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PORPHYRINS

28.* MASS SPECTRA OF PORPHYRINS CONTAINING β-DIKETONE RESIDUES

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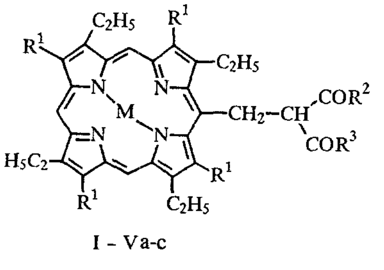
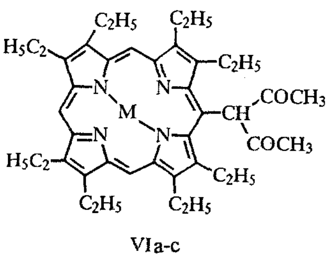
A mass spectrometric investigation has been carried out on chlorins, porphyrins, and their metal complexes containing β-diketone residues in the meso and β-pyrrole positions. Porphyrins containing acetyl or benzoylethyl groups in the meso position are characterized by the loss from the molecular ion M^+ *of a β-diketone residue and then the alkyl substituents of the porphyrin nucleus. Diacetylcyclopropylchlorins are characterized by the sequential loss from the molecular ion of an acetyl residue and a molecule of ketene.*

A procedure developed by us is one of the promising methods of modifying porphyrins and chlorins to create biologically active compounds. It is based on the reaction of porphyrins containing mesodimethylaminomethyl [2], β-(1-alkoxyethyl) [3], or β-hydroxy or vicinal diol groups [4] with CH acids, especially acetylacetone, in the presence of $Zn(OAc)_2$. While developing this method we found that other β-diketones (such as dibenzoylmethane or benzoylacetone) may be used for modifying porphyrins. The presence of a β-diketone residue in the porphyrin or chlorin molecule may create a site for the formation of externally-bound metal complexes.

In the present work the mass spectrometric behavior of β-diketones containing porphyrin or chlorin residues in place of one or two hydrogen atoms, and also of their metal complexes, is considered. We investigated the following compounds: porphyrins containing in the meso position acetyl(benzoyl) ethyl groups [compounds (I-V)] or a diacetylmethyl group [compound (VI)], 3-(octaethyl-5-porphyrinyl)-2,4-pentanedione (VII), the acetylacetonate derivatives of hematoporphyrin IX dimethyl ester [compounds (VIII), (IX)], diacetyl substituted cyclopropyletiochlorin I [compound (X)], and the tetraethyl ester of cyclopropylcoprochlorin I [compound (XI)]. According to literature data [5, 6] the mass spectral decomposition of functionally substituted porphyrins depends to a significant degree on the nature of the substituent and its position in the porphyrin nucleus. This is displayed particularly in the mass spectra of meso substituted porphyrins [7, 8] for which steric factors play a significant role.



I - Va-c



VIa-c

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*For Communication 27, see [1].

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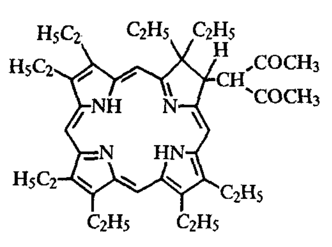
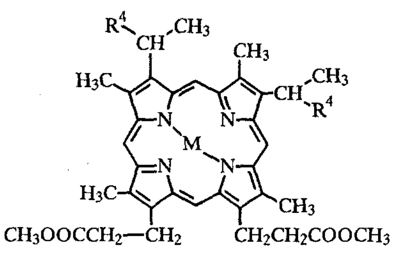
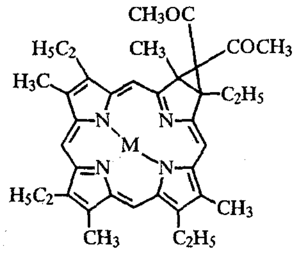


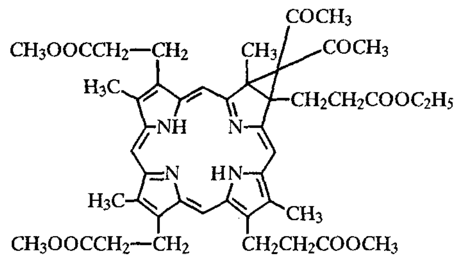
VII



VIIIa, IXa-c



Xa-c



XI

Ib,c $R^1 = R^2 = R^3 = CH_3$; IIa $R^1 = R^2 = CH_3$, $R^3 = C_6H_5$; IIIa—c $R^1 = CH_3$, $R^2 = R^3 = C_6H_5$; IV a-c $R^1 = C_2H_5$, $R^2 = CH_3$, $R^3 = C_6H_5$; V a-c $R^1 = C_2H_5$, $R^2 = R^3 = C_6H_5$; VIIIa $R^4 = CH_2COCH_3$; IXa-c $R^4 = CH(COCH_3)_2$; I—XIa M = 2H; I—XIb M = Zn; I—XIc M = Cu

The main ion peaks and their intensities in the mass spectra of compounds (I)-(VIa-c) are given in Table 1.* The molecular ion peaks M^+ are the most intensive only in the spectra of compounds (VIa-c). The additional methylene group between the porphyrin nucleus and the pentane-2,4-dione residue leads apparently to the possibility of thermal decomposition as a result of which the intensity of the M^+ ion peaks is reduced. Decomposition of the M^+ ions of compounds (Ia-c)-(VIa-c) (Scheme 1) occurs predominantly with fission of the meso substituent (fragment F_8) or part of it (fragment F_4). The peaks of the F_4 ions are maximal in the spectra of compounds (Ib) and (Ic). Loss of a molecule of ketene or an acetyl(benzoyl) residue by the M^+ ion (fragments F_1-F_3) is less probable and the intensity of these ions does not exceed 4%. Apart from these ions intense peaks were present in the spectra of compounds (Ia-c)-(VIa-c) for the β-diketone ions and for their decomposition products (fragments F_9-F_{12}).

The formation of the $M_1{}^+$ and $M_2{}^+$ ion peaks present in the spectra of compounds (IIa) and (IIIa-c)-(Va-c), which are maximal in intensity, is explained by the thermal decomposition of meso substituted porphyrins to ethylporphyrin (or octaethylporphyrin) and their meso methyl analogues. The fact that these ions are not formed from the M^+ ions was confirmed in [8] when studying the mass spectra of meso amino-substituted porphyrins. Their occurrence is caused seemingly by intermolecular interaction of the corresponding porphyrins in the ion source before ionization [9].

The mass spectrum of compound (VII) contains a maximum M^+ ion peak, the fragmentation of which occurs mainly by the sequential fission of ethyl and acetyl residues (Scheme 2). Another breakdown route is linked with the elimination of a pentanedione radical and then a molecule of ethylene or an ethyl radical (see Scheme 1 at top of the following page).

The presence of a small number of intense ion peaks is a characteristic of the spectra of compounds (VIIIa) and (IXa-c) (Table 2). The main decomposition process of the M^+ ions of these compounds is the formation of $[M-R^4]^+$ and $[M-2R^4]^+$ ions. Low intensity ion peaks are present in the spectra of these compounds which are caused by the decomposition of the methyl propionate substituents (fission of OCH_3, $COOCH_3$, CH_2COOCH_3 radicals), typical of hematoporphyrin derivatives [10].

There were only two intense peaks in the spectra of compounds (Xa-c) and (XI) (Table 3). The M^+ ion peak was maximal in intensity and the other large peak was of the ion formed by loss of an acetyl residue. The intensity of the other ion peaks did not exceed 10%.

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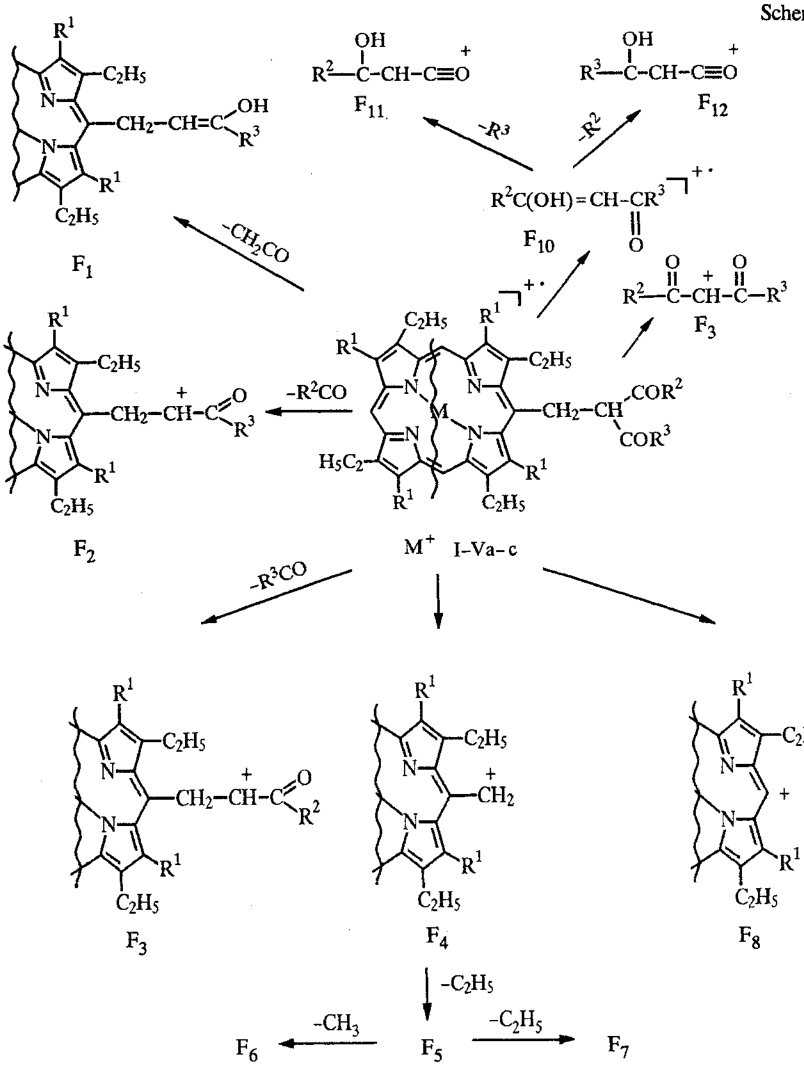
*The m/z values given in Tables 1-3 and in the text for the spectra of compounds (Ib)-(VIb) and (Ic)-(VIc) correspond to the ^{64}Zn and ^{63}Cu isotopes.

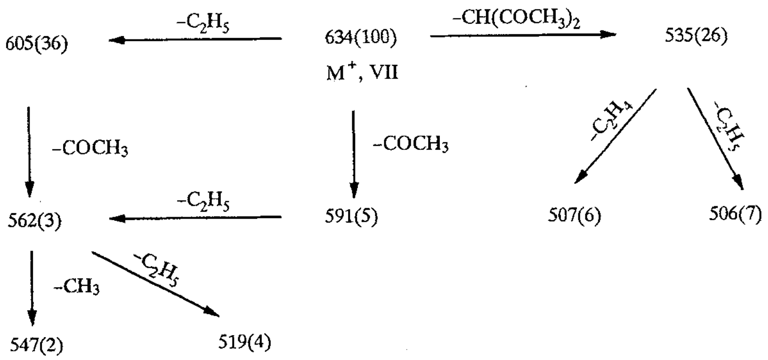
TABLE 1. Characteristic Ion Peaks and Their Intensities in the Mass Spectra of Compounds (Ib), (Ic), (IIa), and (IIIa-c)-(VIa-c)

Fragment	Values of m/z (intensity, %)														
	Ib	Ic	IIa	IIIa	IIIb	IIIc	IVa	IVb	IVc	Va	Vb	Vc	VIa	VIb	VIc
M^+	652(36)	651(32)	652(32)	714(4)	776(7)	775(55)	708(50)	770(44)	769(61)	770(26)	832(25)	831(37)	632(100)	694(100)	693(100)
F_1	610(2)	609(3)	610(2)	—	—	—	666(2)	—	—	—	—	—	590(4)	652(3)	651(3)
F_2	609(1)	608(2)	609(3)	—	—	—	665(4)	—	—	—	—	—	589(3)	651(1)	650(1)
F_3	—	—	547(6)	609(2)	—	670(4)	603(8)	665(1)	664(1)	665(11)	727(2)	726(3)	—	—	—
F_4	553(100)	552(100)	491(78)	491(8)	553(16)	552(62)	547(63)	609(90)	608(66)	547(42)	609(47)	608(52)	533(60)	595(48)	594(44)
F_5	524(11)	523(11)	462(6)	462(2)	524(5)	523(10)	518(5)	580(9)	579(13)	518(4)	580(8)	579(10)	504(5)	566(8)	565(7)
F_6	509(10)	508(9)	447(6)	447(4)	509(8)	508(12)	503(5)	565(6)	564(9)	503(4)	565(7)	564(7)	489(5)	551(6)	550(5)
F_7	495(7)	494(5)	433(3)	433(3)	495(5)	494(8)	489(3)	551(6)	550(6)	489(2)	551(6)	550(5)	—	—	—
F_8	539(13)	538(10)	477(14)	477(7)	539(16)	538(13)	533(11)	595(10)	594(14)	533(11)	595(19)	594(11)	—	—	—
F_9	—	—	161(11)	223(28)	223(36)	223(47)	161(13)	161(10)	161(9)	223(9)	223(11)	223(24)	—	—	—
F_{10}	100(4)	100(2)	162(16)	224(31)	224(48)	224(52)	162(23)	162(18)	162(11)	224(7)	224(8)	224(15)	100(1)	100(6)	100(2)
F_{11}	85(6)	85(4)	147(15)	147(14)	147(18)	147(29)	147(21)	147(17)	147(9)	147(1)	147(4)	147(6)	85(3)	85(7)	85(3)
F_{12}	—	—	85(4)	—	—	—	85(6)	85(10)	85(2)	—	—	—	—	—	—
$[C_6H_5CO]^+$	—	—	105(43)	105(46)	105(23)	105(67)	105(50)	105(34)	105(20)	105(3)	105(11)	105(16)	—	—	—
$[C_6H_5]^+$	—	—	77(27)	77(20)	77(13)	77(47)	77(30)	77(19)	77(12)	77(3)	77(7)	77(9)	—	—	—
$[CH_3CO]^+$	43(19)	43(12)	43(14)	—	—	—	43(14)	43(14)	43(4)	—	—	—	43(4)	43(17)	43(12)
M_1^+	554(74)	553(59)	492(100)	492(42)	554(100)	553(71)	548(100)	610(100)	609(100)	548(100)	610(100)	609(100)	534(34)	596(38)	595(31)
M_2^+	540(47)	539(37)	478(31)	478(100)	540(34)	539(100)	534(41)	596(51)	595(28)	534(16)	596(48)	595(28)	—	—	—
M^{2+}	326(2)	325,5(2)	326(1)	357(0,1)	388(0,3)	387,5(0,4)	354(1)	385(1)	384,5(1)	385(0,2)	416(0,1)	415,5(0,1)	316(4)	347(5)	346,5(2)
M_1^{2+}	277(9)	276,5(5)	246(8)	246(5)	277(15)	276,5(6)	274(10)	305(15)	304,5(8)	274(9)	305(8)	304,5(10)	267(7)	298(9)	297,5(8)
M_2^{2+}	270(10)	269,5(7)	239(4)	239(11)	270(8)	269,5(13)	267(6)	298(12)	297,5(3)	267(2)	298(6)	297,5(3)	—	—	—
$[M_1-C_2H_5]^+$	525(17)	524(16)	463(7)	463(14)	525(9)	524(24)	519(5)	581(9)	580(10)	519(2)	581(10)	580(8)	—	—	—

Scheme 1.



Scheme 2



In addition, there were doubly charged M^{2+} ion peaks in the mass spectra of all the compounds studied and M_1^{2+} and M_2^{2+} ion peaks in the spectra of compounds (Ia-c)-(VIa-c). The M_3^+ ion peaks present in the spectra of compounds (Xa-c) and (XI) have the structure of octaethylporphyrin and coproporphyrin, respectively. Their origin is explained above.

The mass spectra of the porphyrins studied and their Zn and Cu complexes are practically identical, i.e., the presence of the metal does not affect the main decomposition processes of the M^+ ions.

It has been established by studying the mass spectra of compounds (I)-(XI) that the loss of a β-diketone residue and then alkyl substituents of the porphyrin ring from the M^+ ion is a characteristic of mesoacetyl(benzoyl) ethylporphyrins. The main

TABLE 2. Characteristic Ion Peaks and Intensities in the Mass Spectra of Compounds (VIIIa) and (IXa-c)

Fragment	Values of m/z (intensity, %)			
	VIIIa	IXa	IXb	IXc
M^+	706 (100)	790 (100)	852 (100)	851 (100)
$[M\text{-}CH_3]^+$	—	775 (0,3)	837 (0,1)	836 (0,2)
$[M\text{-}OCH_3]^+$	675 (2)	759 (4)	821 (2)	820 (2)
$[M\text{-}COCH_2]^+$	664 (2)	748 (8)	810 (8)	809 (12)
$[M\text{-}COCH_3]^+$	663 (1)	747 (3)	809 (1)	808 (1)
$[M\text{-}R^4]^+$	649 (18)	691 (56)	753 (50)	752 (46)
$[M\text{-}COCH_2\text{-}OCH_3]^+$	633 (1)	717 (1)	779 (1)	778 (1)
$[M\text{-}COCH_2\text{-}COOCH_3]^+$	605 (1)	689 (5)	751 (1)	750 (1)
$[M\text{-}COCH_2\text{-}R^4]^+$	—	649 (5)	711 (5)	710 (7)
$[M\text{-}2R^4]^+$	592 (2)	592 (14)	654 (16)	653 (17)
$[M\text{-}R^4\text{-}HR^4]^+$	591 (4)	591 (13)	653 (13)	652 (10)
$[M\text{-}2R^4\text{-}CH_2COOCH_3]^+$	519 (1)	519 (4)	581 (5)	580 (4)
$[M\text{-}2HR^4\text{-}CH_2COOCH_3]^+$	517 (1)	517 (2)	579 (3)	578 (3)
$[HR^4]^+$	58 (4)	100 (5)	100 (16)	100 (3)
$[HR^4\text{-}CH_3]^+$	43 (10)	85 (8)	85 (21)	85 (3)
$[CH_3CO]^+$	—	43 (5)	43 (56)	43 (6)
M^{2+}	353 (2)	395 (5)	426 (3)	425,5 (2)

TABLE 3. Characteristic Ion Peaks and Their Intensities in the Mass Spectra of Compounds (Xa-c) and (XI)

Fragment	Values of m/z (intensity, %)			
	Xa	Xb	Xc	XI
M^+	576(100)	638(100)	637(100)	864(100)
$[M\text{-}COCH_3]^+$	533(48)	595(58)	594(55)	821(140
$[M\text{-}COCH_3\text{-}COCH_2]^+$	491(2)	553(6)	552(3)	779(1)
$M_3{}^+$	478(8)	540(16)	539(7)	766(3)
$[COCH_3]^+$	43(2)	43(4)	43(2)	43(2)
M^{2+}	288(9)	319(10)	318,5(8)	432(2)

decomposition processes of the M^+ ions of acetylacetonate derivatives of hematoporphyrin IX are linked with fission of one or two β-diketone residues. The fragmentation of diacetylcyclopropylchlorins by electron bombardment is accompanied chiefly by the formation of ions caused by the sequential loss of an acetyl residue and a ketene molecule.

EXPERIMENTAL

Compounds (IIa)-(Va) were obtained by heating mesodimethylaminomethyletioporphyrin I and mesodimethylaminomethyloctaethylporphyrin with acetylacetone, dibenzoylmethane, or benzoylacetone in CCl_4 in the presence of an excess of zinc acetate according to the method of [2], with subsequent demetallation of the Zn complexes with conc. HCl. Porphyrin (IXa) was obtained by the method of [3], porphyrin (VIa) and the chlorins (Xa) and (XI) by the method of [4]. Chlorin (VII) was obtained from 1,1,7,8,12,13,17,18-octaethyl-2-hydroxychlorin by the method of [2]. Porphyrin (VIIIa) was obtained by heating porphyrin (IXa) with KOH in methanol with subsequent esterification of the intermediate diacid with 3% H_2SO_4 in methanol. The purity and homogeneity of samples of porphyrins and chlorins were confirmed by elemental analysis and TLC on silica gel.

The mass spectra were obtained on a Finnigan MAT 90 instrument with an ionization energy of 70 eV by direct insertion of samples into the ion source. The evaporation temperature of samples was 250-300°C, the temperature of the ionization chamber was 220°C.

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