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Note

Gas–liquid chromatographic analyses

XXXIII*. Retention increments for *o*-chloro and *o*-methoxy substitution in isomeric chloroanisoles

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The retention indices of several groups of chlorinated aromatics on both non-polar and polar capillary columns have been reported, the retention index increments for each position of chlorine substitution and the effect of operating temperature on the values being discussed[1]. Recently, the retention enhancements of hydroxy, methoxy and acetoxy groups introduced into various non-chlorinated and chlorinated positions of isomeric chlorobenzenes have been investigated, the effects of the substituents on both non-polar and polar capillary columns being examined[1].

This paper extends the earlier studies with chlorinated anisoles[2] and veratroles[3] (1,2-dimethoxybenzenes) by showing the retention enhancements that occurred on non-polar (SE-30) and polar (OV-351) capillary columns due to an additional chlorine atom and methoxy group introduced into the *o*-position of isomeric chloroanisoles. The effects of both substituents are compared and discussed, together with the incremental effect of an additional chlorine atom in isomeric veratroles.

EXPERIMENTAL

Materials

Anisole was a commercial product (Fluka, Buchs, Switzerland); chloroanisoles were prepared from the commercial chlorophenols (Fluka) and veratrole and chloroveratroles from the commercial catechol (Fluka) and synthetic chlorocatechols[4,5] by using the general methylation procedure with dimethyl sulphate[6].

Methods

Gas chromatographic (GC) analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the operating conditions described earlier[2,3]. The colums used were a vitreous-silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused-silica

* For Part XXXII, see ref. 1.

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OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The data presented were recorded isothermally at 160°C.

The retention indices of the components were calculated as described previously[2,3].

RESULTS AND DISCUSSION

The retention increments of an additional chlorine atom introduced into the *ortho*-positions of isomeric chloroanisoles, obtained on both columns, are presented in Table I and Fig. 1.

The increments for the *o*-chloro isomers on SE-30 are in the range 148–224 retention index units (i.u.) and on OV-351 181–349 i.u., the differences between the columns varying from 33 to 125 i.u. On both stationary phases the greatest retention

TABLE I

INCREMENTAL EFFECTS DUE TO AN ADDITIONAL CHLORINE ATOM INTRODUCED INTO THE *o*-POSITIONS OF ISOMERIC CHLOROANISOLES, OBTAINED ON NON-POLAR AND POLAR CAPILLARY COLUMNS AT 160°C

Anisole isomer substituted*		*Anisole isomer* formed*		*ΔI***		$\Delta I_{OV\text{-}351}/\Delta I_{SE\text{-}30}$	$\Delta I_{OV\text{-}351} - \Delta I_{SE\text{-}30}$
				Non-polar (SE-30) column	*Polar (OV-351) column*		
Anisole		2-	(*o*-)	219	317	1.45	98
2-	(*o*-)	2,6-	(*o*,*o*'-)	99	42	0.42	−57
3-	(*m*-)	2,3-	(*o*,*m*'-)	224	349	1.56	125
3-	(*m*-)	2,5-	(*o*,*m*-)	179	264	1.47	85
4-	(*p*-)	2,4-	(*o*,*p*-)	178	249	1.40	71
2,3-	(*o*,*m*-)	2,3,6-	(*o*,*o*',*m*-)	62	−34	−0.55	−96
3,4-	(*m*,*p*-)	2,3,4-	(*o*,*m*,*p*-)	203	305	1.50	102
2,4-	(*o*,*p*-)	2,4,6-	(*o*,*o*',*p*-)	61	−68	−1.11	−137
3,5-	(*m*,*m*'-)	2,3,5-	(*o*,*m*,*m*'-)	194	285	1.47	91
2,5-	(*o*,*m*'-)	2,3,6-	(*o*,*o*',*m*-)	107	51	0.48	−56
3,4-	(*m*,*p*-)	2,4,5-	(*o*,*m*',*p*-)	148	181	1.22	33
2,3,4-	(*o*,*m*,*p*-)	2,3,4,6-	(*o*,*o*',*m*,*p*-)	32	−133	−4.16	−165
3,4,5-	(*m*,*m*',*p*-)	2,3,4,5-	(*o*,*m*,*m*',*p*-)	179	260	1.45	81
2,3,5-	(*o*,*m*,*m*'-)	2,3,5,6-	(*o*,*o*',*m*,*m*'-)	81	−14	−0.17	−95
2,4,5-	(*o*,*m*',*p*-)	2,3,4,6-	(*o*,*o*',*m*,*p*-)	87	−9	−0.10	−96
2,3,4,5-	(*o*,*m*,*m*',*p*-)	2,3,4,5,6-	(*o*,*o*',*m*,*m*',*p*-)	66	−61	−0.92	−127
Summary of values:							
			(*o*-)	148–224	181–349	1.22–1.56	33–125
			(*o*,*o*'-)	32–107	−133 to 51	−4.16 to 0.48	−165 to −56

* For the retention indices of anisoles, see ref. 2.

** ΔI (i.u.) = $I_{(n+1)\text{Cl anisole}} - I_{n\text{Cl anisole}}$.

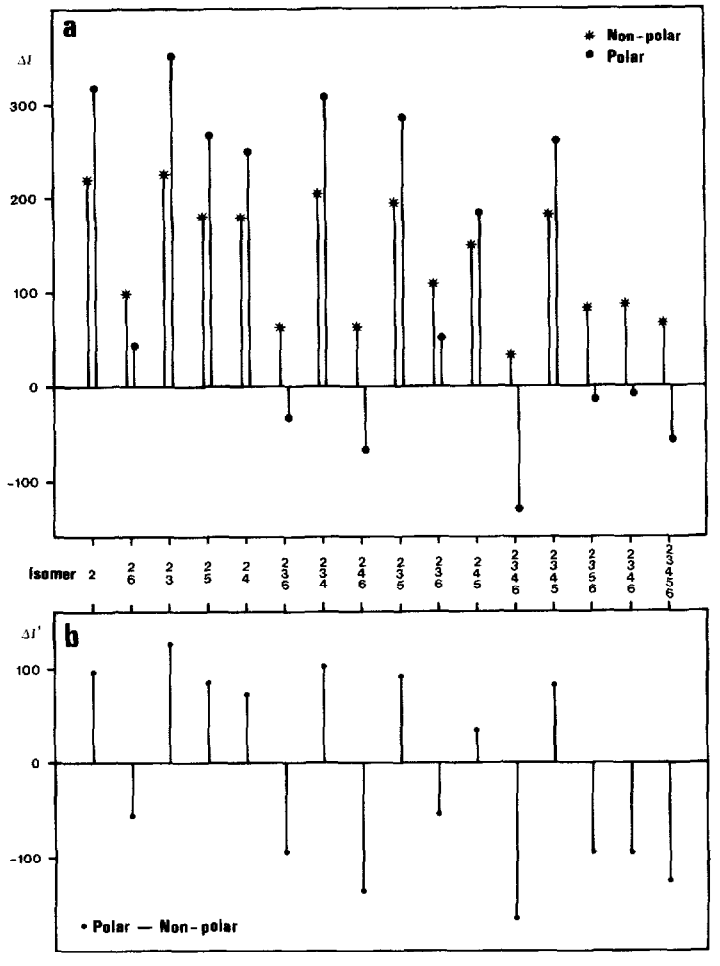

Fig. 1. (a) Incremental effects due to an additional chlorine atom introduced into the *o*-positions of isomeric chloroanisoles, obtained on non-polar (SE-30) and polar (OV-351) capillary columns at 160°C (Table I). ΔI (i.u.) = $I_{(n+1)\text{Cl anisole}} - I_{n\text{Cl anisole}}$. The numbers of the isomers indicate the positions of chlorination. (b) Differences between the retention increments on polar and non-polar columns, *i.e.*, $\Delta I'$ (i.u.) = $\Delta I_{\text{OV-351}} - \Delta I_{\text{SE-30}}$ (Table I).

enhancements occurred with chlorine substitution in the *m*- and *p*-isomers, the increment for the 2,3-(*o,m*-)isomer being even higher than that for the 2-(*o*-) isomer. The lowest enhancements were shown by the *o,o'*-isomers, *i.e.*, 32–107 i.u. on SE-30 and from −133 to 51 i.u. on OV-351, with differences from −165 to −56 i.u. between the columns. Unlike the non-polar column, some reduced retentions occurred on polar OV-351, the reduction of the 2,3,4,6-(*o,o',m,p*-) isomer being highest (−133 i.u.) (Fig. 1a). These reductions are due to the relatively higher retention times of the vicinally substituted chloroanisoles, giving with further chloro substitution the *o,o'*-isomers, where the steric effect occurring with the *o*-isomers is prevented owing to the two competing chlorine atoms adjacent to the methoxy group[1,2].

Table II and Fig. 2 show the incremental effects of an additional methoxy group, introduced into the non-chlorinated *ortho*-positions of isomeric chloroanisoles; the differences between the *o*-chloro and *o*-methoxy substitutions in chloroanisoles, *i.e.*, the incremental effects due to the replacement of an *o*-chlorine atom in chloroanisoles with a methoxy group, are shown in Table III and Fig. 3.

TABLE II

INCREMENTAL EFFECTS DUE TO AN ADDITIONAL METHOXY GROUP INTRODUCED INTO THE NON-CHLORINATED *o*-POSITIONS OF ISOMERIC CHLOROANISOLES, OBTAINED ON NON-POLAR AND POLAR CAPILLARY COLUMNS AT 160°C

Anisole isomer substituted*		*Veratrole isomer** formed*		ΔI***		$\frac{\Delta I^{OV\text{-}351}}{\Delta I_{SE\text{-}30}}$	$\Delta I_{OV\text{-}351} - \Delta I_{SE\text{-}30}$
				Non-polar (SE-30) column	*Polar (OV-351) column*		
Anisole		Veratrole		234	330	1.41	96
2-	(*o*-)	3-	(*o*-)	163	173	1.06	10
3-	(*m*-)	3-	(*o*-)	177	235	1.33	58
3-	(*m*-)	4-	(*m*-)	216	331	1.53	115
4-	(*p*-)	4-	(*m*-)	207	303	1.46	96
2,3-	(*o*,*m*-)	3,4-	(*o*,*m*-)	142	150	1.06	8
3,4-	(*m*,*p*-)	3,4-	(*o*,*m*-	166	228	1.37	62
2,4-	(*o*,*p*-)	3,5-	(*o*,*m*'-)	140	120	0.86	−20
3,5-	(*m*,*m*'-)	3,5-	(*o*,*m*'-)	169	225	1.33	56
2,5-	(*o*,*m*'-)	3,6-	(*o*,*o*'-)	79	−6	−0.08	−85
3,4-	(*m*,*p*-)	4,5-	(*m*,*m*'-)	198	304	1.54	106
2,3,4-	(*o*,*m*,*p*-)	3,4,5-	(*o*,*m*,*m*'-)	125	108	0.86	−17
3,4,5-	(*m*,*m*',*p*-)	3,4,5-	(*o*,*m*,*m*'-)	159	232	1.46	73
2,3,5-	(*o*,*m*,*m*'-)	3,4,6-	(*o*,*o*',*m*-)	66	−25	−0.38	−91
2,4,5-	(*o*,*m*',*p*-)	3,4,6-	(*o*,*o*',*m*-)	70	−20	−0.29	−90
2,3,4,5-	(*o*,*m*,*m*',*p*-)	3,4,5,6-	(*o*,*o*',*m*,*m*'-)	57	−39	−0.68	−96
Summary of values:							
			(*o*-)	125–177	108–235	0.86–1.46	−20 to 73
			(*o*,*o*'-)	57–79	−39 to −6	−0.68 to −0.08	−96 to −85
			(*m*-)	198–216	303–331	1.46–1.54	96–115

* For the retention indices of anisoles, see ref. 2.
** For the retention indices of veratroles, see ref. 3.
*** ΔI (i.u.) = $I_{nCl\ veratrole} - I_{nCl\ anisole}$.

The increments fall into three groups, *viz.*, 125–177 and 108–235 i.u. (from −20 to 73 i.u.) for the *o*-isomers, 57–79 and from −39 to −6 i.u. (from −96 to −85 i.u.) for the *o*,*o*'-isomers and 198–216 and 303–331 i.u. (96–115 i.u.) for the *m*-isomers on SE-30 and OV-351, respectively, the differences between the columns, *i.e.*, $\Delta I_{OV\text{-}351} - \Delta I_{SE\text{-}30}$ given in parentheses (Table II and Fig. 2).

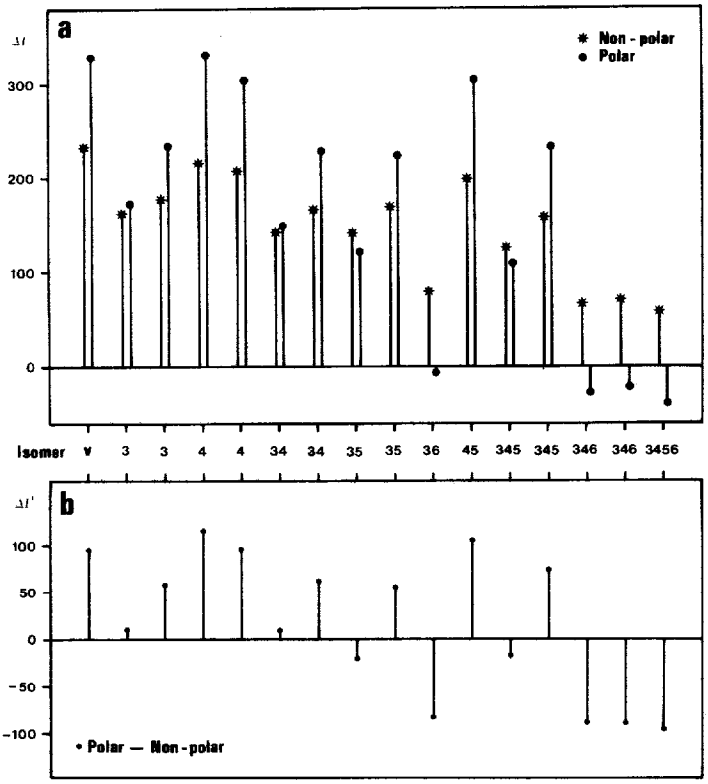

Fig. 2. (a) Incremental effects due to an additional methoxy group introduced into the non-chlorinated *o*-positions of isomeric chloroanisoles, obtained on non-polar (SE-30) and polar (OV-351) capillary columns at 160°C (Table II). ΔI (i.u.) = $I_{nCl\ veratrole} - I_{nCl\ anisole}$. The numbers of the isomers indicate the positions of chlorination; v = veratrole. (b) Differences between the retention increments on polar and non-polar columns, *i.e.*, $\Delta I'$ (i.u.) = $\Delta I_{OV\text{-}351} - \Delta I_{SE\text{-}30}$ (Table II).

Generally, the greatest enhancement on both columns is shown by the parent component, veratrole, the increments 234 (SE-30) and 330 i.u. (OV-351) being 15 and 13 i.u. higher, respectively, than those of 2-(*o*-) chloroanisole (Table III and Fig. 3). The higher increments of the *m*-isomers are from the parent component, the adjacent chlorine atom in the *o*-isomers and particularly the two adjacent chlorine atoms in the *o,o'*-isomers decreasing the interaction between the methoxy groups and the stationary phase, shown from the lower retention enhancements or reductions of the *o*- and *o,o'*-isomers.

The effects mentioned above are shown in Table III, Fig. 3 and Table IV. It is apparent that the methoxy group has a greater effect than the chlorine atom substituted in the *o*-position without an adjacent chlorine atom, *i.e.*, with geminal chloro substitution as presented in Table III, the $\Delta I_{OCH_3} - \Delta I_{Cl}$ differences on SE-30 and OV-351 varying in the ranges 29–93 and 54–241 i.u., respectively. On the other hand, lower retention enhancements are observed with the methoxy substitution adjacent to the chlorine atom than with the corresponding chlorine substitution, *i.e.*, with vicinal chloro substitution as presented in Table III, the $\Delta I_{OCH_3} - \Delta I_{Cl}$ differences

TABLE III

INCREMENTAL EFFECTS DUE TO THE REPLACEMENT OF AN *o*-CHLORINE ATOM IN CHLOROANISOLES WITH A METHOXY GROUP, OBTAINED ON NON-POLAR AND POLAR CAPILLARY COLUMNS AT 160°C

Anisole isomer substituted*		*Veratrole isomer** formed*		ΔI***		$\frac{\Delta I^{OV\text{-}351}}{\Delta I_{SE\text{-}30}}$	$\Delta I_{OV\text{-}351} - \Delta I_{SE\text{-}30}$
				Non-polar (SE-30) column	*Polar (OV-351) column*		
2-	(*o*-)	Veratrole		15	13	0.87	− 2
2,3-	(*o,m*-)	3-	(*o*-)	−47	−114	2.43	−67
2,6-	(*o,o'*-)	3-	(*o*-)	64	131	2.05	67
2,4-	(*o,p*-)	4-	(*m*-)	29	54	1.86	25
2,5-	(*o,m'*-)	4-	(*m*-)	37	67	1.81	30
2,3,4-	(*o,m,p*-)	3,4-	(*o,m*-)	−37	−77	2.08	40
2,3,6-	(*o,o',m*-)	3,4-	(*o,m*-)	80	184	2.30	154
2,3,5-	(*o,m,m'*-)	3,5-	(*o,m'*-)	−25	−60	2.40	35
2,4,6-	(*o,o',p*-)	3,5-	(*o,m'*-)	79	188	2.38	109
2,3,6-	(*o,o',m*-)	3,6-	(*o,o'*-)	−28	−57	2.04	29
2,4,5-	(*o,m',p*-)	4,5-	(*m,m'*-)	50	123	2.46	73
2,3,4,5-	(*o,m,m',p*-)	3,4,5-	(*o,m,m'*-)	−20	−28	1.40	8
2,3,4,6-	(*o,o',m,p*-)	3,4,5-	(*o,m,m'*-)	93	241	2.59	148
2,3,4,6-	(*o,o',m,p*-)	3,4,6-	(*o,o',m*-)	−17	−11	0.65	−6
2,3,5,6-	(*o,o',m,m'*-)	3,4,6-	(*o,o',m*-)	−15	−11	0.73	−4
2,3,4,5,6-	(*o,o',m,m',p*-)	3,4,5,6-	(*o,o',m,m'*-)	− 9	22	−2.44	31
Summary of values:							
Substitution of a vicinal chlorine atom				−47 to −9	−114 to 22	−2.44 to 2.43	−67 to 40
Substitution of a geminal chlorine atom				29–93	54–241	1.81–2.59	25–154

* For the retention indices of anisoles, see ref. 2.
** For the retention indices of veratroles, see ref. 3.
*** ΔI (i.u.) = $I_{(n-1)Cl\ veratrole} - I_{nCl\ anisole}$.

on SE-30 and OV-351 being in the ranges from −47 to −9 and from −114 to 22 i.u., respectively. Pentachloroanisole and tetrachloroveratrole are the diverging components in this respect, the latter having a 22 i.u. higher retention time on OV-351.

The incremental effects of an additional chlorine atom in isomeric veratroles (Table IV) are generally lower than those with anisoles as presented in Table I and ref. 2, *i.e.*, 52–150 i.u. on Se-30 and from −67 to 168 i.u. on OV-351 for *o*-substitution and 150–201 i.u. on SE-30 and 162–287 i.u. on OV-351 for *m*-substitution. The limiting values are shown by the 3,4-(*o,m*-) → 3,4,6-(*o,o',m*-) isomers and 3,5-(*o,m'*-) → 3,4,5-(*o,m,m'*-) isomers.

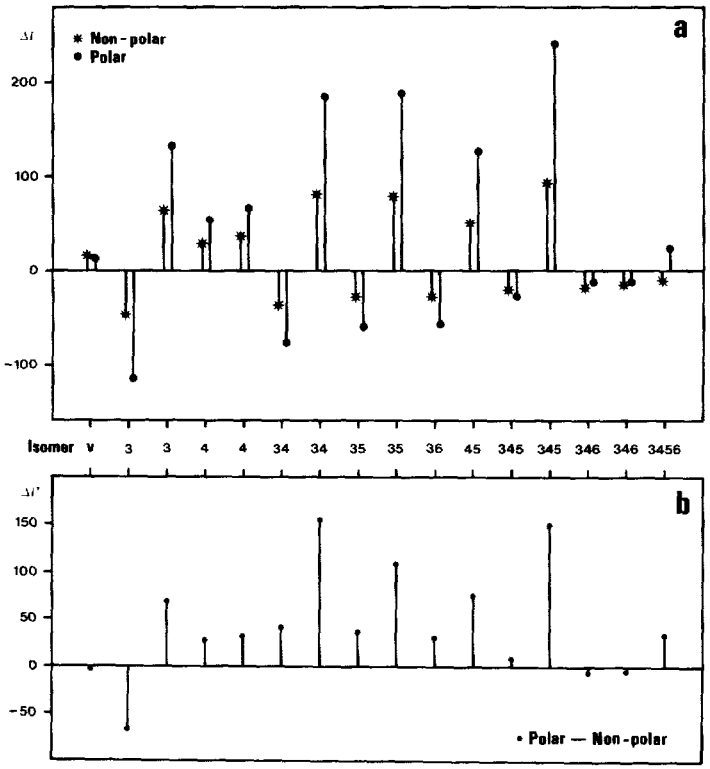

Fig. 3. (a) Incremental effects due to the replacement of an *o*-chlorine atom in chloroanisoles with a methoxy group, obtained on non-polar (SE-30) and polar (OV-351) capillary columns at 160°C (Table III). ΔI (i.u.) = $I_{(n-1)\text{Cl veratrole}} - I_{n\text{Cl anisole}}$. The numbers of the isomers indicate the positions of chlorination; v = veratrole. (b) Differences between the retention increments on polar and non-polar columns, *i.e.*, $\Delta I'$ (i.u.) = $\Delta I_{\text{OV-351}} - \Delta I_{\text{SE-30}}$ (Table III).

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TABLE IV

INCREMENTAL EFFECTS DUE TO AN ADDITIONAL CHLORINE ATOM INTRODUCED INTO ISOMERIC VERATROLES, OBTAINED ON NON-POLAR AND POLAR CAPILLARY COLUMNS AT 160°C

Veratrole isomer substituted*		*Veratrole isomer* formed*		*ΔI***		$\frac{\Delta I^{OV\text{-}351}}{\Delta I_{SE\text{-}30}}$	$\Delta I_{OV\text{-}351} - \Delta I_{SE\text{-}30}$
				Non-polar (SE-30) column	*Polar (OV-351) column*		
Veratrole		3-	(*o*-)	148	160	1.08	12
Veratrole		4-	(*m*-)	187	256	1.37	19
3-	(*o*-)	3,4-	(*o,m*-)	189	264	1.40	75
4-	(*m*-)	3,4-	(*o,m*-)	150	168	1.12	18
3-	(*o*-)	3,5-	(*o,m'*-)	150	162	1.08	12
4-	(*m*-)	3,5-	(*o,m'*-)	111	66	0.59	−45
3-	(*o*-)	3,6-	(*o,o'*-)	81	23	0.28	−58
4-	(*m*-)	4,5-	(*m,m'*-)	182	244	1.34	62
3,4-	(*o,m*-)	3,4,5-	(*o,m,m'*-)	162	185	1.14	23
3,5-	(*o,m'*-)	3,4,5-	(*o,m,m'*-)	201	287	1.43	86
4,5-	(*m,m'*-)	3,4,5-	(*o,m,m'*-)	130	109	0.84	−21
3,4-	(*o,m*-)	3,4,6-	(*o,o',m*-)	52	−67	−1.29	−119
3,5-	(*o,m'*-)	3,4,6-	(*o,o',m*-)	91	35	0.38	−56
3,6-	(*o,o'*-)	3,4,6-	(*o,o',m*-)	160	174	1.09	14
3,4,5-	(*o,m,m'*-)	3,4,5,6-	(*o,o',m,m'*-)	77	−11	−0.14	−88
3,4,6-	(*o,o',m*-)	3,4,5,6-	(*o,o',m,m'*-)	187	241	1.29	54
Summary of values:							
o-Substitution				52–150	−67 to 168	−1.29 to 1.12	−119 to 18
m-Substitution				15–201	162–287	1.08–1.43	12–86

* For the retention indices of veratroles, see ref. 3.

** ΔI (i.u.) = $I_{(n+1)\text{Cl veratrole}} - I_{n\text{Cl veratrole}}$.

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