Fast and efficient green synthesis of thiosulfonate S-esters by microwave-supported permanganate oxidation of symmetrical disulfides

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Potassium permanganate absorbed on copper(II) sulfate pentahydrate has been found to be an efficient, inexpensive, and green oxidation agent for the synthesis of “symmetrical” thiosulfonate S-esters by oxidation of the corresponding symmetrical disulfides. The oxidation reactions were carried out under solvent-free reaction conditions within 15 min under the influence of microwave irradiation, as well as (for comparison) supported by conventional heating, to afford yields of the thiosulfonate S-esters in the range of 60–83%. The oxidation reaction appears to proceed (at least partly) via an intermediate symmetrical vic-disulfoxide.

Keywords: thiosulfonate S-esters; disulfides; oxidation; potassium permanganate; microwave irradiation

1. Introduction

Thiosulfonate S-esters (general formula: R1-SO2-S-R2), in the following for simplicity referred to as thiosulfonates, have been known as existing molecular species for more than 80 years, during which they have attracted considerable attention as reactive and synthetically

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Scheme 1. Possible obtainable products by the oxidation of symmetric disulfides.

useful reagents within general and industrial organic chemistry,[1] as powerful sulfenylating reagents,[2] and as blocking agents in protein chemistry.[3] Based upon their synthetic availability, the thiosulfonates have often been divided into two subgroups, the “symmetrical” thiosulfonates ($R_1^1 = R_2^2$), and the “asymmetrical” thiosulfonates ($R_1^1 \neq R_2^2$).[1]

“Symmetrical” thiosulfonates have been prepared by oxidation of the corresponding symmetrical disulfides by means of hydrogen peroxide,[4–7] m-chloroperbenzoic acid (MCPBA) and other peroxy acids,[7–12] dimethyldioxirane (DMD),[10] sulfoxides in the presence of a rhenium catalyst,[13] triphenylphosphite ozonide,[14] tetrabutylammonium peroxymonosulfate,[15] and dinitrogen tetroxide.[16,17] Symmetrical disulfides can also be converted into the corresponding thiosulfonates by chlorosolvolysis [18–21] and by means of Selectfluor™ (1-chloromethyl-4-fluoro-1,4-diazeniabicyclo[2.2.2]octane bis(tetrafluoroborate)).[22,23]

Since a symmetrical disulfide is the product formed primarily upon oxidation of a thiol, it has naturally been attempted with some success to synthesize “symmetrical” thiosulfonates directly from thiols, for example, by means of chlorosolvolysis [21] and by oxidation with dinitrogen tetraoxide [24–26] or hydrogen peroxide in the presence of titanium tetrachloride.[27] Very recently the direct oxidation of thiols into the corresponding thiosulfonates by means of zinc dichromate trihydrate has also been reported.[28]

The oxidation potentialities of symmetrical disulfides are well investigated and perceived (Scheme 1).[29] Thus, depending on the nature of the disulfide, the nature of the oxidation agent, the molar ratio between the disulfide and the oxidation agent, and the reaction conditions in general, the oxidation can result in the formation of the fairly stable thiosulfinate $3$, the most stable and most useful thiosulfonate $4$, the sulfinyl sulfoxide $6$, or the vic-disulfone $7$. The vic-disulfoxide $5$ has hitherto not been isolated, but there are strong evidences [7,10,11,30,31] for its transient existence as a reactive intermediate in the controlled oxidation of thiosulfonates ($3$) into the corresponding thiosulfonates ($4$).[7,10–12,30–34] Under appropriate conditions, the thermally relatively less stable thiosulfinates ($3$) can undergo disproportionation to form a 1:1 mixture of the corresponding thiosulfonate ($4$) and the disulfide ($2$).[35–39] Some non-oxidative synthetic routes to thiosulfonates depend on the interaction of zinc on sulfinyl chlorides [40–43] or sulfonyl chlorides.[44,45] The latter type of compounds can also be converted into “symmetrical” thiosulfonates upon treatment with potassium iodide in anhydrous acetone containing catalytic amounts of pyridine [46] or with samarium powder in N,N-dimethylformamide.[47]

In continuation of our investigations of the utility of potassium permanganate [48] absorbed on copper sulfate pentahydrate as a versatile, efficient, and “green” oxidation agent,[49–52] we turned our attention toward the stable and useful thiosulfonates as target compounds. The KMnO$_4$ promoted oxidation process is recognized as “green” (friendly to the environment) because manganese dioxide (MnO$_2$), the co-product formed by the reduction of KMnO$_4$, can be isolated easily and subsequently recycled.[53] KMnO$_4$ promoted oxidation reactions of organic
sulfur compounds have been reported quite extensively. However, our literature search on the formation of thiosulfonates (as the product of a KMnO₄ promoted oxidation of symmetric disulfides) revealed only one single item, describing the conversion of diphenyl disulfide by means of KMnO₄ in boiling propionic acid to form S-phenyl benzenethiosulfonate in the yield of 8%.

2. Result and discussion

Preliminary attempts to synthesize a “symmetrical” thiosulfonate directly from the pertinent thiol by means of the oxidation agent xPP/yCSP (x mmol of potassium permanganate absorbed on y mmol of copper sulfate pentahydrate) turned out to be quite unsuccessful irrespective of the nature of the thiol as well as the nature of xPP/yCSP (i.e. the ratio x/y). The direct oxidation of the thiol easily leads to the risk of explosion under strong oxidation condition and is difficult to be performed with simple alkanethiols in gas phase (e.g. methanethiol, ethanethiol, propanethiol, etc.); while the oxidation of disulfides happens safely. Moreover, the easy conversion of the thiol into the corresponding symmetrical disulfide takes place under reaction conditions drastically different from those required to bring about the subsequent conversion of the disulfide into the corresponding thiosulfonate with low product selectivity and yield. Therefore, we decided to focus on the conversion of the symmetrical disulfide (2) into the corresponding thiosulfonate (4) as the main subject of this investigation (Scheme 2), since the starting materials, the symmetrical disulfides (2), appeared to be available either commercially or obtainable easily by KMnO₄ promoted oxidation of the pertinent thiols.

In search for the reaction conditions for maximum conversion of the symmetrical disulfides into the corresponding “symmetrical” thiosulfonates two series of introductory experiments were carried out, using dibutyl disulfide as the arbitrarily chosen model substance. In the first series of experiments, the ratio x:y in the oxidation reagents xPP/yCSP was varied and examined under solvent-free reaction conditions while assisted by microwave irradiation for obtaining the highest degree of conversion. The results demonstrated a choice of 1:3 as the best molar ratio, corresponding to the oxidation agent PP/3CSP.

In the next series of experiments, the molar ratio between dibutyl disulfide and PP/3CSP was varied and examined under the same reaction conditions as described above. After four experiments with increasing amounts of PP/3CSP relative to the 1.5 mmol of dibutyl disulfide (Figure 2), an amount of 6.0 mmol of PP/3CSP finally resulted in complete conversion of the disulfide into 97% of S-butyl butanethiosulfonate and 3% of a by-product having the same molecular weight as the thiosulfonate, but nevertheless also a completely different mass spectrum, as disclosed clearly by the GC/MS-analysis of the product mixture. The only plausible structure attributable to the by-product will be that of the vic-disulfoxide 5 (Scheme 1, R = butyl). However, the subsequent purification of the product mixture by column chromatography resulted in the isolation of only one product – that is, the thiosulfonate S-ester. Evidently, the transiently
Figure 1. Influence of the molar ratio between KMnO₄ and CuSO₄·5H₂O in the oxidation agent KMnO₄/CuSO₄·5H₂O on the efficiency of the oxidation of dibutyl disulfide into S-butyl butanethiosulfonate under solvent-free reaction conditions and assistance by microwave irradiation (250 W, 9 min., dibutyl disulfide: 1.5 mmol, KMnO₄: 6 mmol).

Figure 2. Influence of the molar ratio between dibutyl disulfide and PP/3CSP on the efficiency of the oxidation of dibutyl disulfide into S-butyl butanethiosulfonate under solvent-free reaction conditions and assistance by microwave irradiation (250 W, 9–12.5 min).

formed vic-disulfoxide cannot survive under the conditions of the chromatographic separation. This observation confirms earlier statements as regards the existence and the stability of vic-disulfoxides.[7,9,10,11,30,31,34,58]

Upon replacement of microwave irradiation by ultrasound irradiation, but otherwise under the same reaction conditions as described above, the conversion of dibutyl disulfide into the corresponding thiosulfonate S-ester amounted to only 6%, even after 5 h of ultrasound irradiation. This observation led us to conclude, that the oxidation of the disulfide into the corresponding thiosulfonate S-ester fundamentally requires a sufficiently high reaction temperature. In order to confirm this conclusion, the same oxidation reaction as described above, that is, the oxidation
Table 1. The optimized yield following the molar ratio of disulfides and **PP**/**CSP** under solventless conditions.\(^a\)

| Entry | Product | Method A Yield (GC, time\(^b\), P\(^c\)) | Method B Yield (GC, time\(^b\), Temp.\(^d\)) |
|-------|---------|----------------------------------------|------------------------------------------|
| 1     | ![Image] | 82 (100, 11.2, 250)                    | 80 (100, 11.2, 103)                      |
| 2     | ![Image] | 83 (100, 9.0, 250)                     | 78 (97, 9.0, 101)                       |
| 3     | ![Image] | 63 (72, 3.45, 250)                     | 68 (89, 3.45, 100)                      |
| 4     | ![Image] | 80 (97, 12.5, 250)                    | 73 (100, 12.5, 103)                    |
| 5     | ![Image] | 68 (91, 3.5, 150)                     | 63 (83, 3.5, 100)                      |
| 6     | ![Image] | 75 (95, 4.4, 250)                     | 65 (89, 4.4, 98)                       |
| 7     | ![Image] | 70 (86, 4.6, 250)                     | 71 (89, 4.6, 96)                       |
| 8     | ![Image] | 60 (62, 10.4, 500)                    | 68 (87, 10.4, 91)                      |

\(^a\)Yields were determined by GC/MS.
\(^b\)time = reaction time in minutes.
\(^c\)P = power of microwave oven (Watt).
\(^d\)temp. = reaction temperature (°C).

of dibutyl disulfide into \(S\)-butyl butanethiosulfonate, was carried out at the same temperature as measured by the end of the microwave-assisted experiment, but now with the microwave irradiation being replaced by conventional heating. The latter reaction, which was carried out within the same period of time as found optimal for the microwave-assisted reaction, afforded a somewhat lower yield of \(S\)-butyl butanethiosulfonate, while not even traces of the \(vic\)-disulfoxide could be detected (Table 1).

Subsequently, seven additional symmetrical disulfides (R-S-S-R), representing an appropriate selection of aliphatic, cyclic, and aromatic species (\(R = Me, Et, Pr^t, Bu^t, n-C_8H_{17}, cyclohexyl,\) and \(C_6H_5\)) were subjected to solvent-free oxidation by **xPP**/**yCSP** under microwave irradiation as well as under conventional heating conditions (Scheme 2). The reaction conditions found optimum for the oxidation of dibutyl disulfide into \(S\)-butyl butanethiosulfonate were intended to be used as starting reaction conditions also for the seven additional symmetrical disulfides.

However, it very soon became evident that the oxidation of a symmetrical disulfide into the corresponding thiosulfonate \(S\)-ester depends decisively on the nature of the disulfide R-group. Therefore, for each of the symmetrical disulfides chosen, a series of experiments were performed
in order to determine the optimum reaction conditions for total or maximum conversion into the corresponding thiosulfonate $S$-ester. The microwave-assisted permanganate oxidation of the chosen eight symmetrical disulfides was found to give yields of the corresponding thiosulfonate $S$-esters in the range of 60–83% within 4–13 min (Method A, Table 1). In all cases, except a single one (diphenyl disulfide) the crude product mixture contained also a minor amount (3–14%, determined by GC/MS) of the corresponding vic-disulfoxide 5 (Scheme 1), but these apparently very unstable species never survived the subsequent purification by means of column chromatography.

As described above for the oxidation of dibutyl disulfide into $S$-butyl butanethiosulfonate, all of the seven additionally selected symmetrical disulfides were also found able to undergo oxidation into the corresponding thiosulfonate $S$-esters by means of conventional heating to the same temperature as measured by the end of the microwave-assisted oxidation reactions. The yields of the thiosulfonate $S$-esters obtained under the conditions of conventional heating (Method B, Table 1) are comparable to or slightly lower than those obtained under the assistance of microwave irradiation.

Inspired by the successful syntheses of “symmetrical” thiosulfonate $S$-esters by microwave-assisted permanganate oxidation of symmetrical disulfides, we investigated the reactivity of three asymmetrical disulfides toward PP/3CSP under microwave irradiation and solvent-free conditions as before. However, the results were quite disappointing (Scheme 3): 6 different products were observed in varying amounts (depending evidently on the nature of $R_1$ and $R_2$), apparently owing to the occurrence of a complicated combination of oxidation and disproportionation processes. In this respect our results are comparable to those reported earlier for the oxidation of asymmetrical disulfides by means of hydrogen peroxide,[7] $m$-chloroperbenzoic acid,[7] and sodium periodate.[33]

3. Conclusion

Comprehensive experimental work has made it possible for us to introduce a new, efficient, fast, and green (eco-friendly) synthetic method for the preparation of “symmetrical” thiosulfonate $S$-esters in fair to high yields by solvent-free oxidation of symmetrical disulfides by means of PP/3CSP under the assistance of microwave irradiation, subsidiarily also under the influence of conventional heating.

4. Experimental

4.1. Instrumentation and chemicals

4.1.1. Instrumentation

Microwave irradiations were performed by means of a CEM MDS 200 batch microwave oven. Ultrasound irradiation was performed by means of a BRANSON 1210E-MT ultrasonic bath,
operating at frequency 47 kHz. GC/MS analyses were performed on a Hewlett Packard 5890 GC 5971A MS apparatus equipped with a J&W DB-5MS capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness) and a Hewlett Packard 7673A autosampler. NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer.

4.1.2. **Chemicals**

All commercially available chemicals used were from Aldrich. All synthesized symmetric as well as asymmetric disulfides used as starting materials were analyzed for authenticity and purity by NMR and GC/MS before being used.

4.1.2.1. **Preparation of commercially unavailable disulfides.** Finely ground solid potassium permanganate (KMnO₄, 70 mmol, 11.06 g) was added slowly in small portions during 2 h into a 500 mL round bottom flask containing 210 mmol of the pertinent thiol (1-butanethiol, 2-methyl-2-propanethiol, cyclohexanethiol, or 1-octanethiol). The exothermal reaction was performed with magnetic stirring, and the reaction flask should be placed in an ice/water bath to prevent potential superheating of the more or less inflammable thiols. Subsequently, the reaction mixture was stirred for 6 h at room temperature. Then, the reaction mixture was extracted with 4 × 50 mL of diethyl ether. The combined extracts were filtered through a 1.5–2 cm layer of celite 545, and then dried by anhydrous Na₂SO₄. After removal of the solvent by rotary evaporation, the disulfide was obtained in an almost quantitative yield as a colorless oil of purity > 99% (according to analysis by GC/MS). The ¹H and ¹³C NMR spectra of all of the four disulfides synthesized were compatible with those reported in the literature.

- **Dibutyl disulfide:** ¹H NMR (CDCl₃): δ_H = 2.69 (t, J = 7.2 Hz, 4H), 1.61–1.71 (m, 4H), 1.36–1.48 (m, 4H), 0.93 (t, J = 7.2 Hz, 6H). ¹³C NMR (CDCl₃): δ_C = 38.90 (2C), 31.33 (2C), 21.67(2C), 13.71 (2C). MS: m/z = 178[M]⁺, 122, 87, 79, 57, 41.
- **Di-t-butyl disulfide:** ¹H NMR (CDCl₃): δ_H = 1.31 (s, 18H). ¹³C NMR (CDCl₃): δ_C = 46.1 (2C), 30.6 (6C). MS: m/z = 178[M]⁺, 122, 107, 57, 41.
- **Dioctyl disulfide:** ¹H NMR (CDCl₃): δ_H = 2.68 (t, J = 7.2 Hz, 4H), 1.62–1.72 (m, 4H), 1.28–1.42 (m, 20H), 0.88 (t, J = 7.2 Hz, 6H). ¹³C NMR (CDCl₃): δ_C = 39.2 (2C), 31.8 (2C), 29.26 (2C), 29.23 (2C), 29.21 (2C), 28.6 (2C), 22.7 (2C), 14.1 (2C). MS: m/z = 290[M]⁺, 178, 145, 115, 102, 87, 71, 57.
- **Dicyclohexyl disulfide:** ¹H NMR (CDCl₃): δ_H = 2.64–2.74 (m, 2H), 1.98–2.10 (m, 4H), 1.74–1.86 (m, 4H), 1.56–1.66 (m, 2H), 1.15–1.40 (m, 10H). ¹³C NMR (CDCl₃): δ_C = 49.9 (2C), 32.9 (4C), 26.1 (4C), 25.7 (2C). MS: m/z = 230[M]⁺, 148, 113, 83, 55, 41.

4.1.2.2. **Preparation of oxidant xPP/yCSP.** The copper sulfate pentahydrate was dissolved completely in de-ionized water. Then, the pertinent amount of KMnO₄ was added, followed by a sufficient volume of de-ionized water to obtain a homogeneous solution. The solution was stirred for 10 min at 80°C. Subsequently water was removed from the solution by rotational evaporation, until the weight of the remaining solid mass was equal to the sum of the weights of the original ingredients. Finally, the obtained solid mass was ground in a mortar into a fine homogeneous powder.

4.2. **Typical procedures**

4.2.1. **Oxidation of dibutyl disulfide into the corresponding thiosulfonates by PP/3CSP under solvent-free reaction conditions assisted by microwave irradiation (Method A)**

A pertinent quantity of finely ground PP/3CSP (6 mmol, 5.45 g) was added to a test tube (h = 20.0 cm, d = 3.0 cm) containing also the disulfide (1.5 mmol). The test tube was placed
into a beaker available in the microwave oven. For each of the disulfides, an irradiation programme was applied to determine the most efficient reaction conditions (with respect to maximum yield of product, most convenient irradiation power (W), and the shortest reaction time (minutes)), see Table 1. For every experiment, the temperature of the reaction mixture was measured immediately after reaction stop. After cooling, the reaction mixture was stirred with 50 mL of chloroform during 30 min and then filtered through a 2 cm layer of celite. Subsequently, the solvent was removed from the extract by rotational evaporation, and the remaining crude product was analyzed by GC/MS and NMR spectroscopy. Finally, the thiosulfonate was purified by flash column chromatography (7 g silica gel, Daviscil, grade 710, 4–20 µm, 60 A, 99%) using as eluent a mixture of hexane and dichloromethane.

4.2.2. Oxidation of dibutyl disulfide into corresponding thiosulfonates by PP/3CSP under solvent-free reaction conditions assisted by conventional heating (Method B)

A test tube ($h = 20.0 \text{ cm, } d = 3.0 \text{ cm}$) containing a pertinent quantity of finely ground PP/3CSP (6 mmol, 5.45 g) and the disulfide (1.5 mmol) was placed in an oil bath heated to the temperature measured by the reaction stop of the parallel reaction run under microwave irradiation. The test tube was kept in the oil bath for a period of time corresponding exactly to that found at optimum by Method A. After cooling, the reaction mixture was worked up as described in Method A.

4.3. Spectroscopic data

The identity and purity of all of the thiosulfonates synthesized were ensured by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy as well as by GC/MS. Furthermore, all of the thiosulfonates were also analyzed by IR spectroscopy in order to obtain information concerning the occurrence of conformational isomerism.[59] The observed $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopic data for the eight thiosulfonate S-esters synthesized are listed below, and all of them were found compatible with those reported in the literature.[60–62]

- **Methyl methanethiosulfonate**: $^1\text{H}$ NMR (CDCl$_3$): $\delta_H = 3.32$ (s, 3H), 2.71 (s, 3H). $^{13}\text{C}$ NMR (CDCl$_3$): $\delta_C = 48.89$, 18.36. MS: $m/z = 126[M]^+$, 111, 95, 81, 64.

- **Ethyl ethanethiosulfonate**: $^1\text{H}$ NMR (CDCl$_3$): $\delta_H = 3.33$ (q, $J = 7.5 \text{ Hz, 2H}$), 3.16 (q, $J = 7.2 \text{ Hz, 2H}$), 1.48 (t, $J = 7.2 \text{ Hz, 3H}$), 1.43 (t, $J = 7.5 \text{ Hz, 3H}$). $^{13}\text{C}$ NMR (CDCl$_3$): $\delta_C = 57.15$, 30.68, 15.20, 8.39. MS: $m/z = 154[M]^+$, 139, 125, 95, 62.

- **i-Propyl 1-methylethanesulfonate**: $^1\text{H}$ NMR (CDCl$_3$): $\delta_H = 3.61–3.73$ (m, 1H), 3.27–3.41 (m, 1H), 1.48 (d, $J = 2.4 \text{ Hz, 6H}$), 1.46 (d, $J = 2.1 \text{ Hz, 6H}$). $^{13}\text{C}$ NMR (CDCl$_3$): $\delta_C = 63.59$, 43.03, 24.34 (2C), 16.39 (2C). MS: $m/z = 182[M]^+$, 140, 117, 103, 76, 61, 43.

- **n-Butyl butanethiosulfonate**: $^1\text{H}$ NMR (CDCl$_3$): $\delta_H = 3.30$ (t, $J = 7.8 \text{ Hz, 2H}$), 3.14 (t, $J = 7.5 \text{ Hz, 2H}$), 1.84–1.95 (m, 2H), 1.68–1.78 (m, 2H), 1.38–1.56 (m, 4H), 0.97 (t, $J = 7.2 \text{ Hz, 3H}$), 0.95 (t, $J = 7.5 \text{ Hz, 3H}$). $^{13}\text{C}$ NMR (CDCl$_3$): $\delta_C = 62.46$, 35.95, 31.66, 25.51, 21.75, 21.29, 13.56, 13.46. MS: $m/z = 210[M]^+$, 121, 89, 56, 41.

- **t-Butyl 1,1-dimethylethanesulfonate**: $^1\text{H}$ NMR (CDCl$_3$): $\delta_H = 1.62$ (s, 9H), 1.47 (s, 9H). $^{13}\text{C}$ NMR (CDCl$_3$): $\delta_C = 68.13$, 56.43, 31.56 (3C), 23.77 (3C). MS: $m/z = 210[M]^+$, 146, 89, 57.

- **n-Octyl octanethiosulfonate**: $^1\text{H}$ NMR (CDCl$_3$): $\delta_H = 3.29$ (t, $J = 7.8 \text{ Hz, 2H}$), 3.13 (t, $J = 7.8 \text{ Hz, 2H}$), 1.86–1.93 (m, 2H), 1.69–1.79 (m, 2H), 1.38–1.46 (m, 2H), 1.28–1.35 (m, 18H), 0.88 (t, $J = 6.9 \text{ Hz, 6H}$). $^{13}\text{C}$ NMR (CDCl$_3$): $\delta_C = 62.74$, 36.28, 31.74, 31.70, 29.68, 29.08, 29.02, 28.96, 28.93, 28.60, 28.00, 23.54, 22.62, 22.60, 14.08, 14.07. MS: $m/z = 323[M]^+$, 177, 145, 112, 69, 55, 41.
**Cyclohexyl cyclohexanethiosulfonate**: $^1$H NMR (CDCl$_3$): $\delta_H = 3.42$–$3.53$ (m, 1H), $3.02$–$3.12$ (m, 1H), $2.28$–$2.38$ (m, 2H), $2.06$–$2.11$ (m, 2H), $1.90$–$2.00$ (m, 2H), $1.20$–$1.80$ (m, 14H). $^{13}$C NMR (CDCl$_3$): $\delta_C = 71.51$, $50.4$, $34.30$ (2C), $26.27$ (2C), $25.94$ (2C), $25.25$ (2C), $25.17$, $25.10$. MS: $m/z = 262$[M]$^+$, $149$, $117$, $83$, $64$, $55$, $41$.

**Phenyl benzenethiosulfonate**: $^1$H NMR (CDCl$_3$): $\delta_H = 7.29$–$7.61$ (m, 10H). $^{13}$CNMR (CDCl$_3$): $\delta_C = 142.92$, $136.57$, $133.65$ (2C), $131.42$ (2C), $129.44$, $128.81$ (2C), $127.81$ (2C), $127.54$. MS: $m/z = 250$[M]$^+$, $184$, $141$, $125$, $109$, $77$, $65$, $51$.

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**Supplemental data**

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