

Olefinic Isothiocyanates and Iminodithiocarbonates from the Liverwort *Corsinia coriandrina*

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The chemical investigation of the liverwort *Corsinia coriandrina*, Corsiniaceae, resulted in the isolation, structure elucidation and synthesis of four sulfur- and nitrogen-containing compounds. The coriandrins were identified as (Z)- and (E)-2-(4-methoxyphenyl)ethenyl isothiocyanates, while the O-

methyltridentatols contain the corresponding (Z)- and (E)-S,S-dimethyl 2-(4-methoxyphenyl)ethenyliminodithiocarbonate structures.

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Introduction

Of the numerous natural products that contain both sulfur and nitrogen atoms, organic isothiocyanates are one of the largest and most abundant groups. Hundreds of isothiocyanates with varying carbon skeletons that originate from amino acid or terpene-derived precursors of higher plants, fungi, blue-green algae and marine organisms have previously been reported.^[1–3] Within the plant kingdom more than 120 isothiocyanates formed from amino acid metabolism are known to be prominent among various dicotyledonous angiosperms and clustered within the Brassicaceae (Cruciferae). When plant cells are disrupted in herbivore attack β -thioglucoside-*N*-hydroxyiminosulfates (glucosinolates) are converted by a β -thioglucosidase (myrosinase) into the corresponding isothiocyanates; this process constitutes a chemical defence mechanism that deters attack by various herbivores and also antimicrobial activity against a number of fungal and bacterial plant pathogens.^[3]

The fact that mosses (Bryophytes) and, in particular, liverworts (Hepaticae) are rarely attacked by herbivores or microorganisms has caused much speculation about the specific constituents responsible for this inertness. It is known that liverworts accumulate secondary metabolites with a large variety of structures, mainly terpenoids and aromatic compounds, within special compartments of the cell.^[4,5] These essential oils are believed to act as a chemical defence. In contrast to higher plants, sulfur- and nitrogen-containing metabolites are virtually unknown in liverworts. Although a number of their constituents apparently originate from amino acid metabolism, their biogenesis involves early

deamination. The only known nitrogen-containing natural products in liverworts are the 6- and 7-prenylindoles in some *Riccardia* species.^[6,7] Sulfur-containing metabolites are equally rare: isotachins with a β -S-methylthio-(*E*)-acrylate structure have been obtained from *Isotachis japonica* and *Balantiopsis rosea*.^[8,9]

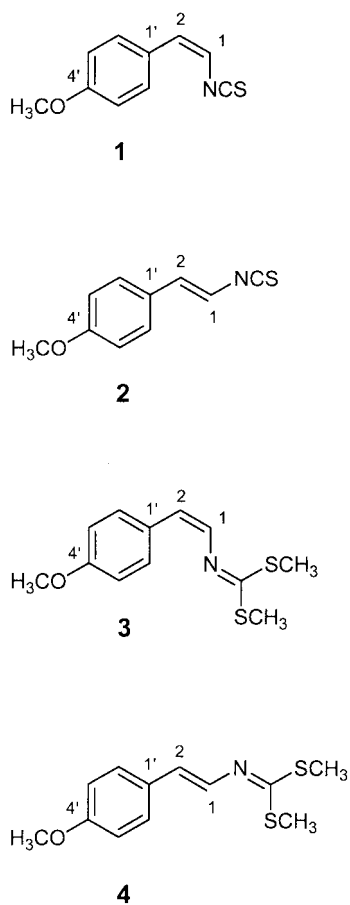
In previous publications, the liverwort-specific dormancy-inducing factor, lunularic acid, and its decarboxylation product, lunularin,^[10] as well as the flavonols, quercetin and kaempferol,^[11,12] and some fatty acids^[13] were described as natural constituents of the liverwort *Corsinia coriandrina* (Corsiniaceae), a relict member of the Marchantiales distributed in Mediterranean areas.^[14] We now report on the isolation, identification and synthesis of the first sulfur- and nitrogen-containing metabolites **1–4** of the liverwort *Corsinia coriandrina* (Scheme 1). The coriandrins are major constituents of the essential oil and were identified as the (Z)- and (E)-configured 2-(4-methoxyphenyl)ethenyl isothiocyanates **1** and **2**, while the O-methyltridentatols are minor constituents representing the (Z)- and (E)-configured S,S-dimethyl 2-(4-methoxyphenyl)ethenyliminodithiocarbonate structures **3** and **4**.

Results and Discussion

From the thallus cell material of *Corsinia coriandrina* (Spreng.) Lind. (Corsiniaceae), collected in Andalusia (Spain) at an elevation of about 500 m above sea level, the essential oil was obtained by hydrodistillation or extraction with diethyl ether and then analysed by GC and GC–MS. α -Pinene, (*E*)- β -caryophyllene and (*E*)-nerolidol were identified as major constituents of the oil by comparison of the mass spectra and retention indices with a spectral library established under identical experimental conditions.^[15] In addition, several known and unknown mono-, sesqui- and

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Scheme 1. Coriandrins **1**, **2** and *O*-methyltridentatols **3**, **4** from *Corsinia coriandrina*.

diterpenoids, unbranched oxygenated aliphatics and fatty acids were detected as minor constituents. Dimethyltrisulfide and dimethyltetrasulfide,^[16,17] as well as *S*-methyl methanethiosulfonate,^[18,19] previously reported from various biological sources, were identified in a liverwort for the first time.

A new nitrogen-containing compound, which we like to call coriandrin (**1**), with a signal for the molecular ion at $m/z = 191$ $[M]^+$, was observed as a major constituent of the diethyl ether extract (20.4% of the total volatiles). After flash chromatographic prefractionation, coriandrin (**1**) was isolated by repeated column chromatography. It was established by high-resolution mass spectrometry that coriandrin **1** has the molecular formula of $C_{10}H_9NOS$ with seven units of unsaturation. One *para*-disubstituted benzene unit, one methoxy group and a (*Z*)-configured ethenyl residue were observed in its 1H NMR spectrum (Table 1), in agreement with carbon signals for one methyl group, six methine groups and three quaternary carbons in its ^{13}C PENDANT spectrum (Table 2). By inspection of the H,H-COSY, HMQC and HMBC spectra a (*Z*)-2-(4-methoxyphenyl)ethenyl skeleton was identified which accounts for five of the seven units of unsaturation. The remaining quaternary carbon was only observed by H,C-correlation signals in its HMBC spectrum at $\delta_C = 135.6$ ppm. From its chemical

shift as well as intensive valence vibration bands at $\tilde{\nu} = 2096$ and 2058 cm^{-1} in its GC-FTIR spectrum, the heterocumylene substituent was identified as an isothiocyanate group,^[2] from which a structure of (*Z*)-2-(4-methoxyphenyl)ethenyl isothiocyanate was established for coriandrin (**1**). Small amounts of the isomeric (*E*)-coriandrin (**2**) were also detected in the diethyl ether extract of *C. coriandrina* (3.4% of the total volatile components).

In addition to the coriandrins **1** and **2** minor quantities of two isomeric sulfur- and nitrogen-containing compounds (**3**, **4**), with a signal for the molecular ion at $m/z = 253$ $[M]^+$, were observed in the diethyl ether extract of *C. coriandrina* (1.6 and 1.0% of the total volatile components, respectively). After column-chromatographic prefractionation, **3** and **4** were isolated by preparative thin-layer chromatography. High-resolution mass spectrometry afforded the molecular formula of $C_{12}H_{15}NOS_2$ with six units of unsaturation. The high sulfur content of the compounds was also indicated by a relatively intense signal at $[M + 2]^+$ (9%). The mass spectra of **3** and **4** exhibited some similarities to those of the coriandrins **1** and **2**, suggesting a similar carbon skeleton. A 2-(4-methoxyphenyl)ethenyl structure was deduced from the 1H NMR spectrum (Table 1) in agreement with the long-range coupling correlations in the H,H-COSY spectrum. Although predominantly present as the (*Z*) isomer **3**, the corresponding (*E*) isomer **4** was also detected. Nevertheless, the heteroatomic substituent of **3** and **4** could not be identified from the spectroscopic data owing to signals in the 1H NMR spectrum overlapping with signals from impurities and because of missing correlations in the H,H-COSY and H,H-TOCSY spectra. Inspection of the mass spectrometric fragmentation pattern, in combination with the HRMS measurements, excluded the presence of a heterocyclic moiety as the signal at $m/z = 206$ $[M - SCH_3]^+$ is the base peak, which suggests an *S*-methyl *N*-methylthiocarbamate or an *S,S*-dimethyl iminodithiocarbonate substituent. The structures of **3** and **4** were consequently proposed to be *S,S*-dimethyl (*Z*)- and (*E*)-2-(4-methoxyphenyl)ethenyliminodithiocarbonate as 4-methoxyphenylethanal and *S,S*-dimethyl dithiocarbonate were observed as cleavage products of the labile enamine intermediate formed upon hydrolysis of the compounds. The free phenols and *O*-sulfates corresponding to **3** and **4** have previously been described from the marine hydroid, *Tridentata marginata*, Sertulariidae, and were called tridentatols.^[20,21]

The structures of the coriandrins **1**, **2** and *O*-methyltridentatols **3**, **4** were finally confirmed by their synthesis (Scheme 2). While a synthetic access to (*E*)-*O*-methyltridentatol A (**4**) has already been described^[22] we have established a different pathway to (*Z*)- and (*E*)-*O*-methyltridentatol (**3** and **4**), which also provided (*Z*)- and (*E*)-coriandrin (**1** and **2**) as synthetic intermediates. 2-Hydroxy-2-(4-methoxyphenyl)ethylammonium chloride (**5**) was prepared in 70% yield over two steps from 2-bromo-1-(4-methoxyphenyl)ethanone. Treatment of **5** with thionyl chloride afforded the 2-chloro derivative **6** in 80% yield.^[23] Standard thiophosgenation procedures failed owing to hydrolysis of the benzylic chlorine followed by cyclisation to oxazolidine-

Table 1. ^1H NMR spectroscopic data for coriandrins **1**, **2** and *O*-methyltridentatols **3**, **4**.^[a]

H atom	(<i>Z</i>)- 1	(<i>E</i>)- 2	(<i>Z</i>)- 3	(<i>E</i>)- 4
SCH ₃	—	—	2.15, 6 H, br. s	2.11, 3 H, br. s
SCH ₃	—	—	—	2.27, 3 H, br. s
1	5.18, 1 H, d, 8.2	5.52, 1 H, d, 13.7	7.16, 1 H, d, 8.5	7.93, 1 H, d, 13.2
2	5.45, 1 H, d, 8.2	5.98, 1 H, d, 13.7	5.98, 1 H, d, 8.5	6.96, 1 H, d, 13.2
2',6'	7.37, 2 H, d, 8.8	6.74, 2 H, d, 8.7	7.86, 2 H, d, 8.8	7.28, 2 H, d, 8.5
3',5'	6.60, 2 H, d, 8.8	6.60, 2 H, d, 8.9	6.84, 2 H, d, 8.8	6.70, 2 H, d, 8.8
4'-OCH ₃	3.20, 3 H, s	3.22, 3 H, s	3.31, 3 H, s	3.27, 3 H, s

[a] Measured in $[\text{D}_6]\text{C}_6\text{H}_6$ (500 MHz); δ_{H} in ppm, integral, multiplicity, *J* in Hz; assignments made by COSY experiments.

Table 2. ^{13}C NMR spectroscopic data for coriandrins **1**, **2** and *O*-methyltridentatols **3**, **4**.^[a]

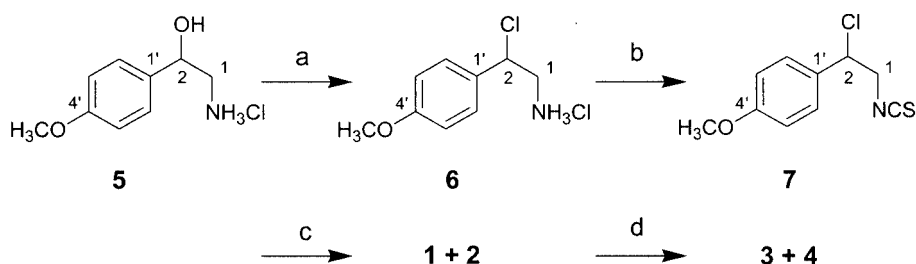
C atom	(<i>Z</i>)- 1	(<i>E</i>)- 2	(<i>Z</i>)- 3	(<i>E</i>)- 4
SCH ₃	—	—	15.1, q	15.1, q
N=C	135.6, s	134.2, s	162.0, s	159.6, s
1	111.3, d	113.5, d	131.4, d	132.9, d
2	127.8, d	131.2, d	121.9, d	127.8, d
1'	126.9, s	130.6, s	130.5, s	130.2, s
2',6'	130.6, d	128.1, d	132.0, d	128.1, d
3',5'	114.6, d	114.7, d	114.2, d	114.8, d
4'	160.7, s	160.9, s	159.3, s	159.8, s
4'-OCH ₃	55.0, q	55.0, q	55.0, q	55.0, q

[a] Measured in $[\text{D}_6]\text{C}_6\text{H}_6$ (100 MHz); δ_{C} in ppm, multiplicity; assignments made by PENDANT, HMQC and HMBC experiments.

2-thiones and, consequently, a less nucleophilic solvent system had to be explored. After liberation of the free base with the sterically hindered Hünig base in diethyl ether, condensation with thiocarbonyl dichloride under basic conditions furnished 2-chloro-2-(4-methoxyphenyl)ethyl isothiocyanate (**7**) in moderate yield. Through gas-phase dehydrochlorination a mixture of the (*Z*)- and (*E*)-2-(4-methoxyphenyl)ethenyl isothiocyanates **1** and **2** was obtained in almost quantitative yield. The geometrical isomers were separated by preparative gas chromatography. Nucleophilic addition of (sodium 18-crown-6) methanethiolate complex to a mixture of **1** and **2** or pure (*Z*)-configured **1** and methylation of the resulting intermediates afforded a (*Z*)/(*E*)

mixture of the *S,S*-dimethyl 2-(4-methoxyphenyl)ethenyl-iminodithiocarbonates **3** and **4**, which were separated by preparative gas chromatography using a column packed with a cyclodextrin derivative.^[24] The MS, IR and NMR spectroscopic data of natural and synthetic (*Z*)- and (*E*)-coriandrin as well as (*Z*)- and (*E*)-*O*-methyltridentatol are completely identical. While (*E*)-*O*-methyltridentatol **A** (**4**) exhibits two ^1H NMR signals for the methylthio groups in different solvents, (*Z*)-*O*-methyltridentatol **B** (**3**) displays only one signal (Table 1) as a result of *syn-anti* topomerisation, which has also been reported for other *S,S*-dimethyl iminodithiocarbonates.^[21,25]

The coriandrins **1**, **2** and *O*-methyltridentatols **3**, **4** are the first examples of these classes of compounds to be identified among the liverworts. Their presence as natural constituents of *Corsinia coriandrina* has been confirmed by the independent detection of these compounds by Asakawa in samples collected in France and Turkey.^[26] The coriandrins **1,2** are rare examples of olefinic isothiocyanate compounds, like axisothiocyanate-4 from the marine sponge *Axinella cannabina*.^[27] The unusual *S,S*-dimethyl iminodithiocarbonate substructure of the tridentatols has so far only been encountered among the cruciferous phytoalexins methoxybrassinin A and B^[25] as well as wasalexin A and B.^[28] Furthermore, the observed co-occurrence of the structurally related isothiocyanates **1** and **2** and the *S,S*-dimethyl iminodithiocarbonate compounds **3** and **4** in the liverwort *Corsinia coriandrina* is similar to the presence of glucosinolate-derived isothiocyanates and the above-mentioned phytoalexins in some Cruciferae species.^[3,25,28,29]



a: SOCl_2 (CHCl_3); b: 1. *N*-Et-*i*-Pr₂N (Et_2O), 2. SCl_2 (Et_2O); c: Δ (210 °C, g);
d: 1. NaSCH_3 , [18]crown-6 (THF), 2. CH_3I

Scheme 2. Synthetic pathway to coriandrins **1**, **2** and *O*-methyltridentatols **3**, **4**.

Experimental Section

General Experimental Procedures: Gas chromatograms were recorded with a HRGC 5300 Mega instrument (Carlo Erba) equipped with 25 m fused-silica capillary columns containing polysiloxanes CPSil-5 and CPSil-19 (Chrompack). Hydrogen at an inlet pressure of 0.5 bar was used as the carrier gas with a split injection at 200 °C (split ratio: 1:30) and a flame ionisation detector at 250 °C; temperature program: 50–250 °C at 3 °C/min. GC-EIMS and GC-HREIMS were measured with a HP 5890 gas chromatograph (Hewlett Packard) equipped with a 25 m CPSil-5 CB fused-silica capillary column (Chrompack) coupled to a VG Analytical 70–250S mass spectrometer; temperature program: 80–270 °C at 10 °C/min. GC-FTIR spectra were recorded with a HP 5890 gas chromatograph (Hewlett Packard) equipped with a 30 m Innowax fused-silica capillary column and coupled to a HP 5965 A infrared spectrometer (Hewlett Packard); temperature program: 80–270 °C at 10 °C/min. NMR spectra were recorded with an AMX 400 spectrometer (Bruker) for ¹H NMR (400.1 MHz), broadband-decoupled ¹³C NMR and ¹³C PENDANT (Polarisation Enhancement that is Nurtured During Attached Nucleus Testing) spectra (100.6 MHz) and with an AMX 500 spectrometer (Bruker) for ¹H NMR, H,H-COSY, H,H-TOCSY, HMQC and HMBC spectra (¹H: 500.1 MHz; ¹³C: 125.8 MHz). Homonuclear ¹H connectivities were determined by performing COSY and TOCSY experiments. One-bond heteronuclear ¹H–¹³C connectivities were determined by using a HSQC pulse sequence [interpulse delay set for ¹J(C,H) = 145 Hz]. Two- and three-bond ¹H–¹³C connectivities were determined by gradient-selected HMBC experiments optimized for ^{2,3}J = 7.7 Hz. Preparative GC was carried out with a modified Varian 1400 instrument equipped with stainless steel columns (1.85 m × 4.3 mm) packed with 10% polydimethylsiloxane SE-30 on Chromosorb W-HP or 6% heptakis(6-*O*-*tert*-butyldimethylsilyl)-2,3-di-*O*-methyl-β-cyclodextrin in SE-52 (50%, w/w) on Chromosorb W-HP. Helium was used as the carrier gas at a flow rate of 120 mL/min with a flame ionisation detector at 250 °C and an injector temperature of 210 °C. Eluting compounds were trapped in Teflon tubes cooled with liquid nitrogen.^[24]

Plant Material: *Corsinia coriandrina* (Spreng.) Lind. was collected at an elevation of approximately 500 m near Tarifa, Andalusia (Spain), in March 2003 (about 30 g fresh weight) and at 350 m near St. Bartolomeo, Andalusia, in April 2004 (about 40 g fresh weight). The liverwort was identified by Professor R. Mues (Universität des Saarlandes, Germany) and Dr. H. Muhle (University of Ulm, Germany).

Hydrodistillation and Extraction: Carefully cleaned fresh plant material of *Corsinia coriandrina* (30 g) was homogenized in water with a blender and hydrodistilled for 2 h to give the essential oil, which was collected in *n*-hexane. The remaining aqueous homogenate was extracted with diethyl ether and the organic phase was separated, dried with Na₂SO₄ and concentrated in vacuo. Air-dried plant material (10 g) was crushed under liquid nitrogen and extracted with diethyl ether.

Isolation of the Coriandrins 1 and 2: The crude essential oil was purified by chromatography on silica gel 60 (Merck) with an *n*-hexane/diethyl ether gradient. Repeated column chromatography with an *n*-hexane/dichloromethane gradient gave approximately 2 mg (*Z*)-coriandrin (**1**) with about 5% of (*E*)-coriandrin (**2**).

(*Z*)-Coriandrin [(*Z*)-2-(4-Methoxyphenyl)ethenyl Isothiocyanate] (1**):** Pale yellow oil. For ¹H and ¹³C NMR ([D₆]benzene) data, see Table 1 and Table 2, respectively. GC-FTIR: $\tilde{\nu}$ = 2200, 2096 (s, NCS), 2058 (s, NCS), 1609 (C=C), 1512 (C=C), 1398, 1260 (COC),

1177, 1042, 832 cm⁻¹. EIMS (70 eV): *m/z* (%) = 191 (100) [M]⁺, 176 (54), 161 (6), 148 (14), 132 (4), 121 (25), 116 (6), 104 (14), 96 (4), 89 (16), 77 (10), 63 (13), 51 (8), 45 (5). HR-EIMS: *m/z* = 191.0405 [M]⁺; calcd. for C₁₀H₉NOS: 191.0405; Δ = 0.0 ppm.

(*E*)-Coriandrin [(*E*)-2-(4-Methoxyphenyl)ethenyl Isothiocyanate] (2**):** Pale yellow oil. For ¹H and ¹³C NMR ([D₆]benzene) data, see Table 1 and Table 2, respectively. GC-FTIR: $\tilde{\nu}$ = 2096 (s, NCS), 2055 (s, NCS), 1610 (C=C), 1513 (C=C), 1251 (COC), 1176, 1042 cm⁻¹. EIMS (70 eV): *m/z* (%) = 191 (100) [M]⁺, 176 (58), 161 (6), 148 (16), 132 (5), 121 (30), 116 (7), 104 (19), 96 (7), 89 (24), 77 (17), 63 (44), 51 (17), 45 (13). HR-EIMS: *m/z* = 191.0410 [M]⁺; calcd. for C₁₀H₉NOS: 191.0405; Δ = 2.6 ppm.

Isolation of the *O*-Methyltridentatols 3 and 4: The crude diethyl ether extract was purified by chromatography on silica gel 60 (Merck) with an *n*-hexane/diethyl ether gradient. Preparative thin-layer chromatography with an eluent of *n*-hexane/ethyl acetate (10:1) afforded approximately 0.3 mg (*Z*)-*O*-methyltridentatol B (**3**) with about 20% of (*E*)-*O*-methyltridentatol A (**4**).

(*Z*)-*O*-Methyltridentatol B [*S,S*-Dimethyl (*Z*)-2-(4-Methoxyphenyl)ethenyliminodithiocarbonate] (3**):** Pale yellow oil. For ¹H and ¹³C NMR ([D₆]benzene) data, see Table 1 and Table 2, respectively. EIMS (70 eV): *m/z* (%) = 253 (87) [M]⁺, 238 (1), 206 (100), 191 (49), 176 (21), 158 (45), 148 (3), 133 (36), 118 (8), 103 (10), 96 (14), 89 (19), 77 (13), 63 (12), 51 (7), 45 (10), 39 (7). HR-EIMS: *m/z* = 253.0624 [M]⁺; calcd. for C₁₂H₁₅NOS₂: 253.0595; Δ = 11.5 ppm; *m/z* = 206.0642 [M – SCH₃]⁺; calcd. for C₁₁H₁₂NOS: 206.0640; Δ = 1.0 ppm.

(*E*)-*O*-Methyltridentatol A [*S,S*-Dimethyl (*E*)-2-(4-Methoxyphenyl)ethenyliminodithiocarbonate] (4**):** Pale yellow oil. For ¹H and ¹³C NMR ([D₆]benzene) data, see Table 1 and Table 2, respectively. EIMS (70 eV): *m/z* (%) = 253 (85) [M]⁺, 238 (1), 206 (100), 191 (49), 176 (22), 158 (36), 148 (3), 133 (43), 118 (9), 103 (11), 96 (13), 89 (20), 77 (13), 63 (12), 51 (7), 45 (10), 39 (7). HR-EIMS: *m/z* = 253.0621 [M]⁺; calcd. for C₁₂H₁₅NOS₂: 253.0595; Δ = 10.3 ppm; *m/z* = 206.0642 [M – SCH₃]⁺; calcd. for C₁₁H₁₂NOS: 206.0640; Δ = 1.0 ppm.

Synthesis of 2-Chloro-2-(4-methoxyphenyl)ethylammonium Chloride (6**):** A suspension of 2-hydroxy-2-(4-methoxyphenyl)ethylammonium chloride (**5**) (620 mg, 3.0 mmol) in chloroform (5 mL) at 0 °C was treated with a solution of thionyl chloride (820 mg, 6.9 mmol) and dimethylformamide (100 μ L) in chloroform (2 mL). After 14 h solvent and excess reagent were evaporated in vacuo at 20 °C and the residue was treated with cold ethanol (3 mL). The product was filtered, washed with cold ethanol (3 × 1 mL) and diethyl ether (2 mL) and dried in vacuo to give **6** (540 mg, 2.4 mmol, 80% yield). White solid. ¹H NMR ([D₆]DMSO): δ = 2.71 (m, 1 H, 1-H), 2.83 (m, 1 H, 1-H'), 3.80 (s, 3 H, 4'-OCH₃), 5.31 (dd, 1 H, *J* = 9.6, 4.7 Hz, 2-H), 6.85 (d, 2 H, *J* = 8.7 Hz, 3',5'-H), 7.32 ppm (d, 2 H, *J* = 8.9 Hz, 2',6'-H). ¹³C NMR ([D₆]DMSO): δ = 45.6 (t, 1-C), 55.6 (q, 4'-OCH₃), 59.9 (d, 2-C), 114.6 (d, 3',5'-C), 127.3 (d, 2',6'-C), 129.9 (s, 1'-C), 160.2 ppm (s, 4'-C). EIMS (70 eV): *m/z* (%) = 185 (40) [M – HCl]⁺, 156 (91), 155 (100), 150 (51), 134 (47), 121 (49), 91 (33), 77 (32), 65 (12), 44 (14), 36 (51).

Synthesis of 2-Chloro-2-(4-methoxyphenyl)ethyl Isothiocyanate (7**):** A suspension of 2-chloro-2-(4-methoxyphenyl)ethylammonium chloride (**6**) (444 mg, 2.0 mmol) in diethyl ether (8 mL) at 0 °C was treated with *N*-ethyl-diisopropylamine (1 mL, 5.8 mmol). After stirring for 1 h the resulting suspension was filtered and the solution added dropwise to a solution of thiocarbonyl dichloride (400 μ L, 4.0 mmol) in diethyl ether (8 mL) at 0 °C. After 30 min ice (8 g) was added and then the organic layer was separated and dried with

Na₂SO₄. The product was purified by chromatography on silica with an *n*-hexane/diethyl ether mixture (8:1) as eluent to give **7** (164 mg, 720 µmol, 36% yield) as colorless crystals. ¹H NMR ([D₆]benzene): δ = 2.96 (dd, 1 H, *J* = 14.5, 6.4 Hz, 1-H), 3.07 (dd, 1 H, *J* = 14.7, 7.1 Hz, 1-H'), 3.20 (s, 3 H, 4'-OCH₃), 4.26 (t, 1 H, *J* = 6.7 Hz, 2-H), 6.61 (d, 2 H, *J* = 8.7 Hz, 3',5'-H), 6.86 ppm (d, 2 H, *J* = 8.7 Hz, 2',6'-H). ¹³C NMR ([D₆]benzene): δ = 52.1 (t, 1-C), 55.1 (q, 4'-OCH₃), 60.5 (d, 2-C), 114.7 (d, 3',5'-C), 129.0 (d, 2',6'-C), 129.8 (s, 1'-C), 135.3 (s, NCS), 160.9 ppm (s, 4'-C). EIMS (70 eV): *m/z* (%) = 227 (8) [M]⁺, 191 (63), 176 (36), 157 (56), 155 (100), 148 (9), 134 (45), 121 (20), 119 (22), 104 (12), 91 (40), 77 (23), 65 (25), 63 (26), 51 (22), 45 (8), 39 (21). HR-EIMS: *m/z* = 227.0170 [M]⁺; calcd. for C₁₀H₁₀NOS³⁵Cl: 227.0172; Δ = 0.9 ppm.

Synthesis of (Z)- and (E)-Coriandrin (1 and 2): A solution of 2-chloro-2-(4-methoxyphenyl)ethyl isothiocyanate (**7**) (100 mg, 440 µmol) in diethyl ether (2.0 mL) was dehydrochlorinated in 100 µL portions at 210 °C in the injector port of a preparative gas chromatograph and the reaction products were separated using a polysiloxane SE-30 column (155 °C, isotherm) to give (Z)-2-(4-methoxyphenyl)ethenyl isothiocyanate (**1**) (32 mg, 168 µmol, 38% yield) and (E)-2-(4-methoxyphenyl)ethenyl isothiocyanate (**2**) (50 mg, 262 µmol, 60% yield) that were identical to (Z)- and (E)-coriandrin isolated from *Corsinia coriandrina*.

Synthesis of (Z)- and (E)-O-Methyltridentatol (3 and 4): A solution of (Z)-2-(4-methoxyphenyl)ethenyl isothiocyanate (**1**) (20 mg, 105 µmol) in *n*-hexane (500 µL) was added dropwise to a solution of sodium methanethiolate (75 mg, 1.1 mmol) and 18-crown-6 (290 mg, 1.1 mmol) in dry tetrahydrofuran (500 µL). After 30 min methyl iodide (160 mg, 1.1 mmol) was added. After stirring for 30 min. water (3 mL) was added and the aqueous phase extracted with diethyl ether (2 × 3 mL). The combined organic phases were dried with Na₂SO₄ and concentrated in a stream of nitrogen. The reaction products were isolated by preparative gas chromatography by using a heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin column (180 °C, isotherm) to give (Z)-*O*-methyltridentatol B (**3**) (12 mg, 47 µmol, 45% yield) and (E)-*O*-methyltridentatol A (**4**) (14 mg, 55 µmol, 52% yield) that were identical to the natural products isolated from *Corsinia coriandrina*.

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