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Synthesis, spectra and biological activity of some new telluronium heterocyclic β-diketonates

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Abstract

Some new triphenyltelluronium heterocyclic β-diketonates have been prepared and characterized on the basis of analytical, molecular weight measurement, IR, proton and ^{13}C NMR and mass spectral data. From the IR and proton and ^{13}C NMR spectra of the compounds, it is inferred that both the enolic oxygen and acetyl or benzoyl oxygen of β-diketonates are involved in the bonding and acquired a stable pentacoordination around tellurium with a distorted octahedral structure. Finally, the newly synthesized compounds have been screened for their activity in vitro against the cellulose degrading fungi such as *Aspergillus niger* and *Curvularia lunata* and found that these compounds show promising fungicidal activity.

Introduction

Recently there was considerable interest in the research on β-diketones and their metal complexes due to their wide spectrum of applications e.g. metal extractants [1], NMR shift reagents [2,3] and in laser technology [4]. The complexing behaviour of heterocyclic β-diketones with non-transitional elements has not been well studied. The oxygen and nitrogen heterocyclic β-diketones such as 3-acetyl-6-methyl-2*H*-pyran-2,4(3*H*)-dione (also called dehydroacetic acid, DHA), 8-acetyl-4-methyl umbelliferone (AMU), 4-benzoyl-3-methyl-1-phenyl-pyrazolone-5 (BMPP) and 4-acetyl-3-methyl-1-phenylpyrazolone-5 (AMPP) are reported to be excellent chelating agents and possess various physiological applications [5–7]. Literature survey reveals that significantly less attention has been directed to the triphenyltellurium

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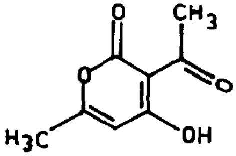
(TPT) derivatives when compared to other triorganotellurium compounds [8,9]. The heterocyclic β-diketonates of tellurium have not been well studied nor their applications fully explored. Hence, we report here the synthesis, spectra and fungicidal activity of new compounds obtained by interaction of triphenyltellurium with DHA, AMU, BMPP and AMPP.

Experimental

DHA (I) was obtained from Fluka, Switzerland. Triphenyltelluronium chloride, the β-diketones AMU (II), BMPP and AMPP (III) were prepared by reported procedures [10–13]. The sodium salts of the β-diketones were used for the preparation of complexes.

Synthesis of triphenyltelluronium heterocyclic β-diketonates

A solution of triphenyltelluronium chloride (2 mmol) in the minimum amount of hot water was mixed with an aqueous solution of the respective sodium salts of β-diketones (2 mmol). The resulting crystalline precipitate, which separated out instantaneously, was filtered, washed with 2–3 small aliquots of cold water, then recrystallized from benzene (TPTDHA and TPTAMU) and acetone (TPTBMPP and TPTAMPP).



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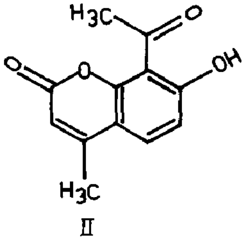

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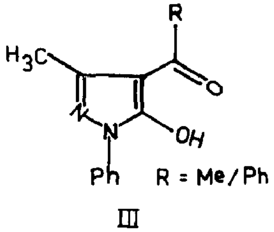

III

Physical measurements. Conductivity measurements in acetone and acetonitrile solutions were carried out using an ELICO conductivity bridge type CM 82T. Molecular weights were determined cryoscopically in nitrobenzene. IR Spectra (4000–200 cm^{-1}) were obtained from KBr and polyethylene discs with a Perkin–Elmer-983 spectrophotometer. Proton and ^{13}C NMR spectra were obtained at 90 and 25 MHz using EM-390 and JEOL FX-90 Q NMR spectrophotometers respectively. Mass spectra were obtained at 70 eV with an AE1 MS9 instrument.

Results

Analytical data, molecular weight measurement data, IR, ^{1}H and ^{13}C NMR, and mass spectral data are presented in Tables 1–6, respectively. The fungicidal activity of the new compounds (at 500 ppm) is expressed in terms of average percentage of inhibition of fungal growth after 4 and 10 days of incubation. The percentages of inhibition were calculated from the eq. 1 and the results are given in Table 7.

$$\text{inhibition } (\%) = \frac{100\,(C-T)}{C}$$

Where C = diameter (mm) of the fungus colony in control plate and T = diameter (mm) of the fungus colony in treated plates.

Discussion

The new compounds, triphenyltelluronium dehydroacetic acid (TPTDHA), triphenyltelluronium 8-acetyl-4-methyl umbelliferone (TPTAMU), triphenyltelluronium 4-benzoyl-3-methyl-1-phenyl-pyrazolone-5 (TPTBMPP) and triphenyltelluronium 4-acetyl-3-methyl-1-phenyl-pyrazolone-5 (TPTAMPP) are stable in air and to moisture, they decompose or melt in the range of 180–245 °C, and are soluble in most of the polar organic solvents and in hot water. The purity of the compounds was checked by TLC using appropriate solvents.

The elemental analyses (Table 1) show that the telluronium to β-diketone ratio is 1/1, and the molecular weight measurements data in nitrobenzene (Table 2) also reveal that at higher concentrations (5–10 mM), the molecular weights are very

Table 1

Analytical data of the new tellurium heterocyclic β-diketonates

Compound	Colour	M.p.[a] (°C)	Analysis (Found (calcd.) (%))				Λ_M[b] (Acetone)	Λ_M[b] (Acetonitrile)
			C	H	N	Te		
TPT DHA	Light brown	188	59.6	4.0	–	24.1	15.9	21.2
			(59.4)	(4.2)		(24.2)		
TPT AMU	Light Yellow	180 (dec.)	62.4	4.2	–	22.3	15.5	19.6
			(62.5)	(4.1)		(22.2)		
TPT BMPP	Yellow	242	66.3	4.5	4.3	20.1	27.7	28.5
			(66.1)	(4.4)	(4.4)	(20.0)		
TPT AMPP	Yellow	217	62.9	4.7	4.8	22.2	23.8	25.3
			(62.8)	(4.5)	(4.9)	(22.2)		

[a] Uncorrected melting points. [b] Concentration at 10^{-3} M.

Table 2

Molecular weight measurement data

Compound	Formula wt.	Concentration (mM)	Molecular wt.
TPT DHA	525.6	1.78	327.9
		3.89	353.8
		7.14	508.5
		10.86	527.4
TPT AMU	575.6	1.58	309.9
		4.26	385.2
		7.32	583.2
		11.27	610.3
TPT BMPP	635.6	1.93	318.9
		4.12	405.4
		6.84	614.7
		12.18	731.1
TPT AMPP	573.6	1.62	312.6
		4.11	369.3
		7.48	589.7
		10.99	619.4

Table 3

Tentative IR band assignments (cm^{-1})

DHA	TPT DHA	AMU	TPT AMU	BMPP/ AMPP	TPT BMPP/ TPT AMPP	Assignment
3030sh	–	3300–2600br	–	3100–2600br	–	ν(OH...O) chelates
1710s	1710s	1740s	1735s	–	–	ν(C=O) lactone ring
1640s	1620s	1625s	1600s	1640–1600vs	1605–1590vs	ν(C=O) benzoyl/ acetyl
–	–	–	–	1575m 1528–1506s	1586–1580m 1530–1514sh	Pyrozolone ring stretching
1260s	1275s	1205s	1225s	1368–1360s	1380–1374s	ν(C–O) enolic
–	–	–	–	1118–1105s	1120–1115s	Pyrozolone ring breathing
1000m	995m	1060m	1070m	–	–	ν(C–O–C) ring
–	375s	–	350s	–	350– 345s	ν(Te–O)
–	260s	–	257s	–	260– 255s	ν(Te–C)

close to the expected values for monomers. The molar conductance values of these compounds in acetone and acetonitrile (10^{-3}–10^{-5} *M*) indicate the moderately electrolytic behaviour, but these values are low for 1/1 electrolytes [14].

The IR spectra of the compounds (Table 3) show the absence of ν(O–H...O) peaks (present in the free β-diketone) which confirms the cleavage of intramolecular hydrogen bonding with subsequent deprotonation and participation of enolic oxygen in bonding [7,5]. This is further confirmed by a positive shift of 15–20 cm^{-1} in ν(C–O) (enolic) values. The ν(C=O) of acetyl in TPTDHA, TPTAMU and TPTAMPP, and of benzoyl in TPTBMPP suffered a negative shift from the free β-diketones of 20–25 cm^{-1}, which certainly indicates its coordination to the metal ion [15]. The bands at 1710 and 1740 cm^{-1} in DHA and AMU, respectively, are assigned to ν(C=O) of the lactone ring and these are not altered during the complexation, thereby indicating the non-participation of this group in coordination. In the far IR region, the bands at 345–375 and 250–260 cm^{-1} are attributed to ν(Te–O) and ν(Te–C) modes, respectively [9].

Table 4

^{1}H nuclear magnetic resonance spectra [a]

Compound	Ring CH_3	Acetyl CH_3	Lactone ring proton	Aromatic ring protons		Phenyl protons	TePh protons		Hydroxyl protons
				H(1)	H(2)		I	II type	
DHA	2.30	2.60	5.80	–	–	–	–	–	11.1
TPT DHA	2.30	2.80	5.70	–	–	–	7.2	7.5(m)	–
AMU	2.30	2.70	5.75	6.35–6.50	7.10–7.20	–	–		10.95
TPT AMU	2.30	3.00	5.70	6.10–6.20	7.00–7.10		7.3	7.5(m)	–
BMPP	2.07	–	–	–	–	7.2–8.1(m)	–		11.17
TPT BMPP	2.05	–	–	–	–	7.2–8.1(m)	7.3	7.5(m)	–
AMPP	2.12	2.45	–	–	–	7.2–8.0(m)	–		12.27
TPT AMPP	2.08	2.60	–	–	–	7.1–8.1(m)	7.25	7.5(m)	–

[a] Chemical shift, δ(ppm) relative to TMS in $CDCl_3$ solvent.

Table 5

Major chemical shifts in ^{13}C NMR spectra of β-diketones and their metal complexes

Compound	Chemical shifts, δ (ppm)					
	C(4)	C(5)	C(7)	O=C–R	TePh$_3$	
					I	II type
DHA	168.9	–	–	204.9	–	–
TPT DHA	177.1	–	–	190.1	129	134
AMU	–	–	159.3	198.6	–	–
TPT AMU	–	–	172.0	186.4	128	135
BMPP	–	165.2	–	191.3	–	–
TPT BMPP	–	175.0	–	180.5	130	133
AMPP	–	163.6	–	189.4	–	–
TPT AMPP	–	170.3	–	175.9	131	134

The proton NMR data of the β-diketones and their complexes are compiled in Table 4. The assignment of all proton signals have been made. It is clear from the spectra that the enolic protons of β-diketones are lost during complex formation which confirms participation of the enolic oxygen in bonding. The acetyl protons ($COCH_3$) in TPTDHA, TPTAMU and TPTAMPP appear downfield at 0.2–0.3 ppm from the free β-diketones, probably due to deshielding effects by the carbonyl group coordinated to telluronium. The signals of two different multiplets observed at 7.2–7.3 and 7.5 ppm are due to the two types of phenyls attached to the telluronium in the compounds. This clearly shows that the phenyl group on the *z*-axis is different from the other two phenyls which are on the *y*- and *x*-axis of a distorted octahedron. The integration of the proton signals clearly shows the appropriate proton ratio present in the compounds.

^{13}C NMR data (Table 5) show that the carbon atoms of acetyl or benzoyl carbonyls of β-diketones are shielded to the extent of 10–15 ppm and the carbon atoms C(4), C(7) and C(5) in DHA, AMU and BMPP or AMPP, respectively, are deshielded to about 6–13 ppm during complexation [16]. Hence it further supports the chelation of the ligands and bonding through both oxygen atoms. The signals at 129–131 and 133–135 ppm are attributed to two distinct phenyls attached to the central telluronium.

Mass spectral studies of telluronium salts have been useful to provide support for the concept of association of cations and anions in the gas phase [17]. The spectra of the synthesized compounds (Table 6) show the presence of the Ph_3Te^+, Ph_2Te^+, $PhTe^+$, Ph_2^+, and Ph^+ regularly as major high m/e peaks. None of the compounds shows ions containing telluronium beyond m/e 368; however, some higher mass fragments are observed. Correlation of these fragments could not be made with the components of the compounds and may probably arise from pyrolysis of the material in the source of the instrument. The significant parent ion of dicarbonyl is clearly seen.

On the basis of above data, it is proposed that the triphenyltelluronium is bonded through both oxygens of the enolic and acetyl or benzoyl groups of the β-diketones and form stable pentacoordinate [18] complexes with distorted octahedral geometry in which the vacant site is occupied by a lone pair of electrons on tellurium.

Table 6

Mass spectral data

Fragment	TPT DHA m/e	TPT AMU m/e	TPT BMPP m/e	TPT AMPP m/e
Ph_3Te^+	361	361	361	361
Ph_2Te^+	284	284	284	284
$PhTe^+$	207	207	207	207
Ph_2^+	154	154	154	154
Ph^+	77	77	77	77
Dicarbonyl ion	176	217	277	215

Table 7

Fungicidal screening-inhibition (%)

Compound	*Aspergillus niger*		*Curvularia lunata*	
	4 days	10 days	4 days	10 days
DHA	65.66	38.46	66.33	42.50
AMU	57.05	43.29	52.11	44.66
BMPP	86.10	64.00	57.80	40.35
AMPP	82.72	78.50	75.80	51.95
TPT DHA	94.44	55.55	72.22	50.00
TPT AMU	77.77	66.66	77.77	50.00
TPT BMPP	100.00	75.00	66.66	43.75
TPT AMPP	100.00	90.00	95.00	60.00

Physiological activity

The preliminary screening of the newly synthesized telluronium compounds has been carried out in vitro using an agar plate technique [19] against *Aspergillus niger* Van Tiegh and *Curvularia lunata* (Wakker) Boedijn, the organisms capable of degrading cellulose and its related materials such as wood, paper, leather etc. It is observed that these compounds when compared to free β-diketones (38.46–86.10%) were showing excellent inhibition (50–100%) and are effective over the growth rate of fungi at 4 and 10 days of incubation (Table 7). Hence the newly synthesized compounds may be useful as promising fungicides.

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