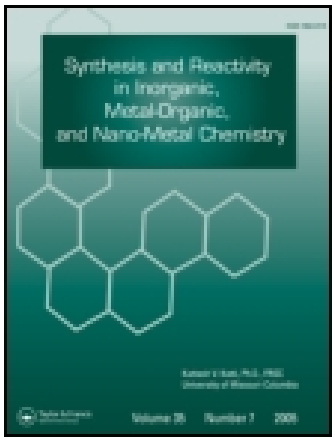

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Synthesis, Spectral and In Vitro Biological Studies of Bis-Triorganogermyl(substituted)propionates of Triarylantimony(V) X-ray Studies of Triphenylgermyl-n-propyl Propionic Acid

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New compounds of Bis-triorganogermyl(substituted) propionates of triarylantimony(V) with general formula ($^{1}R_3$-GeCHR^{2}CH$_2$CO$_2$)$_2$SbAr$_3$ have been synthesized and characterized by various techniques such as elemental analyses; FT-IR, ^{1}HNMR, ^{13}CNMR and mass spectrometry. All these compounds have distorted trigonal bipyramidal geometry around antimony in both solid states as well as in non-coordinated solvents. The single X-ray analysis of precursor triphenylgermyl-n-propyl propionic acid (Ph$_3$GeCH-(n-C$_3$H$_7$)CH$_2$COOH) have revealed dimeric structure of molecule through strong hydrogen bonding in conventional manner in which germanium has slightly distorted tetrahedral geometry. Selected numbers of compounds screened against different strains of bacteria and fungus show good activity.

Keywords antimony carboxylates, germanium, X-ray studies, biological studies

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INTRODUCTION

Triorganoantimony(V) carboxylates of the type $R_3Sb(O_2CR)_2$ have been studied because of their wide range of biological and catalytic applications.[1–3] Their structures have been studied with the help of vibrational spectroscopy and X-ray diffraction.[4] Organogermanium compounds are another class that has a wide range of biological applications.[5,6] When both organogermanium and organoantimony compounds are coupled then the activity of these complexes is enhanced. The bioassay results showed that triarylantimony compounds containing germanium have relatively higher antitumour activities than the simple triphenylgermyl propionic acid.[7] In order to investigate their further biological activity and structure, we present in this paper the synthesis, structural characterization and antimicrobial studies of triorganogermyl (substituted) propionates of triarylantimony(V) which contain two active centers, namely the triarylantimony moiety and triorganogermyl substituted propionic acid. At the same time we are interested to study the nature of bonding in triphenylgermyl-n-propyl propionic acid in which germanium atom adopted slightly distorted tetrahedral geometry.

RESULTS AND DISCUSSION

The different triorganogermyl substituted propionic acids have been synthesized according to the reported method.[8] The title compounds (**1–11**) were synthesized as shown in (Eq. (1)) by stirring 2:1 molar ratio of triorganigermyl substituted propionic acid and triarylantimony(V) dibromide in the presence of triethylamine in toluene under mild conditions.[9]

$$2\,{}^{1}R_3GeCHR^2CH_2CO_2H + Ar_3SbBr_2 \xrightarrow[\text{r.t.8h}]{Et_3N,\ \text{Toluene}} ({}^{1}R_3GeCHR^2CH_2CO_2)_2Sb(Ar)_3 + Et_3N\cdot HCl \quad (1)$$

$R^1 = Ph,\quad Ar = p-CH_3C_6H_4$ (**1 − 6**)

$R^1 = p-CH_3C_6H_4,\quad Ar = Ph$ (**7 − 11**)

$R^2 = p-ClC_6H_4$ (**1**), $o-CH_3OC_6H_4$ (**2**),

$p-CH_3OC_6H_4$ (**3**, **8**), $m-CH_3OC_6H_4$ (**9**)

$p-CH_3C_6H_4$ (**4**, **7**), $n-C_3H_7$ (**5**), CH_3 (**6**, **10**), C_6H_5 (**11**).

The products were purified by crystallization from CH_2Cl_2 and petroleum ether. The yield obtained is 70–80%. All compounds are white powder, which are easily soluble in $CHCl_3$, CH_2Cl_2 and DMSO. They are unaffected by atmospheric moisture showing no decomposition over a period of several weeks. The physical data of synthesized compounds are given in Table 1.

Infrared Spectroscopy

The infrared spectra of these compounds have been recorded in the range of 4000–400 cm^{-1}. Tentative assignments have been made on the basis of earlier publications,[10,11] and the important data are listed in Table 2. The formation of the complex is evidenced by the absence of the broad band of ν(OH) in the 3500–3300 cm^{-1} region by deprotonation and coordination of germyl substituted propionic acid with antimony. Further, the IR data support the molecular constitution of title compounds. In the majority of organoantimony (V) compounds, the antimony has generally a coordination number of five. Because of the vacant 5d orbital, antimony atom can accept lone electron pairs of ligands and may have a coordination number of six or seven.[12,13] When there are interactions between the antimony atom and carbonyl oxygen atoms of the carboxylates groups, the asymmetric absorption vibration frequencies $\nu_{asy}(CO_2)$ of carbonyl groups decrease, and the symmetric absorption vibration frequencies $\nu_{sym}(CO_2)$ increase. Therefore, the difference, $\Delta\nu(CO_2)$ decrease.[14] In the IR spectra of synthesized compounds, the carboxylates bands are observed in the characteristic regions: $\nu(CO_2)_{asym}$ between 1603 to 1666 cm^{-1} and $\nu(CO_2)_{sym}$ between 1308 to 1360 cm^{-1}, respectively. On the basis of the difference $\Delta\nu(CO_2)$, these compounds can be divided into two classes. Compounds (**4**) show low $\Delta\nu$ value, ca.279 cm^{-1}, while all other compounds show high $\Delta\nu$ values between 323–347 cm^{-1}, indicating stronger interactions between the carbonyl oxygen atoms of the carboxylates groups and the antimony atom in the former and weaker interactions or no interaction between the antimony atom and the carbonyl oxygen atoms of carboxylates of the latter groups.[15] In addition, the frequencies ν(Sb-C) appeared between 459–484 cm^{-1} consistent with literature. [16]

NMR SPECTROSCOPY

^{1}H NMR

The chemical shift of various protons in the compounds is listed in Table 3. All protons in the compounds have been identified by intensity and multiplicity pattern and the total number of protons calculated from the integeration curve is in agreement with the expected molecular composition. The signals of the aromatic protons of substituted phenyl group of the germyl and antimony moiety are complex and are observed as multiplet in the region 6.8–7.2 ppm, while the substituent on the phenyl group observed as sharp singlet in the region 2.14–2.54 ppm, respectively. Another characteristic feature of these compounds is presence of GeCH chiral center and CH_2 is a prochiral center and three hydrogen of the unit $GeCHCH_2$, corresponds to an ABX system. The subspectral analysis of the ABX spectra revealed that the eight-lines portion (two pseudo-quartets) of the spectrum is made up of two AB sub-spectra in the range of 2.12–2.81 ppm, whereas the X part of the spectrum consists of four detectable lines with equal intensity in the range of 3.15–3.82 ppm. The interesting observation for this ABX system is diasterotopy. The two protons of methylene group (A, B) being diasterotopic, coupled to the third proton (X) of the chiral center giving three chemical shifts, υ_A, υ_B and υ_X and three suitable coupling constants, J_{AB}, J_{AX} and J_{BX}, as shown in Table 3.[17]

^{13}C NMR

^{13}C NMR spectral data of triorganoantimony carboxylates containing germanium is given in Table 4. The number of signals found corresponds with the presence of magnetically non-equivalent carbon atoms, which was assigned by comparison with the experimental chemical shift with those calculated from the incremental method.[18] The position of carboxylate carbon in all synthesized compounds move to a lower field, as compared with the germyl substituted propionic acid ligand indicating participation of carboxylic group in coordination to antimony atom. The group with strong electron withdrawing effect e.g., methoxy group attached to phenyl ring (R^1) resonate at low field, while the methyl substituent on the phenyl group of germyl and antimony moiety appear at 21.21–22.05 ppm and 21.56–22.85 respectively.

MASS SPECTROMETRY

The main mass spectral data of representative compounds (**1**, **10**) are listed in Table 5. Mass spectral data support the

TABLE 1
Physical data of triorganoantimony derivatives of general formula: $R^1_3GeCHR^2CH_2COO)_2SbAr_3$

Comp. no.	R^1	R^2	Ar	Molecular formula	M. Wt.	M.P. °C	Yield %	Elemental analysis found (Calcd.) C %	Elemental analysis found (Calcd.) H %
1	C_6H_5	*p*-ClC_6H_4	*p*-$CH_3C_6H_4$	$C_{75}H_{65}O_4Ge_2SbCl_2$	1368	143–144	71	65.73 (65.78)	4.74 (4.75)
2	C_6H_5	*o*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4$	$C_{77}H_{71}O_6Ge_2Sb$	1359	185–188	64	67.96 (67.99)	5.20 (5.22)
3	C_6H_5	*p*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4$	$C_{77}H_{71}O_6Ge_2Sb$	1359	225–227	81	67.94 (67.99)	5.20 (5.22)
4	C_6H_5	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	$C_{77}H_{71}O_4Ge_2Sb$	1327	185–187	76	69.65 (69.63)	5.38 (5.35)
5	C_6H_5	n-C_3H_7	*p*-$CH_3C_6H_4$	$C_{69}H_{71}O_4Ge_2Sb$	1231	248–249	59	67.28 (67.26)	5.69 (5.76)
6	C_6H_5	CH_3	*p*-$CH_3C_6H_4$	$C_{65}H_{63}O_4Ge_2Sb$	1175	251–252	65	66.40 (66.38)	5.31 (5.36)
7	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	C_6H_5	$C_{80}H_{77}O_4Ge_2Sb$	1369	235–237	65	70.13 (70.12)	5.64 (5.62)
8	*p*-$CH_3C_6H_4$	*p*-$CH_3OC_6H_4$	C_6H_5	$C_{77}H_{77}O_6Ge_2Sb$	1402	189–190	63	68.49 (68.47)	5.51 (5.49)
9	*p*-$CH_3C_6H_4$	*m*-$CH_3OC_6H_4$	C_6H_5	$C_{80}H_{77}O_6Ge_2Sb$	1402	211–213	71	68.65 (68.49)	5.60 (5.64)
10	*p*-$CH_3C_6H_4$	CH_3	C_6H_5	$C_{80}H_{69}O_4Ge_2Sb$	1217	209–212	75	67.10 (67.05)	5.65 (5.66)
11	*p*-$CH_3C_6H_4$	C_6H_5	C_6H_5	$C_{78}H_{73}O_4Ge_2Sb$	1341	213–215	85	69.77 (69.79)	5.41 (5.44)

TABLE 2
Characteristics IR absorption frequencies in cm^{-1} of triarylantimony carboxylate derivatives with general formula: $R^1_3GeCHR^2CH_2COO)_2SbAr_3$

Comp.	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	ν(Ge-C)	ν(Sb-C)	ν(Sb-O)
1	1658	1335	323	652	476	567
2	1660	1313	347	657	470	583
3	1655	1321	334	658	469	520
4	1642	1363	279	667	484	578
5	1665	1340	325	657	482	585
6	1656	1317	339	645	479	563
7	1653	1313	340	659	459	590
8	1655	1323	332	660	461	591
9	1661	1327	325	648	467	588
10	1649	1310	339	651	462	573
11	1654	1326	328	654	461	563

TABLE 3
^{1}H NMR data[a–f] of triarylantimony(V) derivatives $R^1_3GeCHR^2CH_2COO)_2SbAr_3$

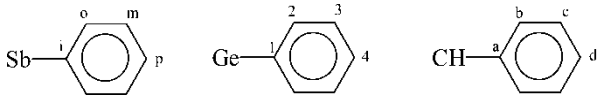
Comp.	CH	CH_2	R^2	ArSb	R^1Ge
1	2.98–3.12 (m, 2H)	2.29–2.41 (m, 4H)	7.11–7.14 (m, 8H)	6.82–7.09 (m, 12H) 2.33 (s, 9H)	7.22–7.35 (m, 30H)
2	3.26 [q,^3J(7.3)]	2.62 [dd,^3J(14.9,6.8)] 2.81 [dd,^3J(14.9,5.1)]	7.0–7.15 (m, 14H) 3.19 (s,6H)	6.85–6.91 (m, 12H) 2.38 (s, 9H)	7.21–7.29 (m, 30H)
3	3.38 [q,^3J(7.1)]	2.59 [dd,^3J(15.8,7.1)] 2.75 [dd,^3J(15.8,4.9)]	7.15–7.19 (m, 14H)	6.65–6.85 (m, 12H) 2.37 (s, 9H)	7.21–7.35 (m, 30H)
4	3.38 [q,^3J(6.9)]	2.55 [dd,^3J(15.6,6.7)] 2.65 [dd,^3J(15.6,4.7)]	6.85–6.89 (m, 14H) 2.25 (s, 6H)	6.67–6.78 (m, 12H) 2.35 (s, 9H)	7.18–7.25 (m, 30H)
5	3.29 [q,^3J(7.4)]	2.29 [dd,^3J(15.5,6.9)] 2.36 [dd,^3J(15.5,5.8)]	0.81 [t,^3J(7.0)] 2.07–2.61 (m, 8H)	7.14–7.29 (m, 12H) 2.31 (s, 9H)	7.34–7.55 (m, 30H)
6	3.15–3.33 (m, 2H)	2.24–2.61 (m, 4H)	8.5 [d,^3J(6.9)]	6.84–6.99 (m, 12H) 2.42 (s, 9H)	7.12–7.40 (m, 30H)
7	3.35–3.41 (m, 2H)	2.65–2.85 (m, 4H)	7.05–7.18 (m, 8H) 2.27 (s, 6H)	6.8–6.85 (m, 15H)	7.21–7.32 (m, 24H) 2.31 (s, 9H)
8	3.38–3.45 (m, 2H)	2.60–2.75 (m, 4H)	7.15–7.19 (m, 8H) 3.81 (s, 6H)	6.6–6.7 (m, 15H)	7.2–7.5 (m, 24H) 2.39 (s, 6H)
9	3.35–3.41 (m, 2H)	2.69–2.72 (m, 4H)	6.9–7.23 (m, 8H) 3.75 (s, 6H)	6.51–6.80 (m, 15H)	7.1–7.4 (m, 24H) 2.29 (s, 6H)
10	2.95–3.21 (m, 2H)	2.42–2.71 (m, 4H)	0.91 (d, 6H) ^3J[7.1]	6.8–6.95 (m, 15H)	7.20–7.35 (m, 24H) 2.31 (s, 6H)
11	3.38–3.40 (m, 2H)	2.57–2.61 (m, 4H)	6.61–7.11 (m, 10H)	7.12–7.2 (m, 15H)	7.12–7.2 (m, 24H) 2.24 (s, 6H)

[a] In $CDCl_3$ at 295 K.
[b] Chemical shifts in ppm. $^nJ(^1H - ^1H)$ in Hz.
[c] Multiplicity is given as s = singlet, d = doublet, dd = doublet of double, m = multiplet.
[d] R^1 = Ph Ar = *p*-$CH_3C_6H_4$ (**1**–**6**).
[e] R^1 = *p*-$CH_3C_6H_4$ Ar = Ph (**7**–**11**).
[f] R^2 = *p*-ClC_6H_4 (**1**), *o*-$CH_3OC_6H_4$ (**2**), *p*-$CH_3OC_6H_4$ (**3**, **8**), *p*-$CH_3C_6H_4$ (**4**, **7**), n-C_3H_7 (**5**), CH_3 (**6**, **10**), *m*-$CH_3OC_6H_4$ (**9**), C_6H_5 (**11**).

TABLE 4
^{13}C NMR data[(a–c)] of triarylantimony(V) derivatives of general formula $R^1_3GeCHR^2CH_2COO)_2SbAr_3$

Comp.	1	2	3	4	5	6	7	8	9	10	11
R^2a	135.76	130.41	130.24	138.24	23.64	16.84	137.63	133.65	139.57	16.35	140.15
b	131.48	128.54	127.51	133.74	22.48		135.35	129.27	138.61		138.40
c	126.93	115.30	113.85	125.42	—		128.43	157.10	157.81		129.35
d	129.08	157.50	157.42	129.41	14.66		133.61	113.33	113.84		136.17
s	—	54.13	55.47	21.55	—		23.42	55.52	55.92		—
CH	32.17	26.15	31.95	32.34	33.98	31.67	30.01	29.77	32.33	33.62	30.97
CH_2	43.82	37.5	39.24	38.51	38.40	37.89	38.15	38.52	37.91	38.41	40.13
R^1Ge 1	136.06	141.52	141.53	141.12	137.16	139.45	139.02	138.63	140.21	139.37	140.75
2	135.39	136.42	136.45	135.89	136.11	138.31	136.51	137.79	139.37	138.91	139.46
3	127.42	128.41	129.50	130.51	130.23	126.23	129.42	130.59	129.24	129.54	130.61
4	129.87	131.67	133.86	133.85	134.51	132.37	134.35	134.06	134.71	134.62	134.27
s	—	—	—	—	—	—	21.85	21.45	22.05	21.96	21.21
ArSb i	131.04	137.10	141.75	141.51	136.15	139.12	138.51	135.47	138.11	137.61	139.71
o	130.41	134.71	136.41	134.45	135.79	137.41	134.23	132.08	135.46	135.42	135.34
m	126.39	127.25	128.31	126.30	129.20	129.63	127.05	128.87	128.35	128.91	129.81
p	128.76	133.52	133.40	128.54	134.08	133.81	130.42	133.69	133.96	133.67	133.63
s	22.16	21.20	22.10	22.85	21.97	21.43	—	—	—	—	—
CO	177.47	178.69	178.41	177.50	178.53	177.31	178.51	177.21	178.04	177.83	177.29

[a]In $CDCl_3$ at 297 K, Chemical shifts in ppm.
[b]R^1 = Ph, Ar = *p*-$CH_3C_6H_4$ (**1**–**6**), R^1 = *p*-$CH_3C_6H_4$, Ar = Ph (**7**–**11**), s = substituent on phenyl.
[c]R^2 = *p*-ClC_6H_4 (**1**), *o*-$CH_3OC_6H_4$ (**2**), *p*-$CH_3OC_6H_4$ (**3**, **8**), *p*-$CH_3C_6H_4$ (**4**, **7**), n-C_3H_7 (**5**), CH_3 (**6**, **10**). *m*-$CH_3OC_6H_4$ (**9**), C_6H_5 (**11**).



proposed structure of compounds. Fragmentation pattern mainly depends on the structure of the compounds and the properties of the carbonyl group. Decarboxylation and dealkylation from the metal atom are the main breakdown patterns for the synthesized compounds.

X-ray Studies of $(C_6H_5)_3GeCH(n\text{-}C_3H_7)CH_2COOH$

The crystal structure of $(C_6H_5)_3GeCH(n\text{-}C_3H_7)CH_2COOH$ was determined by X-ray diffraction method (Figure 1). Selected bond lengths and bond angles are presented in Table 6. In the crystal structure, the central germanium atom is four coordinated and attained slightly distorted tetrahedral geometry. The C-Ge-C angles lie in the range of 107.61(7) to 112.18(7)°. The Ge-C^3_{sp} distance is significantly longer, 1.972(17), than Ge-$C_{aromatic}$ distance between the germanium and three phenyl rings which are identical within experimental error with mean value of 1.955(17)Å. The two C-O bond lengths [C(1)-O(1): 1.308(2) and C(1)-O(2): 1.230(2)Å] clearly differentiate between single and double bond. The molecule form dimeric pairs about inversion center through strong hydrogen-bonding interaction between carboxylic acid groups. Detail of hydrogen bonding geometry of the title compound is given in Table 7.

BIOLOGICAL STUDIES

The in vitro biological activities of the selected compounds have been determined against various bacteria and fungi by agar well diffusion and agar well dilution protocol.[19,20] The results are given in Table 8 and Table 9.

The antibacterial activity was studied against six different types of bacteria, *E. coli, B. substilis, S. flexinari, S. aureus, P. aeruginosa and S. typhi.* The antibacterial effects of these complexes have been compared with the reference drug (imipenum). The screening tests of organoantimony derivatives containing germanium revealed that all compounds show moderate activity for all types of tested bacteria except compound (**1**), which shows significant activity. The greater activity of this compound is probably due to the presence of chlorine in ligand acid, which itself is antibacterial.[21] The antibacterial data indicate that the nature of aryl group may also affect the activity of the compounds. However, the enhanced antibacterial activity in organoantimony(V) derivatives is associated with the phenyl group and is decreased in substituted triaryl antimony(V) carboxylates containing germanium.[11]

The selected organoantimony(V) derivatives containing germanium have been screened against various fungal

TABLE 5
Mass spectroscopic data of compounds (**1** and **10**)

	Compound (**1**)			Compounds (**10**)	
m/z	Fragments	Intensity (%)	m/z	Fragments	Intensity (%)
1368	$[(C_6H_5)_3GeCH(ClC_6H_4)CH_2CO_2)_2Sb(CH_3C_6H_4)_3]^+$	n.o	1218	$[((CH_3C_6H_4)_3GeCH(CH_3)CH_2COO)_2Sb(C_6H_5)_3]^+$	n.o
881	$[(C_6H_5)_3GeCH(ClC_6H_4)CH_2COO)Sb(CH_3C_6H_4)_3]^+$	29.6	785	$[((CH_3C_6H_4)_3GeCH(CH_3)CH_2COO)Sb(C_6H_5)_3]^+$	21.76
790	$[(C_6H_5)_3GeCH(ClC_6H_4)CH_2COO)Sb(CH_3C_6H_4)_2]^+$	15.4	708	$[((CH_3C_6H_4)_3GeCH(CH_3)CH_2COO)Sb(C_6H_5)_2]^+$	34.64
487	$[(C_6H_5)_3GeCH(ClC_6H_4)CH_2COO)$	25.8	554	$[(CH_3C_6H_4)_3GeCH(CH_3)CH_2COOSb]^+$	15.42
394	$[Sb(CH_3C_6H_4)_3]^+$	18.9	433	$[(CH_3C_6H_4)_3GeCH(CH_3)CH_2COO]^+$	35.78
368	$[(C_6H_5)_2GeCH(ClC_6H_4)CH_2COO)$	38.4	361	$[CH(CH_3)CH_2COOSb(C_6H_5)_2]^+$	18.15
305	$[(C_6H_5)_3Ge]^+$	94.5	332	$[(C_6H_5)_3Sb]^+$	76.20
303	$[Sb(CH_3C_6H_4)_2]^+$	76.5	347	$[(CH_3C_6H_4)_3Ge]^+$	82.14
228	$[(C_6H_5)_2Ge]^+$	64.5	352	$[CHCO_2Sb(C_6H_5)_2]^+$	39.27
226	$[(C_6H_5)_2Ge\text{- }2H]^+$	24.5	275	$[(C_6H_5)_2Sb]^+$	100
212	$[Sb(CH_3C_6H_4)]^+$	100	256	$[(CH_3C_6H_4)_2Ge]^+$	89.32
			252	$[(CH_3C_6H_4)_2Ge - 4H]^+$	57.14
182	$[(CH_3C_6H_4)_2]^+$	65.3	198	$[(C_6H_5)Sb]^+$	64.91
153	$[SbO_2]^+$	5.2	165	$[(CH_3C_6H_4)Ge]^+$	44.28
151	$[(C_6H_5)Ge]^+$	20.6	153	$[SbO_2]^+$	13.72
121	$[Sb]^+$	2.01	121	$[Sb]^+$	12.46
91	$[CH_3C_6H_4]^+$	54.6	91	$[(CH_3C_6H_4)]^+$	59.81
75	$[GeH]^+$	8.01	74	$[Ge]^+$	4.41

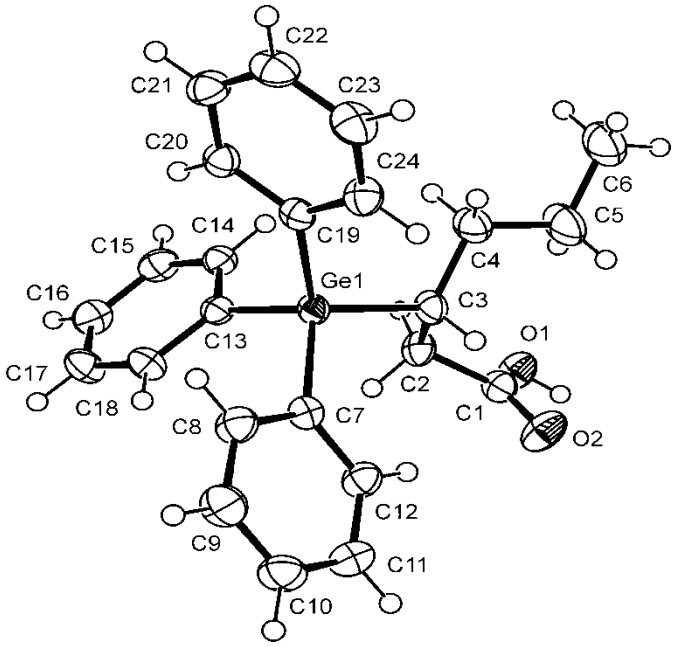


FIG. 1. X-ray structure of $(C_6H_5)_3GeCH(n\text{-}C_3H_7)CH_2COOH$.

strains such as *Trichophyton longifusus, Candida albicans, Aspergillus flavus, Microsporum canis, Fusarium solani and Candida glaberata.* The standard antifungal drugs used were Amphotericin B and Miconazole for comparison test. Screening results of organoantimony(V) show that the substituted triarylantimony(V) derivatives containing germanium show good antifungal activity as seen in Table 9.

Bioactive compounds are often toxic to shrimp larvae. So, cytotoxicity of synthesized compounds was determined by in vitro lethality to shrimp larvae. The shrimp larvae have been extensively used as a tool to monitor the cytotoxicity of samples under study.[22,23] The standard cytotoxic drug used was Etoposide and the results obtained are listed in Table 10. It has been observed that all the test samples show cytotoxicity with LD_{50} values in the range of 7.21–258.61 μg/mL for organoantimony(V) derivatives indicated the diversity in toxic behavior. Data suggested that the compounds (**3**–**5**) possess low toxicity. The majority of compounds shows nearly equal LD_{50} values and are toxic to some extent.

EXPERIMENTAL

Chemicals

Substituted propeonic acids were purchased from Aldrich (Germany), while germanium dioxide (99.9% purity) was procured from the People's Republic of China and were used as received. R_3Sb was synthesized and converted into corresponding dibromide by direct bromination.[19] The solid product was crystallized from a toluene-petroleum ether mixture. All chemical reactions were carried out in organic solvents, which were dried over sodium benzophenone prior to use in accordance to standard methods.[24]

Instrumentation

Elemental analyses were carried out at Midwest Micro-Lab, Indianapolis, Indiana, USA. Melting points were determined

TABLE 6
Selected bond lengths [Å] and bond angles [°] of $(C_6H_5)_3GeCH(n\text{-}C_3H_7)CH_2COOH$

Bond lengths			
Ge(1)-C(7)	1.950(17)	C(2)-C(3)	1.544(2)
Ge(1)-C(19)	1.952(16)	C(3)-C(4)	1.524(2)
Ge(1)-C(13)	1.955(17)	C(10)-C(11)	1.379(3)
Ge(1)-C(3)	1.972(17)	C(11)-C(12)	1.389(3)
O(1)-C(1)	1.308(2)	C(13)-C(18)	1.392(2)
O(2)-C(1)	1.230(2)	C(13)-C(14)	1.399(2)
C(1)-C(2)	1.498(2)	C(14)-C(15)	1.387(3)
Bond angles			
C(7)-Ge(1)-C(19)	109.73(7)	C(3)-C(4)-C(5)	114.94(16)
C(7)-Ge(1)-C(13)	107.61(7)	C(6)-C(5)-C(4)	112.97(19)
C(19)-Ge(1)-C(13)	109.58(7)	C(12)-C(7)-C(8)	117.82(16)
C(7)-Ge(1)-C(3)	107.59(7)	C(9)-C(8)-C(7)	121.15(17)
C(19)-Ge(1)-C(3)	112.18(7)	C(10)-C(9)-C(8)	119.82(18)
C(13)-Ge(1)-C(3)	110.02(7)	C(18)-C(13)-Ge(1)	120.66(13)
O(2)-C(1)-O(1)	123.11(16)	C(14)-C(13)-Ge(1)	121.58(12)
O(2)-C(1)-C(2)	121.57(15)	C(20)-C(19)-Ge(1)	121.60(12)
O(1)-C(1)-C(2)	115.30(16)	C(24)-C(19)-Ge(1)	120.54(13)

TABLE 7
Hydrogen bonds [Å and °] for Ia_2

D—H- - -A	d(D—H)	d(D- - -A)	d(D- - -A)	<(DHA)
O(1)—H(1)- - O(2)#1	0.84	1.77	2.607(2)	175

Symmetry transformations used to generate equivalent atoms: #1−x−1, −y, −z+2.

TABLE 8
Antibacterial activity data of triorganoantimony(V) derivatives containing germanium (in vitro)

Name of bacteria	Zone of inhibition of sample (mm)										% Zone of inhibition of std. drug (mm)
	1	2	3	4	5	6	7	8	9	10	
Escherichia coli	32	30	19	30	16	23	18	14	23	17	33
Bacillus subtilis	30	23	18	24	—	19	18	—	13	24	30
Shigella flexenari	33	24	—	—	—	—	—	—	—	21	35
Staphylococcus aureus	18	38	24	24	26	32	26	19	27	23	43
Pseudomonas aeruginosa	22	22	—	17	13	15	12	13	18	16	25
Samonella typhi	39	38	32	36	22	31	29	21	15	19	40

Concentration of sample = 5 mg/mL of DMSO.
Concentration of standard drug (Imipenum) = 10 μg/mL.
(—) = No activity.

TABLE 9
Antifungal activity data of triorganoantimony(V) derivatives containing germanium (in vitro)

Name of fungus	Zone of inhibition of sample										Std. drug MIC μg/mL	% Inhibition
	1	2	3	4	5	6	7	8	9	10		
Trichophyton longifusus	68	65	—	45	30	48	45	38	—	37	Miconazole	70
Candida albicans	95	12	—	38	45	—	—	—	—	25	Miconazole	110
Aspergillus flavus	—	35	—	10	—	—	12	13	—	—	Amphotericin B	20
Microsporum canis	—	78	48	55	30	65	68	63	—	—	Miconazole	98
Fusarium solani	65	65	25	—	30	43	45	39	43	56	Miconazole	73
Candida glaberata	105	102	68	65	48	85	97	71	69	74	Miconazole	110

Concentration of sample = 400 μg/mL of DMSO.
Incubation temperature (period) = 27 ± 1°C (7 days).
(—) = No activity.

with a Mitamura Riken Kogyo (Japan) and are uncorrected. IR were recorded on a Bio-Rad Excalibure FT-IR Model FTS 3000 MX using KBr disc. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer using deuterated solvents and TMS as a reference operating at 300 and 75.5 MHz respectively. The crystallographic data were collected at 173 K on a Nonius Kappa CCD diffractometer.

Synthesis

The compounds were synthesized under mild conditions as per the literature method.[11] Typically, to 3-triorganogermyl (substituted) propionic acid (1 mmol) and triethylamine (0.8 cm^3) in toluene (50 cm^3) were added respectively to Ar_3SbBr_2 (0.5 mmol). The reaction mixture was stirred at room temperature for eight hours and filtered. The filtrate

TABLE 10
Cytotoxicity data (a–d) of triorganoantimony(V) derivatives containing germanium

Comp. no.	LD_{50} (μg/mL)	Comp. no.	LD_{50} (μg/mL)
1	24.65	**6**	10.43
3	256.43	**8**	7.21
4	254.71	**9**	9.45
5	258.61	**10**	18.62

[a]Organism = Brine shrimp (in vitro).
[b]Std. drug = Etoposide.
[c]Conc. of std. drug = λ_{50}(μg/mL) = 7.46.
[d]LD_{50} = Lethal dose at which 50% organisms die.

was evaporated under reduced pressure. The obtained solid was washed several times with n-hexane to get a pure product.

Crystal Structure Determination

Suitable crystals of $(C_6H_5)_3GeCH(n\text{-}C_3H_7)CH_2COOH$, were isolated for X-ray analysis dissolving the respective compound (0.5 g) in chloroform (5.0 mL), to which a few drops of acetone were added. Slow evaporation of the solvent at room temperature over a period of several days yielded fine crystals, which were subsequently washed with acetone. A colorless prismatic crystal was mounted on glass fiber and used for data collection. The cell constants obtained from the refinement of total reflections in the range of $3.3 < \theta < 27.5^\circ$ corresponded to a primitive triclinic cell.

Diffraction measurements were carried out at 173(2) K on a Nonius Kappa CCD diffractometer for a colorless prismatic crystal of size 0.20 x 0.16 x 0.08 mm^3. The data were corrected for Lorentz and polarization effects and for absorption, using the multi-scan method.[25] The structure was refined using SHELXL-97.[26] The details of crystal data and structure refinement have been listed in Table 11.

TABLE 11
Crystal data and structure refinement of $(C_6H_5)_3GeCH(n\text{-}C_3H_7)CH_2COOH$

Empirical formula	$C_{24}H_{26}GeO_2$
Formula weight	419.04
Crystal system	Triclinic
Space group	P-1
a(Å)	9.858(2)
b(Å)	10.995(2)
c(Å)	11.260
β(°)	69.114(9)
Volume	1056.9(3)Å^3
Z	2
Absorption coefficient	1.464 mm^{-1}
θ_{max}(°)	27.5
Reflections collected	9111
Independent reflections	4810 [R(int) = 0.016]
Reflected observed (>2σ)	—
Max. and min. transmission	0.892 and 0.758
Goodness-of-fit on F^2	1.03
Final R indices [I > 2sigma(I)]	R1 = 0.028, wR2 = 0.065
R indices (all data)	R1 = 0.031, wR2 = 0.067
δ_{max}(e · Å^{-3})	0.58

SUPPLEMENTARY DATA

A complete list of crystallographic data and parameters including atomic coordinates has been deposited at Cambridge Crystallographic Data Center as CCDC Number: 261766. Copies of the data can be obtained on request to CCDC, 12 Union Road, Cambridge CB21 EZ, UK. E-mail: deposited@ccdc.cam.ac.uk or ⟨http://www.ccdc.cam.ac.uk⟩.

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