of water. After filtration, concentration *in vacuo*, and fractionation of the residual oil, 6.5 g. (51%) of product was obtained, b.p. 136–146° (0.6 mm.), n_D^{28} 1.5353.

Anal. Calcd. for $C_{16}H_{26}N_2$: C, 78.11; H, 10.65; N, 11.39. Found: C, 78.52; H, 10.25; N, 10.81.

[1-Methyl-2-(octahydro-1-azocinyl)-2-phenethyl]guanidine sulfate was prepared from 5 g. (0.02 mole) of 1-methyl-2-(octahydro-1-azocinyl)-2-phenethylamine and 2.83 g. (0.01 mole) of 2-methylthiopseudourea sulfate. Recrystallization from ethanol-ether gave 4.1 g. (61%) of crystalline material, m.p. 145–155° dec.

Anal. Calcd. for $C_{34}H_{42}N_8O_4S$: C, 60.49; H, 8.66; N, 16.60. Found: C, 60.40; H, 8.37; N, 16.81.

Hexahydro-5-oxo-1,4-thiazepine. With moderate cooling, 12.7 g. (0.19 mole) of sodium azide was slowly added to 15 g. (0.13 mole) of tetrahydro-1-thiopyran-4-one[15] in 65 ml. of concd. hydrochloric acid. After the addition was completed, stirring was continued for an additional 4 hr. at room temperature. Solid sodium carbonate was then added until the solution was slightly alkaline, sufficient water being added to dissolve salts present. After extraction with chloroform, drying, and concentrating to a low volume, petroleum ether was added to precipitate the product. Recrystallization was from carbon tetrachloride–heptane to give 11.5 g. (63%) of product, m.p. 115–118°.

Anal. Calcd. for C_5H_9NOS: C, 45.84; H, 6.93; N, 10.69; S, 24.48. Found: C, 45.13; H, 6.79; N, 10.10; S, 24.23.

1,4-Hexahydrothiazepine. To a solution of 5.9 g. (0.15 mole) of lithium aluminum hydride in 800 ml. of ether was added, with stirring, 12 g. (0.09 mole) of solid hexahydro-5-oxo-1,4-thiazepine. After refluxing for 24 hr., the mixture was carefully decomposed with 20 ml. of water. After filtration and concentration of the filtrate, the residue was fractionated to give 9.5 g. (88%) of product, b.p. 192–193° n_D^{27} 1.5342.

Anal. Calcd. for $C_5H_{11}NS$: C, 51.32; H, 9.48; N, 11.97; S, 27.41. Found: C, 51.23; H, 8.96; N, 11.22; S, 27.85.

The *hydrochloride salt* was recrystallized from isopropyl alcohol–ether to give material which melted at 210–212°.

Anal. Calcd. for $C_5H_{12}ClNS$: C, 39.25; H, 7.91; N, 9.16; Cl, 23.17. Found: C, 39.08; H, 7.89; N, 9.06; Cl, 23.04.

[2-(Octahydro-1-azocinyl)ethylamino]-2-imidazoline hydroiodide. To 4 g. (0.025 mole) of 2-(octahydro-1-azocinyl)-ethylamine in 10 ml. of water was added 6.26 g. (0.025 mole) of 2-methylthio-2-imidazoline[16] hydroiodide and the mixture warmed on the steam bath until evolution of methyl mercaptan ceased. The oil which separated on cooling was dissolved in ethanol and reprecipitated by addition of ether. This low melting material amounted to 6 g. (67%).

Anal. Calcd. for $C_{12}H_{25}IN_4$: C, 40.91; H, 7.16; N, 15.92. Found: C, 39.66; H, 7.25; N, 15.65.

[2-(Octahydro-1-azocinyl)ethyl]-2-thiopseudourea dihydrochloride. 2-(Octahydro-1-azocinyl)ethylchloride hydrochloride[5] (2 g.; 0.01 mole) was added with stirring to a solution of 0.8 g. (0.01 mole) of thiourea in 26 ml. of ethanol and refluxed for 6 hr. The solid which separated after cooling was recrystallized from ethanol to give 1.6 g. (56%) of material, m.p. 212–215°.

Anal. Calcd. for $C_{10}H_{23}Cl_2N_3S$: C, 41.70; H, 8.05; N, 14.59. Found: C, 41.59; H, 7.96; N, 14.37.

Acknowledgment. The authors wish to express their appreciation to Mr. Louis Dorfman and his associates for the microanalyses.

SUMMIT, N. J.

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(16) S. R. Aspinall and E. J. Bianco, *J. Am. Chem. Soc.* **73**, 602 (1951).

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

Anthochlor Pigments. XIV. The Pigments of *Viguiera multiflora* (Nutt.) and *Baeria chrysostoma* (F. and M.)

MASAME SHIMOKORIYAMA AND T. A. GEISSMAN

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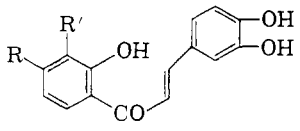
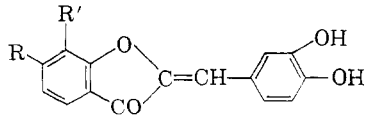
The flower petals of two composites, neither of which is a member of the subtribe Coreopsidinae, have been found to be pigmented with chalcones and aurones. The presence of these (anthochlor) pigments in plants not in the subtribe of which they have heretofore seemed to be characteristic offers further evidence concerning their biosynthetic relationships. As in earlier examples, a chalcone is accompanied by the structurally corresponding aurone in each instance of its occurrence.

The designation "anthochlor" has been applied to the polyhydroxychalcones and -aurones (2-benzal-3-coumaranones) typified by the widely distributed compounds butein (I) and sulfuretin (V):



I. Butein, R = OH, R′ = H
II. Coreopsin, R = *O*-glucosyl, R′ = H
III. Okanin, R = R′ = OH
IV. Marein, R = *O*-glucosyl, R′ = OH



V. Sulfuretin, R = OH, R′ = H
VI. Sulfurein, R = *O*-glucosyl, R′ = H
VII. Maritimetin, R = R′ = OH
VIII. Maritimein, R = *O*-glucosyl, R′ = OH

Pigments of these classes that contain a resorcinol-derived ring (as in I and II) rather than one derived from phloroglucinol[1] occur in numerous genera of compositae, and most characteristically

in members of the tribe Heliantheae, subtribe Coreopsidinae.[2]

The recognition, by qualitative tests, of the presence of anthochlor pigments in *Viguiera multiflora* Nutt., a member of the Heliantheae but not of the Coreopsidinae, and in *Baeria chrysostoma* F. and M., a member of the tribe Helenieae, was of special interest, as it indicated a chemical relationship between these species that was not forecast by their taxonomic classification. Accordingly, a detailed study of these two species was undertaken with a view to establishing the identity of all of their flavonoid pigments.

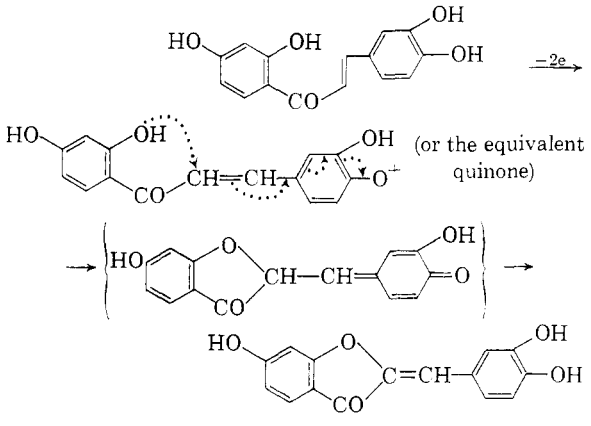
Viguiera multiflora flowers were separated into ray and disc flowers and the former examined in detail. Chromatographic separation of the constituents of an alcoholic extract led to the isolation of coreopsin (II) and quercimeritrin (quercetin 7-glucoside) in crystalline form, and to the identification by spectrometric and chromatographic methods of sulfurein (VI), sulfuretin (V), butein (I), and caffeic and chlorogenic acids. From experience in work with other plants containing chalcone and aurone glycosides, it is probable that the aglucons butein and sulfuretin are hydrolytic artefacts that arose after the flowers were collected.

The whole flower heads of *Baeria chrysostoma* were extracted and the constituents separated by chromatography on paper. The following compounds were isolated in crystalline form: butein, caffeic acid, quercetin, isoquercitrin, coreopsin, okanin (III), and marein (IV). In addition to these, sulfurein, sulfuretin, maretimein (VIII), maritimetin (VII), and chlorogenic acid were identified by spectrometric, chromatographic and chemical procedures.

These findings show that *Viguiera multiflora* and *Baeria chrysostoma* have patterns of pigmentation that are remarkably similar to these previously found in certain *Coreopsis* species. Butein and its 4′-glucoside, coreopsin, have been identified in a number of *Coreopsis* and *Cosmos* species, and constitute what are probably the commonest of the naturally occurring anthochlor pigments.[3-5] The corresponding aurone, sulfuretin, and its 6-glucoside, sulfurein,[6] have been found in *Cosmos sulfureus*,[7] the yellow *Dahlia variabilis*,[8] and in *Coreopsis gigantea* and *C. maritima*.[9] The presence of caffeic and chlorogenic acids is so common in numerous composites as to make their discovery in the present study quite unexceptional. Quercetin 7-glucoside (quercimeritrin) is known to occur in the sunflower, *Helianthus annuus*,[10] but has not previously been found in other genera of the tribe. The flavones that have so far been found to co-occur with anthochlor pigments are luteolin in *Cosmos sulfureus*,[7] its 7-glucoside in *Coreopsis maritima*,[8] and isoquercitrin in *Cosmos sulfureus*.[4]

It is interesting to note that *Baeria chrysostoma* contains nearly the same pigment complex as does *Coreopsis maritima*[9]; the exception is that in *Baeria* isoquercitrin (quercetin 3-glucoside), and in *C. maritima* luteolin 7-glucoside, accompany the chalcones coreopsin and marein and the aurones sulfurein and maritimein.

The presence of the chalcone-aurone pairs coreopsin-sulfurein (in *Viguiera* and *Baeria*) and marein-maritimein (in *Baeria*) emphasizes further the close interrelationship of chalcones and aurones and supports the hypothesis that aurones are directly derived from chalcones by way of an oxidation reaction. The conversion of 3,4-dihydroxychalcones into aurones occurs with ease under ordinary conditions. Butein, when allowed to stand in alcoholic solution slowly changes into sulfuretin, and it has been found experimentally that in air in the presence of alkali the change is rapid.[11] The formulation of this reaction in the following way suggests possible implications in the oxidation of other 3,4-dihydroxylated flavonoid compounds:



(1) It is of interest to note that aurones based upon the phloroglucinol ring have not been found in the Compositae, but are present in such diverse genera as *Oxalis* and *Antirrhinum*; see ref. 2.

(2) T. A. Geissman, J. B. Harborne, and M. K. Seikel, *Les Heterocycles Oxygenes*, Colloques Internat. du Centre National de Recherche Scientifique, Lyon, 1955, pp. 277–285.

(3) T. A. Geissman, *J. Am. Chem. Soc.*, **63**, 656; **63**, 2689 (1941); T. A. Geissman and C. D. Heaton, *J. Am. Chem. Soc.*, **65**, 677; **66**, 486 (1944); M. K. Seikel and T. A. Geissman, *J. Am. Chem. Soc.*, **72**, 5720 (1950).

(4) M. Shimokoriyama and S. Hattori, *J. Am. Chem. Soc.*, **75**, 1900 (1953).

(5) T. A. Geissman and L. Jurd, *J. Am. Chem. Soc.*, **76**, 4475 (1954).

(6) L. Farkas, L. Pallos, and Z. Paál, *Chem. Ber.*, **92**, 2847 (1959).

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(8) C. G. Nordstrom and T. Swain, *Chem. and Ind.*, 823 (1953); *Arch. Biochem. Biophys.*, **60**, 329 (1956).

(9) T. A. Geissman, J. B. Harborne, and M. K. Seikel, *Arch. Biochem. Biophys.*, **78**, 825 (1956).

(10) C. E. Sando, *J. Biol. Chem.*, **68**, 407 (1926).

(11) J. B. Harborne and T. A. Geissman, unpublished observations in this laboratory.

It is of interest to note that in studies of this reaction in which various model compounds were examined, 4-hydroxyl and 4-hydroxyl-3-methoxylchalcones were not converted into aurones.[11]

The fact that all of the flavonoid compounds known to be present in the *Viguiera* and *Baeria* species examined contain the 3,4-dihydroxyphenyl residue indicates their close biosynthetic relationship. The presence of quercimeritrin in *Viguiera* and of isoquercitrin in *Baeria*, along with the 6-(aurone numbering) and 4'-(chalcone numbering) glycosides of the anthochlor pigments indicates that the processes of glycosylation in the flavone and anthochlor pigments bear no direct connection with each other.

The taxonomic relationships suggested by these findings offer attractive ground for speculation but must be assessed with caution. That anthochlor pigmentation is not a purely accidental feature is shown by the fact that it is highly characteristic of the sub-tribe Coreopsidinae (being found, for example, in *Cosmos, Coreopsis, Dahlia, Bidens*) but is encountered only rarely outside of that group of genera. Qualitative tests in this laboratory have shown that *Viguiera laciniata* and *Baeria macrantha* also contain pigments of this class, an indication that it is the genera *Viguiera* and *Baeria* that are so characterized and not simply the two species *V. multiflora* and *B. Chrysostoma*. That these observations suggest that there is a closer relationship between *Viguiera* and the genera of the Coreopsidinae than between *Viguiera* and other genera of the Heliantheae is a reasonable speculation; but by the same token, *Baeria*, of the tribe Helenieae, should be considered to be more closely related to members of another taxonomic tribe than with those of its own, no other of which has been found to be anthochlor-pigmented.

EXPERIMENTAL

General remarks. The filter paper used for the isolation of the pure compounds described below was Whatman No. 3 paper (19 × 45 cm.) that had been prewashed with butanol: 27% acetic acid (1:1) (BAW); 30% acetic acid (AA); and 50% ethanol, in this order, each for 3 days. In the preparation of solutions for spectrophotometric measurements, Whatman No. 1 paper, prewashed as above, was used, and the final operation was carried out by the half-banding method.[12] All solvents were freshly distilled. For the elution of glycosides and chlorogenic acid, 50% aqueous ethanol was used; for aglycones and caffeic acid, 95% ethanol. In determining shifts in absorption spectra caused by aluminum chloride, 3 drops of 5% ethanolic aluminum chloride were added to the sample and blank solutions (3 ml.) in the spectrophotometer cuvettes. Where identifications were made by chromatographic and spectrometric means, authentic samples were used as standards for comparison.

Viguiera multiflora. Flowers were collected near Gothic, Colorado, in August, 1959. The whole flower heads were dried at once in a current of warm air. The rays were separated, and 8 g. was extracted five times, each with 80 ml. of methanol. The combined extracts were filtered and evaporated under reduced pressure and the aqueous concentrate washed thoroughly with benzene and with petroleum ether (b.p. 20–40°), and then exhaustively extracted with ethyl acetate (20 times). Evaporation of the ethyl acetate solution yielded a residue that was dissolved in 8 ml. of 50% ethanol. A similar extract of the disc florets gave a paper chromatogram that was nearly the same as that of the ray flowers; it was not studied in detail.

To each of four Whatman No. 3 sheets was applied 1 ml. of the stock solution; development with BAW gave five distinct bands. These were eluted and purified by repeated chromatography with BAW and AA.

Bands 1 and 2 contained caffeic acid, butein, and sulfuretin (band 1) and quercetin and chlorogenic acid. These were readily identified by comparison with authentic specimens and by their ultraviolet absorption spectra.

Band 3 gave butein on hydrolysis. When the eluate was evaporated and the residue dissolved in 2 ml. of 30% ethanol, coreopsin crystallized (18 mg.). It melted at 213–214° (reported[10] m.p. 209–211°, 215–216°).

Anal. Calcd. for $C_{21}H_{22}O_{10}\cdot{}^1/_2H_2O$: C, 56.88; H, 5.23. Found: C, 57.15; H, 5.25.

Band 4 contained as its chief component sulfurein, identified by its ultraviolet absorption and chromatographic comparison with authentic material.

Band 5 contained a flavone glycoside. When the eluate was evaporated and dissolved in 1 ml. of 50% ethanol, 3 mg. of the crystalline glycoside separated. Recrystallization from 40% ethanol gave 2 mg. of pure material, m.p. 247–248°. It was identified as quercimeritrin (reported[10] m.p. 247–249°) from the following observations: It showed chromatographic behavior identical with that of authentic quercimeritrin and showed exactly the same color reactions, the bright green-yellow fluorescence (in ultraviolet light) with aluminum chloride being characteristic of flavonols with free 3-hydroxyl groups; it gave quercetin on hydrolysis.

Baeria chrysostoma. Whole flower heads of *B. chrysostoma*, collected in the vicinity of Los Angeles, were dried, ground, and extracted exhaustively with methanol. An ethyl acetate solution was prepared and chromatographed on Whatman No. 3 paper as described for *Viguiera multiflora*. Four distinct bands were developed.

Band 1 was eluted and the eluate evaporated under reduced pressure. A solution of the residue in 3 ml. of 30% ethanol was cooled and soon deposited 16 mg. of crystalline butein. The mother liquor was separated on paper with 30% acetic acid as developing solvent. The two bands that were formed contained caffeic acid (A) and butein plus sulfuretin (B). From the eluate of B was obtained a further 5 mg. of crystalline butein; sulfuretin was identified by chromatographic comparison with authentic material and by its ultraviolet absorption spectrum. The butein, m.p. 213–214°, was analyzed.

Anal. Calcd. for $C_{15}H_{12}O_5\cdot H_2O$: C, 62.06; H, 4.86. Found: C, 62.54; H, 5.17.

Band 2 yielded an eluate that deposited quercetin (11 mg.) on concentration. This was identified by its melting point and chromatographic properties. The mother liquor contained chlorogenic acid.

Band 3 was eluted and the eluate concentrated to 5 ml. and kept at 0°. Crystalline okanin (106 mg.) separated. Recrystallized from 40% ethanol, the okanin melted at 235–240° (reported[13] m.p. 235–240°).

Anal. Calcd. for $C_{15}H_{12}O_6\cdot{}^1/_2H_2O$: C, 60.61; H, 4.41. Found: C, 60.91; H, 4.39.

The mother liquor from the crystalline okanin was further separated by chromatography on paper with 30% acetic acid. Four bands were formed; these contained, respectively, A) chlorogenic acid; B) isoquercitrin, obtained in crystalline

(12) T. A. Geissman, J. B. Harborne, and M. K. Seikel, *J. Am. Chem. Soc.*, **78**, 825 (1956).

(13) F. E. King and T. J. King, *J. Chem. Soc.*, 569 (1951).

form (24 mg., m.p. 196–198°, identified by comparison with an authentic specimen; C) coreopsin, obtained in crystalline form (18 mg.), m.p. 213–214°, and sulfurein; and D) additional okanin, from which 50 mg. of crystalline material was isolated, and maritimetin.

Band D, after elution and concentration of the eluate to 5 ml., yielded 309 mg. of marein. This was crystallized as bright orange aggregates from 50% ethanol. When hydrolyzed with 5% hydrochloric acid it gave a mixture of okanin and the isomeric flavano-okanin. The presence of marein in the mother liquors was readily established by paper chromatographic comparison with authentic material and by spectral measurements.

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LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY OF NATURAL PRODUCTS, NATIONAL HEART INSTITUTE, NATIONAL INSTITUTES OF HEALTH, U. S. PUBLIC HEALTH SERVICE, DEPARTMENT OF HEALTH, EDUCATION AND WELFARE]

Alkaloids of *Ormosia jamaicensis* (Urb.)—Jamaicensine and Jamaidine

H. A. LLOYD AND E. C. HORNING

Received May 2, 1960

Jamaicensine, $C_{14}N_{22}N_2O$, and jamaidine, $C_{15}H_{24}N_2O_2$, have been isolated from seeds of *Ormosia jamaicensis* (Urb.) and *O. panamensis* (Benth.) Jamaicensine closely resembles, but may not be identical with, a new alkaloid angustifoline isolated recently from *Lupinus angustifolius*. Jamaidine is isomeric with hydroxylupanine but not identical with it.

Three isomeric bases of formula $C_{20}H_{33}N_3$ present in seeds of *Ormosia panamensis* (Benth.) and other *Ormosia* species were described in a previous paper.[1] Several additional alkaloids, two of which were oxygen-containing, were also found in seeds of *Ormosia* species which were examined, except for *O. stipitata* (Schery).[2] The oxygen-containing alkaloids have now been isolated and characterized. Seeds of *O. panamensis* and *O. jamaicensis* (Urb.) were used as the source of these compounds. The extraction process was carried out as described previously,[1] in such a way as to yield an ether solution that contained the three major bases (panamine, ormosanine, ormosinine) and a chloroform solution that contained two major components and several minor ones. Chromatography on alumina provided these two components in pure form. They were named jamaicensine and jamaidine.

Jamaicensine (m.p. 80.5–81°) was found to have an empirical formula $C_{14}H_{22}N_2O$ through analysis of the base and a number of derivatives. The hydrochloride and picrate were formed in 1:1 ratio of acid to base, and a determination of the neutral equivalent showed that only one basic group was present. A strongly positive Simon test indicated that this was a secondary amino group. This was confirmed through the preparation of an acetyl and a benzoyl derivative, and through the preparation of *N*-methyljamaicensine. The latter compound gave a negative Simon test. Additional analytical determinations indicated that one active hydrogen atom was present in the alkaloid, and that no C-methyl, *N*-methyl or *O*-methyl groups were present. No absorption was found through the ultraviolet region (above 220 mμ). The infrared absorption spectrum showed a strong carbonyl band at 1625 cm.$^{-1}$; this suggested that the oxygen atom was present in an amide group, possibly of the α-piperidone type. Strong absorption bands at 919 and 998 cm.$^{-1}$ and absorption at 3078 cm.$^{-1}$ in the carbon-hydrogen region suggested that a vinyl group $RCH{=}CH_2$ was present.[3] When the alkaloid was hydrogenated in acetic acid solution with platinum (Adams' catalyst), dihydrojamaicensine was formed. The infrared spectrum of this compound retained the carbonyl (amide) absorption band, but the bands at 3078 and 998 cm.$^{-1}$ were no longer present and only a weak band remained at 919 cm.$^{-1}$. Additional evidence for a terminal methylene group was obtained by oxidation of the alkaloid with a periodate-permanganate mixture; formaldehyde was isolated as the dimedone derivative.

The reduction of the ethylenic double bond and of the carbonyl (amide) group was effected in hydrochloric acid solution with a platinum catalyst. Dihydrodesoxyjamaicensine contained no oxygen and the infrared spectrum showed no evidence of a carbonyl or a terminal methylene group. This reduction method is applicable to lactams of the sparteine family.[4] The sum of evidence suggests that jamaicensine is a tricyclic base containing a lactam group, a secondary amino group, and a side chain with a vinyl group.

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