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Synthesis and Langmuir isotherms of difluorostearic acids

David O'Hagan [a,*], Itsumaro Kumadaki [b], Michael Petty [c], Hiroaki Takaya [b], Christopher Pearson [c]

[a] *Department of Chemistry, Science Laboratories, University of Durham, South Road, Durham, DH1 3LE, UK*
[b] *Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka 573-01, Japan*
[c] *School of Engineering, Science Laboratories, University of Durham, South Road, Durham, DH1 3LE, UK*

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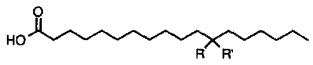
Abstract

The CF_2 containing 6,6- and 10,10-difluorooctadecanoic acids **7** and **8**, respectively have been synthesised and their Langmuir isotherms evaluated. In marked contrast to the behaviour of octadecanoic acid (stearic acid) **1** it is demonstrated that spreading on an aqueous subphase generates an unstable monolayer which reorganises to a more stable bilayer structure. Grazing incidence X-ray scattering and ellipsometric measurements after deposition of **8** from the subphase onto a silicon wafer, confirmed a bilayer structure. These observations reinforce our earlier conclusions with 12,12-difluorooctadecanoic acid that substitution of CH_2 by CF_2 leads to increased conformational flexibility of a hydrocarbon chain.

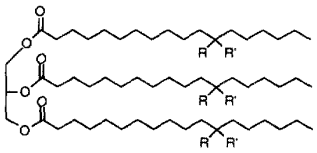
Keywords: Langmuir isotherms; Octadecanoic acids; CF_2

1. Introduction

The selective replacement of hydrogen atoms by fluorine is a current interest in bio-organic and materials chemistry [1–4]. The steric influence of the fluorine atom is greater than hydrogen (van der Waal's radii 1.47 vs. 1.2 Å) [5] but the evidence suggests [6] that a single substitution does not normally induce a serious steric perturbation. However the progressive replacement of H's for F's becomes increasingly disparate and most notably, the $-CH_3$ and $-CF_3$ groups are not isosteric [7]. Recently we reported [8] a study which involved the progressive replacement of the C-12 methylene group of stearic acid by CHF and CF_2. This was designed to assess the influence of fluorine substitution in the middle of a hydrocarbon chain. Langmuir isotherms of the resultant 12-monofluoro **2** and the 12,12-difluoro **3** stearic acids, were recorded after spreading onto a water subphase.



R = H, R' = H **1**
R = F, R' = H **2**
R = F, R' = F **3**



R = H, R' = H **4**
R = F, R' = H **5**
R = F, R' = F **6**

Both stearic acid **1**, the parent hydrocarbon, and the monofluorinated stearic acid **2** behaved classically, generating a stable monolayer where the area occupied by each molecule (molecular area) was 0.21 ± 0.01 and 0.23 ± 0.01 nm^2 on the aqueous subphase, respectively. However the monolayer of 12,12-difluorostearic acid **3** on the aqueous subphase was unstable and after an initial compression, reorganised to a bilayer. The isotherm from this latter experiment is shown in Fig. 1. The stearic acids **2** and **3** were then esterified with glycerol to generate their corresponding tristearins **5** and **6**,

* Corresponding author. Fax: +44-191-384-4737.

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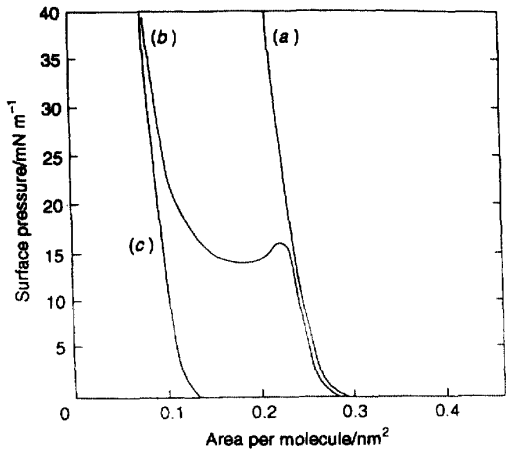


Fig. 1. Langmuir isotherms of 12,12 difluorostearic acid **3** showing condensed pressure vs. area curves for the three successive compressions: (a) first; (b) second; (c) third compression.

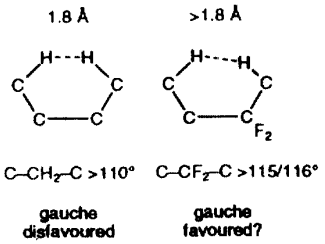
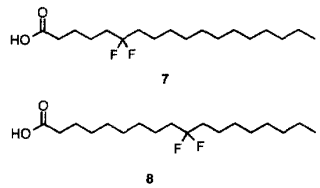


Fig. 2. The CF_2 group increases the C–C–C angle and increases the H···H distance between 1,4-hydrogens lowering the energy of attainment of *gauche* conformations.

respectively, and the polymorphic behaviour of the tristearins was evaluated by differential scanning calorimetry (DSC) and X-ray powder diffraction analyses. The CHF substituted tristearin **5** displayed similar polymorphic behaviour to **4**, the parent hydrocarbon system, however the CF_2 substituted tristearin **6** had a unique polymorphism [8]. In general the phases had lower melt transitions and the melting point of **6** (57.7°C) was significantly lower than **4** and **5** (72 and 73°C).

We attributed this phenomenon to increased conformational flexibility of the hydrocarbon chain induced by the CF_2 group. In hydrocarbon chains *gauche* conformations are disfavoured due to 1,4-hydrogen interactions and such chains prefer to adopt *anti-zig-zag* conformations. However the introduction of a CF_2 group widens the C–C–C angle from 109° in C–CH_2–C to 115/116° in C–CF_2–C [8] as illustrated in Fig. 2. This widening of the angle increases the 1,4-hydrogen distance and relaxes the 1,4-interactions such that *gauche* conformations are now more accessible, thus the CF_2 containing chains display a higher degree of conformational flexibility relative to the hydrocarbon chains.

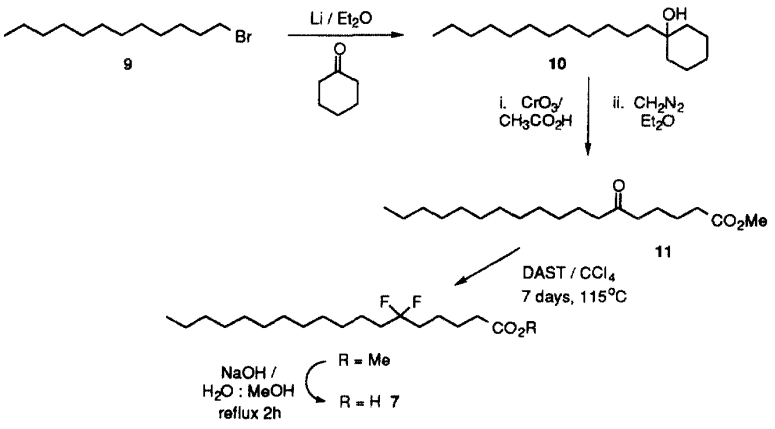


In order to explore this phenomenon further we now report the preparation of 6,6-difluorostearic **7** and 10,10-difluorostearic **8** acids for Langmuir isotherm analysis. It was anticipated that the 6,6-difluoro compound **7** would form less stable monolayers on the surface of water than the 10,10-difluoro compound **8** as the *gauche* turns associated with the CF_2 group should penetrate deeper into the monolayer in the former case and destabilise the integrity of the film. In the event this was borne out in the study.

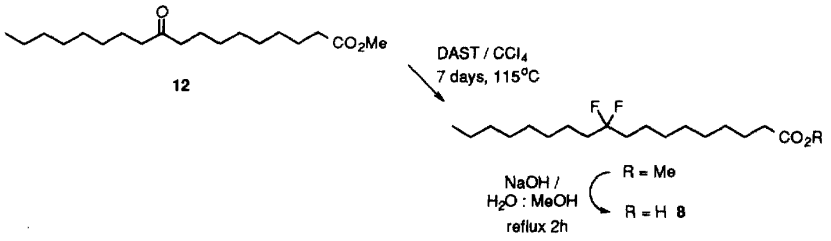
2. Results

2.1. Synthesis of 7 and 8

Compound **7** presented the greater synthetic challenge and was prepared as illustrated in Scheme 1. Metal exchange of 1-bromododecane **9** with lithium followed by treatment with cyclohexanone generated tertiary alcohol **10** in 56% yield.



Scheme 1.



Scheme 2.

Oxidative ring opening to give 6-oxooctadecanoic acid and then esterification with diazomethane furnished methyl 6-oxooctadecanoate **11**. Finally treatment with diethylamino sulfurtrifluoride (DAST) and then hydrolysis gave the required compound **7**.

Compound **8** was prepared in a straightforward manner after DAST treatment of 12-oxooctadecanoic acid **12** followed by hydrolysis as shown in Scheme 2.

2.2. Langmuir isotherms

With compounds **7** and **8** in hand, Langmuir isotherms were recorded for each material after spreading onto water. The materials were dissolved in dichloromethane to a concentration of approximately 1 g l^{-1} and applied to the subphase surface using a microsyringe. The isotherms were recorded on a purified water subphase adjusted to pH 4.8 with HCl, with a constant compression rate (3.0×10^{-3} nm^2 $molecules^{-1}$ s^{-1}). The layer was compressed until a surface pressure of 40 mN m^{-1} was reached at which point the direction of the barriers was reversed. The barriers were fully opened and then immediately recompressed.

The resultant isotherm recorded at 21°C for **8** is shown in Fig. 3a. Compound **8** displayed the characteristics initially of a monolayer however this monolayer collapsed on the second compression and reorganised as a bilayer as indicated by the plateau in that isotherm. The bilayer remained stable for subsequent compressions. This behaviour is entirely consistent with that observed previously [8] for 12,12-difluorostearic acid **3** shown in Fig. 1. Again the area of the resultant bilayer was less than half that of the monolayer suggesting some elements of a multilayer component in the thermodynamically more stable sub-structure. A more detailed analysis of the Langmuir film of **8** was conducted by lowering the temperature of the subphase to 17 and 15°C as illustrated in Fig. 3b and c, respectively. The isotherms reveal that the monolayer is more stable at 17°C requiring more compressions (six) before reorganisation to the bilayer occurs. And at 15°C the transition is less facile where successive compressions result in an incremental reduction in the surface area with each compression, until a bilayer is fully established. By comparison spreading of 6,6-difluorostearic acid **7** onto the aqueous subphase generated the expanded isotherm shown in Fig. 4 indicative of a conformationally more dynamic monolayer. The surface pressure begins to increase at 0.37 nm^2 (vs. 0.28 nm^2 for **8**) and then plateaus, indicative of a phase transition. It is again apparent that after the first compression a reorganisation of a monolayer to a bilayer takes place, and this now emerges as a characteristic feature of these CF_2 containing stearic acids.

2.3. Multilayer deposition

To obtain X-ray and ellipsometry data, 10,10-difluorostearic acid **8** was deposited onto a silicon wafers. Compound **8** could not be deposited using conventional vertical dipping

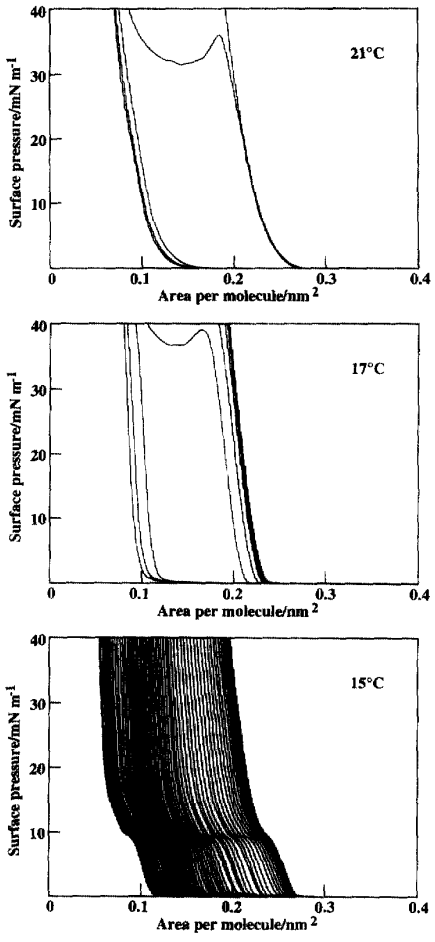


Fig. 3. Langmuir isotherms of 10,10-difluorostearic acid **8** showing condensed pressure vs. area curves for repeated compressions: (a) at 21°C, (b) at 17°C and (c) at 15°C.

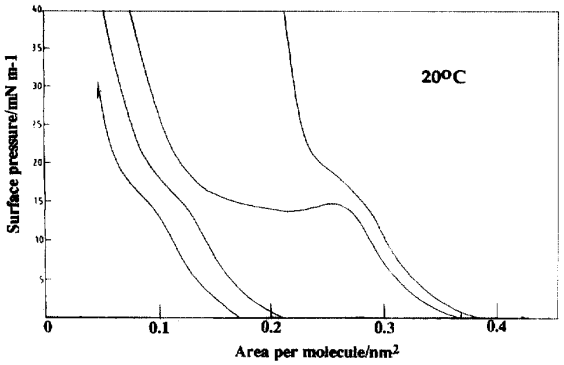


Fig. 4. Langmuir isotherms of 6,6-difluorostearic acid **7** showing condensed pressure vs. area curves for repeated compressions at 20°C.

but it was possible to obtain a multilayer film on hydrophilic silicon using a horizontal dipping technique. A pure water subphase at a temperature of 18.5°C was adjusted to pH 4.8 ± 0.1 with HCl solution. A suitable volume (200 μl) of a solution of **8** in dichloromethane, with a concentration of 1 $g\,l^{-1}$, was then applied dropwise to the surface. After 10 min, to allow evaporation of the solvent, consecutive compression isotherms were recorded at a speed of $1.6 \pm 0.2 \times 10^{-3}$ nm^2 $molecule^{-1}$ s^{-1}, until the structure of the film was observed to change from the regime with large area per molecule to that having small molecular area. The surface pressure of the floating layer was then controlled at 30 mN m^{-1} and the subphase area, monitored using a chart recorder, allowed to stabilise before deposition was started.

Hydrophilic silicon substrates ((100) orientation) were clamped above, with faces almost parallel to, the subphase. The substrates were lowered, at a speed of 2 mm min^{-1}, through the surface of the subphase until submerged. The direction of the dipping motor was then reversed and the substrates raised back up through the air/water interface. Five, ten and fifteen dipping cycles were performed (samples 1, 2 and 3), allowing a drying time of 1 h between cycles. Although a plot of trough area vs. time obtained during the dipping experiment did not record significant film transfer, visual examination of the substrates revealed patchy film on both sides, especially the lower face.

2.4. X-ray analysis

The results of the grazing incidence specular X-ray scattering measurements performed on the organic film that was deposited on the lower face of sample 2 are shown in Fig. 5. Two Bragg peaks are evident at angles of $\theta = 0.946°$ and $\theta = 0.1884°$, corresponding to first and second order reflections of a d spacing in the organic film of $d = 4.23 \pm 0.01$ nm. The length of a molecule of compound **8**, derived from a standard molecular model, is 2.5 ± 0.1 nm, indicating a maximum bilayer thickness of 5.0 ± 0.2 nm. The d spacing obtained from X-ray measurements is smaller than this value,

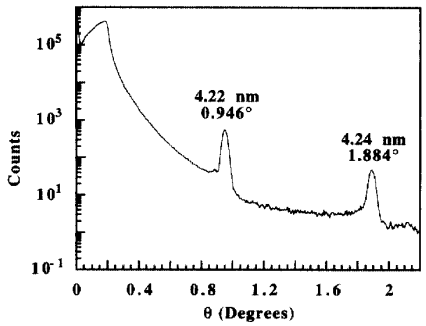


Fig. 5. Grazing incidence specular X-ray scattering scan of 10,10-difluorostearic acid **8** deposited onto a silicon(100) substrate from a floating layer on water after 10 dipping cycles.

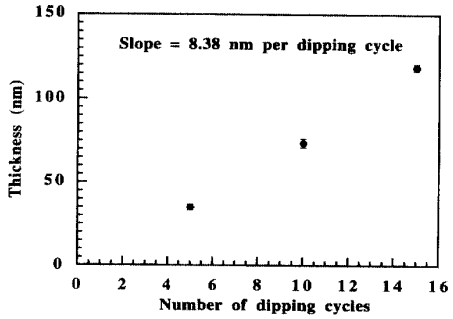


Fig. 6. Plot of film thickness vs. the number of dipping cycles for multilayer films of **8** in a silicon wafer substrate as measured by ellipsometry.

suggesting some degree of tilting or interdigitation of the molecules in the multilayer film.

2.5. Ellipsometry

Using a Rudolph Research Auto El IV ellipsometer operating at 632.8 and 546.1 nm, the overall thicknesses of the organic layers were measured, at areas of best quality, of samples 1, 2 and 3. These thicknesses are plotted against the number of dipping cycles in Fig. 6. The slope of this graph gives a value of 8.38 ± 0.35 nm per cycle. It is poignant that this value is double the d spacing obtained using X-ray scattering indicating that two bilayers of compound **8** were transferred onto the substrate during each dipping cycle. The result provides further evidence that in the low area per molecule regime, compound **8** forms a bilayer at the air/water interface.

3. Discussion

Stearic acid **1** forms very stable monolayers at the air/water interface. However, it is now clear that substitution of a CH_2 for a CF_2 group in a stearic acid alters dramatically the nature of the material and disrupts the integrity of a floating layer. In the cases studied (**3**, **7** and **8**) this substitution is made sufficiently remote from the carboxylate group such that the modified behaviour is unlikely to be attributed to a

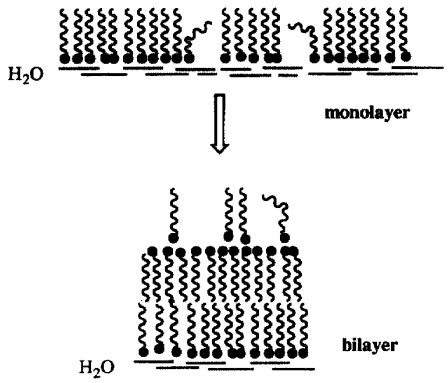


Fig. 7. Schematic representation of monolayer and bilayer structures for **7** and **8** on a water subphase.

change in the nature (e.g., acidity) of the carboxylate. There may be a steric component contributing to monolayer destabilisation, however the marked change in behaviour reinforces our earlier conclusion that increased conformational disorder arises by such a substitution. The situation is demonstrated most forcefully by comparing the Langmuir isotherm of 6,6-difluorostearic acid **7** with that of 10,10-difluorostearic **8** acid at 20 and 21°C, respectively. In the former case the CF_2 group is closer to the carboxylate group which associates with the aqueous subphase. Thus, as anticipated, conformational disorder has a greater destabilising effect on the integrity of the monolayer by comparison with the 10,10-difluoro system. Rearrangement to a bilayer presumably stabilises the system to a greater extent overriding much of the conformational disorder apparent in the monolayer. This is shown schematically in Fig. 7 (below).

A bilayer structure for the thermodynamically more stable film from 10,10-difluorostearic acid **8** was supported by X-ray analysis after repetitive deposition onto silica. However, it is a consistent feature revealed by the Langmuir isotherms that the area of the bilayer is always less than 50% that of the monolayer [8]. This is most readily explained by some degree of bilayer stacking, perhaps with the effect of neutralising the impact of the exposed carboxylates at the air interface as illustrated in Fig. 7, however the details of such a structure remain to be confirmed.

In conclusion, CF_2 groups destabilise the integrity of hydrocarbon packing in monolayers (or membranes) when they are introduced in the place of a CH_2 group. This extends our previous conclusions. When spread onto the surface of water the monolayer finds stability in reorganising to generate a bilayer structure.

4. Experimental details

4.1. General procedures

Melting points were measured on a micro-melting point apparatus, Model MP (Yanagimoto, Kyoto, Japan) without correction. ^1H NMR spectra were recorded on JEOL FX90Q and JNM-GX400 spectrometers and ^{19}F NMR spectra were measured on Hitachi R-1500 and JEOL FX90Q spectrometers. Benzotrifluoride (BTF) was used as an internal standard and 64 ppm was added to convert to a common standard scale from $CFCl_3$. IR spectra were recorded on Hitachi 270-30 Infrared Spectrophotometer.

4.2. 1-Dodecylcyclohexanol **10**

To a suspension of Li (0.557 g, 80.2 mmol) in dry Et_2O (40 ml), 1-bromododecane (1.0 g, 4.01 mmol) was added at room temperature under an atmosphere of Ar, and the mixture was sonicated for 10 min to start the reaction. After the reaction started, a solution of 1-bromododecane (9.0 g, 36.1 mmol) in dry Et_2O (100 ml) was added dropwise in 3 h, and the mixture was stirred further 1 h. Cyclohexanone (5.91 g, 60.2 mmol) was added to the mixture, then the whole was stirred overnight. After addition of saturated NH_4Cl, the mixture was stirred for 30 min and extracted into Et_2O. The Et_2O layer was washed with saturated NaCl and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, CH_2Cl_2) to give 1-dodecylcyclohexanol **10** (6.0 g, 22.3 mmol, 55.7%) as a pale yellow oil. MS m/z: 268 (M^+). HRMS Calcd. $C_{18}H_{36}O$: 268.277. Found: 268.277. IR (KBr) cm^{-1}: 3420.0 (OH), 2928.0, 2860.0 (C–H). ^1H NMR ($CDCl_3$) δ: 0.88 (3H, t, J=7.0 Hz), 1.2–2.45 (32H, m), 2.83–2.92 (1H, m).

4.3. 6-Oxooctadecanoic acid

CrO_3 (0.25 g, 2.50 mmol) was added to a solution of 1-dodecylcyclohexanol **10** (1.0 g, 3.72 mmol) in acetic acid (37.5 ml) and stirred vigorously at room temperature for 5 min. CrO_3 (2.75 g, 27.5 mmol) was further added in small portions at 30°C with ice-cooling. After stirring for 3 h, H_2O (37.5 ml) was added and the reaction extracted into Et_2O. The Et_2O layer was washed with H_2O, extracted with 5% NaOH and the aqueous layer acidified with 36% HCl and then extracted into Et_2O. The Et_2O layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was recrystallized from hexane to give 6-oxo-octadecanoic acid (0.645 g, 2.16 mmol, 58.1%) as colourless plates. Mp. 79.5–80.5°C. MS m/z: 298 (M^+). IR (KBr) cm^{-1}: 3300–2500 (OH), 2960.0, 2924.0, 2856.0 (C–H), 1710.0 (COOH, C=O).

4.4. Methyl 6-oxooctadecanoate

A solution of CH_2N_2 (excess) in Et_2O (100 ml) was added to a solution of 6-oxooctadecanoic acid (0.7 g, 2.35 mmol) in Et_2O (50 ml), and the mixture was stirred at room temperature for 1 h. The reaction was then treated with acetic acid to decompose excess CH_2N_2. The Et_2O layer was washed with saturated $NaHCO_3$ and H_2O and then dried over $MgSO_4$. After evaporation of the solvent under vacuum, the residue

was purified by column chromatography (SiO_2, hexane–Et_2O, 1:1) and recrystallized from hexane to give methyl 6-oxooctadecanoate **11** (0.70 g, 2.24 mmol, 95.3%) as colourless plates. Mp 45.0–46.0°C. MS *m/z*: 312 (M^+). HRMS Calcd. $C_{19}H_{36}O_3$: 312.266. Found: 312.265. Anal. Calcd. $C_{19}H_{36}O_3$: C, 73.03; H, 11.61. Found C, 72.93; H, 11.34. IR (KBr) cm^{-1}: 2960.0, 2924.0, 2856.0 (C–H), 1740.0 ($COOCH_3$), 1708.0 (C=O). ^1H NMR ($CDCl_3$) δ: 0.88 (3H, t, $J=7.0$ Hz), 1.15–1.38 (18H, m), 1.47–1.70 (6H, m), 2.32 (2H, t, $J=6.5$ Hz), 2.38 (2H, t, $J=7.0$ Hz), 2.41 (2H, t, $J=6.5$ Hz), 3.66 (3H, s).

4.5. Methyl 6,6-difluorooctadecanoate

A solution of methyl 6-oxooctadecanoate **11** (1.80 g, 5.76 mmol) and DAST (5.00 g, 31.0 mmol) in dry CCl_4 (40 ml) was sealed in a stainless steel tube and shaken at 115°C for 7 days. The mixture was poured onto ice water and extracted into Et_2O. The CCl_4 and Et_2O layers were combined, washed with H_2O and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, hexane–Et_2O, 9:1) and recrystallized from hexane to give methyl 6,6-difluorooctadecanoate (0.521 g, 1.56 mmol, 27.1%) as colourless plates. Mp 37.0°C. MS *m/z*: 314.0 ($M-HF$). HRMS Calcd. $C_{19}H_{35}O_2F$ ($M-HF$): 314.262. Found: 314.263. IR (KBr) m^{-1}: 2920.0, 2852.0 (C–H), 1742.0 ($COOCH_3$). ^1H NMR ($CDCl_3$) δ: 0.88 (3H, t, $J=7.0$ Hz), 1.15–1.38 (18H, m), 1.38–1.60 (4H, m), 1.67 (2H, quin, $J=7.62$), 1.72–1.90 (4H, m), 2.33 (2H, t, $J=3.97$ Hz), 3.67 (3H, s). ^{19}F NMR ($CDCl_3$) δ: −32.9 (2F, quin, $J=16.1$ Hz).

4.6. 6,6-Difluorooctadecanoic acid 7

Methyl 6,6-difluorooctadecanoate (**4**, 0.482 g, 1.44 mmol) was added to a solution of NaOH (1.2 g, 30 mmol) in H_2O (10 ml) and CH_3OH (10 ml), and the mixture was heated under reflux for 2 h. The solvent was then evaporated under reduced pressure and the residue acidified with 10% HCl, and extracted into Et_2O. The Et_2O layer was washed with H_2O and dried over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from hexane to give 6,6-difluoro-octadecanoic acid **7** (0.40 g, 1.25 mmol, 86.6%) as colourless plates. Mp 81.0–81.5°C. MS *m/z*: 300.0 ($M-HF$). HRMS Calcd. $C_{18}H_{33}O_2F$ ($M-HF$): 300.246. Found: 300.246. Anal. Calcd. $C_{18}H_{34}O_2F_2$: C, 67.46; H, 10.69. Found: C, 67.47; H, 10.49. IR (KBr) cm^{-1}: 3700–2400 (OH), 2960.0, 2920.0, 2856.0 (C–H), 1706.0 (COOH). ^1H NMR ($CDCl_3$) δ: 0.88 (3H, t, $J=6.84$ Hz), 1.15–1.38 (18H, m), 1.38–1.49 (2H, m), 1.49–1.59 (2H, m), 1.69 (2H, quin, $J=7.82$), 1.73–1.90 (4H, m), 2.38 (2H, t, $J=7.33$). ^{19}F NMR ($CDCl_3$) δ: −33.0 (2F, quin, $J=16.1$ Hz).

4.7. Methyl 10,10-difluorooctadecanoate

A solution of methyl 10-oxooctadecanoate **12** (Aldrich, 2.50 g, 8.00 mmol) and DAST (5.00 g, 31.0 mmol) in dry CCl_4 (50 ml) was sealed in a stainless steel tube and stirred at 115°C for 7 days. The mixture was poured into ice water and extracted into Et_2O. The CCl_4 and Et_2O layers were combined and washed with H_2O and dried over $MgSO_4$. After the evaporation of the solvent, the residue was purified by column chromatography (SiO_2, hexane–Et_2O, 9:1) and recrystallized from hexane to give methyl 10,10-difluoro-octadecanoate (0.90 g, 2.69 mmol, 33.6%) as colourless plates. Mp 34.0–34.5°C. MS *m/z*: 294.0 ($M-2HF$). HRMS Calcd. $C_{19}H_{34}O_2$ ($M-2HF$): 294.256. Found: 294.256. IR (KBr) m^{-1}: 2928.0, 2856.0 (C–H), 1740.0 ($COOCH_3$). ^1H NMR ($CDCl_3$) δ: 0.88 (3H, t, $J=6.7$ Hz), 1.15–1.38 (18H, m), 1.38–1.53 (4H, m), 1.62 (2H, quin, $J=6.8$), 1.70–1.88 (4H, m), 2.30 (2H, t, $J=7.62$ Hz), 3.67 (3H, s). ^{19}F NMR ($CDCl_3$) δ: −32.6 (2F, quin, $J=16.1$ Hz).

4.8. 10,10-difluorooctadecanoic acid 8

Methyl 10,10-difluorooctadecanoate (**6**, 0.566 g, 1.69 mmol) was added to a solution of NaOH (1.0 g, 25 mmol) in H_2O (10 ml) and CH_3OH (10 ml) and the mixture was heated under reflux for 2 h. After evaporation of CH_3OH, the residue was acidified with 10% HCl, and extracted into Et_2O. The Et_2O layer was washed with H_2O and dried over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from hexane to give 10,10-difluoro-octadecanoic acid **8** (0.495 g, 1.54 mmol, 91.2%) as colourless plates. Mp 74.0–74.5°C. Anal. Calcd. $C_{18}H_{34}O_2F_2$: C, 67.46; H, 10.69. Found: C, 67.44; H, 10.49. IR (KBr) cm^{-1}: 3600–2400 (OH), 2924.0, 2856.0 (C–H), 1706.0 (COOH). ^1H NMR ($CDCl_3$) δ: 0.88 (3H, t, $J=6.8$ Hz), 1.15–1.39 (18H, m), 1.39–1.53 (4H, m), 1.64 (2H, quin, $J=7.3$ Hz), 1.70–1.88 (4H, m), 2.35 (2H, t, $J=7.3$ Hz). ^{19}F NMR ($CDCl_3$) δ: −32.6 (2F, quin, $J=16.1$ Hz).

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