Synthesis and Structure of a New Chiral Oxaziridine from (3-Oxo-camphorsulfonyl)imine

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Oxidation of (3-oxo-camphorsulfonyl)imine (**1**) by magnesium monoperoxyphthalate does not lead to the oxaziridine obtained with 3-chloro-perbenzoic acid, but to a new chiral oxaziridine containing an additional oxygen atom (Baeyer-Villiger type oxidation). The structure of the product is established by X-ray crystallography, and reaction pathways for the oxidation of **1** by peracids are discussed.

Introduction

Chiral N-sulfonyl-oxaziridines have been introduced in organic chemistry as mild oxidation reagents, leading to high enantioselectivities, for alkenes, enolates, and sulfides [1–5]. Further applications, *e.g.* for enantioselective oxidations of phosphites, are expected [6]. For the oxidation of sulfides to chiral sulfoxides, the (3-oxo-camphorsulfonyl)-oxaziridine **3** [5] gives the highest enantiomeric excess, and is therefore of considerable interest. Generally, these oxaziridines are prepared from the corresponding N-sulfonyl-imines by oxidation with peracids. In the case of the oxaziridine **2,** 3-chloroperbenzoic acid (MCPA) gives the best results, while oxidations with peracetic acid are less reproducible. Recently, warnings with respect to potential safety hazards of MCPA have led to suggestions of safer substitutes. In particular, the magnesium salt of monoperoxyphthalic acid (MPPA), a bleaching agent produced on an industrial scale, is a prominent candidate for this purpose. In a first publication, oxidation of sulfides to sulfoxides and of amines to N-oxides, epoxidation of alkenes, and Baeyer-Villiger oxidation of ketones have been shown to proceed with excellent results [7]. We therefore tried to replace MCPA in the oxidation of the sulfonylimine **1** by MPPA. To our surprise, no trace of the oxaziridine **3** was observed, and even no trace of the Baeyer-Villiger product **6,** which is a normal by-product of the MCPA oxidation of **1.** Instead, a high yield of a new compound **7** was obtained by excess MPPA, which we identified by spectroscopic data and an X-ray structure analysis as (4aS,9aR)-10,10-dimethyl-6,7-dihydro-4H-4a,7-methano-oxazirino[3,2-j]oxepino[3,4-c]isothiazol-9-(5H)-one-3,3-dioxide, more conveniently named as camphorlactone-sulfonyloxaziridine. Its formation and the different pathways for the oxidations of **1** by MCPA and MPPA are shown in Scheme 1.

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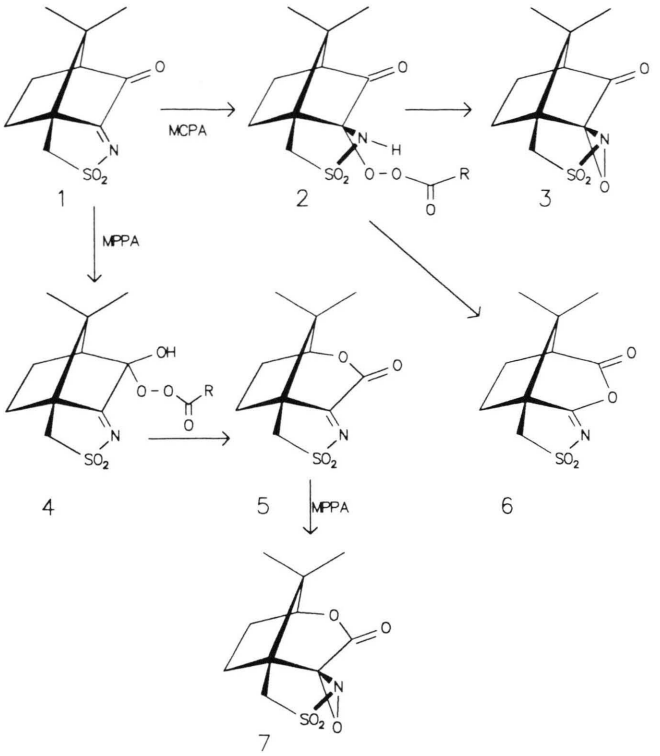
Results and Discussion

Molecular structure of camphorlactone-sulfonyl-oxaziridine (**7**)

The structure of the new oxaziridine **7** was unequivocally established by X-ray crystallography (Tables I, II).

In accord with the chirality of **7,** the compound crystallizes in the non-centrosymmetric space group $P2_12_12_1$. The asymmetric unit contains two independent molecules which show no significant discrepancies. Both molecules have the same expected absolute configuration which was checked independently by refinement of the enantiomeric species (see Experimental part). In the crystal, there are no close contacts between the individual molecules.

As evident from Fig. 1, the oxidation with MPPA leads to an insertion of an oxygen atom (O5) between the carbonyl C atom C1 and the bridgehead carbon C6. The second step of the oxidation, resulting in the formation of the oxaziridine ring, proceeds



Scheme 1. Oxidation of (3-oxo-camphorsulfonyl)-imine (**1**) by MCPA (3-chloroperbenzoic acid) and MPPA (magnesium monoperoxyphthalate).

with complete stereoselectivity and places the oxygen atom O3 in an *endo* position with respect to the bicyclic lactone-imine skeleton. This is certainly due to the methyl group C9 at the bridging C atom C7 which effectively shields the five-membered ring S, N, C2, C3, C10 at the opposite side (Fig. 2). The same stereoselectivity has been observed in the case of other camphorsulfonyl-oxaziridines [2, 5], obviously for the same reasons. This shielding should also contribute to the high enantioselectivities in the oxidation reactions of the camphor-type oxaziridines. Compared with the X-ray structure of another camphor-derived oxaziridine [3], **7** is a more spherical molecule with a much stronger shielded oxaziridine unit (Fig. 2), and thus, better enantioselectivities can be expected.

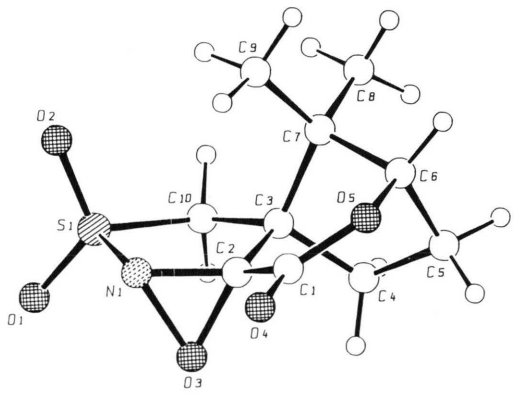


Fig. 1. Molecular structure of one of the two independent molecules of **7** (SCHAKAL; atoms with arbitrary radii).

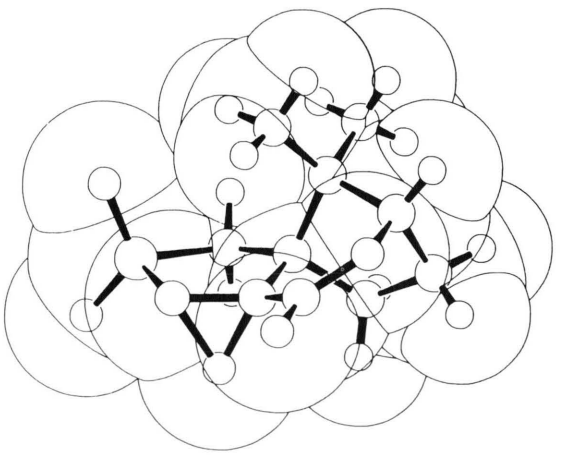


Fig. 2. Space filling representation of the molecule shown in Fig. 1.

Table I. Fractional atomic coordinates and equivalent isotropic displacement parameters of **7** (U_{eq} = $1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$).

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
S1	0.28338(6)	0.2655(1)	0.86557(2)	0.091
O1	0.2817(2)	0.2570(4)	0.81831(6)	0.112
O2	0.3201(2)	0.1021(3)	0.89033(7)	0.154
O3	0.3392(2)	0.6209(3)	0.86252(6)	0.084
O4	0.5048(2)	0.7369(4)	0.93141(6)	0.115
O5	0.3499(2)	0.7291(3)	0.97932(6)	0.088
N1	0.3893(2)	0.4385(4)	0.88135(7)	0.092
C1	0.4000(3)	0.6887(5)	0.93983(8)	0.081
C2	0.3219(3)	0.5757(4)	0.90770(8)	0.069
C3	0.1901(2)	0.5242(4)	0.92062(8)	0.068
C4	0.1109(3)	0.7047(4)	0.91955(9)	0.110
C5	0.1330(3)	0.8043(4)	0.96426(9)	0.122
C6	0.2211(3)	0.6721(4)	0.98868(8)	0.071
C7	0.1961(2)	0.4723(4)	0.97123(8)	0.062
C8	0.0703(3)	0.4046(5)	0.98812(9)	0.102
C9	0.2957(3)	0.3306(4)	0.98433(8)	0.088
C10	0.1470(2)	0.3733(4)	0.88812(8)	0.088
S2	1.01815(6)	−0.1399(1)	0.79183(2)	0.074
O6	1.1164(2)	−0.0635(3)	0.76573(6)	0.112
O7	1.0340(2)	−0.3190(3)	0.81314(6)	0.107
O8	0.9477(2)	0.1947(3)	0.81431(6)	0.089
O9	0.8608(2)	0.2233(4)	0.90282(6)	0.115
O10	0.6881(2)	0.0743(3)	0.88419(6)	0.095
N2	0.9896(2)	0.0141(3)	0.83589(6)	0.080
C11	0.8029(3)	0.1300(5)	0.87648(8)	0.083
C12	0.8611(2)	0.0677(4)	0.83240(8)	0.076
C13	0.7814(2)	0.0373(4)	0.79902(7)	0.056
C14	0.6909(2)	−0.1068(4)	0.77876(9)	0.102
C15	0.5834(3)	0.1209(5)	0.81291(9)	0.130
C16	0.6159(3)	−0.0228(5)	0.84891(9)	0.100
C17	0.6954(2)	−0.1738(4)	0.82587(8)	0.090
C18	0.6124(3)	−0.2919(5)	0.7951(1)	0.136
C19	0.7606(3)	−0.3085(5)	0.8581(1)	0.129
C20	0.8708(2)	−0.1235(4)	0.76500(8)	0.071

Table II. Important distances (Å) and angles (deg.) for both independent molecules of **7** with estimated standard deviations in units of the last significant figure given in parentheses.

S1–O1	1.426(2)	S2–O6	1.427(2)
S1–O2	1.428(2)	S2–O7	1.427(2)
S1–N1	1.739(3)	S2–N2	1.743(2)
S1–C10	1.792(3)	S2–C20	1.790(2)
N1–C2	1.448(4)	N2–C12	1.443(3)
N1–O3	1.506(3)	N2–O8	1.499(3)
C2–O3	1.412(3)	C12–O8	1.405(3)
C2–C3	1.521(4)	C12–C13	1.517(4)
C3–C10	1.519(4)	C13–C20	1.534(4)
C2–C1	1.511(4)	C12–C11	1.535(3)
C1–O4	1.209(3)	C11–O9	1.206(3)
C1–O5	1.339(3)	C11–O10	1.321(3)
O5–C6	1.476(3)	O10–C16	1.486(3)
C7–C6	1.527(4)	C17–C16	1.534(4)
C7–C3	1.570(3)	C17–C13	1.563(4)
C10–S1–N1	98.1(1)	C20–S2–N2	98.5(1)
S1–N1–C2	106.7(2)	S2–N2–C12	106.1(2)
S1–N1–O3	105.0(1)	S2–N2–O8	104.5(1)
C2–N1–O3	57.1(2)	C12–N2–O8	57.0(1)
N1–O3–C2	59.4(2)	N2–O8–C12	59.5(2)
C3–C2–N1	116.9(2)	C13–C12–N2	117.8(2)
C3–C2–O3	115.1(2)	C13–C12–O8	115.5(2)
C3–C2–C1	119.0(2)	C13–C12–C11	118.8(2)
N1–C2–O3	63.6(2)	N2–C12–O8	63.5(2)
N1–C2–C1	115.0(2)	N2–C12–C11	114.0(2)
C1–C2–O3	115.2(2)	C11–C12–O8	115.3(2)
C2–C3–C10	106.8(2)	C12–C13–C20	106.2(2)
C3–C10–S1	106.9(2)	C13–C20–S2	106.5(2)

The aforementioned five-membered ring is almost planar. A moderate envelope conformation results from an interplanar angle of 20.8/21.1° between the best plane through S1, N1, C2, C10 and the plane containing C10, C3, C2. The oxaziridine ring forms an angle of 85.4/85.7° with the plane through S1, N1, C2, C10. (Values for both independent molecules are given in each case).

Conformation of **7** *in solution*

As the new oxaziridine **7** is of potential interest as chiral oxidizing agent, considerable interest in the solution structure exists. Although no dramatic deviations from the solid state structure should be expected, we have conducted an analysis of nuclear Overhauser enhancement effects using the two-dimensional technique in a rotating frame (ROESY) [8–11]. The assignment of the ^{1}H NMR signals is based mainly on two-dimensional CH-correlation [12].

The strongest NOE effects are found between the two methyl groups of the bridge, and between the geminal protons of the CH_2–SO_2 unit. Weaker effects are evident between the bridgehead proton and the CH_2–CH_2 group region. Because of extreme overlap of the signals, no conclusive assignment could be made in this complex multiplet structure. However, the NOE effects allow to assign the dublet at 3.50 ppm to the proton at C10 which is directed upward (*exo*), because it shows a correlation with the methyl groups, while no such correlation can be found with the dublet at 3.34 ppm. Thus, it seems certain that the general structure of **7,** as determined by X-ray crystallography, is maintained in solution, as well as its conformational rigidity.

If the excess of MPPA in the oxidation of the imine **1** is not sufficient, a byproduct is observed, which we identified as the Baeyer-Villiger product **5.** Obviously, it is an intermediate in the formation of the oxaziridine **7.** The NMR data of the new compounds **5** and **7** are listed in the Tables III and IV, together with those of their precursor **1** and of the products **3** and **6,** formed by the oxidation of **1** with MCPA.

The general pattern of both ^{1}H and ^{13}C NMR spectra of all the compounds is quite similar and reflects the rigid structure in solution. The main difference between the MCPA- and the MPPA-derived series lies in the chemical shifts of the bridgehead CH group (C6) (2.70 to 3.16 and 51.5 to 59.1 ppm in **1, 3,** and **6** *vs.* 4.60 to 4.88 and 89.9 to 91.4 ppm in **5** and **7**), which is due to the absence or presence, respectively, of the oxygen atom O5.

Thus, we may conclude that the solution structure is very similar to the solid state structure, and the conformation adopted by the oxaziridine ring, which is completely shielded from attack from the upper side, can be considered to be favorable for enantioselective oxidations.

Pathways for the oxidation of **1**

The different results in the oxidation of (3-oxocamphorsulfonyl)imine (**1**) by MCPA and MPPA are mainly due to steric effects, which play a prominent role in the chemistry of the oxidations of bicyclic systems [13]. Already in the first publication on the peracid oxidation of ketones [14], Baeyer and Villiger observed that camphor is converted to the lactone with oxygen insertion between carbonyl and the CH_2 group. This regioselectivity must be due to sterical hinderance, because 2-norbornanone gives the normal Baeyer-Villiger product with oxygen insertion between carbonyl and bridgehead carbon [15, 16].

The Baeyer-Villiger oxidation has been demonstrated by kinetic measurements and careful product analysis [17] to proceed *via* the so-called Criegee-intermediates [18], like **4,** and, by oxygen migration to the nitrogen, oxaziridines are formed from analogous intermediates like **2** [19, 20]. The greater migration tendency of secondary alkyls, as compared with primary alkyl groups [13, 17], explains the regioselectivity in the case of sterically less problematic compounds like 2-norbornanone.

Although a comparatively new compound with more technical than chemical applications, MPPA has been studied by X-ray crystallography [21]. A central octahedral $Mg(H_2O)_6$-unit is surrounded by two mono-peroxy-phthalate anions in a sandwich-like manner, and the water molecules are linked by hydrogen bridges to the carboxylate groups of the anions. It is very probable that the general arrange-

Comp.	H6	H5	H4	H10	H8, H9
1	2.79 (d, 4.8 Hz)	1.80–2.10 (m, 2H)	2.20–2.40 (m, 2H)	3.24 3.45 (2d, 13.6 Hz)	0.99 1.17 (2s)
3	2.70 (d, 4.8 Hz)	1.78–2.28	(m, 4H)	3.37 3.60 (2d, 14.4 Hz)	1.17 1.24 (2s)
6	3.16 (d, 6.4 Hz)	1.70–2.40	(m, 4H)	3.89 3.98 (2d, 14.3 Hz)	0.98 1.06 (2s)
5	4.88 (d, 4.4 Hz)	2.16–2.37 (m, 2H)	2.44–2.63 (m, 2H)	3.90 3.94 (2d, 14.5 Hz)	1.11 1.12 (2s)
7	4.60 (d, 4.6 Hz)	2.12–2.43	(m, 4H)	3.34 3.50 (2d, 14.2 Hz)	1.12 1.38 (2s)

Table III. ^{1}H NMR spectra of **1, 3, 5, 6,** and **7.** Compounds **5** and **6** in d_6-DMSO, other compounds in $CDCl_3$. The numbering of the atoms follows Fig. 1.

Comp.	C3	C2	C1	C6	C5	C4	C7	C10	C8, C9
1	62.8	181.5	197.7	59.1	22.7	28.1	44.7	50.1	18.4 20.2
3	59.7	89.7	201.1	51.5	22.2	27.5	44.0	48.9	17.2 21.3
6	61.3	166.8	178.7	51.9	23.5	31.8	53.1	59.0	18.6 19.8
5	63.2	156.6	173.0	89.9	28.5	30.3	46.8	49.0	16.6 20.3
7	83.6	117.8	160.6	91.4	28.2	30.2	46.3	47.3	18.3 20.3

Table IV. ^{13}C NMR spectra of the compounds **1, 3, 5, 6,** and **7.** Compounds **5** and **6** in d_6-DMSO, other compounds in $CDCl_3$. The numbering of the carbon atoms follows Fig. 1.

ment of this sandwich is maintained in solution, and thus the oxidizing agent is much bulkier than MCPA or its (monomeric) anion. Therefore, MCPA follows the general tendency of peracids and attacks the imine double bond of **1,** leading to **2** which then may rearrange with loss of the benzoate to give the oxaziridine **3,** or undergo a migration of the carbonyl group to form the normal Baeyer-Villiger product **6.** This is completely analogous to the formation of anhydrides from 1,2-dicarbonyl compounds with peracids [22]. On the other hand, MPPA, as a much more voluminous reagent, reacts more rapidly with the sterically less hindered carbonyl group of **1** to give the Criegee-intermediate **4,** which then rearranges with alkyl migration to the lactone-imine **5** but not with migration of the imine group to **6,** as this compound could never been detected in oxidations with MPPA. A final, slower oxidation at the imine leads to the oxaziridine **7.**

What remains to be explained, is the slow conversion of the Baeyer-Villiger product **6** to the oxaziridine **3** which takes place in dimethyl sulfoxide solution [5]. A mechanism can be conceived starting with addition of an anion to the imine function and continuing with a rearrangement to form the new C–C-bond and the oxaziridine ring. However, this has to be inspected more closely by detailed kinetic measurements.

Conclusion

Camphorlactone-sulfonyloxaziridine **7** was prepared by the oxidation of (camphorsulfonyl)imine **1** with MPPA. That **7** is obtained, and not **3,** can be understood in terms of sterical effects in the formation of the Criegee-intermediates in the Baeyer-Villiger oxidation process. This result clearly demonstrates that MPPA cannot simply be considered as a convenient substitute for MCPA. Deviations in the reactivity pattern should always be expected when a different sterical environment of the oxidant may lead to different approaches to the substrate. The characteristic structure of the oxaziridine **7,** as elucidated by X-ray crystallography and NOE measurements, suggests important applications in enantioselective oxidations of various functional groups. Preliminary experiments show that **7** is a far stronger oxidizing agent than (3-oxo-camphorsulfonyl)oxaziridine **3,** as it oxidizes dimethyl sulfoxide rapidly to dimethyl sulfone, while **3** leaves it unchanged, at least at room temperature. We will report on the enantioselectivities obtained in the oxidations with **7** in due course.

Experimental

NMR spectra have been measured with a Bruker AM 360 spectrometer at 360.13 MHz (^{1}H) and 90.556 MHz (^{13}C), in $CDCl_3$, unless otherwise stated. IR spectra have been obtained with a Perkin-Elmer 257 spectrophotometer, and optical rotations have been determined with a Roussel Jouan Digital 71 polarimeter. Mass spectra have been measured with a Varian CH5 instrument.

X-ray structure determination

Syntex-P2_1 diffractometer, Mo–K_α radiation, λ = 0.71069 Å, graphite monochromator, T = −50 °C.

Crystal data: $C_{10}H_{13}NO_5S$, M_r = 259.283, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 10.805(1), b = 7.047(1), c = 30.152(2) Å, V = 2295.9 Å^3, Z = 8, d_{calcd} = 1.500 g/cm^3, μ(Mo–K_α) = 2.8 cm^{-1}, F(000) = 1088. The integrated intensities of 4403 reflexions were measured, corrected for Lp effects, and merged to give 3810 independent data, 3567 of which with $F_o > 4.0\sigma(F_o)$ were deemed "observed" and used for all further calculations (ω scans, $\Delta\omega$ = 0.8°, hkl range: +12, +8, ±35, $(\sin\vartheta/\lambda)_{max}$ = 0.583 Å^{-1}). The structure was solved by direct methods (SHELXS-86, MS-DOS version) and completed by Fourier syntheses. 24 hydrogen atoms were located in difference maps, 2 were calculated at idealized geometrical positions. They were included at constant positions into structure factor calculations, while all other atoms were refined with anisotropic displacement parameters. Refinement converged at $R(wR)$ = 0.033(0.038), w = $1/\sigma^2(F_o)$ for 308 refined parameters. 8 structure factors were suppressed in the final refinement cycles, because they were found to result from faulty intensity measurements. The absolute configuration of **7** was independently checked by refinement of the inverse coordinate set which resulted in slightly larger R values (0.034/0.039). The residual electron density was featureless ($\Delta\varrho_{fin}$(max/min) = 0.35/−0.46 e/Å^3). Table I contains the atomic coordinates, Table II distances and angles for both independent molecules. Further crystal structure data have been deposited*.

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Preparation of the compounds

(4aS,9aR)-10,10-Dimethyl-6,7-dihydro-4H-4a,7-methano-oxazirino[3,2-j]oxepino[3,4-c]isothiazol-9(5H)-one-3,3-dioxide (**7**) *and (3aS)-9,9-Dimethyl-5,6-dihydro-3H-3a,6-methano-oxepino[3,4-c]isothiazol-7(4H)-one-2,2-dioxide* (**5**)

A solution of 22.7 g (100 mmol) (3-oxo-camphorsulfonyl)imine (**1**) [5] in 200 ml of dichloromethane and a solution of 18.6 g (200 mmol) $NaHCO_3$ in 100 ml of water are cooled to 0 °C. A saturated solution of 124 g (200 mmol) 80% commercial magnesium peroxyphthalate in 200 ml of water is added slowly with vigorous stirring. Stirring is continued for 24 h at room temperature. The phases are separated, and the aqueous phase is extracted with 100 ml of dichloromethane. The organic phases are dried with sodium sulfate, and the solvent is evaporated. The residue is recrystallized from acetone. The yield of **7** is 15.5 g (60%).

The mother liquor of the recrystallization often contains the lactone-imine (**5**). It may be isolated by evaporation of the solvent and recrystallization from ethanol, where **7** is only sparingly soluble. However, the following procedure is more convenient:

To a solution of 2.59 g (10 mmol) oxaziridine **7** in 50 ml of dichloromethane, a solution of 0.78 g (10 mmol) of dimethyl sulfoxide in 10 ml of dichloromethane is added dropwise. After stirring for one hour at room temperature, the volatile components are evaporated and the residue is washed with water and recrystallized from acetone. The yield of **5** is 2.19 g (90%).

5: M.p.: 264–265 °C, IR (KBr): 1770 s, 1755 vs (C=O), 1625 s (C=N). MS: 243 (m^+), 94 (100%). $[\alpha]_D^{22} = +3.4°$ (c = 1, acetone).

$C_{10}H_{13}NO_4S$ (243.28)

Calcd	C 49.37	H 5.39	N 5.76,
Found	C 49.08	H 5.42	N 5.70.

7: M.p.: 202–204 °C, IR (KBr): 1755 vs (C=O). MS: no molecular ion; 215 (10%), 44 (100%). $[\alpha]_D^{22} = +92.0°$ (c = 1, acetone).

$C_{10}H_{13}NO_5S$ (259.28)

Calcd	C 46.32	H 5.05	N 5.40,
Found	C 46.07	H 5.00	N 5.35.

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