908. *Compounds of Curcumin and Boric Acid. Part III.* Infra-red Studies of Rosocyanin and Allied Compounds.*

By L. J. Bellamy, G. S. Spicer, and J. D. H. Strickland.

The infra-red spectra of curcumin and rosocyanin are compared with the spectra of their related acetylacetone complexes, and with the corresponding beryllium compounds. The spectra support the structures postulated in Parts I and II.*

Curcumin and its condensation products with boron and beryllium are too complex to permit of any simple interpretation of their infra-red spectra in terms of structure. Nevertheless a certain amount of positive information can be obtained in this way and some tentative conclusions can be drawn when the spectra are considered in conjunction with the chemical data (Spicer and Strickland, preceding papers), and with the spectra of the simpler acetylacetone complexes which constitute a part of these molecules.

Acetylacetone has been studied by Kohlrausch and Pongratz (*Ber.*, 1934, **67**, 976, 1465) and Kahovec and Kohlrausch (*Ber.*, 1940, **73**, 1304 *et seq.*) who have shown that the Raman spectrum permits the possibility of the existence of four enolic forms; Rasmussen, Tunni-

---

* Parts I and II, preceding papers.

cliffe, and Brattain (*J. Amer. Chem. Soc.*, 1949, **71**, 1068) presented very strong evidence that it exists mainly as a chelated monoenolic form in which the enolic hydroxyl group is strongly bonded by hydrogen to the remaining carbonyl group with resonance stabilisation of the whole. This is reflected in the infra-red spectrum by very considerable shifts of the CO and OH stretching frequencies. The spectra of acetylacetone complexes have been examined by Morgan (U.S. Atomic Energy Commission, 1949, Report No. 12,659, p. 16) and especially by Lecomte (*Discuss. Faraday Soc.*, 1950, No. 9, p. 125) who has given the spectra of 11 metallic complexes. Their results in relation to the complexes of curcumin will be discussed.

EXPERIMENTAL

All the spectra were obtained with a Perkin Elmer 21B recording spectrometer with rock-salt optics. Samples were examined as solid pastes ground in paraffin and pressed between rock-salt plates. The results obtained, insofar as they are relevant to the discussion, are summarised in the Table. For convenience, the characteristic frequencies which we find for acetylacetone and its acetyl derivative are included although these are in agreement with those reported by Rasmussen *et al.* (*loc. cit*).

DISCUSSION

Curcumin.—Curcumin, examined in the solid state, shows no absorption in the regions corresponding to normal or αβ-unsaturated ketones. The only absorptions in the double-bond region are a single strong band at 1625 cm.$^{-1}$ and two others of medium intensity at 1600 and 1500 cm.$^{-1}$. The latter pair arises from the C=C vibrations of the aromatic rings. The analogy with acetylacetone is clear, and the 1625 cm.$^{-1}$ band must arise from a similar chelated type of keto–enol system. The fact that the frequency is a little higher than for acetylacetone indicates a slightly weaker chelation and this is not unexpected in view of the strong external conjugation of the double bond in the chelated ring. The C=C vibration is not apparent and is probably hidden by the aromatic absorption at 1600 cm.$^{-1}$, as this is roughly the position in which a strongly conjugated C=C absorption would be expected.

Confirmation of the chelated structure is afforded by the examination of the OH stretching vibrations. In addition to the OH stretching vibration of the phenolic hydroxyl groups, which shows normal hydrogen bonding and absorption near 3400 cm.$^{-1}$, there is also evidence of broad absorptions near 2600 cm.$^{-1}$, corresponding to the chelated hydroxyl group. We therefore regard curcumin as existing wholly in the keto–enol form (I) in which a strong chelated bond closes a cyclic structure.

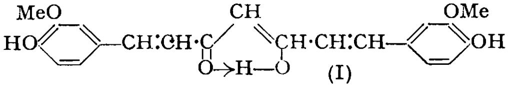
Curcumin also shows strong absorption at 962 cm.$^{-1}$, which we attribute to the –CH=CH– (*trans-*)double bond (Sheppard and Sutherland, *Proc. Roy. Soc.*, 1949, *A*, **196**, 195).

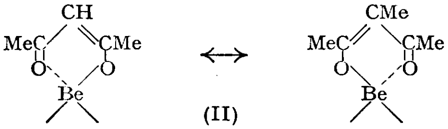
Acetylacetone Complexes.—The boron complex of acetylacetone has been examined and also, for comparison, the beryllium compound which was studied earlier by Lecomte (*loc. cit.*). The most obvious feature of the spectrum of the latter is the further displacement of the carbonyl absorption, the 1600 cm.$^{-1}$ band of acetylacetone being replaced by bands at 1560 and 1515 cm.$^{-1}$. Lecomte attributed these to the carbonyl and to the C=C absorption, respectively. The further shift of the carbonyl to 1560 cm.$^{-1}$ represents a marked further weakening of the bond to an extent approximating to that found in ionised carboxylic acids, which Lecomte postulates might occur in the resonant cyclic system (II).

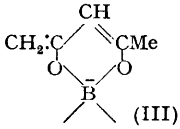
The assignment of the C=C vibration at 1515 cm.$^{-1}$ represents a very marked weakening also of the double bond beyond even that given by a long chain of conjugated double bonds (Blout, Fields, and Karplus, *J. Amer. Chem. Soc.*, 1948, **70**, 194) but it is not possible to predict the possible influence of a structure such as (II) on the bond length.

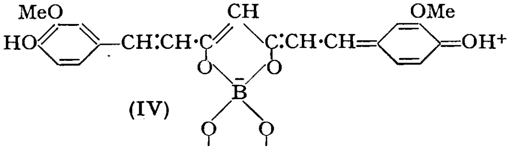
We find that the spectrum of this complex also shows a strong band at 822 cm.$^{-1}$ which may be associated with the CH bending vibration of a double bond of the type $\overset{|}{\mathrm{C}}\mathrm{H}{=}\mathrm{C}{<}$. There is no absorption at 900 cm.$^{-1}$ where double bonds of the type $>\mathrm{C}{=}\mathrm{CH}_2$ might be expected to absorb.

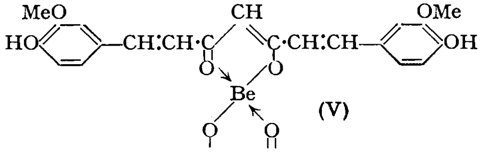
The spectra of the great majority of the metal acetylacetone complexes described by Lecomte and by Morgan (*loc. cit.*) are essentially similar. On the other hand, the complex with boron shows a spectrum so different as to suggest that the structures may not be the same. For example, in the double-bond region we find only a single band at 1560 cm.$^{-1}$ which must correspond to either the carbonyl or the C═C absorption or both. It is tempting to conclude that both absorptions coincide, but if the structure is similar to that of the beryllium complex it is difficult to see why the C═C bond should be so much stronger in the boron complex. Also, as will be seen later, a similar situation arises with the boron and the beryllium complexes of curcumin which show one and two bands, respectively, in this region. The band of the boron–curcumin complex is not in the same place as in the acetylacetone complex and it is unlikely that the C═O and C═C vibrations would again be coincident at a different frequency. The alternative is to suppose that either the C═O or the C═C vibration is absent from the boron–acetylacetone compound. This can be visualised on the basis of the structure (III), in which all the C–O–B links are equal and have no double-bond character. Such a structure would be expected to show a strong absorption band near 900 cm.$^{-1}$ arising from the out-of-plane CH deformations of the CH_2═C group. A band of 884 cm.$^{-1}$ is in fact shown by the boron and not by the beryllium acetylacetone complex. Against this is the fact that a structure such as (III) cannot be satisfactorily incorporated in the formula for the complex as a whole whilst retaining the formal positive charge which the complex is known to possess. This difficulty does not arise in the case of rosocyanin (cf. Part I). In addition, very little is known of the frequencies of out of plane ═CH vibrations in resonant structures, so that the evidence afforded by these observations can only be regarded as very tentative.


(I)


(II)


(III)


(IV)


(V)

Insofar as account can be taken of ═CH vibrations both beryllium and boron compounds show absorption near 820 cm.$^{-1}$ corresponding to the CH═C linkage. The 1560 cm.$^{-1}$ band in the boron compound could be attributed to the C═C vibrations and with the conjugated structure postulated this frequency would be expected to be different from the C═C vibrations in the chelated beryllium compound.

Rosocyanin and the Beryllium–Curcumin Complex.—The spectrum of rosocyanin is very different, in the double-bond region, from that of curcumin. The strong band originally present at 1625 cm.$^{-1}$ has vanished, and the spectrum now shows a very small band at 1530 cm.$^{-1}$. The aromatic C═C ring vibrations now occur at 1587 and 1500 cm.$^{-1}$ and are much more intense.

As with the boron acetylacetone complex the 1530-cm.$^{-1}$ band could well be interpreted as arising from a resonating carbonyl structure or a conjugated C═C group or both. However, the fact that the corresponding beryllium curcumin complex shows two strong bands in this region suggests that the cases are parallel and that the boron complex is associated with reaction with a dienol form. We would therefore assign to rosocyanin the partial structure (IV).

With such a structure in which the conjugation is increased, the C═C vibration would be expected to be more intense, and at lower frequency, than in curcumin. Similarly, the shift in this vibration from 1560 to 1530 cm.$^{-1}$ on passing from the boron acetylacetone to the boron curcumin complex would be expected from the increased conjugation. The alteration in the nature of the bonding in one of the aromatic rings might also be expected to cause a small frequency change, and the movement of one of the aromatic vibrations from 1600 cm.$^{-1}$ in curcumin to 1587 cm.$^{-1}$ in rosocyanin is in line with similar changes in quinones. The occurrence of both 1605 and 1587-cm.$^{-1}$ absorptions may be slight evidence for the presence of both types, but could be interpreted in other ways. The 962-cm.$^{-1}$ band assigned to the $-\mathrm{CH}{=}\mathrm{CH}-$ grouping in curcumin is notably weakened, although still present, in rosocyanin.

Absorption bands (*cm.*$^{-1}$).

Group	Normal frequency range	Acetyl-acetone	Acetyl-acetone acetate	Boron acetyl-acetone complex	Beryl-lium acetyl-acetone complex	Curcumin	Beryl-lium curcumin complex	Boron curcumin complex (roso-cyaninn)
OH (H bonded)	3500—3200	—	—	—	—	3400	—	—
OH (chelated) ...	2800—2500	2600	—	—	—	2600	—	—
CO (conjugated)	1690—1660	—	1695	—	—	—	—	—
CO (chelated) ...	*ca.* 1600	1600	—	—	1560	1625	1605	—
$-\mathrm{C}{=}\mathrm{C}-$	1680—1600 (lower bottom limit if heavily conjugated)	1600	1633	1560	1515	1600 ?	1510	1530
$-\mathrm{C}{=}\mathrm{C}-$ (rings) ...	*ca.* 1600 and 1500	—	—	—	—	1600, 1500	1600, 1500	1605, 1587, 1500
$-\mathrm{CH}{=}\mathrm{CH}-$ (*trans*)	near 965	—	—	—	—	962(s)	970	962(m)
$-\mathrm{CH}{=}\mathrm{C}<$	near 825	—	840	820	822	—	—	—
$\mathrm{CH_2}{=}\mathrm{C}<$	near 900	980	—	884	—	—	—	—
CO (ester)	near 1740	—	1765	—	—	—	—	—

This infra-red evidence for the structure of rosocyanin is therefore in accord with the chemical evidence.

The beryllium curcumin complex shows strong absorptions at 1605 and 1510 cm.$^{-1}$ in addition to the bands arising from the aromatic ring. The intensity of the absorption shown at 970 cm.$^{-1}$ is comparable with that shown by curcumin itself. We therefore regard this complex as differing from the boron complex and more closely resembling the acetylacetone complex, with the partial structure (V). The 1605-cm.$^{-1}$ band would then be assigned to the resonant $\mathrm{C}{=}\mathrm{O}$ vibration and the 1510-cm.$^{-1}$ band to the $\mathrm{C}{=}\mathrm{C}$ vibration.

Rubrocurcumin.—The spectrum of rubrocurcumin is in many respects similar to that of rosocyanin, especially in the important 1650—1450-cm.$^{-1}$ region. To this extent it affords reasonably good evidence that closely related structures are involved. However it also shows two strong absorptions at 1810 and 1770 cm.$^{-1}$. These must be carbonyl bands, and if they can be presumed to arise from one or both of the oxalate residues it is an indication that it forms an integral part of the molecules. These frequencies could correspond to ketones of vinyl ester type (Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073; Short, *J.*, 1952, 206). Any ionic oxalate present could not be readily detected as absorptions appear in any case in the expected region owing to the chelated structure.

This compound is however so complex that the interpretation of its infra-red spectrum must be very uncertain, especially as in this case it has not proved possible to isolate a similar beryllium complex for comparison.

Acknowledgment is made to the Chief Scientist, Ministry of Supply, for permission to publish this paper.

CHEMICAL INSPECTORATE, ROYAL ARSENAL, WOOLWICH, S.E.18. [*Received, July 2nd,* 1952.]