APPENDIX

Ultraviolet Absorption Spectra of some Polyhydroxyanthraquinones

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In an endeavour to obtain guidance as to the location of the hydroxyl groups of polyhydroxyanthraquinones isolated from natural sources, and, in particular, of asperthecin, the ultraviolet absorption spectra of some of the natural and synthetic hydroxyanthraquinones of known constitution were examined in ethanolic solution and compared. Briggs, Nicholls & Paterson (1952) had made such determinations on compounds containing up to two free α-hydroxyl groups, but it appeared desirable to extend these observations to compounds of higher α-hydroxyl content. The wavelength and molar extinction coefficients of the maxima of the curves obtained are shown in Table 1 (p. 486). The absorption spectra were determined by means of a Hilger and Watts 'Uvispek' spectrophotometer.

Nearly all the curves show two major bands or groups of maxima (group *A*, lower λ and group *B*, higher λ) separated by a deep trough in the region 300–400 mμ. Chrysophanol and emodin (and ω-hydroxyemodin, the curve for which is almost indistinguishable from that of emodin) each containing two α-hydroxyl groups, are similar spectrographically; the additional hydroxyl group in the β- position present in emodin has only a small effect on the λ-values of the maxima, although the log ε values of the peaks in group *A* are considerably altered. In anthragallol (two β-, one α-OH) all the maxima occur at lower λ and the 285–290 band is intensified, relative to the other maxima of group *A*.

Islandicin and helminthosporin (three α-OH), which differ only in the position of the methyl group, show a general displacement of the bands towards the longer wavelengths only small in group *A*, but very marked in group *B*, with the appearance of fine structure in the latter group, three or four maxima being revealed in this range. The addition of a further α-hydroxyl group, represented by cynodontin (four α-OH) produces even further bathochromic displacement in group *B*, whereas in catenarin (three α-, one β-OH) the additional β-hydroxyl group has little effect on group *B* but seems to enhance the fine structure of group *A*, where there are now four clearly marked maxima as in emodin.

Rufigallic acid (two α, four β-OH) has one feature which distinguishes it from all the other compounds examined, namely a peak in the 350 mμ. region (anthragallol has a slight inflexion at this point). It is also characterized by a very high maximum at 295 mμ., even higher than anthragallol, although the general form of the curve is similar in the two cases, particularly in the group *B* region.

These results confirm the observations of Briggs *et al.* (1952) that the major band in the region from 350 mμ. upward is greatly affected by the number of α-hydroxyl groups, the presence of β-hydroxyl groups having little effect. It seems, however, that the number and position of the maxima in the lower wave band region (below 350 mμ.) is considerably influenced by the β-hydroxyl groups.

If the absorption spectrum of asperthecin is compared with the curves for those substances of known constitution which have been examined, it is evident that the closest resemblance is presented by the spectrum of catenarin. The resemblance is particularly marked in the group *B* portion, which suggests that three and not more than three α-hydroxyl groups are present in asperthecin. The differences in the group *A* portion of the curves could well be accounted for by the additional nuclear hydroxyl present in asperthecin, which if the above deduction is correct, must be in the β- position.

SUMMARY

1. The ultraviolet absorption spectra of nine natural and synthetic polyhydroxyanthraquinones of known structure have been determined.

2. From a comparison of these spectra with that of asperthecin it is concluded that the molecule of asperthecin probably has three α-hydroxyl groups in its structure.

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REFERENCE

Briggs, L. H., Nicholls, G. A. & Paterson, R. M. L. (1952). *J. chem. Soc.* p. 1718.

Table 1. *Ultraviolet spectra of polyhydroxyanthraquinones in ethanol*

Substituted anthraquinone	λ 210–240		λ 240–265		λ 265–287		λ 287–320		λ 320–480		λ 480–520		λ 520–560	
	mμ.	log ε	mμ.	log ε	mμ.	log ε	mμ.	log ε	mμ.	log ε	mμ.	log ε	mμ.	log ε
Chrysophanol (2-methyl-4:5-dihydroxy)	225	4·56	255	4·34	277·5	4·04	287·5	4·07	430	4·08	—	—	—	—
Emodin (2-methyl-4:5:7-trihydroxy)	222	4·55	252	4·26	265	4·27	289	4·34	437	4·10	—	—	520–30*	2·38
ω-Hydroxyemodin (2-hydroxymethyl-4:5:7-trihydroxy)	222·5	4·46	250·5	4·21	266	4·21	289·5	4·26	436	4·04	—	—	510–20*	2·92
Anthragallol (1:2:3-trihydroxy)	213	4·25	241 245	4·28 4·30	—	—	287	4·49	414	3·81	—	—	—	—
Islandicin (2-methyl-1:4:5-trihydroxy)	232	4·52	252·5	4·28	—	—	289	3·86	390–402* 466–70*	3·32 3·98	492 513	4·09 3·96	527	3·92
Helminthosporin (2-methyl-4:5:8-trihydroxy)	231	4·53	255	4·15	—	—	289	3·79	405–15*	3·85	480 490 510	3·99 4·01 3·89	525	3·81
Catenarin (2-methyl-1:4:5:7-tetrahydroxy)	231	4·51	255	4·23	280	4·24	298	4·03	—	—	488·5 508	4·16 4·06	515–525*	3·99
Cynodontin (2-methyl-1:4:5:8-tetrahydroxy)	221 237·5	4·22 4·32	—	—	—	—	296	3·63	—	—	518	3·90	545 558	3·88 3·94
Rufigallic acid (1:2:3:5:6:7-hexahydroxy)	213 222	4·21 4·18	258	3·85	—	—	295	4·64	349 438	3·92 3·92	—	—	—	—
Asperthecin	237·5	4·41	262·5	4·49	286·5	4·27	318	4·02	—	—	484 510	4·24 4·23	545–55*	3·66

* Inflexion.