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SYNTHESIS AND CHARACTERIZATION OF ETHYLPHENYLSTANNYLENE DERIVATIVES OF ETHYLENE GLYCOL, CYTIDINE AND 3,5-DIIODOSALICYLIC ACID *

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Summary

The synthesis and characterization of the ethylphenylstannylene derivatives of ethylene glycol, cytidine, and 3,5-diiodosalicylic acid are described.

Introduction

Ethylphenyltin oxide is almost insoluble in water and in organic solvents, but is nevertheless characterized by a T/C value of 147% against P388 lymphocytic leukaemia in mice [1]. We have prepared the ethylphenylstannylene derivatives of ethylene glycol, cytidine, and 3,5-diiodosalicylic acid in the hope of enhancing the bio-availability of the ethylphenyltin oxide moiety. Furthermore, the five- and six-membered rings present in these compounds might influence favourably their rate of hydrolysis, which seems to play a fundamental role in the reaction process of platinum compounds with DNA [2] and hence on their anti-tumour properties: too good leaving groups on the platinum complexes lead to toxic compounds, whereas bad leaving groups lead to inactive compounds. Chloride and carboxylate anions lie in between these two extremes, and are used for first and second generation anti-tumour platinum drugs [3]; our hope is that the organotin diolates and carboxylates discussed in this paper will have similarly favourable rates of hydrolysis. The results of in vitro and in vivo tests will be presented elsewhere.

Synthesis of ethylphenyltin dibromide

Ethylphenyltin oxide has been prepared previously by Bulten [1]. However, spectral properties of ethylphenyltin oxide or of the intermediate ethylphenyltin dibromide have not been reported before, and we present them below.

* Dedicated to Prof. J. Tirouflet on the occasion of his retirement.

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TABLE 1

270 MHz ^{1}H NMR SPECTRUM OF A $CDCl_3$ SOLUTION (10 mg/0,5 l) OF ETHYLPHENYLTIN DIBROMIDE (1)

H	δ (ppm)	intensity	J (Hz)	pattern
CH_3	1.47	3.03	$^3J(H^a-H^b) = 8$	triplet
CH_2	2.03	1.97		quartet
Phenylprotons				
ortho	7.65–7.62	2.06	$^3J(Sn-H) = 38$	
meta, para	7.52–7.47	2.93		

	J ($^{117/119}Sn-^1H$) (Hz)
$^3J(H^a-Sn)$	144/151
$^2J(H^b-Sn)$	53/57

TABLE 2

67,89 MHz ^{13}C NMR-SPECTRUM OF A $CDCl_3$ SOLUTION (0,3 ml/2 ml) OF ETHYLPHENYLTIN DIBROMIDE (1), DECOUPLED. (The numbering of the different atoms is given in Table 1.)

C	δ (ppm)	J (Hz)
a	10.02	
b	18.59	$^1J(C_b-Sn) = 476$
ipso	138.70	
ortho	134.66	$^2J(C_{ortho}-Sn) = 61$
meta	131.30	$^3J(C_{meta}-Sn) = 70$
para	129.37	$^4J(C_{para}-Sn) = 20$

The assignment of the signals of the different carbon atoms was made by a comparative study with existing data on analogous tin compounds [4], and additivity rules.

TABLE 3

70 eV EI MASS SPECTRUM OF ETHYLPHENYLTIN DIBROMIDE (1)

Ion	M	I (%)
Sn^+	120	23
$SnPh^+$	197	58
$SnBr^+$	199	100
$SnPhEt^+$	226	0.4
$SnPhBr^+$	276	4
$SnBr_2^+$	278	0.6
$SnPhEtBr^+$	305	17
$SnEtBr_2^+$	307	< 0.3
$SnPhBr_2^+$	355	39
$SnPhEtBr_2^+$	384	0.8

Ethylphenyltin dibromide, **1**, was prepared from ethyltriphenyltin and bromine in methanol. Its spectroscopic properties are given in Tables 1 to 4.

Synthesis of ethylphenyltin oxide

Ethylphenyltin oxide, **2**, has been prepared by the reaction of a NaOH solution in water/methanol with ethylphenyltin dibromide. Its IR-spectrum (see Table 5)

TABLE 4

IR-SPECTRUM (NaCl) OF ETHYLPHENYLTIN DIBROMIDE (**1**)

Energy (cm^{-1})	Assignment
3060	C–H aromatic stretch
2995	asym. stretch CH_3
2920	asym. stretch CH_2
2865	sym. stretch CH_3
1480	scissoring CH_2
1450	C=C ring stretch
1430	asym. bending CH_3
1380	sym. bending CH_3
1300 and 1225	twisting + wagging CH_2
1183	C–H deformation of Sn–Et
1069	C–H deformation of Sn–Ph
730	rocking CH_2
695	C–H out of plane

clearly shows that the tin–phenyl and tin–ethyl bonds are still present, and furthermore a O–Sn–O stretching band is visible, confirming the polymeric structure of the oxide (cf. ref. 5 for a comparison with di-n-butyltin oxide).

The 70 eV EI mass spectrum of ethylphenyltin oxide shows four important tin-containing fragment-ions (Sn^+: 30%; SnH^+: 9%; $PhSn^+$: 70%, and Ph_2EtSn^+ [recombination]: 13%, compared to the base peak, Bu^+). The experimentally observed low intensities are due to the low volatility of this compound.

The Mössbauer spectrum of ethylphenyltin oxide, compound **2**, ($IS = 0.98$ mm/s; $QS = 2.08$ mm/s) is analogous to those found for other diorganotin oxides (n-Bu_2SnO: 0.98; 2.06 mm/s [7]; Et_2SnO: 0.99; 2.02 mm/s [8]).

The structure of compound **2** was confirmed by its reaction with ethylene glycol, to yield 2-ethyl-2-phenyl-1,3-dioxa-2-stannacyclopentane, **3**.

TABLE 5

IR-SPECTRUM (3 mg/63,9 mg KBr) OF ETHYLPHENYLTIN OXIDE (**2**)

Energy (cm^{-1})	Assignment
3060	C–H aromatic stretch
2960	asym. stretch CH_3
2940	asym. stretch CH_2
2860	sym. stretch CH_3
1480	scissoring CH_2
1450	C=C ring stretch
1430	asym. bending CH_3
1375	sym. bending CH_3
1190	C–H deformation of Sn–Et
1075	C–H deformation of Sn–Ph
725	rocking CH_2
700	C–H out of plane bend
670	ν (O–Sn–O) [6]

TABLE 6

IR-SPECTRUM (2 mg/ 67.9 mg KBr) OF 2-ETHYL-2-PHENYL-1,3-DIOXA-2-STANNACYCLOPENTANE (3)

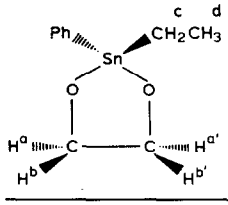
Energy (cm^{-1})	Assignment
3040	C–H aromatic stretch
2920	asym. stretch CH_3
2860	sym. stretch CH_3
1480	scissoring CH_2
1450	C=C ring stretch
1425	asym. bending CH_3
1190	C–H deformation of Sn–Et
1060	*C–O–Sn asym. stretch in five membered ring* [10]
890	*C–O–Sn sym. stretch in five membered ring* [10]
730	rocking CH_2
695	C–H out of plane bend
670	*ν(O–Sn–O) [6] [11]*
660	C=C ring bend

Synthesis and characterization of 2-ethyl-2-phenyl-1,3-dioxa-2-stannacyclopentane

Compound **2** reacts with ethylene glycol in benzene and the water formed can be distilled off as the benzene-water azeotrope, (cf. ref. 9) to yield 2-ethyl-2-phenyl-1,3-dioxa-2-stannacyclopentane, **3**. The IR spectrum of **3** shows bands due to the presence of the C–O–Sn and O–Sn–O groups (see Table 6). The 270 MHz ^1H NMR spectrum of a $CDCl_3$ solution of 2-ethyl-2-phenyl-1,3-dioxa-2-stannacyclopentane, **3**, clearly shows the diastereotopic ethylene protons of the five-membered ring (AA′BB′ pattern around 3.7 ppm). The other observed signals are shown in Table 7.

TABLE 7

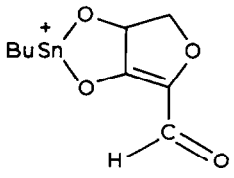
270 MHz ^1H NMR DATA OF A $CDCl_3$ SOLUTION (13 mg/0,5 ml) OF 2-ETHYL-2-PHENYL-1,3-DIOXA-2-STANNACYCLOPENTANE (3)



H	δ (ppm)	J (Hz)	pattern
c	1.50	$^3J(H^c–H^d) = 7$	quartet
d	1.30		triplet
Phenyl protons			
ortho,	7.53–7.56	$^3J(Sn–H) = 22$	
meta, para	7.36–7.38		

Synthesis and characterization of the ethylphenylstannylene derivative of cytidine

The ethylphenylstannylene derivative, **4**, of cytidine was prepared in the same way as compound **3**, but in methanol as solvent. Its 70 eV EI mass spectrum exhibits only two fragment-ions, Sn^+ and $PhSn^+$, possibly again due to the low volatility of the compound. In contrast, the mass spectra of the di-n-butylstannylene derivatives of adenosine (m.p. 207–210 °C), which exhibits a doublet in its Mössbauer spectrum centered at 1.00 mm/s (*QS* 2.12 mm/s), and of uridine (m.p. 236–239 °C; *IS* 1.26 mm/s; *QS* 3.05 mm/s) contain much more useful information: the 70 eV El mass spectrum of the di-n-butylstannylene derivative of uridine exhibits the molecular ion minus a hydrogen ($m/z = 475$, $I < 1\%$), and this loses butene (419, 2%) or octane (361, 14%) and oxygen (345, 7%). An ion is found at m/z 305 (50%) that could be



and this loses CH_2 (291, 7%), CH_2 again (277, 5%), then formaldehyde (221, 21%) or formic acid (205, 28%). There is also an ion at $m/z = 307$ (21%), that loses CH_2 (293, 21%) then propene (251, 14%). Bu_2SnH^+ (235, 14%), Bu_2Sn^+ (234, 7%), $BuSnH_2^+$ (179, 57%), $BuSn^+$ (177, 100%), $PrSnH_2^+$ (165, 50%), $PrSn^+$ (163, 21%), $SnOH^+$ (137, 28%), SnH^+ (121, 64%) and Sn^+ (120, 28%) are also present.

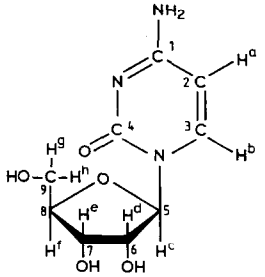
The 70 eV EI mass spectrum of the di-n-butylstannylene derivative of adenosine is analogous to that just described: it exhibits the molecular ion minus a hydrogen (500, 18%) that loses octane (386, 4%), then water (368, 86%), with again additional ions at $m/z = 307$ (18%), 305 (46%), 293 (18%), 291 (9%), 235 (14%), 234 (14%), 221 (14%), 205 (22%), 193 (27%), 191 (36%), 179 (64%), 177 (82%), 165 (41%), 163 (27%), 137 (41%), 121 (45%), and 120 (18%). The base peak is at $m/z = 254$, an ion not present in the mass spectrum of the di-n-butylstannylene derivative of uridine, and this overlaps with other ions at $m/z = 253$ and 256. The reason for the presence of such an intense fragment-ion at $m/z = 254$ is not clear: a possible structure might be adenine-Sn^+, which would explain why it is not seen in the mass spectrum of the di-n-butylstannylene derivative of uridine, but this would mean that a rearrangement of the adenine moiety to tin has occurred. If this were the case, a uracil-Sn^+ ion at $m/z = 231$ (that is not observed experimentally) would be expected in the mass spectrum of the di-n-butylstannylene derivative of uridine.

The Mössbauer spectrum of the ethylphenylstannylene derivative, **4**, of cytidine shows two doublets (IS_1 1.09 mm/s; QS_1 2.35 mm/s; IS_2 0.67 mm/s; QS_2 1.92 mm/s), owing to the presence of the two expected diastereoisomers, with either the phenyl or ethyl group lying under the ribose ring.

The IR spectrum of compound **4** between 800 and 1100 cm^{-1} shows bands from the functional groups of the ribose moiety and the pyrimidine base. However, at 900 cm^{-1} and 1075 cm^{-1}, there are two bands that are absent from the spectrum of free cytidine and that may be due to the presence of the C–O–Sn group in compound **4**. These values are in agreement with those observed for compound **3**, although they are much more clearly seen there (see Table 6).

TABLE 8

67.89 MHz ^{13}C NMR SPECTRUM (UNCOUPLED) OF A DMSO-d_6 SOLUTION (40 mg/2 ml) OF THE ETHYLPHENYLSTANNYLENE DERIVATIVE OF CYTIDINE (**4**)



Free cytidine			Compound **4**	
C	δ (ppm) (4)	δ (ppm) (exp)	C	δ (ppm)
3	166.7	165.6	3′	165.4
4	156.9	155.4	4′	155.3
1	142.8	141.5	1′	141.5
2	95.7	93.8	2′	93.8
5	90.1	89.2	5′	91.6
8	85.3	84.0	8′	86.5
7	75.1	74.0	7′	79.1 [a]
6	70.6	69.4	6′	73.2 [a]
9	61.9	60.6	9′	61.7
			Et: CH_2	13.7 [a]
			CH_3	10.1 [a]
			Ph: *ipso*^{1}	144.2
			ipso^2	141.9
			ortho^1	136.7
			ortho^2	135.8
			meta^1	129.3
			meta^2	128.9
			para^1	128.6
			para^2	128.3

[a] Signal split owing to the presence of two diastereomers (see text)

The ^{13}C NMR spectra of DMSO-d_6 solutions of cytidine and of compound **4** are compared in Table 8. In the latter case, besides each signal of free cytidine, a signal due to compound **4** can be seen, except for C(1) and C(2), which is due either to the co-crystallisation of cytidine with **4**, or to partial hydrolysis by the water present in the very hygroscopic DMSO. For the ribose ring, these are shifted towards lower field. The C(6) and C(7) signals are the more shifted (3.8 and 5.1 ppm, respectively), and the C(5) and C(8) signals are less shifted (2.4 and 2.5 ppm). The signal of C(9) is only shifted by 1.1 ppm. This shows that the hydroxyl groups of C(6) and C(7) have reacted with ethylphenyltin oxide. The expected signals of the carbon atoms of the ethyl and phenyl groups are also clearly seen (see Table 8). The low solubility of compound **4** accounts for the low signal-to-noise ratio; because of this couplings between ^{13}C and ^{117}Sn and ^{119}Sn are not observed. Furthermore, the signals of the C(6) and C(7) atoms of the ribose ring in compound **4** are split, as was expected because of the presence of two diastereoisomers. The signals of the carbon atoms of

the phenyl and ethyl groups of compound **4** are also split for the same reason. The signals of the carbon atoms of the pyrimidine base are hardly shifted at all, which confirms that the ethylphenylstannylene moiety lies under the ribose ring, far from the pyrimidine base, and is therefore not bound to carbon C(9).

The ^{1}H 270 MHz NMR spectrum of compound **4** also shows that free cytidine is present, but is very complicated, especially in the region of the protons of the ribose moiety. Wagner was unable to interpret the high resolution spectrum of the di-n-butylstannylene derivative of cytidine [12].

Synthesis and characterization of the ethylphenylstannylene derivative of 3,5-diiodosalicylic acid

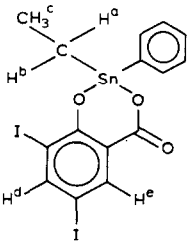
The ethylphenylstannylene derivative of 3,5-diiodosalicylic acid, compound **5**, was also prepared analogously. Its ^{1}H NMR, mass and IR spectra are given in Tables 9, 10 and 11. Because of its low solubility, its ^{13}C NMR spectrum could not be recorded.

As for compound **3**, the chemical shift difference between the methyl and methylene protons of the ethyl group of compound **5** in the ^{1}H NMR spectrum is very small indeed (see Table 9). Furthermore, Sn–H couplings are present, and the methylene protons are diastereotopic. This accounts for the fact that no precise determination of these chemical shifts could be achieved. The Mössbauer spectrum of compound **5** exhibits the expected doublet ($IS = 0.77$ mm/s; $QS = 2.40$ mm/s).

In the IR spectrum of compound **5** (see Table 10), the C=O stretch band is absent. This may be due to the fact that, in the solid state, the carbonyl group coordinates to the tin atom of another molecule to bring about sp^3d^2 hybridisation.

TABLE 9

270 MHz ^{1}H NMR OF A DMSO-d_6 SOLUTION (13,4 mg/0,5 ml) OF THE ETHYLPHENYLSTANNYLENE DERIVATIVE of 3,5-DIIODOSALICYLIC ACID, (**5**)



H	δ (ppm)	J (Hz)	pattern
a, b	≈1.30	^2J(H ^{a}–H ^{b}) ≈ 34	doublet of quartets for both H atoms
c	1.15	^3J(H ^{a}–H ^{c}) ≈ 5 ^3J(H ^{b}–H ^{c}) ≈ 5	triplet
d	8.14		
e	7.37		
Phenyltin protons			
ortho		7.97	
meta, para		7.82	

TABLE 10

IR-SPECTRUM (1,5 mg/65,2 mg KBr) OF THE ETHYLPHENYLSTANNYLENE DERIVATIVE OF 3,5-DIIODOSALICYLIC ACID (**5**)

Energy (cm^{-1})	assignment
3060	C–H arom. stretch
2960	asym. CH_3 stretch
2920	asym. CH_2 stretch
2860	sym. CH_3 stretch
1550	C=C ring stretch of 1,2,3,5-tetrasubst. benzene
1440	C=C ring stretch of monosubst. benzene
1420	asym. CH_3 bending
1370	sym. CH_3 bending
1235	*C–O–Sn asym. stretch in 6-ring [10]*
1190	C–H deformation of Sn–Et
1090	*C–O–Sn sym. stretch in 6-ring [10]*
800	CH wagging (isolated H in 1,2,3,5-tetrasubst. benzene)
715	ring deformation
680	*ν(O–Sn–O) [11]*

The bands corresponding to the OH bending (at 1430 cm^{-1} and 1300 cm^{-1}) and the OH out of plane band at 900 cm^{-1}, which were present in the spectrum of 3,5-diiodosalicylic acid, have disappeared, and new bands at 1235 cm^{-1} and 1090 cm^{-1} have appeared in the IR spectrum of compound **5**, corresponding to the presence of C–O–Sn moiety in a six-membered ring, together with the O–Sn–O stretching at 680 cm^{-1}. Its mass spectrum (see Table 11) exhibits the expected peaks with however low intensities compared to that of the base peak, Et^+. Strangely enough, the 70 eV EI mass spectrum of the di-n-butylstannylene derivative, **6**, of 3,5-diiodosalicylic acid [13] (m.p.: 234–237 °C) is quite different from that of compound **5**: the molecular ion is present and exceptionally intense (83%); loss of a butyl group from the molecular ion is not observed, but the ion $HSnC_7H_2O_3I_2^+$ ($m/z = 509$, 33%) is present and loses CO_2 (465, 53%), then HI (337, 33%). Many other ions can be seen: Bu_2SnI^+ (361, 97%), $BuHSnI^+$ (305, 33%), ISn^+ (247, 100%), Bu_2SnH^+ (234, 3%), $BuSnH_2$(179, 30%), $BuSn^+$ (177, 27%), $SnOH^+$ (137, 20%), SnH^+ (121, 43%) and Sn^+ (120, 17%). The Mössbauer spectrum of compound **6** exhibits the expected doublet (*IS* 1.25 mm/s; *QS* 3.23 mm/s); its NMR spectrum could not be recorded even in DMSO, because its too low solubility.

TABLE 11

70 eV EI MASS SPECTRUM OF THE ETHYLPHENYLSTANNYLENE DERIVATIVE OF 3,5-DI-IODOSALICYLIC ACID (**5**) (Base peak: 29 (Et^+))

Ion	*M*	*I* (%)
Sn^+	120	3.4
$SnPh^+$	197	3.9
$SnPhEtI^+$	353	2.7
$SnHC_7H_2O_3I_2^+$	509	0.1
$SnEtC_7H_2O_3I_2^+$	537	0.7
$SnPhEtC_7H_2O_3I_2^+$	614	0.01

The 70 eV EI mass spectrum of the di-n-butylstannylene derivative, **7**, of salicylic acid (m.p.: 227–229 °C) [13] is again quite different from those of compounds **5** and **6**, because it exhibits a rather intense ion exhibiting the isotopic distribution of a ditin ion at $m/z = 512$ (I = 35%), that might be $(C_7H_4O_3Sn)_2^+$; besides the molecular ion (MI) (370, 30%) and an ion at $MI + 1$ (27%), the $BuSnC_7H_4O_3^+$ ion is present but of low intensity (313, 1%), whereas $HSnC_7H_4O_3^+$ is intense (257, 81%) and loses CO_2 (213, 100%). An ion at $m/z = 212$ is also present (46%), and an unidentified one at $m/z = 184$ (34%), together with $BuSn^+$ (9%), $SnOH^+$ (19%), SnH^+ (26%) and Sn^+ (33%). The Mössbauer spectrum of compound **7** is characterized by an isomer shift of 1.20 mm/s and a quadrupole splitting of 3.1 mm/s, comparable to those found for compound **6**. Its solubility is again too low even in DMSO to permit recording of a satisfactory proton NMR spectrum.

Experimental

Synthesis of ethylphenyltin dibromide (1)

To 10.00 g (0.0264 mole) ethyltriphenyltin suspended in 50 ml methanol, bromine was added dropwise (1 drop every 2 s) from a buret. After the addition of 1.35 ml (0.0264 mole) the decoloration was slower and so 1 drop was added every 10 s. After the addition of 2.45 ml (0.0476 mole), the solution was colourless and no precipitate remained. The last 0.15 ml bromine were added and a yellow colour remained for a longer period and disappeared only after some time. The solvent was evaporated off and the residual mixture kept at 45 °C under 0.4 Torr to constant weight. 10.45 g. of a yellow-brown liquid was obtained, which gave a white precipitate with ethanolic silver nitrate. TLC on SiO_2 with hexane + 5% CH_2Cl_2 as eluant gave only one spot, with $R_f = 0.20$.

Synthesis of ethylphenyltin oxide, compound 2

To a solution of 2.28 g (57.1 mmole) NaOH in a mixture of 250 ml water and 250 ml methanol was added a solution of 9.63 g. (25 mmole) ethylphenyltin dibromide in 150 ml methanol (at 1 drop/s). The fine precipitate formed was filtered off on a Büchner funnel, washed with 300 ml of water, then with 300 ml of ether, and finally with 300 ml of methanol, and left on the Büchner funnel under reduced pressure for 30 min to yield 5.08 g of a white powder (yield: 84%). Because of its low solubility NMR spectra could not be obtained. Characterization was by IR, mass and Mössbauer spectroscopy.

Synthesis of substituted 1,3-dioxa-2-stannacycloalkanes

The procedure described in ref. 9 was used to prepare 2-ethyl-2-phenyl-1,3-dioxa-2-stannacyclopentane, **3** (4 mmole; 100 ml benzene), and the one described in ref. 12, to prepare the ethylphenylstannylene derivative, **4**, of cytidine (6.2 mmole; 160 ml methanol). TLC on SiO_2 (elution with hexane + 15% CH_2Cl_2 for **3**, and with methanol for **4**) caused the hydrolytic opening of the five-membered ring. However, a DMSO solution of compound **4** (10 mg/0.5 ml) remains clear for at least two weeks, which means that no ethylphenyltin oxide, which is insoluble in that solvent, is formed.

Synthesis of the ethylphenylstannylene derivative of 3,5-diiodosalicylic acid (5)

1.638 g 3,5-diiodosalicylic acid (4.2 mmole) and 1.03 g ethylphenyltin oxide (4.2 mmole) was added to a mixture of 200 ml benzene and 15 ml methanol and the mixure refluxed for 1 h at 65 °C. 26 ml of the solvent were distilled off at 67 °C with a Dean–Stark head, then 39 ml between 67 and 80 °C and finally 100 ml of benzene at 80 °C. The white suspension filtered off on the Büchner funnel, washed with dry benzene and left on the Büchner funnel under reduced pressure for 1 h. 1.26 g of a white solid (m.p. > 350 °C) was obtained. The filtrate was evaporated and the solid residue dried in a desiccator (P_2O_5) to yield a second fraction (0.97 g., m.p. > 350 °C). The infra-red and mass spectra of both fractions were identical, and so were considered to be identical. Again TLC and SiO_2 (elution with methanol) caused hydrolysis of the ethylphenylstannylene derivative of 3,5-diiodosalicylic acid.

The ^1H NMR spectra were recorded on a Bruker AM 270 instrument with TMS as internal standard. The mass spectra were recorded on a MS 902 S instrument of AEI (source temperature: 200 °C, pressure: 10^{-7} Torr).

The Mössbauer spectra were recorded on an Elscint MVT-4 instrument on Promeda ($Ca^{119}SnO_3$, source from Amersham, sample temperature: −196 °C). The IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. The melting points were determined on a Reichert-Thermopan melting point microscope.

TLC was performed with Polygram SIL G/UV 254 plates of Macherey–Nagel.

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