Supplementary Information.

Results

Mass spectroscopy of peaks at RT 7.74 min, RT 8.92 min, RT 9.96 min, RT 10.89 min in Fig. S2A showed very similar mass spectra like the internal standard (RT 11.33, 3-hydroxyheptadecanoic acid). Only in the higher mass region, the fragments are shifted by either 14 or 28 m/z. Therefore the peaks were identified as the methyl esters of 3-hydroxydecanoic acid (RT 7.74 min), 3-hydroxydodecanoic acid (RT 8.92 min), 3-hydroxytetradecanoic acid (RT 9.96 min) and 3-hydroxyhexadecanoic acid (RT 10.89 min), respectively. Three additional peaks eluting before the saturated C12, C14 and C16, 3-hydroxyfatty acid methyl esters had a similar mass spectrum (see example Fig. S2C of peak at RT 9.86 min) but the $M^+ - 15$ Peak was 2 masses lower and indicates a molecule lacking 2 hydrogen atoms, this could be derived from mono-unsaturated fatty acid methyl esters.

Localization of double bonds via dimethyl disulfide (DMDS), based on [1, 2]

After DMDS derivatization, new peaks appeared (Fig. S3A) and their molecular peaks of m/z 394 (RT 11.45 min, Fig. S3D), m/z 422 (RT 12.40 min, Fig. S3B) and m/z 450 (RT 13.21 min, Fig. S3C) revealed that they might have been formed by addition of one DMDS (M=94) to m/z 300 (mono-unsaturated 3-OH-dodecanoic methyl ester), m/z 328 (mono-unsaturated 3-OH-tetradecanoic methyl ester) and m/z 356 (mono-unsaturated 3-OH-hexacanoic methyl ester), respectively. According to the fragmentation pattern (Fig. S3E), fragments are formed as a result of the cleavage of the bond between the carbon atom bearing the methylthiol group. The fragment comprising the methylated carboxy

group further fragments by losing m/z 32 (methanethiol). Fig. S3E shows this fragmentation for the DMDS derivatized 3-hydroxy-7-tetradecenoic methyl ester (m/z 422) where the double bond is in the ω7 position. The characteristic fragments m/z 422, m/z 277, m/z 245 and m/z 145 were also seen in the mass spectrum of peak RT 12.40 (Fig. 3SB). The mass spectrum of peak RT 13.21 (Fig. S3C) was very similar, only the fragments in the higher mass region were shifted by 28 mass units. This is consistent when the double bond is now again in ω7 position (m/z 145) but - since the chain is 2 carbon atoms longer - has moved from position 7 to position 9 (m/z 305, m/z 273). The structure of peak RT 13.21 was therefore determined to be the DMDS derivate of 3-hydroxy-9-hexadecenoic methyl ester (m/z 450). The only peaks showing a molecular peak of m/z 394 (DMDS adduct of 3-hydroxy-dodecenoic methyl ester) were RT 11.42 and RT 11.45 with a very similar mass spectrum (Fig. S3E for RT 11.45). Since it was lacking the characteristic pair of fragments in the higher mass region the localization of the double bond remained unclear.

References

1. Dunkelblum, E., Tan, S.H., Silk, P.J. *Journal of Chemical Ecology*, Vol 11, No. 3, 1985

2. Bauer, S.: *Die Zusammensetzung der Oberflaechenwachse von Tomaten, Paprika und Auberginen*, Dissertation, University of Muenster, Germany 2003

Figure Legends.

Fig. S1. Sequence alignment of bacterial carboxy methyl transferases. Sequences were from *M. marinum* (Mmar_3356), *Mycobacterium ulcerans Agy99* (Mul_1287), *Mycobacterium avium 104* (MAV_2179), *Mycobacterium sp. KMS* (MKMS_3444), *Mycobacterium sp. JLS* (Mjls_3393), *Mycobacterium vanbaalenii PYR-1* (Mvan_3770), *Mycobacterium gilvum PYR-GCK* (Mflv_2764), *M. smegmatis* (Msmeg_4347) *and A. thaliana* jasmonate methyltransferases (JMT).

Fig. S2. (A) Section of GCMS TIC trace where relevant compounds eluted. (B) Mass spectrum of compound at RT 9.96 min. (C) Mass spectrum of compound at RT 9.86 min. (D) Mass spectrum of compound at RT 8.83 min. (E) Mass spectrum of compound at RT 10.81 min.

Fig. S3. (A) Section of GCMS TIC trace where relevant compounds eluted. (B) Mass spectrum of compound at RT 12.40 min. (C) Mass spectrum of compound at RT 13.21 min. (D) Mass spectrum of compound at RT 11.45 min. (D) Proposed fragmentation of DMDS- and TMS-derivatized 3-hydroxy-7-tetradecenoic acid.