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Sweetness-Vibrational Spectra Relationship in Aldopyranoses and Sucrose/Galactosucrose System

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Correlation of the *RS* relative sweetnesses of 6 aldopyranoses, maltose and lactose on the structures of their PM3 vibrational spectra are analysed. The QSAR correlations of *log*(*RS*) *versus* squares of ν(OH) stretching, δ(COH) bending and T(OC) torsion calculated frequencies are examined. High correlations are found for ν^2(4-OH), δ^2(4-COH) and T^2(4-OC) parameters, so the corresponding vibrations are called "*sweet vibrations*". Computational QSAR procedure with two ν^2(O–H) vibrational parameters is applied to localize AH,B Shallenberger glycophore. The high correlation reached by author for ν(4-OH) and ν(3-OH) frequencies makes agree 4-OH, O-3 structure with AH,B glycophore. It allows to recover B = O-3 subsite, which is inactive in aldopyranoses due to *electrostatic model.* Analysis of the PM3 vibrational spectra of sucrose, galactosucrose and their chlorodeoxy derivatives is carried out. Based on QSAR procedure with four ν^2(O–H) vibrational parameters one can define Nofre-Tinti four-subsite sweetener in sucrose and galactosucrose molecules. Computations indicate for contribution of 4-OH, 3-OH pyranose groups and 1'-OH, 6'-OH fructofuranose groups. It speaks well for XH1, B2, E1, E4 sweetener in the sucrose/galactosucrose structure.

Key words: QSAR on sweetness, aldopyranoses, chlorodeoxy sucrose/galactosucrose derivatives, vibrational spectroscopic parameters, ν^2(O–H) vibrational parameters

The sweetness depends on the molecular structure. The pairs of the functional groups such as hydroxyl groups, aminogroups and ether oxygen were usually present in the structure of sweet tasting compound and they were called "glycophores" [1–4]. The sweet taste-eliciting group for the sugars was a glycol, (-CHOH-CHOH-) unit. The OH groups contributing to a structural unit from the so called AH,B glycophore [1–3]. Birch and Lee have accepted [4] that AH is formed by H atom of 4-OH hydroxyl group, whereas B is O-3 atom of 3-OH group in aldopyranoses. The 4-OH$^{\delta(+)}$,O-3$^{\delta(-)}$ charged glycophore may interact with corresponding $\mathbf{XH}^{(+)}$ and $\mathbf{Y}^{(-)}$ receptor dipoles forming two hydrogen bonds:

$$\text{4-OH}^{\delta(+)},\ \text{O-3}^{\delta(-)} + \mathbf{XH}^{(+)},\mathbf{Y}^{(-)} \rightarrow \text{4-OH}^{\delta(+)}\text{—}\mathbf{Y}^{(-)},\mathbf{XH}^{(+)}\text{—O-3}^{\delta(-)} \qquad (1)$$

glycophore receptor glycophore—receptor complex

Under biochemistry progress after 1990, Nofre and Tinti [5] distinguished in aldopyranoses $\{XH_2,XH_1,B_1,B_2,AH_1,AH_2\}$ six subsite sweetener. In this notation XH_1 and B_2 Nofre-Tinti sweetener subsites corresponds to AH and B Shallenberger sweeteners, respectively. QSAR correlations of $ln(RS_j^{expl})$ against some PM3 quantum parameters in our previous paper [6], have shown that B_2 Nofre-Tinti or B Shallenberger sweetener is almost inactive in aldopyranoses. So, the reaction (1) may be shorten to the expression:

$$\text{4-OH}^{\delta(+)} + \mathbf{XH}^{(+)},\mathbf{Y}^{(-)} \rightarrow \text{4-OH}^{\delta(+)}\text{—}\mathbf{Y}^{(-)},\mathbf{XH}^{(+)} \qquad (2)$$

Due to the mentioned investigations [6], sweetness of aldopyranoses depends on Q_j(O-4) and Q_j(H-04) net charges of both the atoms of 4-OH group, but especially on Q_j(H-04) net charge. H-04 is identified as AH Shallenberger sweetener.

Höltje and Kier [7] have found that experimental $log\ RS_j^{expl}$ for a set of sweet 1-X_j-2-amino-4-nitrobenzenes with different X_j glycophores indicates a linear correlation against calculated intermolecular interaction energies, ΔE_j(Gly-Rec), in the sweet substance—receptor complexes.

$$log(RS_j^{expl}) = b_1 \Delta E_j(\text{Gly-Rec}) + b_0 \qquad (3)$$

In this paper new aspects of *Molecular Electron Structure – Sweetness Relationship* theory [6,8] are found, which were based on a simplified theory of intermolecular interaction between glycophore and the sweet taste receptor. An estimation of the interaction integrals, as common constant coefficients for all the sugar of the set, have performed from QSAR correlation of $log(RS_j^{expl})$ against PM3 quantum parameters of isolated sugar molecules. Presently, the serious part of modifications belongs to vibrational spectroscopic investigations. The intermolecular interaction effects on vibrational frequencies of the COH moiety have been observed [9].

In order to relate the sweetness with the vibrational spectrum of a molecule, a simplified consideration is carried out. Previously [6], we demonstrated a great contribution of electrostatic interactions of q_j(H-04) net charge with $q(k)$ net charges of receptor atoms to ΔE_j(H04-Rec) energy. On other hand, q_j(H-04) interacts with $q_j(i)$ net charges of the sugar atoms being in a neighbourhood, in good deal with q_j(O-4), forming the ΔE_j(H04-O4) electrostatic intramolecular energy. Both the energy terms may be described by

$$\Delta E_j(\text{H04-Rec}) = q_j(\text{H04}) \sum_{k \in Rec} \frac{q(k)}{r_{\text{H04},k}} = a_1 \cdot q_j(\text{H04}) \qquad (4)$$

$$\Delta E_j(\text{H04-O4}) = q_j(\text{H04}) \cdot \frac{q_j(\text{O4})}{r_{\text{H04,O4}}} = a_2 \cdot q_j(\text{H04}) \qquad (5)$$

where a_2 is a constant for the small changes of q_j(O4), a_1 is a constant for all the sugar in the set [6] and r are distances between corresponding atoms. Putting Gly = H-04 in eq. (3) and combining both latter equations with (3) we receive

$$log(RS_j^{expl}) = c_1 \Delta E_j(\text{H04-O4}) + c_0 \tag{6}$$

It is well shown from (6), that $log(RS_j^{expl})$ can be approximated by a linear function of H-04—O4 interaction energy. Since *j*-(4-OH) group is accepted as a single oscillator with $\bar{\nu}_j$ frequency, such energy may be represented by potential energy of ν_j(4-OH) stretching vibration, denoted by U_j. In consequence ΔE_j(H04-O4) energy takes the form:

$$\Delta E_j(\text{H04-O4}) = U_j = \frac{1}{2}\omega_j^2 \vec{Q}_j^2 = 2\pi^2 c^2 \bar{\nu}_j^2 \vec{Q}_j^2 \tag{7}$$

$\vec{Q}_j$ vector of the normal mode is normalized by $\vec{Q}_j^2 = 1$ condition in Gaussian-98 output. Putting (7) to (6) we receive QSAR correlation equation:

$$log(RS_j^{expl}) = a \cdot \bar{\nu}_j^2 + b \tag{8}$$

where *a* and *b* are common constants for a given sugar set. The latter equation is the base for a new form of sweetness theory, which may be called *Sweetness-Vibrational Spectra Relationship.*

In this paper we examine all the correlations of $log(RS_j^{expl})$ against $\bar{\nu}_j^2$ for ν(*n*-OH) stretching, δ(*n*-COH) angle bending and T(*n*-OC) torsion vibrations, with *n* = 1, 2, 3, 4, 6 position in aldopyranose ring. This analysis should answer, which frequencies are related with the sweet taste of aldopyranoses. The maximal value of R_n correlation coefficient indicates *n*-position of the one-center glycophore. On other hand, a localization and structure of multicenter glycophore requires to create a QSAR multiple correlation equation. We take under consideration only ν(*n*-OH) vibrations as the most dominating in the corresponding normal modes. Then, due to (8), QSAR multiple correlation equation for this type of vibrations is expressed by (9):

$$log(RS_j^{expl}) = a_0 + \sum_n a_n \bar{\nu}_j^2(n - \text{OH}) \qquad \text{for } n = 1, 2, 3, 4, 6 \text{ in aldopyranoses,} \tag{9}$$

The above equation is very suitable in the localization of two-center AH,B Shallenberger glycophore or XH1,B2 Nofre-Tinti sweetener. Although experimental localization is well known, the calculations due to *electrostatic model* [6] cannot localize B2 subsite.

AH,B Shallenberger and existing till now schemes are not sufficient to determination of the structure and localization of the glycophore in sucrose and galactosucrose system. Sucrose is the most important sweetener in food technology, but its sweetening mechanism requires further investigations. Krutošikowa and Uher [10] have suggested that two Kier triangle glycophores may be found in sucrose/galactosucrose structure: 2-OH—O-1'—O-4 and 2-OH—O-1'—O-6', which become especially active, since glucopyranose 4-OH, fructofuranose 1'-OH and 6'-OH are substituted by chlorine. It does not explain quntitative relations among RS_j^{expl} values of these derivatives as well as the *6-OH deoxychlorination negative effect* [8] .

In our previous paper [8] a great contribution of E1 and E4 sweetener subsites, as the strong electronodonors, has been proved. The *charge-transfer and dispersion model* presenting in the latter paper omitted two-center XH1,B2 (AH,B) glycophore, which provides about 40% of sweetness in an unsubstituted sucrose. This theory explained the *6-OH deoxychlorination negative effect* by a strong decrease of electrostatic motion of XH2 subsite during chlorination. It seems that this effect is rather deeply hidden in the electronic structure of galactosucrose and encoded in the system of eight $\nu(n\text{-OH})$ stretching vibrations for n = 6, 4, 3, 2, 1', 3', 4' and 6'. Computational QSAR multiple correlation analysis of these vibrations may decode this effect.

CALCULATIONS

1. Recalculation RS_j(mole/mole) into RS_j(%/%) relative sweetness. The RS_j is calculated for equimolar solutions (mole/mole) in QSAR correlation equations. On other hand, RS_j is measured usually for equiper cent solutions (%/%). Therefore, (9a) is necessary for a mutually recalculation of RS_j(mole/mole) into RS_j(%/%),

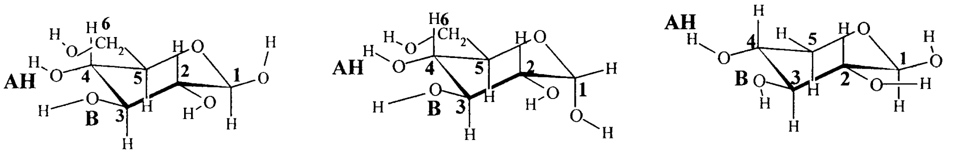
$$\frac{RS_j(\%/\%)}{RS_j(mole/mole)} = \frac{M_0}{M_j} \tag{9a}$$

where M_j is molecular weight of j-sugar and M_0 represents molecular weight of standard sugar = sucrose.

2. Initial geometry of the sugars. The 6 aldopyranoses, maltose and lactose are taken into account (Fig. 1). Maltose and lactose are treated as the compounds formed by aldopyranose units. The intial 3D geometries are found by the application of "*Add H & Model Build*" function from menu *Build* using HyperChem-5.0 program [11]. This function is very suitable as starting point to find proper OH-conformer of a given aldopyranose free molecule. Then MM+ chemical mechanics procedure of self-consistent geometry with Fletcher-Reeves convergence is accepted and PM3 semiempirical quantum procedure is applied [12] with the Polak-Ribiere convergence.

The self-consistent geometries of chlorodeoxy derivatives of sucrose and galactosucrose (Fig. 2) are calculated in the same manner.

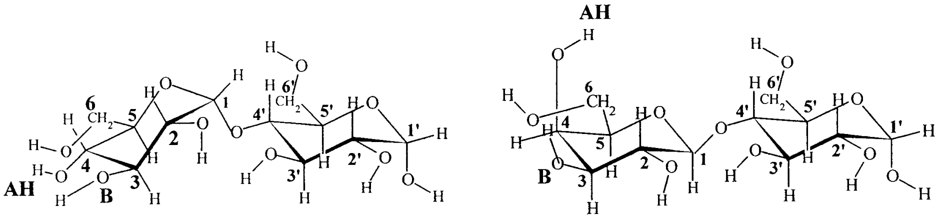
3. Vibrational spectra. The calculations of the harmonic vibrational spectra are based on *GF*-Wilson analysis. Formerly, during the time of worse computerization, the force constants (*F* –matrix) were calculated by the use of Urey-Bradley force field [9,13,14]. Presently, they are calculated as the second derivatives of U total energy of the molecule in respect to the mass-weighted Cartesian internal coordinates [15]. PM3 harmonic vibrational spectra were calculated for 6 aldopyranoses, maltose, lactose as well as sucrose, galactosucrose and their chlorodeoxy derivatives, starting from their previously fixed PM3 geometries. Vector contributions of internal vibrations to a given normal mode are shown by animate normal vibration, created by HyperChem-5.0 program. Description of a normal mode distinguishes the following internal vibrations: **(1)** ν(X–Y) stretching vibration of the X–Y bond, **(2)** δ(X–Y–Z) bending defomation of the angle, **(3)** T(O–C) torsion vibration of C–O bond as produced by out-off-plane movement of H atom from the COH plane. X, Y and Z letters denote the atoms.



1. β-Glucose
α-D-glucopyranose

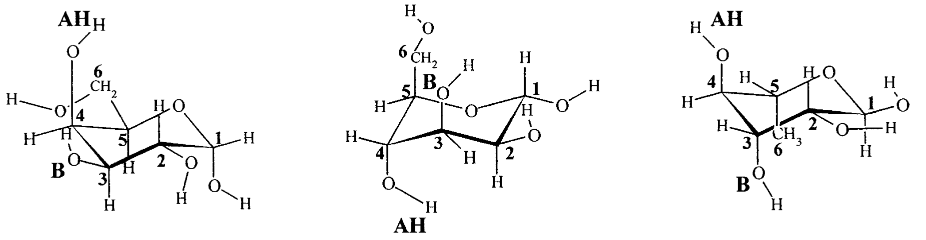
2. α-Glucose
α-D-glucopyranose

5. Xylose
β-D-Xylopyranose



3. Maltose

4. Lactose



6. Galactose
α-D-galactopyranose

7. Mannose
α-D-mannopyranose (1*C*)

8. Rhamnose
6-dezoxy-α-L-mannopyranose

Figure 1. Numeration of the carbon atoms and localization of AH,B Shallenberger glycophore in all the 6 aldopyranoses, maltose and lactose.

RESULTS AND DISCUSSION

1. QSAR on aldopyranose sweetness with vibrational parameters. Results of the PM3 vibrational analyses on 6 aldopyranoses and 2 dialdopyranoses – maltose and lactose (Fig. 1) are shown in Tabs. 1, 2 and 3. Due to the sweetness theory, we limit them to frequencies of n-COH moieties with $n = 1, 2, 3, 4, 6$. The normal mode frequencies (in cm^{-1}) with strong domination of ν(n-OH) stretching vibrations are listed in Tab. 1. The frequencies with superiority of δ(n-COH) bending vibrations are shown in Tab. 2 and with overweight of T(OC) torsion frequencies are presented in Tab. 3. The selection of the domination of ν(C–O) stretching vibration in any normal mode by animation is difficult, because ν(C–O) are coupled with ν(C–C) stretchings and other vibrations.

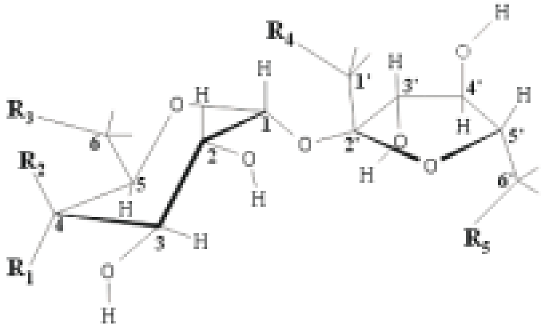


Figure 2. Numeration of carbon atoms (1 – 6, 1' – 6') in *R* – substituted sucrose/galactosucrose derivatives. The *R*-substituent positions form the following derivatives:

	R_1	R_2	R_3	R_4	R_5	
1.)	H	Cl	OH	Cl	Cl	1',4,6'-trichloro-1',4,6'-trideoxy-galactosucrose
2.)	H	Cl	Cl	Cl	Cl	1',4,6,6'-tetrachloro-1',4,6,6'-tetradeoxy-galactosucrose
3.)	H	Cl	OH	OH	OH	1',4-dichloro-1',4-dideoxy-galactosucrose
4.)	OH	H	OH	Cl	Cl	1',6'-dichloro-1',6'-dideoxy-sucrose
5.)	Cl	H	Cl	Cl	Cl	1',4,6,6'-tetrachloro-1',4,6,6'-tetradeoxy-sucrose
6.)	OH	H	OH	OH	Cl	6'-chloro-6'-deoxy-sucrose
7.)	OH	H	OH	Cl	OH	1'-chloro-1'-deoxy-sucrose
8.)	Cl	H	OH	OH	OH	4-chloro-4-deoxy-sucrose
9.)	OH	H	OH	OH	OH	sucrose
10.)	H	OH	OH	OH	OH	galactosucrose

Analysis of Table 1, 2 and 3 reveals satisfactory QSAR correlations of $log(RS_j^{expl})$ *versus* ν_j^2(4-OH), δ_j^2(4-COH) and T_j^2(4-OC) squares of normal mode frequencies (cm^{-1}) independently, manifested by relatively high ***R*** coefficients, **0.94169, 0.91304** and **0.98842**, respectively. Therefore, **ν_j(4-OH), δ_j(4-COH) and T_j(4-OC)** vibrations may be called **"sweet vibrations".**

Apart of vibrations, RS_j^{expl} relative sweetnesses correlate with A_j calculated integrated intensities of the IR "sweet" bands. It is especially well observed in case of strong characteristic ν_j(4-OH) bond vibrations, Table 1. The *R* coefficients of the correlation between RS_j^{expl} and A_j are situated in the parentheses, in bottom of Tab. 1. High correlation is observed for ν_j(4-OH), which reaches ***R* = 0.9838.** The A_j values rapidly lower together with the decrease of sweetness of aldopyranose. It means that "sweet" bands should disappear in IR spectra of the weakly sweet sugars.

In order to establish the localization of two-center glycophore, (9) is taken into consideration with five ν_j(*n*-OH) frequencies, $n = 1, 2, 3, 4, 6$, for all eight sugars, $j = 1, 2,..8$. The computational QSAR with two spectroscopic parameters leads to the set:

***n* = 3, 4 (*R* = 0.9880),** $n = 4, 6$ ($R = 0.9873$), $n = 2, 4$ ($R = 0.9852$), $n = 3, 6$ ($R = 0.9768$),...

The best correlation belongs to system of 3-OH, 4-OH hydroxylic group. For this case the QSAR correlation equation takes the form:

$$log(RS_j) = 0.50983 \cdot 10^{-6} \cdot \bar{\nu}_j^2(3\text{-OH}) - 0.477136 \cdot 10^{-6} \cdot \bar{\nu}_j^2(4\text{-OH}) - 1.270428 \qquad (10)$$

Table 1. PM3 vibrational spectra of aldopyranose free molecules. Comparison of the ν(O–H) stretching frequencies (cm^{-1}) and their A_j integrated intensities (km/mole) in parentheses – with RS_j relative sweetnesses of the aldopyranoses. R are correlation coefficients for:
(a) $ln(RS_j) = a\ \nu_j^2(n\text{-OH}) + b$ linear regression equations, (b) $RS_j = a\ A_j + b$ equations. α-D-mannose is represented by 1C ring-conformer.

Pyranose j	ν(1-OH)	ν(2-OH)	ν(3-OH)	**ν(4-OH)**	ν(6-OH)	**RS_j** (mole/mole)
β-D-glucose	3867.52 (3.54)	3894.73 (8.08)	3897.25 (10.63)	**3803.43 (59.81)**	3908.19 (6.84)	**0.421**
α-D-glucose	3912.76 (7.09)	3895.04 (8.56)	3899.04 (10.49)	**3803.46 (57.23)**	3908.57 (6.28)	**0.368**
maltose	—	3876.25 (2.33)	3895.68 (7.33)	**3804.68 (54.56)**	3908.37 (6.87)	**0.330**
lactose	—	3888.23 (10.43)	3873.57 (6.82)	**3851.64 (15.17)**	3886.84 (2.99)	**0.200**
β-D-xylose	3816.16 (14.34)	3898.22 (6.73)	3898.55 (11.73)	**3897.13 (8.24)**	—	**0.175**
α-D-galactose	3900.29 (9.89)	3875.73 (3.64)	3874.20 (5.29)	**3868.57 (3.62)**	3879.45 (2.48)	**0.168**
α-D-mannose	3897.47 (5.98)	3868.10 (4.23)	3863.31(61.98)	**3871.89 (3.69)**	3902.59 (5.85)	**0.158**
rhamnose	3817.70 (12.87)	3896.86 (9.68)	3894.92 (9.36)	**3899.14 (3.64)**	—	**0.158**
R	0.3371$^{a.)}$ (0.6851)$^{b.)}$	0.2453$^{a.)}$ (0.0537)$^{b.)}$	0.5738$^{a.)}$ (0.2967)$^{b.)}$	**0.9417$^{a.)}$** **(0.9838)$^{b.)}$**	0.7339$^{a.)}$ (0.7316)$^{b.)}$	

Table 2. PM3 vibrational spectra of aldopyranose free molecules. Comparison of the δ(COH) bending frequencies (cm^{-1}) with RS_j relative sweetnesses. R are correlation coefficients for $\log(RS_j) = a\delta_j^2(n\text{-COH}) + b$ linear regression equations. α-D-mannose is represented by 1C ring-conformer.

Pyranose j	δ(1-COH)	δ(2-COH)	δ(3-COH)	**δ(4-COH)**	δ(6-COH)	RS_j (mole/mole)
β-D-glucose	1390.98	1426.76	1412.38	1520.07	1397.90	0.421
α-D-glucose	1362.70	1432.98	1411.09	1520.97	1389.73	0.368
maltose	—	1396.65	1423.32	1520.40	1388.85	0.330
lactose	—	1394.27	1405.71	1492.76	1386.55	0.200
β-D-xylose	1566.71	1402.91	1498.31	1419.00	—	0.175
α-D-galactose	1389.47	1408.45	1397.86	1400.16	1368.90	0.168
α-D-mannose	1419.10	1406.92	1416.72	1392.06	1383.75	0.158
rhamnose	1561.14	1416.44	1420.16	1371.84	—	0.158
R	0.57468	0.49160	0.22639	**0.91304**	0.78722	

Table 3. PM3 vibrational spectra of aldopyranose free molecules. Comparison of the T(OC) torsion frequencies (cm^{-1}) with RS_j relative sweetnesses in pyranoses. R are correlation coefficients for the particular $log(RS_j) = a\mathrm{T}_j^2(m\text{-OC}) + b$ linear regression equation. α-D-mannose is represented by 1C ring-conformer.

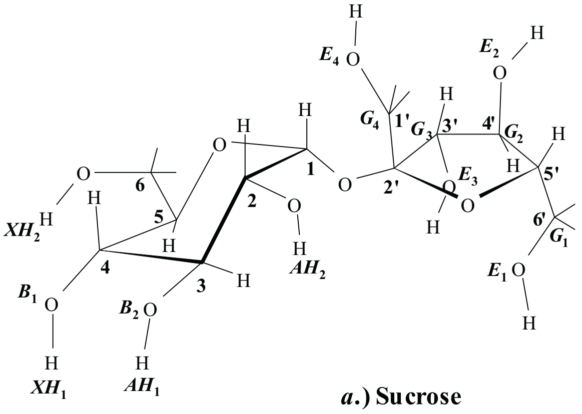
Pyranose j	T(1-OC)	T(2-OC)	T(3-OC)	T**(4-OC)**	T(6-OC)	RS_j (mole/mole)
β-D-glucose	304.32	270.40	307.93	401.98	211.80	0.421
α-D-glucose	134.53	218.05	306.71	394.06	208.52	0.368
maltose	—	361.73	286.42	392.36	204.82	0.330
lactose	—	298.57	386.10	375.71	311.53	0.200
α-D-galactose	266.75	396.07	350.77	373.89	325.03	0.168
α-D-mannose	196.18	349.97	257.51	372.64	218.18	0.158
R	0.12691	0.65263	0.23204	**0.98842**	0.63882	

The latter equation is suitable for calculation of RS_j relative sweetness of aldopyranoses from ν(O–H) vibrational frequencies of 4-OH and 3-OH groups, since PM3 quantum method is used. Results of these calculations are listed in Table 4. Satisfactory agreement is observed between experimental and calculated values. We support, that AH,B Shallenberger, or XH1,B2 Nofre-Tinti sweetener subsites are localized on 4-O$\underline{\text{H}}$,$\underline{\text{O-3}}$ moiety. Taking into account the presence of O-3 oxygen atom, it allows to recover B2 subsite, which is inactive in aldopyranoses due to the *electrostatic model* [6].

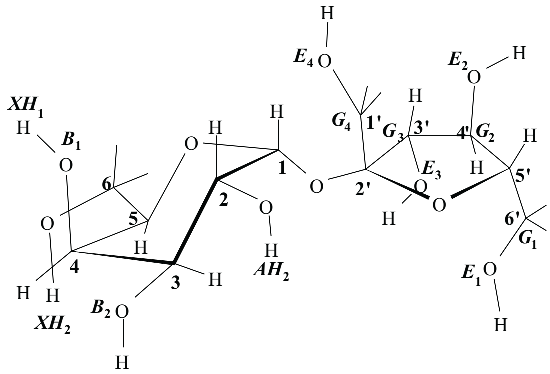
Table 4. Calculated and experimental values of the *RS* relative sweeteness for aldopyranoses. Calculations were carried out according to QSAR correlation equation (Eq. 10) with two vibrational spectroscopic parameters for two-center glycophore.

Aldopyranose	*RS* (calc.) %/%	*RS* (expl.) %/%
β-D-glucopyranose	0.707	0.800
α-D-glucopyranose	0.719	0.700
β-D-xylopyranose	0.398	0.400
α-maltose	0.363	0.330
rhamnose	0.338	0.330
α-D-galactopyranose	0.331	0.320
α-D-mannopyranose (1C)	0.292	0.300
α-lactose	0.200	0.200

2. Structure and localization of four-subsite sweetener in sucrose/galactosucrose molecular system. Chemical formulas of sucrose, galactosucrose and their chlorodeoxy derivatives are shown in Fig. 2. The localization of Nofre-Tinti sweetener subsites in sucrose and galactosucrose is presented in Fig. 3. The *charge-transfer and dispersion model* presented in the paper [8] indicates for a great activity of E1 and E4 sweetener subsites in above compounds. These subsites are situated on O-6' and O-1' fructofuranose oxygen atoms, respectively, in sucrose and galactosucrose. Mentioned model excellently explains the effects of strong increase of sweetness, when OH groups with these oxygen atoms are subsituted by chlorine. On other hand, *charge-transfer and dispersion model* completely neglect less active subsites in glucopyranose moiety, XH1 and B2, equivalent to AH,B glycophore. QSAR multiple correlation establishes four-subsite sweetener by the use of (9) with the eight ν_j(n-OH) frequencies, n = 4, 3, 2, 1, 1', 3', 4' and 6' for all ten sugars, j = 1, 2,..10. Results of the computational correlation procedure are listed in Table 5. They choose the 4-OH, 3-OH aldopyranose frequencies and 1'-OH, 6'-OH fructofuranose groups by highest value of multiple correlation coefficient R = 0.98857. It speaks for the four-subsite XH1, B2, E4, E1 sweetener. In this way AH,B Shallenberger glycophore is present in sucrose and galactosucrose. The corresponding QSAR correlation equation has the following form:



***a.*) Sucrose**



***b.*) Galactosucrose**

Figure 3. a.) Location of Nofre-Tinti sweetener subsites in sucrose molecule.
b.) Location of these subsites in galactosucrose.

$$\begin{aligned} log(RS_j) = &- 0.761875\cdot 10^{-7}\cdot\bar{\nu}_j^2(\text{4-OH}) + 0.544904\cdot 10^{-5}\cdot\bar{\nu}_j^2(\text{3-OH}) - \\ &- 0.750269\cdot 10^{-7}\cdot\bar{\nu}_j^2(\text{1'-OH}) - 0.662605\cdot 10^{-7}\cdot\bar{\nu}_j^2(\text{6'-OH}) - 79.27555 \end{aligned} \qquad (11)$$

(11) allows to calculate the RS_j relative sweetness of sucrose, galactosucrose and their chlorodeoxy derivatives from the vibrational frequencies of 4-OH, 3-OH, 1'-OH and 6'-OH groups. The results of calculations are listed in Table 6. They satisfactory reproduce the very high sweetness of chlorodeoxy derivatives of sucrose and galactosucrose. (11) is also a key in explanation of *6-OH deoxychlorination negative effect* in galactosucrose based on ν(O-H) vibrational frequencies. The calculations reproduce excellently twice greater sweetness of 1',4,6'-trichloro-1',4,6'-trideoxy-galactosucrose in relation to sweetness of 1',4,6,6'-tetrachloro-1',4,6,6'-tetradeoxy-galactosucrose.

Table 5. Determination of the contribution of OH groups to four-center glycophore from all the eight OH groups in sucrose/galactosucrose structure, based on QSAR correlation equation with $\nu^2(n\text{-OH})$ spectroscopic parameters. R = coefficient of multiple correlation, S^2 = remainder variance, Err = relative error. Hydroxylic groups belonging to fructofuranose moiety are marked by italic letters. Four-group set indicating the best correlation is shown using bold fashion.

	R	S^2	*Err*	I	II	III	IV
1.	**0.98857**	**0.07911**	**0.22769**	**4-OH**	**3-OH**	***1’-OH***	***6’-OH***
2.	0.98656	0.09286	0.29261	4-OH	3-OH	*1’-OH*	*3’-OH*
3.	0.98474	0.10532	0.56407	*1’-OH*	*3’-OH*	*4’-OH*	*6’-OH*
4.	0.97461	0.17442	0.76105	6-OH	4-OH	*1’-OH*	*6’-OH*
5.	0.97269	0.18741	1.82912	4-OH	*1’-OH*	*3’-OH*	*4’-OH*
6.	0.97168	0.19423	0.67811	6-OH	4-OH	*1’-OH*	*3’-OH*
7.	0.97139	0.19624	1.97215	4-OH	2-OH	*1’-OH*	*6’-OH*
8.	0.96717	0.22470	2.43283	4-OH	*1’-OH*	*4’-OH*	*6’-OH*
9.	0.96693	0.22630	2.22411	4-OH	2-OH	*1’-OH*	*3’-OH*
10.	0.96605	0.23222	0.97641	6-OH	*1’-OH*	*3’-OH*	*4’-OH*

Table 6. Calculated values of the ν(O–H) stretching vibrations refered to the four-center glycophore. The *RS* relative sweetnesses of chlorodeoxy sugars due to QSAR correlation equation (11) and comparison with the corresponding measured values.

Abbreviated name of the chlorodeoxysugar a.)	ν(O-H) frequencies in cm^{-1}				*RS*(calc.) mole/mole	*RS* (expl.) mole/mole
	4-OH	3-OH	*1’-OH*	*6’-OH*		
1’,4,6’-trichloro-G	–	3897.3	–	–	3098.20	2323.26
1’,4,6,6’-tetrachloro-G	–	3888.0	–	–	1250.64	1215.52
1’,4-dichloro-G	–	3900.8	–	3823.0	470.12	664.65
1’,6’-dichloro-S	3805.9	3896.9	–	–	234.76	553.87
1’,4,6,6’-tetrachloro-S	–	3877.3	–	–	436.34	243.10
6’-chloro-S	3803.4	3898.5	3881.5	–	20.16	21.08
1’-chloro-S	3802.7	3897.9	–	3797.0	28.55	21.08
4-chloro-S	–	3876.1	3877.5	3853.7	3.02	5.27
sucrose	3803.1	3897.3	3877.6	3852.1	1.90	1.00
galactosucrose	3850.0	3873.9	3879.0	3807.6	0.19	0.20

a.) G = galactosucrose, S = sucrose. For example 1’,4,6’-trichloro-G abbreviated name is equivalent to 1’,4,6’-trichloro-1’,4,6’-trideoxy-galactosucrose.

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REFERENCES

1. Shallenberger R.S., *Food Technology*, **52**, 72 (1998).
2. Shallenberger R.S., *J. Food Sci.*, **28**, 584 (1963).
3. Shallenberger R.S., *Agr. Sci. Rev.*, **2**, 11 (1964).
4. Birch G.G. and Lee C.K., *The Theory of Sweetness* in *Developments in Sweetness 1.* Applied Science Publishers Ltd., London – 1979, pp 165–186.
5. Nofre C. and Tinti J.M., *Food Chem.*, **56**, 263 (1996).
6. Pietrzycki W., *Polish J. Chem.*, **75**, 1569 (2001).
7. Höltje H.D. and Kier L.B., *J. Pharm. Sci.*, **63**, 1722 (1974).
8. Pietrzycki W., *Polish J. Chem.*, **76,** 875 (2002).
9. Pietrzycki W., *Polish J. Chem.,* **50**, 1555 (1976).
10. Krutošikova A. and Uher M., *Natural and Synthetic Sweet Taste Substances*, (in Polish), PWN, Warszawa, 1990.
11. Hypercube, Inc., 419 Philip Street, Waterloo, Ontario N2L 3X2, Canada.
12. Stewart J.J.P., *J. Comput. Chem.*, **10,** 209, 221 (1989).
13. Pietrzycki W., *Polish J. Chem.*, **47**, 1475 (1973).
14. Czuchajowski L., Pietrzycki W. and Rożek-Cicha J., *Bull. Acad. Polon, Sci., Ser. Chim.*, **22**, 225 (1974).
15. Pietrzycki W., *Polish J. Chem.*, **71**, 1462 (1997).