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SUPPLEMENTRY INFORMATION

Bio-Inspired Surfactants Capable of Generating Plant Volatiles

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Synthesis

a) *Synthesis of Farnesol based Surfactants:* In a typical procedure farnesol (9.09 g, 40 mmol) was treated with bromoacetic acid (5.56 g, 40 mmol) under solvent free conditions for 18 hours at 68 ºC. The reaction mixture was dissolved in 100 ml of hexane, washed twice with 100 mL of water, separated, dried using Na_2SO_4 and removed under reduced pressure in a rotary flash evaporator at 40 °C. Subsequent purification by silica gel (200-400 mesh) column chromatography using hexane yielded pure farnesyl-2-bromoacetate in 46% isolated yield. The procedure was repeated to build up the amount of pure farnesyl-2-bromoacetate. Farnesyl-2-bromoacetate (3.43 g, 10 mmol) was dissolved in 3.43 mL of dry chloroform and treated with *N*-methyl imidazole (0.82 g, 10 mmol) or tropine (1.41 g, 10 mmol) or pyridine (0.79 g, 10 mmol) for 20 minutes at 45 ºC under inert conditions. The crude reaction mixture after the removal of chloroform under reduced pressure was subsequently washed twice with 50 mL of hexane and precipitated in a cold diethyl ether-acetone (95:5) mixture under inert nitrogen atmosphere. The precipitates upon drying in a rotary flash evaporator at 50 °C for 2 hours gives pure 1-methyl-3-(2-oxo-2-((farnesyl)oxy)ethyl)-1*H*-imidazol-3-ium bromide (Far[Im]Br) or 3-hydroxy-8-methyl-8-(2-oxo-2-((farnesyl)oxy)ethyl)-8-azabicyclo[3.2.1]octan-8-ium bromide (Far[Trop]Br) or 1-(2-oxo-2-((farnesyl)oxy)ethyl)pyridin-1-ium bromide (Far[Py]Br) in 78-82% isolated yield.

b) *Synthesis of Citronellol based Amphiphile:* Citronellol (1.56 g, 10 mmol) was reacted with bromoacetic acid (1.39 g, 10 mmol) under solvent free conditions for 18 hours at 68 ºC. The reaction mixture was dissolved in 25 ml of hexane, washed twice with 25 mL of water, separated, dried using Na_2SO_4 and removed under reduced pressure in a rotary flash evaporator at 40 °C. Subsequent purification on a silica gel (200-400 mesh) column chromatography using hexane yielded pure corresponding bromoacetates in 46-48% isolated yield. Respective

bromoacetate was reacted with *N*-methyl imidazole (0.82 g, 10 mmol) for 20 minutes at 45 ºC under inert conditions. The crude reaction mixture was washed twice with hexane and cold precipitated in a diethyl ether-acetone (95:5) mixture under inert nitrogen atmosphere. The precipitates upon drying in a rotary flash evaporator at 50 °C for 2 hours gives pure citronellol based cationic amphiphiles in 78-82% isolated yield.

Instrumentation, Materials and Methods

Instrumentation: ^{1}H NMR (300 MHz) spectra was recorded using a Varian NMR instrument. Chemical shifts are recorded in ppm (δ) in $CDCl_3$ and D_2O. For HRMS analyses ESI ionization and a TOF analyzer were used.

Materials: Tropine was purchased from MP Biomedicals, France. farnesol, nerol, bromoacetic acid and *N*-methylimidazole were purchased from ACROS, USA. Pyridine, diethyl ether, hexane and acetone were purchased from Fisher Scientific, USA. Millipore water was used in all experiments.

Method:

Pendent drop method for determination of surface properties of surfactants:

The surface tension at water−air interface was investigated using the pendant drop technique[1,2] (Attention Theta tensiometer, Biolin Scientific, Finland). The tensiometer is a real-time droplet analyzer that allows continuous droplet profile extraction. An inverted 16-gauge needle is submerged in the aqueous phase such that the tip is visible in the frame of capture. A gas tight syringe [1 mL] (Hamilton Co., USA) is mounted in a microsyringe pump (Harvard Apparatus) to ensure instantaneous creation of a droplet of a preset volume. Before the droplet is formed, the image capture software is triggered, collecting images at 2 frames for the first 10 min and 1 frame/min thereafter, for a total aging time of 3600 s (1 h). Edge detection is used to identify the droplet shape, with the surface tension determined using the Young−Laplace equation.

Experimental runs of 3600 s are chosen as surfactant solution attains equilibrium within the chosen time frame.

The physical and thermodynamic parameters[3] were calculated according to following equations:

The maximum surface excess concentration at the air/water interface, Γ_{max} is calculated by applying the Gibbs adsorption isotherm equation:

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right)_T \qquad (1)$$

Here, γ denotes the surface tension, R is the gas constant, T is the absolute temperature, and C is the surfactant concentration. The value of n is taken as 2. The area occupied per surfactant molecule (A_{min}) at air water interface is obtained by using following equation:

$$A_{min} = 1/N\,\Gamma_{max} \qquad (2)$$

Where N is Avogadro's number and A_{min} is in nm^2. The values of Γ_{max} and A_{min} are shown in Table 1. The A_{min} values of these surfactants have been found to be exceptionally low indicating tighter packing of the surfactant molecule at the interface. Other important parameters such as γ_{cmc} (affinity to reduce surface tension at cmc) and π_{cmc} of these surfactants have been calculated from the plot of decrease in surface tension versus log of concentration and have been shown in Table 1. The affinity to reduce surface tension of aqueous system by these surfactants depends upon the nature of hydrophilic head group attached to surfactant molecule.

Gibbs free energy of micellization (ΔG^o_{mic}) is calculated by following equation:

$$\Delta G^o_{mic} = (1+\beta)\,RT\ln X_{cmc} \qquad (3)$$

Where X_{cmc} is the cmc in molar fraction, X_{cmc} = cmc/55.4, where cmc is in mol/L, and 55.4 comes from 1 L of water corresponding to 55.4 mol of water at 25 ºC. β is the degree of counterion binding to micelles.

Similarly Gibbs free energy of adsorption (ΔG^o_{ads}) is calculated by following equation:

$$\Delta G^\circ_{ads} = \Delta G^\circ_{mic} - \frac{\pi_{cmc}}{\Gamma} \qquad (4)$$

Here, π_{cmc} denotes the surface pressure at the cmc ($\pi_{cmc} = \gamma_o - \gamma_{cmc}$, where γ_o and γ_{cmc} are the surface tensions of water and the surfactant solution at cmc, respectively).

Conductivity Measurements: Conductivity was measured on VWR SB80PC auto temperature conductivity meter equipped with a conductivity cell having a cell constant of 1. The solutions were thermostated at 25.0 $\pm$ 0.1 °C in thermostated glass vessel controlled by VWR temperature controller. For the determination of cmc adequate quantity of a concentrated surfactant solution was added in order to change the surfactant concentration from concentrations well below the critical micelle concentration (cmc) to up to at least 1-2 times the cmc. Degree of counterionbinding (β) has been calculated as (1-α), where $\alpha = S_{micellar}/S_{premicellar}$ *i.e*; ratio of the slope after and before cmc.[4]

Time dependent NMR investigations: 50 mM concentration of surfactant solution was prepared by dissolving appropriate amount of individual amphiphiles in D_2O. ^1H NMR of surfactant solutions was recorded at different time interval.

Headspace GC-MS analysis: 50 mM aqueous solution of Far[Im]Br, Far[Trop]Br and Far[Py]Br was prepared in standard GC-MS bottle (headspace vial). The samples were analyzed based on the isomerization and hydrolysis rate determined by ^1H NMR data (after 72 hours in case of Far[Im]Br, 48 hours in case of Far[Trop]Br and 24 hours in case of Far[Py]Br) for the volatiles produced at air-interface. Subsequently, samples were withdrawn from same bottle after their complete hydrolysis (i. e. after 144 hours for Far[Im]Br, 120 hours in case of Far[Trop]Br and 60 hours in case of Far[Py]Br) for determination of volatiles produced inside micelle core. Analysis was conducted using a GC/MS-QP2010 Plus (Shimadzu, Kyoto, Japan) equipped with a headspace injection system. Vials were incubated for 5 min at 75 °C, and 1 mL of the headspace air were directly transferred to the injection port in splitless manner to a RESTEK®-5MS (crossbond ® 5% diphenyl/95% dimethyl polysiloxane 30 m × 0.25 mm, 0.25 μm). Carrier gas was helium, with a column flow of 1.0 mL/min and a linear velocity of 38 cm/s. The temperature

program started at 150 °C with a gradient of 7 °C/min up to 195 °C followed by a gradient of 15 °C/min up to 300 °C with a hold for 5 and 3 min at 195 °C and 300 °C respectively.

Supporting Figures

Fig. S1 Time dependent ^{1}H NMR studies of 50 mM solution of Far[Im]Br in D_2O. The NMR spectra shown at different time interval: 0 hour, after 36 hours, 72 hours, 96 hours and 120 hours respectively at 25 °C and the surfactants solution were kept at 25 °C. The surfactant starts to degrade after 36 hours and completely degrades in 120 hours (degradation time determined by recording NMR on short time interval).

Fig. S2 Time dependent ^{1}H NMR studies of 50 mM solution of Far[Im]Br in D_2O. The NMR spectra shown at different time interval 0 hour, after 24 hours, 48 hours, 72 hours and 96 hours respectively at 25 °C and the surfactants solution were kept at 25 °C. The surfactant starts to degrade after 18 hours and completely degrades in 110 hours (degradation time determined by recording NMR on short time interval).

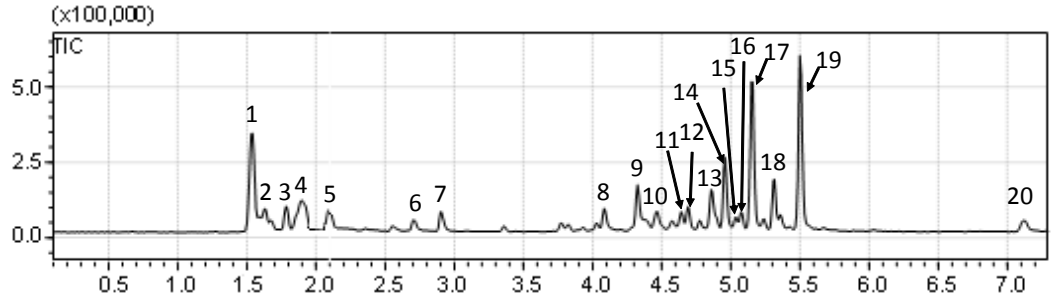

Fig. S3 Headspace analysis of 50 mM aqueous solution of Far[Im]Br. Headspace was collected after 144 h. The main components were identified by mass spectra of computerized libraries. The chemical structure of major molecules generated inside the micelle core are 2: (*Z*)-3,4-dimethyl pent-2-ene, 3: 2,7-dimethyloxepine, 4: 5-isopropyl-2-methyl-2-vinyltetrahydrofuran, 5: 2-(5-methyl-5-vinyltetrahydrofuran-2-yl)propan-2-ol, 6: (Z)-4,8-dimethylnona-3,7-dien-2-one, 7: 4,8-dimethylnona-3,8-dien-2-one, 8: (*Z*)-β-farnesene, 9: (*E*)-β-farnesene, 10: (*Z,E*)-α-farnesene, 11: (*Z,Z*)-α-farnesene, 12: (*E,Z*)-α-farnesene, 13: (*E,E*)-α-farnesene, 14: β-bisabolene, 15: isopulegol acetate, 16: α-bergamotene, 17: (*Z*)-nerolidol 18: α-bisabolene, 19: (*E*)-nerolidol and 20: α-bisabolol. Peak 1 corresponds to unidentified hydrolyzed imidazolium based ionic liquid derivative.

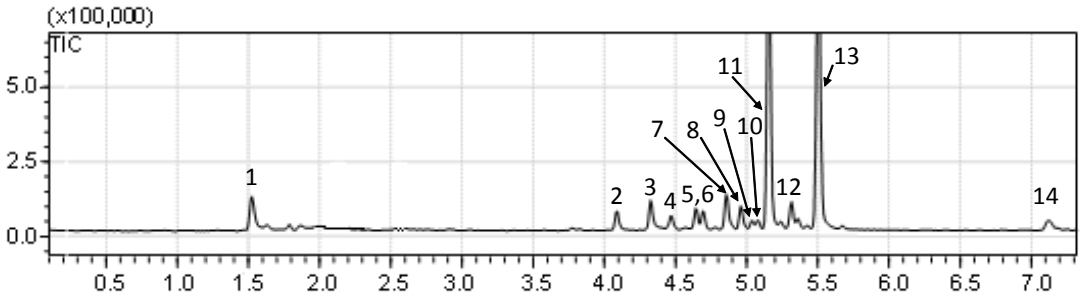

Fig. S4 Headspace analysis of 50 mM aqueous solution of Far[Py]Br. Headspace was collected after 60 h. The main components were identified by mass spectra of computerized libraries. The chemical structure of major molecules generated inside the micelle core are 2: (*Z*)-β-farnesene, 3: (*E*)-β-farnesene, 4: (*Z,E*)-α-farnesene, 5: (*Z,Z*)-α-farnesene, 6: (*E,Z*)-α-farnesene, 7: (*E,E*)-α-farnesene, 8: β-bisabolene, 9: α-bergamotene, 10: isopulegol acetate, 11: (*Z*)-nerolidol, 12: β-bisabolene, 13: (*E*)-nerolidol and 14: α-bisabolol. Peak 1 corresponds to unidentified hydrolyzed pyridinium based ionic liquid derivative.

Spectral Data of Compounds

(1) 1-methyl-3-(2-oxo-2-((farnesyl)oxy)ethyl)-1*H*-imidazol-3-ium bromide **(1: Far[Im]Br):** Slightly yellowish viscous liquid, Yield 81% (with respect to starting farnesyl-2-bromoaectate); 500 MHz ^{1}H NMR ($CDCl_3$) δ ppm: 1.52-1.64 (m, 12H), 1.89-2.02 (m, 8H), 4.02 (s, 3H), 4.64-4.65 (d, *J* = 10.0 Hz, 2H), 5.01 (m, 2H), 5.26 (m, 1H), 5.36 (s, 2H), 7.51 (s, 1H), 7.56 (s, 1H), 9.95 (s, 1H). 75 MHz ^{13}C NMR ($CDCl_3$) δ ppm: 16.83, 17.91, 23.65, 25.94, 26.36, 26.86, 32.11, 37.24, 39.84, 50.47, 63.79, 112.20, 124.20, 124.65, 131.57, 131.81, 135.88, 135.99, 144.76, 144.88, 165.09. ESI-HRMS positive ions *m/z*: calculated 345.2542 for (M^+−Br^-) or M^+, found 345.2558.

(2) 3-hydroxy-8-methyl-8-(2-oxo-2-((farnesyl)oxy)ethyl)-8-azabicyclo[3.2.1]octan-8-ium bromide (**2: Far[Trop]Br**): White waxy solid, Yield 85% (with respect to starting farnesyl 2-bromoaectate); 500 MHz ^{1}H NMR ($CDCl_3$) δ ppm: 1.52-1.64 (m, 12H), 1.88-2.03 (m, 8H), 2.12-2.22 (m, 5H), 2.49-2.52 (m), 2.74-2.76 (m, 2H), 3.47 (s, 3H), 4.20 (m, 1H), 4.42 (s, 2H), 4.52 (s, 2H), 4.63-4.64 (m, 2H), 5.00 (m, 2H), 5.23 (m, 1H). 75 MHz ^{13}C NMR ($CDCl_3$) δ ppm: 16.81, 17.87, 23.61, 25.28, 25.93, 26.88, 32.13, 34.60, 34.70, 39.86, 42.09, 42.20, 58.51, 59.48, 59.73, 63.74, 68.01, 112.20, 124.20, 124.65, 131.81, 135.88, 144.88, 165.09. ESI-HRMS positive ions *m/z*: calculated 404.3165 for (M^+−Br^-) or M^+, found 404.3141.

(3) 1-(2-oxo-2-((farnesyl)oxy)ethyl)pyridin-1-ium bromide **(3: Far[Py]Br):** Slightly yellowish viscous liquid, Yield 81% (with respect to starting farnesyl 2-bromoaectate); 500 MHz ^{1}H NMR ($CDCl_3$) δ ppm: 1.56-1.67 (m, 12H), 1.93-1.99 (m, 8H), 4.71 (m, 2H), 5.04 (m, 2H), 5.29 (m, 1H), 6.20 (s, 2H), 8.03 (dt, *J* = 34.1, 7.0 Hz, 2H), 8.51 (t, *J* = 7.7 Hz, 1H), 9.39 (dd, J = 16.9,5.4 Hz, 2H). 75 MHz ^{13}C NMR ($CDCl_3$) δ ppm: 16.80, 17.80, 23.60, 25.91, 26.38, 26.84, 32.11, 39.84, 61.27, 64.23, 117.30, 123.41, 124.19, 127.28, 128.30, 131.47, 131.71, 135.84, 144.48, 146.57, 146.91, 166.00. ESI-HRMS positive ions *m/z*: calculated 342.2433 for (M^+−Br^-) or M^+, found 342.2438.

(4) 3-(2-((citronellyl)oxy)-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium bromide **(Cit[Im]Br):** Colorless liquid, Yield 86%; 500 MHz ^{1}H NMR ($CDCl_3$) δ ppm: 0.81 (dd, *J* = 20.7,6.4 Hz, 3H), 1.11 (m, 1H), 1.25 (m, 1H), 1.41-1.60 (m, 9H), 1.88-1.90 (m), 4.02 (s, 3H), 4.15-4.16 (m, 2H),

5.00 (t, J = 6.8 Hz, 1H), 5.39 (s, 2H), 7.53 (s, 1H), 7.60 (s, 1H), 10.05 (s, 1H). 75 MHz ^{13}C NMR ($CDCl_3$) δ ppm: 17.74, 19.34, 25.55, 29.42, 35.08, 36.74, 37.04, 50.24, 65.32, 123.65, 124.05, 124.44, 131.26, 137.56, 137.96, 166.41. ESI-HRMS positive ions *m/z*: calculated 279.2073 for (M^+−Br^-) or M^+, found 279.2055.

(5) Farnesyl-2-bromoaectate: Colorless liquid, Yield 46%; 500 MHz ^{1}H NMR ($CDCl_3$) δ ppm: 1.57-1.68 (m, 12H), 1.95-2.08 (m, 8H), 3.80 (s, 2H), 4.66-4.67 (t, J = 9.9 Hz, 2H), 5.06 (t, J = 6.3 Hz, 2H), 5.17 (m, 1H). 75 MHz ^{13}C NMR ($CDCl_3$) δ ppm: 16.74, 17.89, 23.57, 25.89, 26.33, 26.92, 32.18, 39.72, 40.00, 63.31, 117.62, 123.71, 124.49, 131.49, 135.87, 143.75, 167.41.

(6) Citronellyl-2-bromoacetate: Colorless liquid, Yield 58%; 500 MHz ^{1}H NMR ($CDCl_3$) δ ppm: 0.90 (d, J = 6.5 Hz, 3H), 1.13-1.20 (m, 1H), 1.29-1.36 (m, 1H), 1.41-1.48 (m, 1H), 1.51-1.72 (m, 8H), 1.90-2.01 (m, 2H), 3.80 (s, 2H), 4.14-4.23 (m, 2H), 5.05 (t, J = 6.7 Hz). 75 MHz ^{13}C NMR ($CDCl_3$) δ ppm: 17.84, 19.61, 25.53, 26.08, 26.34, 29.50, 35.38, 37.06, 65.91, 124.83, 131.51, 167.46.

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