***Supplementary Material***

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1. Materials

*Escherichia coli* DH5α was used for DNA manipulation. The plasmid containing the CvFAP gene (short length; comprises residues 62-654) was a courtesy of Prof Frank Hollmann (Huijbers et al., 2018). Competent *E. coli* BL21 (DE3) cells were transformed with the plasmid for recombinant enzyme production.

*Solvent and reagent:* Tris base (Sigma-Aldrich), HCl 37 % (Vetec Química), Kanamycin (Fluka), Bradford protein assay reagent (Bio-Rad), methyl sulfoxide (Tedia), Ethyl Acetate (Tedia), Ethanol (Vetec Química), Methanol (Vetec Química), Sodium sulphate anhydrous (Vetec Química), Palmitic acid (Sigma-Aldrich).

*Equipments:*Analytical Balance Mettler Toledo, Magnetic Stirrer Heating Plate - Model 753A – FISATOM, Asia System 110 Continuous Flow – Syrris, Orbital Shaker Incubator Marconi, GC-FID Hewlett–Packard (HP) Model GC-6890C, Shimadzu GC2014 GC-FID – Cpsil 5 CB column (50 m × 0.53 mm × 1.0 µm), PTFE-coil (1/16), Portable digital KR812 luximeter (until 200000 lux), Ultrasonic Sonicator VIBRA-CELL VCX 500 Sonics (USA).

1. Gas Chromatography Analysis

Samples were prepared by diluting 20 μL of reaction crude in 980 μL of ethyl acetate. Conversion percentages were analyzed by chromatogram areas using the Shimadzu GC2014 GC-FID – Cpsil 5 CB column (50 m × 0.53 mm × 1.0 µm). Injection temperature 260 °C, injection split ratio 20.0, carrier gas was N2, pressure 89.0 kPa, column flow 4.86 mL.min−1. The oven temperature setting was: 110 °C, heated at 25 °C min−1 to 190 °C for 3 min, and remained heating at 25 °C min−1 to 280 °C. Conversion percentages were analyzed by chromatogram area based on a calibration curve.

1. Preparation of the enzymatic extract

The enzyme expression was performed as described by Huijbers and coworkers (2018). After enzyme expression, cells were harvested by centrifugation (11000 g at 4 °C for 10 min), washed twice with washing buffer (50 mM Tris-HCl buffer, pH 8, containing 100 mM NaCl), resuspended in the same buffer with the addition of 1 mM PMSF and 20 % glycerol, and stored at -80 ºC. The cells were prepared for lysis by centrifugation and resuspension in lysis buffer (100 mM Tris-HCl buffer, pH 8.5, containing 1 mM PMSF and 5 % glycerol). Cells lysis were performed by VIBRA-CELL VCX 500 Sonics (USA) instrument using the following settings: 30 % amplitude; 15 min sonication; ON/OFF pulses of 10 son and 30 s off. The total extract obtained were frozen with liquid nitrogen and stored in -80 ºC to be used in the photocatalytic reactions. The total protein concentration of the extracts was determined and standardized by Smith (1985) assays.

1. Batch reactions

## *4.1. Photocatalytic reactions in batch with 300 W blue LED lamp*

Photoenzymatic decarboxylation reactions were performed at 37 oC in a total volume of 1.0 mL Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent. To a transparent glass vial (total volume 1.5 mL) were added 0.3 mL DMSO, palmitic acid (13 mM), 0.7 mL Tris-HCl buffer (pH 8.5, 100 mM) containing the cell extract (5.6 mg.mL-1 of total protein). The vial was sealed and exposed at 6 cm from 300 W blue LED source under constant and gentle magnetic stirring for 30 min to give the product (99 % yield). After 30 min aliquots were withdrawn and the substrates and products were extracted with twice the volume of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

## *4.2. Reaction 1 – Photocatalytic reactions in batch with solar light in 5.6 mg.mL-1 of total protein*

The photoenzymatic decarboxylation reactions using solar light exposition were carried out in a transparent jacketed reactor (total volume 25 mL) at 35 ºC. The reactions were performed in a total volume of 10.0 mL Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent and 13 mM of palmitic acid as substrate. The enzymatic extract was used in a 5.6 mg.mL-1 final concentration. The reactor was exposed to solar rays (127.4 x 103 lux) at summer season under constant and gentle magnetic stirring starting at 11 h a.m. (-22.8601423, -43.2297134) for 2 h. Aliquots (100 μL) were withdrawn hourly and the substrates and products were extracted with 1 mL of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

|  |  |
| --- | --- |
| **Time (h)** | **Conv. (%)\*** |
| 0 | 0 |
| **1** | **>99** |
| 2 | >99 |

\*Calculated by integration of chromatogram peak area.

*4.3. Reaction 2 – Screening of shorter reaction times in 5.6 mg.mL-1 of total protein*

The photoenzymatic decarboxylation reactions using solar light exposition were carried out in a transparent jacketed reactor (total volume 25 mL) at 35 ºC. The reactions were performed in a total volume of 10.0 mL Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent and 13 mM of palmitic acid as substrate. The enzymatic extract were used in a 5.6 mg.mL-1 final concentration. The reactor was exposed to solar rays (131.3 x 103 lux) at summer season under constant and gentle magnetic stirring starting at 11 h a.m. (-22.8601423, -43.2297134) for 60 min. Aliquots (100 μL) were withdrawn every 10 min and the substrates and products were extracted with 1 mL of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

|  |  |
| --- | --- |
| **Time (min)** | **Conv. (%)\*** |
| 0 | 0 |
| 10 | 90 |
| **20** | **>99** |
| 30 | >99 |
| 40 | >99 |
| 50 | >99 |
| 60 | >99 |

\*Calculated by integration of chromatogram peak area.

## *4.4. Reaction 3 – Kinetic photocatalytic reactions in batch with solar light in 5.6 mg.mL-1 of total protein*

The photoenzymatic decarboxylation reactions using solar light exposition were carried out in a transparent jacketed reactor (total volume 25 mL) at 35 ºC. The reactions were performed in a total volume of 10.0 mL Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent and 13 mM of palmitic acid as substrate. The enzymatic extract was used in a 5.6 mg.mL-1 final concentration of total protein. The reactor was exposed to solar rays (123.1 x 103 lux) at summer season under constant and gentle magnetic stirring starting at 11 h a.m. (-22.8601423, -43.2297134) for 20 min. Aliquots (100 μL) were withdrawn and the substrates and products were extracted with 1 mL of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

|  |  |
| --- | --- |
| **Time (min)** | **Conv. (%)\*** |
| 0 | 0 |
| 5 | 34 |
| 7 | 42 |
| 10 | 67 |
| 12 | >99 |
| 15 | >99 |
| **20** | **>99** |

\*Calculated by integration of chromatogram peak area.

*4.5. Reaction 4 – Photocatalytic reactions in batch with solar light in 2.8 mg.mL-1 of total protein and different acid concentrations*

The photoenzymatic decarboxylation reactions using solar light exposition were carried out in a transparent jacketed reactor (total volume 10 mL) at 35 ºC. The reactions were performed in a total volume of 2.0 mL Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent and palmitic acid in different concentrations as substrate. The enzymatic extract was used in a 2.8 mg.mL-1 final concentration of total protein. The reactor was exposed to solar rays (118.1 x 103 lux) at summer season under constant and gentle magnetic stirring starting at 11 h a.m. (-22.8601423, -43.2297134) for 60 min. Aliquots (100 μL) were withdrawn and the substrates and products were extracted with 1 mL of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

|  |  |
| --- | --- |
| **Acid concentration (mM)** | **Conv. (%)\*** |
| **13** | **>99** |
| 19.5 | 96 |
| 26 | 49 |
| 34.5 | 36 |

\*Calculated by integration of chromatogram peak area.

*4.6. Reaction 5 – Photocatalytic reactions in batch with solar light in 2.8 mg.mL-1 of total protein*

The photoenzymatic decarboxylation reactions using solar light exposition were carried out in a transparent jacketed reactor (total volume 10 mL) at 35 ºC. The reactions were performed in a total volume of 2.0 mL Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent and 13 mM of palmitic acid as substrate. The enzymatic extract was used in a 2.8 mg.mL-1 final concentration of total protein. The reactor was exposed to solar rays (116.5 x 103 lux) at summer season under constant and gentle magnetic stirring starting at 11 h a.m. (-22.8601423, -43.2297134) for 40 min. Aliquots (100 μL) were withdrawn every 10 min and the substrates and products were extracted with 1 mL of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

|  |  |
| --- | --- |
| **Time (min)** | **Conv. (%)\*** |
| 0 | 0 |
| 10 | 58 |
| **20** | **>99** |
| 30 | >99 |
| 40 | >99 |

\*Calculated by integration of chromatogram peak area.

*4.7. Reaction 6 – Photocatalytic reactions on cloudy days with lower intensity solar light in 2.8 and 5.6 mg.mL-1 of total protein*

The photoenzymatic decarboxylation reactions using lower intensity solar light exposition were carried out in a transparent jacketed reactor (total volume 10 mL) at 35 ºC. The reactions were performed in a total volume of 2.0 mL Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent and 13 mM of palmitic acid as substrate. The enzymatic extract was used in a 2.8 and 5.6 mg.mL-1 final concentrations of total protein. The reactor was exposed to solar rays (41 x 103 lux) at summer season under constant and gentle magnetic stirring starting at 11 h a.m. (-22.8601423, -43.2297134) for 60 min. Aliquots (100 μL) were withdrawn and the substrates and products were extracted with 1 mL of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

|  |  |  |
| --- | --- | --- |
| **Time** | **Concentration (mg.mL-1)** | **Conv. (%)\*** |
| 0 | 2.8 | 0 |
| 5.6 | 0 |
| 20 | 2.8 | 69 |
| 5.6 | 87 |
| 60 | 2.8 | >99 |
| 5.6 | >99 |

\*Calculated by integration of chromatogram peak area.

*4.8 Reaction 7 – Lower protein concentrations for photocatalytic reactions with solar light*

The photoenzymatic decarboxylation reactions using solar light exposition were carried out in a transparent jacketed reactor (total volume 10 mL) at 35 ºC. The reactions were performed in a total volume of 2.0 mL Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent and 13 mM of palmitic acid as substrate. Different enzymatic extract concentrations were used. The reactor was exposed to solar rays (109 x 103 lux) at summer season under constant and gentle magnetic stirring starting at 11 h a.m. (-22.8601423, -43.2297134) for 60 min. Aliquots (100 μL) were withdrawn and the substrates and products were extracted with 1 mL of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

|  |  |  |
| --- | --- | --- |
| **Concentration (mg.mL-1)** | **Time (min)** | **Conv. (%)\*** |
| 5.6 | 20 | >99 |
| 60 | >99 |
| **2.8** | **20** | **>99** |
| 60 | >99 |
| 1.4 | 20 | 23 |
| 60 | 51 |
| 0.7 | 20 | 5.4 |
| 60 | 8.6 |
| 0.56 | 20 | 4 |
| 60 | 8.5 |

\*Calculated by integration of chromatogram peak area.

## *4.9. Reaction 8 – Scale up evaluation*

The scale up of photoenzymatic decarboxylation reactions using lower intensity solar light exposition were carried out in a transparent jacketed reactor (total volume 10 mL) at 35 ºC. The reactions were performed in different volumes using Tris-HCl buffer (pH 8.5, 100 mM) containing 30 vol % DMSO as cosolvent and 13 mM of palmitic acid as substrate. The enzymatic extract was used in a 2.8 mg.mL-1 final concentration of total protein. The reactor was exposed to solar rays (116 x 103 lux) at summer season under constant and gentle magnetic stirring starting at 11 h a.m. (-22.8601423, -43.2297134) for 20 min. Aliquots (100 μL) were withdrawn and the substrates and products were extracted with 1 mL of ethyl acetate. The remaining organic phase was analyzed by gas chromatography.

|  |  |
| --- | --- |
| **Volume (mL)** | **Conv. (%)\*** |
| 2 | >99 |
| 4 | >99 |
| 8 | >99 |

\*Calculated by integration of chromatogram peak area.

5. Foton emission assay

The evaluation of the flux of photons emitted by the lamps used in photocatalytic reactions was performed using a luxmeter and in presence of a light beam regulator. The Lux value was converted to PPFD (Photosynthetic Photon Flux Density) via the website (https://www.waveformlighting.com/horticulture/convert-lux-to-ppfd-online-calculator)

|  |  |  |  |
| --- | --- | --- | --- |
| **Light Source** | **Lux** | | **PPFD (μmol.s-1.m-2)** |
| Blue Lamp 300 W | | 2750 | 317.77 |
| Sun (sunny day) | | 570 | 13.11 |
| Sun (cloudy day) | | 183 | 4.21 |

6. Chromatograms

* 1. Standard chromatograms

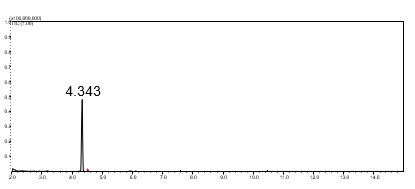


Figure S1: Pentadecane.

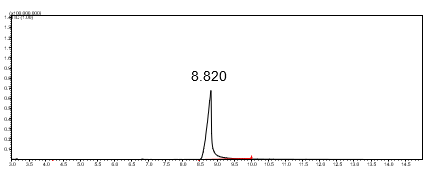


Figure S2: Palmitic acid.

## *6.2. Reaction 3 (item 4.4) chromatograms*

4.0

4.5

5.0

5.5

6.0

6.5

7.0

7.5

8.0

8.5

9.0

9.5

10.0

10.5

11.0

11.5

12.0

12.5

0.25

0.50

0.75

1.00

1.25

1.50

8.560/100.000

Figure S3: Zero time reaction with 13 mM of palmitic acid (0% of conversion).

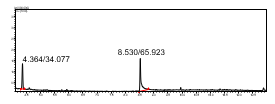


Figure S4: Reaction after 5 min with 13 mM of palmitic acid (34% of conversion).

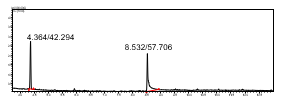


Figure S5: Reaction after 7 min with 13 mM of palmitic acid (43% of conversion).



Figure S6: Reaction after 10 min with 13 mM of palmitic acid (67% of conversion).

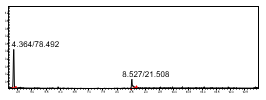


Figure S7: Reaction after 12 min with 13 mM of palmitic acid (78% of conversion).

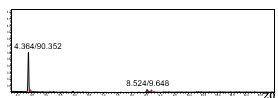


Figure S8: Reaction after 15 min with 13 mM of palmitic acid (90% of conversion).

## *6.3. Reaction 4 (item 4.5.) chromatograms*

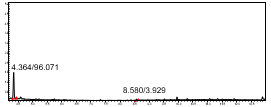


Figure S9: Reaction after 1 h using with 19.5 mM of palmitic acid (96% of conversion).

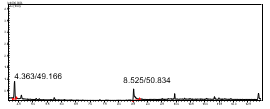


Figure S10: Reaction after 1 h using with 26 mM of palmitic acid (49% of conversion).

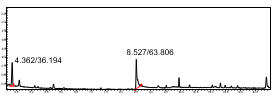


Figure S11: Reaction after 1 h using with 34.5 mM of palmitic acid (36% of conversion).

## *6.4. Reaction 9 (item 4.10.) chromatograms*

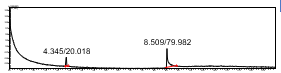


Figure S12: Reaction after 30 min without sunlight component filter and 13 mM of palmitic acid (20% of conversion).

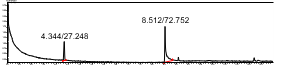


Figure S13: Reaction after 60 min without sunlight component filter and 13 mM of palmitic acid (27% of conversion).

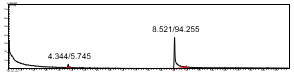


Figure S14: Reaction after 60 min with FGL400 sunlight component filter and 13 mM of palmitic acid (6% of conversion).

# *7. Emission spectrum of lamps*

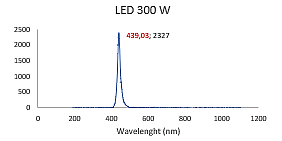


Figure S15: Emission spectrum of 300 W blue LED lamps (439 nm).

# *9. References*

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