repeatedly with small portions of butyl alcohol. The deeply-colored butyl alcohol solution was diluted with about an equal volume of ether and extracted with 5% sodium carbonate solution. The deep red alkaline extract was acidified and the resulting deep yellow-brown solution washed with ether which removed very little of the color. In the preliminary run (50 g.) some of the water-soluble pigment separated at this point but in the larger run this did not occur even after several days. The solution was extracted with butyl alcohol and with this extract were combined the butyl alcohol extracts of aqueous solutions (A) and (B) above. The butyl alcohol solution was diluted with ether and petroleum ether (equal volumes of each) and washed first with water, then with dilute alkali. The combined aqueous extracts were acidified and extracted with ether. During the ether extraction a tar separated from the aqueous solution. This tar dissolved in alkali with a deep red color but no crystalline material could be obtained from it. The pigment still remaining in the aqueous solution was taken up in butyl alcohol and again transferred to water. The aqueous solution obtained was evaporated under reduced pressure and the tarry residue acetylated with sodium acetate–acetic anhydride. After decomposition of the acetylation mixture a tarry product resulted, part of which was insoluble in ether. The ether-soluble part could not be crystallized and was saponified with cold aqueous potassium hydroxide (5 g. in 75 ml. of water). The deep red alkaline solution resulting from this treatment was washed with ether, acidified and saturated with ammonium sulfate. On standing a granular, but amorphous, brown-yellow precipitate appeared. This weighed 0.34 g It was acetylated by boiling with 1 g. of sodium acetate and 5 ml. of acetic anhydride. After decomposing the acetylation mixture with ice-water the resulting tarry substance was taken up in a small volume of ether. On standing a substance separated from the ether as soft white needles, 0.31 g., m. p. 171–172°. After two recrystallizations from alcohol it had m. p. 172.5–173°. *Anal.* Found: C, 56.22, 56.15, 56.39; H, 5.01, 5.20, 4.69. These figures are not in agreement with those calculated for the acetate of a butein hexoside (C, 57.69; H, 4.98) but do check those calculated for the acetate of a pentahydroxychalcone **hexoside** (C, 56.46; H, 4.87).

The acetate gives an orange color in concentrated sulfuric acid. It is insoluble in aqueous sodium hydroxide and when warmed with alcoholic sodium hydroxide it dissolves to give an intensely bluish-red solution. Acidification of this solution causes the color to change to yellow and from this acid solution ether extracts very little color. When a solution of the acetate in concentrated sulfuric acid was diluted drop by drop with water and the resulting yellow solution nearly neutralized with sodium hydroxide, the yellow color could be extracted by ether. These facts suggest that the acetate is derived from a polyhydroxychalcone glycoside but attempts to recover a crystalline compound after hydrolysis have so far been unsuccessful.

Summary

The flowers of *Coreopsis gigantea* contain butein and a second pigment which appears to be a glycoside of a polyhydroxychalcone.

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