Tin(IV) Compounds Derivatives of Reaction Between Organotin(IV), $SNCL_4$ and Rutin Trihydrate: Characterization and Hypolipidemic Effects.

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ABSTRACT

Equimolar reactions involving $SnClPh_3$, $SnCl_2Ph_2$, $SnCl_3Ph$ and $SnCl_4$ and rutin trihydrate (Quercetin-3-rutinoside) produced organotin(IV) polymers, which have been characterized by infrared spectroscopy, ^1H, ^{13}C and ^{119}Sn NMR, Mössbauer spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and microanalysis. The NMR (^1H, ^{13}C) and ^{119}Sn Mössbauer spectroscopy have revealed dephenylation of the starting organotin(IV) materials. The overall data have revealed a six-coordination for the Sn(IV) centre in solution as well as in solid state. DSC and GPC techniques have confirmed the formation of macromolecules for those adducts with an average molar mass higher than $7.0x10^4$ g/mol. The hypolipidemic effect of total cholesterol reduction in male New Zealand rabbits was comparable to calcic atorvastatin, a commercial drug for treatment of hyperlipidemic patients.

INTRODUCTION

Flavonoids form part of a wide class of metabolites, which are derivatives of biosynthetic routes involving acetate, chickimate and other subunits. They have been acknowledged as the origin of the colour from a variety of flowers as well as the flavour of all sorts of food and drinks. Those compounds are chemically classified according to the functional group within the structural arrangement. More than 4000 flavonoids have been identified and some of them are predominantly found in citric fruits and vegetables /1/. The pharmacological properties of flavonoids have attracted interest in several fields of research, for

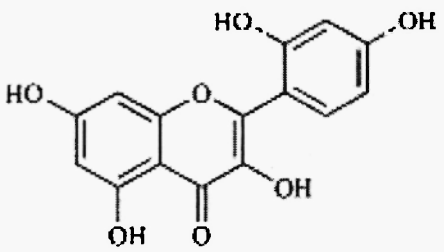
instance, in the treatment of diabetes and cancer therapy of human colon adenocarcinoma cells /2/. The effects of flavonoids in hyperlipidemic rats and rabbits /3-5/ have given promising results concomitant to the statistical work on coronary disease as the main cause of death in people with age over 45 /6/. The information above. together with the recognized biological properties of organotin compounds such as anti-inflammatory /7/, antifungal /8, 9/ and antitumoral /10, 11/ activity, has motivated us to investigate the hypolipidemic effects of Sn(IV)-flavonoid derivative complexes in hyperlipidemic rabbits.

In coordination chemistry, flavonoids can be used as ligands owing to the available electrons on the heteroatoms such as oxygen (see Figure 1). These compounds can perform a variety of bonding modes leading to a number of geometrical patterns. The literature provides a few complexes with this class of compounds, mainly from the first row of transition metals /12/, and in addition, Sn(IV) complexes derivatives of reaction between n-dibutyltin(IV)-oxide and rutin trihydrate /13/.

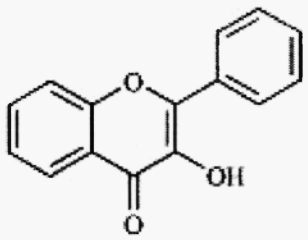
The required knowledge about the coordination chemistry of organotin(IV) complexes with flavonoids has led us to choose $SnClPh_3$, $SnCl_2Ph_2$, $SnCl_3Ph$ and $SnCl_4$ as starting materials to carry on research for new compounds with rutin trihydrate. The present work reports the characterization of the products by ^1H, ^{13}C and ^{119}Sn NMR, infrared and ^{119}Sn Mössbauer spectroscopy, as well as the preliminary results of hypolipidemic effects in New Zealand rabbits.

MATERIALS AND METHODS

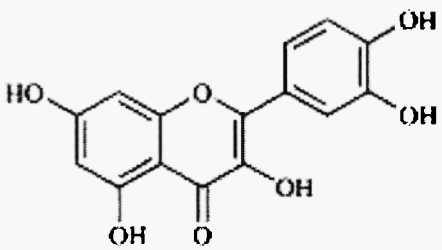
The ^1H and ^{13}C NMR spectra were obtained using a Bruker Advance DPX 200 (200 MHz) spectrometer with tetramethylsilane ($SiMe_4$) as internal standard ($\delta = 0$) in deuterated methanol. The ^{119}Sn NMR spectra were measured using a Bruker DRX400 (400 MHz) with tetramethyltin(IV) ($SnMe_4$) as external standard ($\delta = 0$) in CH_3OH and DMSO, ^{119}Sn Mössbauer spectroscopy data were collected at 78 K in constant acceleration equipment moving a $CaSnO_3$ source at room temperature. All Mössbauer spectra were computer-fitted assuming Lorentzian single lines. Infrared spectra were recorded on a Perkin Elmer Spectrum 1000 grating spectrometer, using Nujol suspension between CsI windows, scanning from 4000 to 223 cm^{-1}. The microanalysis was carried out using a Perkin Elmer 2004 CHNS/O and the cholesterol analysis on an Alize Analyzer. The molecular mass of each compound was obtained by GPC through a GPC803D-GPC802D 2 x 300 x 8 mm column in dimethylformamide (DMF) using a Shimadzu device, and the DSC analysis a Shimadzu - DSC50. The biological research was set by the use of six groups (six animals each) of male New Zealand rabbits, fifty days old with a weight-average of 1.2 Kg. Those were fed with hyperlipidemic diet (RCAC = ration + cholesterol 0.5% + colic acid 0.1%) and treated daily with capsules containing 5 mg of the appropriate test substance such as rutin, Sn(IV)-rutin products (**1**, **2**, **3**, **4**), and calcic atorvastatin, a commercial drug. The control groups were treated with ration and RCAC. All Sn(IV) reagents were obtained from Aldrich, and rutin trihydrate from Sigma Company. Schlenk glassware, nitrogen atmosphere and magnetic stirring were used throughout the experiments. Chloride was investigated by qualitative analysis against silver nitrate.



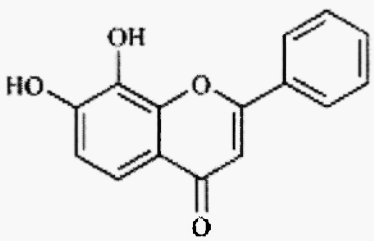
Morin



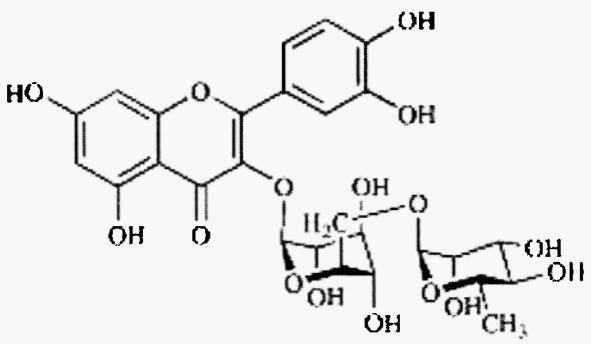
3-Hydroxy-flavone



Quercetin



7,8-Dihydroxy-flavone



Rutin

Fig. 1: Common flavonoids found in vegetables and fruits.

Preparation of [Sn(rutinate)2(rutin)]

Equimolar reactions between organotin(IV) reagents and rutin trihydrate were carried out in methanol. The yellow mixture was kept stirring for more than 14 h at room temperature, except in the case of **1** (65°C). The yellow solid obtained by removal of half of the solvent was filtered off and washed with acetonitrile or chloroform. The removal of the solvent in the case of **3** left behind a carroty oil, that was dissolved again in diethyl ether, stirred for approximately 1 h, and then the solvent was removed under reduced pressure. This procedure was repeated several times. At last, the diethyl ether was replaced by a mixture of diethyl ether/hexane (1:2) and the solution was left to stand for 4 days, in which a pale yellow solid separated and was treated as described above.

[Sn(rutinate)$_2$(rutin)]·H_2O·4CH_3OH (**1**): Yield: 0.97g (60%). mp(°C): 176; Anal. Calcd. for $C_{85}H_{104}O_{53}Sn$: C, 48.79; H, 5.01; Found: C, 48.88; H, 5.44; Mol Weight (g/mol): 8.4 x 10^3; IR (nujol/CsI, cm^{-1}): ν(C=O) 1655, ν(Sn-O) 456; NMR: ^{1}H (CD_3OD, 200 MHz), δ 7.50 (m, Ar, 2H), δ 6.71 (d, Ar, 1H), δ 6.20 (d, Ar, 1H), δ 6.02 (d, Ar, 1H), δ 4.94 (d, CH, 1H), δ 4.78 (s, H_2O, OH), δ 4.39 (s, CH, 1H), δ 3.01-3.80 (m, CH, CH_2, 10H); δ 0.98 (d, CH_3, 3H); ^{13}C (CD_3OD, 300 MHz,), δ 178.1 (C=O), 164.8, 161.7, 158.1, 157.2, 148.5, 144.6, 134.4 122.3, 121.8, 116.5, 114.8, 104.3, 98.7, 93.6 (Quercetin, 15C); δ 103.5, 101.2, 76.9, 76.0, 74.5, 72.7, 71.0, 70.8, 70.1, 68.5, 67.3 (CH_2), 16.7 (CH_3) (3-Rutinoside, 12 C); ^{119}Sn (CH_3OH, 400 MHz): δ -186.6.

[Sn(rutinate)$_2$(rutin)]·6CH_3OH (**2**): Yield: 1.00g (63%). mp(°C): 172; Anal. Calcd. for $C_{87}H_{110}O_{54}Sn$: C, 48.87; H, 5.18; Found: C, 48.69; H, 5.32; Mol Weight (g/mol): 9.7 x 10^3; IR (nujol/CsI, cm^{-1}): ν(C=O) 1656, ν(Sn-O) 435; NMR: ^{1}H (CD_3OD, 200 MHz), δ 7.55 (m, Ar, 2H), δ 6.75 (d, Ar, 1H), δ 6.25 (d, Ar, 1H), δ 6.07 (d, Ar, 1H), δ 4.98 (d, CH, 1H), δ 4.78 (s, H_2O, OH), δ 4.41 (d, CH, 1H), δ 3.20 – 3.85 (m, CH, CH_2, 10H); δ 1.01 (d, CH_3, 3H); ^{119}Sn (CH_3OH, 400 MHz, R_{int} %): δ -527.3 (58), -534.1 (100), -546.9 (80).

[Sn(rutinate)$_2$(rutin)]·2H_2O·5CH_3OH (**3**): Yield: 0.63g (55%). mp(°C): 178; Anal. Calcd. for $C_{86}H_{110}O_{55}Sn$: C, 48.21; H, 5.17; Found: C, 48.13; H, 5.43; ; Mol Weight (g/mol): 9.0 x 10^3; IR (nujol/CsI, cm^{-1}): ν(C=O) 1658, ν(Sn-O) 455; NMR: ^{1}H (CD_3OD, 200 MHz), δ 7.50 (m, Ar, 2H), δ 6.74 (d, Ar, 1H), δ 6.23 (s, Ar, 1H), δ 6.05 (s, Ar, 1H), δ 4.96 (d, CH, 1H), δ 4.78 (s, H_2O, OH), δ 4.40 (s, CH, 1H), δ 3.10 – 3.75 (m, CH, CH_2, 10H); δ 1.02 (d, CH_3, 3H); ^{119}Sn (CH_3OH, 400 MHz, R_{int} %): δ -534.1 (70), -546.9 (100), -572.5 (70),-585.6 (86).

Preparation of [SnCl(rutinate)].3CH3OH (4)

Tin(IV) chloride (0.65g, 0.29 ml, 2.52 mmol) was transferred by syringe onto a yellow acetonitrile solution (40 ml) of rutin trihydrate (1.60g, 2.41 mmol) at room temperature, immediately yielding a yellow gold precipitate. After 30 minutes stirring, the solid was removed by filtration in air and washed with methanol. Yield: 1.80g (80%). mp(°C): 167; Anal. Calcd. for $C_{30}H_{40}O_{19}ClSn$: C, 41.95; H, 4.69; Found: C, 41.66; H, 4.94; Mol Weight (g/mol): 8.3 x 10^3 and 2.6 x 10^5; IR (nujol/CsI, cm^{-1}): ν(C=O) 1654, ν(Sn-O)

457, ν(Sn-Cl) 360; NMR: ^{1}H (CD_3OD, 200 MHz), δ 7.64 (m, Ar, 2H), δ 6.87 (d, Ar, 1H), δ 6.38 (d, Ar, 1H), δ 6.19 (d, Ar, 1H), δ 5.10 (d, CH, 1H), δ 4.93 (s, H_2O, OH), δ 4.51 (s, CH, 1H), δ 3.01 – 3.95 (m, CH, CH_2, 10H); δ 1.11 (d, CH_3, 3H); ^{119}Sn (CH_3OH, 400 MHz, R_{int} %): δ -527.3 (100), -546.3 (50), -559.4 (20), -622.3 (20); ^{119}Sn (DMSO, 400 MHz, R_{int} %): δ -524 (100), -543.8(50), -556.9(33), -619.9(18), -636.2(10).

RESULTS AND DISCUSSION

The compounds **1**, **2**, **3**, and **4** are soluble in methanol, dimethyl formamide and dimethyl sulfoxide. Only **3** presented an oily aspect during its preparation, which is most likely a consequence of solvent trapping by intermolecular hydrogen bonding. Qualitative analysis has shown a complete loss of chloride in **1**, **2** and **3**, but not in **4**. The compounds are hygroscopic solids but air stable materials. They should be stored in desiccators containing anhydrous calcium chloride under vacuum to avoid moisture. Before running the elemental analysis, samples of the complexes were kept in desiccators for a week over calcium chloride. As a polydentate ligand, rutin allows several coordination modes towards Sn(IV) as shown in Figure 2.

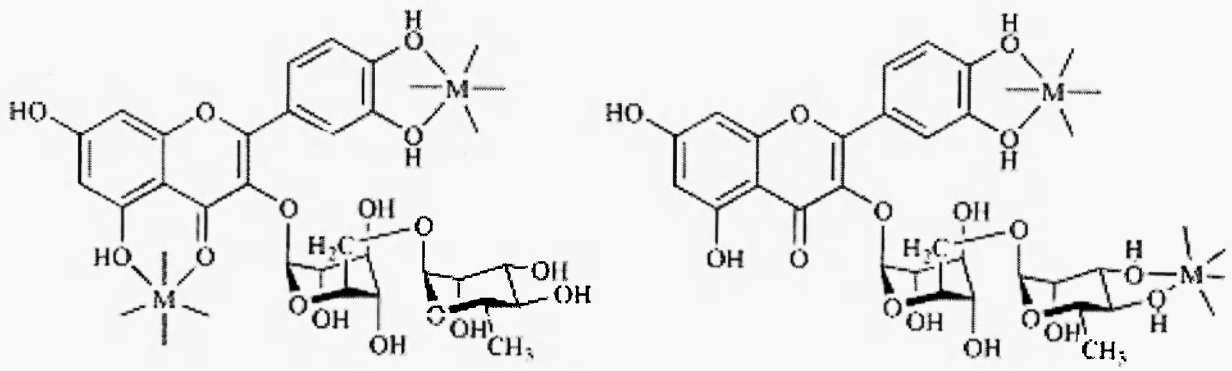
The OH groups attached to the aromatic and aliphatic ring of rutin can bind to metals in mono-, bidentate and chelate modes. It is also conceivable that rutin can act as tridentate or tetradentate ligand whereas both mono- and chelate bonding modes coexist towards an Sn(IV) centre. Loss of one, two or more hydrogen atoms from quercetin or 3-rutinoside moieties, or even from both, lead to rutinate-anion. The information concerning structural features provided by each technique employed in the present work is discussed below.

Infrared Spectroscopy

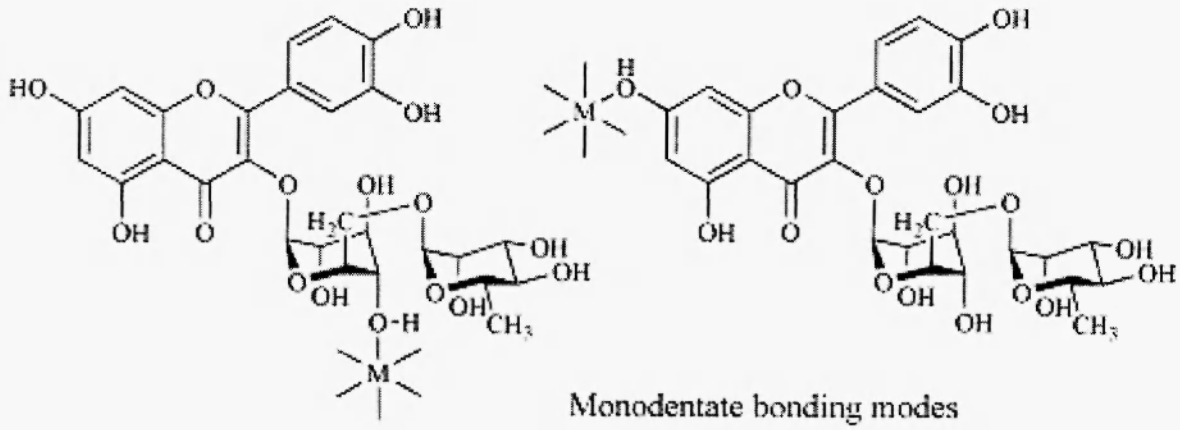
The infrared spectrum of rutin trihydrate exhibited a C=O band at 1654 cm^{-1}, which remained unchanged upon coordination to the Sn(IV) nucleus. All complexes revealed a broad band at 3450 cm^{-1}, caused by the vibrational stretching of the OH group, and another one around 450 cm^{-1} assigned to the Sn-O bond. In addition, only an infrared band at 360 cm^{-1} was displayed in **4** due to the vibrational stretching of the Sn-Cl bond /14, 15/. Consequently, the infrared spectroscopy points out that the coordination towards the Sn(IV) does not occur through the carbonyl group of rutin, since the displacement of the vibrational C=O stretching is not significant enough to suggest it. At the low frequency, however, the metal-oxygen bond strongly indicates coordination of rutin, where the oxygen might come from aromatic or aliphatic groups.

NMR Spectroscopy

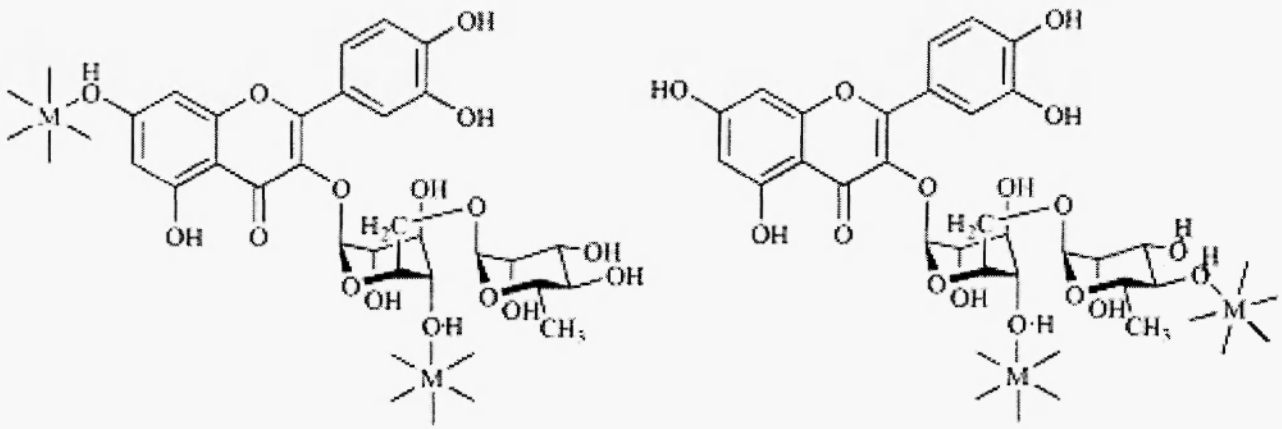
The ^{1}H NMR spectra of **1**, **2** and **3** show no signals correlated to the phenyl groups from the starting materials $SnClPh_3$, $SnCl_2Ph_2$ and $SnCl_3Ph$, which usually are found approximately at δ 7.50. The proton integration of all complexes matches the number of hydrogen atoms belonging to the 3-rutinoside and quercetin moiety (see Figure 1). The signals of all OH groups from rutin could not be seen as a consequence of deuterium exchanging with the solvent. Those materials are most likely to be hygroscopic due to the intense signal around δ 4.85, which confirms the presence of water. The chemical shift and the spectral pattern of rutin trihydrate, when in comparison to the assigned peaks of **1**, **2** and **3** including **4**, were



Bridging chelate bonding modes



Monodentate bonding modes



Bridging bidentate bonding modes

Fig. 2: Possible bridging chelate, bidentate and monodentate bonding modes of rutin bound to a six-coordinate metal centre.

essentially unchanged upon coordination, suggesting all hydrogen atoms in the same magnetic environment.

The ^{13}C NMR of rutin showed a signal at δ 178, assigned to C=O moiety, which remained upon coordination to Sn(IV) in **1**, **2**, **3** and **4**. The magnetic resonance of methyl and methylene groups was identified at δ 16.7 and 67.3 respectively by the use of DEPT 35 technique for the free rutin as well as the Sn(IV) derivative complexes. All aromatic and aliphatic carbon atoms of both the 3-rutinoside and quercetin moiety were observable in the ^{13}C NMR spectra of **1**, **2**, **3** and **4**, and no signal could be correlated to the phenyl groups from the starting materials. The chemical shift and the spectral pattern of the assigned peaks were remarkably unaffected as well by comparison to those of the free rutin trihydrate. In other words, the structural features of those compounds cannot be distinguished by these NMR techniques. On the other hand, loss of phenyl groups has been recognized before /16, 17/, as in the reaction of thiophene-2-carboxaldehyde thiosemicarbazone with $SnCl_3Ph$[9]. Time of reaction /18/ and solvent mixtures /17/ seem to play an important role in the dephenylation reaction. The latter has also been established under the stimulus of solar /19/ and UV-light /20/. However, the mechanism of dephenylation is still questionable. accounting for the fact that the same result was achieved whether the reaction was carried out under the solar light or in the dark.

The correlation between chemical shift and coordination number on the Sn nucleus is well-known in ^{119}Sn NMR. Coordinating solvents can greatly influence the ^{119}Sn chemical shift where the resulting species are believed to form dimers or tetramers by auto-association. The literature provides some examples for dialkoxide and trialkoxide organotin compounds /21/, where the chemical shift towards low frequency is approximately 120 and 250 for five- and six-coordinate tin-oxygen compounds respectively. The ^{119}Sn NMR spectra of **2**, **3** and **4** in CH_3OH displayed several peaks at low frequency, contrarily to **1**. The latter exhibited a singlet at δ -187, which is remarkably close to that of $SnClPh_3$ (δ -177) in the same solvent, suggesting that both have six-coordinate Sn(IV) by means of solvent coordination. The number of ^{119}Sn peaks exposed in the spectrum of **2**, **3** and **4**, were even lower than the common range assigned to hexacoordinated organotin complexes in solution as well as to organotin-oxo oligomers in solid state /22, 23/. A slight difference in chemical shift was revealed for those peaks in **4** by replacing CH_3OH with DMSO, a strong coordinating solvent. This is evidence for the absence of correlation between the number of peaks and solvent interaction by means of coordination. The number of observed signals in **2**, **3** and **4** is most likely related to the effect of subtle magnetic variation surrounding the Sn(IV) nucleus, caused by the spatial arrangements of the bulky coordinating ligand. In this context, the only signal exhibited in the spectrum of **1** suggests no magnetic variation surrounding the Sn(IV), indicating coordination through the quercetin moiety whereas the conformation of the aromatic rings is retained. On the other hand, chair and boat spatial conformations are expected for the 3-rutinoside moiety. In view of that, possible structural arrangements surrounding the Sn(IV) can be envisaged as shown in Figure 3. The water and methanol molecules are trapped in the lattice by hydrogen bonding.

^{119}Sn Mössbauer Spectroscopy

A recent Mössbauer study on coordination chemistry involving n-dibutyltin(IV)-oxide with several flavonoids, including rutin, has pointed out the Sn(IV) centre as penta- and hexacoordinated[13]. Table 1 shows

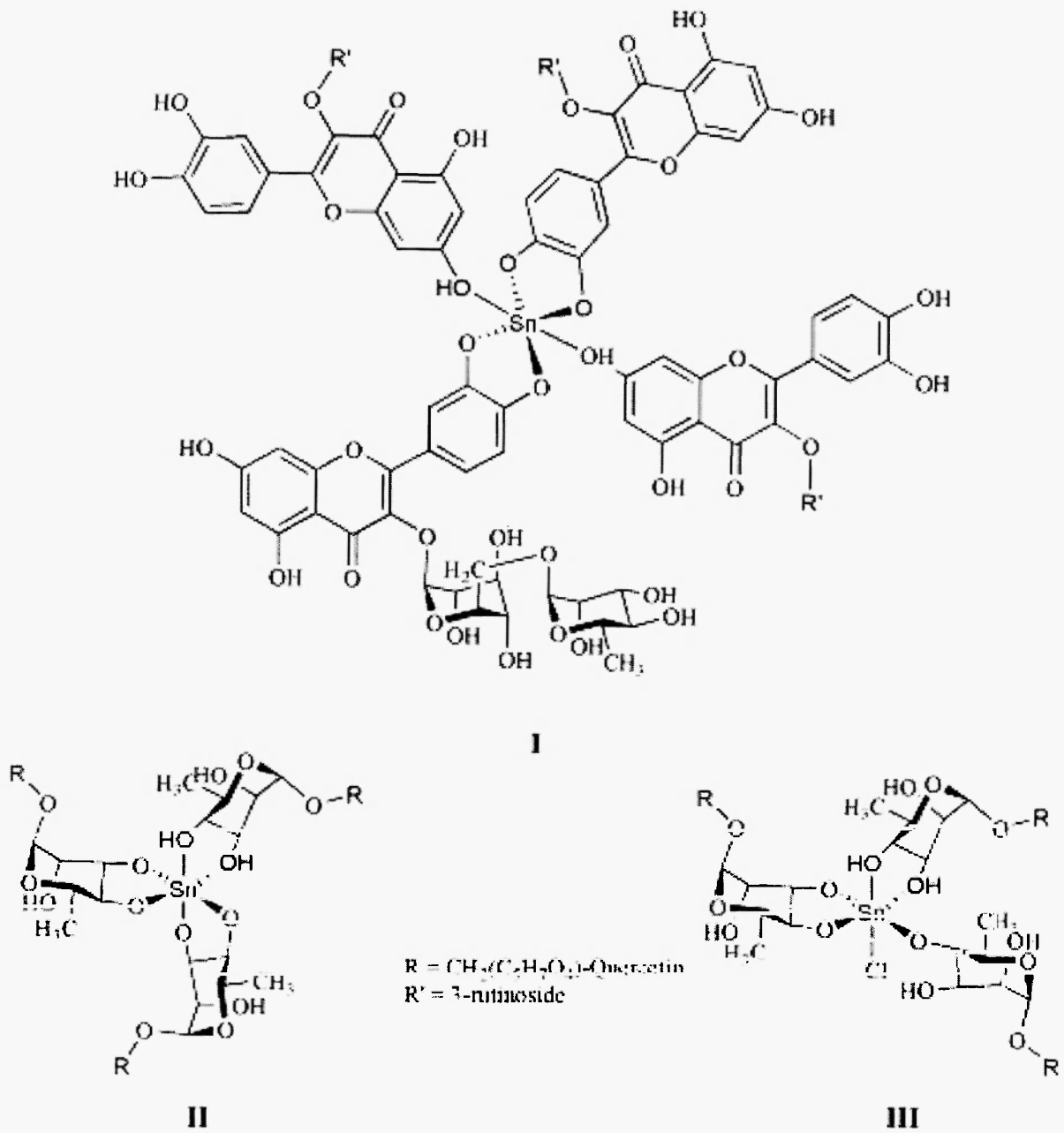


Fig. 3: Possible spatial arrangements of rutin towards a six-coordinate Sn(IV) centre through 3-rutinoside (**II**, **III**) and quercetin (**I**) moiety, leading to monomeric species.

the Mössbauer parameters for the compounds prepared in this work as well as literature data for comparison.

The isomer shifts (δ) of **1**, **2**, **3** and **4** are quite intriguing, for the reason that the values are amazingly lower in comparison to the starting materials. The overall δ value of those is even inferior to that of **5** and **6**, derivatives of the reaction between n-dibutyltin(IV)-oxide and rutin. Low values of δ are related to the decrease of *s* density at the Sn(IV) nucleus upon coordination, consequently increasing its coordination number. In **1**, **2**, and **3**, δ was as low as in the SnO_2 (**10**), suggesting the same octahedral pattern as for this polyoxide /24, 25/. The upper value of **4** can be reasonably compared to the polymeric materials **7** and **9**, which have four chloride ions occupying the edges of an octahedron.

Table 1

Mössbauer parameters of the Sn(IV)-rutin derivatives and literature data for comparison.

Product	δ(mm/s)	Δ(mm/s)	Γ(mm/s)	Ref.
$[SnClPh_3]$	1.33(1)	2.54(1)		29
$[SnCl_2Ph_2]$	1.41(1)	2.83(1)		29
$[SnCl_3Ph]$	1.16	1.76		30, 31
$[SnCl_4]$	0.82	0.00		30-32
1. $[Sn(L)_2(rutin)]$	0.01(5)	0.56(5)	1.40(1)	thiswork
2. $[Sn(L)_2(rutin)]$	0.08(5)	0.56(5)	1.01(8)	this work
3. $[Sn(L)_2(rutin)]$	0.14(2)	0.59(5)	0.99(5)	this work
4. $[SnCl(L)]\cdot H_2O$	0.29(2)	0.55(5)	0.96(5)	this work
5. $[SnBu_2(rutin)]$[a]	0.80	2.62		12
6. $[Sn_2Bu_4(rutin)]$[a]	0.78	2.49		33
8. $[OSnPh_2]_n$	0.89(9)	2.00(9)		34
9. $[SnCl_4(pyz)]_n$	0.52	0.92		35
10. SnO_2	0.04(1)	0.78(2)		this work

[a] trigonal bipyramidal arrangement; H_2salen (N,N'-ethylenebis(salicylideneimine); pyz = pyrazine; L = rutinate.

A remarkable aspect concerning the data in Table 1 in comparison to **1**, **2**, **3** and **4** is that all starting materials as well as **5**, **6** an **8** have appreciable quadrupole splitting (Δ), due to the difference in electronegativity between chloride, butyl and phenyl groups, as well as the C-Sn-C angle which is closely related to the electron field gradient (EFG) perceived by the Sn atom. For all complexes prepared in the present work, very low values of Δ have been observed, which reinforce the presence of a weaker EFG owing to the lack of contribution from phenyl groups. Therefore, this is a strong evidence of dephenylation in those reactions as pointed out by ^1H and ^{13}C NMR spectroscopy. The extremely low values found for both Mössbauer parameters suggest a symmetrical environment for the Sn(IV) nucleus, which is assumed to be at the centre of an octahedron in the solid state surrounded by six oxygen atoms in **1**, **2** and **3** and **5**. plus a chloride in **4**.

Interestingly, the linewidth (Γ) of **1**, **2**, **3** and **4** was large, as shown in Table 1, which could be caused by the poor crystalline degree of the sample or the thickness effect of the absorber, or even by both factors. Large linewidth, however, has been reported for linear organotin polymers by molecular dynamics studies /26/. The number of tin atoms in the repeating unit of the polymer is closely correlated to the Γ value. For that reason, the large values of linewidth found in this work have led us to suppose the formation of polymeric or oligomeric materials. Molecular measurements by gel permeation chromatography (GPC) have confirmed this assumption, although the values of δ and Δ can also be helpful to distinguish polymerization in organotin compounds, as is the case of methacryl derivatives of butyltin, where those parameters drop off on passing from monomeric to polymeric species /27/.

Thermal Analysis and Gel Permeation Cromatography

Gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) were employed to gain information on the molar mass and phase transitions in those materials. The GPC measurements have effectively established the formation of macromolecules. The weight-average molar mass of **1**, **2** and **3** are identical from the molar mass point of view considering the accuracy of GPC evaluation. The polydispersity (Mw/Mn) values were of 1.3, which is commonly found for polymer systems. In the case of **4**, the molar mass distribution has shown two peaks with a polydispersity around 2.0, characteristic of polymer systems as well. In the latter, both peaks belong to the same material diverging from each other in molar mass, or the chain size. The DSC technique has revealed a curve pattern typical of polymer systems /28/. All compounds prepared in this work have presented similar thermal behaviour.

Two thermal phenomena, glass transition (T_g) and melting point (T_m), typical parameters of semicrystalline polymers, were observed by DSC. For all systems prepared, the T_m could be determined by the endothermic change observed around 180°C and the glass transition in the range of 0-50°C, owing to the inflection point as shown in Figure 4. The endothermic event between 50 to 100°C is probably related to the loss of water and methanol molecules. The melting points obtained by DSC were very close indeed for **1**, **2**, and **3**. This proximity in melting point is a result of the closeness in molar masses between those as well as an indication that all have the same intersegment interaction, unlike **4**, for which the melting point was 8, 5 and 11°C below in comparison to the former three, respectively.

Hypolipidemic Effects

All six groups of rabbits (six animals each) were fed with a hyperlipidemic diet in order to enhance the blood cholesterol concentration. The data were statistically worked out by the Tukey and Dunnet methods. The best achievement in cholesterol reduction was obtained after 15 days of treatment with complex **4**. This reduction was surprisingly similar to that of calcic atorvastatin, a well-known medication for hyperlipidemic patients, for the same experiment as shown in Table 2. Further work to assemble more information will be developed in order to establish possible side effects such as liver and kidney damage.

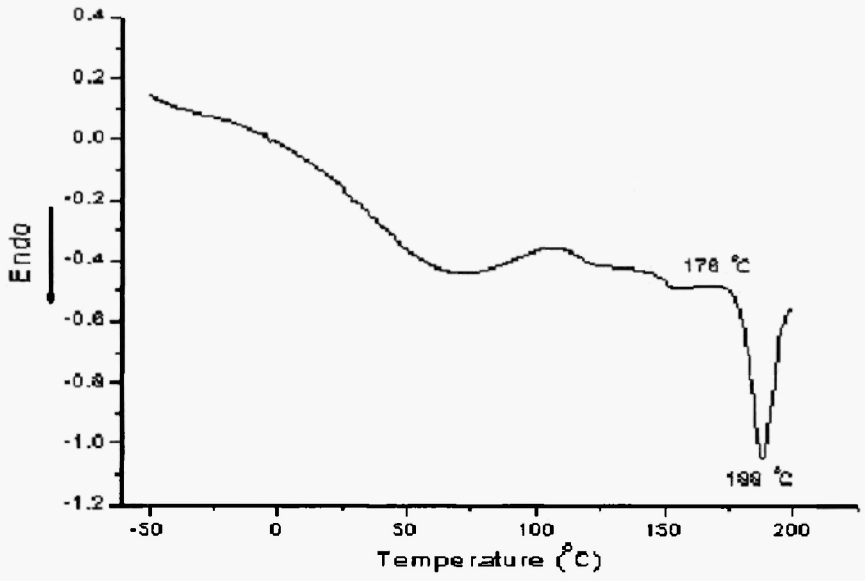


Fig. 4: DSC curve of $[Sn(rutinate)_2(rutin)]\cdot H_2O\cdot 4CH_3OH$ (**1**) monitored at a heating rate of 20°C/min, in nitrogen atmosphere.

Table 2

Average total seric cholesterol concentration in male rabbits treated by RCAC plus test substance in capsules.

	days of treatment (cholesterol conc.)		
Product	zero (mg/dl) †	15 (mg/dl) †	% reduction ‡
Control group 1**	151.27	99.20	--
Control group 2**	128.82	1,012.22	--
RCAC plus rutin	134.23	986.70	-2.52
RCAC plus **1**	140.10	900.66	-25.71
RCAC plus **2**	163.53	751.95	-11.02
RCAC plus **3**	124.45	788.65	-22.09
RCAC plus **4**	172.23	633.07	-37.46
RCAC plus CA*	169.60	615.84	-39.16

* Commercial drug (calcic atorvastatin); ** Control groups treated with ration (1) and RCAC (2). RCAC = hyperlipidemic diet (ration + cholesterol 0.5% + colic acid 0.1%). † - Tukey's statistical method; ‡ - Percentage is related to RCAC.

CONCLUDING REMARKS

Several attempts to achieve suitable crystals for crystallography studies have failed, as usual for polymeric systems. Nevertheless, Mössbauer spectroscopy has revealed six-coordinate Sn(IV) nucleus for all polymeric materials in solid state and reinforced the evidence for a dephenylation reaction on the organotin(IV) reagents, previously observed by NMR techniques. The number of signals observed by ^{119}Sn NMR in those compounds most likely indicates the coordination site from rutin in **1** belongs to quercetin, whereas for **2**, **3** and **4** it involves both the 3-rutinoside and quercetin moieties. Although **1**, **2,** and **3** have the same molecular formula, the stereochemistry of the ligand upon coordination as well as the coordination site is still doubtful without molecular structural determination, and this applies to **4** as well. Low-molecular-mass oligomers are always present in step polymerisation, which does not invalidate the GPC results /28/. In this context, **1**, **2,** and **3** are better conceived as oligomers and **4** as a mixture of an oligomer and a polymer, accounting for the differences in weight-average molecular mass results.

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