TABLE II

ULTRAVIOLET SPECTRA AND R_f VALUES OF MARITIMEIN AND RELATED AURONES

Aurone	λ_{max}[d] 95% EtOH				EtOH–NaOEt	R_f BAW	R_f 30% HOAc	R_f 50% HOAc	Colors UV	Colors UV/NH_3	Colors 1% aq. Na_2CO_3 spray
Maritimein	242	274	330	419	505	0.42	0.21	0.37	Y	R	P
Maritimetin	..	270	355[a]	413	Dec.	.53	.10	.24	Y	R	Pk
6,7,3′,4′-Tetrahydroxy	252	268	355[a]	415[c]	Dec.	.53	.09	.24	Y	R	Pk
Methylated maritimein			[b]	408	No shift	.88	.53	.75	YG	YG	..
Methylated maritimetin			[b]	403	No shift	.82	.17	.54	YG	YG	..
6,7,3′,4′-Tetramethoxy	256	268[a]	340[a]	404	No shift	.82	.18	.54	YG	YG	..
Leptosin	257	276.5	328.5	411	522	.51	.33	.52	Y	R	P
Leptosidin	257	272	340	406	396, 459	.76	.19	.41	Y	OR	Pk
6-Methoxy-7,3′,4′-trihydroxy	245	272	337	413	355, 477	.69	.18	.40	Y	R	P
6,7-Dimethoxy-3′,4′-dihydroxy	257	272	332.5	406	312, 487	.78	.19	.47	Y	R	P
Hydrolyzate of methylated maritimein	[b]		...	401	425	.83	.17	.50	YG	O	..
6-Hydroxy-7,3′,4′-trimethoxy	255	268	...	401	424	.83	.18	.50	YG	O	..
7-Hydroxy-6,3′,4′-trimethoxy	243	266	358	411	362, 447	.83	.20	.52	G	B	..

[a] Inflection. [b] Not measured in this region. [c] Max. at 413 in presence of trace of acid. [d] The spectra of these compounds do not shift on adding EtOH–$AlCl_3$.

acetone and the product was identical with authentic 6,7,-3′,4′-tetramethoxyaurone.

Maritimein was methylated with methyl sulfate, potassium carbonate and acetone. The spectrum of the methylated product did not shift in the presence of alkali, indicating that complete methylation had taken place. This product was hydrolyzed for three hours with dilute 2 *N* acid at 100°. The cooled solution was extracted with ethyl acetate and the organic extract was dried and evaporated. The residue was identical with authentic 6-hydroxy-7,3′,4′-trimethoxyaurone (VI) (see Table II).

Synthesis of Aurones.—The method used was exactly that described earlier.[6] The preparation of 6,7,3′,4′-tetrahydroxyaurone will be described elsewhere.[8] The other new aurones are described here.

6-Hydroxy-7-methoxycoumaranone and veratraldehyde gave **6-hydroxy-7,3′,4′-trimethoxyaurone**, yellow needles, m.p. 204–205°, from aqueous acetic acid.

Anal. Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.92. Found: C, 65.82; H, 5.19.

7-Hydroxy-6-methoxycoumaranone and veratraldehyde gave **7-hydroxy-6,3′,4′-trimethoxyaurone**, yellow needles, m.p. 210–211°, from aqueous acetic acid.

Anal. Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.92. Found: C, 65.79; H, 5.30.

Acknowledgments.—The authors thank the U. S. Public Health Service for a research grant (G-3667), and Eli Lilly and Company for a Fellowship to J. B. H. A gift of 6,7,3′,4′-tetrahydroxyflavanone from Dr. M. K. Seikel is gratefully acknowledged.

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

Anthochlor Pigments. XIII. The Ultraviolet Absorption Spectra of Phenolic Plant Pigments. Polyhydroxyaurones

BY T. A. GEISSMAN AND J. B. HARBORNE

RECEIVED JULY 25, 1955

As an aid in the identification of aurone plant pigments, the ultraviolet spectra of twenty-seven hydroxylated or methoxylated aurones have been measured in both neutral and in alkaline solution. While the presence of a 4- or 3′-hydroxyl-, or a 5-hydroxyl- in a 6-hydroxyaurone, does not change the spectra appreciably, a 6-hydroxyl group has a pronounced hypsochromic effect on aurone spectra. The following hydroxyl groups are bathochromic: 2′-, 4′-, 7- in the presence of 6-, and 3′ in the presence of 4′-. These results are interpreted as being partly due to cross conjugation. Comments are included on the spectra of aurone glycosides and the spectra in alkaline solution.

Although aurones (benzalcoumaran-3-ones) (*e.g.*, I) have been known for a long time, it is only recently that they have been found to occur in nature. Three such compounds have been isolated as glycosides from the flower petals of certain *Compositae*, especially the genus *Coreopsis*, and other plants in these laboratories[1] and elsewhere.[2–4] They are leptosidin (I, R = H, R′ = OMe), aureusidin (I, R = OH, R′ = H) and sulfuretin (I, R = R′ = H). Because of their bright golden yellow colors, these substances are important contributors to the pigmentation of the flowers in which they occur.

Recent chromatographic and spectral studies of the petal extracts of *Coreopsis maritima* Hook. have revealed the presence of a new aurone glycoside, maritimein, in this plant. As only micro quantities of this new compound were available, the absorption spectra of a number of polyhydroxyaurones were measured in order to provide a means of identifying its structure. No comprehensive study has previously been made of the spectra of these

(1) (a) T. A. Geissman and C. D. Heaton, THIS JOURNAL, **65**, 677 (1943); **66**, 486 (1944); (b) T. A. Geissman and M. K. Seikel, *ibid.*, **72**, 5725 (1950); (c) T. A. Geissman and W. Mojé, *ibid.*, **73**, 5765 (1951).

(2) M. Shimokoriyama and S. Hattori, *ibid.*, **75**, 1900 (1953).

(3) A. Ballio, S. Dittrich and G. B. Marini-Bettolo, *Gazz. chim. ital.*, **83**, 224 (1953).

(4) C. G. Nordstrom and T. Swain, *Chemistry and Industry*, 823 (1953).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF POLYHYDROXYAURONES

[a] Indicates inflection

	Aurones		λ_{max} (log ϵ) in 95% EtOH				λ_{max} (log ϵ) in EtOH–NaOEt color of alkaline soln.	
II	Parent compd.	max.	251(4.10)	.....	316.5(4.27)	379(4.06)	.....	
		min.		279(3.85)	349(3.81)		.....	
III	4-Hydroxy-	max.	225[a](4.14)	.....	307(4.26)	389(4.25)	443(4.27)	
		min.		253(3.75)	344(3.72)		yellow	
IV	4-Methoxy-	max.	225(4.12)	261(3.86)	308(4.25)	387(4.33)	.....	
		min.	252(3.81)	268(3.83)	342(3.74)		.....	
V	6-Hydroxy-	max.	229(4.10)	257[a](3.92)	344(4.43)	.....	402(4.39)	
		min.		276(3.80)			yellow	
VI	2'-Hydroxy-	max.	250(4.07)	270(4.11)	317(4.05)	402(4.27)	367(4.01)	499(4.24)
		min.	257(4.00)	293(3.93)	342(3.90)		carmine red	
VII	3'-Hydroxy-	max.	252(4.03)	268(4.12)	316(4.21)	381(4.29)	330(4.17)	381(4.30)
		min.		286(3.90)	341(3.95)		yellow	
VIII	4'-Hydroxy-	max.	.....	260(4.32)	346(4.07)	405(4.47)	358(3.70)	487(4.65)
		min.		307(3.67)	353(4.06)		orange	
IX	3',4'-Dihydroxy-	max.	259(4.09)	277(4.16)	330(3.87)	415.5(4.43)	516(4.47)	
		min.	265(4.08)	302(3.65)	343(3.85)		deep purple	
X	3'-Hydroxy-4'-methoxy-	max.	257(4.08)	276(4.12)	325(3.90)	409(4.32)	393(4.21)	463(4.07)
		min.	262(4.07)	299(3.66)	343(3.86)		orange	
XI	4'-Hydroxy-3'-methoxy-	max.	262[a](4.07)	275(4.12)	327(3.79)	413(4.38)	347(3.79)	510(4.56)
		min.		304(3.65)	331(3.78)		carmine red	
XII	6,7-Dihydroxy-	max.	242[a](3.93)	.....	321(4.15)	379(4.19)	430, 520(unstable)	
		min.		271(3.51)	339(4.10)		violet	
XIII	6-Hydroxy-7-methoxy-	max.	228(4.16)	.....	315[a](4.16)	361(4.34)	375[a](4.32)	422(4.47)
		min.		273(3.70)			yellow	
XIV	7-Hydroxy-6-methoxy-	max.	243[a](4.00)	.....	323(4.28)	385(4.22)	330(4.39)	458(3.91)
		min.		272(3.56)	353(4.16)		orange yellow	
XV	6,7-Dimethoxy-	max.	257[a](3.79)	.....	345[a](4.33)	368(4.35)	.....	
		min.		273(3.62)			.....	
XVI	5,6-Dihydroxy-	max.	230[a](3.93)	273(3.97)	347(4.49)	.....	382(4.42)	505(3.95)
		min.	252(3.75)	285(3.89)			red	
XVII	5,6-Dimethoxy-	max.	230(4.01)	263(4.02)	344(4.51)	.....	.....	
		min.	250(3.86)	281(3.80)			.....	
XVIII	4,4'-Dihydroxy-	max.	230(4.14)	253(4.07)	337(4.09)	408(4.51)	385(4.16)	473(4.64)
		min.	247(4.04)	280(3.82)	357(4.00)		orange	
XIX	6,4'-Dihydroxy-	max.	234(4.01)	254(4.09)	.....	388(4.44)	454(4.65)	
		min.	238(4.00)		287(3.60)		yellow	
XX	6-Hydroxy-4'-methoxy-	max.	245(4.21)	.....	370(4.47)	387(4.48)	405(4.60)	
		min.		288(3.70)			yellow	
XXI	5,6,4'-Trihydroxy-	max.	258(4.05)	271[a](3.99)	.....	381(4.55)	435(4.61)	
		min.			295(3.73)		orange	
XXII	4,6,4'-Trihydroxy-	max.	225(4.21)	245[a](4.09)	345[a](4.27)	392(4.50)	352(4.30)	445(4.59)
		min.		279(3.47)			deep yellow	
XXIII	6,7,4'-Trihydroxy-	max.	241(4.12)	.....	355[a](4.22)	407(4.39)	508 (unstable)	
		min.		288(3.50)			crimson	
XXIV	4,3',4'-Trihydroxy-	max.	256(3.91)	274(4.02)	310(3.92)	416(4.47)	360, 510 (unstable)	
		min.	258(3.90)	293(3.84)	342(3.79)		crimson	
XXV	6,3',4'-Trihydroxy-	max.	257(4.13)	270(4.09)	.....	399(4.55)	464 (unstable)	
		min.	265(4.08)		295(3.86)		orange red	
XXVI	5,6,3',4'-Tetrahydroxy-	max.	.....	266(4.10)	.....	395(4.53)	(very unstable)	
		min.	240(3.85)		297(3.75)		red	
XXVII	6,7,3',4'-Tetrahydroxy-	max.	252(4.01)	268(3.95)	355[a](4.19)	415(4.48)	(very unstable)	
		min.		294(3.57)			purple	
XXVIII	4,6,3',4'-Tetrahydroxy-	max.	254(3.95)	269(3.90)	336(4.16)	399(4.44)	(very unstable)	
		min.	263(3.89)	288(3.66)			red	

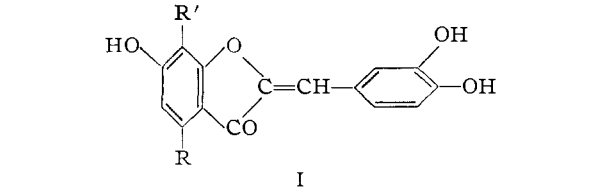
pigments. Geissman and Seikel[1b] have recorded and commented on the spectra of aureusidin and leptosidin and their glycosides. Geissman and Jurd[5] have confirmed the structure of sulfurein, sulfuretin 6-glucoside, by comparison of the spec-

(5) T. A. Geissman and L. Jurd, THIS JOURNAL, 76, 4475 (1954).

tra of the natural and synthetic methylated derivatives. Also the structure of the two different glucosides of aureusidin has been proved by the aid of spectral measurements.[6] A systematic study of the spectra of mono- and polyhydroxyaurones has therefore been made in order to aid in the identification of new aurones and in the hope of finding useful correlations between structure and absorption spectra in this class of compounds.

The absorption maxima and minima in both neutral and in alkaline solution of twenty-seven hydroxylated or methoxylated aurones are presented in Table I. As will be seen, the majority of aurones show four maxima, two of which are in the 240–280 mμ range. These two maxima may be attributed to the contributions from the simpler vibrations in the aurone molecule (*e.g.*, of the phenyl group of the A ring (*cf.* XXIX) with the adjacent carbonyl group). No attempt will be made here to analyze the slight variations of these short wave length maxima. Of much more interest are the two (sometimes single) maxima in the range above 300 mμ, which can be attributed to the resonance contributions of the carbonyl group with the different conjugated systems in the aurone molecule. These maxima are considerably shifted by the introduction of hydroxyl or alkoxyl substituents, especially in the 6-, 7- and 4′-positions.

Monohydroxyaurones.—Aurones absorb at longer wave lengths than any of the other closely related flavonoid plant pigments, *e.g.*, the flavanones, chalcones and especially the isomeric flavones. For example, the long wave length band of flavone is at 297 mμ and that of aurone is at 379 mμ; that of 2′-hydroxychalcone is intermediate at 312 mμ. This greater shift toward the visible region has been ascribed to three factors: (1) the greater strain in the five-membered heterocyclic ring,[1b] (2) the presence of an exocyclic double bond,[1b] and (3) the chromolatory effect of the A-benzene ring in conjugation with the —C=CH—B ring through the ether oxygen atom.[7] A fourth factor, that of cross-conjugation, is now advanced. There are present in the aurone molecule two opposed resonating systems, namely, that of the carbonyl group with the B ring through the ethylene double bond (see XXIX), and that of the carbonyl group with the A ring. Comparisons with the flavone series, where the exocyclic double bond of an aurone is readily accommodated inside the 6-membered γ-pyrone ring, making resonance structures such as XXX important contributors, suggests that in flavones cross-conjugation is not likely to be such an important factor. This is borne out by the following observations.



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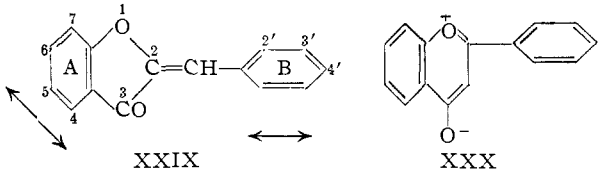


XXIX XXX

A comparison of the long wave length maxima of simple monohydroxyaurones and the related flavones is given in Table II.

TABLE II

LONG WAVE LENGTH BANDS OF FLAVONES AND AURONES[a]

	Flavones		Aurones	
Substituent	λ_{max}	$\Delta\lambda$	λ_{max}	$\Delta\lambda$
Parent compd.	297	..	379	..
3′-Hydroxy	297	0	381	+2
7-Hydroxy[b]	308	+11	344	−35
2′-Hydroxy	..	..	402	+23
4′-Hydroxy	327	+30	405	+26
5-Hydroxy[c]	337	+40	389	+10

[a] $\Delta\lambda$ = difference in mμ between the maximum of the parent compound and that of the substituted compound. [b] This is the 6-position in the aurone series. [c] This is the 4-position in the aurone series.

As may be seen from Table II, the effect of introducing hydroxyl groups into the B ring of the aurone molecule is approximately the same as in the flavone series and does not require comment. However, the presence of a hydroxyl group in the A ring *para* to the carbonyl group causes a small bathochromic shift in the case of the flavones but a large hypsochromic shift in the aurone series. This may be explained by considering the effect of the two opposed systems in the aurones, as mentioned above. In aurone itself, the 316.5 mμ maximum can be attributed to the absorption of the resonance system, A-ring—C=O, and the 379 mμ maximum to the resonance system, B-ring—CH=C—C=O. In 6-hydroxyaurone, the contribution of the first system is greatly strengthened by the presence of the hydroxyl group in a conjugate position, and the contribution of the second species will be diminished, producing a maximum at 344 mμ intermediate between the two aurone maxima, the net effect being a hypsochromic shift. This result is illustrated in Fig. 1, which shows the spectra of aurone and its 6- and 4′-hydroxy derivatives.

In contrast to the effect of a 6-hydroxyl substituent, the introduction of a 4-hydroxyl group does not change the general shape of the spectra of aurone to any great extent. The small bathochromic shift of 10 mμ, given by 4-hydroxyaurone (λ_{max}, 389 mμ) as compared to aurone, is a much smaller shift than that given by the introduction of a 5-hydroxyl group in flavone (see Table II), indicating that some cross-conjugation is present in 4-hydroxylated aurones. But a 4-hydroxyl group, because of its position adjacent to the carbonyl group, is not able to provide the same directional cross-conjugation that the 6-hydroxyl group does in the "A-ring carbonyl" system. Furthermore, hydrogen bonding between the 4-hydroxyl and 3-carbonyl, although probably only a very minor factor, will tend to increase the contribution of the "B-ring" system.

That there is only a small degree of hydrogen

(6) T. A. Geissman and J. B. Harborne, THIS JOURNAL, **77**, 4622 (1955).

(7) A. E. Bradfield and A. E. Flood, *J. Chem. Soc.*, 4740 (1952).

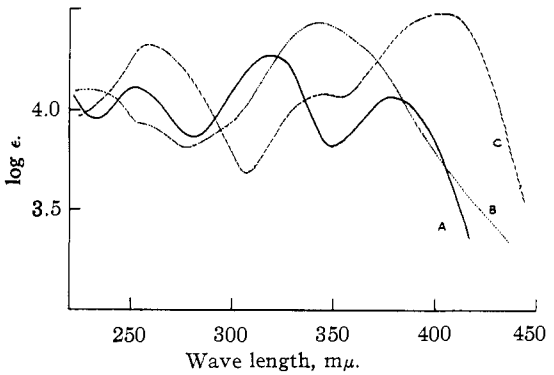


Fig. 1.—Ultraviolet absorption spectra, in 95% ethanol, of: A, aurone; B, 6-hydroxyaurone; C, 4′-hydroxyaurone.

bonding between the 4-hydroxyl and 3-carbonyl group in aurones is already known from chemical evidence (*e.g.*, the ease of methylation of the 4-hydroxyl group). A study of the spectra of 4-hydroxy- and 4-methoxyaurone in ethanol and cyclohexane further shows that there is only a small amount of hydrogen bonding, since the hypsochromic shift of the longer wave length bands caused by methylation is very small, even in the non-hydroxylic solvent

	λ_{max} in 95% EtOH	λ_{max} in cyclohexane
4-Hydroxyaurone	307, 389	305, 320, 384
4-Methoxyaurone	308, 387	303, . . . , 376

This may be compared, for example, with *o*-hydroxyacetophenone (λ_{max} 327 mμ, 95% EtOH; 329 mμ, hexane)[8] and *o*-methoxyacetophenone (λ_{max} 305 mμ, 95% EtOH; 300 mμ, hexane)[8] where the removal of normal hydrogen bonding causes hypsochromic shifts of 22–29 mμ, depending on the solvent. This lack of hydrogen bonding reflects the lack of polarity in the carbonyl group of aurones, which prefers to remain in the >C=O form. Steric factors cannot be important here, since normal chelation, *e.g.*, with aluminum ion,[9] takes place between the 4-hydroxyl and the 3-carbonyl groups.

Polyhydroxyaurones.—Cross-conjugation accounts for the large hypsochromic shift of the long wave length band of 6-hydroxyaurone as compared with aurone itself, and similar but smaller hypsochromic shifts in polyhydroxyaurones bearing a 6-hydroxyl group can be similarly accounted for. Thus, the introduction of a 6-hydroxyl group into 4′-hydroxyaurone (λ_{max} 405 mμ) and 3′,4′-dihydroxyaurone (λ_{max} 415.5 mμ) causes hypsochromic shifts of 17 and 13 mμ, respectively. As expected, the further addition of a 4-hydroxyl group, giving 4,6,4′-trihydroxy- and 4,6,3′,4′-tetrahydroxyaurone does not alter the spectra appreciably. In the same way, the addition of a 4-hydroxyl group to 4′-hydroxy- and 3′,4′-dihydroxyaurone, giving XVIII and XXIV, does not have much effect on the corresponding spectra.

3′,4′-Dihydroxyaurone absorbs 10.5 mμ further in the visible than 4′-hydroxyaurone—the well known effect of a hydroxyl group increasing the resonance contribution of an adjacent hydroxyl group although not itself in a conjugate position. A comparable example is that of methyl *p*-hydroxycinnamate (λ_{max} 312.5 mμ) and methyl 3,4-dihydroxycinnamate (λ_{max} 322.5 mμ), where the shift is almost identical. A methoxyl group in the 3′-position is also effective in this respect (*cf.* XI, Table I) and the isomeric 3′-hydroxy-4′-methoxyaurone (X) absorbs 4 mμ further in the visible than 4′-hydroxyaurone.

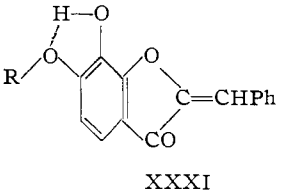
The effects on the visible spectra of introducing 5- and 7-hydroxyl groups into 6-hydroxy-, 6,4′-dihydroxy- and 6,3′,4′-trihydroxyaurone are summarized in Table III, and illustrated in Figs. 2–5. It will be seen that the introduction of a 5-hydroxyl group causes only very small shifts in the long wave length spectra of these three compounds. Therefore, it cannot contribute to any large extent to the resonance hybrids of the respective compounds. On the other hand, the introduction of a 7-hydroxyl group into a 6-hydroxyaurone has a large bathochromic effect, which is very nearly equal to the original hypsochromic effect of the 6-hydroxyl group, as is shown in Table III.

TABLE III

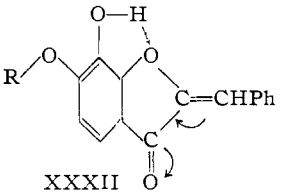
INTRODUCTION OF 5- AND 7-HYDROXYL GROUPS INTO AURONES

Aurone	λ_{max}, mμ	Aurone	λ_{max}, mμ
6-OH	344	6,7,4′-triOH	407
5,6-diOH	347	4′-OH	405
6,7-diOH	379	6,3′,4′-triOH	399
Parent compd.	379	5,6,3′,4′-tetraOH	395
6,4′-diOH	388	6,7,3′,4′-tetraOH	415
5,6,4′-triOH	381	3′,4′-diOH	415.5

This effect has been studied more closely in the case of 6,7-dihydroxyaurone (XII) and the spectra of its partially and fully methylated derivatives have also been taken (*cf.* XII–XV, also Fig. 5). Methylation of the 7-hydroxyl group causes a hypsochromic shift, indicating that the original bathochromic effect might be partially due to hydrogen bonding of the 7-hydroxyl group with either the 6-hydroxyl (or methoxyl) group XXXI or the ether oxygen atom of the aurone as in XXXII. In both cases, the effectiveness of the "A-ring carbonyl"



XXXI



XXXII

resonance will be reduced, the effectiveness of the "B-ring-C=C-carbonyl" resonance will be increased, thus leading to the over-all bathochromic shift that is actually observed. In effect, then, the 7-hydroxyl, and not the 5-hydroxyl, group is bathochromic in 6-hydroxyaurones because of its unique position with ether oxygen atoms which are in conjugation with the carbonyl group adjacent to it on either side and thus, for steric reasons, hydrogen bonding becomes an important factor.

Aurone Glycosides.—The glycosides of all the known naturally occurring aurones all have

(8) R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940).
(9) J. B. Harborne, *Chemistry and Industry*, 1142 (1954).

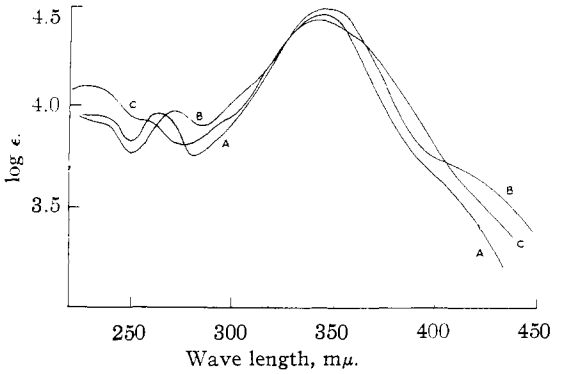


Fig. 2.—Ultraviolet absorption spectra, in 95% ethanol, of: A, 5,6-dimethoxyaurone; B, 5,6-dihydroxyaurone; C, 6-hydroxyaurone.

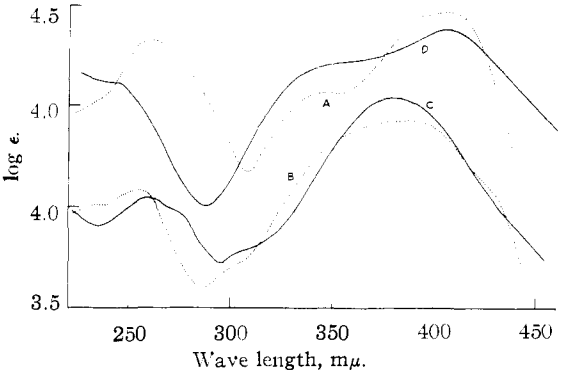


Fig. 3.—Ultraviolet absorption spectra, in 95% ethanol, of: A, 4′-hydroxyaurone; B, 6,4′-dihydroxyaurone; C, 5,6,4′-trihydroxyaurone; D, 6,7,4′-trihydroxyaurone.

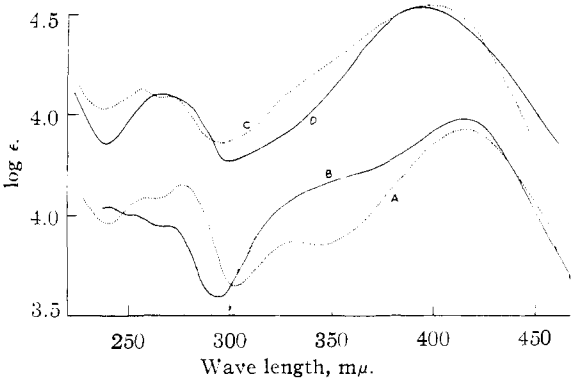


Fig. 4.—Ultraviolet absorption spectra, in 95% ethanol, of: A, 3′,4′-dihydroxyaurone; B, 6,7,3′,4′-tetrahydroxyaurone; C, 6,3′,4′-trihydroxyaurone; D, 5,6,3′,4′-tetrahydroxyaurone.

maxima which are shifted between 4 to 6 mμ further toward the visible as compared with their aglycones. Furthermore, the spectra of the glycoside acetates differ in several details from the spectra of the aglycone acetates, which they would be expected to resemble more closely than they do.[1b] Both these results are different from experience in related compounds, such as the flavones, where the presence of a sugar molecule does not usually alter the spectra. Thus the spectra of both apigenin and luteolin glycosides are identical with the spectra of

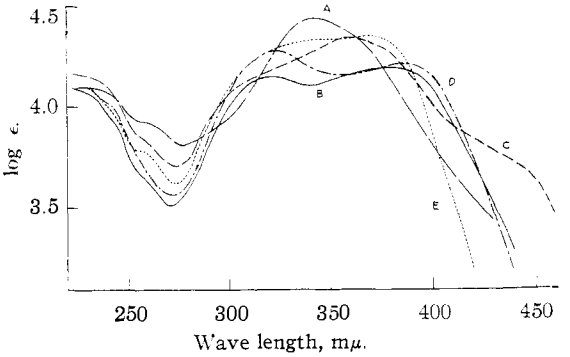


Fig. 5.—Ultraviolet absorption spectra, in 95% ethanol, of: A, 6-hydroxyaurone; B, 6,7-dihydroxyaurone; C, 6-hydroxy-7-methoxyaurone; D, 6-methoxy-7-hydroxyaurone; E, 6,7-dimethoxyaurone.

their respective aglycones.[10] The difference thus disclosed may now be explained, since the sugar residues of all the known aurone glycosides are attached to the A ring of the aurone molecule at the 4-, 6- or 7-positions, which are all in some way involved in the "A-ring carbonyl" resonance. The presence of a sugar residue on these hydroxyl groups will abolish the ability of these groups to ionize and thus decrease their ability to resonate through the benzene ring with the carbonyl group. There will thus be a diminution of the "A-ring carbonyl" contribution and a consequent increase in the contribution of the opposing system, thus accounting for the small observed bathochromic shift.

Alkaline Spectra.—The long wave length band of the majority of polyhydroxyaurones listed in Table I undergoes pronounced shifts in the presence of ethanolic sodium ethoxide, although in a few cases decomposition occurs before measurements can be taken. The colors in alkaline solution are also characteristic, and indicate approximately the magnitude of the spectral shift, from the original pale yellow to deep yellow, orange, red, violet or blue. In general, the magnitude of the shift is comparable with those recorded for simpler phenolic compounds, although there is an increase in the shift shown by aurones as a result of the added opportunity for resonance over the whole aurone molecule. Thus, 6-hydroxyaurone ($\Delta\lambda_{alk}$, 58 mμ)[11] has a larger shift than 4-hydroxyacetophenone ($\Delta\lambda_{alk}$, 50 mμ) and 4′-hydroxyaurone ($\Delta\lambda_{alk}$, 82 mμ) a larger shift than 4-hydroxybenzalacetophenone, *p*-HO—C_6H_4—CH=CHCOCH$_3$, ($\Delta\lambda_{alk}$, 69 mμ).

The effects of cross-conjugation are considerably more pronounced in the alkaline than in the neutral spectra. However, it is not possible to relate the magnitude of the alkaline shift to the position of the hydroxyl groups in more than the very simplest cases. This is because of uncertainties regarding the extent to which polyhydroxyaurones are ionized, and also because some aurones—particularly those with *o*-dihydroxyl groupings—are very unstable in alkaline solution. In the simpler cases where only one or two hydroxyl groups are involved, the relationship of alkaline shifts and posi-

(10) C. G. Nordstrom and T. Swain, *J. Chem. Soc.*, 2764 (1953).

(11) $\Delta\lambda_{alk}$ is the difference between the maxima of the long wave length bands in neutral and in alkaline solution.

tion of hydroxyl groups has already been dealt with in the 4,6,3′,4′-tetrahydroxyaurone series.[6] These cross-conjugated effects are best illustrated here by the results shown in Table IV.

TABLE IV

Aurone	λ_{max}, 95% EtOH	λ_{max}, EtOH/ NaOEt	$\Delta\lambda_{alk}$, mμ
6-Hydroxy-	344	402	58
6-Hydroxy-3′,4′-methylenedioxy	397	408	11
6-Hydroxy-3′,4′-dimethoxy	396	410	14
6-Hydroxy-4′-methoxy	387	405	18
6,4′-Dihydroxy	388	454	66
4′-Hydroxy	405	487	82

evaporated. The resulting crude ω-chloroketone was heated directly with anhydrous sodium acetate (50 g.) in ethanolic solution (50 cc.) at 100° for 2 hours. After the addition of water, the solution was extracted with ether and this extract was dried and evaporated. The product crystallized from a large volume of water (norite) to give **5,6-dihydroxycoumaranone** as colorless needles, m.p. 260° dec. It gave an intense green color with aqueous ferric chloride; yield 4.4 g. (18% over-all).

Anal. Calcd. for $C_8H_6O_4$: C, 57.84; H, 3.64. Found: C, 57.59; H, 3.69.

Preparation of Aurones.—The aurones were all prepared by the method, described earlier,[5] of condensing the respective coumaranones with the appropriate aromatic aldehyde. Many of these aurones have been described before, and their properties agreed with those recorded in the literature. The new aurones are listed in Table V.

TABLE V

NEW AURONES

Aurone	M.p., °C.	Properties	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
4-Hydroxy-	141–143	Yellow needles[c]	$C_{15}H_{10}O_3$	75.95	75.63	4.46	4.23
4-Methoxy-	149	Pale yellow needles[c]	$C_{16}H_{12}O_3$	76.03	76.17	5.13	4.80
3′-Hydroxy-	190–191	Yellow plates[d]	$C_{15}H_{10}O_3$	75.55	75.63	4.44	4.23
6-Hydroxy-7-methoxy-	160–162	Yellow needles[e]	$C_{16}H_{12}O_4$	71.64	71.62	4.72	4.51
5,6-Dihydroxy-	245	Orange red plates[e]	$C_{15}H_{10}O_4$	70.34	70.87	4.14	3.97
5,6-Dimethoxy-	168	Lemon yellow needles[b,f]	$C_{17}H_{14}O_4$	72.34	72.32	5.18	5.00
4,4′-Dihydroxy-	237–238	Yellow orange needles[e]	$C_{15}H_{10}O_4$	70.68	70.87	4.12	3.97
6,4′-Dihydroxy-	288[a]	Yellow needles[c]	$C_{15}H_{10}O_4$	70.63	70.87	4.13	3.97
6-Hydroxy-4′-methoxy-	259	Pale yellow needles[e]	$C_{16}H_{12}O_4$	71.76	71.63	4.64	4.51
3′-Hydroxy-4′-methoxy-	180	Orange plates[e]	$C_{16}H_{12}O_4$	71.39	71.63	4.82	4.51
3′-Methoxy-4′-hydroxy-	195–196	Deep yellow needles[e]	$C_{16}H_{12}O_4$	71.63	71.63	4.78	4.51
5,6,4′-Trihydroxy-	320[a]	Yellow needles[d]	$C_{15}H_{10}O_5$	66.41	66.66	3.91	3.73
4,6,4′-Trihydroxy-	295–300[a]	Yellow needles[e]	$C_{15}H_{10}O_5$	66.59	66.66	3.96	3.73
4,3′,4′-Trihydroxy-	310[a]	Yellow needles[e]	$C_{15}H_{10}O_5$	66.53	66.66	3.98	3.73
5,6,3′,4′-Tetrahydroxy-[b]	298[a]	Orange powder[b,g]	$C_{15}H_{10}O_6$	61.46	62.94	3.86	3.52
6,7,3′,4′-Tetrahydroxy-	292[a]	Orange needles[h]	$C_{15}H_{10}O_6$	62.88	62.94	3.70	3.52

[a] M.p. with decomposition. [b] Prolonged drying failed to remove traces of moisture (*e.g.*, $C_{15}H_{10}O_6 \cdot {}^1/_2H_2O$ requires C, 61.03; H, 3.76%). The tetraacetate was prepared, pale green needles, m.p. 234° (*Anal.* Calcd. for $C_{23}H_{18}O_{10}$: C, 60.79; H, 3.99. Found: C, 60.56; H, 4.03). Crystallizing solvent: [c] petroleum ether; [d] aqueous ethanol; [e] aqueous acetic acid; [f] ethanol; [g] ethyl acetate–petroleum ether; [h] water.

Experimental

5,6-Dihydroxycoumaranone.—A solution of hydroxyhydroquinone (18.6 g.) and chloroacetonitrile (14 cc.) in dry ether (300 cc.) containing anhydrous zinc chloride (10 g.) was saturated with dry hydrogen chloride and then kept at 0° for 2 days. After decanting the ether, the residue was washed with fresh dry ether and then hydrolyzed with water (300 cc.) for one hour at 100°. The cold solution was then extracted thrice into ether, and this extract was dried and

Acknowledgments.—This work was supported by a research grant (G-3667) from the U. S. Public Health Service and a Grant-in-Aid from Eli Lilly and Company, to whom the authors express their thanks. The authors are grateful to Dr. F. M. Dean for helpful comments.

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