Tetrahedron, 1961, Vol. 14, pp. 223 to 229. Pergamon Press Ltd. Printed in Northern Ireland

THE INTENSITIES OF THE CARBONYL BANDS IN THE INFRA-RED SPECTRA OF 2- AND 4-QUINOLONES

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Abstract—The intensities of the carbonyl bands in the infrared spectra of sixty-five 2- or 4-quinolones have been measured. The results indicate that the high intensities of 2-quinolones distinguish them from 4-quinolones. Some applications in alkaloid chemistry are discussed, including proof that the ring system of maculosidine (XXVII) is linear.

IT is often important in the chemistry of quinoline alkaloids to distinguish between a 2- and 4-quinolone. The different criteria which have been adopted for this purpose have recently been summarised by Rapoport and Holden.[1] One distinction was based on the infra-red spectra of model compounds, amongst which 2-quinolones were found to absorb at 1660–1650 cm^{-1}, and 4-quinolones at 1630–1620 cm^{-1}.[2,3] However, increasing numbers of 2- and 4-quinolones have since been found which absorb in the same frequency region, namely 1647–1631 cm^{-1}.[4,5] It has been noticed, on the other hand, that the 2-quinolone absorption band has a characteristic shape and high intensity,[5] and it is now shown that 2- and 4-quinolones may be differentiated by measuring the carbonyl intensities.

The determination of infra-red spectra in the solid state suffers from the disadvantage that frequency and relative intensity changes are often observed, depending on the state of division of the sample.[6] Owing to the low solubility of many quinolones in common infra-red solvents, very few quinolones have had their spectra measured in solution. The author has tested methylene bromide and bromoform as solvents, but many quinolones, notably 4-quinolones and 4-hydroxy-2-quinolones are sparingly soluble even in these. It was found, however, that almost all the quinolones which were tried, were soluble in dimethylsulphoxide. This has only low absorption in the carbonyl region and would be a suitable solvent but for the fact that it dissolves, to a significant extent, the potassium bromide of which cells are generally composed. However, potassium bromide was found to be virtually insoluble in mixtures of 1 part dimethylsulphoxide with 3 or 4 parts of chloroform. These mixtures readily dissolved the quinolones and, where spectra could be obtained in chloroform or methylene bromide as well as in the sulphoxide–chloroform mixture, results proved to be similar.

Integrated intensities were calculated by the method of Cabana and Sandorfy.[7] In the few cases where shoulders occurred on the high frequency side of bands, these were included in the intensity calculations using the Cabana–Sandorfy treatment for

[1] H. Rapoport and K. G. Holden, *J. Amer. Chem. Soc.* **82**, 4395 (1960).
[2] B. Witkop, J. P. Patrick and M. Rosenblum, *J. Amer. Chem. Soc.* **73**, 2641 (1951).
[3] M. F. Grundon, N. J. McCorkindale and M. N. Rodger, *J. Chem. Soc.* 4284 (1955).
[4] J. R. Price and J. B. Willis, *Aust. J. Chem.* **12**, 589 (1959).
[5] M. F. Grundon and N. J. McCorkindale, *J. Chem. Soc.* 2177 (1957).
[6] R. N. Jones and C. Sandorfy, *Technique of Organic Chemistry* Vol IX, pp. 294–297. Interscience, New York (1956).
[7] A. Cabana and C. Sandorfy, *Spectrochim. Acta* **16**, 335 (1960).

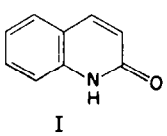
TABLE 1. INTEGRATED BAND INTENSITIES (IN ABSOLUTE UNITS) OF 2-QUINOLONES AND N-METHYL-2-QUINOLONES

No.	Structure	ν_{max} (cm^{-1})	ε^{a}_{max}	A_s† $\times 10_7$	$A_{1/4}$† $\times 10^7$	$A_{1/2}$† $\times 10^7$	A_m† $\times 10_7$
1	I	1658[a]*	1451	48·8	53·1	62·0	50·5
		1659[c]*	1528	51·6	54·1	63·3	53·2
2	I, 4-NHPh[9,10]	1645[a]	1854	42·6	43·5	49·4	46·1
3	II[11]	1641[a]	1274	39·4	39·8	47·7	42·2
4	II, 8-MeO[11]	1640[b]	1734	65·8	68·7	68·7	65·5
5	II, 7-MeO[12]	1642[a]	1201	51·8	53·8	60·2	55·5
6	II, 5:8-diMeO[11]	1649[c]	2047	56·8	55·6	54·9	56·8
7	II, 8-Ph[11]	1634[b]	1676	76·7	77·8	84·0	79·3
8	II, 5:6-benzo[11]	1640[a]	1550	67·2	67·9	80·9	75·6
9	II, 8-MeO_2C[11]	1637[a]	1603	61·6	63·4	71·6	66·1
10	III, 4-OH[5,9]	1640[d]	1658	45·7	44·1	42·9	43·4
11	IV[8,9]	1656[d]	2061	47·7	44·6	48·2	47·8
12	V[9,13]	1644[d]	1717	51·6	49·5	57·7	54·1
13	VI[14]	1660[a]	1358	46·3	47·4	45·9	46·1
14	VI, 8-MeO[15]	1657[b]	1674	55·6	60·3	64·8	58·3
		1657[c]	1630	51·8	55·3	60·2	54·1
15	VI, 7-MeO[15]	1657[c]	1438	52·0	55·5	59·2	55·8
16	VI, 5:8-diMeO[15]	1655[c]	1714	61·1	62·6	72·0	66·2
17	VI, 8-Ph[15]	1657[c]	1406	46·6	47·0	55·3	50·0
18	VI, 8-MeO_2C[15]	1658[c]	1636	60·3	58·1	69·2	64·5
19	VI, 5:6-benzo[15]	1658[a]	1614	59·2	60·5	72·1	63·1
20	VII	1654[c]	1436	57·6	58·5	69·4	58·2
21	VII, 5:8-diMeO	1651[c]	1526	59·6	58·9	69·6	63·3
22	VII, 8-MeO_2C	1653[c]	1428	62·4	57·4	72·0	66·5

* Peaks marked with an asterisk had a shoulder on the high frequency side of the main band. This was included in the calculations.

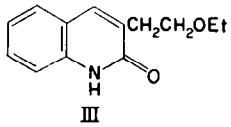
† A_s is the value of the integrated intensity computed by the method of segments. $A_{1/4}$ and $A_{1/2}$ are those based on $\Delta\nu^a_{1/4}$ and $\Delta\nu^a_{1/2}$, A_m is the mean of $A_{3/4}$, $A_{1/2}$, $A_{1/4}$ and $A_{1/8}$.

[a] Chloroform-dimethylsulphoxide (3:1)
[b] Chloroform-dimethylsulphoxide (4:1)
[c] Chloroform
[d] Methylene bromide



I

II R = OH
VI R = $OCOCH_3$
VII R = Cl
VIII R = OMe

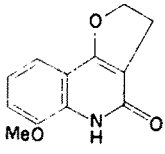


III

[9] Sample kindly provided by Dr. M. F. Grundon, Queen's University, Belfast.
[10] F. H. S. Curd, C. G. Raison and F. L. Rose, *J. Chem. Soc.* 899 (1947).
[11] Preparation as for compound no. 5 (*cf.* ref. 12).
[12] R. G. Cooke and H. F. Haynes, *Aust. J. Chem.* 7, 273 (1954).
[13] M. F. Grundon and N. J. McCorkindale, *J. Chem. Soc.* 3448 (1957).
[14] T. Ohta, *J. Pharm. Soc. Japan* 73, 63 (1953).
[15] Preparation as for compound no. 13 (*cf.* ref. 14).

TABLE 1 (*contd.*)

No.	Structure	ν_{max} (cm^{-1})	ε^{a}_{max}	A_s $\times 10^7$	$A_{1/4}$ $\times 10^7$	$A_{1/2}$ $\times 10^7$	A_m $\times 10^7$
23	VII, 8-MeO	1653[c]	1324	50·9	52·4	59·2	54·6
24	III, 4-Cl[5,9]	1651[d]	1510	52·2	52·3	58·5	54·8
25	I, 3-HO_2C[16]	1638[a,*]	1008	33·7	42·1	30·5	33·0
26	I, 4-HO_2C[17]	1666[a]	1431	49·3	50·8	56·3	51·4
27	VIII[14]	1650[c]	1443	53·0	58·7	59·8	55·8
28	VIII, 8-MeO[18]	1648[c]	1761	59·2	58·8	66·6	62·6
29	VIII, 7-MeO[18]	1647[c]	1402	54·9	57·0	62·7	59·3
		1649[b]	1426	47·7	47·6	58·7	51·4
30	VIII, 6-MeO[18]	1650[c]	1339	42·0	44·0	45·2	43·9
31	VIII, 5:8-diMeO[18]	1646[c]	1741	62·6	63·2	74·1	68·2
		1648[b]	1552	57·2	56·7	69·4	63·9
32	VIII, 6:8-diMeO[18,19]	1648[c]	1273	34·3	35·8	37·3	35·5
33	VIII, 8-Ph[18]	1648[c]	1510	56·4	58·3	67·5	61·2
34	IX[3]	1651[a]	1391	56·3	55·9	61·0	58·5
		1649[d]	1498	53·7	54·3	58·5	57·2
35	X[20]	1652[a,*]	1297	34·7	38·0	37·4	36·8
36	XI	1638[a,*]	1366	41·3	45·3	45·9	40·7
37	XII[14]	1630[b]	1042	45·2	42·9	54·0	49·4
38	XII, 8-MeO_2C[21]	1632[a]	1137	38·8	41·5	46·8	41·8
39	XII, 7-MeO[12]	1626[a]	1076	38·9	41·4	48·2	41·7
40	XIII[21]	1639[a]	1353	41·7	46·6	52·3	43·2
41	XIV[21]	1636[c]	1269	35·5	35·7	38·6	37·5
		1635[a]	1205	36·3	37·7	37·4	36·8
42	XIV, 7-MeO[21]	1632[c]	1292	41·3	41·8	46·2	42·6
43	XIV, 8-MeO_2C[21]	1640[b]	1352	53·2	52·2	60·4	55·2
44	XV[22]	1659[d]	1787	60·3	59·7	67·1	62·9



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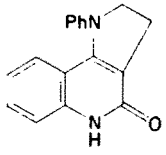
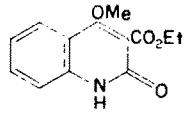


V



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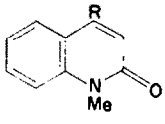
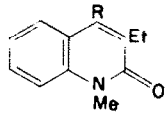
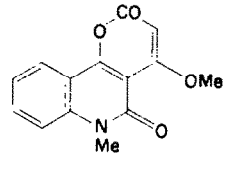


X R = H
XI R = OH
XIII R = OMe



XII R = OH
XIV R = OMe



XV

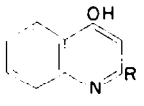
[16] P. Friedlander and C. F. Goering, *Ber. Dtsch. Chem. Ges.* **17**, 459 (1884).
[17] Sample kindly supplied by Dr. J. D. Loudon, Glasgow University.
[18] Preparation as for compound no. 27 (*cf.* ref. 14).
[19] R. H. Prager, E. Ritchie and W. C. Taylor, *Aust. J. Chem.* **13**, 385 (1960).
[20] Sample kindly supplied by Dr. A. Kent, Glasgow University.
[21] Preparative method as in ref. 12.
[22] M. F. Grundon and N. J. McCorkindale, unpublished work. *Cf.* R. E. Bowman, A. Campbell and E. M. Turner, *J. Chem. Soc.* 444 (1959).

TABLE 2. INTEGRATED BAND INTENSITIES (IN ABSOLUTE UNITS) OF 4-QUINOLONES AND N-METHYL-4-QUINOLONES

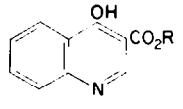
No.	Structure	ν_{max} (cm^{-1})	ε^{a}_{max}	A_s $\times 10^7$	$A_{1/4}$ $\times 10^7$	$A_{1/2}$ $\times 10^7$	A_m $\times 10^7$
45	XVI[23]	1635[b]	689	21·5	20·1	21·4	20·9
		1636[a]	580	16·3	17·0	17·5	16·4
46	XVI, 8-MeO[24]	1632[a]	501	10·3	9·9	10·5	10·2
47	XVII[17,25]	1638[a]	524	14·9	17·1	16·8	15·8
48	XVII, 5:8-diMeO[25]	1639[a]	883	22·1	20·3	20·3	21·1
49	XVII, 6:8-diCl[17,25]	1639[a]	671	16·2	15·7	18·2	17·8
50	XVIII,[26]	1633[a]	676	8·9	9·9	10·9	9·7
51	XIX[23]	1624[a]	794	22·6	22·4	28·2	24·5
52	XIX, 8-Ph[27]	1629[c]	615	25·1	25·0	30·3	27·3
		1626[a]	682	25·8	25·6	27·9	26·6
53	XIX, 8-MeO_2C[28]	1645[a]	413			12·4*	
54	XIX, 8-MeO[24]	1622[a]	412	13·1	12·9	15·7	14·4
55	XX, 5:8-diMeO[27]	1629[a]	819	24·6	25·7	29·1	25·8
56	XXI[17]	1632[a]	421	12·9	12·3	12·7	12·7
57	XXI, 7-Cl[17]	1632[a]	620	21·8	21·3	20·3	21·1
58	XXII[17]	1630[a]	460			13·9*	
59	XXII, 6-Cl[17]	1633[a]	572			20·7*	
60	XVI, 8-Ph[27,29]	1629[c]	1390	22·2	21·3	22·1	21·7
61	XVI, 7:8-benzo[27,30]	1632[a]	1169	18·8	20·1	20·1	19·5
62	XXIII, 8-Ph[31]	1628[a]	991	22·0	23·8	26·2	23·7
63	XXIII, 2-Me[31]	1624[a]	952	20·5	22·3	24·1	21·8
64	XXIII, 2-Ph[32]	1622[a]	722	16·6	16·9	22·3	18·6
65	XXIII[31,33]	1629[a]	760	20·5	22·2	25·6	22·2

* In this case it was not found possible to measure the quarter and eighth band widths owing to the presence of an adjoining peak on both sides of the carbonyl band.

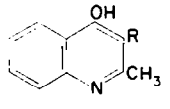
[a] Chloroform-dimethylsulphoxide (3:1) [b] Chloroform-dimethylsulphoxide (4:1) [c] Chloroform



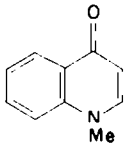
XVI R = H
XVII R = Me
XVIII R = Ph



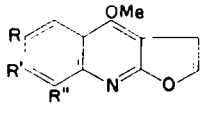
XIX R = Et
XX R = H



XXI R = CO_2Et
XXII R = $COCH_3$



XXIII



XXIV R = R' = R'' = H
XXV R = R' = H; R'' = OMe
XXVI R = R'' = H; R' = OMe
XXVII R = R'' = OMe; R' = H

[23] C. C. Price and R. M. Roberts, *J. Amer. Chem. Soc.* **68**, 1204 (1946)
[24] W. M. Lauer R. T. Arnold, B. Tiffany and J. Tinker, *J. Amer. Chem. Soc.* **68**, 1268 (1946).
[25] M. Conrad and L. Limpach, *Ber. Dtsch. Chem. Ges.* **21**, 1965 (1888).
[26] R. C. Fuson and D. M. Burness, *J. Amer. Chem. Soc.* **68**, 1270 (1946)
[27] Preparation by the Price–Roberts method (*cf.* ref. 23).
[28] M. F. Grundon and V. Boekelheide, *J. Amer. Chem. Soc.* **74**, 2637 (1952).
[29] C. E. Kaslow and M. Hayek, *J. Amer. Chem. Soc.* **73**, 4986 (1951).
[30] R. E. Foster, R. D. Lipscomb, T. J. Thompson and C. S. Hamilton, *J. Amer. Chem. Soc.* **68**, 1327 (1946
[31] Methylation as in the preparation of compound no. 64 (*cf.* ref. 32).
[32] R. Johnstone, J. R. Price and A. R. Todd, *Aust. J. Chem.* **11**, 562 (1958).
[33] E. Spath and A. Kolbe, *Monatsh.* **53**, 421 (1922).

unsymmetrical bands. Shoulders on the low frequency side were not included, since these might be attributable to ring vibrations. Intensities are given in absolute units, cm, c/s, molecule, ln.

The results given in Tables 1–2 support the generalization that the amide carbonyl absorption of 2-quinolones is considerably more intense than that of 4-quinolones. The carbonyl intensities found for the 4-quinolones (8·9–25·8 units) are comparable to those found for a group of anilides (Table 3), and to those recorded[8] for some acetamides, benzamides and acetanilides (11·6–22·5 units). The carbonyl intensities of the 2-quinolones lie in a higher range (33·7–76·7 units). Accordingly, despite the fact that a number of the 2- and 4-quinolones examined absorb in the same frequency range (1649–1626 cm^{-1}), the high peak intensities of the 2-quinolones allow them to be distinguished from the 4-quinolones.

The apparent molecular extinction coefficients (ε^a_{max}) corresponding to the carbonyl absorption are again large in the case of 2-quinolones (1000–2000). Although the majority of the 4-quinolones had ε^a_{max} values considerably less than 900, four had higher values (compounds nos. 60–63), and, on the basis of ε^a_{max} value alone, would be indistinguishable from 2-quinolones. The carbonyl bands of these were, however, narrow and the integrated areas were therefore similar to those of other 4-quinolones.

Comparing the results obtained by the different methods of intensity estimation (Tables 1–2), it may be seen that intensity values given by $A_{1/4}$ (i.e. based on $\Delta\nu^a_{1/4}$, the apparent quarter band width) and by A_m (the mean of $A_{3/4}$, $A_{1/2}$, $A_{1/4}$ and $A_{1/8}$) allow the same empirical classification of the quinolones as the more accurate values given by the method of segments (A_s). $A_{1/2}$ is not quite so satisfactory in this respect. The results agree with the suggestion of Cabana and Sandorfy[7] that, for symmetrical bands, $A_{1/4}$ is a more useful approximation of the intensity than $A_{1/2}$.

The structures of some of the quinolones examined are relevant to the structures of different alkaloids. The carbonyl intensities of ethyl dictamnate (IX) (53·7 units), derived from the alkaloid dictamnine (XXIV), and of 2-phenyl-4-quinolone (8·9 units) and 1-methyl-2-phenyl-4-quinolone* (16·6 units), derived from the alkaloid 4-methoxy-2-phenylquinoline,[34] are in accord with their respective structures.

Hydrogenolysis of many furoquinoline alkaloids gives rise to a 3-ethyl-4-methoxy-2-quinolone, which may be synthesised.[35] It is assumed in the synthesis that diazomethane effects selective methylation of the 4-hydroxy group in the corresponding 4-hydroxy-2-quinolone. If the 2-quinolone structure of these hydrogenolysis products is established, it follows that the furan oxygen in the respective alkaloids is attached to the 2- rather than the 4- position. Seven 3-ethyl-4-methoxy-2-quinolones are included in Table 1, three of which (compounds nos. 27–29) correspond to the alkaloids of established structure dictamnine (XXIV),[5] fagarine (XXV)[5] and evolitrine (XXVI)[36] respectively. The high carbonyl intensities of these three quinolones (47·7–59·2 units) reaffirms their 2-quinolone structure.

The structure of the alkaloid maculosidine, however, has not been established rigorously, and the linear arrangement of its ring system rests on the properties of the hydrogenolysis product, assigned the structure XXVII on spectral grounds (λ_{max} 280 mμ, ν_{max} (in Nujol) 1646 cm^{-1}). Compound no. 32, synthesized during the

* This compound has also been isolated recently from natural sources.[1]

[8] H. W. Thompson and D. A. Jameson, *Spectrochim. Acta* **13**, 236 (1958).

TABLE 3. INTEGRATED BAND INTENSITIES (IN ABSOLUTE UNITS) OF ANILIDES

No.	Structure	ν_{max} (cm^{-1})	ε^{a}_{max}	A_s $\times 10^7$	$A_{1/4}$ $\times 10^7$	$A_{1/2}$ $\times 10^7$	A_m $\times 10^7$
66	Acetanilide	1682[b]	447	14·9*	16·3	19·5	17·7
67	*p*-Cl-acetanilide[17]	1686[a]	405	14·9*	15·2	16·2	15·5
68	*p*-MeO-acetanilide	1684[b]	475	18·9*	19·3	20·8	19·9
		1676[a]	509	19·0	19·5	21·6	20·4
69	*o*-Cl-acetanilide[17]	1693[a]	319	16·4	19·5	20·0	19·8
70	2:4-diMeO-acetanilide[17]	1680[a]	351	13·8	14·1	17·3	15·7
71	α-Et-malon-di-*o*-anisidide†	1681[a]	324	15·3	16·9	15·2	15·5

* Thompson and Jameson[8] report the integrated intensities of compounds no. 66–68 as 15·1, 14·7 and 16·8 units respectively (chloroform solutions).
† Intensity per carbonyl group.
[a] Chloroform-dimethylsulphoxide (3:1).
[b] Chloroform.

present work, was identical with an authentic sample of the hydrogenolysis product. It was found that in KBr, the carbonyl frequency was unexpectedly low, 1626 cm^{-1}. However, the method of synthesis and the high carbonyl intensity (34·3 units) of this compound confirm it as a 2-quinolone, and hence the linear structure of the alkaloid.

EXPERIMENTAL

The infra-red spectra were determined on a Unicam SP100 instrument (Mark II), using a diffraction grating and with spectral slit widths of 4·0–4·7 cm^{-1}. The measurements were carried out on 6–12 mg samples dissolved in 5 cm^3 of solvent, using 0·5 mm cells.

The compounds examined were purified commercial samples or were prepared by standard methods. References to known compounds and preparative methods are included in Tables 1–3, and the properties of new compounds are noted briefly below.

M.p.s were measured on a Kofler block and are uncorrected.

3-Ethyl-4-hydroxy-8-methoxy-2-quinolone. (II, 8-MeO). M.p.226–227° (alcohol). (Found: C, 66·0; H, 5·7; N, 6·2. $C_{12}H_{13}O_3N$ requires: C, 65·7; H, 6·0; N, 6·4%).

3-Ethyl-4-hydroxy-5:8-dimethoxy-2-quinolone (II, 5:8-diMeO). M.p.217–218° (alcohol). (Found: C, 62·4; H, 5·7; N, 5·5. $C_{13}H_{15}O_4N$ requires: C, 62·6; H, 6·1; N, 5·6%).

3-Ethyl-4-hydroxy-8-phenyl-2-quinolone (II, 8-Ph). M.p.233–235° (alcohol). (Found: C, 76·7; H, 5·4; N, 5·4. $C_{17}H_{15}O_2N$ requires: C, 77·0; H, 5·7; N, 5·3%).

5:6-Benzo-3-ethyl-4-hydroxy-2-quinolone (II, 5:6-benzo). M.p.270–275° (acetic acid). (Found: C, 75·6; H, 5·4; N, 6·0. $C_{15}H_{13}O_2N$ requires: C, 75·3; H, 5·5; N, 5·9%).

3-Ethyl-4-hydroxy-8-methoxycarbonyl-2-quinolone (II, 8-MeO_2C). M.p.245° (alcohol). (Found: C, 63·2; H, 4·8; N, 5·5. $C_{13}H_{13}O_4N$ requires: C, 63·2; H, 5·3; N, 5·7%).

4-Acetoxy-3-ethyl-8-methoxy-2-quinolone (VI, 8-MeO). M.p.180–182° (alcohol). (Found: C, 64·4; H, 5·6. $C_{14}H_{15}O_4N$ requires: C, 64·4; H, 5·8%).

4-Acetoxy-3-ethyl-7-methoxy-2-quinolone (VI, 7-MeO). M.p.223° (aqueous alcohol). (Found: C, 64·1; H, 5·9. $C_{14}H_{15}O_4N$ requires: C, 64·4; H, 5·8%).

4-Acetoxy-3-ethyl-5:8-dimethoxy-2-quinolone (VI, 5:8-diMeO). M.p.184–188° (aqueous alcohol). (Found: C, 62·0; H, 6·0. $C_{15}H_{17}O_5N$ requires: C, 61·9; H, 5·9%).

4-Acetoxy-3-ethyl-8-phenyl-2-quinolone (VI, 8-Ph). M.p.215–217° (alcohol). (Found: C, 74·3; H, 5·5. $C_{19}H_{17}O_3N$ requires: C, 74·3; H, 5·6%).

4-Acetoxy-3-ethyl-8-methoxycarbonyl-2-quinolone (VI, 8-MeO_2C). M.p.171–172° (alcohol). (Found: C, 62·5; H, 5·0. $C_{15}H_{15}O_5N$ requires: C, 62·3; H, 5·2%).

4-Acetoxy-5:6-benzo-3-ethyl-2-quinolone (VI, 5:6-benzo). M.p.266–271° (alcohol), (Found: C, 72·8; H, 5·2; N, 5·1. $C_{17}H_{15}O_3N$ requires: C, 72·6; H, 5·4; N, 5·0%)

[34] S. Goodwin, A. F. Smith, and E. C. Horning, *J. Amer. Chem. Soc.* **79**, 2239 (1957).
[35] T. Ohta and Y. Mori, *Ann. Rep. Tokyo Coll. Pharm.* **5**, 48 (1955).
[36] T. Ohta and Y. Mori, *J. Pharm. Soc. Japan* **78**, 446 (1958).

4-Chloro-3-ethyl-2-quinolones (compounds nos. 20–23) were prepared conveniently in 50–60% overall yield from the appropriate 3-ethyl-4-hydroxy-2-quinolone by successive treatments with phosphorus oxychloride and acetic acid.[37] When, however, this process was applied to 3-ethyl-4-hydroxy-2-quinolone (II, 8-Ph), a 55% yield of 4-acetoxy-3-ethyl-8-phenyl-2-quinolone was obtained, identical (m.p., mixed m.p. and infra-red spectrum) with a sample prepared as above.

4-Chloro-3-ethyl-2-quinolone (VII). M.p.222–225° (aqueous alcohol). (Found: C, 63·6; H, 4·9. $C_{11}H_{10}ONCl$ requires: C, 63·6; H, 4·9%).

4-Chloro-3-ethyl-5:8-dimethoxy-2-quinolone (VII, 5:8-diMeO). M.p.201–204° (alcohol). (Found: 58·1; H, 5·0. $C_{13}H_{14}O_3NCl$ requires: C, 58·3; H, 5·3%).

4-Chloro-3-ethyl-8-methoxycarbonyl-2-quinolone (VII, 8-MeO_2C). M.p. 142–142·5° (aqueous alcohol). (Found: C, 58·9; H, 4·2. $C_{13}H_{12}O_3NCl$ requires: C, 58·8; H, 4·6%).

4-Chloro-3-ethyl-8-methoxy-2-quinolone (VII, 8-MeO). M.p. 206–208° (alcohol). (Found: C, 60·6; H. 5·2. $C_{12}H_{12}O_2NCl$ requires: C, 60·6; H, 5·1%).

3-Ethyl-4:8-dimethoxy-2-quinolone (VIII, 8-MeO). M.p.116–118° (light petroleum, b.p. 60–80°). (Found: C, 67·1; H, 6·4. $C_{13}H_{15}O_3N$ requires: C, 66·9; H, 6·5%).

3-Ethyl-4:7-dimethoxy-2-quinolone (VIII, 7-MeO). M.p. 152·5–154° (benzene–light petroleum). (Found: C, 67·4; H, 6·3. $C_{13}H_{15}O_3N$ requires: C, 66·9; H, 6·5%).

3-Ethyl-4:6-dimethoxy-2-quinolone (VIII, 6-MeO). M.p. 167–169° (benzene–light petroleum). (Found: C, 66·9; H, 6·6; N, 6·3. $C_{13}H_{15}O_3N$ requires: C, 66·9; H, 6·5; N, 6·0%).

3-Ethyl-4:5:8-trimethoxy-2-quinolone (VIII, 5:8-diMeO). M.p. 149–150° (benzene–light petroleum). (Found: C, 64·0; H, 6·4. $C_{14}H_{17}O_4N$ requires: C, 63·9; H, 6·5%).

3-Ethyl-4:6:8-trimethoxy-2-quinolone (VIII, 6:8-diMeO). M.p. 130–131° (light petroleum, b.p. 60–80°). (Found: C, 64·0; H, 6·6; N, 5·5. Calc. for $C_{14}H_{17}O_4N$: C, 63·9; H, 6·5; N, 5·3%). There was no depression in m.p., on admixture with an authentic sample* of the hydrogenolysis product of maculosidine, m.p. 130–131°†. The ultra-violet and infra-red spectra of the product were identical with those of the authentic sample.

3-Ethyl-4-methoxy-8-phenyl-2-quinolone (VIII, 8-Ph). M.p. 135–136° (light petroleum, b.p. 60–80°). (Found: C, 77·6; H, 5·8. $C_{18}H_{17}O_2N$ requires: C, 77·4; H, 6·1%).

3-Ethyl-4-hydroxy-8-methoxycarbonyl-1-methyl-2-quinolone (XII, 8-MeO_2C). M.p. 242–243° (aqueous alcohol). (Found: C, 64·4; H, 5·4; OMe, 11·4. $C_{14}H_{15}O_4N$ requires: C, 64·4; H, 5·8; one OMe, 11·9%).

3-Ethyl-4-methoxy-1-methyl-2-quinolone (XIV). M.p. 82–83·5° (light petroleum, b.p. 40–60°). (Found: C, 71·9; H, 6·9. $C_{13}H_{15}O_2N$ requires: C, 71·9; H, 7·0%).

3-Ethyl-4:7-dimethoxy-1-methyl-2-quinolone (XIV, 7-MeO). B.p. 160–180° (bath temp.)/0·1 mm, m.p. 72–74° (light petroleum, b.p. 40–60°). (Found: C, 68·1; H, 6·9. $C_{14}H_{17}O_3N$ requires: C, 68·0; H, 6·9%).

3-Ethyl-4-methoxy-8-methoxycarbonyl-1-methyl-2-quinolone (XIV, 8-MeO_2C). M.p. 119–120° (light petroleum b.p. 40–60°). (Found: C, 65·4; H, 6·1. $C_{15}H_{17}O_4N$ requires: C, 65·4; H, 6·2%).

5:8-Dimethoxy-2-methyl-4-quinolone (XVII, 5:8-diMeO). M.p. 216–217° (dimethylformamide.) (Found: C, 65·9; H, 5·8; N, 6·6. $C_{12}H_{13}O_3N$ requires: C, 65·7; H, 6·0; N, 6·4%).

3-Ethoxycarbonyl-8-phenyl-4-quinolone (XIX, 8-Ph). M.p. 245–248° (pyridine–alcohol). (Found: C, 73·7; H, 5·0; N, 5·1. $C_{18}H_{15}O_3N$ requires: C, 73·7; H, 5·2; N, 4·8%).

3-Carboxy-5:8-dimethoxy-4-quinolone (XX, 5:8-diMeO). M.p. 270–271° (acetone). (Found: C, 57·5; H, 4·6; N, 5·5. $C_{13}H_{11}O_5N$ requires: C, 57·8; H, 4·5; N, 5·6%).

8-Phenyl-4-quinolone (XVI, 8-Ph). M.p. 203·5–204·5°‡ (aqueous alcohol). (Found: C, 81·1; H, 4·8; N, 6·5. Calc. for $C_{15}H_{11}ON$: C, 81·4; H, 5·0 N, 6·3%).

α-Ethyl-malondi-o-anisidide. M.p. 152–154° (alcohol). (Found: C, 67·1; H, 6·6; N, 8·1. $C_{19}H_{22}O_4N_2$ requires: C, 66·7; H, 6·5; N, 8·2%).

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† Prager *et al.*[19], give m.p. 126–127°.

‡ Kaslow and Hayek[29] give m.p. 204°.

[37] T. Sato and M. Ohta, *Bull. Chem. Soc. Japan* **30**, 708 (1957).