THE MASS SPECTRA OF ACRIDONES*

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Summary

The mass spectra of 34 acridones have been determined and interpreted with the aid of both high-resolution measurements and deuterium labelling studies. The spectra contain pronounced molecular ions and are free of skeletal rearrangement fragments. The fragmentation patterns are dependent on the nature and position of substituents, and therefore mass spectrometry can be a useful aid to structure determination in this class of naturally occurring compounds.

Although the mass spectra of several furoquinoline alkaloids¹ and of acridine^{2a} have been described, no study of acridones has been reported.

The mass spectra of the acridone derivatives (I)-(XXXIV) are reported in Figures 1–9 and Table 1. Exact mass measurements (Table 2) confirm the composition of many ions in the spectra. Structures written for fragment ions serve the important purpose of relating fragmentation processes to the structure of the molecule in the ground state. These structures are nominal only, as it has been recently suggested that neither the benzene³ nor the furan⁴ molecular ions have the structure of the intact molecules. The presence of an asterisk in either the text or a figure denotes the presence of an appropriate metastable ion for the process indicated.

The mass spectrum (Table 1) of acridone (I) is unexceptional and is summarized in Scheme 1. Exact mass measurements establish the composition of the major ions. Loss of carbon monoxide from the molecular ion produces an ion $(m/e \ 167)$ represented as the carbazole radical ion a, which may fragment further^{2b} by loss of HCN and a hydrogen radical to $b \ (m/e \ 139)$. The mass spectrum (Fig. 1 and Scheme 1) of *N*-methylacridone (II) fragments by either of the processes M⁺-Me⁺-CO-HCN (to $b, \ m/e \ 139$) or M⁺-CHO⁺-CH₂N⁺ (to the biphenylene radical ion $e, \ m/e \ 152$).

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TABLE 1

MASS SPECTRA OF ACRIDONE DERIVATIVES (I)-(XXXIV)

For compounds marked ^a, all peaks greater than 5% of the base peak were recorded; for components marked ^b, 10%. For compound (XXX), because of the complexity of its spectrum, only peaks greater than 20% of the base peak were recorded

(I) ^a	m e I (%)	$83 \cdot 5$ 9	113 11 8	5 139 7 19	9 140 9 18	166 3 24	3 167 4 58	7 168 3 (3 198 3 100	5(M))	196 19			
(III) <i>p</i>	m/e I (%) m/e I (%) m/e I (%)	151 24 273 19 366 14	$\begin{array}{ccccccc} 152 & 153 \\ 33 & 14 \\ 285 & 286 \\ 16 & 83 \\ 367 & 368 \\ 100 & 16 \end{array}$	164 58 287 29 369 41	165 32 288 82 370 6	169 20 289 15	178 37 322 10	179 41 324 15	180 15 326 10	207 12 350 15	243 18 352 27	245 19 354 16	271 19 365 54	
(IV)ª	m/e I (%) m/e I (%)	77 12 11 227 19	$\begin{array}{cccc} 28 & 140 \\ 6 & 6 \\ 254 & 255 \\ 20 & 100 \end{array}$	154 9 (M)	168 6 256 29	169 8	182 12	183 9	184 13	199 11	200 8	212 19	225 30	226 54
(V)*	m/e I (%)	140 6	$\begin{array}{ccc} 155 & 168 \\ 6 & 6 \end{array}$	183 14	196 23	198 7	211 18	$\begin{array}{c} 226 \\ 24 \end{array}$	254 56	255 8	269 100	(M)	270 19	
(VII) ^b	m/e I (%) m/e I (%)	77 1 18 212 11	$\begin{array}{cccc} 01 & 102 \\ 16 & 22 \\ 228 & 229 \\ 100 & 17 \end{array}$	$128 \\ 22 \\ 242 \\ 18$	129 39 256 78	130 20 257 14	140 11 271(34	156 16 M)	157 20	185 65	186 11	198 14	199 11	
(VIII) ^a	m/e I (%) m/e I (%)	$\begin{array}{ccc} 77 & 1 \\ 15 \\ 256 \\ 14 \end{array}$	15 128 13 8 270 271 100 23	142 8 284 23	143 11 285(74	170 18 M) 2	171 17 286 16	184 6	199 3 9	200 8	212 9	226 7	242 59	243 13
(IX) ^a	m/e I (%) m/e I (%) m/e I (%)	77 1 10 253 26 313(M 37	15 128 10 9 254 255 8 34 () 314 14	154 7 268 9	170 12 269 8	171 8 270 24	183 8 280 20	184 9 284 20	198 6 296 11	213 8 298 100	226 18 299 26	$240 \\ 8 \\ 300 \\ 20$	241 8	242 28
(X) ^b	m/e I (%) m/e I (%)	77 8 37 1 183 67	$egin{array}{cccc} 9 & 102 \ 6 & 14 \ 184 & 185 \ 21 & 16 \end{array}$	103 15 199 12	113 21 211 32	114 15 212 60	115 14 213 17	126 21 240 34	$127 \\ 35 \\ 241 \\ 14$	128 18 269 100	140 32 (M)	154 50 270 27	155 14	182 42
(XIV)ª	m/e I (%) m/e I (%)	77 1 10 299(M 59	15 158 12 24 300 13	170 7	198 5	226 6	228 8	254 34	255 8	256 9	284 100	285 20		
(XV) ^b	m/e I (%)	77 1. 16	$58 159 \\ 18 25$	253 16	$\frac{254}{26}$	$\begin{array}{c} 255\\11\end{array}$	284 73	$\begin{array}{c} 285\\ 100 \end{array}$	286 20	299 40	300 64	301 12	$ d_0 = d \\ d_1 = d $	41%, 59%)

TABLE 1 (Continued)

- (XVI)^b m|e50 51 63 75 76 77 81 83 113 114 115 116 127 128 130 I (%) 18 14 14 15 33 20 14 25 19 30 50 12 45 35 22 139 140 143 154 155 168 170 171 182 183 198 210 211 m/eI(%)22 $\mathbf{34}$ 17 19 14 1731 322719 30 44 22 212 224 225 227 228 238 239 240 253 254 255 256 m|e|226I (%) 16 37 15 $\mathbf{24}$ 153278 23 17 18 5828 100 284 285 299(M) 300 m/e257266 270 271I(%)18 $\mathbf{29}$ 1530 96 17 90 $\mathbf{22}$
- 76 77 102 114 127 128 129 130 140 141 142 154 169 182 (XVII)^b m/eI (%) 15 221516 1515 16 14 1214 1214 20 12 184 197 212 224 225 238 240 252 253 255 268 269 270 m/e I (%) 11 1216 2511 12 20 70 16 $\mathbf{28}$ 32 16 100 271 280 285 298 313(M) 314 m/eI (%) 2246 3252 100 $\mathbf{28}$
- 77 102 114 115 127 128 129 130 141 154 158 169 170 182 (XVIII)^b m/eI (%) 18 1516 18 13 13 12 $\mathbf{20}$ 14 4013 14 17 12 254 255 268 269 270 283 284 285 294 295 226 238 240 m/e1253 17 53I(%)10 1217 5720 78 17 100 24 310 312 313 327(M) 328 m/eI(%)36 88 18 83 $\mathbf{22}$
- $(XX)^{b}$ 77 102 114 129 159 169 197 212 225 238 254 m|e268 270 271 I (%) 12 7 7 6 14 9 7 6 6 9 13 1280 17 280 284 298 299 313(M) 314 m/eI(%)1216 100 $\mathbf{24}$ 7815
- (XXI)^b 77 102 114 115 130 158 169 170 240 254 m/e268270 284285I (%) 15121214 $13 \quad 24 \quad 23$ $\mathbf{24}$ 11 3216 65 68 13294 310 312 313 327(M) 328 m/eI(%) $\mathbf{21}$ 22100 19 6214
- (XXII)^b 77 130 158 159 170 186 226 228 242 243 m/e254258 284285I(%)2018 $\mathbf{34}$ 22 15 22 11 11 12 25 $\mathbf{43}$ 28100 19 286 299 300 301 331(M) m/eI(%)61 84 2030 11
- $(XXIII)^{b} m/e$ 77 104 115 130 158 159 226 228 243 254258 270 284285I (%) 22 $\mathbf{28}$ 40 2016 14 10 18 234230 12 100 18 286 287 299 300 315 343(M) m/eI(%)86 1284 2511 2
- (XXIV)^b m/e77 89 103 115 130 131 144 158 159 228 242 243 258268I (%) 17 16 10 20 17 20 17 31 31 11 1238 $\mathbf{22}$ 14 271 286 287 301(M) 302 m|e|I(%)18 100 25 70 16
- (XXV)^a 77 115 130 158 186 214 228 229 242 256 257 270 285 m/e300 7 8 38 8 6 17 I(%)108 $\mathbf{24}$ 8 8 8 8 100 m/e 301 315(M) 316 I (%) 20 43 12

TABLE 1 (Continued)

(XXVI) ^b	m/e	158	228	242	256	257	270	272	284	285	287	288	289	300
	I(%)	51	19	36	14	48	15	20	93	20	11	12	14	100
	m/e	301	315(M) 3	316									
	I (%)	31	94		24									
(XXVII) ^b	m/e	77	158	228	242	257	258	270	272	282	286	300	301	
	I (%)	13	30	15	25	70	14	15	32	16	11	100	25	
	m/e	315(M) 3	816										
	I (%)	59		15										
(XXX)	m/e	228	254	255	256	257	258	270	271	283	284	285	286	298
	I(%)	50	29	40	70	32	22	60	4 0	27	34	21	22	30
	m/e	299	314	315	316	317	318	330	331	332		$(d_1$	= 25,	$d_2 = 37$,
	I (%)	21	100	68	74	98	26	20	30	24			d_{s}	= 38%
(XXXI) ^b	m/e	158	228	240	242	256	270	284	285	286	3 00	301	310	326
	I(%)	26	22	11	27	22	22	22	16	46	55	12	11	20
	m/e	328	329	343((M) 3	344								
	I (%)	100	22	51		11								
(XXXIII) ^a	m/e	63	77	16.5	160	·5 2	04 2	09 2	48 2	63 2	64 2	65 2	76 27	7 291
	I(%)	7	6	11	7		7	9	10	12	30	12	12 1	0 11
	m/e	292	293	306	307	321((M)	322						
	I (%)	30	10	100	26	68		21						
(XXXIV) ^b	m/e	77	154	196	212	213	225	226	241	242	254	255	3 09(M	I) 3 10
·	I (%)	12	12	14	13	14	45	17	100	25	44	11	100	23



d, m/e 180



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The spectrum (Table 1) of the dibromoacridone (VI) retains some of the features of the spectrum of N-methylacridone. The major fragmentation follows the pathway $M^+-Br\cdot-Me\cdot-CO-Br\cdot$, while the biphenylene radical ion e, m/e 152 (33%) of the base peak) is formed by the scheme $M^+-Br\cdot-Br\cdot-CO-HCN$.

Compound	m/e	Composition	Compound	m/e	Composition
(I)	167	C ₁₀ H _o N	(XIV)	158	C ₁₀ H _s NO
\ -7	139	C ₁₁ H ₇			
(II)	194	C ₁₃ H ₈ NO		294 284	$C_{17}H_{12}NO_4$ $C_{15}H_{10}NO_5$ (80%)
	180	$C_{12}H_{10}N$	1		$C_{16}H_{14}NO_4 (20\%)$
	166	C ₁₂ H ₈ N		270	$C_{15}H_{12}NO_4$
	152	$C_{12}H_8$		268	$C_{15}H_{10}NO_4$
	140	$C_{10}H_6N$			
			- (XXIV)	268	$C_{15}H_{10}NO_4$
(VI)	266	$C_{17}H_{16}NO_2$		258	$C_{14}H_{12}NO_4$
	240	$C_{15}H_{14}NO_2$		144	$C_6H_8O_4$
	226	$C_{14}H_{12}NO_2$			
	210	$C_{13}H_8NO_2 (60\%)$	(XXXI)	326	$C_{19}H_{20}NO_4$
		$C_{14}H_{12}NO (40\%)$		310	$C_{18}H_{16}NO_4$
	196	C ₁₃ H ₁₀ NO		300	$C_{16}H_{14}NO_5 (85\%)$
	183	C ₁₂ H ₉ NO	1		$C_{17}H_{18}NO_4$ (15%)
	168	$C_{12}H_{10}N$		270	$C_{15}H_{12}NO_4 (90\%)$
					$C_{14}H_8NO_5$ (10%)
(IX)	284	$C_{16}H_{14}NO_4$		256	$C_{14}H_{10}NO_4$ (80%)
	270	$C_{15}H_{12}NO_4$			$C_{15}H_{14}NO_{3}$ (20%)
	255	$C_{15}H_{13}NO_3$		242	$C_{13}H_8NO_4$ (80%)
	253	$C_{15}H_{11}NO_3$ (60%)		000	$C_{14}H_{12}NO_3$ (20%)
	040	$C_{16}H_{15}NO_2 (40\%)$		228	$C_{13}H_{10}NO_3$
	242	$\begin{array}{c c} U_{14}H_{12}NU_{3} \\ C H NO (500()) \end{array}$		014	
	220	C H NO (50%)	(AAAII)	200	$\begin{array}{c} \mathbf{U}_{17}\mathbf{H}_{16}\mathbf{N}\mathbf{U}_{5} \\ \mathbf{U}_{17}\mathbf{H}_{16}\mathbf{N}\mathbf{U}_{5} \\ \mathbf{U}_{17}\mathbf{H}_{16}\mathbf{N}\mathbf{U}_{5} \end{array}$
	100	$C_{14}H_{12}NO_2 (50\%)$		300	$C_{16}H_{14}NO_5 (60\%)$
	198	C = H NO (50%)		20.0	C H NO
	170	$C = 12 M NO_2 (50 \%)$		290	C H NO
	170	01111810		290	C H NO (409/)
	240	CHNO		201	$C_{16}H_{14}NO_4$ (40 /0)
(21)	237	$C_{14}H_{10}HO_3$		270	$C_{15}H_{10}NO_5(007_0)$
	201	$C_{15}H_{11}NO_2$		2.0	$C_{15}H_{12}(O_4 (00))$
	212	$C_{14}H_{10}NO_2$		256	$C_{14}H_{g1}(O_{5}^{-}(O_{70}^{-}))$
	196	$C_{13}H_{10}(0)$			$C_{15}H_{14}(0_3)$ (20%)
		$C_{13}H_{10}(0, (5\%))$		242	$C_{14}H_{10}NO_{4}(60\%)$
	182	C.H.NO			$C_{12}H_{a}NO_{4}(40\%)$
	154	C.H.N		228	C.,H.,NO.
	127	$C_{10}H_{7}$ (60%)			- 1310 3
		$C_{0}H_{*}N$ (40%)	(XXXIV)	254	C ₁₅ H ₁₀ NO.
·	• ••• •• • • •			241	C ₁₄ H ₁₁ NO.
(XIII)	144	C ₉ H ₆ NO		225	C ₁₄ H ₁₁ NO ₂
. ,	128	C ₉ H ₆ N			

 TABLE 2

 EXACT MASS MEASUREMENTS IN THE SPECTRA OF COMPOUNDS (I-XXXIV)

Acridones containing oxygenated substituents behave characteristically upon electron impact. Compounds containing either C2 or C4 substituents decompose simply by fragmentations which proceed through either of these substituents.



The fragmentations occur by concerted processes which specifically involve the nitrogen atom. If 2- and 4-alkoxyl substituents are absent, the fragmentations are complex and non-specific. This feature has been investigated by studying the fragmentation modes of various compounds labelled in different positions with either ethoxyl or OCD_8 groups. During the course of this investigation, it became apparent

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that if an hydroxyl substituent at C1 was converted into the 1-ethyl ether, the presence of this substituent could be unequivocally detected by a specific "ortho-effect" (see McLafferty⁵) involving the adjacent carbonyl group. Finally, the spectrum of an alkoxy N-methylacridone differs from that of the corresponding alkoxy



acridone in being completely shifted by m/e 14 to higher mass values. These observations are of considerable use for the structure elucidation of acridones and they are illustrated by a consideration of the mass spectra of the substituted acridones (IV)-(XXXII).

⁵ McLafferty, F. W., in "Mass Spectrometry of Organic Ions." p. 337. (Academic Press: New York 1963.)

MASS SPECTRA OF ACRIDONES

In order to rationalize the fragmentation processes of alkoxyacridones, it is convenient to start with a discussion of the 1,2,3,4-tetrasubstituted derivatives (XXIV-XXXII) because of the information available from labelling studies. The overall fragmentations of these compounds are complex; nevertheless those processes which originate from the molecular ions give considerable insight into the orientation of substituents. The spectra of (XXIV), (XXV), (XXVI), (XXVII), (XXX), and (XXXI) are recorded in Table 1, while those of (XXVIII), (XXIX), and (XXXII) are illustrated in Figures 2–4. Specific features of these spectra are summarized in Table 3. It can be seen that M^+ —Me· ions are the base peaks of

Compound	M+-Me·	M^+-CD_3 ·	M+-Et·	Compound	M+-Me·	M^+ - CD_3 ·	$\mathrm{M}^+-\mathrm{Et}\cdot$
(XXIV) (XXV) (XXVI) (XXVII) (XXVII)	100 100 100 100 100			(XXIX) (XXX) (XXXI) (XXXI) (XXXII)	40 60 100 70	60 40 —	0

 TABLE 3

 RELATIVE ABUNDANCE OF IONS IN THE SPECTRA OF COMPOUNDS (XXIV-XXXII)

the spectra of all compounds containing only methoxyl groups (and for those which in addition contain hydroxyl substituents). When a 1-ethoxyl substituent is present (as in XXXI), the spectrum (Tables 1 and 2) is extremely complex, and no ion corresponding to the process M^+ -Et is observed. However, when a 4-ethoxyl group is present (XXXII; Fig. 2 and Table 2), the M^+ -Et \cdot cation is the base peak of the spectrum, indicating a large contribution to the total ion current due to the general fragmentation from the 4-substituent. It seems reasonable (see above) that fragmentations may proceed by concerted mechanisms via the 2- and 4substituents. To establish this point the labelled methyl ethers (XXIX) and (XXX) were synthesized (cf.⁶) and their spectra determined. The mass spectra (Figs. 3 and 4; Table 1) of melicopicine (XXVIII) and of compounds (XXIX) and (XXX) establish that 60% of the M+-Me cation originates by the loss of a methyl radical from the 2-methoxyl group, while 40% is produced by fragmentation of the 4-methoxyl substituent. In addition, all fragment ions below m/e 271 in the spectrum (Fig. 4) of (XXIX) have lost the label (i.e. after the loss of the second methyl radical). This establishes fragmentations through the substituents at C2 and C4 (see Scheme 2). Similar effects have recently been observed in the spectra of coumarins,⁷ flavones,⁸ and spermatheridine alkaloids.⁹

The spectra of the naturally occurring acridones (and their derivatives) which contain methylenedioxy groups illustrate the features described above.

- ⁶ Van der Merwe, K. J., Steyne, P. S., and Eggers, S. H., Tetrahedron Lett., 1964, 3923.
- ⁷ Shapiro, R. H., and Djerassi, C., J. org. Chem., 1965, 30, 955.
- ⁸ Bowie, J. H., and Cameron, D. W., Aust. J. Chem., 1966, 19, 1627.
- ⁹ Bick, I. R. C., Bowie, J. H., and Douglas, G. K., Aust. J. Chem., in press.

The mass spectra of evoxanthine (XI) and (XII) are illustrated in Figures 5 and 6. Compound (XII) behaves simply on electron impact, fragmenting initially through the 2-methoxyl substituent probably to i (m/e 240) and then by the processes indicated



in Figure 5 and Scheme 3. Evoxanthine (XI) exhibits a very complex spectrum (Fig. 6), and it is suggested that the M^+ -CO ion originates by decomposition of





Scheme 3

the methylenedioxy group $(j \rightarrow k)$ and that the acridone carbonyl group is probably lost last. Attempts to confirm this suggestion by ¹⁸O labelling were unsuccessful, as no exchange of the carbonyl oxygen could be detected with ¹⁸OD₂ in dioxan alone or in the presence of acid, or in pyridine with ¹⁸OD⁻. The absence of any nucleophilic additions to the carbonyl group will be reported on in a subsequent communication. The spectrum (Table 1) of norevoxanthine (X) is similar to that of evoxanthine, exhibiting analogous fragmentation processes.





this class of compound. The isomeric pairs (XIV) and (XIX), melicopidine (XVII) and melicopine (XX), and (XVIII) and (XXI) exhibit very similar spectra. The only difference in the spectra (Table 1) of (XVII) and (XX), and of (XVIII) and





An additional feature of 1,2,3,4-tetrasubstituted acridones is that the compounds having either hydroxyl groups (XIII, XIV, XIX, XXII, XXIV, XXV, XXVI, and XXVII) or ethoxyl substituents (XVIII, XXI, XXIII, XXXI, and XXXII) (which may fragment by elision of ethylene to give the corresponding phenol radical ion), exhibit the prominent ions (25-50%) of the base peak) l (m/e 144) and m(m/e 158) in the spectra of acridones and N-methylacridones respectively. On the other hand, these ions are either absent or very small in the spectra of those compounds containing only methoxyl and/or methylenedioxy groups. Although there is no firm evidence to suggest the origin of these ions, hydrogen transfer from the hydroxyl group [as proved by the spectrum of (XV)] to ring B, is a prerequisite for their formation. Indeed, the spectrum of (XXIV) (which contains two hydroxyl groups) exhibits m (m/e 158, 31% of the base peak), and n (m/e 159, 31% of the base peak) which have resulted from one and two hydrogen transfers respectively. The presence of such ions in the spectrum of an acridone indicates 1,2,3,4-tetrasubstitution and may be used to determine the substituent on nitrogen, and to detect the number of hydroxyl groups (or potential hydroxyl radical ion producers, e.g., ethoxyl and probably acetoxyl groups) on ring A.



The mass spectra (Table 1) of xanthoxoline (VII) and of the other 1,2,3oxygenated acridones are unexceptional. However, the spectra (Table 1) of the two ketals (XXII) and (XXIII) show some interesting features. Compound (XXII), on electron impact, loses methanol from its molecular ion to produce the normelicopine radical ion (m/e 299), which fragments as described earlier (Fig. 8). The mass spectrum of (XXIII) affords verification of the structure of this compound, as the major fragmentation involves the elision of C_2H_4O from the molecular ion with concomitant hydrogen rearrangement, probably by a concerted mechanism (see o), to again furnish the normelicopine radical ion. The spectrum (Table 1) of acronycine (XXXIII) can be likened to that of 2,2-dimethylchromene,^{10,11} while the spectrum (Table 1) of (XXXIV) may be explained by reference to the mass

¹⁰ Barnes, C. S., and Occolowitz, J. L., Aust. J. Chem., 1964, 17, 975.

¹¹ Willhalm, B., Thomas, A. F., and Gantschi, F., Tetrahedron, 1964, 20, 1185.

spectra of chromans¹¹ and flavans.¹² The compositions of many ions in these spectra are recorded in Table 2.

The mass spectra (Tables 1 and 2; Fig. 9) of the 1,3-disubstituted acridones (IV-VI) reflect the complexity of fragmentation modes when an acridone lacks either a C2 or C4 substituent. In the spectrum (Fig. 9) of 1-ethoxy-3-methoxy-



N-methylacridone (VI), complex decomposition patterns can be seen to originate from either the ethoxyl or methoxyl groups.

Further examination of the spectrum (Fig. 9) of (VI) shows the presence of the process $M^+-OH \cdot -H_2$ to give an ion m/e 264. Comparison of the spectra of all other 1-ethoxyacridones shows this to be a general process, not observed in

RELATIVE ABUNDANCES (/0) OF MOTT. TONS IN THE SPECIFIC OF ETHOXYACRIDONES										
Compound	M+-OH·	$\mathbf{M^{+}\!-\!OH}\cdot -\mathbf{H}_{2}$	Compound	M+-OH·	$\mathbf{M^{+}\!-\!OH^{\cdot}\!-\!H_{2}}$					
(\mathbf{VI})	50	18	(XXI)	22	1					
(IX)	11	2	(XXXI)	20	2					
(XVIII)	36	3	(\mathbf{XXXII})	<u> </u>	<u> </u>					

Table 4 relative abundances (%) of $\mathrm{M}^+{-}\mathrm{OH}\cdot$ ions in the spectra of ethoxyacridones

either the spectrum of a 4-ethoxyacridone (Tables 1 and 4) or in those of other acridones studied. The compositions of these ions have been established in the spectra of (VI) and (XXXI). This process may be plausibly represented (e.g. in the case of (VI)) by the bond-forming process (VI) $\rightarrow p \rightarrow q$ (Scheme 4). Electron impact processes involving loss of hydroxy radicals and water from compounds containing ethoxyl groups adjacent to carbonyl functions will be reported in a future publication.

¹² Pelter, A., Stainton, P., and Barber, M., J. heterocyclic Chem., 1965, 2, 262.

In summary, mass spectrometry provides valuable information regarding the type of substituents at the 1,2 and 4 positions of the acridone nucleus, and in some cases, allows the determination of the substituent on nitrogen. This technique, in



conjugation with other physical methods, should prove of considerable value in the structure elucidation of acridones.

EXPERIMENTAL

All mass spectra were determined with a Hitachi Perkin-Elmer RMU 6D mass spectrometer operating at 75 eV and with a source and inlet temperature of approximately 200°. Exact mass measurements were determined with an A.E.I. MS9 mass spectrometer with a resolution of 14000 (10% valley definition) using heptacosafluorotributylamine to provide reference masses. All measurements were correct to within 15 p.p.m.

Compounds (V), (XVII), (XX), (XXVIII), and (XXXIII) were isolated from Acronychia baueri, and compounds (IV), (XIV), (XIX), and (XXV) derived from them.¹³ Compounds (VII), (XI), and (XVI) were isolated from Evodia xanthoxyloides and compounds (VIII), (X), and (XIII) derived from them.¹⁴ Compound (III) was prepared by the method of Acheson,¹⁵ (XXII) and (XXIII) by that of Prager and Thredgold.¹⁶ Compounds (VI), m.p. 134°; (IX), m.p. 132°; (XVIII), m.p. 95–96°; (XXI), m.p. 153–154°; and (XXXI) (non-crystalline gum¹⁷) were prepared by ethylating the corresponding 1-hydroxy compound with ethyl iodide in the presence of silver oxide. Compounds (XXIX) and (XXX) were prepared from melicopidine and melicopine respectively by opening the methylenedioxy group with sodium methoxide to give (XXVI) and (XXVII),¹⁷ and methylating with deuterodiazomethane in dioxan/ether.⁶ Compound (XXXII) was prepared by ethylation of (XXVII) with ethyl iodide.¹⁷ Compound (XXXIV), m.p. 214–216°, was prepared by hydrogenation of noracronycine, a method found superior to that of Brown *et al.*¹⁸ The spectrum of (XV) was obtained by introducing (XIV) directly into the source with deuterium oxide.¹⁹

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¹³ Lahey, F. N., and Thomas, W. C., Aust. J. scient. Res. A, 1949, 2, 423.

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