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Note

Calculation of retention indices of pyrazines on the basis of molecular structure

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Pyrazines have been characterized as the chemicals that contribute to roasted or toasted flavours and a number of pyrazines have been found in various foods[1]. Almost all known volatile food constituents could be analysed by using gas chromatographic (GC) retention indices and GC–mass spectrometric techniques[2]. The retention indices predicted from the structure and/or topology of the solute molecules are often in good agreement with experimental values (*e.g.*, for benzene and its derivatives[3], isoalkanes[4] and polychlorinated biphenyls[5]). The aim of this work was to derive the relationships between the molecular structures of pyrazines and their retention indices.

EXPERIMENTAL

Pyrazines were commercially available (Ogawa, Tokyo, Japan, Pyrazine Specialties).

GC analyses were carried out on a Hewlett-Packard Model 5710A gas chromatograph equipped with a flame ionization detector and a fused-silica capillary column. Two types of wall-coated open tubular fused-silica capillary column were used: 50 m × 0.22 mm I.D. coated with Carbowax 20M (CW-20M) and 50 m × 0.22 mm I.D. coated with OV-101. The columns were prepared in our laboratory[6]. The carrier gas (nitrogen) flow-rate was 0.67 ml/min. The column temperature was programmed from 80 to 200°C at 2°C/min. The splitting ratio was 1:100 and the temperatures of the injector and detector were 250°C.

RESULTS AND DISCUSSION

Table I shows the retention indices (I) of 27 pyrazines on CW-20M and OV-101 columns. $I_{obsd.}^{CW\text{-}20M}$ and $I_{obsd.}^{OV\text{-}101}$ indicate the retention indices on CW-20M and OV-101, respectively. The retention index of a pyrazine derivative can be represented as the sum of the increment for the substituent groups and the retention index of pyrazine:

$$I^{st.ph.} = I_{p}^{st.ph.} + \Sigma\delta I_{m(i)}^{st.ph.} + \Sigma\delta I_{d(i)}^{st.ph.} \quad (1)$$

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TABLE I

RETENTION INDICES OF PYRAZINES ON CW-20M AND OV-101

$D = I^{st.ph.}_{obsd.} - I^{st.ph.}_{calcd.}$

Compound	$I^{CW\text{-}20M}_{obsd.}$	$I^{CW\text{-}20M}_{calcd.}$	D	$I^{OV\text{-}101}_{obsd.}$	$I^{OV\text{-}101}_{calcd.}$	D
Pyrazine	1179			710		
2-Methylpyrazine	1235	1235	0	801	800	+1
2,3-Dimethylpyrazine	1309	1309	0	897	890	+7
2,5-Dimethylpyrazine	1290	1291	− 1	889	890	−1
2,6-Dimethylpyrazine	1300	1291	+ 9	889	890	−1
2,3,5-Trimethylpyrazine	1366	1365	+ 1	981	980	+1
Tetramethylpyrazine	1439	1439	0	1067	1070	−3
2-Methoxy-3-methylpyrazine	1339	1346	− 7	954	956	−2
2-Ethoxy-3-methylpyrazine	1385	1388	− 3	1029	1025	+4
2-Acetylpyrazine	1571	1567	+ 4	993	998	−5
2-Acetyl-5-methylpyrazine	1625	1623	+ 2	1093	1088	+5
2-Acetyl-6-methylpyrazine	1618	1623	− 5	1089	1088	+1
2-Acetyl-3-methylpyrazine	1567	1563	+ 4	1061	1059	+2
2-Acetyl-3,5-dimethylpyrazine	1629	1619	+10	1153	1149	+4
2-Acetyl-3,6-dimethylpyrazine	1615	1619	− 4	1144	1149	−5
2-Acetyl-3-ethylpyrazine	1617	1612	+ 5	1138	1138	0
2-Ethylpyrazine	1300	1300	0	894	891	+3
2-Ethyl-5-methylpyrazine	1357	1356	+ 1	980	981	−1
2-Ethyl-6-methylpyrazine	1353	1356	− 3	977	981	−4
2-Ethoxy-3-ethylpyrazine	1439	1437	+ 2	1101	1104	−3
2-Ethyl-3-methylthiopyrazine	1695	1693	+ 2	1237	1237	0
2-Ethyl-3-methoxypyrazine	1400	1395	+ 5	1037	1035	+2
2,3-Diethyl-5-methylpyrazine	1459	1463	− 4	1137	1138	−1
2-Vinylpyrazine	1392	1392	0	907	907	0
2-Methoxypyrazine	1306	1306	0	877	877	0
2-Isopropyl-3-methoxypyrazine	1400	1396	+ 4	1078	1074	+4
2-Isopropyl-3-methylthiopyrazine	1692	1694	− 2	1273	1276	−3

where $I^{st.ph.}$ = retention index of the pyrazine derivative on a stationary phase (st.ph.), $I^{st.ph.}_{p}$ = retention index of pyrazine, $\delta I^{st.ph.}_{m(x)}$ = increment of $I^{st.ph.}$ for a substituent group that does not have a neighbouring (2,3- or 5,6-position) group and $\delta I^{st.ph.}_{d(x)}$ is the increment of $I^{st.ph.}$ for a substituent group that has a neighbouring group.

TABLE II

INCREMENTS OF $I^{st.ph.}$ FOR SUBSTITUENT GROUPS OF PYRAZINES

Substituent group (X)	$\delta I^{CW\text{-}20M}_{m(X)}$	$\delta I^{CW\text{-}20M}_{d(X)}$	$\delta I^{OV\text{-}101}_{m(X)}$	$\delta I^{OV\text{-}101}_{d(X)}$
CH_3	56	65	90	90
C_2H_5	121	114	181	169
$COCH_3$	388	319	288	259
OCH_3	127	102	167	156
OC_2H_5	–	144	–	225
$CH=CH_2$	213	–	197	–
$CH(CH_3)_2$	–	115	–	208
SCH_3	–	400	–	358

The increments were determined from the observed $I^{st.ph.}$ values and the above relationships. The values assigned are shown in Table II. For example, the $I^{CW\text{-}20M}$ value of 2,3,5-trimethylpyrazine is predicted as follows.

From Tables I and II:

$\delta I^{CW\text{-}20M}_{m(methyl)}$ = 56 i.u. (the increment for a 5-methyl group)

$2\delta I^{CW\text{-}20M}_{d(methyl)}$ = 130 i.u. (the sum of the increments for 2- and 3-methyl groups: 2 × 65 i.u.)

$I^{CW\text{-}20M}_{p}$ = 1179 i.u.

Total = 1365 i.u.

The observed $I^{CW\text{-}20M}$ value was 1366 i.u. The calculated $I^{st.ph.}$ values are compared with the observed values in Table I. The difference between the observed and the calculated values seems to correspond to the increment based on the positional relationship.

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