VISIBLE FLUORESCENCE AND CHEMICAL CONSTITUTION OF COMPOUNDS OF BENZO-PYRONE GROUP

Part IV. Further Study of γ-Pyrone Derivatives

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IN the first part[1] of this series a general study of both the α and γ types of benzo-pyrones was made; in the subsequent two papers[2] the coumarins received detailed attention and attempts were made to explain the special features that were noted. As a result of synthetic work in our laboratories during the following years a large number of chromones, flavones, flavanones and isoflavones have become available. These have now been examined for their fluorescence in sulphuric acid solution and the results recorded here. Alkaline solutions were unsuitable because of the deep colour which these substances develop. For the observation of the fluorescence a pyrex test tube and diffuse light were employed and the light was concentrated by using a flat-bottomed round flask containing water. Brighter light such as direct sunlight passed through a similar condenser or reflected sunlight was not quite suitable because under these conditions even the pyrex tube started emitting a weak bluish-violet fluorescence. In those cases where the solution was deep yellow, brown or red it was diluted suitably with more sulphuric acid and the fluorescence observed. In all cases the intensity was checked after an hour; but no fading was noted in any case. The following table gives the list of compounds which show fluorescence:—

Compound	Colour of the solution	Fluorescence
Chromones		
7-OH-2-Me	Pale yellow	Bright violet
7-OMe-2-Me	do.	Strong bluish-violet
7-OH-3-OMe-2-Me	Colourless	do.
7-OAc-3-OMe-2-Me	do.	do.
7-Allyloxy-3-OMe-2-Me	do.	Blue
7-OH-8-allyl-3-OMe-2-Me	Pale yellow	Bluish-green
7-Allyloxy-8-allyl-3-OMe-2-Me	do.	do.
7: 3-Dimethoxy-2 : 8-dimethyl	Yellowish-brown	do.

Compound	Colour of the solution	Fluorescence
Flavones		
6-Hydroxy	Pale yellow	Blue
7 : 3′ : 4′-Trihydroxy	Pale red	Pale violet
7 : 3-Dihydroxy	Pale brown	Violet-blue
7 : 3 : 4′-Trihydroxy	Pale Yellow	Strong bluish-green
Robinetin	Orange	Strong green
5 : 7-Dihydroxy	Bright yellow	Blue
Apigenin	do.	Strong blue
3 : 5 : 7 : 4′-Tetrahydroxy	Brighter yellow	Intense blue
Quercetin	Brownish-yellow	Intense greenish-blue
Myricetin	Yellow	Bluish-green
Morin	do.	Strong greenish-blue
3 : 6 : 7-Trihydroxy	Pale yellow	Pale blue
3 : 6 : 7 : 4′-Tetrahydroxy	Almost colourless	Bright blue
3 : 6 : 7 : 3′ : 4′-Pentahydroxy	Yellow	Blue
3 : 6 : 7 : 3′ : 4′ : 5′-Hexahydroxy	do.	Bluish-green
Baicalein (natural)	Pale yellow	Pale blue
5 : 6 : 7 : 3′ : 4′-Pentahydroxy	Deep yellow	do.
Nor-tangeretin	Yellow	Blue
Gossypetin (natural)	Reddish-brown	Prominent blue
Hibiscetin (synthetic)	Brownish-yellow	Weak blue
3 : 7-Dihydroxy-4′-methoxy	Yellow	Bright blue
5-Hydroxy-7-methoxy	Bright yellow	Blue
5-Hydroxy-7 : 2′-dimethoxy	Pale yellow	do.
5 : 7-Dihydroxy-4′-methoxy	Bright yellow	Strong blue
5 : 7-Dihydroxy-3′ : 4′-dimethoxy	Brighter yellow	Blue
5-Hydroxy-7 : 3′ : 4′-trimethoxy	do.	do.
5 : 7-Dihydroxy-3′ : 4′ : 5′-trimethoxy	do.	do.
5 : 7-Dihydroxy-3-methoxy	Bright yellow	do.
5 : 7-Dihydroxy-3 : 4′-dimethoxy	Brighter yellow	Intense blue
Pentamethyl gossypetin (5-OH)	Bright yellow	Weak blue
7-Methoxy	Colourless	Strong blue
3 : 7 : 4′-Trimethoxy	Yellow	Greenish-blue
Pentamethyl robinetin	Bright yellow	Weak green
Kanugin	Deep red	Strong green
3 : 7 : 8 : 3′ : 4′-Pentamethoxy	Bright yellow	Weak blue
5 : 7 : 4′-Trimethoxy	Almost colourless	do.
3 : 5 : 7-Trimethoxy	Yellow	Bluish-green
3 : 6 : 7 : 3′ : 4′ : 5′-Hexamethoxy	do.	Weak bluish-green
Hexamethyl myricetin	Bright yellow	Green
3 : 5 : 7 : 8-Tetramethoxy	Yellow	Weak blue
Heptamethyl hibiscetin	Deep orange-yellow	Blue

Compound	Colour of the solution	Fluorescence
3:5:6:7-Tetramethoxy	Almost colourless	Feeble blue
Tangeretin	Deep yellow	Greenish-blue
3:5:6:8:4′-Pentamethoxy	do.	Blue
5:6:7:3′:4′-Pentamethoxy	Yellow	Light blue
5:6:7:8-Tetramethoxy	Pale yellow	do.
5:6:7:8:4′-Pentamethoxy	Yellow	do.
3:5:6:7:8-Pentamethoxy	do.	Weak blue
Dimethyl calycopterin	do.	Light blue
Isoflavones		
7-Hydroxy-2-Me	Light yellow	Bluish-violet
7-Methoxy-2-Me	Colourless	do.
7-Allyloxy-2-Me	Pale yellow	Dull blue
7-Hydroxy-8-allyl-2-Me	Colourless	Greenish-blue
7-Methoxy-8-allyl-2-Me	do.	Bluish-violet

The following compounds do not show any fluorescence on dissolution in concentrated sulphuric acid; the colour of the solution is given within brackets:—

**Chromones.*—7-Hydroxy-3-acetyl-2-methyl (pale yellow); 7-Methoxy-3-acetyl-2-methyl (very pale yellow); 7-Hydroxy-3-methoxy-8-aldehydo-2-methyl (yellow); 5:7-Dihydroxy-2-methyl (pale yellow); 5-Hydroxy-7-methoxy-2-methyl (colourless); 3:5:7-Trihydroxy-2-methyl (pale yellow); 5:7-Dihydroxy-3-methoxy-2-methyl (pale yellow); 5-Hydroxy-3:7-dimethoxy-2-methyl (pale yellow); 7:8-Dihydroxy-3-acetyl-2-methyl (yellow); 7:8-Diacetoxy-3-acetyl-2-methyl (yellow); 7:8-Dihydroxy-2-methyl (pale yellow); 7:8-Dimethoxy-2-methyl (colourless); 7:8-Dihydroxy-3-methoxy-2-methyl (pale yellow); 3:7:8-Trimethoxy-2-methyl (pale yellow); 3:5:7:8-Tetrahydroxy-2-methyl (orange-red); 3:5:7:8-Tetramethoxy-2-methyl (lemon yellow).

Flavones.—5-Hydroxy (red); 5-Methoxy (pale yellow); 3:5:4′-Trihydroxy (pale yellow); 3:5:3′:4′-Tetrahydroxy (yellowish-brown); 3:5:3′:4′-Tetramethoxy (pale red); Isokanugin (yellow); 6-Hydroxy-5-aldehydo (orange); 5:6-Dihydroxy (deep yellow); 5-Hydroxy-6-methoxy (bright yellow); 5:6-Dimethoxy (bright yellow); 3:5:6-Trihydroxy (yellow); 3:5:6:4′-Tetrahydroxy (yellow); 3:5:6:3′:4′-Pentahydroxy (yellow); 5:7-Dihydroxy-8-aldehydo (reddish-yellow); 5-Hydroxy-7:2′-dimethoxy (yellow); Primetin (brownish-yellow); 5-Hydroxy-8-methoxy (deep yellow);

* Some of these exhibit some fluorescence when their solutions in sulphuric acid are allowed to stand for over 24 hours.

3:6:7-Trimethoxy (almost colourless); 7:8-Dihydroxy (bright yellow); 3:7:8-Trihydroxy (yellow); 3:7:8-Trimethoxy (pale yellow); 3:7:8:4'-Tetramethoxy (deep yellow) 3:7:8:3':4'-Pentahydroxy (yellow); 3:7:8:3':4':5'-Hexahydroxy (pale yellow); Nor-wogonin (yellow); Wogonin dimethyl ether (yellow); 5:7:8:2'-Tetramethoxy (yellow); Oroxylin-A (orange); 3:5:6:7:3':4':5'-Heptamethoxy (yellow); Pentamethyl herbacetin (deep yellow); 6:7:8:4'-Tetrahydroxy (pale yellow); 3:6:7:8:4'-Pentamethoxy (yellow); 5:6:7:8-Tetrahydroxy (orange); 5:6:7:8:3':4'-Hexahydroxy (brownish-yellow); 3:5:6:7:8:3':4':5'-Octamethoxy (yellow).

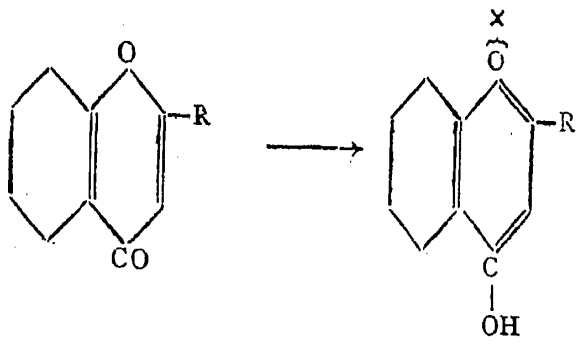
Flavanones.—7-Methoxy (bright yellow); 5:7-Dihydroxy (bright yellow); 5-Hydroxy-7-methoxy (bright yellow); 5:7:4'-Trihydroxy (bright yellow); 7-Methoxy-5:4'-dihydroxy (bright yellow); 5-Hydroxy-7:4'-dimethoxy (yellow); 5:7:3':4'-Tetrahydroxy (orange-yellow).

Isoflavones.—7-Hydroxy-2-methyl-8-aldehydo (colourless); 7-Hydroxy-2-methyl-8-acetyl (colourless); 5:7-Dihydroxy (yellow); 5-Hydroxy-7-methoxy (very pale yellow); 5:7-Dihydroxy-2-methyl (pale yellow); 5-Hydroxy-7-methoxy-2-methyl (pale yellow); 5:7-Dimethoxy-2-methyl (colourless); 7:8-Dihydroxy-2-methyl (pale yellow); 7:8-Dimethoxy-2-methyl (pale yellow); Prunetin (very pale yellow); Santal (pale greenish-yellow).

Discussion

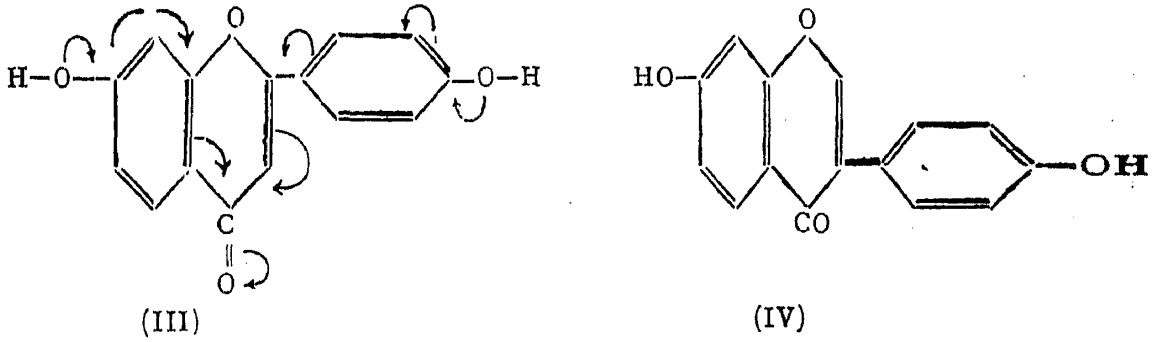
In the case of the chromone derivatives the relationship between fluorescence and chemical constitution seems almost parallel to that found in the coumarin field. Chromone itself has been reported to exhibit strong blue fluorescence in concentrated sulphuric acid whereas coumarin does not. A greater tendency to fluoresce seems to be exhibited by the chromone derivatives all through. This may be explained as due to the greater readiness with which the γ-pyrone structure (I) undergoes changes into the pyronium or hydroxy-pyrylium salts (II) which seem to be the real fluorescent substances in acid solution. The pyrone double bond is quite essential not only in the coumarins but also in the chromones. The flavanones which do not have this double bond are non-fluorescent.

The influence of the hydroxyl and methoxyl groups is most favourable to fluorescence in γ-pyrone derivatives when they are present in the 7-position and the 6-position is the next best whereas 5 and 8 positions are highly disadvantageous. The explanation offered earlier in regard to the behaviour of coumarins and pyrylium salts may be applicable to the present case also because they all refer to oxonium salts.[3] Formyl and acetyl groups reduce



(I) (II)

fluorescence while methyl has no appreciable effect. In the case of the coumarins it was pointed out that a phenyl group in the 3-position greatly enhances fluorescence whereas such a group in the 4-position has no advantage. Analogous features are noticed even in the chromones. A 2-phenyl derivative (flavone) is markedly more fluorescent whereas a 3-phenyl derivative (isoflavone) seems to be just the same as the corresponding chromone without the phenyl group. This difference could be attributed to the presence of conjugation between the C=O group and the phenyl group when present in the 2-position and its absence when the phenyl group is present in the 3-position (formulæ III and IV). Further it would appear that in regard to fluorescence in sulphuric acid solution conjugation of the hydroxyl group with the carbonyl group is a favourable feature and the electromerisations involved are given in the following formula. The importance of this feature is shown by the marked effect of a hydroxyl group in the 4'-position of the flavones (III) increasing the fluorescence considerably while in the isoflavone series (IV) no such influence is noticeable.



(III) (IV)

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References

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