425. *The Constitution of Tannins. Part IV. Absorption Spectra of Natural Phlobatannins and Synthetic Flavpinacols.*

By Alfred Russell, John Todd, and Cecil L. Wilson.

It has been shown (this vol., pp. 218, 1066, 1506) that the reduction by zinc dust and dilute alcoholic acid of 2-hydroxy-polyhydroxychalkones containing suitably oriented phenolic hydroxyl groups produces amorphous substances, which are qualitatively indistinguishable from natural phlobatannins and are probably flavpinacols. Since tannins can be recognised qualitatively only, it may be inferred that natural phlobatannins are flavpinacols hydroxylated in the manner indicated by the fission products which they yield on fusion with alkali.

Broadly speaking, this view is in harmony with the speculations of Freudenberg (" Tannin, Cellulose, Lignin," Berlin, 1933), who considers that phlobatannins are polymerides of 3-hydroxyflavans on account of the resemblance which catechin (3 : 5 : 7 : 3′ : 4′-pentahydroxyflavan), although not a tannin, bears to natural phlobatannins. The fact, however, that catechin is the only member of its class known to occur naturally, whereas a large number of phlobatannins are known, makes it unlikely that phlobatannins are hydroxyflavans polymerised at the 3-position.

Their amorphous nature precludes quantitative comparison of natural phlobatannins and synthetic flavpinacols. Accordingly, attention has been directed to comparative physicochemical measurements which are, at least partly, quantitative. Results, which could not be interpreted, were obtained in an attempted comparison of molecular weights by viscosity measurements along lines similar to those advocated by Staudinger (*Ber.*, 1932, **65**, 267) for complex aliphatic compounds. Absorption spectra measurements have, however, given results which confirm, beyond reasonable doubt, the view that phlobatannins are polyhydroxyflavpinacols. The absorption spectra of polyhydroxyflavpinacols are indistinguishable from those of typical natural phlobatannins, which, fortunately, are banded in a sufficiently characteristic manner (cf. curves for gallotannin and ellagic acid, containing the essential structures of the few natural tannins which are not phlobatannins, with those for hemlock and mimosa tannins).

FIG. 1.

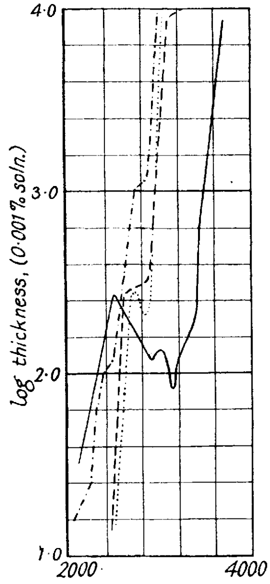


FIG. 2.

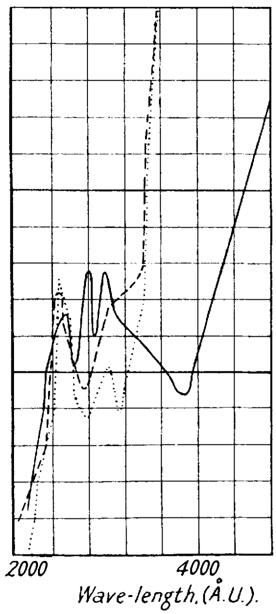


FIG. 3.

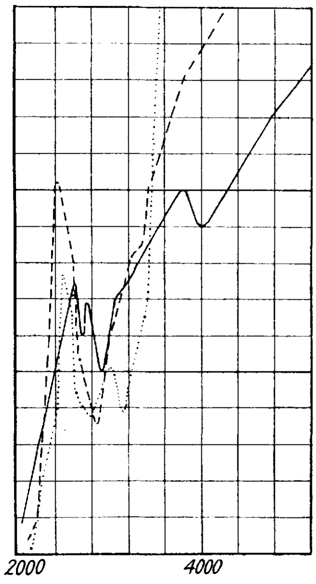


FIG. 1.

– – – – *Acetophenone.*
. . . . *Benzaldehyde.*
——— *Chalkone.*
–·–·–· *Bis-reduction product of chalkone.*

FIG. 2.

– – – – *Resacetophenone.*
. . . . *Protocatechualdehyde.*
——— 2 : 4 : 3′ : 4′-*Tetrahydroxychalkone.*

FIG. 3.

– – – *Phloracetophenone.* . . . . . *Protocatechualdehyde.* ——— 2 : 4 : 6 : 3′ : 4′-*Pentahydroxychalkone.*

Absorption curves are included for all the essential starting materials, for the intermediate polyhydroxychalkones, and for a number of 4-hydroxyflavpinacols, whose properties will be described later.

The Baly tube method was employed and the solvent was absolute alcohol showing no absorption above λ 2350. The instrument was a Hilger Medium Quartz Spectrograph (E2) having a dispersion sufficient to differentiate four of the seven absorption bands of benzene recorded by Baly and Collie (J., 1905, **87**, 1332) at λ 2410 (two bands), 2490, 2560, and 2610 (three bands).

Results.—Where possible these are given in tabular form.

Acetophenone (Fig. **1**). General absorption with a pronounced extension of the curve at λ 2620—2880 (cf. Baly and Collie, *loc. cit.*, p. 1343).

Hydroxy-ketones. The effect of introducing phenolic hydroxyl groups into acetophenone is very marked; the three derivatives examined have a similar banded structure (Table I). The extension measured may, of course, be a weak band.

TABLE I.

Ketone.	Head of band.	Extension.
Resacetophenone (Fig. 2)	2780	3000—3300
Phloracetophenone (Fig. 3)	2860	3200—3380
Gallacetophenone (Fig. 4)	2800	3260—3400

Benzaldehyde (Fig. 1). The absorption measured agrees with that recorded by Baly and Collie (*loc. cit.*); a small band with its head at λ 2850.

FIG. 4. FIG. 5. FIG. 6.

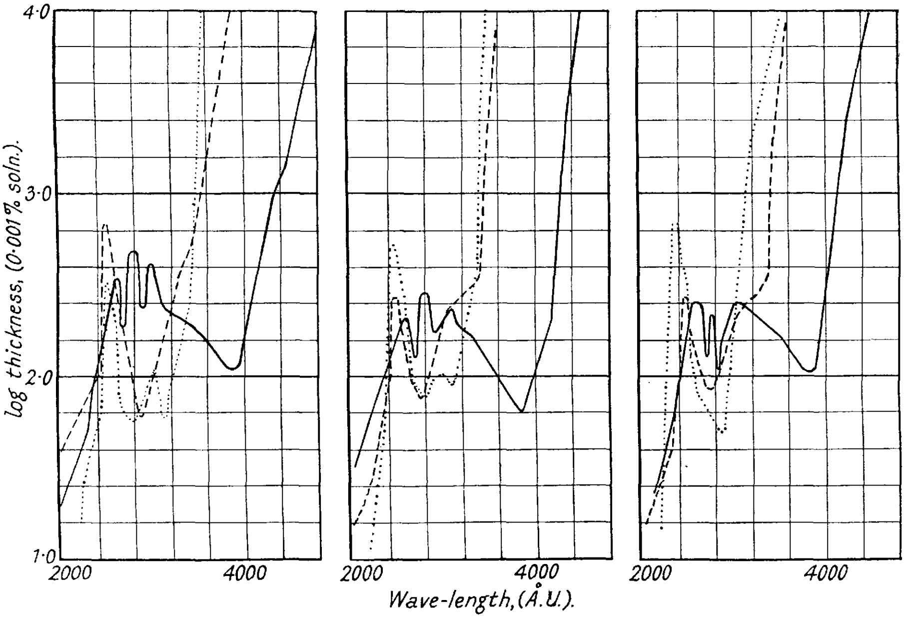


FIG. 4.

– – – – *Gallacetophenone.*
.... *Protocatechualdehyde.*
——— 2 : 3 : 4 : 3′ : 4′-*Pentahydroxychalkone.*

FIG. 5.

– – – – *Resacetophenone.*
.... *Vanillin.*
——— 2 : 4 : 4′-*Trihydroxy*-3′-*methoxychalkone.*

FIG. 6.

– – – – *Resacetophenone.* .... p-*Hydroxybenzaldehyde.* ——— 2 : 4 : 4′-*Trihydroxychalkone.*

Hydroxy-aldehydes. Again the effect of introducing phenolic groups is very marked.

TABLE II.

Aldehyde.	Inflexion.	Band head.	Band head.
p-Hydroxybenzaldehyde (Fig. 6) *	2650	2880	—
Protocatechualdehyde (Fig. 2)	—	2760	3120
Vanillin (Fig. 5) †	—	2780	3120

* Cf. Tuck, J., 1909, **95**, 1809. † Cf. Purvis, J., 1914, **105**, 2482.

The two bands given by protocatechualdehyde and vanillin merge, in greater thicknesses of solution, into one broad band.

Benzylideneacetophenone (*Chalkone*) (Fig. 1). The spectrum shows two bands: a weak one at λ 2880 and a stronger one at λ 3125, the two merging into one broad band. This is similar to the curve given by Stobbe and Ebert (*Ber.*, 1911, **44**, 1289), who found a broad band with its head at λ 2857 and an extension of the curve at λ 3100—3300, but totally unlike that given by Shibata and Nagai (*J. Chem. Soc. Japan*, 1923, **43**, 101), who found one broad band with its head at λ 3300. A repetition, using chalkone that had been further recrystallised twice, served only to verify the results now given.

Chalkone reduction product, $C_{30}H_{26}O_2$ (Fig. 1) (this vol., p. 1069). The absorption is general; the curve shows two small extensions at λ 2370—2500 and λ 2730—2880 which may be weak bands. It seems to be indicated, however, that reduction of chalkone destroys, or modifies considerably, the centres of absorption, a view which is in harmony with the change 2-hydroxychalkone ⟶ flavpinacol.

FIG. 7. FIG. 8. FIG. 9.

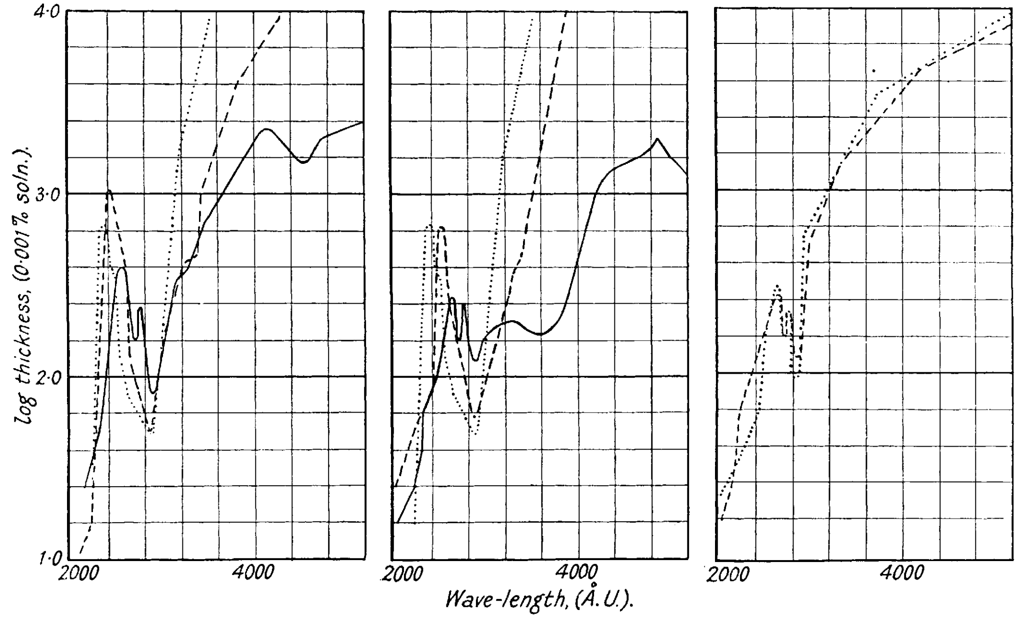


FIG. 7.

– – – – *Phloracetophenone.*
.... p-*Hydroxybenzaldehyde.*
——— 2 : 4 : 6 : 4′-*Tetrahydroxychalkone.*

FIG. 8.

– – – – *Gallacetophenone.*
.... p-*Hydroxybenzaldehyde.*
——— 2 : 3 : 4 : 4′-*Tetrahydroxychalkone.*

FIG. 9.

– – – – *Hemlock tannin.* .... *Mimosa tannin.*

TABLE III.

Chalkone.	Fundamental bands.		Extension.	Colour band.
2 : 4 : 3′ : 4′-Tetrahydroxy (Fig. 2)	2670	2900	3160—3380	3840
2 : 4 : 6 : 3′ : 4′-Pentahydroxy (Fig. 3)	2700	2880	3160—3300	3970
2 : 3 : 4 : 3′ : 4′-Pentahydroxy (Fig. 4)	2700	2890	3100—3500	3860
2 : 4 : 4′-Trihydroxy-3′-methoxy (Fig. 5)	2670	2910	3120—3320	3840
2 : 4 : 4′-Trihydroxy (Fig. 6)	2690	2810	3150—3400	3760
2 : 4 : 6 : 4′-Tetrahydroxy (Fig. 7)	2700	2880	3100—3300	4570
2 : 3 : 4 : 4′-Tetrahydroxy (Fig. 8)	2700	2880	3560	above 5000

2-*Hydroxy-polyhydroxychalkones.* The introduction of phenolic hydroxyl groups into chalkone modifies its spectrum considerably. This effect might be expected, since it corresponds to the change from chromogen to chromophore and indicates that it would be of interest to make a comprehensive examination of the absorption spectra of hydroxychalkones. The spectra are all very similar and show two, what may be called, fundamental bands in the ultra-violet region, an extension or shallow band at about λ 3100—3300, and a deep well-marked band partly in the visible region, accounting for the yellow-orange colour of hydroxychalkones. Table III shows the band measurements.

Flavpinacols. The curves show a close similarity in the ultra-violet region to those of the chalkones above, but the "colour band" has disappeared. Since bis-(7 : 4′-dihydroxy)-flavpinacol also shows a band above λ 5000, it is possible that reduction has shifted the "colour band" of the chalkones further towards the red end of the spectrum and out of the region examined for the other flavpinacols. It seems more likely, however, that the extra band in bis-(7 : 4′-dihydroxy)flavpinacol is due to the presence of a trace of unreduced chalkone, since an extension of the curve at about λ 3300 corresponds to the extension of the corresponding 2 : 4 : 4′-trihydroxychalkone.

FIG. 10.

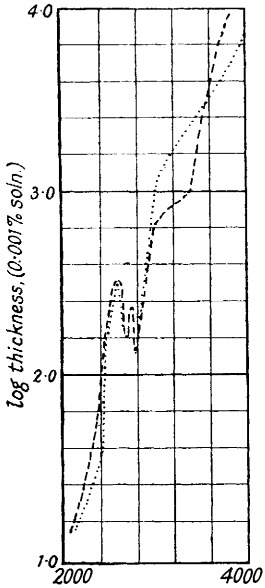


FIG. 11.

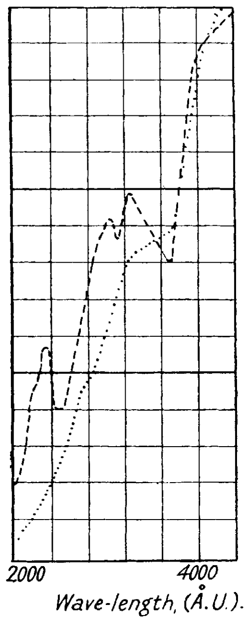


FIG. 12.

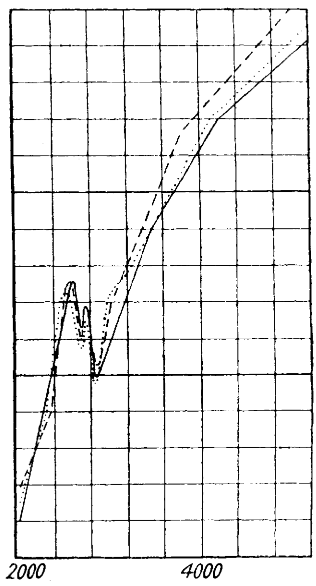


FIG. 10.

– – – – *Methylated hemlock tannin.*
.... *Methylated mimosa tannin.*

FIG. 11.

– – – – *Ellagic acid.*
.... *Gallotannin.*

FIG. 12.

– – – – *Bis-*(5 : 7 : 3′ : 4′*-tetrahydroxy)flavpinacol.* ——— *Bis-*(7 : 8 : 3′ : 4′*-tetrahydroxy)flavpinacol.*
.... *Bis-*(7 : 3′ : 4′*-trihydroxy)flavpinacol.*

3′ : 4′*-Dihydroxy-polyhydroxyflavpinacols* (qualitatively indistinguishable from phlobatannins: cf. this vol., pp. 218, 1066).

TABLE IV (FIG. 12).

Flavpinacol.	Band head.	Band head.
Bis-(7 : 3′ : 4′-trihydroxy)	2700	2850
Bis-(5 : 7 : 3′ : 4′-tetrahydroxy)	2700	2880
Bis-(7 : 8 : 3′ : 4′-tetrahydroxy)	2700	2890

4′*-Hydroxy-polyhydroxyflavpinacols.*

TABLE V (FIG. 13).

Flavpinacol.	Band head.	Band head.
Bis-(7 : 4′-dihydroxy)	2690	2820
Bis-(5 : 7 : 4′-trihydroxy)	2700	2890
Bis-(7 : 8 : 4′-trihydroxy)	2690	2900

Natural phlobatannins (Table VI) *and methylated natural phlobatannins* (Table VII).

TABLE VI (FIG. 9).

Tannin.	Band head.	Band head.
Hemlock	2710	2860
Mimosa	2700	2860

TABLE VII (FIG. 10).

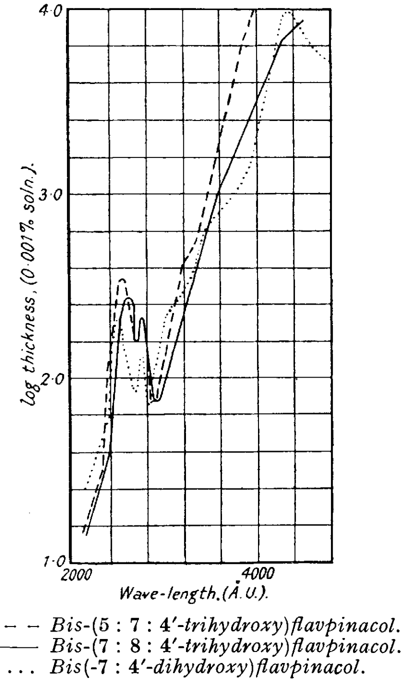
Parent tannin.	Band head.	Band head.
Hemlock	2700	2800
Mimosa	2700	2810

Ellagic acid (B.D.H.), $C_{14}H_6O_8$ (Fig. 11). Three bands are measured at λ 2480, λ 3140, and λ 2680, the first of which is probably the diphenyl band (cf. Adam and Russell, J., 1930, 202).

Gallotannin, extracted from oak galls (Fig. 11). The absorption appears to be general, but two extensions at λ 2740—2920 and at λ 3300—3740 may be weak bands.

In interpreting the results given above it has been found most convenient to consider the various spectra as grouped in the Figures. Fig. 1 shows the two starting materials, benzaldehyde and acetophenone, chalkone, the condensation product of these, and the bis-reduction product of chalkone. Each of Figs. 2—8 shows a hydroxy-aldehyde, hydroxy-ketone, and the corresponding chalkone. Figs. 9 and 10 show the characteristics of the phlobatannin spectrum—two narrow bands at λ 2700 and λ 2800—2900. Fig. 11 shows the totally different spectra given by the two natural tannins which are known not to be phlobatannins. Figs. 12 and 13 for flavpinacols show that reduction of 2-hydroxychalkones removes the "colour band," or shifts it far into the red region, and reduces the spectrum to one exactly like the characteristic phlobatannin spectrum.

FIG. 13.



Discussion.—Without extensive speculation the results may be summarised. The absorption spectra of synthetic flavpinacols are entirely similar to those of typical natural phlobatannins, consisting of two sharply defined bands at λ 2700 and λ 2800—2900. The parent chalkones (of the flavpinacols) also show two bands in approximately the same positions, but all have, in addition, a broad characteristic band in the violet region with its head at, in the different cases, from λ 3700 to λ 3900, complementary to the visible colour of chalkones and differentiating the spectra very sharply from those of flavpinacols.

Considered in conjunction with the spectra, the differences in colour between the chalkone and the flavpinacol solutions are explained. In all cases the solutions of hydroxychalkones are strongly coloured, with colours varying from bright yellow to deep orange-red. On dilution, the colour weakens but persists. Flavpinacol and phlobatannin solutions, on the other hand, rapidly lose their red colour on dilution.

The hydroxychalkone spectrum is, broadly speaking, the sum of the spectra of hydroxy-aldehyde and hydroxy-ketone plus a characteristic band in the visible region due to the chromophoric characteristic of 2-hydroxychalkones. On reduction, the chromogenic group is destroyed by ring closure, the visible band disappears, and the reduction products give spectra which are closely similar to those of typical natural phlobatannins.

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