Reductive desulfurization of allylic thiols by HS^-/H_2S in water gives clue to chemical reactions widespread in natural environments

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Desulfurization of *E*-phyt-2-ene-1-thiol 1 in water.

Typically, *E*-phyt-2-ene-1-thiol **1** (20mg, $6.41 \cdot 10^{-5}$ mol; 0.40 g/L) was reacted at 50°C in a septum-sealed vial with an argon degassed H_2S-saturated aqueous solution (50 mL) containing lauric acid sodium salt (1, 5, or 10 g/L) for 15 to 180 days. The reaction mixture was extracted with dichloromethane (3X). The crude extract was then chromatographed on a silica gel column (hexane) to separate the alkenes from the organic sulfur compounds (thiols and polysulfides). The alkenes were quantified by gas chromatography using squalane as internal standard. Highest yield of phytenes (3.8%) were obtained after 180d. with 10 g/L of surfactant; after 15d. and 1 g/L of surfactant, 0.1% yield was obtained. The sulfur compounds were transformed into thiols following the procedure described in the next paragraph and analyzed by gas chromatography-mass spectrometry.

The same procedure was used for experiments involving ^{34}S-labeled *E*-phyt-2-ene-1-thiol **14** in water.

Desulfurization of ^{34}S-labeled *E*-phyt-2-ene-1-thiol in DMF/H_2O.

To a solution of ^{34}S-labeled *E*-phyt-2-ene-1-thiol **14** (7mg, $2.24 \cdot 10^{-5}$ mol, $^{32}S/^{34}S$: 1/1) in 3.5 ml DMF/H_2O (3/1; v/v) were added 102mg ($1.38 \cdot 10^{-3}$ mol) of NaSH, H_2O. The reaction mixture was stirred under nitrogen at 70°C. After 3hours, the reaction mixture was poured into water, neutralised with a 1M HCl aqueous solution and extracted with cyclohexane. The crude extract was chromatographed on a small silica gel column (hexane) to yield the phytenes (**2**-**5**) (Rf>0.8) and a mixture of *E*- and *Z*-phyt-2-ene-1-thiols and polysulfides **7** (Rf≈0.5). An aliquot (2/3) of the mixture of thiols and polysulfides was dissolved in MeOH/Et_2O (1/1; v/v). MeONa (15mg) and EtSH (300µL) were added and the mixture kept under nitrogen at room temperature for 3 hours. AcOH (100µL) was then added and the solvents evaporated. The crude mixture was then chromatographed on a small silica gel column (hexane) to yield a mixture of *E*- and *Z*-phyt-2-ene-1-thiols (≈4mg; $^{32}S/^{34}S$: 2/1 determined by gas chromatography-mass spectrometry). $^{32}S/^{34}S$ ratios were identical for both isomers.

Spectroscopic data

Z-phyt-2-ene **4**

*NMR data***,** (Brucker ARX-500) δ_H (C_6D_6, 500 MHz): 0.913 (3H, *d*, *J*= 6.5 Hz, CH_3-16 or 16'), 0.914 (3H, *d*, *J*= 7 Hz, CH_3-16 or 16'), 0.93 (3H, *d*, *J*= 6.5 Hz, CH_3-8' or 12'), 0.94 (3H, *d*, *J*= 6.5 Hz, CH_3-8' or 12'), 0.98 (3H, *t*, *J*= 7.5 Hz, CH_3-1), 1.7 (3H, *ddd*, *J*= 1 Hz, *J*= 1 Hz, *J*= 1 Hz, CH_3-4'), 2.05 (2H, *q*, *J*= 7.5 Hz, H-2), 2.08 (2H, *m*, H-5), 5.23 (1H, *dd*, *J*= 7.0 Hz, *J*= 7.0 Hz, H-4).

MS data (Finnigan MAT TSQ 700) EI (70 eV), *m*/*z* (rel. int.): 280([M+] $C_{20}H_{40}$, 19%), 140(15), 125(38), 111(48), 97(23), 83(57), 70(57), 55(100).

E-phyt-2-ene **5**

NMR data, δ_H (C_6D_6, 500 MHz): 0.914 (3H, *d*, *J*= 6.5 Hz, CH_3-16 or 16'), 0.915 (3H, *d*, *J*= 6.5 Hz, CH_3-16 or 16'), 0.93 (3H, *d*, *J*= 6.5 Hz, CH_3-8' or 12'), 0.95 (3H, *d*, *J*= 7.0 Hz, CH_3-8' or 12'), 1.01 (3H, *t*, *J*= 7.5 Hz, CH_3-1), 1.61 (3H, *br s*, CH_3-4'), 2.00 (2H, *q*, J= 7.5 Hz, H-2), 2.11 (2H, *m*, H-5), 5.27 (1H, *qt*, *J*= 1.5 Hz, *J*= 7.0 Hz, H-4).

MS data EI (70 eV), *m*/*z* (rel. int.): 280([M+] $C_{20}H_{40}$, 21%), 140(16), 125(40), 111(51), 97(27), 83(66), 70(68), 55(100).

E-phyt-2-ene-1-thiol ($^{32}S/^{34}S$: 1/1) **14**

NMR data, δ_H ($CDCl_3$, 500 MHz) : 0.83 (3H, *d*, *J*= 6.5 Hz, CH_3–8' or 12'), 0.84 (3H, *d*, *J*= 6.5 Hz, CH_3–12' or 8'), 0.86 (6H, *d*, *J*= 6.5 Hz, CH_3–16 and 16'), 1.40 (1H, *t*, *J*= 7.0 Hz, –CH_2–S<u>H</u>), 1.52 (1H, *non.*, *J*= 6.5 Hz, CH–15), 1.64 (3H, *d*, *J*= 1.0 Hz, CH_3–4'), 1.96 (2H, *t*, *J*= 7.5 Hz, CH_2–4), 3.16 (2H, *dd*, *J*= 7.5, 7.0 Hz, CH_2–1), 5.33 (1H, *tq*, *J*= 7.5, 1.0 Hz, CH–2).

MS data EI (70 eV), *m*/*z* (rel. int.): 314([M+] $C_{20}H_{40}{}^{34}S$, 4.9%), 312([M+] $C_{20}H_{40}{}^{32}S$, 4.9%), 139(9), 125(27), 111(55), 97(63), 83(65), 69(84), 57(100).