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Lutz Stoeber[a]; Andres Sustic[b]; William J. Simonsick Jr.[c]; Otto Vogl[de]
[a] Allied Signal Inc., Engineering Plastics, Morristown, NJ, U.S.A. [b] H. B. Fuller Co., St. Paul, MN, U.S.A. [c] Du Pont Performance Coatings, Marshall R & D Laboratories, E.I. du Pont de Nemours & Co., Philadelphia, PA, U.S.A. [d] Six Metrotech Center, Polytechnic University, Brooklyn, NY, U.S.A. [e] Department of Polymer Science, University of Massachusetts, Amherst, MA, U.S.A.

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FUNCTIONAL POLYMERS 64. POTASSIUM IONIZATION OF DESORBED SPECIES (K^+IDS) OF 2(2-HYDROXYPHENYL)2H-BENZOTRIAZOLES

Lutz Stoeber,[1,†] Andres Sustic,[1,‡] William J. Simonsick, Jr.,[2] and Otto Vogl[1,*]

[1]Polytechnic University
Six Metrotech Center
Brooklyn, NY 11201

[2]Du Pont Performance Coatings
Marshall R & D Laboratories
E.I. du Pont de Nemours & Co.
Philadelphia, PA 19146

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ABSTRACT

Mass spectrometry using the potassium ionization of desorbed species (K^+IDS) technique was found to be an unusually fruitful method to characterize 2(2-hydroxyphenyl)2H-benzotriazole derivatives. This class of compounds has the proper molecular weight range of 200 up to more than 1000 daltons (Da) and the

†Present address: Allied Signal Inc., Engineering Plastics, 101 Columbia Road, Morristown, NJ 07962
‡Present address: H. B. Fuller Co., 1200 Willow Lake Blvd., St. Paul, MN 55110
*Author to whom correspondence should be addressed at Department of Polymer Science, University of Massachusetts, Amherst, MA, 01003-4350. Tel.: 413-577-1628; Fax: 413-545-0082; E-mail: vogl@polysci.umass.edu

proper volatility to show readily desirable concentrations in the mass spectrometer. This class of compounds is stable under the conditions of measurement which allows the determination of their purity. 2(2-Hydroxyphenyl)2H-benzotriazoles have recently been used most extensively for the ultraviolet stabilization of polymeric materials. In this work, over 100 2(2-hydroxyphenyl)2H-benzotriazoles have been characterized by K^+IDS mass spectrometry.

INTRODUCTION

Potassium Ionization of Desorbed Species (K^+IDS) is a mass spectrometric technique for the determination of compounds with molecular weights between 100 and 2000 daltons (Da) with minimal molecular fragmentation [1-4]. Sample molecules are deposited in close proximity to a filament where they are radiatively heated at a very fast rate and intact molecules evaporate with minimal thermal decomposition. Subsequently, the molecules are ionized by an ionization technique based upon the thermionic emission of potassium from an aluminosilicate matrix containing K_2O. The molecular weight is determined by subtracting from the mass of the pseudomolecular ion peak, $[M]K^+$, the average atomic weight of the potassium ion, 39.1 Da. An improved computerized procedure to rapidly and effectively make molecular weight determinations of organic compounds including the detection of oligomers was developed [5]. This technique has been most useful for the analysis of oligomer compositions obtained from the study of the embryonic state of polymerizations [6] or for the characterization of modern coatings components [7, 8].

Over the last decade and a half, we have studied intensively the synthesis, characterization and photochemistry of 2(2-hydroxyphenyl)2H-benzotri-azole derivatives. First, we investigated the 5-vinyl- and 5-isopropenyl-substituted 2(2-hydroxyphenyl)2H-benzotriazoles [9-20], the UV ineffective 4-hydroxy compounds, and the multi benzotriazole substituted multiphenols [21-24] and the multinuclear phenols [25]. Resorcinol and phloroglucinol provided an excellent source for 4-substituted and 4,6-disubstituted 2(2-hydroxy-phenyl)2H-benzotriazoles [26-34], and also 2(2-hydroxyphenyl)2H-benzotria-zoles that have substituents in the 5'-position. These compounds allowed the synthesis of 2(2-hydroxyphenyl)2H-benzotriazoles with significant absorption at 400 nm which is required for optical UV lens applications [35-37]. 2(2Hydroxy-phenyl)2H-benzotriazoles with substitution on the 5 position in the phenyl ring provided a new family of compounds. One group of these compounds had a tert. butyl group in

the 3-position and allowed the synthesis of surface active UV stabilizers with long fluorocarbon, silicon and hydrocarbon chains. Surface active polymerizable ultraviolet 2(2-hydroxyphenyl)2H-benzotriazoles were made be reacting the 3-unsubstituted 2(2-hydroxyphenyl)2H-benzotriazoles with methylol(meth)acrylamide or methylolmaleimide to give the 3-methyleneamido- compounds. The 3-tert. butyl- 5-(3'-hydroxypropyl) 2(2-hydroxyphenyl)2H-benzotriazoles reacted with unsaturated carboxylic acid derivatives and provided UV stabilizers for drying oils and oriental lacquer compositions [55].

In addition to the synthesis of regular 2(2-hydroxyphenyl)2H-benzotriazoles, 2(2-hydroxyphenyl)2H-benzotriazoles suitable for incorporation into condensation polymers, i.e., polyesters, polycarbonates and polyamides, were also synthesized and studied.

Polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles were incorporated into polymers by copolymerization, by grafting, by addition to double bond present in the polymer structures and by polymer reactions.

The polymer effect of the 2(2-hydroxyphenyl)2H-benzotriazole moiety was also investigated, as was the photochemistry and the photophysics of 2(2-hydroxyphenyl)2H-benzotriazoles, the as well as fundamentals and the "polymer effects."

EXPERIMENTAL

Measurements

Molecular weight determinations (reported as monoisotopic values in Daltons, Da) [where one Dalton is defined as 1/12 of the mass of an atom of carbon of the isotope mass of carbon 12] were obtained using the K^+IDS measurement technique. They were performed on a modified Finnigan 4615B quadrupole GC/MS system. An EI source configuration was used in all experiments.The experimental details of the K^+IDS technique can be found in Reference 4.

Molecular Weight Calculations

K^+IDS is a soft ionization technique affording molecular ions as $[M]K^+$ with little or no fragmentation. Therefore, we will only discuss the molecular ion region of the spectra and the mass definitions pertaining to this region [38]. The nominal mass, which is what we will report throughout the manuscript, is calculated using the most abundant isotopes without considering the mass defect i.e., H =I, C = 12, N =14, 0 = 16, F = 19, Cl = 35, K = 39, etc. The monoisotopic

mass calculated from the most abundant isotopes takes into account the mass defect i.e., H = 1.0078, C = 12.0000, N = 14.003 1, 0 = 15.9993, F = 18.9984, Cl = 34.9688, K = 39.0984. Unfortunately, quadrupole mass spectrometers do not have enough resolving power (R~1000) to provide such exact mass data. However, ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry has recently been shown to furnish isotopic fine structure for proteins [40] The average mass is calculated from the average masses of the elements and is then weighed for abundance i.e., H = 1.008, C = 12.01, N = 14.01, 0 = 15.96, F = 19.00 Cl = 35.46, K = 39.11.

Selected 2(2-Hydroxyphenyl)2H-benzotriazoles

A selected group of 2(2-hydroxyphenyl)2H-benzotriazole derivatives are mentioned specifically, the rest of the compounds are shown in Tables 1 to 8 [9-34, 41-64]

Substituted 2(2,4-Dihydroxyphenyl)2H-benzotriazoles
2(2,4-Dihydroxyphenyl)-2H-benzo-triazole (BDH)

The K^+IDS spectrum of BDH showed the pseudomolecular ion peak $[M]K^+$ at 266 Da, corresponding to a species with a nominal molecular weight of 227 Da; the nominal molecular weight of BDH is 227 Da. There is also a minor peak at 304 Da, ca. 10% abundance, which we attribute to the potassium salt of $[BDH]K^+$ [where the H of the phenolic hydroxyl group is replaced by K].

2(2,4-Dihydroxyphenyl)2H-5'-fluorobenzotriazole (FBDH). The K^+IDS spectrum of FBDH showed the pseudomolecular ion base peak at 245 Da, which corresponds to the molecular weight of FBDH. This is quite interesting because we expected the peak at 284 Da (245 + 39). As will become evident soon, this is also the case for most of the 2(2,4-dihydroxy-phenyl)2H-benzotriazoles that have an electron donating group in the 5 position of the benzotriazole ring, vide INFRA. The K^+IDS spectrum showed also the expected isotope peaks at 246 and 247 Da supporting a compound with a molecular formula of $[C_{12}H_8N_3ClO_3]K^+$.

2(2,4,6-Trihydroxyphenyl)2H-5'-chlorobenzotriazole (CIBTH). The K^+IDS spectrum of CIBTH showed the pseudomolecular ion peak at 277 Da plus isotopes. The ions at mass 277-281 Da are due to the more complex chlorine containing isotope distribution. Once again, no potassium is involved in the ions which closely corresponds to the molecular weight of ClBTH (277 Da). We anticipated a peak at 316 Da (277 + 39). The isotope peaks observed at 278 Da, 279 Da and 280 Da, display a characteristic one-chlorine isotope pattern.

2(2,4-Dihydroxyphenyl)2H-5'-chlorobenzotriazole (ClBDH). The K^+IDS spectrum of ClBDH showed the base peak at 261 Da, which is due to the monoisotopic peak of CIBDH (261 Da). The peak was expected at 261 + 39 = 300 Da. Adjacent isotope peaks are also observed at 262 Da, 263 Da, and 264 Da and display the expected one-chlorine isotope pattern.

2(2,4-Dihydroxyphenyl)2H-5',6'-dichlorobenzotriazole (DClBDH). The K^+IDS spectrum of DClBDH showed the pseudomolecular ion peak at 296 Da which corresponds to the molecular weight of DClBDH. There are less abundant peaks corresponding to the isotope peaks of C, N, H, K and especially Cl. There is also a peak at 295 Da, about 90% the intensity of the base peak. This ion peak is most probably due to the loss of one proton from the molecule. Another species giving a peak of about 50% the intensity of the base ion peak, appears at 262 Da, a difference of 34 Da with respect to DClBDH. This ion peak could be due to DClBDH replacing one chlorine atom for a hydrogen atom, the hydrogen atom coming from the species with MW 295 Da.

2(2,4-Dydroxy-5-phenyl]2H-1,3-bis-(5'-chlorobenzotriazole) (ClDBDH). The K^+IDS spectrum of ClDBDH showed the pseudomolecular ion peak at 451 Da. There is a ^{13}C isotope peak at 452 Da and a more intense chlorine ^{37}Cl peak at 453 Da. The weighted average of these peaks will yield the average molecular weight of ClDBDH.

2(2-Hydroxy-5-[2-hydroxyethylphenyl])2H-benzotriazole (HHEPB). The K^+IDS spectrum of HHEPB (255 Da) showed the pseudomolecular ion peak at 294 Da, which corresponds to a molecular weight of 255 Da (294- 39). No isotope peak was observed at 295 Da which we attribute to a weak signal but there was a small ion peak (<10%) at 296 Da, whose origin is due to the pseudomolecular ion peak, $[M]K^+$, for the potassium ^{41}K isotope.

2(2-Hydroxy-5-[3-carboxyethylphenyl]2H-benzotriazole (BHPA). The K^+IDS spectrum of BHPA showed the pseudomolecular peak at 322 Da. After subtracting the atomic weight of the potassium ion, a molecular weight of 283 Da was calculated. The calculated average molecular weight is 283 Da. The isotope peaks are small, but support a C, H, O, and N containing compound.

2(2-Hydroxynaphthalene)2H-benzotriazole (1B2HN) and 2(4-hydroxynaphthalene)2H-benzotriazole (4B1HN). The K^+IDS spectra of 1B2HN and 2B1HN were almost identical to each other, with the pseudomolecular ion peak found at 300

Da, which corresponds to a compound with a molecular weight of 261 Da. For the two compounds, the nominal molecular weight is 261 Da; 1B2HN and 4B1HN are isomers thus one expects identical K^+IDS spectra. 1B2HN has the hydroxyl group *ortho*- to the benzotriazole moiety while 4B1HN has the hydroxyl group *para*- to the benzotriazole group. The K^+IDS spectrum of 4B1HN is very clean, the only ion peaks appearing correspond to the isotopes at 301Da, 302 Da, and 303 Da. The isotope patterns support structures with a molecular formula of $[C_{16}H_{11}N_3O]K^+$.

2[2-Hydroxy-(polydimethylsiloxanylethyl-3-carboxyethyl)phenyl]2H-benzo-triazol (PDMS-BHMPA). The methylene carbinol terminated polydimethylsiloxane used in this work is an ethylene oxide-dimethylsiloxane-ethylene oxide block terpolymer consisting of 75-80% ethylene oxide units. The K^+IDS spectrum of the product showed several ion peaks ranging from 215 Da up to 906 Da, with the peaks decreasing in intensity after the base peak at 447 Da, the peak which corresponds to a species with a molecular weight of 408 Da. The molecular weight of BHMPA is 380 Da. A molecular weight of 408 Da could indicate that under the experimental conditions at which the K^+IDS spectrum was obtained there was a substantial amount of fragmentation implying decomposition. As evidenced in the spectrum, the more intense peaks are separated by an average 44 Da, which is the weight of one oxyethylene unit. Starting at 215 Da, there are at least 18 peaks separated by 44 Da, so that the poly(dimethyl siloxane) oligomer must have some chains with at least 19 dimethylsiloxane units. On the other hand, the reported average molecular weight of the carbinol terminated PDMS is 1250 Da which would give an average number of dimethylsiloxane units of 5 to 6.

2[2-Hydroxy-(2-perfluoroalkylethyl 3-carboxethyl)[phenyl]2H-benzotriazol (PFAE-BHMPA). The K^+IDS spectrum of PFAE-BHMPA showed a base peak at 864 Da due to the pseudomolecular ion and corresponding to a species with a molecular weight of 725 Da. Both the elemental analysis and the K^+IDS spectrum appear to agree on a molecular weight of 825-827 Da for PFEA-BHMPA, which would correspond to a species for which the perfluroalkylethyl part of the molecule has on the average 7 perfluoromethylene units, corresponding to a molecular weight for the perfluoroalkylethyl group of 461 Da. There is also a much smaller peak, ca. 5% of the intensity of the base peak, with a molecular weight of 725 Da, possibly the ionized PFEA-BHMPA, and finally, there is a peak at 964 Da, ca. 28% as intense as the base peak, corresponding to a species with a molecular weight exactly 100 Da higher than PFAE-BHMPA. These differences are due to a species with two additional difluoromethylene groups (C_2F_4 = 100 Da).

2(2,4-Dihydroxy-6-methylpyrimidyl)2H-benzotriazole (BDMPy). The K^+IDS spectrum showed a pseudomolecular ion peak at 282 Da which would correspond to a species with a molecular weight of 243 Da, which is the molecular weight of BDMPy. There is a much smaller peak due to a pseudomolecular ion with a weight of 306 Da, which would correspond to a species with a molecular weight of 267 Da, 24 Da heavier than BDMPy.

Polymerizable Substituted 2(2,4-Dihydroxyphenyl)2H-benzotriazoles

2(2-Hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)2H-benzotriazole (BDHG). The K^+IDS spectrum of BDHG showed a pseudomolecular ion peak at 408 Da. The molecular weight of BDHG was found to be 369 Da, which agrees with the calculated nominal molecular weight of 369 Da. There are some less intense secondary peaks (<20% of base peak intensity) found at 409, 410, and 411 Da, which are due to isotopes. Another cluster of peaks was observed at 476 Da which corresponds to a species with an extra methacryloyl group (mass of group minus condensation unit), probably from substitution also on the second - hindered 2-hydroxy-group.

2(2-Hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)2H-5'-chloro-benzotriazole (CIBDHG). The K^+IDS spectrum of CIBDHG gave a pseudomolecular ion peak at 442 Da, which corresponds to a molecular weight for CIBDHG of 403 Da. The calculated average molecular weight is 403,83 Da . There is a less intense secondary peak at 443 Da (< 25%), due to hydrogen and carbon isotopes, and another one found at 444 Da (< 40%) due to the chlorine 37 isotope. In the lower molecular weight range, there is another peak (ca. 35%) which belongs to a species with a molecular weight of 323 Da, a weight difference of 80 Da. This peak does not show the chlorine isotope ion peak.

2(2-Hydroxy-3-acrylamidomethyl-5-methylphenyl)2H-benzotriazole (2H3A5M). The K^+IDS spectrum showed the pseudomolecular ion peak at 347 Da which gives for 2H3A5M a molecular weight of 308 Da; the calculated molecular weight is 308 Da. Present also are isotope peaks at 348 Da, 349 Da and 350 Da supporting a molecular formula of $[C_{17}H_{16}N_4O_2]K^+$.

2(2-Hydroxy-3-methacrylamidomethyl-5-(2-carboxyethyl) phenyl)2H-benzotri-azole (BHMPA). The K^+IDS spectrum of BHMPA showed some interesting features. It showed the pseudomolecular ion peak at 419 Da, which corresponds to a compound with a molecular weight of 380 Da, while the calculated molecular weight of BHMPA is 380 Da. The spectrum showed also several additional smaller

peaks. One peak, with ca. 25% abundance, appeared at 433 Da. This would correspond to a compound with an additional nitrogen atom or an additional methylene group. Moreover, there are smaller peaks found at 516 Da (ca. 15% intensity), 617 Da (ca. 10%) and 714 Da (ca. 3%). The weight differences are 97 Da, 101 Da, and 97 Da, respectively. The weight of the methacrylamidomethyl moiety is 98 Da. This data would appear to indicate that there has been multiple substitutions on the phenyl ring, with molecules having up to three methacrylamidomethyl groups. On the other side, there are several peaks with lower MW. Of the more relevant ones, there is one at 380 Da ($[M]K^+$ minus 39 Da) with a ca. 15% abundance which corresponds to the molecular ion peaks. Another peak is found at 322 Da, a difference of 97 Da with respect to the pseudomolecular ion peak. This could mean that while some ions are losing methacrylamidomethyl groups, other ions are gaining units of that molar mass. The ion peak corresponding to the potassium salt of the carboxylate was not observed.

2(2-Hydroxy-3-methacrylamidomethyl-5-methylphenyl)2H-benzotriazole (2H3M5M). The K^+IDS spectrum of 2H3M5M showed the pseudomolecular ion peak at 361 Da which gave for 2H3M5M a molecular weight of 322 Da; the calculated molecular weight is 322.37 Da. Isotope ion peaks at 362 Da, 363 Da and 364 Da support a compound with a molecuar formula of $[C_{18}H_{18}N_4O_2]K^+$.

2(2-Hydroxy-3-tert-pentyl-5-methacrylamidomethylphenyl) 2H-benzotriazole (2H3T5M). The K^+IDS spectrum of 2H3T5M showed the pseudomolecular ion peak at 417 Da, which corresponds to a species with a molecular weight of 378 Da, while the calculated nominal molecular weight of 2H3T5M is 378 Da. A second ion peak appeared at 795 Da, with a much lower abundance (ca. 16%). This peak is due to the potassium bound dimer and can be reduced by using less sample. We have seen these adducts in previous studies [38].

2(2-Hydroxy-4-methacryloxyphenyl)2H-benzotriazole (BDHM). The K^+IDS mass spectrum for BDHM showed a pseudomolecular ion peak at 334 Da which corresponds to a species with a molecular weight of 295 Da. The molecular weight of BDHM is 295 Da. Also present are the isotope peaks. There is another peak with ca. 60% relative abundance at 629 Da, which is due to the potassium bound dimer.

2(2-Hydroxy-4-acryloxyphenyl)2H-benzotriazole (BDHA). The K^+IDS mass spectrum for BDHA showed a pseudomolecular ion peak at 320 Da which corresponds to a species with MW 281 Da, the nomial molecular weight of BDHA.

Also present are the isotope peaks. There is another peak with ca.18% relative abundance at 601 Da, which is due to the potassium bound dimer. This dimerization phenomenon has already been observed before for BDHM and for 2H3T5M, and could possibly be due to some particular instrumental conditions with a gas phase concentration being too high, which creates favorable conditions for the formation of potassium bound dimers. Also included is a peak with ca. 13% abundance at 374 Da, a difference of 54 Da with respect to the pseudomolecular ion peak, apparently the reaction product of two acryloyl groups (72 Da) on both hydroxyl groups with a corresponding loss of water (72-18 = 54). This di-functional impurity in the mono functional acryloyl compound is not very desirable because it causes crosslinking on polymerization.

RESULTS AND DISCUSSION

We have analyzed over 100 2(2-hydroxy-phenyl)2H-benzotriazoles and 2(2-hydroxyphenyl)2H-benzotriazole derivatives by K^+IDS spectrometry. Most of them are ultraviolet stabilizers and intermediates. We also investigated a few 2(4-hydroxyphenyl)2H-benzotriazoles. The results are shown in Tables 1-9. We found excellent agreement between the calculated and experimental values of the molecular weights. The Tables show the structural formulae, molecular formulae, references, calculated molecular weights [M]. Found [M] were obtained by subtracting K^+ from the experimentally determined $[M]K^+$, shown in the last column as $[M]K^+$. The preparation of the compounds was described previously, and is shown in the references. Many of the compounds are mentioned in References 54 and 62.

K^+IDS Spectra of 5-substituted 2(2,4-dihydroxyphenyl)2H-benzotriazoles

The 2(2,4-dihydroxyphenyl)2H-benzotriazole derivatives show interesting and highly useful K^+IDS spectra. For example, we have selected 2(2,4-dihydroxyphenyl)2H-benzotriazoles such as FBDH, ClBDH, MoBDH, and DClBDH, substituted in the 5' (and 6'-position for DClBDH) positions of the benzotriazole ring as specific examples. Typically, for compounds with an electron donating substituent, the mass-charge-ration m/z, of the pseudomolecular ion peak matches the molecular weight of the non-ionized molecule.

This phenomenon was not observed in the spectrum of unsubstituted BDH. One possible explanation is that the presence of such electron active groups as -F, -Cl, or even $–OCH_3$ in the 5'-position (and 6'-position) of the ben-

zotriazole ring, lower the ionization potential of the molecule to such an extent that there is an electron transfer process involving the potassium ion and the substituted 2(2,4-dihydroxyphenyl)2H-benzotriazole, leading to the formation of a positively charged molecular ion which is mass filtered and detected. Of the trihydroxy compounds, only ClBTH follows the behavior of the substituted d-hydroxy compounds while the K^+IDS spectrum of MBTH shows the pseudomolecular ion peak.

Interestingly, this phenomenon is not observed in the spectrum of ClBDHG in which the 4-hydroxyl on the phenoxy ring has been replaced by the 3-methacryloxy-2-hydroxypropoxy substituent. Nor is it observed in the K^+IDS spectrum of the 5'-substituted dihydroxy-di-benzotriazole MDBDH (Table 7) for which the pseudomolecular ion peak appears at a weight equivalent to $[MDBDH]K^+$, the expected molecular weight. The same predicted behavior is observed in the spectra of the 2(2-hydroxy-5-alkylphenyl)2H-benzotriazoles HHEPB, BHPA and 2H5M.

It also appears that the presence of at least two electron donating hydroxyl groups in the benzene ring, one *ortho* and the other *para* to the benzotriazole ring, including the electron donating substituent in 5'-, provides a suitable environment for an electron transfer to the potassium ion to occur. Why would an electron donating group such as the 3-methacryloxy-2-hydroxypropoxy or a second benzotriazole ring not have a similar effect is not known at this moment.

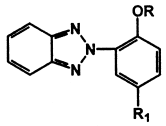
Table 1 shows the 2(2-hydroxy-5-phenyl)2H-benzotriazole derivatives, both a group of 2(2-hydroxy-5-phenyl)2H-benzotriazole derivatives with a free hydroxy group and another group as their acetyl-derivatives.

Table 2 describes derivatives of 2(2-hydroxy-3-tert. butyl-5-sub-stituted)2H-benzotriazoles. Tertiary butyl groups in the *ortho*-position are often used in phenolic antioxidants and ultraviolet stabilizers, including 2(2-hydroxyphenyl)2H-benzotriazoles to enhance their activity and increase their solubility in the polymer to be stabilized. Some of these stabilizers have been used for the stabilization of oriental lacquers [55], others as surface active UV stabilizers [62-64].

Table 3 shows polymerizable derivatives with a polymerizable group in the 3-position. They include 2(2-hydroxyphenyl)2H-benzotriazoles with methyleneacrylamido- and methylenemethacrylamido groups and one methylenemaleimido derivative.

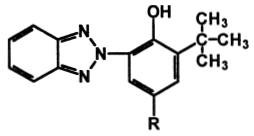
Table 4 describes 2(2-hydroxyphenyl)2H-di-benzotriazole derivatives derived from resorcinol, 2(2,4-)2H-benzotriazole derivatives and from phloroglucinol, 2(2,4,6-trihydroxyphenyl)2H-benzotriazole derivatives.

TABLE 1.



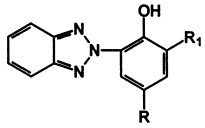
			Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
R= —H							
	R_1=	$-CH_3$	$C_{13}H_{11}N_3O$	-	225.25	264	225
		$-C_2H_5$	$C_{14}H_{13}N_3O$	15	239.28	278	239
		$-CH(OH)CH_3$	$C_{14}H_{13}N_3O_2$	18	255.28	294	255
		$-CH(OCH_3)CH_3$	$C_{15}H_{15}N_3O_2$	18	269.30	308	269
		$-CH=CH_2$	$C_{14}H_{11}N_3O$	15	237.26	276	237
		$-COCH_3$	$C_{14}H_{11}N_3O_2$	18	253.26	292	253
		$-CH(CH_3)_2$	$C_{15}H_{15}N_3O$	18	253.30	292	253
		$-COH(CH_3)_2$	$C_{15}H_{15}N_3O_2$	18	269.30	308	269
		$-CCH_3=CH_2$	$C_{15}H_{13}N_3O$	18	251.29	290	251
		$-CH_2CH_2OH$	$C_{14}H_{13}N_3O_2$	60	255.28	294	255
		$-CH_2CH_2OCOCCH_3=CH_2$	$C_{18}H_{17}N_3O_3$	60	323.35	362	323
		$-CH_2CH_2OCH_2CHOHCH_2OCOCCH_3=CH_2$	$C_{21}H_{23}N_3O_5$	54	397.43	436	397
		$-CH_2CH_2COOH$	$C_{15}H_{13}N_3O_3$	60	283.29	322	283
R= $-OCCH_3$							
	R_1=	$-C_2H_5$	$C_{16}H_{15}N_3O_2$	15	281.31	320	281
		$-CHBrCH_3$	$C_{16}H_{14}N_3O_2Br$	15	360.21	399	360
		$-CH(OH)CH_3$	$C_{16}H_{15}N_3O_3$	18	297.31	336	297
		$-CH(OCH_3)CH_3$	$C_{17}H_{17}N_3O_3$	18	311.34	350	311
		$-CH=CH_2$	$C_{16}H_{13}N_3O_2$	15	279.30	318	279
		$-COCH_3$	$C_{16}H_{13}N_3O_3$	18	295.30	334	295
		$-CCH_3=CH_2$	$C_{17}H_{15}N_3O_2$	18	293.32	332	293

TABLE 2.



			Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
R= $-C(CH_3)_3$			$C_{20}H_{25}N_3O$	-	323.44	362	323
R= $-CH_2NHCOCCH_3=CH_2$			$C_{22}H_{26}N_4O_2$	54	378.47	417	378
R= $-CH_2CH_2COOR_1$							
	R_1=	$-H$	$C_{19}H_{21}N_3O_3$	62	339.39	378	339
		$-CH_3$	$C_{20}H_{23}N_3O_3$	62	353.42	392	353
		$-CH_2CH_2OH$	$C_{21}H_{25}N_3O_4$	54	383.44	422	383
		$-(CH_2)_{15}CH_3$	$C_{36}H_{53}N_3O_3$	62	563.83	602	563
		$-(CH_2)_{17}CH_3$	$C_{37}H_{57}N_3O_3$	62	591.88	630	591
		$-CH_2CH_2(CF_2)_5CF_3$	$C_{27}H_{24}N_3O_3F_{13}$	62	685.49	724	685
		$-CH_2(CF_2)_6CF_3$	$C_{27}H_{22}N_3O_3F_{15}$	62	721.47	760	721
		$-CH_2CH_2(CF_2)_{11}CF_3$	$C_{33}H_{24}N_3O_3F_{25}$	62	985.53	1024	985
R= $-CH_2CH_2CH_2R_2$							
	R_2=	$-OH$	$C_{19}H_{23}N_3O_2$	62	325.41	364	325
		$-OCOCH=CH_2$	$C_{22}H_{25}N_3O_3$	59	379.45	418	379
		$-OCOCCH_3=CH_2$	$C_{23}H_{27}N_3O_3$	59	393.49	432	393
		$-OCO(CH_2)_{16}CH_3$	$C_{37}H_{67}N_3O_3$	59	591.88	630	591
		Oleate	$C_{37}H_{55}N_3O_3$	59	589.86	628	589
		Linolate	$C_{37}H_{53}N_3O_3$	59	587.85	626	587
		Linolenate	$C_{37}H_{51}N_3O_3$	59	585.83	624	585
		Stearic (see above)	$C_{37}H_{57}N_3O_3$	59	591.88	630	591
		Acetic	$C_{21}H_{25}N_3O_3$	59	367.45	406	367

TABLE 3.



			Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
R_1= $-CH_2NHCOCH=CH_2$							
R= $-CH_2CH_2COOR_2$							
	R_2=	—H	$C_{19}H_{18}N_4O_4$	62	366.38	405	366
		$-(CH_2)_{15}CH_3$	$C_{35}H_{50}N_4O_4$	62	590.81	629	590
		$-(CH_2)_{17}CH_3$	$C_{37}H_{54}N_4O_4$	62	618.86	657	618
R_1= $-CH_2NHCOCCH_3=CH_2$							
R= $-CH_2CH_2COOR_2$							
	R_2=	—H	$C_{20}H_{20}N_4O_4$	54	380.40	419	380
		$-CH_2CH_2(CF_2)_7CF_3$	$C_{30}H_{23}N_4O_4F_{17}$	54	826.52	865	826

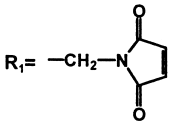
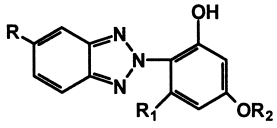
R_1= $-CH_2NHCOCH=CH_2$							
	R=	$-CH_3$	$C_{17}H_{16}N_4O_2$	54	308.34	347	308
R_1= $-CH_2NHCOCCH_3=CH_2$							
	R=	$-CH_3$	$C_{18}H_{18}N_4O_2$	54	322.37	361	322
R_1= 							
	R=	$-CH_3$	$C_{18}H_{14}N_4O_3$	41	334.33	373	334

TABLE 4.



			Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
—H	R_1= —H						
		R_2= —H	$C_{12}H_9N_3O_2$	20	227.22	266	227
		—$COCH=CH_2$	$C_{15}H_{11}N_3O_3$	23	281.27	320	281
		—$COCCH_3=CH_2$	$C_{16}H_{13}N_3O_3$	23	295.30	334	295
		—$CO(CH_2)_8CH=CH_2$	$C_{23}H_{27}N_3O_3$	29	393.49	432	393
		—$CH_2CH(OH)CH_2OCOCH=CH_2$	$C_{18}H_{17}N_3O_5$	54	355.35	366	327
		—$CH_2CH(OH)CH_2OCOC(CH_3)=CH_2$	$C_{19}H_{19}N_3O_5$	54	369.38	408	369
	R_1= —OH						
		R_2= —H	$C_{12}H_9N_3O_3$	26	243.22	No	243
		—$CO(CH_2)_8CH=CH_2$	$C_{23}H_{27}N_3O_4$	29	409.49	448	409
—OH	R_1= —H	R_2= —H	$C_{12}H_9N_3O_3$	-	243.22	282	243
	R_1= —OH	R_2= —H	$C_{12}H_9N_3O_4$	-	259.22	298	259
—Cl	R_1= —OH	R_2= —H	$C_{12}H_8N_3O_3Cl$	-	277.67	316	277
	R_1= —H	R_2= —$CH_2CH(OH)CH_2OCOCH=CH_2$	$C_{19}H_{18}N_3O_5Cl$	-	403.83	442	403
—OCH_3	R_1= —H	R_2= —H	$C_{13}H_{11}N_3O_3$	-	257.25	296	257
		—$COCH=CH_2$	$C_{16}H_{13}N_3O_4$	-	311.30	350	311
		—$COCCH_3=CH_2$	$C_{17}H_{15}N_3O_4$	-	325.32	364	325
		—$CH_2CH(OH)CH_2OCOC(CH_3)=CH_2$	$C_{20}H_{21}N_3O_6$	-	399.40	438	399
	R_1= —OH	R_2= —H	$C_{13}H_{11}N_3O_4$	-	273.25	312	273
		—$COCCH_3=CH_2$	$C_{17}H_{15}N_3O_5$	-	341.32	380	341

Table 5 shows the experimental and calculated molecular weights of 5' and 6' substituted 2(2-hydroxyphenyl)2H-benzotriazole derivatives, where the sustituents are in the benzene ring of the benzotriazole moiety.

In Table 6, 2(2,4-dihydroxyphenyl)2H-benzotriazole and 2(2,4,6-trihydroxyphenyl)2H-benzotriazole derivatives are shown, including polymerizable 2(2-hydroxyphenyl)2H-benzotriazole type ultraviolet stabilizers.

Table 7 also shows 2(2,4-dihydroxyphenyl)2H-di-benzotriazole and 2(2,4,6-trihydroxyphenyl)2H-di-benzotriazole derivatives with substituents like hydroxy-, methoxy-, carbomethoxy-, carboxy-, and chlorine in the benzene ring of the benzotriazole moiety. Some are suitable polymerizable ultraviolet stabilizers that have been incorporated into polyesters and polyamides.

Table 8 contains 2(2-hydroxy-3-phenyl)2H-benzotriazole and derivatives and their intermediates. 2(4-Hydroxyphenyl)2H-benzotriazoles are ultraviolet absorbers but not ultraviolet stabilizers.

Table 9 shows 2(2-hydroxy)2H-benzotriazole derivatives derived from naphthols, 4-hydroxybipenyl and one hydroxypyrimidine.

In all Tables, we report the calculated average molecular weight, the nominal mass of the experimentally measured $[M]K^+$ and finally the nominal mass of the compound obtained by subtracting the nominal mass of potassium, 39 Da from the measured $[M]K^+$.

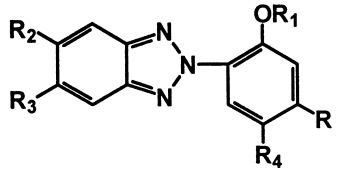
Calculated Isotope Distributions

In Figures 1 through 12 we present a graphical comparisons of the theoretical isotope distribution with the measured distribution for the molecular ion region of the a few selected stabilizers. Along with the comparison plots we also report the average mass of the ion calculated from the elements and weighted for abundance. In addition, we report the monoisotopic masses calculated from the isotopes taking into account the mass defects and the corresponding theoretical isotope envelopes with the theoretical abundancies. All theoretical calculations were performed using ISOPRO, version 3.02 [40].

The isotopes of 41K (7.4%) and 37Cl (32.5%) are important. Fluorine has monoisotopic. Measurements of the masses, as determined by mass spectrometry does not give the "average" mass but masses that can be resolved to about one Dalton. However, the average mass can be calculated by averaging the total isotope envelope.

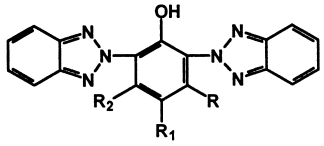
For example, 2(2,4-diydroxyphenyl)2H-benzotriazole of an average mass of 265.32 does not only consist of $C_{12}H_9O_2N_3$, which one would normally assume as $^{12}C_{12}{}^{1}H_9{}^{16}O^{14}N_3$, or the potassiated ion $^{12}C_{12}{}^{1}H_9{}^{16}O^{14}N^{39}$ K, but also other

TABLE 5.



					Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
R= —H	R_1= —H	R_2= $-C_2H_5$	R_3= —H	R_4= $-CH_3$	$C_{15}H_{15}N_3O$	17	253.30	253	292
		R_2= $-CH=CH_2$	R_3= —H	R_4= $-CH_3$	$C_{15}H_{13}N_3O$	17	251.28	251	290
	R_1= $-COCH_3$	R_2= $-C_2H_5$	R_3= —H	R_4= $-CH_3$	$C_{17}H_{17}N_3O_2$	17	295.34	295	334
		R_2= $-CH=CH_2$	R_3= —H	R_4= $-CH_3$	$C_{17}H_{15}N_3O_2$	17	293.32	293	332
R= —OH	R_1= —H	R_2= $-Cl$	R_3= —H	R_4= —H	$C_{12}H_8N_3O_2Cl$	60	261.66	261	300
				$-CH_2NHCOCH=CH_2$	$C_{16}H_{13}N_4O_3Cl$	60	344.75	344	383
				$-CH_2NHCOC(CH_3)=CH_2$	$C_{17}H_{15}N_4O_3Cl$	60	358.78	358	397
			R_3= $-Cl$	R_4= —H	$C_{12}H_7N_3O_2Cl_2$	60	296.11	295	334
		R_2= —F	R_3= —H	R_4= —H	$C_{12}H_8N_3O_2F$	60	245.21	245	284
		R_2= —H	R_3= —H	R_4= $-COCH_3$	$C_{14}H_{11}N_3O_3$	33	269.25	269	308
				R_4= $-COC_6H_5$	$C_{19}H_{13}N_3O_3$	33	331.33	331	370
		R_2= $-OCH_3$	R_3= —H	R_4= $-COCH_3$	$C_{15}H_{13}N_3O_4$	33	299.28	299	338
				R_4= $-COC_6H_5$	$C_{20}H_{15}N_3O_4$	33	361.35	361	400

TABLE 6.



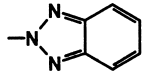
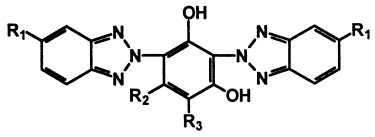
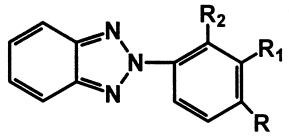
			Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
R= —OH							
	R_2= —H	R_1= —H	$C_{18}H_{12}N_6O_2$	20	344.33	383	344
		—$COCH_3$	$C_{20}H_{14}N_6O_3$	22	386.37	425	386
		—$CH=CH_2$	$C_{20}H_{14}N_6O_2$	32	370.37	409	370
		—$CCH_3=CH_2$	$C_{21}H_{16}N_6O_2$	32	384.40	423	384
		—$CH(OH)CH_3$	$C_{20}H_{16}N_6O_3$	32	388.39	427	388
		—$COH(CH_3)_2$	$C_{21}H_{18}N_6O_3$	32	402.41	441	402
		—COC_6H_5	$C_{25}H_{16}N_6O_3$	22	448.44	487	448
	R_2= —OH	R_1= —H	$C_{18}H_{12}N_6O_3$	20	360.33	399	360
			$C_{24}H_{15}N_9O_3$	25	477.44	516	477
R= —$OCOCH=CH_2$	R_2= —H	R_1= —H	$C_{21}H_{14}N_6O_3$	24	398.38	437	398
	R_2= —OH	R_1= —H	$C_{21}H_{14}N_6O_4$	24	414.38	453	414
R= —$OCOCCH_3=CH_2$	R_2= —H	R_1= —H	$C_{22}H_{16}N_6O_3$	24	412.41	451	412
	R_2= —OH	R_1= —H	$C_{22}H_{16}N_6O_4$	24	428.41	467	428
R= —$OCO(CH_2)_8CH=CH_2$							
	R_2= —OH	R_1= —H	$C_{29}H_{30}N_6O_4$	29	526.59	565	526

TABLE 7.



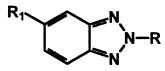
			Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
R_1= —OCH_3	R_2= —H						
		R_3= —H	$C_{20}H_{16}N_6O_4$	26	404.38	443	404
		—$CH_2NHCOCH{=}CH_2$	$C_{24}H_{21}N_7O_5$	26	487.48	526	487
		—$COCH_3$	$C_{22}H_{18}N_6O_5$	26	446.42	485	446
	R_2= —OH						
		R_3= —H	$C_{20}H_{16}N_6O_5$	26	420.38	459	420
R_1= —OH	R_2= —H						
		R_3= —H	$C_{18}H_{12}N_6O_4$	26	376.33	415	376
	R_2= —OH						
		R_3= —H	$C_{18}H_{12}N_6O_5$	26	392.33	431	392
R_1= —COOH	R_2= —H						
		R_3= —H	$C_{20}H_{12}N_6O_6$	48	432.35	471	432
R_1= —$COOCH_3$	R_2= —H						
		R_3= —H	$C_{22}H_{16}N_6O_6$	48	460.40	499	460
R_1= —$OCOCH_3$	R_2= —H						
		R_3= —H	$C_{22}H_{16}N_6O_6$	48	460.40	499	460
R_1= —Cl	R_2= —H						
		R_3= —H	$C_{18}H_{10}N_6O_2Cl_2$	60	413.24	452	413

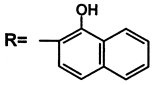
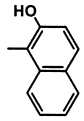
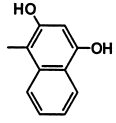
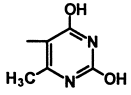
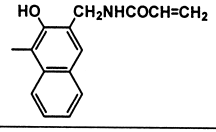
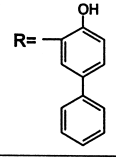
TABLE 8.



			Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
R= —OH	R_1= —H						
		—C_2H_5	$C_{14}H_{13}N_3O$	16	239.28	278	239
		—CH=CH_2	$C_{14}H_{11}N_3O$	16	237.26	276	237
	R_1= —C_2H_5						
		R_2= —H	$C_{14}H_{13}N_3O$	16	239.28	278	239
	R_1= —CH=CH_2						
		R_2= —H	$C_{14}H_{11}N_3O$	16	237.26	276	237
R= —$OOCCH_3$	R_1= —H						
		R_2= —C_2H_5	$C_{16}H_{15}N_3O_2$	16	281.31	320	281
		—$CHBrCH_3$	$C_{16}H_{14}N_3O_2Br$	16	360.21	399	360
		—CH=CH_2	$C_{16}H_{13}N_3O_2$	16	279.30	318	279
	R_1= —C_2H_5						
		R_2= —H	$C_{16}H_{15}N_3O_2$	16	281.31	320	281
	R_1= —$CHBrCH_3$						
		R_2= —H	$C_{16}H_{14}N_3O_2Br$	16	360.21	399	360
	R_1= —CH=CH_2						
		R_2= —H	$C_{16}H_{13}N_3O_2$	16	279.30	318	279

TABLE 9.



		Molecular Formula	Ref.	Calc. Avg. Weight (Da)	Nominal $[M]K^+$ (Da) (exp)	Nominal [M] (Da) (calc)
R_1= —H						
	R= 	$C_{16}H_{11}N_3O$	60	261.28	300	261
		$C_{16}H_{11}N_3O$	60	261.28	300	261
		$C_{16}H_{11}N_3O_2$	60	277.28	316	277
		$C_{11}H_9N_5O_2$	54	243.22	282	243
		$C_{20}H_{16}N_4O_2$	54	344.37	407	368
R_1= —Cl	R= 	$C_{18}H_{12}N_3OCl$	54	321.77	360	321

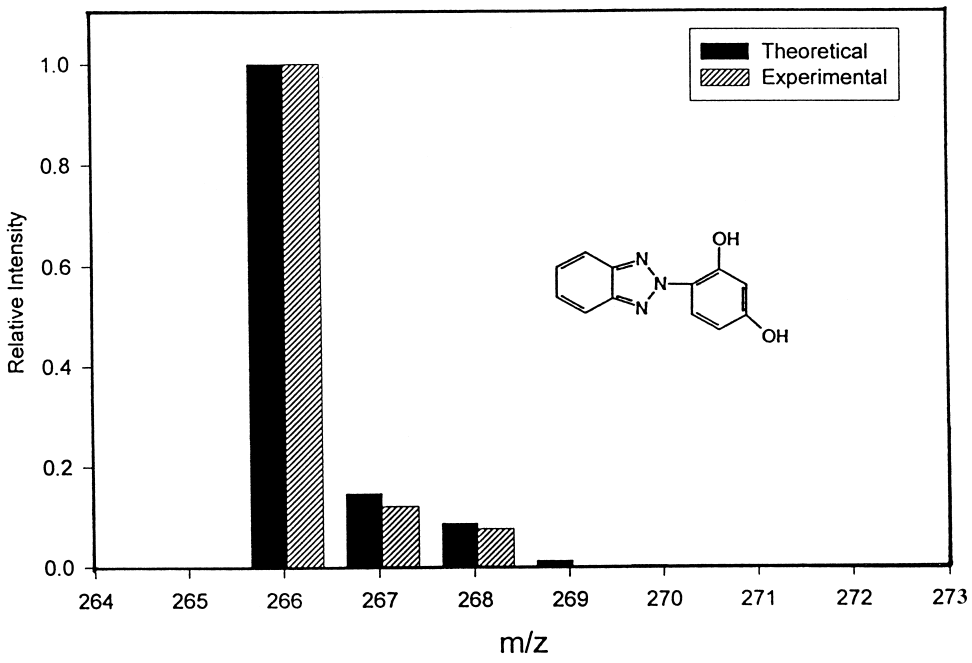


Figure 1. Isotope Distributions 2(2,4-Dihydroxyphenyl)2H-Benzotriazole $[C_{12}H_9N_3O_2]K^+$.

important isotopes, such as $^{13}C_{12}{}^{1}H_9{}^{16}O^{15}N^{39}K$ and $^{13}C_{12}{}^{1}H_9{}^{16}O^{15}N^{41}K$. All the ions of the various isotope atomic masses are detectable if the mass spectrometer sensitivity is capable of determining them. More easily detected are the isotope ions that have higher percentages of isotopes that occur naturally in higher proportions such as in the case of chlorine where the isotope ratio ^{35}Cl:^{37}Cl is 67.5:32.5 or nearly 2:1.

The following calculations were made to demonstrate the isotope distribution of a few interesting 2(2-hydroxyphenyl)2H-benzotriazole derivatives [63, 64]:

Figures 1, 3, 4, 5, 6, 8, 9, 10, 11, and 12 show the bar charts of the K^+IDS spectra with isotope distribution of the respective 2(2-hydroxy-phenyl)2H-benzotriazoles derivatives.and also the calculated isotope mass spectra. In mass spectrometry the spectra are represented as line drawings (65). Figures 2 and 7 show the Gaussian peaks computed at the resolution of 10,000 routinely achieved by FT-MS (38). These data are typically presented in the bar graph form as seen in Figures 1 and 6.

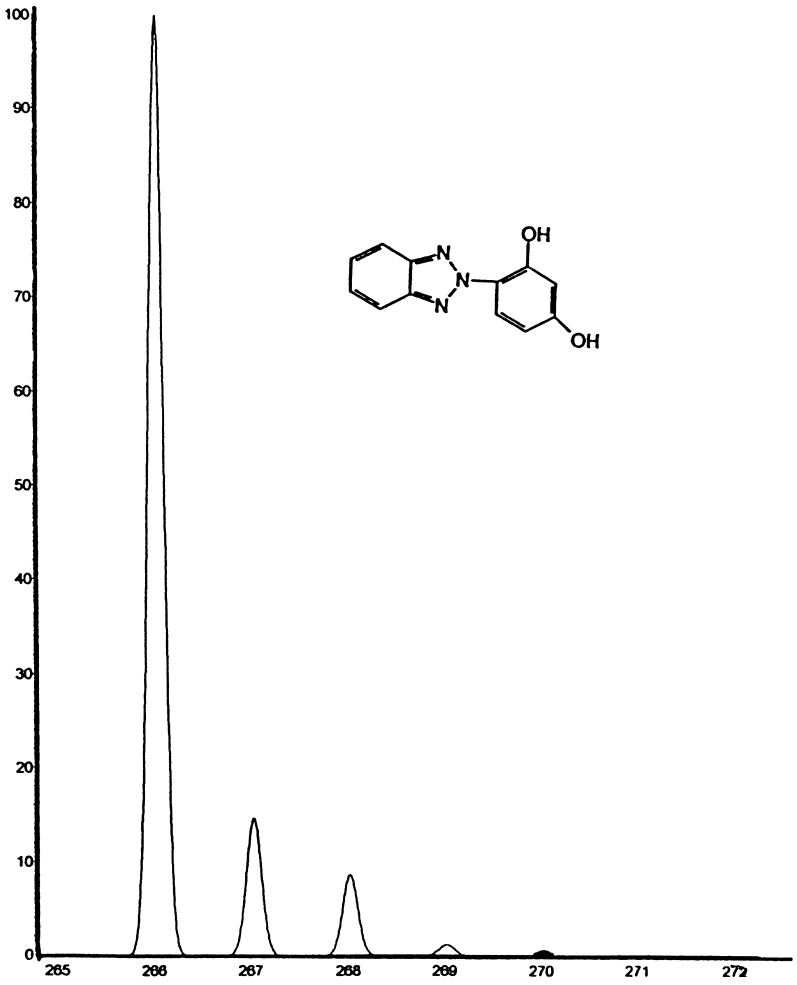


Figure 2.

2(2,4-Diydroxyphenyl)2H-benzotriazole: 266.32

m/z	266.03	267.04	268.03	269.03	270.04
(a)	100	14.18	8.63	1.12	0.10

2(2-Hydroxy-4-[3-methacryloxy-2-hydroxypropoxy]phenyl)2H-benzotriazole: 408 48

m/z	408.10	409.10	410.10	411.10	412.10	413.10
(a)	100	22.69	10.66	2.03	0.27	0.028

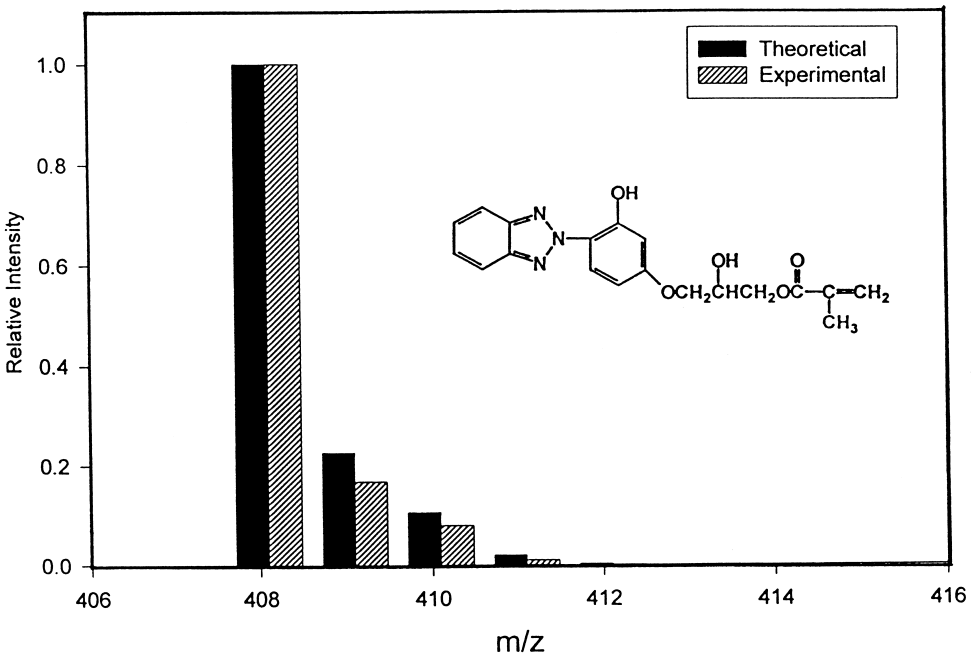


Figure 3. Isotope Distributions 2(2,-Hydroxy-4-[3-methacryloxy-2-hydroxypropoxy]phenyl)2H-Benzotriazole $[C_{19}H_{19}N_3O_5]K^+$.

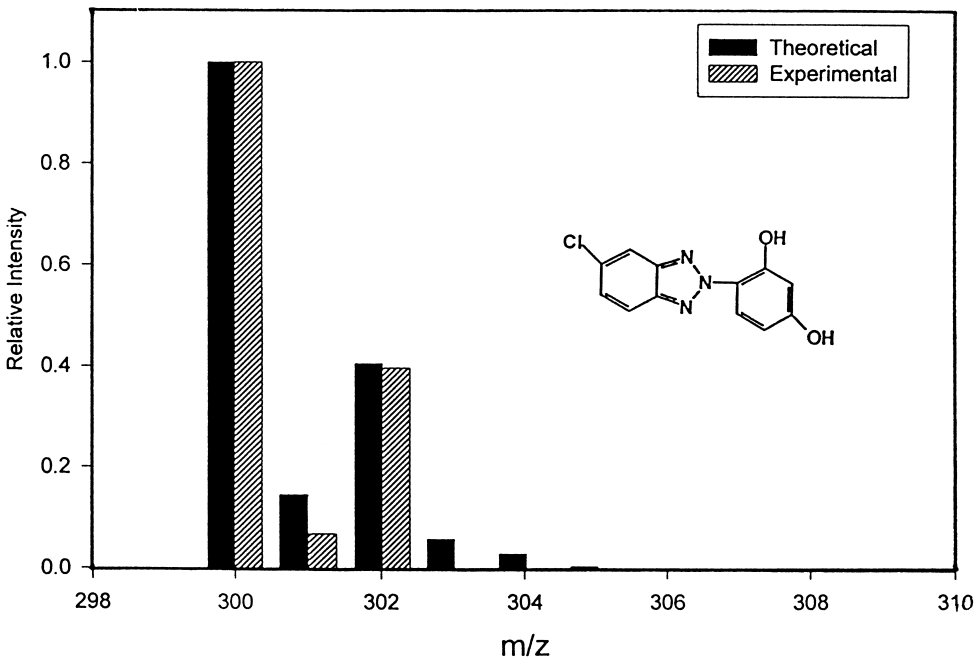


Figure 4. Isotope Distributions 2(2,4-Dihydroxyphenyl)2H-5'-chlorobenzotriazole $[C_{12}H_8N_3O_3Cl]K^+$.

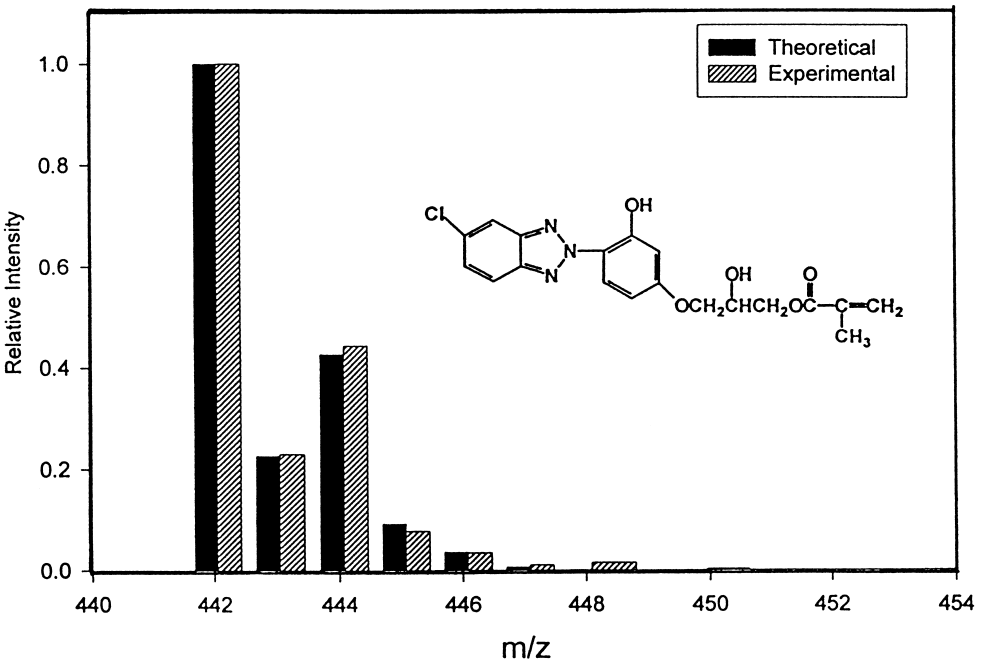


Figure 5. Isotope Distributions 2(2-Hydroxy-4-[3-methacryloxy-2-hydroxypropoxy]phenyl)2H-5'-chlorobenzotriazozle $[C_{19}H_{18}N_3O_5Cl]K^+$.

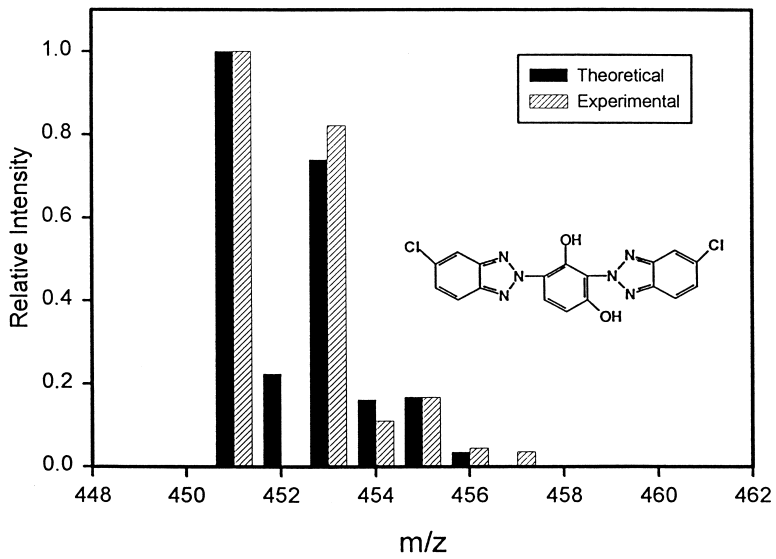


Figure 6. Isotope Distributions 2,4-Bis(4-chloro-2H-benzotriazole-2-yl) 1,3-dihydroxybenzene $[C_{18}H_{10}Cl_2N_6O_2]K^+$.

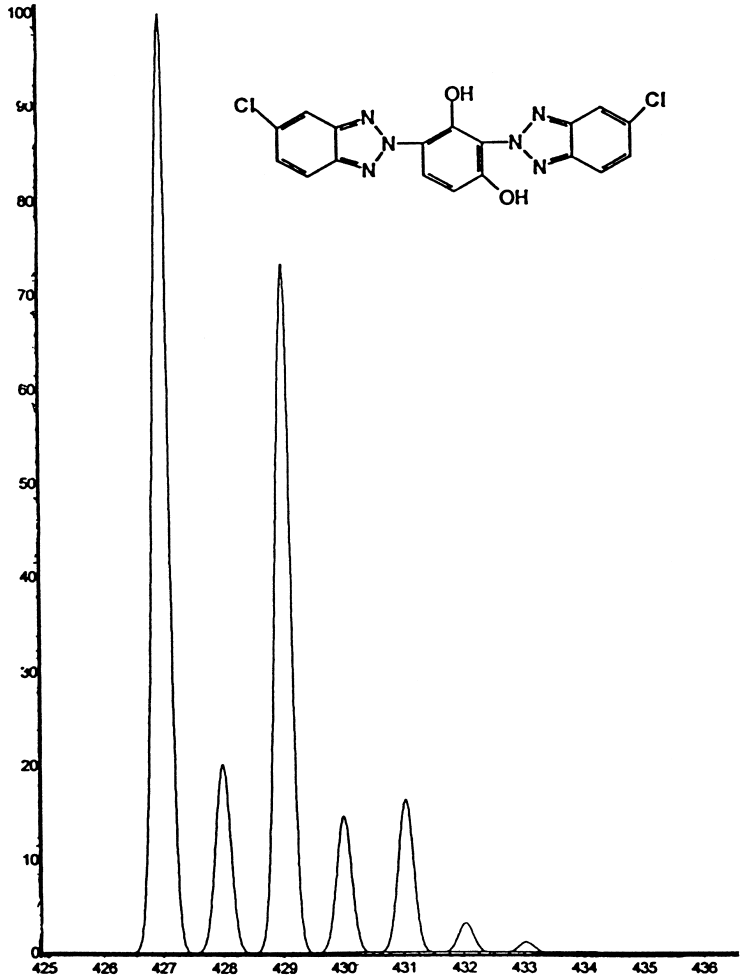


Figure 7.

2(2,4-Diydroxyphenyl)2H-5'-chlorobenzotriazole: 300.77

m/z	299.99	301.00	302.02	303.02	304.02	304.03	305.03
(a)	100	14.63	40.62	5.80	2.86	0.36	0.032

2(2-Hydroxy-4-[3-methacryloxy-2-hydroxypropoxy]phenyl)2H-5'chloro-benzotriazole: 442.93

m/z	442.06	443.06	444.08	445.08	446.09	447.09	448.09
(a)	100	22.69	42.64	9.32	3.67	0.68	0.088

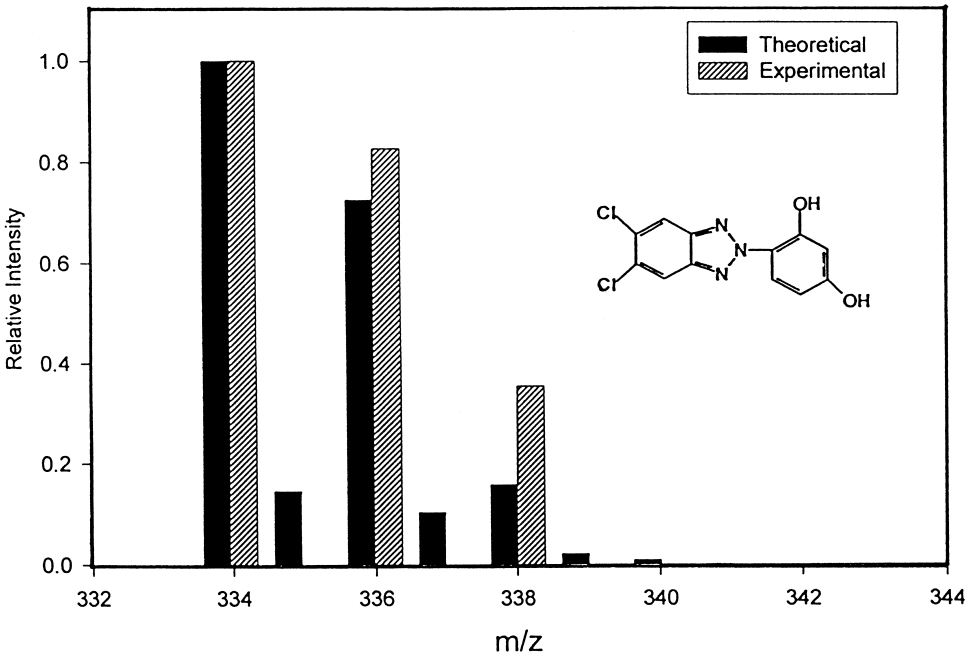


Figure 8. Isotope Distributions 2(2,4-Dihydroxyphenyl)2H-5,6"-dichlorobenzotriazozle $[C_{12}H_7N_3O_2Cl_2]K^+$.

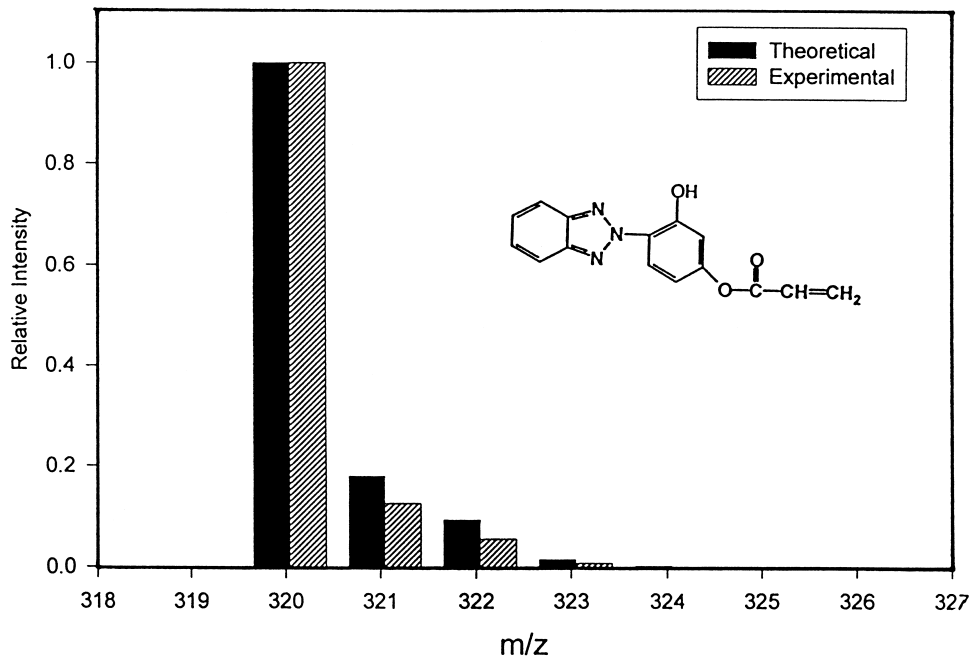


Figure 9. Isotope Distributions 2(2-Hydroxy-4-acryloxyphenyl)2H-Benzotriazole $[C_{15}H_{11}N_3O_3]K^+$.

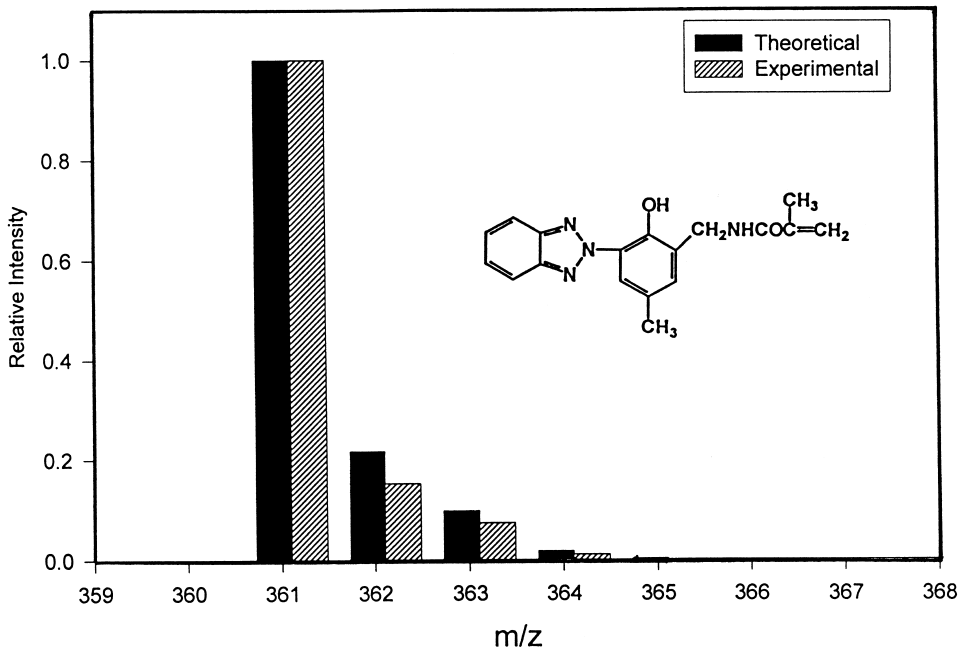


Figure 10. Isotope Distributions 2(2-Hydroxy-3-methacrylamidomethyl-5-methylphenyl)-2H-benzotriazole $[C_{18}H_{18}N_4O_2]K^+$.

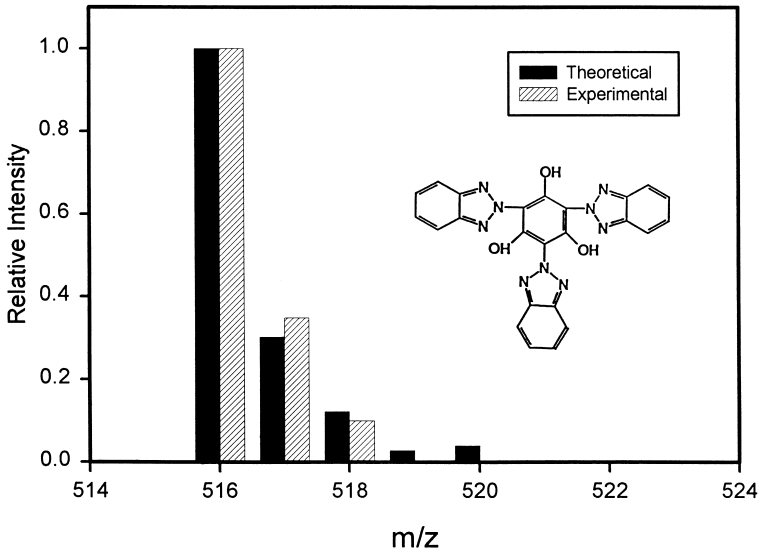


Figure 11. Isotope Distributions 2,4,6-[Tri(2H-benzotiazole-2-yl)]1,3,5-trihydroxybenzene $[C_{24}H_{15}N_9O_3]K^+$.

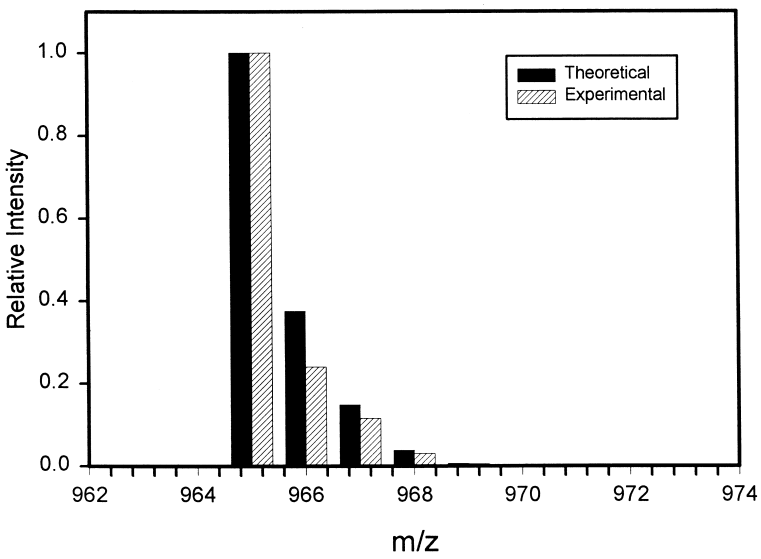


Figure 12. Isotope Distributions 2-Perfluorodecylethyl-3'(52H-benzotriazole-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl]propionate $[C_{32}H_{23}F_{21}N_4O_4]K^+$.

2(2,4-Dihydroxyphenyl)2H-1,3-bis(5'-chloro-benzotriazole): 452.34

m/z	450.99	451.99	453.01	454.02	455.04	456.04	457.05	458.05	459.05
(a)	100	22.44	73.96	16.20	16.83	3.50	1.16	0.20	0.02

2(2,4-Dihydroxyphenyl)2H-5'6"-dichlorobenzotriazole: 335.23

m/z	333.96	334.96	335.98	336.99	338.00	339.01	340.01	341.02
(a)	100	14.92	72.58	10.46	15.83	2.21	0.95	0.15

2(2-Hydroxy-4-acryloxyphenyl)2H-benzotriazole: 320.37

m/z	320.04	321.0	322.04	323.05	324.05
(a)	100	18.05	9.35	1.49	0.16

2(2-Hydroxy-3-methacrylamidomethyl-5-methylphenyl)2H-benzotriazole: 361.46

m/z	361.1	362.11	363.11	364.11	365.11
(a)	100	21.80	9.87	1.80	0.20

2(2,4,6-Trihydroxyphenyl)2H-1,3,5-tribenzotriazole: 516.54

m/z	516.09	517.10	518.10	519.10	520.10	521.10	522.10
(a)	100	30.29	2.20	2.77	0.39	0.04	0.0001

2(2-Hydroxy (3',3',4',4',5',5',6',6',7',7',8',8',9',9',10',10',11',11', 12',12',13', 13',13',-dodecyl fluoro-undodecyl) 3'carboxypropyl-phenyl)2H-benzotriazole: 965.66

m/z	965.10	966.11	967.11	968.11	969.11	970.11	971.11
(a)	100	37.58	14.75	3.77	0.68	0.08	0.007

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