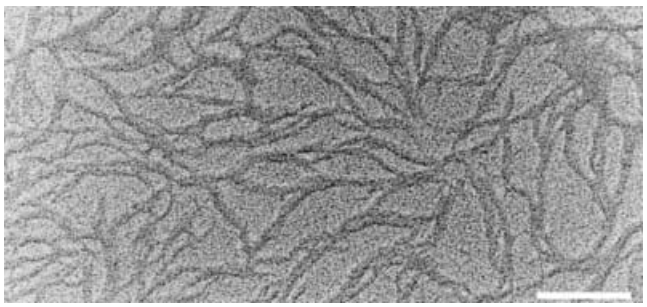

Figure 3. Transmission electron micrograph of a 1/1 mixture of **A***n*Bu and potassium picrate (3 mM in $CHCl_3/CH_3CN$ (1.7/1.0)). The white bar (bottom right) represents 200 nm. The sample was prepared as described in ref. [3d]).

foldamer[16] and generates a polar inner void towards the center of which all the napy electrical dipoles are directed. This arrangement induces cation complexation, which in turn promotes the multiple supramolecular association of ligands, through effects such as ion–dipole interaction and π stacking between the aromatic rings.

The hierarchical self-organization observed amounts to a sort of effector-induced growth process and is reminiscent of the self-assembly of the tobacco mosaic virus, where the formation of the helical protein coat results from the induced association of the peptide components by the nucleic acid strand occupying the central void of the polymolecular architecture. The formation of cation-containing polymolecular stacks of helical monomeric components suggests that such entities may potentially act as transmembrane ion channels[1, 17] that would not only conduct ions but also build up solely if suitable ions are present, thus presenting a most intriguing ability to perform a cation-selective self-regulation of ion flow.

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The Determination of the Absolute Configurations of Diastereomers of (*S*)-Camphanoyl 3-Hydroxy-5-oxohexanoic Acid Derivatives by X-ray Crystallography**

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Polyketides form a major class of secondary metabolites,[1] produced by fungi, lichens, and higher plants. 6-Methylsalicylic acid (6-MSA) is one of the simplest aromatic compounds produced by a polyketide biosynthesis pathway. It is assembled from one molecule of acetyl-coenzyme A (acetyl-CoA),

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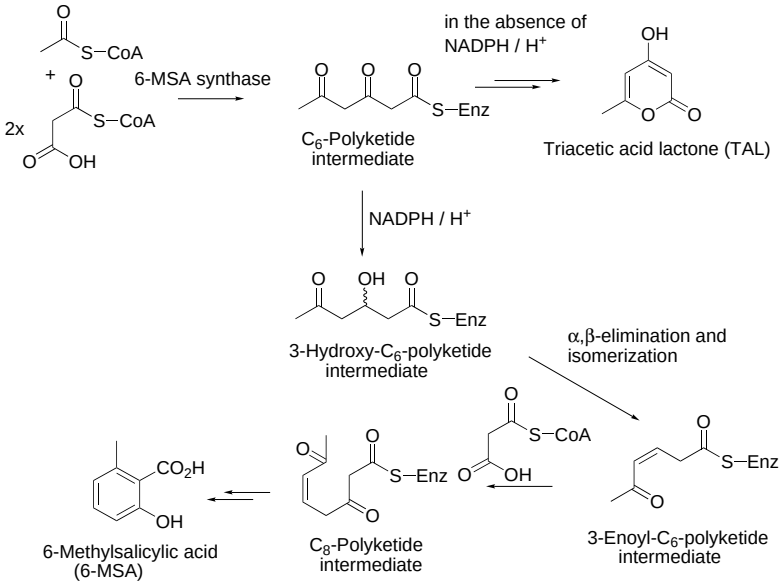
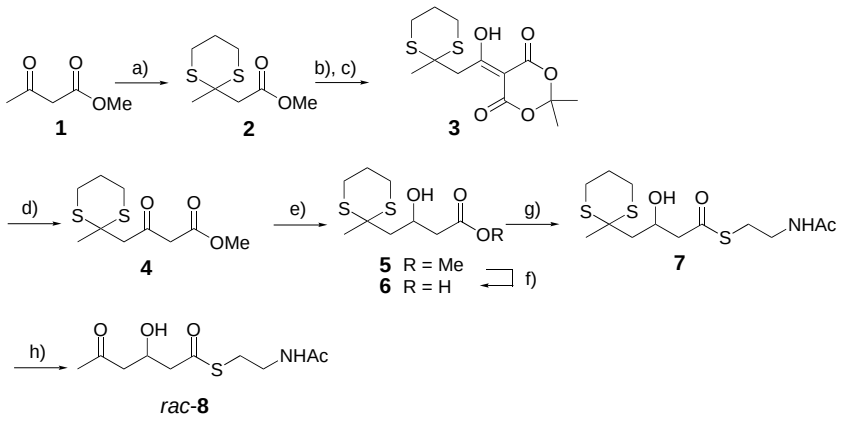
three molecules of malonyl-CoA, and one molecule of nicotinamide adenine dinucleotide phosphate, reduced form (NADPH), by the enzyme 6-methylsalicylic acid synthase[2] (Scheme 1). The mechanism of action of this multifunctional enzyme commences with a starter molecule, acetyl-CoA, which undergoes two successive Claisen condensations with two molecules of malonyl-CoA, to form an enzyme-bound C_6-triketide intermediate. This compound is then reduced with NADPH to the corresponding 3-hydroxy-5-oxohexanoyl (3-hydroxy-C_6) intermediate, followed by α,β-elimination and isomerization, to yield a *cis*-5-oxohex-3-enoyl (3-enoyl-C_6) intermediate. A final Claisen condensation with a third malonyl-CoA then occurs, which leads to the production of a C_8 intermediate, which dehydrates and cyclizes to form 6-methylsalicylic acid. In the absence of NADPH, the C_6-triketide intermediate is eliminated from the enzyme and cyclizes prematurely to form triacetic acid lactone (TAL; Scheme 1),[1]. In the presence of NADPH, the resulting hydroxy-C_6 unit is converted through the normal catalytic sequence into 6-MSA. The stereochemical events operating in 6-MSA biosynthesis have been extensively investigated in our laboratory. Specific stereochemical insights were obtained by a series of experiments using chiral (*2R*)[1-^{13}C; 2-^{2}H]-malonyl-CoA and (*2S*)[1-^{13}C; 2-^{2}H]-malonyl-CoA.[3] These were incubated with acetyl-CoA, NADPH, and highly purified 6-MSA synthase. The mass spectra of the mixtures were then analyzed and compared. The results of the analysis indicate that there is a single base at the enzyme active site which can perform the α,β-elimination in the 3-hydroxy-C_6 intermediate and the isomerization process in the next step. A key stage in the enzyme reaction is the reduction of the C_6-triketide to the 3-hydroxy C_6 intermediate. A knowledge of the stereochemistry of this hydroxy-intermediate is essential for a full understanding of the mechanism of the reaction pathway. To analyze the role and stereospecificity of the 3-hydroxy-C_6 intermediate and the timing of its formation in the 6-MSA synthase catalytic cycle, it was necessary to develop a synthesis for both chiral 3-hydroxy-C_6 intermediates as their corresponding 2-(acetylamino)ethyl thioesters (NACs) for incubation these with 6-MSA synthase. There is evidence that NACs are accepted as substrates by some polyketide synthases.[4] The synthesis of the racemic 2-(acetylamino)ethyl 3-hydroxy-5-oxohexanethioate (**8**; Scheme 2) has been achieved in our laboratory by protection of the C_5 ketone with a dithiane group. The synthesis of the mixture has also been reported elsewhere using a different method.[5] Here, we report the resolution of the racemic mixture of **8**, by a method which employs the chiral auxillary, (*S*)-camphanoyl chloride. Subsequent X-ray crystallographic analysis of the corresponding (*S*)-camphanoyl-hydroxy-C_6 derivatives allowed their unambiguous characterization and the assignment of the C3 stereochemistry.

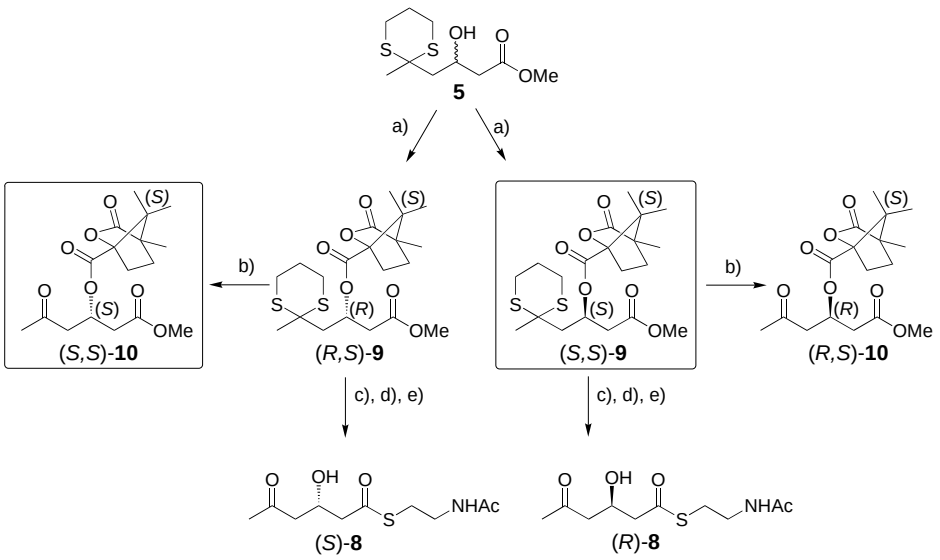


Scheme 1. The biosynthetic pathway for 6-MSA.



Scheme 2. Reagents and conditions: a) $ZnCl_2$, HCl gas, 1,3-propanedithiol, b) 10% NaOH, 90 °C/HCl, c) 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid), *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), d) MeOH, reflux in toluene, e) $NaBH_4$, MeOH, f) 2 M NaOH/HCl, g) $(PhO)_2P(O)(N_3)$, NEt_3, DMAP, *N*-acetylcysteamine, dimethylformamide (DMF), h) MeI, $CaCO_3$, 50 °C. Full experimental details and physical data are given in the Supporting Information.

The synthesis of (*S*)-camphanoyl-hydroxy-C_6 derivatives is shown in Scheme 3. A racemic mixture of **5**, which contains the C_6 backbone, was prepared from 2-methyl-[1,3]dithian-2-yl-acetic acid (**2**)[6] and Meldrum's acid, heated under reflux with methanol in toluene and reduced using $NaBH_4$. Diastereomers methyl (3*R*)- or (3*S*)-[3-(*S*)-camphanoyloxy]-4-(2-methyl-1,3-dithian-2-yl)butanoate ((*R*,*S*)-**9** and (*S*,*S*)-**9**, respectively), were prepared in 45% yield in a ratio of 1:1, by the reaction of the racemic **5** with (*S*)-camphanoyl chloride. The *RS* and *SS* compounds were separated by column chromatography and recrystallized from toluene. Deprotection, achieved by use of trimethyloxonium tetrafluoroborate,[7] afforded the corresponding *keto*-derivatives, methyl (3*S*)- or (3*R*)-[3-(*S*)-camphanoyloxy]-5-oxohexanoate,((*S*,*S*)-



Scheme 3. Reagents and conditions: a) (*S*)-camphanoyl chloride, NEt_3, DMAP, 1,2-dichloroethane (DCE), b) $Me_3O^+BF_4^-$, dichloromethane (DCM), c) 3.5 M HCl/2 M NaOH, HCl, d) $(PhO)_2P(O)(N_3)$, *N*-acetylcysteamine, DMF, e) MeI, $CaCO_3$, 50 °C[8]. The boxed structures have been determined by X-ray crystallography.

10 and (*R*,*S*)-**10**, respectively),[8] which were also recrystallized from toluene, each in approximately 85% yield.

The X-ray crystal structures of (*S*,*S*)-**9** (Figure 1) and (*S*,*S*)-**10** (Figure 2) indicate unambiguously that the syntheses of both the *RS* and *SS* diastereomers were successful. Importantly, the X-ray structures confirm that no loss of chirality occurred at C-3 during deprotection. *R*-**8** and *S*-**8** were finally obtained by acid and base hydrolyses, and subsequent deprotection.

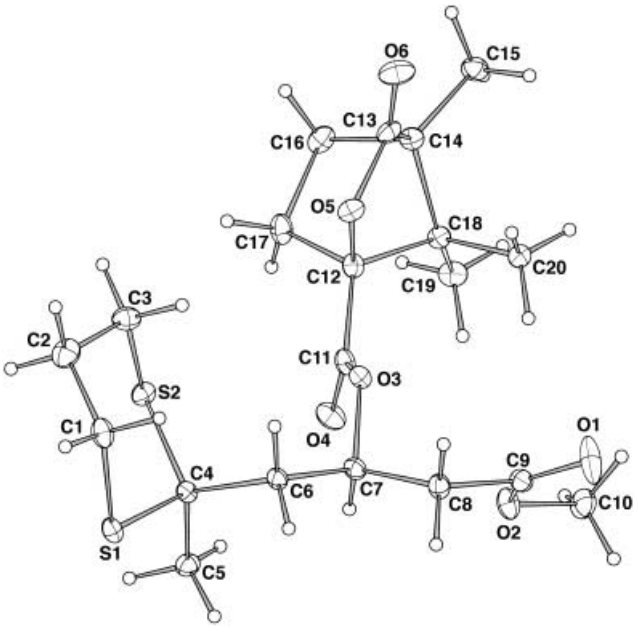


Figure 1. The X-ray crystallographic structure of (*S*,*S*)-**9**.

Incorporation experiments were carried out with *R*-**8** and *S*-**8**, using highly purified 6-methylsalicylic acid synthase, isolated from *Penicillium patulum*, to ascertain whether either could be enzymatically transformed into 6-MSA. This would require the initial transfer of the acyl group to an enzyme thiol, to form a bound 3-hydroxy C_6-intermediate (Scheme 1), followed by dehydration and addition of a malonyl moiety from malonyl-CoA. On incubation with the enzyme, neither intermediate was able to form 6-MSA at a rate significantly greater than that with malonyl-CoA alone, although the enzyme was inhibited by both enantiomers. This result could be predicted, as the natural substrates of 6-MSA synthase are CoA thiolesters rather than *N*-acetylcysteamine thiolesters. Furthermore, observations with other polymerases suggest that such enzymes do not always recognize externally added intermediates or their analogues. For instance, in the tetra-

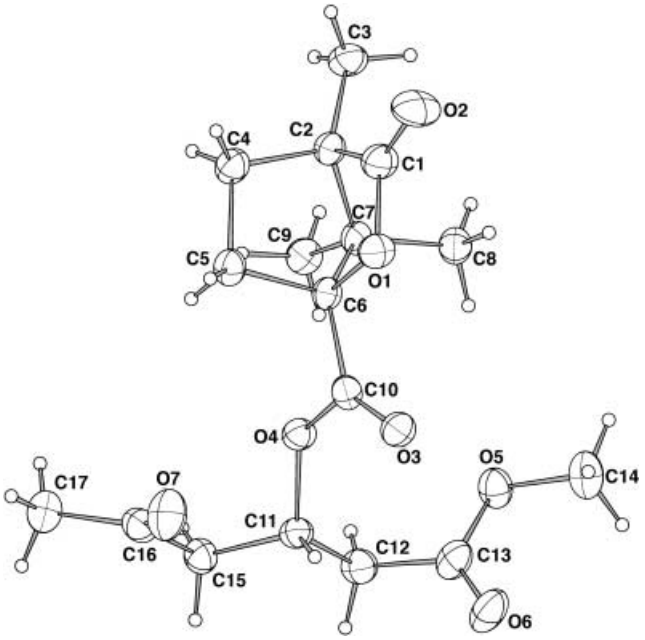


Figure 2. The X-ray crystallographic structure of (*S*,*S*)-**10**.

merization reaction catalyzed by porphobilinogen deaminase, neither dipyrromethanes[9] nor tripyrranes[10] are able to act as substrates, despite their known involvement as enzyme bound species.[11] Thus, the enzyme recognizes only the monopyrrolic building unit, porphobilinogen, rather than more advanced intermediates. A similar observation has been made in fatty acid biosynthesis, in which advanced intermediate thiol esters are not recognized by the enzyme and are not incorporated into palmitic acid.[12] Whilst these results are somewhat disappointing with respect to determination of the absolute stereochemistry of enzyme bound 3-hydroxy-5-oxohexanoyl thiolester intermediate, the synthetic methodology devel-

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oped, and the availability of the two enantiomers, will be useful for investigating other polyketide synthases, some of which can recognize *N*-acetylcysteamine thiol esters.

Experimental Section

3: Compound **2** (3.0 g, 15.6 mmol), Meldrum's acid (2.47 g, 17.1 mmol), and DMAP (2.86 g, 23.4 mmol) were dissolved in CH_2Cl_2 (100 mL). The solution was cooled to $-5\,^{\circ}C$ and a solution of DCC (3.55 g, 17.2 mmol) in CH_2Cl_2 (50 mL) was added dropwise over an hour. The resulting solution was stirred at $4\,^{\circ}C$ for 18 h, during which time crystals of dicyclohexylurea were formed. After filtration, the organic solution was washed with 5% $KHSO_4$, brine, and water, and dried over Na_2SO_4. After filtration and evaporation of the solvent, crystals were obtained (4.5 g). The crystals were recrystallized from *n*-hexane, filtered when hot. Pale yellow crystals were collected (4.2 g, 85%). M.p. = 92–93 °C; IR (Nujol): $\tilde{\nu}$ = 2950, 1755, 1670, 1575, 1210, 1140 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 15.35 (s, 1H; OH), 4.00 (s, 2H; CH_2), 3.15 (m, 2H; CH_2), 2.70 (m, 2H; CH_2), 2.15 (m, 2H; CH_2), 1.79 (s, 6H; 2 × CH_3), 1.75 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 191.6, 160.9, 104.9, 94.0, 48.3, 44.3, 29.5, 27.3, 26.8, 24.5; δ_{DEPT}: [CH_3] 29.5 and 26.8. [CH_2] 44.3, 27.3 and 24.5; ES-MS +ve mode: [$M^+ - H$] 317.0 (84), 212.5 (10); HRMS calcd for $C_{13}H_{18}S_2O_5$: 318.0596, found: 318.0598.

4: Compound **3** (1.2 g, 3.8 mmol) and MeOH (0.6 g, 18.8 mmol) were mixed in dry toluene (20 mL), and the resulting solution was heated under reflux for 3 h. After the evaporation of the solvent, a yellow oil was obtained (0.73 g, 77%). The ratio of the keto to enol forms was about 3.7:1. IR (liquid film): $\tilde{\nu}$ = 2980, 2950, 1760, 1732, 1670, 1640, 1250, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): [keto] δ = 3.76 (s, 3H; CH_3), 3.62 (s, 2H; CH_2), 3.24 (s, 2H; CH_2), 2.80–3.05 (m, 4H; 2 × CH_2), 1.90–2.15 (m, 2H; CH_2) and 1.75 (s, 3H; CH_3); [enol] δ = 12.05 (s, 1H; OH), 5.11 (s, 1H; CH), 3.75 (s, 3H; CH_3), 3.24 (s, 2H; CH_2), 2.80–3.05 (m, 4H; CH_2 + CH_2), 1.90–2.15 (m, 2H; CH_2), and 1.75 (s, 3H; CH_3); HRMS calcd for $C_{10}H_{16}S_2O_3$: 248.0541, found: 248.0539.

5: Compound **4** (2.58 g, 10.4 mmol) was dissolved in MeOH (40 mL) and the solution was cooled to 0 °C. $NaBH_4$ (1.18 g, 31.0 mmol) was added in portions over 15 min and the resulting solution was stirred at 25 °C for an hour. Saturated citric acid was added, and the solution was extracted with ether. The combined ether layers were washed with water and dried over Na_2SO_4. After evaporation of the solvent, a yellow oil was obtained (2.05 g, 79%). IR (LF): $\tilde{\nu}$ = 3520, 2990, 2950, 1745, 1180, 1010 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.38 (m, 1H; CH), 3.65 (s, 3H; CH_3), 3.64 (d, *J* = 3.8 Hz, 1H; OH), 3.00 (m, 2H; CH_2), 2.80 (m, 2H; CH_2), 2.57 (dd, *J* = 15.4 and 7.7 Hz, 1H; CH), 2.52 (dd, *J* = 15.4 and 5.2 Hz, 1H; CH), 2.38 (dd, *J* = 15.0 and 8.8 Hz, 2H; CH_2), 1.85–2.10 (m, 2H; CH_2), and 1.64 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 172.2, 65.7, 51.8, 47.5, 46.7, 42.1, 28.4, 26.8, 26.6 and 24.6; HRMS calcd for $C_{10}H_{18}S_2O_3$: 250.0697, found: 250.0695.

6: The ester **5** was stirred in 2 M NaOH for 18 h at 25 °C, and 2 M HCl was added until pH 4–5 was reached. The solution was extracted with ether. After the work-up, a yellow oil was obtained in approximately 70% yield. IR (LF): $\tilde{\nu}$ = 3450, 3000–2500, 2990, 2960, 1725, 1190, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.42 (m, 1H; CH), 3.02 (m, 2H; CH_2), 2.80 (m, 2H; CH_2), 2.62 (dd, *J* = 15.8 and 7.4 Hz, 1H; CH), 2.54 (dd, *J* = 15.8 and 5.5 Hz, 1H; CH), 2.47 (2H, dd, *J* = 15.0 and 9.5 Hz), 1.85–2.15 (2H, m), and 1.70 (3H, s).

7: Compound **6** (0.28 g, 1.2 mmol), diphenylphosphoryl azide (0.65 g, 2.4 mmol), NEt_3 (0.14 g, 1.4 mmol) and a catalytic amount of DMAP were dissolved in DMF (8 mL), and the solution was stirred at 25 °C under N_2 for 3 h. A solution of *N*-acetylcysteamine (0.42 g, 3.5 mmol) and NEt_3 (0.36 g, 3.6 mmol) in DMF (3 mL), prepared under N_2, was added through a syringe. The solution was stirred at 25 °C for 24 h under N_2. The DMF was then diluted with brine (10 mL) and extracted with ether. The combined ether layers were dried over Na_2SO_4, filtered and evaporated, yielding a yellow oil (0.46 g). The oil was chromatographed in EtOAc : petroleum ether (40–60 °C) (1:2), and purified again by preparative TLC (thin-layer chromatography) with EtOAc:MeOH (5:1). A light yellow oil (0.16 g, 40%) was obtained. R_f = 0.65 (EtOAc:MeOH (5:1)); IR (LF): $\tilde{\nu}$ = 3350, 3120, 2960, 1670, 1560, 1300, 1120, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.00 (s, broad, 1H; NH), 4.45 (m, 1H; CH), 3.75 (s, 1H; OH), 3.45 (m, 2H; CH_2), 3.08 (m, 2H; CH_2), 2.75–3.05 (m, 4H; 2 × CH_2), 2.68 (dd, *J* = 15.0 and 9.0 Hz, 1H; CH), 2.40 (dd, *J* = 15.0 and 4.4 Hz, 1H; CH), 2.05 (m, 2H; CH_2), 1.90 (m, 2H; CH_2), 1.98 (s, 3H; CH_3) and 1.70 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 198.0, 170.4, 66.3, 51.5, 47.3, 46.6, 39.4, 28.8, 28.4, 26.8, 26.6, 24.5 and 23.2; δ_{DEPT} ($CDCl_3$): [CH, CH_3] 66.3, 28.4 and 23.2. [CH_2] 51.5, 46.6, 39.4, 28.8, 26.8, 26.6 and 24.5; ES-MS +ve mode: [M^++Na] 359.5 (91), 238.9 (62), 117.7 (100). HRMS calcd for $C_{13}H_{23}NS_3O_3$: 337.0840, found: 338.0740 (M^++H).

rac-**8**: Compound **7** (35 mg, 0.1 mmol), CH_3I (200 μL) and $CaCO_3$ (20 mg) were mixed and stirred in CH_3CN:H_2O/9:1 (2 mL) at 50 °C. The reaction was monitored at half hourly intervals by TLC. Additional portions of $CH_3I/CaCO_3$ were added to the reaction suspension until the disappearance of the starting material was confirmed by TLC. Four additional portions of $CH_3I/CaCO_3$ were added in total. The solvents were subsequently evaporated and the oil was dried in vacuo. CH_2Cl_2 was added to the residue and filtered. After the TLC separation, a light yellow oil was obtained (11.8 mg, 46%). R_f = 0.53 (EtOAc:MeOH (5:1)); IR (LF): $\tilde{\nu}$ = 3400, 2950, 1710, 1690, 1660, 1550, 1380, 1300 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.82 (s, 1H; NH), 4.54 (m, 1H; CH), 3.46 (m, 2H; CH_2), 3.38 (d, *J* = 3.7 Hz, 1H; OH), 3.07 (t, *J* = 6.3 Hz, 2H; CH_2), 2.81 (dd, *J* = 15 and 7.7 Hz, 1H; CH), 2.73 (dd, *J* = 15 and 5.2 Hz, 1H; CH), 2.70 (d, *J* = 5.9 Hz, 2H; CH_2), 2.20 (s, 3H; CH_3), 1.98 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 208.5, 198.1, 170.5, 64.9, 49.9, 48.9, 39.2, 30.8, 28.9, 23.2; δ_{DEPT} ($CDCl_3$): [CH, CH_3] 64.9, 30.8, 23.2. [CH_2] 49.9, 48.9, 39.2, 28.9; ES-MS +ve mode: [M^++H] 247.9 (95), 229.9 (33), 119.6 (100); HRMS calcd for $C_{10}H_{17}NSO_4$: 247.0878, found: 248.0870 [M^++H].

(*S*,*S*)-**9** and (*R*,*S*)-**9**: To a solution of compound **5** (110 mg, 0.44 mmol), NEt_3 (148 mg, 1.46 mmol), DMAP (54 mg, 0.44 mmol) in DCE (10 mL), (*S*)-camphanoyl chloride (317 mg, 1.46 mmol) in DCE (2 mL) were added and the solution was heated under reflux for 24 h. After cooling, the organic layer was washed with water, sat. $NaHCO_3$ solution, sat. citric acid, and brine (40 mL of each), and dried over anhydrous Na_2SO_4. After evaporation of the solvent, an oil (213 mg) was obtained. The diastereomers were separated using a SiO_2 column, eluted with EtOAc: petroleum ether (40–60 °C)/1:2.

(*S*,*S*)-**9** was obtained as colorless needles (42 mg, 22%) and recrystallized in toluene. M.p. = 116–117 °C. R_f = 0.59; IR (Nujol): $\tilde{\nu}$ = 2950, 1790, 1752, 1740, 1170, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.53 (m, 1H; CH), 3.68 (s, 3H; CH_3), 2.96 (m, 2H; CH_2), 2.70 (m, 4H; 2 × CH_2), 2.30–2.60 (m, 3H; CH + CH_2), 1.80–2.10 (m, 4H; CH + CH + CH_2), 1.65 (m, 1H; CH), 1.62 (s, 3H; CH_3), 1.09 (s, 3H; CH_3), 1.07 (s, 3H; CH_3), and 0.95 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 178.4, 170.1, 166.9, 90.9, 69.6, 54.9, 54.3, 51.9, 46.9, 43.9, 39.8, 30.7, 28.9, 28.3, 26.8, 26.6, 24.6, 16.7, 16.5 and 9.7; ES-MS (+ve mode): [M^++Na] 453.0 (100), 234.9 (20); HRMS calcd for $C_{20}H_{30}O_6S_2$: 430.1484; found: 431.1474 [M^++H].

(*R*,*S*)-**9** was obtained as colorless crystals (43.5 mg, 23%). M.p. = 110–111 °C; R_f = 0.5; IR (Nujol): $\tilde{\nu}$ = 2950, 1800, 1765, 1748, 1185, 1125, 1070 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.53 (m, 1H; CH), 3.68 (s, 3H; CH_3), 2.90 (m, 2H; CH_2), 2.75 (m, 4H; 2 × CH_2), 2.30–2.60 (m, 3H; CH + CH_2), 1.85–2.10 (m, 4H; CH + CH + CH_2), 1.65 (m, 1H; CH), 1.62 (s, 3H; CH_3), 1.09 (s, 3H; CH_3), 1.07 (s, 3H; CH_3), and 0.95 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 178.0, 170.1, 166.7, 90.8, 69.8, 54.8, 54.2, 51.9, 46.9, 44.3, 39.7, 31.0, 29.0, 28.4, 26.8, 26.6, 24.7, 16.8, 16.7, 9.6; ES-MS (+ve mode): [M^++Na] 453.0 (100), 234.9 (20); HRMS calcd for $C_{20}H_{30}O_6S_2$: 430.1484; found: 431.1400 [M^++H].

(*R*,*S*)-**10**: Compound (*S*,*S*)-**9** (18 mg, 0.04 mmol) was dissolved in CH_2Cl_2 (4 mL), trimethoxyoxonium tetrafluoroborate (36.5 mg, 0.25 mmol) was added and the resulting suspension was stirred vigorously at room temperature. The reaction was monitored by TLC. After one hour, water (4 mL) was added and the cloudy solution was stirred for a further 15 min. The organic layer was washed with water (2 × 10 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by preparative TLC (SiO_2) in EtOAc:petroleum ether (40–60 °C) (1:2). Colorless crystals (12 mg, 84.3%) were obtained. M.p. = 60–61 °C. R_f = 0.19; IR (Nujol): $\tilde{\nu}$ = 2940, 1800, 1765 (s. broad), 1730, 1190, 1165, 1125, 1080, 950 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.70 (m, 1H; CH), 3.68 (s, 3H; CH_3), 2.98 (dd, *J* = 17.3 and 7 Hz, 1H; CH), 2.86 (dd, *J* = 17.3 and 6.3 Hz, 1H; CH), 2.77 (dd, *J* = 15.8 and 5.5 Hz, 1H; CH), 2.70 (dd, *J* = 15.8 and 7 Hz, 1H; CH), 2.42 (m, 1H; CH), 2.20 (s, 3H; CH_3), 1.95 (m,

2H; CH_2), 1.68 (m, 1H; CH), 1.10 (s, 3H; CH_3), 1.05 (s, 3H; CH_3), and 0.95 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 204.5$, 178.2, 170.1, 166.6, 90.9, 67.9, 54.9, 54.3, 51.9, 46.6, 38.1, 30.7, 30.5, 28.9, 16.6, 16.4 and 9.7; ES-MS (+ve mode): $[M^+ + Na]$ 363.2 (100), 283.5 (18), 239.1 (20); HRMS calcd for $C_{17}H_{24}O_7$: 340.1522, found: 341.1580 $[M^+ + H]$.

(*S*,*S*)-**10**; The preparation of this compound is as described for (*R*,*S*)-**10**. Starting material (*R*,*S*)-**9** (13.3 mg, 0.03 mmol) was used and the product was obtained as colorless crystals (9 mg, 85.6%). M.p. = 92–93 °C; R_f = 0.19; IR (Nujol): $\tilde{\nu} = 2940$, 1810, 1755 (s. broad), 1722, 1190, 1164, 1120, 950 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 5.70$ (m, 1H; CH), 3.69 (s, 3H; CH_3), 2.98 (dd, $J = 17.3$ and 7 Hz, 1H; CH), 2.86 (dd, $J = 17.3$ and 5.5 Hz, 1H; CH), 2.77 (dd, $J = 15.8$ and 5.5 Hz, 1H; CH), 2.70 (dd, $J = 15.8$ and 6.3 Hz, 1H; CH), 2.40 (m, 1H; CH), 2.20 (s, 3H; CH_3), 1.95 (m, 2H; CH_2), 1.68 (m, 1H; CH), 1.10 (s, 3H; CH_3), 1.05 (s, 3H; CH_3), and 0.95 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 204.4$, 178.2, 170.1, 166.6, 90.9, 67.8, 54.8, 54.3, 51.9, 46.6, 38.0, 30.7, 30.5, 28.9, 16.6, 16.4 and 9.7; ES-MS (+ve mode): $[M^+ + Na]$ 363.0 (100), 283.5 (8), 238.9 (20); HRMS calcd for $C_{17}H_{24}O_7$: 340.1522, found: 341.0980 $[M^+ + H]$.

Crystal Data for *(S,S)*-**9**: $C_{20}H_{30}O_6S_2$, $M_r = 430.56$, Orthorhombic space group $P2_12_12_1$, $a = 6.3432(13)$, $b = 16.713(3)$, $c = 20.190(4)$ Å, $U = 2140.4(7)$ Å^3, $Z = 4$, $\mu(Mo_{K\alpha}) = 0.282$ mm^{-1}, 5375 unique data were produced from 15601 measured reflections ($R_{int} = 0.0891$), $R_1 = 0.0535$ and $wR_2 = 0.1172$.

Crystal Data for *(S,S)*-**10**: $C_{17}H_{24}O_7$, $M_r = 340.36$, Monoclinic space group $P2_1$, $a = 6.175(2)$, $b = 7.547(2)$, c = 19.027(4) Å, $\beta = 98.44(3)°$, $U = 877.1(3)$ Å^3, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.1$ mm^{-1}, 3611 unique data were produced from 16126 measured reflections ($R_{int} = 0.0987$), $R_1 = 0.0528$ and $wR_2 = 0.1179$. CCDC-166921 ((*S,S*)-**9**) and CCDC-127009 ((*S,S*)-**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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A New Mononuclear Iron(III) Complex Containing a Peroxocarbonate Ligand**

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Peroxo iron(III) complexes have been proposed as key intermediates in various oxidation reactions catalyzed by mononuclear non-heme iron enzymes and their functional model complexes.[1] Various types of synthetic mononuclear peroxo–iron(III) complexes with η^2-peroxo,[2, 3] η^1-hydroperoxo,[3, 4] and alkylperoxo[5] ligands have been characterized by spectroscopic studies. However, there is no structurally characterized mononuclear peroxo iron(III) complex to date. It has been shown that the structure, electronic structure, and reactivity of the peroxo complexes can be modified by the coordination environment at an iron(III) center. For instance, a tetradentate tripod ligand, tris(2-pyridylmethyl)amine (TPA), has been shown to form a low-spin η^1-hydroperoxo species, whereas sterically bulky TPA derivatives with 6-methyl groups give low-spin and/or high-spin alkylperoxo species.[5d] Furthermore, interconversion between η^2-peroxo and η^1-hydroperoxo species has been also observed in some complexes, where a change in spin states (high spin and low spin) also occurs.[1c, 3] Most of these peroxo–iron(III) complexes have nitrogen-rich coordination environments, except for the ethylenediaminetetraacetate (EDTA) complex. Thus, it is of interest to investigate how the nature of the donor atoms and the stereochemistry of the supporting ligands influence the formation, structure, and properties of such peroxo–iron(III) complexes. Here, we report the synthesis of a novel mononuclear iron(III) complex with a bidentate peroxocarbonate ligand in a carboxylate-rich coordination environment, $[Fe(qn)_2(O_2C(O)O)]Ph_4P \cdot 1.5\,CH_3OH \cdot 0.5\,(CH_3)_2NCHO$ (**1**; see Figure 1), derived from the reaction of a bis(μ-hydroxo)diiron(III) complex, $[Fe_2(qn)_4(OH)_2] \cdot 2\,H_2O$ (**2**) with H_2O_2 and CO_2, where Hqn is quinaldic acid. Compound **1** is the first

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