

## Photochemical Reaction of Lucigenin: Electron-transfer Reduction of 10,10'-Dimethyl-9,9'-biacridinediium by Counter Anions, followed by Photocyclization

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Lucigenin (1) is a charge-transfer complex between 10,10'-dimethyl-9,9'-biacridinediium (DMBA<sup>2+</sup>) and two nitrate anions. When the complex (1) was irradiated in the charge-transfer absorption band (>510 nm) in deaerated solutions, DMBA<sup>2+</sup> was converted into the reduced form, 10,10'-dimethyl-9,9'-biacridylidene (2). On the other hand, irradiation of (1) with visible light (>420 nm) gave a red product assumed to be 7,16-dimethylbenzo[1,2,3-*kl*:6,5,4-*k'l'*]diacridine (4). A mechanism is suggested which involves electron-transfer photoreduction of DMBA<sup>2+</sup> by counter anions, followed by photocyclization of (2) to give a dihydrophenanthrene-type intermediate (3), and subsequent dehydrogenation.

Lucigenin (1) is a charge-transfer (CT) complex between 10,10'-dimethyl-9,9'-biacridinediium (DMBA<sup>2+</sup>) and two nitrate anions; the cation also forms CT complexes with other anions such as Cl<sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup>, and I<sup>-</sup> showing the CT band at wavelength longer than 500 nm.<sup>1</sup> The absorption intensity of the CT band increases with decreasing solvent polarity, or increasing concentration of the salt of DMBA<sup>2+</sup>. Addition of nucleophiles such as OH<sup>-</sup>, CN<sup>-</sup>, OR<sup>-</sup>, and PhS<sup>-</sup>, of stronger electron-donating power, to the solution of (1) results in reduction of DMBA<sup>2+</sup> to give 10,10'-dimethyl-9,9'-biacridylidene (2) by electron-transfer from the nucleophile.<sup>1</sup> We now report the photolytic behaviour of the CT complex (1). Irradiation of (1) in several solutions by visible light in the absence of molecular oxygen or oxidizing agents afforded the reduced compound (2) or a new red compound (4), depending upon the wavelength of irradiation.

### Results and Discussion

When a deaerated ethanolic solution ( $5 \times 10^{-5}$  mol dm<sup>-3</sup>) of (1) was irradiated with visible light (>420 nm) at 20 °C, the absorption spectrum gradually changed to that of (2), showing a new maximum at 420 nm with decrease in absorption at 360 nm; however, an additional weak broad band around 500 nm was observed as shown in Figure 1(a). On further irradiation, the colour of the reaction mixture changed from yellow to red, and a new absorption maximum was observed at 520 nm. The photoreaction was also monitored by fluorescence measurement. Lucigenin exhibits two fluorescence maxima, at 500 and 480 nm in ethanol under excitation at 430 nm. At the first stage of the photoreaction of (1), the shape of the fluorescence spectrum became very similar to that of (2), with an emission maximum at 500 nm. However, the maximum gradually decreased during further irradiation and the resulting red solution exhibited a new emission maximum at 545 nm, under excitation at 520 nm. The photoformation of compound (4) from (1) proceeded much faster at 30 than at 20 °C.

Similar changes of absorption and fluorescence spectra were also observed in other solvents such as Bu<sup>t</sup>OH, dimethylformamide (DMF), and dimethyl sulphoxide (DMSO). On irradiation of (1) in aqueous solution, absorption and fluorescence maxima gradually decreased; after about 50 h a yellowish substance precipitated on the wall of the cell, but the red product did not form. In a separate experiment (100 mg in 200 cm<sup>3</sup>) the yellowish precipitate (8 mg) was collected and identified as compound (2) by spectrophotometric measurements in benzene. It seems that the insolubility of compound

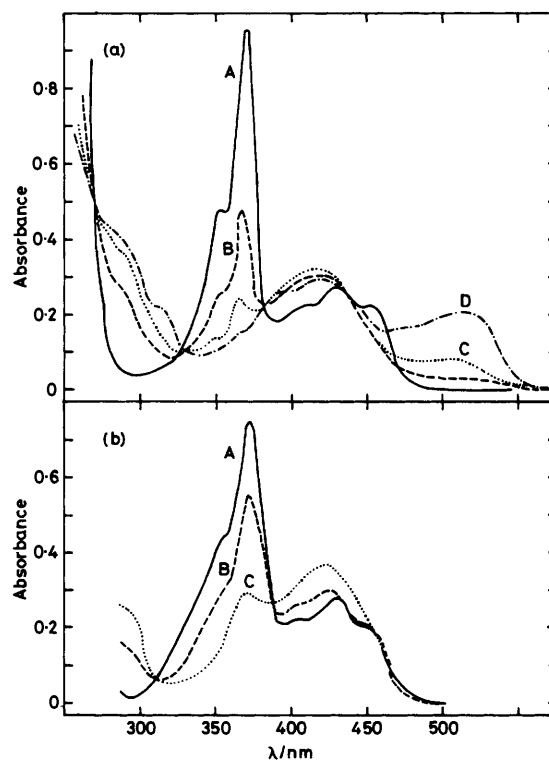
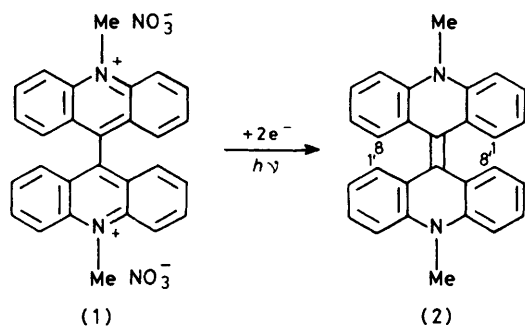


Figure 1. (a) The time-resolved absorption spectra of (1) ( $5 \times 10^{-5}$  mol dm<sup>-3</sup>) in EtOH under irradiation (>420 nm) at 20 °C: A, before irradiation; B, after 145 min irradiation; C, after 260 min irradiation; D, after 8 h irradiation. (b) The time-resolved absorption spectra of (1) ( $5 \times 10^{-5}$  mol dm<sup>-3</sup>) in DMF under irradiation (>510 nm) at 20 °C: A, before irradiation; B, after 200 min irradiation; C, after 16 h irradiation

(2) in H<sub>2</sub>O caused precipitation and suppressed the formation of the red product (4). From these findings it was suggested that photoreduction of (1) is the first step of the photoformation of compound (4), and probably involves electron transfer from the counter anions.

In order to confirm this suggestion, selective excitation of the CT transition of (1) was carried out. A deaerated solution of (1) in DMF ( $5 \times 10^{-5}$  mol dm<sup>-3</sup>) has the absorption spectrum shown in Figure 1(b); no CT band is apparent at wavelengths longer than 500 nm because of the low concentration of (1).



Scheme 1.

However, on excitation in the CT absorption range by light of wavelength longer than 510 nm, the spectrum of (1) gradually changed to give one strongly resembling that of (2), with an isobestic point at 388 nm [Figure 1(b)]. After 16 h irradiation no additional change of the spectrum was observed under CT excitation. In a separate experiment, only two compounds, (1) and (2), were detected on t.l.c. of the reaction mixture. From the last spectrum (curve C) shown in Figure 1(b), the (2):(1) ratio was estimated to be about 3.5:1. The photoreduction of (1) was also monitored by measurement of the fluorescence spectrum with excitation at 430 nm after each irradiation. The positions of the fluorescence maxima of (1) and (2) are almost identical (506 nm) in DMF; thus a shift was not observed, although the intensity was enhanced as the reduction proceeded. From these facts it was concluded that the photoinduced electron-transfer reduction of DMBA<sup>2+</sup> by the counter anions occurred under charge-transfer excitation. Although we could not detect any oxidized species formed from the electron-donating anions, it seems reasonable to rule out the involvement of ethanol in the photoreduction as reported for one-electron photoreduction of bipyridinium salts<sup>2</sup> in primary or secondary alcohols. A similar photoreduction by CT excitation was also observed for DMBA<sup>2+</sup>2I<sup>-</sup> in DMF or Bu<sup>t</sup>OH. The photoreduction is paralleled by the chemical reduction of salts of DMBA<sup>2+</sup> by electron transfer from nucleophiles<sup>1,3</sup> or the electrochemical reduction<sup>4-6</sup> to give (2) as shown in Scheme 1. It is not clear whether the photoreduced product (2) exists in the reaction mixture as a diradical or as a species having a double bond between the two ring systems; however, the precipitated (2) from the aqueous solution exhibited e.s.r. signals showing presence of the diradical. This strongly suggests the presence of the diradical in the photoreduced compound (2) formed in the organic solvents.

When the irradiation of (1) was carried out with light of wavelength longer than 420 nm, which can be absorbed by the reduced compound (2), further photoreaction occurs to give compound (4) *in situ*. This process was confirmed by the following reactions. Subsequent irradiation of the resulting DMF solution [curve C in Figure 1(b)] by light of wavelength longer than 420 nm caused a further change in the absorption spectrum, accompanied by a colour change in the solution. The fluorescence intensity at 506 nm also decreased, with appearance of a new emission maximum at 558 nm. After 2 h irradiation maximal conversion into compound (4) was obtained (monitored by intensity of the fluorescence at 558 nm). In the resulting red solution three main compounds (1), (2), and (4) were detected by t.l.c. Compound (4) was also produced by irradiation of compound (2) at wavelengths longer than 420 nm in benzene at temperatures between 6 and 30 °C. Changes in the absorption spectrum of (2) ( $5 \times 10^{-5}$  mol dm<sup>-3</sup>) under irradiation in deaerated benzene at 20 °C

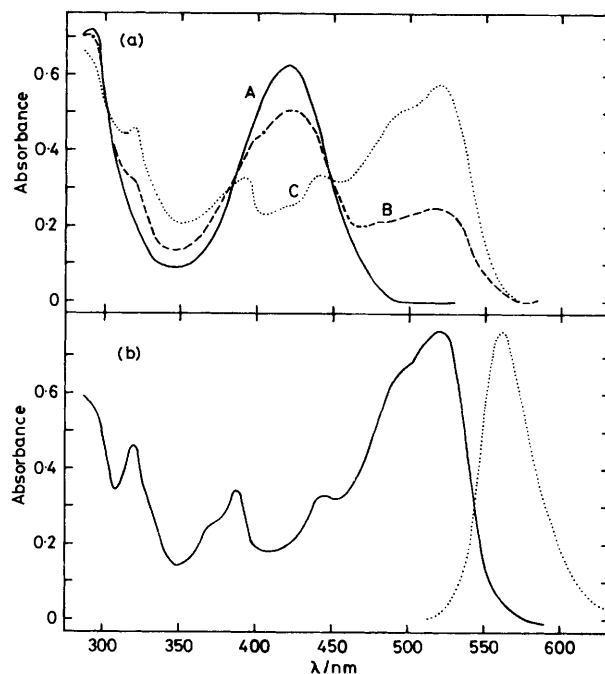


Figure 2. (a) The time-resolved absorption spectra of (2) ( $5 \times 10^{-5}$  mol dm<sup>-3</sup>) in benzene under irradiation ( $>420$  nm) at 20 °C: A, before irradiation; B, after 30 min irradiation; C, after 2 h irradiation. (b) Absorption (full curve) and fluorescence (broken line) spectra of (4) ( $5.4 \times 10^{-5}$  mol dm<sup>-3</sup>) in benzene

are shown in Figure 2(a). During photolysis the fluorescence maximum of (2) (excitation at 430 nm) at 503 nm decreased, with appearance of a new emission band at 550 nm.

In order to determine the structure of compound (4), its preparation from (1) (20 mg) was carried out in ethanol by irradiation with a high-pressure mercury lamp at 30 °C under nitrogen. The irradiation was continued for 9 h and monitored fluorophotometrically until the fluorescence band at 545 nm reached maximal intensity. Extended irradiation brought about further change in the product (4). After the solvent had been distilled off *in vacuo* the resulting reddish-brown residue was purified by column chromatography. From the benzene eluate compound (4) (1 mg) was obtained as red prisms. In this photoreaction of (1), the formation of by-products (probably oxidation products caused by molecular oxygen as impurity, or oxidants formed from the electron-donating nitrate anion) could not be excluded. Therefore, the yield of (4) from (1) was not good. On the other hand, photolysis of (2) in deaerated benzene at 30 °C gave the same product (4) in good yield.

Compound (4) did not exhibit e.s.r. absorption and decomposed at 324 °C. Its absorption and fluorescence spectra in benzene are shown in Figure 2(b). Elemental analysis and mass spectrum [ $m/z$  384 ( $M^+$ )] gave the molecular formula C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>, suggesting its formation by dehydrogenation from (2). The <sup>1</sup>H n.m.r. spectrum is shown in Figure 3(a). Comparison with the spectrum of (2) [Figure 3(b)], shows the following changes: the *N*-methyl signal undergoes an upfield shift from  $\delta$  2.97 to 2.83, and the aromatic proton signals spread over a wider range, indicating the formation of various kinds (shielded and deshielded) of protons. The <sup>13</sup>C n.m.r. spectrum of (4) showed only one methyl carbon signal (at 33.52 p.p.m.) and 13 kinds of aromatic ring carbon atom (106.95–141.09 p.p.m.). It has been reported that dioxanthylene<sup>7</sup> and 10*H*,10'*H*-bianthrylidene<sup>8</sup> undergo photocycliz-

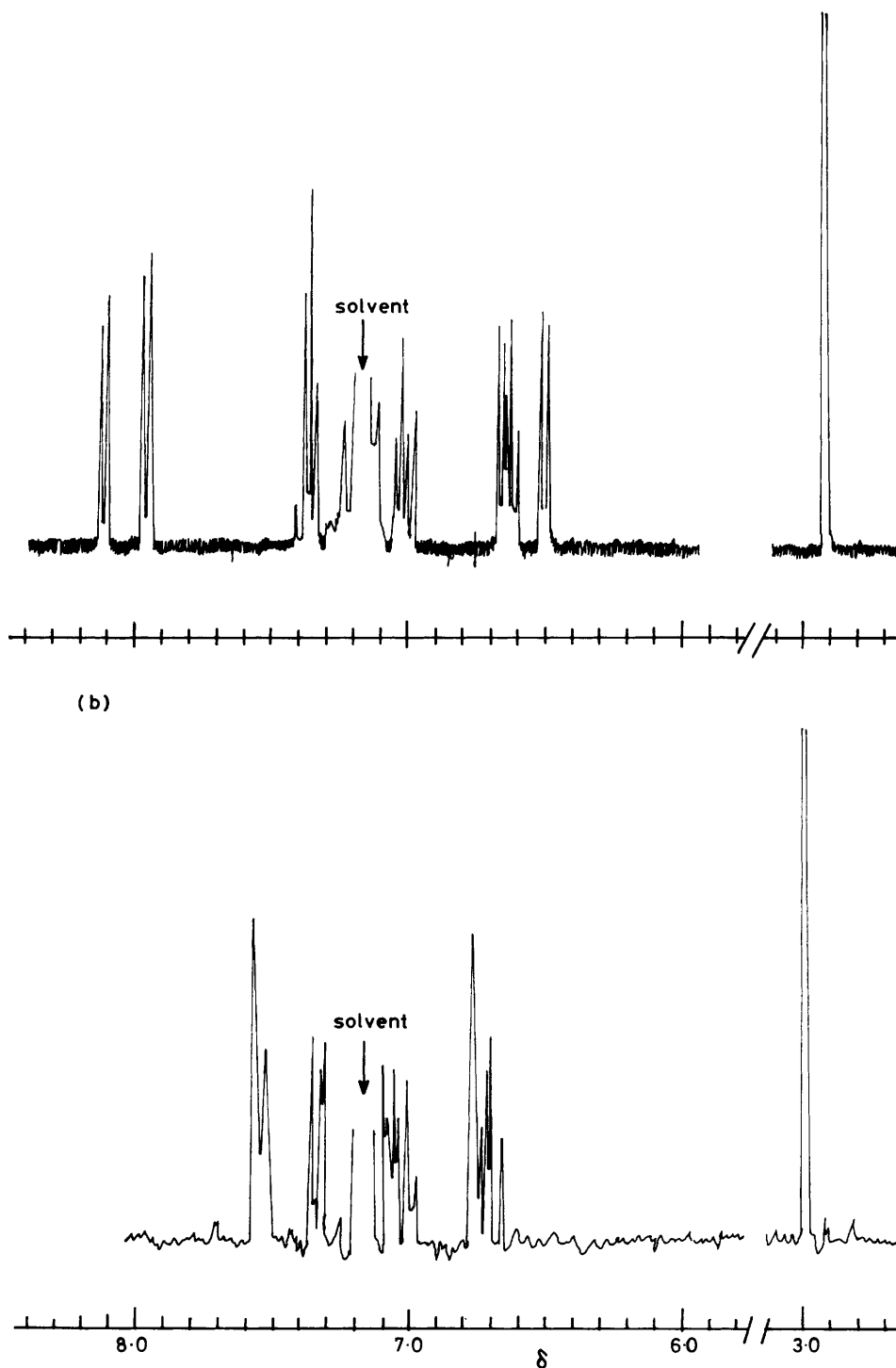
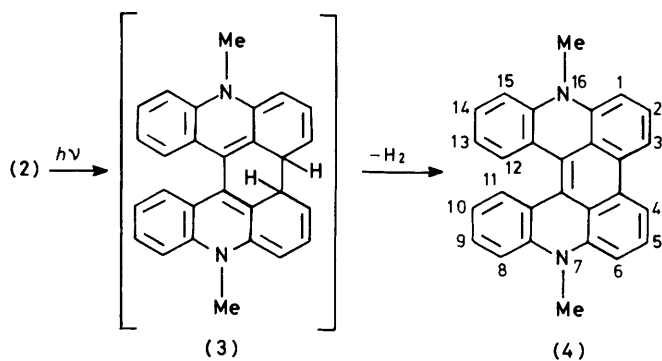


Figure 3. (a)  $^1\text{H}$  N.m.r. spectrum of (4) in  $\text{C}_6\text{D}_6$ . (b)  $^1\text{H}$  N.m.r. spectrum of (2) in  $\text{C}_6\text{D}_6$

ation to give dihydrophenanthrene-type compounds which are transformed into the corresponding dehydrogenation products, helixanthene, and helianthryl, respectively, on addition of oxidizing agents. In view of these facts and of our experimental results, it is considered that compound (4) is a helixanthene-type product, 7,16-dimethylbenzo[1,2,3-*kl*:6,5,4-*k'l'*]diacridine, formed from the dihydrophenanthrene-type photocyclization product (3) as shown in Scheme 2. Although the precursor (3) could not be detected in the

spectrophotometric measurements, dehydrogenation to give (4) from (3) was assumed to proceed with greater facility with oxygen (impurity) in the solution than in the formation of helianthryl or helixanthene from the corresponding precursors.

The structure of compound (4) is supported by the following observations. (a) In the mass spectrum the molecular ion peak is the base peak, and a doubly charged molecular ion peak [ $m/z$  192 ( $M^{2+}$ )] also appears. The fragmentation pattern is very simple: the main fragment ions are only  $m/z$  369 (40%),



Scheme 2.

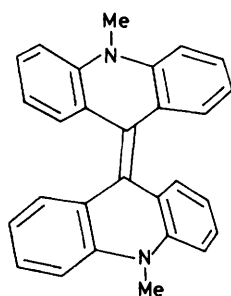
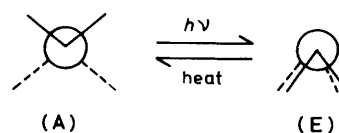


Figure 4. The doubly folded form (A) of (2)

and 354 (10%), corresponding to loss of one and two methyl groups, respectively. These facts reflect the great stability to fragmentation of compound (4), as reported for acridines.<sup>9</sup> (b) It has been reported that the lowest energy state of compound (2) is a doubly folded form (denoted A) as shown in Figure 4,<sup>10</sup> which on irradiation at temperatures down to  $-180^{\circ}\text{C}$  yields an isomer E (Scheme 3). During the A  $\rightarrow$  E process an upfield shift of the *N*-methyl signal, and a downfield shift of the 1,1', and 8,8'-proton signals were observed, resulting from removal of the diamagnetic shielding by the opposite benzene ring.<sup>11</sup> These observations are very similar to the upfield shift of the *N*-methyl signals and downfield shift of the aromatic ring proton signals in the transformation (2)  $\rightarrow$  (4) already described above. In this reaction it is assumed that the doubly folded compound (2) is converted into a configuration similar to that of E, containing a coplanar phenanthrene moiety. The suggested structure of compound (4) is consistent with the following assignments for protons in the <sup>1</sup>H n.m.r. spectrum. The signal shifted downfield to  $\delta$  8.15 (2 H, dd, *J* 1.5 and 8 Hz), is considered to be due to the protons at the 3 and 4 positions (in the phenanthrene moiety). The signal shifted upfield to  $\delta$  6.51 (2 H, d, *J* 8 Hz) can be assigned to the protons at the 11- and 12-position, probably subject to anisotropic shielding by the opposite aromatic rings of the phenanthrene moiety.

### Experimental

Measurements of u.v. spectra were carried out using a Shimadzu UV 200 spectrophotometer. Fluorescence spectra were recorded with a Shimadzu RF-510 fluorophotometer. N.m.r. spectra (<sup>1</sup>H and <sup>13</sup>C) were obtained with a JNM FX-400 or -200 spectrometer. The mass spectrum was run on a Hitachi RMU 6MG spectrometer. Thermal gravity differential thermal analysis (TGDTA) was performed with an ULVAC TGD-300 instrument with Al<sub>2</sub>O<sub>3</sub> as standard.



Scheme 3.

**Starting Materials.**—Lucigenin (1) was synthesized by the method of Decker and Dunnant<sup>12</sup> from 10,10'-dimethyl-9,9'-biacridylidene (2), prepared by reduction of *N*-methylacridone. Purification was achieved by recrystallization from water and then ethanol-methanol (1 : 1 v/v). Compound (2) was purified by recrystallization from pyridine and then benzene.

**Spectrophotometry.**—The sample solution was introduced into a long-necked square 10 mm path length cell clear on all four faces. The solution was degassed by repeated freeze-pump-thaw cycles. The sample was irradiated with a 500 W xenon lamp using a Toshiba glass filter (Y-51 or L-42).

**General Procedure for Preparation of 7,16-Dimethylbenzo[1,2,3-kl:6,5,4-k'l']diacridine (4).**—All irradiations were performed on solutions (150 cm<sup>3</sup>) irradiated by a 400 W high-pressure mercury lamp from inside the sample solution without filter in a thermostatically controlled bath.

**Isolation of the Compound (4) from (2).**—A solution of compound (2) (17 mg) in benzene was irradiated while nitrogen was bubbled through at 30  $^{\circ}\text{C}$ . After 17 h irradiation, the solution was distilled to dryness *in vacuo* under nitrogen. The n.m.r. spectrum showed the ratio of (4) to (2) to be about 5.5 : 1. Repeated column chromatography on alumina with benzene as eluant gave the product (4) as red prisms (8 mg, 47%), m.p. 324  $^{\circ}\text{C}$  (decomp.; from TGDTA);  $\lambda_{\text{max}}$  (C<sub>6</sub>H<sub>6</sub>) 520 ( $\epsilon$  20 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), 443 (8 600), 391 (9 100), and 321 nm (12 000);  $\delta_{\text{H}}$  (400 MHz; solvent C<sub>6</sub>D<sub>6</sub>; standard Me<sub>4</sub>Si) 2.83 (6 H, s, Me), 6.5–8.2 (14 H, m, Ar);  $\delta_{\text{C}}$  (200 MHz; solvent C<sub>6</sub>D<sub>6</sub>; standard Me<sub>4</sub>Si) 33.52 (Me), 106.95, 112.82, 114.16, 114.57, 120.25, 120.40, 125.0, 126.81, 127.78, 128.29, 128.68, 129.17, and 141.09 (Ar) (Found: C, 87.3; H, 5.15; N, 7.15. C<sub>28</sub>H<sub>20</sub>N<sub>2</sub> requires C, 87.45; H, 5.25; N, 7.3%); *m/z* 384 (*M*<sup>+</sup>, 100%), 369 (40), 354 (10), and 192 (*M*<sup>2+</sup>, 8).

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