Infrared and Ultraviolet Spectra of α- and γ-Pyrones

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There have been known a number of pyrone derivatives; both synthetic ones and naturally occurring ones. The characteristic features of infrared and ultraviolet spectra of the pyrone nucleus itself cannot be obtained from those of benzopyrones, i. e. coumarines and chromones, owing to the presence of the fused benzene ring. It is, therefore, necessary to examine the pyrone derivatives without any fused aromatic rings, in order to obtain the spectral properties of pyrones. In connection with the investigation of aureothin$^{1)}$, the studies of various pyrones without aromatic rings were carried out, and in the present paper, the spectroscopic aspects of pyrones are reported.

Infrared Spectra. — Since α- and γ-pyrones show some aromatic nature, the bands associated with the double bonds of the ring as well as carbonyl band are characteristic for the identification of pyrone rings. The effects of the substituents on these bands were examined.

α-Pyrone.—Since the position and the shape of the carbonyl band are, in many cases, sensitive to the condition of measurement$^{2)}$, the band positions were compared in the same

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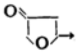
1) Y. Hirata, H. Nakata, K. Yamada, K. Okuhara and T. Naito, *Tetrahedron*, **14**, 252 (1961).

2) As to α-pyrone and 5-methyl-α-pyrone, Jones and his coworkers$^{3)}$ observed anomalous absorption in the carbonyl stretching region; the single absorption band expected for these compounds is replaced by two bands, the relative intensities of which are dependent on the solvent polarity and temperature. Various interpretations including Fermi resonance were presented but they could not reach any conclusion regarding this phenomenon.

3) R. N. Jones, C. L. Angell, T. Ito and R. J. D. Smith, *Can. J. Chem.*, **37**, 2007 (1959).

No.	R_1	R_2	R_3	R_4
1*1	H	H	H	H
2	H	CH_3	H	CH_3
3	Br	CH_3	H	CH_3
4	H	OCH_3	H	CH_3
5	Br	OCH_3	H	CH_3
6*2	H	OH	H	CH_3
7*3	Br	OH	H	CH_3
8	CH_3	OCH_3	CH_3	
9*4	H	H	$COOCH_3$	H
10	H	H	$COOCH_3$	CH_3
11	H	CH_3	COOH	CH_3
12	$COCH_3$	OH	H	CH_3
13	$COCH_3$	OCH_3	H	CH_3
14	NO_2	OH	H	CH_3

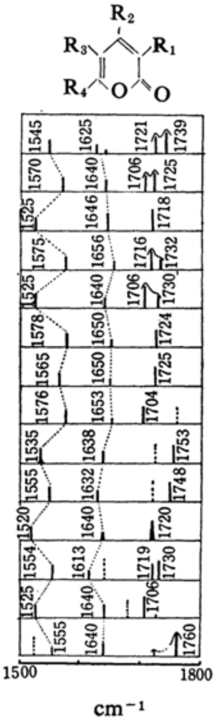
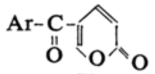


Fig. 1. Infrared spectra of α-pyrone derivatives ($CHCl_3$ solution).

*1 Data from R. N. Jones et al. (Ref. 3)
*2 Dioxane solution.
*3 $\nu_{C=O}$ appears at 1735 cm^{-1} in dioxane solution.
*4 A band written by dotted line is due to a group in side chain.

solvent. The carbonyl frequency was reported[4,5] to be in the range of 1720∼1750 cm^{-1}, and the variance in the band position is mainly due to the substituents, as illustrated later. As characteristic bands of α-pyrones, there appear two bands arising from the double bonds of the ring; one lies usually within the range 1650∼1630 cm^{-1}, and the other within 1570∼1520 cm^{-1}. In general, the lower band shows stronger intensity than the higher one, but the reverse is sometimes observed (4, 6-dimethyl-3-bromo-α-pyrone, methyl coumalate). The infrared spectra of substituted α-pyrones are shown in Fig. 1. In comparison with the conjugated systems of ketones and lactones, the effect of the substituent on the position of a carbonyl band is unique in some respects, which may be ascribed to the aromatic character of the pyrone ring. While an electron-donating substituent conjugated with a $\rangle C=O$ group has a small influence on the carbonyl band (i. e., variance of $\nu_{C=O}$ in No. 2→No. 4 and No. 3→No. 5 in Fig. 1), an electron-attracting group shifts the carbonyl band to a higher frequency[6]. (Changes of $\nu_{C=O}$ in No. 1→No. 9 and No. 1→No. 10. $\nu_{C=O}$ of the type I was reported[8] to fall within 1760∼1750 cm^{-1}). When the



(I)

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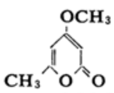
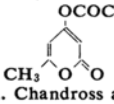
[4] a) R. H. Wiley and C. H. Jarboe, *J. Am. Chem. Soc.*, **78**, 624 (1956); b) R. H. Wiley and C. H. Jarboe, ibid., **78**, 2398 (1956); c) R. H. Wiley, C. H. Jarboe and F. N. Hayes, ibid., **79**, 2602 (1957); d) K. Meyer, *Helv. Chim. Acta*, **38**, 1631 (1955); e) R. H. Wiley and C. L. de Silva, *J. Org. Chem.*, **21**, 841 (1956); f) I. Chimielewska, J. Cieslak and T. Kraczkiewicy, *Roczniki Chem.*, **30**, 1009 (1956); g) I. Chimielewska, J. Cieslak, K. Gorczynska, B. Kontnik and Pitakowska, *Tetrahedron*, **4**, 36 (1958); h) D. Herbest, W. B. Mors, O. R. Gottlieb and C. Djerassi, *J. Am. Chem. Soc.*, **81**, 2427 (1959); i) R. H. Wiley and J. G. Esterle, *J. Org. Chem.*, **22**, 1257 (1957).

[5] Y. Hirata, "Infrared Absorption Spectrum", Vol. 12, Nankodo, Tokyo (1961), pp. 93—105.

[6] A good example reported[7] is the difference of pyrone carbonyl bands of A and B. A compound A has stronger electron-donating group (OCH_3), than a compound B.



1712 (sh.)
1701 cm^{-1} (A)

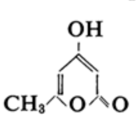


1739 cm^{-1} (B)

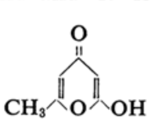
[7] E. A. Chandross and P. Yates, *Chem. & Ind.*, **1960**, 149.

[8] R. H. Wiley and S. C. Slaymaker, *J. Am. Chem. Soc.*, **78**, 2393 (1956).

substituent R_3 in Fig. 1 is an ester group (No. 9, No. 10), there appear two carbonyl bands, one of which at higher frequency is considered to be a band due to a pyrone carbonyl group. It has been known that halogen substitution in the alpha position of a carbonyl group results in a high-frequency shift of the carbonyl absorption as illustrated in α-haloketones[9], α-halo-esters[9] and $\Delta^{\alpha,\beta}$-α-halo-γ-lactone[10]. This general finding is expected for 3-bromo-α-pyrone derivative, but in fact this phenomenon was not an actual case and there was an indication that α-bromination rather resulted in a lowering of a carbonyl frequency[11] (see $\nu_{C=O}$ change in No. 2→No. 3 and No. 4→No. 5 in Fig. 1). This fact would be explicable if a factor leading to a low-frequency shift of $\nu_{C=O}$ (plausible one is $+M$ effect of bromine[12]) is operative in addition to the dipole-dipole interaction which causes a high-frequency shift of carbonyl band. This apparent anomaly is not observed, when the more electronegative substituent is introduced into an α-position of carbonyl group (3-nitro-α-pyrone derivatives), and in this case $\nu_{C=O}$ appears at fairly high frequency region. The effects of substituents on the bands related to the double bonds of pyrone ring seem to be complicated, but the clear points worthy of mention are that two bands appear in every case examined and that the band at a higher frequency is insensitive to the introduction of the substituent whereas the other is deeply influenced. As mentioned before, the carbonyl band differs in shape and position according to the condition of measurement—that is, solution or solid state. A remarkable example is triacetic lactone (II) (No. 6 in Fig. 1), the infrared spectrum of which taken in a solid state is complex in comparison with that in dioxane[13]. Two tautomeric forms IIa, IIb are possible for this compound and it is evident that IIa is an overwhelmingly predominant form in solution on the infrared and ultraviolet evidence (see Fig. 1 and Table I). In the solid state, II exhibits a complicated pattern of bands in 1800∼1500 cm^{-1} region as shown in Fig. 2, and the bands due to strong hydrogen bonds are observed. It should be noted that a spectrum of II is similar to that of methyl-ether of IIa (No. 4 in Fig. 1) in 1000∼700 cm^{-1} region.



IIa



IIb

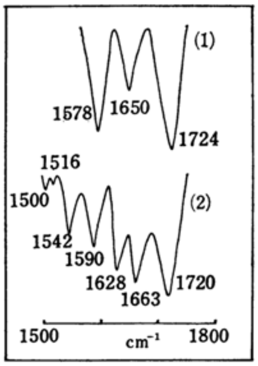


Fig. 2. Infrared spectra of triacetic lactone.
(1) Dioxane (2) KBr

γ-Pyrone.—As in α-pyrone series, the most characteristic frequencies available for detection of a γ-pyrone ring arise from carbonyl and C=C double bond vibrations. Usually a band near 1660 cm^{-1} (first band) is believed to originate from the carbonyl group[4h,14] and the bands (second and third bands) observed in 1650∼1560 cm^{-1} would correspond to the double bonds of γ-pyrone (see Fig. 3). However, intense couplings among $\nu_{C=C}$ and $\nu_{C=O}$ might occur in the compound of this series and the definite assignments of the bands are therefore difficult[15]. According to the data available from literatures[4h,14] and in Fig. 3, the introduction of a substituent makes but a small influence on the position of the first band near 1660 cm^{-1} and no significant change on this band was observed under various conditions of measurement. Though the carbonyl absorption of γ-pyrone itself shows the doublet peaks, no such phenomenon was found on the substituted γ-pyrones examined. In general, there appear two bands (the second band, the third band) associated with the double bonds. In comparison with those of α-pyrone series, the two bands are separated to a smaller

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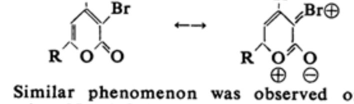
9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen & Co. Ltd., London (1958), p. 400.

10) Y. Hata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1531 (1958).

11) Similar result was obtained under the different conditions; i. e., in carbon tetrachloride solution and in solid state.

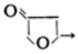
12)



13) Similar phenomenon was observed on 4-hydroxycoumarin. No definite conclusion as to the structure in the solid state was obtained: R. A. Abramovitch and J. R. Gear, *Can. J. Chem.*, **36**, 1501 (1958).

14) a) L. L. Woods, *J. Am. Chem. Soc.*, **77**, 3161 (1955); b) C. D. Hurd and S. Trofimenko, *J. Org. Chem.*, **23**, 1276 (1958); c) R. J. Light and C. R. Hauser, ibid., **25**, 538 (1960).

15) Cook assigned a band of the highest-frequency in 1600 cm^{-1} region to a ring stretching mode on the basis of the magnitude of the band shift observed on the various salts prepared from 2,6-dimethyl-γ-pyrone and Lewis acids: D. Cook, *Can. J. Chem.*, **39**, 1184 (1961).

No.	R_1	R_2	R_3	R_4
1	H	H	H	H
2	CH_3	H	H	CH_3
3	OCH_3	CH_3	CH_3	
4	OCH_3	H	H	CH_3
5*	H	OH	H	H
6*	CH_3	OH	H	H
7	CH_3	OCH_3	H	H
8*	CH_2OH	H	OCH_3	H
9*	CH_2OH	H	OH	H

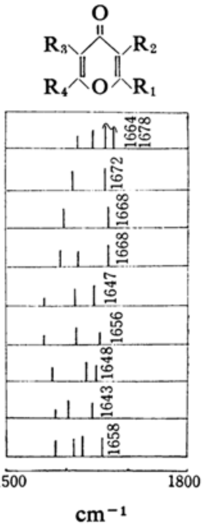


Fig. 3. Infrared spectra of γ-pyrone derivatives ($CHCl_3$ solution).
* KBr

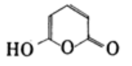
extent and their relative intensities to that of the carbonyl band are fairly strong.

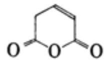
Ultraviolet Spectra. — *α-Pyrone.* — Ultraviolet spectra of a few α-pyrones were already reported[4h,7,16], especially 6-methyl-4-hydroxy-α-pyrone[17]. In order to avoid the factors of conjugation and/or strain, α-pyrone derivatives examined in the present study are those without fused rings—aromatic or alicyclic. In Table I are listed the ultraviolet spectra of various α-pyrones. Almost all the compounds recorded in Table I have their maxima near 300 mμ, and in some type of the substituted pyrones, the second absorption maximum with the higher intensity appears in the short wavelength region (250 mμ). In general, the introduction of substituents such as alkyl, carbonyl, bromine, etc. causes a bathochromic shift of the absorption band near 300 mμ.

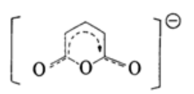
γ-Pyrone. — The absorption maxima of γ-pyrones appear in the shorter wavelength region (near 250 mμ) in comparison with those of α-pyrones. In Table II are shown absorption maxima of some γ-pyrone derivatives. The properties of the substituents are not so widely varied in the present study as well as in the compounds already reported[16c,18], as to permit to infer the substituent effect on the ultraviolet absorption.

On the Structural Problems of Some Pyrone Derivatives.—With these spectral characteristics at hand, the structural problems of pyrones are easily solved in some cases.

1) Tautomerism of Glutaconic Anhydride. — Glutaconic anhydride (III) and its derivatives have been assigned 6-hydroxy-α-pyrone structure (IIIa) on evidence from their chemical behaviors[19].


IIIa


IIIb


IIIc

In the infrared spectra of III, bands appeared at 1805, 1740, 1650 cm^{-1} in the solid state (KBr) and at 1800, 1760, 1650(w) cm^{-1} in chloroform solution and no hydroxyl bands were observed. Thus, it becomes evident that glutaconic anhydride exists as normal anhydride form IIIb in the solid state and chloroform solution. This conclusion is supported from the fact that no strong absorptions ascribable to α-pyrone structure IIIa were detected in the ultraviolet region (chloroform solution). In contrast to the transparency of III in chloroform solution, the ultraviolet absorptions with high intensities (λ_{max} 350 mμ, log ε, 4.21; 233 mμ, log ε, 3.91) were observed in ethanol, which are expected and accounted for by assuming the presence of the anion IIIc, since III is strongly acidic and hence is likely to dissociate in polar solvent such as

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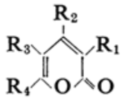
[16] a) R. B. Woodward and G. Small, *J. Am. Chem. Soc.*, **72**, 1297 (1950); b) J. A. Berson, ibid., **74**, 5172 (1952); c) J. A. Berson, W. M. Jones and S. L. F. O'Callaghan, ibid., **78**, 622 (1956); d) S. Pataki and K. Meyer, *Helv. Chim. Acta*, **38**, 1631 (1955).

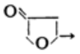
[17] It was established that α-form absorbs at longer wavelength than γ-form when there are two isomeric α- and γ-pyrones such as 6-methyl-2, 4-pyronone[4f,4h].

[18] a) J. A. Berson, *J. Am. Chem. Soc.*, **75**, 3521 (1953); b) W. M. McLamore, E. Gelblum and A. Bavley, ibid., **78**, 2816 (1956).

[19] a) N. Bland and J. F. Thorpe, *J. Chem. Soc.*, **101**, 856 (1912); b) R. H. Wiley and C. H. Jarboe Jr., *J. Am. Chem. Soc.*, **77**, 403 (1955).

Table I. Ultraviolet spectra* of α-pyrone

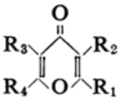


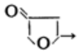
No.	Compound				λ_{max} (mμ)	log ε
	R_1	R_2	R_3	R_4		
1	H	H	CH_3	H	298	3.7**
2	H	CH_3	H	CH_3	290	3.78
3	Br	CH_3	H	CH_3	305	3.89
4	H	CH_3	COOH	CH_3	304	3.79
5	H	CH_3	$COOC_2H_5$	CH_3	292 (246	3.7 3.8)
6	H	H	$COOCH_3$	CH_3	293 (246	3.71 4.03)
7	H	H	$COOCH_3$	H	290 (245	3.61 3.96)
8	H	H	H	COOH	304 (225	3.87 —)
9	H	OH	H	CH_3	284	3.80
10	H	OCH_3	H	CH_3	280	3.86
11	NO_2	OH	H	CH_3	327 (306 (235	3.74 3.70) 3.95)
12	Br	OH	H	CH_3	296	3.94
13	$COCH_3$	OH	H	CH_3	310 (225	4.00 3.95)
14	$COCH_3$	OCH_3	H	CH_3	312	3.75
15	CH_3	OCH_3	CH_3		295	

* Measurements were made in ethanol. Absorption maxima in shorter wavelength region are put in parentheses.

** J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 566 (1941).

Table II. Ultraviolet spectra of γ-pyrone

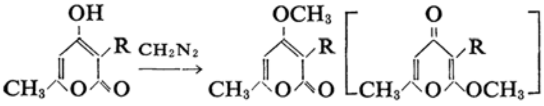


No.	Compound				λ_{max} (mμ)	log ε
	R_1	R_2	R_3	R_4		
1	H	H	H	H	248 (253) (260)	
2	CH_3	H	H	CH_3	247	4.02
3	H	OH	H	H	272	3.82
4	CH_3	OH	H	H	276	3.88
5	CH_3	H	H	OCH_3	240	4.05
6	CH_2OH	H	OH	H	266	3.85
7	CH_2OH	H	OCH_3	H	265	3.86
8		CH_3	CH_3	OCH_3	263 (248	3.90 3.84)

* Measurements were made in ethanol. A figure in parenthesis shows a position of the shoulder of the absorption.

ethanol. Upon addition of a drop of hydrochloric acid, the absorption maximum at 350 mμ disappeared and instead the new absorption appeared at 328 mμ (log ε, 3.04). Considering the α-pyrone structure IIIa, the new absoption, though quite reasonable as to its position, is unusually weak in intensity, implying that the equilibrium between two undissociated forms IIIa, IIIb is in favor of keto-form IIIb even in the polar solvent and a fraction of an enol form IIIa is small[20].

2) Structures of Triacetic Lactone Derivatives.—Both α- and γ-pyrone forms are possible for the 2, 4-pyronone system and it is a matter of importance, which of the two predominates in various substituted 2, 4-pyronones. As shown before, triacetic lactone (No. 6 in Fig. 1) exists as an α-form and the same result was obtained on 4-hydroxycoumarin[21], while the preferential existence of γ-form under the subtle influences of substituents and fused rings was reported[4h,22] in some derivatives of 2, 4-pyronone. There was some confusion as to the structures of triacetic lactone methylether, but two isomers were unambiguously isolated and assignments of the isomers to α- and γ-forms were carried out[23]. As one of the problems regarding the isomeric α- and γ-pyrones, Arndt and Avan reported the methylethers of 3-bromotriacetic lactone and 3-nitrotriacetic lactone[24]. It is evident from the spectral viewpoints (Fig. 1 and Table I) that α-pyrone structures are assigned to 3-bromotriacetic lactone (IV) and 3-nitrotriacetic lactone (V)[25], to which no structural reference was made by Arndt et al. Methylation of IV and V under conditions employed by Arndt et al., gave corresponding methylethers VI, VII.



IV : R=Br VI : R=Br VI′ : R=Br

V : R=NO_2 VII : R=NO_2 VII′ : R=NO_2

Arndt and Avan assigned γ-pyrone structures VI′, VII′ to these methylethers on the basis of their solubilities to concentrated hydrochloric acid. However, this conclusion is unacceptable. The infrared spectrum of bromo-derivative VI in solution is, as shown in Fig. 1, typical of α-pyrone structure and also in solid state the same is true (bands at 1703, 1640 and 1522 cm^{-1}). The ultraviolet spectral result also favors the α-pyrone structure for VI (λ_{max} 305 mμ, log ε, 3.95). Similarly, α-pyrone structure is established for nitro derivative (VII) from the infrared (bands at 1735, 1644, 1543 and 1525 cm^{-1} in chloroform) and ultraviolet (λ_{max} 310 mμ, log ε, 3.68 : 300 mμ, log ε, 3.75) spectral data. Accordingly, the methylethers obtained by Arndt et al., in fact, have α-pyrone structures.

Experimental

Infrared spectra were measured with a Hilger H 800 Model. The ultraviolet spectra were measured with a Beckman DK-2 spectrophotometer.

Synthesis and Characterization of Compounds.—*Dehydroacetic Acid (No. 12 in Fig. 1).*—Commercial sample recrystallized from ethanol, m. p. 107∼108°C.

Dehydroacetic Acid Methylether (No. 13 in Fig. 1). — Prepared as described by Perkin[26], m. p. 89∼90°C.

Triacetic Lactone (No. 6 in Fig. 1).—Obtained by the procedure of Collie[27], m. p. 185∼186°C.

6-Methyl-4-methoxy-α-pyrone (No. 4 in Fig. 1) and 6-Methyl-2-methoxy-γ-pyrone (No. 4 in Fig. 3).—Treatment of triacetic lactone with ethereal diazomethane gave a mixture of two isomers, the separation of which was carried out by the salt formation of γ-pyrone isomer[23b]; α-isomer, m. p. 85∼86°C; γ-isomer, m. p. 93∼94°C.

3-Bromotriacetic Lactone (No. 7 in Fig. 1) and 3-Nitrotriacetic Lactone (No. 14 in Fig. 1).—Prepared as described by Arndt and Avan[24]. Bromo compound decomposed above 210°C. Found : C, 35.51 ; H, 2.53. Calcd. for $C_6H_5O_3Br$: C, 35.14 ; H, 2.46%. Nitro compound had m. p. 162∼164°C. Found : C, 41.83 ; H, 3.16 ; N, 8.23. Calcd. for $C_6H_5O_5N$: C, 42.11 ; H, 2.95 ; N, 8.19%.

6-Methyl-4-methoxy-3-bromo-α-pyrone (No. 5 in Fig. 1) and 6-Methyl-4-methoxy-3-nitro-α-pyrone.—Prepared as described by Arndt and Avan[24]. 3-Bromo compound, m. p. 151∼152°C. Found : C, 38.59 ; H, 3.31. Calcd. for $C_7H_7O_3Br$: C, 38.38 ; H, 3.23%. Nitro compound, m. p. 165∼167°C. Found : C, 45.34 ; H, 3.93 ; N, 7.69. Calcd. for $C_7H_7O_5N$: C, 45.41 ; H, 3.81 ; N, 7.57%.

Isodehydroacetic Acid (No. 11 in Fig. 1).—Prepared from ethyl acetoacetate and concentrated sulfuric acid[28]. M. p. 152∼154°C.

4, 6-Dimethyl-α-pyrone (No. 2 in Fig. 1). — Isodehydroacetic acid (or ethyl isodehydroacetate) was heated with concentrated sulfuric acid at 160°C, and a mixture was diluted with water and extracted with ether[28], m. p. 49∼50°C.

4, 6-Dimethyl-3-bromo-α-pyrone (No. 3 in Fig. 1). — Prepared from 4, 6-dimethyl-α-pyrone[29], m. p. 102∼104°C.

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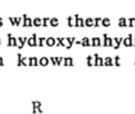
[20] In some cases where there are structural factors that would stabilize the hydroxy-anhydride form as encountered in C, it has been known that α-pyrone structure predominates:



(C)

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Methyl Coumalate (No. 9 in Fig. 1). — Coumalic acid was treated with 1.5 equivalent amount of ethereal diazomethane, m. p. 71~72°C.

Methyl 6-Methylcoumalate (No. 10 in Fig. 1). — Coumalic acid was treated with a large excess amount of diazomethane (3~4 mol. equiv.) at room temperature. In this case, *C*-methylation took place at 6-position of coumalic acid, in addition to *O*-methylation (ester formation). Recrystallization from ether gave rectangular plates, m. p. 83~85°C (reported 86~87°C[30]).

2,6-Dimethyl-γ-pyrone (No. 2 in Fig. 3). — Decarboxylation of dehydroacetic acid, m. p. 128~130°C.

Pyromeconic Acid (No. 5 in Fig. 3). — M. p. 114~115°C.

Maltol (No. 6 in Fig. 3).—M. p. 158~160°C.

Maltol Methylether (No. 7 in Fig. 3). — Prepared from maltol and diazomethane, colorless liquid, b. p. 122~125°C/20 mmHg.

Kojic acid (*No. 9 in Fig. 3*).—M. p. 150~151°C.

Kojic Acid Monomethylether (*No. 8 in Fig. 3*).—Action of ethereal diazomethane on kojic acid gave needles, m. p. 161~163°C.

Glutaconic Anhydride (III). — Prepared by dehydration of glutaconic acid with acetic anhydride and purified by distillation under reduced pressure, m. p. 84~86°C, recrystallization from benzene.

Summary

Effects of substituents on the characteristic bands of pyrones were examined in the infrared spectra. Ultraviolet spectra of various α- and γ-pyrones were recorded and the application of the spectroscopic results obtained, disclosed the problems of tautomerism and isomerism concering some of the pyrone derivatives.

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