phenyl bands. For this reason, it may be impossible to make a satisfactory assignment of the chelated C=O band in these compounds.

Further report on the phenyl band of anthraquinone derivatives will be made in a subsequent paper.

The author wishes to acknowledge the encouragement and helpful advices of Prof. S. Shibata. The infrared measurement was carried out in the Central Clinical laboratory of the Tokyo University Hospital, to the members of which the author's thanks are due. The author is also indebted to Messrs. J. Shoji and T. Tanikawa for their help in the measurement of infrared spectra.

Experimental

Substances examined were prepared by known methods and carefully purified before use. Some of the samples were provided by Mr. M. Takido of the Nihon University and Mr. Y. Hirose of the University of Kumamoto to whom the author is grateful for their kindness. 2-OH-4,5-$(OCH_3)_2$-7-CH_3-anthraquinone (4,5-dimethylemodin) is a new compound which was prepared by the reductive cleavage of diacetyltetramethylskyrin; the details of the preparation methods and physical properties of these compounds will be described in a forthcoming report.

Infrared spectra were measured by a Hilger H 800 double-beam spectrometer fitted with a rock-salt prism. For measurement as a solid, the Nujol mull technique was used. The spectra in dioxane were measured in 1～2% solution (if the sample is only slightly soluble in this solvent, a saturated solution was used), with the cell of 0.1 mm. thickness. A change of the concentration between 0.5% and 2.0% did not affect the position of C=O absorption maximum. For a few compounds, spectra in dilute solution in CCl_4 or $CHCl_3$ were also examined. The data were always carefully corrected by comparing with the absorption maxima of polystyrene film.

Summary

The infrared spectra of about 80 anthraquinone derivatives substituted with acetoxyl, hydroxyl, methoxyl, or methyl group, were measured in the dioxane solution and in the solid state. The effect of substituents on the free and chelated C=O stretching vibration frequencies was discussed.

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6. Osamu Tanaka : Infrared Spectra of Anthraquinone Derivatives. II.* The Relationship between the Absorption Bands in the Region of 1480～1620 cm^{-1} and Hydroxyl, Methoxyl, Acetoxyl, and Methyl Substitutions.

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It has been well known that compounds containing an aromatic ring show skeletal vibration bands within the range of 1480～1620 cm^{-1} (phenyl band) and conjugation of the aromatic ring with C=O, C=C, etc. causes increase of the intensity of these bands.[1～3] Bomstein[4] examined the effect of substituents on the intensity of the phenyl band near 1600 cm^{-1} for the mono- and di-substituted benzene derivatives and reported that the directing influence and orientation of substituents in the ring are the most important factors. However, extensive systematic studies on the phenyl bands of a more complex molecules have not been made.

* Part I : O. Tanaka : This Bulletin, **6**, 18(1958).

** Hongo, Tokyo (田中 治).

1) L.J. Bellamy : "The Infrared Spectra of Complex Molecules," p. 53(1954).
2) R. N. Jones, et al. : "Chemical Applications of Spectroscopy," Ed. W. West, 395(1956).
3) M-L. Josien, J-M. Lebas : Bull. soc. chim. France, **1956**, 53, 57.
4) J. Bomstein : Anal. Chem., **25**, 512(1953).

The infrared studies on the hydroxyanthraquinones and their derivatives have been almost confined to the C=O and O–H stretching absorptions, and works concerning the phenyl band have not been reported.[5] It should be noted that this band sometimes appears near the lower frequency side of the chelated C=O stretching band and causes a confusion in the precise assignment of the chelated C=O stretching band.

In the present work, the author has investigated the relationship between the absorption bands in the region of 1480~1620 cm^{-1} and hydroxyl, methyl, acetoxyl, methoxyl, and methyl substitutions for about 80 anthraquinone derivatives. An empirical correlation was obtained from the results described below, which seemed to be useful for the determination of the types and positions of substituents in the naturally occurring anthraquinones and their derivatives.

Results and Discussion

The results obtained are illustrated in Figs. 1 and 2.

I) The Absorption Bands in the Region of 1560~1620 cm^{-1} (Fig. 1)

The phenyl absorption in this region will be discussed on the following points :

a) The position of absorption maxima.

b) The number of absorption bands.

c) The intensity of absorption band (relative intensity in comparison with the C=O band).

1) Compounds not containing chelated carbonyl group—Anthraquinone itself shows the phenyl band at 1578 cm^{-1} as a solid, the intensity of which is slightly lower than that of the C=O band. In dioxane, this band shifts to 1595 cm^{-1} and its intensity diminishes further.

Almost all the methyl and acetoxyl derivatives possess one sharp phenyl band in the region of 1585~1596 cm^{-1} in the solid state which is always less intense than the C=O band. In solution, its absorption range moves to a slightly higher and narrower region of 1595±3 cm^{-1}, accompanied by a further diminution of its intensity (Fig. 1 group A. I~XI).

The phenyl band observed in most of the acetoxyl and methyl derivatives is postulated as " the standard type of the phenyl band " in substituted anthraquinones.

In 1,3,8-$(OAc)_3$-6-CH_3- and 1,8-$(OAc)_2$-3-CH_3-anthraquinones, an additional band appears on the higher frequency side of the main phenyl band, both in the solid state and in solution, but the intensity of the phenyl bands is also lower than that of the C=O band (Fig. 1 group A XII, XIII).

Effect of methoxyl group—As in the case of the C=O stretching band, the phenyl band is more sensitive to methoxyl substitution at the β-position than that at α-position.

The one α-methoxyl substitution causes a little increase in the intensity of the phenyl band in the solid state but the position of the phenyl absorption maximum is almost unaffected. In the solution, the phenyl band of these compounds is not so different from the standard type (Fig. 1 group B. I~III).

In the β-monomethoxyl derivatives, the phenyl band is always much more intense than the C=O band in the solid state (Fig. 1 group B. IV~IX) and even in dioxane the intensity of this band is sometimes higher than that of the C=O band (Fig. 1 group B. VI, VIII). The position of its absorption maximum is almost similar to that of the standard type but some compounds (Fig. 1 group B. V, IX) show a weak second band or shoulder in the lower frequency region (near 1570 cm^{-1}).

5) Recently, the infrared absorption bands of mono- and di- substituted anthraquinones in the region of 650~900 cm^{-1} were discussed (cf. N. Ōi : This Bulletin, 5, 155(1957)).

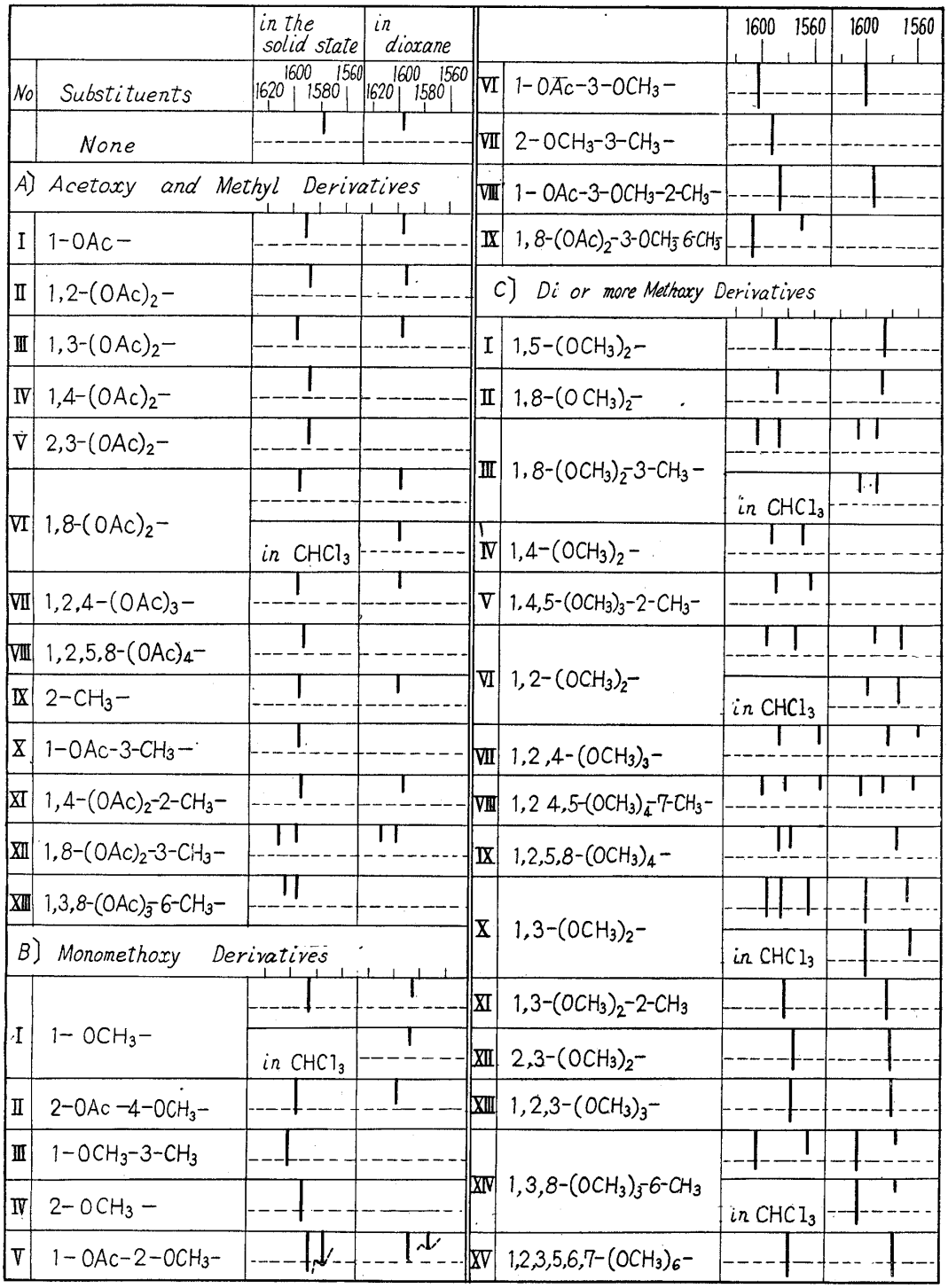


Fig. 1. The Phenyl Band of the Anthraquinone Derivatives in the Region of 1560～1620 cm^{-1} (1)

(Compds. IV, V, VIII, X, and XIII in [A], III, IV, VII, and IX in [B], and IV and V in [C] were not examined in dioxane)

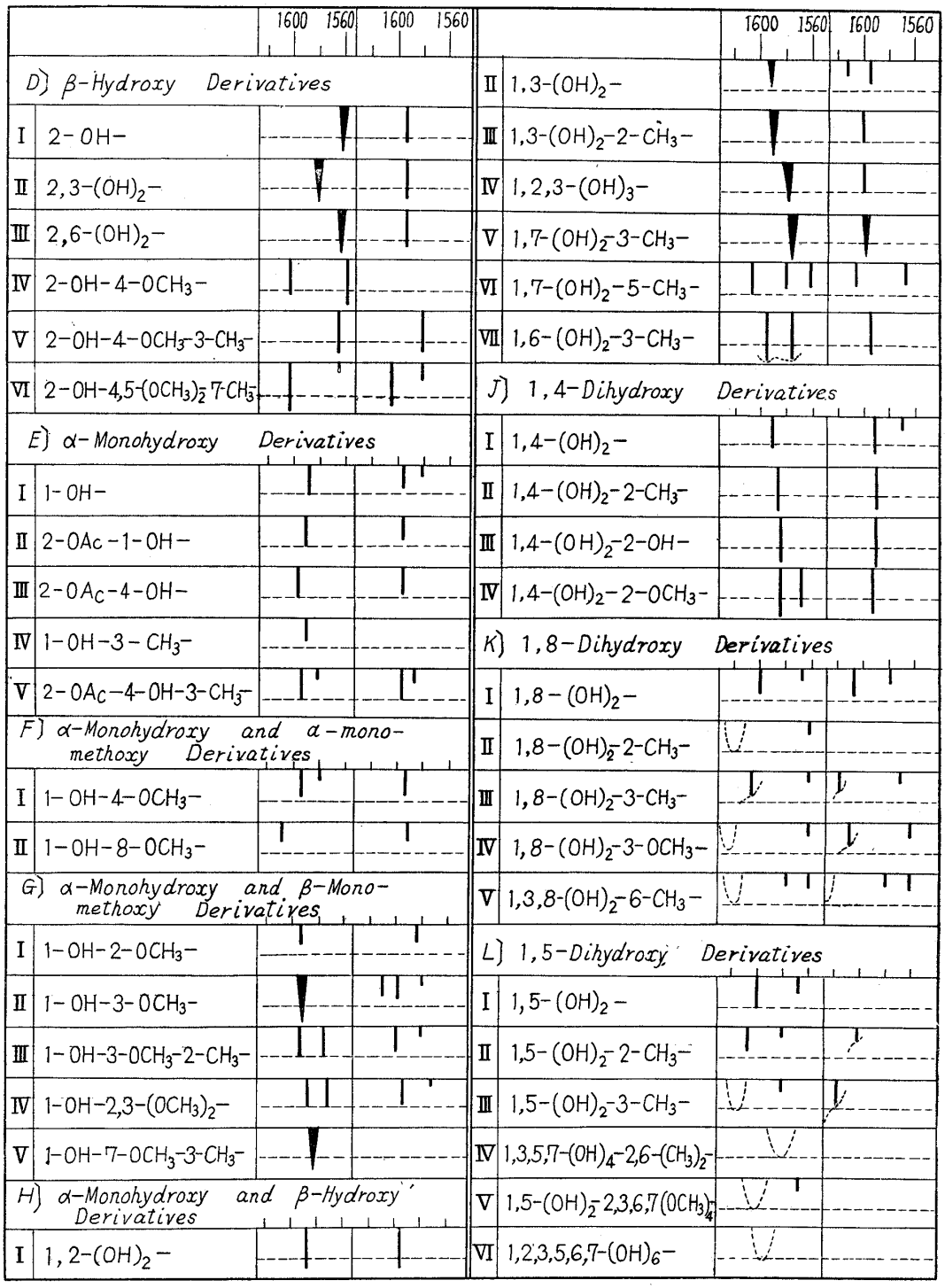
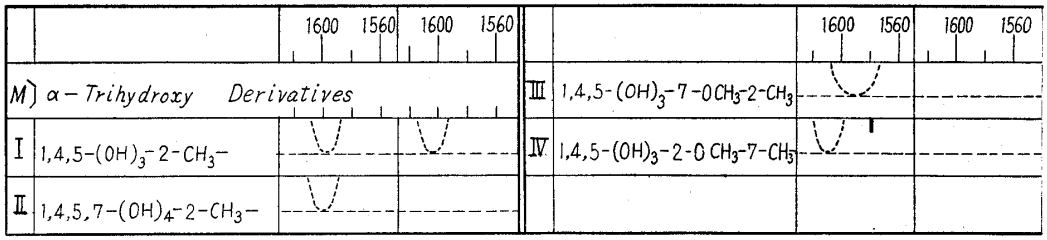


Fig. 1. The Phenyl Band of the Anthraquinone Derivatives in the Region of 1560~1620 cm^{-1} (2)

(Compds. IV in [D] and [E], V in [G], II [K], I, IV, V, and VI in [L], and II~IV in [M] were not examined in dioxane)

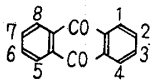
Fig. 1. The Phenyl Band of the Anthraquinone Derivatives in the Region 1560～1620 cm^{-1} (3)



-------- : Intensity of the C=O absorption band (in the case of E-L, the intensity of the chelated C=O band).

: A shoulder.

: The broad absorption band seemed to contain the chelated C=O and phenyl absorption.



α : 1,4,5,8
β : 2,3,6,7

In most of di- or poly-methoxyl derivatives, the phenyl band shifts to a lower frequency from the range of the standard type or an additional absorption band appears in the region of 1560～1580 cm^{-1}, both in the solid state and in solution (Fig. 1, group C). In these compounds with β-methoxyl group, the intensity of the main phenyl band is always considerably higher than that of the C=O band (Fig. 1 group C. X～XV), but if the α-methoxyl substitution occurs at a position *ortho* to the β-methoxyl group, the effect of this β-methoxyl group diminishes, and intensity of the phenyl band becomes lower than that of the C=O band (Fig. 1, group C. VI～IX). In a majority of compounds containing no β-methoxyl groups, intensity of the phenyl bands is also not higher than that of the C=O band (Fig. 1, group C. II～V).

It would therefore seem likely that the phenyl band will afford a reliable means of deducing the presence and orientation of methoxyl groups in the acetates and methyl ethers of the naturally occurring hydroxy-methoxy-anthraquinones.

Effect of β-hydroxyl group—The substitution of hydroxyl group at β-position causes a marked change in the phenyl band (Fig. 1, group D). In the solid state, a very strong broad band appears within the range of 1560～1580 cm^{-1}, or the phenyl band is sometimes split into two absorption bands. In all cases, the main phenyl band is considerably stronger than the C=O band. In dioxane, which forms a solvent-solute complex (see Part I* of this series) with these compounds, these bands are generally displaced toward a higher frequency but the intensity is still somewhat higher than that of the C=O band.

From the alteration of the phenyl band caused by a change in the state of samples, it is suggested that this band is affected by the intermolecular force and this association effect is more clearly apparent in the β-hydroxy derivatives (see Part I* of this series).

Acetoxyl and methyl groups, if present with methoxyl or β-hydroxyl group, appear to play a part in alteration of the phenyl band, but the precise generalization cannot be made.

2) Compounds containing the chelated carbonyl group :

One α-hydroxyl group, which forms a strong, conjugated chelation system, takes only a relatively small part in the alteration of the phenyl band.

In 1-OH-anthraquinone and its acetoxyl or methyl derivative, the weak shoulder sometimes appears on the lower frequency side of the main phenyl band, but the position of this main band shows no marked difference from that of the standard type, and its intensity is always not higher than that of the chelated C=O band, both in the solid state and in dioxane (Fig. 1, group E. I～V).

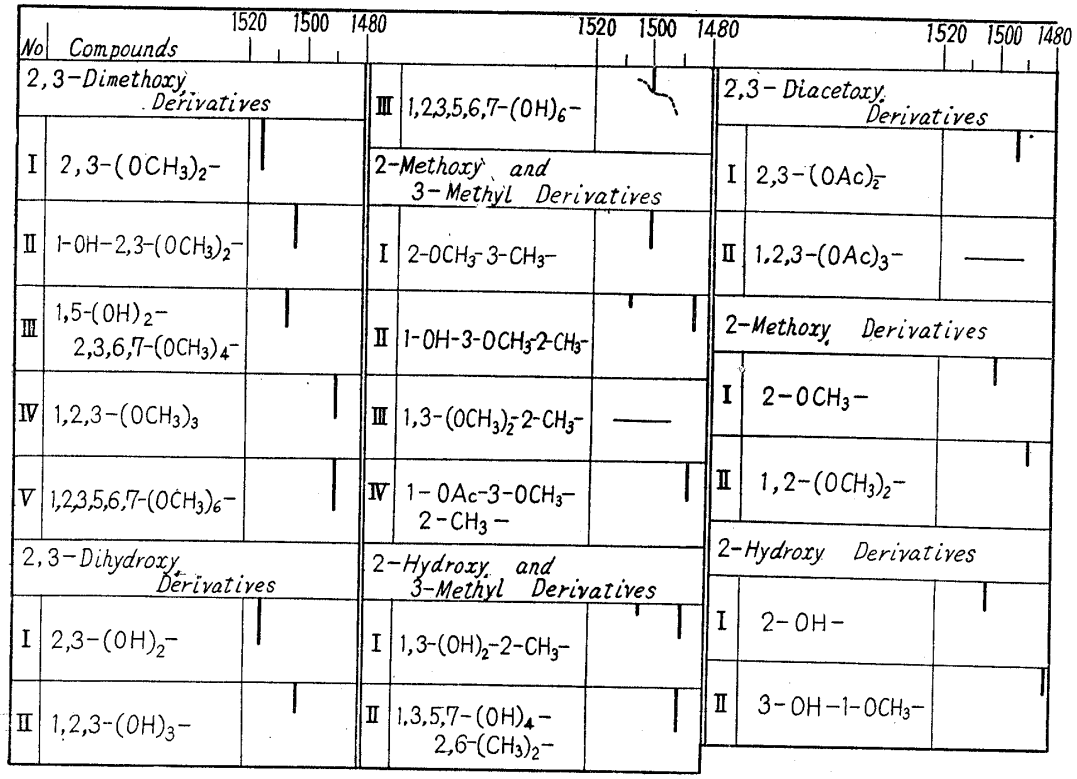
The introduction of α-methoxyl group causes no remarkable change (Fig. 1 group F. I, II), but β-methoxyl substitution except in position *ortho* to the α-hydroxyl (Fig. 1 group G. I) shows a marked alteration in the phenyl band. In the 1-OH-3-OCH_3-derivatives (Fig. 1 group G. II～IV), the phenyl band exhibits an additional band in the lower frequency region of 1570～1580 cm^{-1}, both in the solid state and in dioxane, and the phenyl band in 1-OH-7-OCH_3-3-CH_3-anthraquinone (Fig. 1 group G. V) is much more intense than that of the chelated C=O band.

Similar effect is observed in the β-hydroxyl substitution. In α-monohydroxy and β-hydroxy derivatives (Fig. 1 group H), various changes are observed in the phenyl band, such as the anomalous increase in its intensity (I, III～V, VII), broadening of the band, or the occurrence of the additional band in the lower frequency region (II～VII). These alterations in the phenyl band are always more distinct in the solid state than in dioxane which suggests that the intermolecular association through the hydrogen bonding also plays an important part in the change of the phenyl band in these compounds.

The phenyl band of the 1.4-dihydroxy derivatives—In these compounds, the position of the phenyl absorption maximum does not shift from that of the standard type, but its intensity is higher than that of the chelated C=O band both in the solid state and in dioxane (Fig. 1 group J. I, II). Substitution of β-hydroxyl or β-methoxyl group causes further increase of the intensity or splitting of the phenyl band (Fig. 1 group J. III, IV).

The phenyl band of 1,8- or 1,5-dihydroxy or α-trihydroxy derivatives—In these compounds, a remarkable shift of the phenyl band to a higher frequency is observed. Although in 1,8- and 1,5-$(OH)_2$-anthraquinones (Fig. 1 group K. I, group L. I), the phenyl band near 1600 cm^{-1} can be clearly distinguished from the chelated C=O band, the phenyl band in more complex compounds (Fig. 1 group K. II～V, group. L II～VI,

Fig. 2. The Phenyl Band of the Anthraquinone Derivatives in the Region of 1480～1520 cm^{-1} (in the solid state)



—— : No absorption band is observed in this region.

group M. I ~IV) shifts to a further higher frequency and becomes overlaped partly or completely by the strong chelated C=O band both in the solid state and in dioxane. Besides this main band, a second band of lower intensity sometimes appears in the region of 1560~1580 cm^{-1}.

Owing to this particular feature of the phenyl absorption, α-di- or -trihydroxy derivatives are readily distinguishable from other types of the compound.

II) The Absorption Band in the Region of 1480~1520 cm^{-1} (Fig. 2)

Most of the anthraquinones examined exhibit no marked absorption within the range of 1480~1550 cm^{-1}. If β-monosubstitution or the o-disubstitution at 2,3-position occurs, a medium or a weak absorption band is observed in this region, which is not swamped by the C-H bending vibration band in the measurement as a Nujol paste. As in the case of the phenyl band in the region of 1560~1620 cm^{-1}, the effect of β-hydroxyl and β-methoxyl groups on this band seems to be most marked. In 2,3-$(OH)_2$- and 2,3-$(OCH_3)_2$-anthraquinones, this band appears at the highest frequency region (near 1515 cm^{-1}). When a further substitution occurs at the α-position, this phenyl band always shifts to a lower frequency and in the measurement as Nujol paste, no absorption bands are sometimes observed in this region owing to overlapping with the C-H bending band of Nujol. Besides the phenyl band in the region of 1560~1620 cm^{-1}, the analysis of the phenyl band in this region can provide a further useful information for chemical studies on the anthraquinone derivatives.

The author wishes to acknowlege the encouragement and helpful advices of Prof. S. Shibata. Thanks are due to Mr. Y. Hirose of the University of Kumamoto and Mr. M. Takido of the Nihon University who kindly supplied some of the samples examined. The infrared measurement was carried out at the Central Clinical Laboratory of the Tokyo University Hospital, to the members of which thanks are also due. The author is also indebted to Messrs. J. Shoji and K. Tanikawa for their help in the measurement of the spectra.

Experimental

The compounds examined and the experimental conditions were as previously described (see Part I* of this series). For examinations in the range of 1480~1515 cm^{-1}, the samples were measured as a paste in hexachlorobutadiene. For a few compounds (Fig. 1, group A. VI, group B. I, group C. III, VI, X, XIV), the phenyl band was also measured in a dilute $CHCl_3$ solution in which the phenyl band was almost similar to that in dioxane.

Summary

The infrared spectra of about 80 anthraquinone derivatives substituted with acetoxyl, hydroxyl, methoxyl, and methyl groups were measured as a solid and in solution. The effect of the substituents to the position and intensity of the absorption band in the region of 1480~1620 cm^{-1} was discussed.

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