Iodocyclofunctionalization of (*E*)-1-Trichloroacetimidoalk-2-enes. Synthesis of (±)-*erythro*-Sphinganine Triacetate

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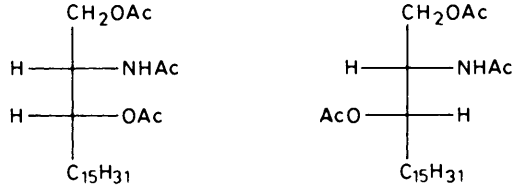
From the iodocyclization of (*E*)-1-trichloroacetimido-octadec-2-ene, 5-iodo-4-pentadecyl-2-trichloromethyl-5,6-dihydro-4*H*-oxazine was unexpectedly obtained, whose structure was assigned from i.r. and ^{1}H n.m.r. spectra. The stereostructure of this oxazine was further confirmed by chemical evidence: thus, the compound was hydrolysed on silica gel to give 2-iodo-3-trichloroacetamido-octadecan-1-ol, and successive treatment with Amberlyst A 26 (CO_3^{2-} form) yielded *cis*-5-hydroxymethyl-4-pentadecyl-4,5-dihydro-oxazole, whose configuration was determined by ^{1}H n.m.r. data. Acidic hydrolysis of this oxazole and acetylation led to *erythro*-3-amino-octadecane-1,2-diol triacetate. To ascertain definitively the structure of this triacetate, 3-trichloroacetamido-octadec-1-ene was cyclized, to yield 5-iodomethyl-4-pentadecyl-4,5-dihydro-oxazole as a 45:55 *cis*:*trans* mixture. After hydrolysis of the *cis*-isomer, treatment with Amberlyst A 26 (AcO^- form), and full acetylation, the aforementioned *erythro*-triacetate was obtained.

Confirming the unequivocal assignment of the stereostructure of 5-iodo-4-pentadecyl-2-trichloromethyl-5,6-dihydro-4*H*-oxazine, its acidic cleavage gave 3-amino-1-iodo-octadecan-2-ol hydrochloride. By treatment of this salt with Amberlyst A 26 (AcO^- form), full acetylation of the product afforded (±)-*erythro*-sphinganine triacetate in good yield, contaminated with a minor amount of the regioisomeric 3-amino-octadecanediol triacetate.

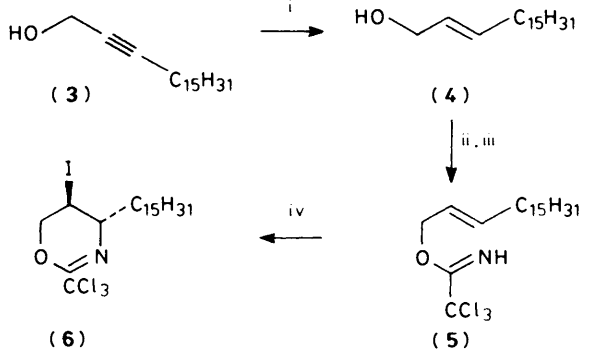
New methods to control the regio- and stereo-chemistry in acyclic systems have attracted much interest, stimulated by the considerable practical importance that such processes have gained for the synthesis of natural products.[1] In the preceding paper[2] from this laboratory, the syntheses of (±)-*erythro*-sphinganine triacetate (**1**) and (±)-*threo*-sphinganine triacetate (**2**) were described, starting from (*Z*)-octadec-2-en-1-ol or octadec-1-en-3-ol, where the iodocyclization always proceeds *via* a 5-*exo* closure.[3]



(**1**) (**2**)

In planning the synthesis of (±)-*erythro*-sphinganine[4] starting from (*E*)-octadec-2-en-1-ol (**4**), new data, which are in contrast with the mechanism previously observed, serve to give us cause for further research into the course of the reaction. We observed that, starting from an *E*-double bond, a 6-*endo* closure was obtained, and we exploited this in a synthesis of (±)-*erythro*-sphinganine triacetate (**1**).

A convenient starting material to compound (**1**) was (*E*)-octadec-2-en-1-ol (**4**), easily obtained by reduction of octadec-2-yn-1-ol (**3**) with $LiAlH_4$ in refluxing tetrahydrofuran (THF).[5] The conversion of enol (**4**) into the corresponding trichloroacetimidate (**5**) in 90% yield was affected by treatment with a catalytic amount of NaH, followed by addition of trichloroacetonitrile at 0 °C in THF.[6] The cyclization of imidate (**5**), performed with *N*-iodosuccinimide (NIS) in $CHCl_3$ at room temperature, gave the 4,5-dihydro-oxazine (**6**) in 80% yield (Scheme 1), whose i.r. absorption at 1 670 cm^{-1} was



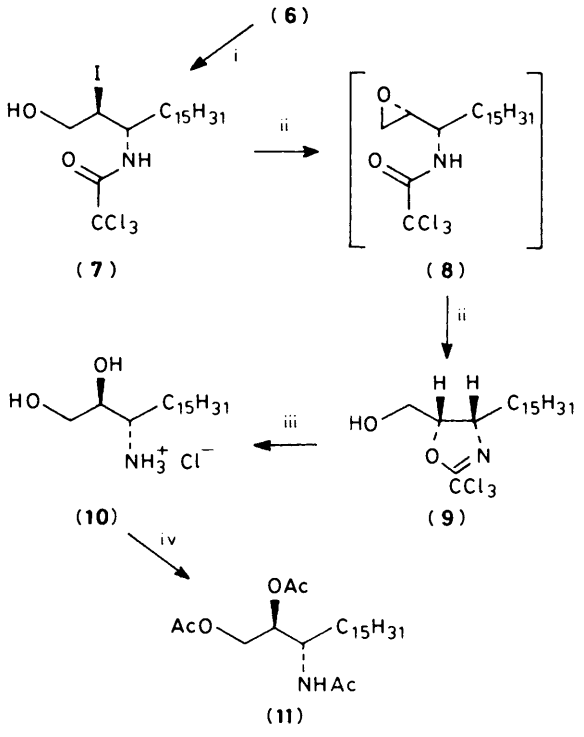
Scheme 1. *Reagents and conditions*: i, $LiAlH_4$, THF, 1 h, reflux; ii, NaH (0.1 equiv.), THF, 1 h, 0 °C; iii, CCl_3CN, THF, 1 h, 0 °C; iv, NIS, $CHCl_3$, 12 h, room temp.

consistent with a C=N stretch in a six-membered ring of 2-trichloromethyl-4,5-dihydro-oxazoles.[7,8] In addition the ^{13}C n.m.r. spectrum disagreed with the five-membered ring structure of the previously described *threo*-4-(1-iodohexadecyl)-2-trichloromethyl-4,5-dihydro-oxazole,[2] (δ_C 71.5 and 61.0 *vs.* δ_C 75.4 and 71.9). From analysis of the ^{1}H n.m.r. spectrum, performed at 300 MHz, we were able to assign a *trans*-relationship from $J_{4H,5H}$ 8 Hz.

This unexpected result required further chemical evidence. Thus the oxazine (**6**) was adsorbed on silica gel for 4 days and the corresponding amide (**7**) was obtained in quantitative yield after elution with AcOEt. Treatment of the iodohydrin (**7**) with Amberlyst A 26 (CO_3^{2-} form) in refluxing benzene afforded, in 70% yield, the *cis*-5-hydroxymethyl-4,5-dihydro-oxazole (**9**), whose i.r. absorption at 1 655 cm^{-1} was in agreement with a C=N stretch in a five-membered ring in this class of compound. The diagnostic feature of its ^{1}H n.m.r. spectrum was the 5-H

resonance, which appeared as a doublet of triplets at δ_H 4.95 with a coupling constant J_{4H-5H} 9 Hz, characteristic of a *cis*-relationship.[9] The *cis*-4,5-dihydro-oxazole formation could be explained by means of a double inversion at C-2: the reaction proceeded through an intermediate epoxide (**8**) which underwent ring opening promoted by nucleophilic attack of the amido group.[10]

The *cis*-5-hydroxymethyl-4,5-dihydro-oxazole (**9**) was then hydrolysed with 2M-HCl in methanol in 2 h at room temperature to give the salt (**10**), which was directly acetylated with acetic anhydride and pyridine. The triacetate (**11**) was isolated in 70% yield and its regiochemistry was determined through ^{1}H n.m.r. spectroscopy, after selective irradiations (see Experimental section); the *erythro*-configuration was assigned to (**11**), since all these reactions proceed with a total retention at chiral centres present in the starting *cis*-5-hydroxymethyl-4,5-dihydro-oxazole (**9**). These reactions are shown in Scheme 2.

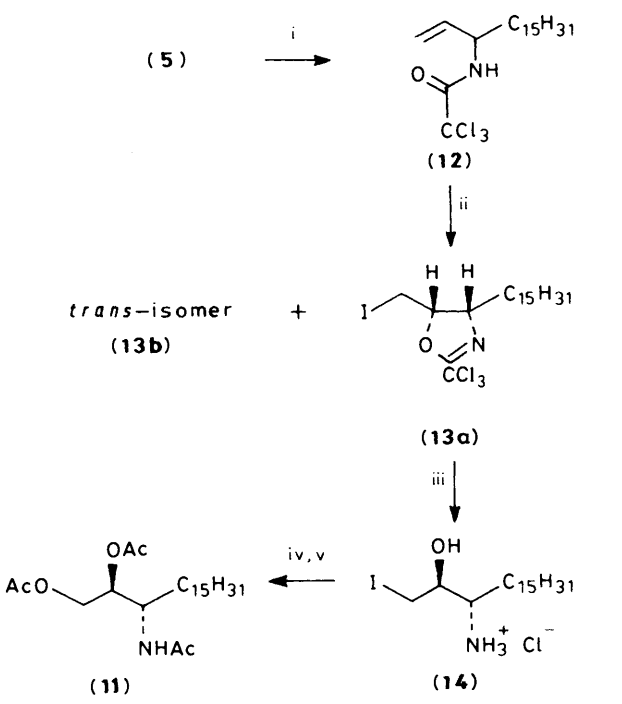


Scheme 2. *Reagents and conditions:* i, SiO_2, 4 days, room temp.; ii, Amberlyst A 26 (CO_3^{2-} form), benzene, 1 h; reflux; iii, 2M-HCl, 2 h, room temp.; iv, Ac_2O, pyridine, 18 h, room temp.

To ascertain definitely the structure of triacetate (**11**), 3-trichloroacetamido-octadec-1-ene (**12**)[6] was cyclized, affording the 4,5-dihydro-oxazole (**13**) in a 45:55 *cis*:*trans* ratio. The mixture was separated by column chromatography on silica gel: *cis*-isomer (**13a**) showed a characteristic coupling constant $J_{4H\ 5H}$ 9 Hz, while *trans*-isomer (**13b**) had J_{4H-5H} 5.5 Hz. After hydrolysis of compound (**13a**) with 2M-HCl in methanol the corresponding hydrochloride (**14**) was obtained in quantitative yield (Scheme 3).[8]

By treatment of salt (**14**) with Amberlyst A 26 (AcO^- form), followed by acetylation in acetic anhydride–pyridine, a triacetate was obtained which, on the basis of ^{1}H and ^{13}C n.m.r. spectra, was identical with compound (**11**), obtained from the 4,5-dihydro-oxazole (**9**).

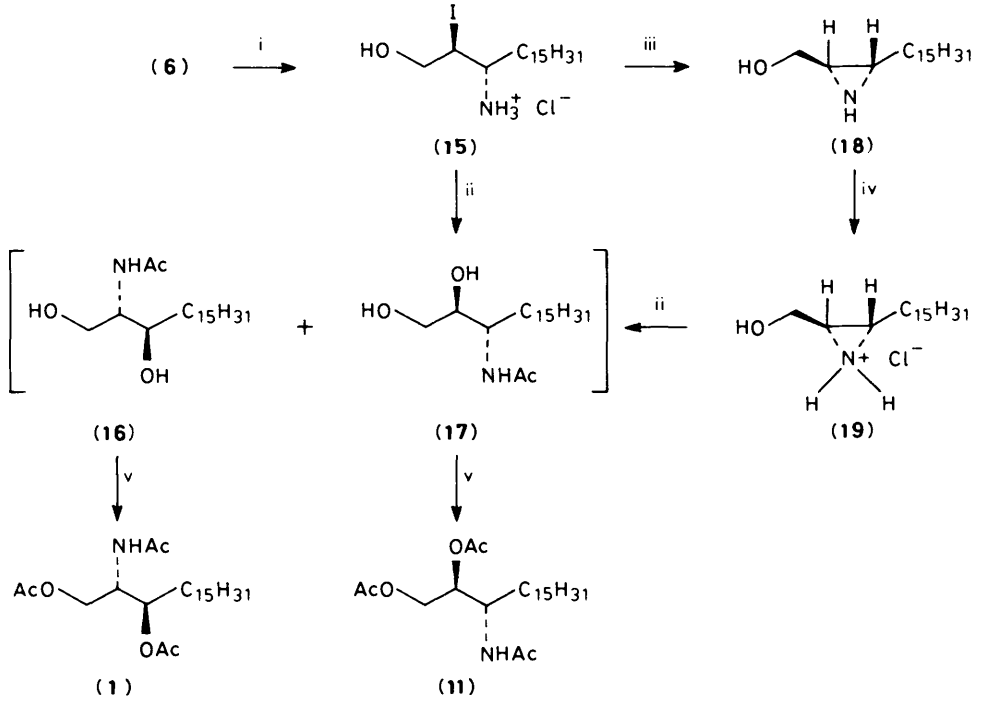
Since from chemical evidence and spectroscopic data the regiochemistry and the *trans*-structure of the 4,5-dihydro-



Scheme 3. *Reagents and conditions:* i, decahydronaphthalene, 12 h, reflux; ii, NIS, $CHCl_3$, 12 h, room temp.; iii, 2M-HCl, 2 h, room temp.; iv, Amberlyst A 26 (AcO^- form), benzene, 12 h, reflux; v, Ac_2O–pyridine, 18 h, room temp.

oxazine (**6**) were unequivocally assigned, this compound was chosen as the key intermediate to the (±)-*erythro*-sphinganine triacetate (**1**). The 4,5-dihydro-oxazine (**6**) was thus hydrolysed with 2M-HCl in acetone for 2 h at room temperature and the corresponding salt (**15**) was isolated in quantitative yield and treated in refluxing benzene for 12 h with Amberlyst A 26 (AcO^- form).[8] The reaction product was directly acetylated and two compounds were obtained in 70:30 ratio, as evidenced by t.l.c., g.l.c., and ^{13}C n.m.r. spectrum of the crude mixture. After silica gel chromatography, the (±)-*erythro*-sphinganine triacetate (**1**) was isolated in 45% yield (m.p. 89—91 °C; lit.,[4d] 90—92 °C) as the major component. The minor one was identical with the regioisomer (**11**) as determined by comparison of its ^{1}H and ^{13}C n.m.r. spectra (Scheme 4). This result was in full agreement with the production of an intermediate aziridine. By treatment of the salt (**15**) in methanol for 1 h at room temperature with Amberlyst A 26 (CO_3^{2-} form), the corresponding *trans*-aziridine (**16**)[2] was isolated simply by filtering off the resin. The aziridine was converted into the corresponding hydrochloride (**19**), which was refluxed in benzene with Amberlyst A 26 (AcO^- form), and the same 70:30 regioisomeric mixture as from the salt (**15**) was obtained.

In conclusion, although the iodocyclization reaction led to an unexpected result in the case of the *E* double bond compounds, we were able to obtain substantial quantities of (±)-*erythro*-sphinganine triacetate (**1**). The contamination by a minor amount of its regioisomer was resolved through a simple chromatographic separation. The dependence of iodocyclization of allylic trichloroacetimidates on the configuration of the double bond certainly requires more investigation: the 5-*exo* closure is probably due to the steric hindrance of the *cis*-substituent on the double bond. On the other hand, where the steric hindrance of the substituent is lacking the 6-*endo* compound is preferred. This problem will be the object of further investigation.



Scheme 4. *Reagents and conditions:* i, 2M-HCl, acetone, 2 h, room temp.; ii, Amberlyst A 26 (AcO^- form), benzene, 12 h, reflux; iii, Amberlyst A 26 (CO_3^{2-} form), benzene, 1 h, reflux; iv, 2M-HCl–MeOH; v, Ac_2O–pyridine, 18 h, room temp.

Experimental

For general conditions, see preceding paper.

2-*Octadec*-2-*yn*-1-*ol* (**3**).—Compound (**3**) was prepared as described in ref. 11, and was obtained as a low melting solid; spectroscopic data as in preceding paper.

(E)-*Octadec*-2-*en*-1-*ol* (**4**).—A solution of ynol (**3**) (5.3 g, 20 mmol) in dry THF (20 ml) was added under an inert atmosphere to a suspension of $LiAlH_4$ (1.52 g, 40 mmol) in dry THF (20 ml) and the mixture was refluxed for 1 h. Then MeOH (10 ml) and saturated aqueous NH_4Cl was successively added and the mixture was extracted with ether. After evaporation of the extract under reduced pressure, the residue was chromatographed on silica gel with cyclohexane–AcOEt (8:2) as eluant and the enol (**4**) (4.8 g, 90%) was obtained as an oil; $\nu_{max.}$ 3 300 and 970 cm^{-1}; $\delta_H(CDCl_3)$ 0.9 (3 H, t), 1.3 (26 H, m), 1.8—2.2 (2 H, m), 3.85 (1 H, s, OH), 4.05 (2 H, d, *J* 6 Hz), and 5.65 (2 H, m); $\delta_C(CDCl_3)$ 133.1, 128.8, 63.5, 32.0, 31.8, 29.5, 29.2, 29.0, 28.2, and 13.9.

(E)-1-*Trichloroacetimidoyloxyoctadec*-2-*ene* (**5**).—To a suspension of NaH (50% in oil; 100 mg, 2 mmol; previously washed with dry pentane) in dry THF (20 ml) under an inert atmosphere at 0 °C was added a solution of (*E*)-octadec-2-en-1-ol (**4**) (5.4 g, 20 mmol) in dry THF (30 ml). After 1 h the clear solution was added dropwise at 0 °C to a solution of trichloroacetonitrile (3.15 g, 22 mmol) in dry THF (30 ml). The reaction mixture was allowed to warm to room temperature, then MeOH (5 ml) was added and the solvent was removed under reduced pressure. The residue was chromatographed through silica gel with cyclohexane–AcOEt (95:5) as eluant and imidate (**5**) was obtained (5.8 g, 70%) as an oil; $\nu_{max.}$ 3 340 and 1 660 cm^{-1}; $\delta_H(CDCl_3)$ 0.9 (3 H, t), 1.3 (26 H, m), 1.9—2.3 (2 H, m), 4.8 (2 H, m), 5.65 (2 H, m, *J* 9 Hz) and 8.3 (1 H, br s, NH); $\delta_C(CDCl_3)$ 137.2, 123.0, 70.0, 32.3, 31.9, 29.7, 29.5, 29.4, 29.2, 28.9, 22.7, and 14.1.

trans-5-*Iodo*-4-*pentadecyl*-2-*trichloromethyl*-5,6-*dihydro*-4H-1,3-*oxazine* (**6**).—To a solution of imidate (**5**) (6.2 g, 15 mmol) in $CHCl_3$ (150 ml) was added NIS (3.6 g, 16 mmol) and the mixture was stirred for 12 h. Then 10% aqueous $Na_2S_2O_3$ was added; the organic layer was separated and the solvent was removed under reduced pressure. After chromatography through silica gel with cyclohexane as eluant, the *oxazine* (**6**) was recovered as a clear oil (7.3 g, 90%); $\nu_{max.}$ 1 675 cm^{-1}; $\delta_H(CDCl_3)$ 0.85 (3 H, t), 1.25 (26 H, m), 1.53 (2 H, m), 3.7 (1 H, dt, *J* 4 and 8 Hz, CHN), 4.2 (1 H, m, CHI), and 4.32 and 4.50 (2 H, *AB*X, *J* 10 Hz, CH_2O); $\delta_C(CDCl_3)$ 71.5, 61.0, 34.2, 31.9, 29.7, 29.3, 24.8, 22.7, 21.3, and 14.1 (Found: C, 36.0; H, 5.25; N, 2.05. $C_{20}H_{35}Cl_3INO$ requires C, 36.09; H, 5.30; N, 2.10%).

erythro-2-*Iodo*-3-*trichloroacetamido*-*octadecan*-1-*ol* (**7**).—The 4,5-dihydro-oxazine (**6**) (8.1 g, 15 mmol) was adsorbed on silica gel and after 4 days the product was eluted with AcOEt. The solvent was then stripped off under reduced pressure and the *amide* (**7**) was recovered in quantitative yield as an oil; $\nu_{max.}$ 3 450, 1 700, and 1 510 cm^{-1}; $\delta_H(CCl_4)$ 0.85 (3 H, t), 1.2 (26 H, m), 1.6—1.8 (2 H, m), 3.5—4.2 (4 H, m), 4.4 (1 H, br s, OH), and 7.3 (1 H, d, *J* 7 Hz, NH); δ_C 65.4, 54.8, 38.7, 32.7, 31.8, 29.6, 29.3, 28.6, 25.8, 22.6, and 14.0 (Found: C, 35.1; H, 5.4; N, 2.0. $C_{20}H_{37}Cl_3INO_2$ requires C, 35.14; H, 5.46; N, 2.05%).

cis-5-*Hydroxymethyl*-4-*pentadecyl*-2-*trichloromethyl*-4,5-*dihydro*-*oxazole* (**9**).—To a solution of amide (**7**) (5.6 g, 10 mmol) in dry benzene (20 ml) was added Amberlyst A 26 (CO_3^{2-} form) (10 g; ~3.8 mequiv. g^{-1}) was added and the suspension was refluxed for 1 h. Then the resin was filtered off and the solvent was removed under reduced pressure. The residue was chromatographed through silica gel with cyclohexane–AcOEt (8:2) as eluant, to give the *oxazole* (**9**) (3.0 g, 70%) as a clear oil; $\nu_{max.}$ 3 400 and 1 655 cm^{-1}; $\delta_H(CDCl_3)$ 0.85 (3 H, t), 1.3 (26 H, m), 1.6—1.8 (2 H, m), 3.5—4.7 (3 H, m), 4.7—5.2 (1 H, dt, *J* 9 Hz), and 5.6 (1 H, br s, OH) $\delta_C(CDCl_3)$ 86.6, 68.5, 60.9, 32.3, 32.2, 32.0,

30.0, 29.7, 27.5, 22.7, and 14.1 (Found: C, 55.9; H, 8.5; N, 3.3. $C_{20}H_{36}Cl_3NO_2$ requires C, 56.01; H, 8.46; N, 3.27%).

erythro-3-*Acetamido*-1,2-*diacetoxyoctadecane* (**11**).—To a solution of the oxazole (**9**) (2.1 g, 5 mmol) in methanol (60 ml) was added 2M-HCl (5 ml) and the mixture was stirred at room temperature for 2 h. The solvent was then stripped off under reduced pressure and the salt (**10**) was directly acetylated with acetic anhydride (0.5 ml) in pyridine (3 ml) at room temperature. After 18 h the organic phase was removed under reduced pressure and the crude product was chromatographed through silica gel, with cyclohexane–AcOEt (1:1) as eluant, to give the title compound (**11**) (1.5 g, 70%) as a clear oil; $\nu_{max.}$ 3 300, 1 730, 1 640, and 1 540 cm^{-1}; $\delta_H(CDCl_3)$ 0.88 (3 H, t), 1.25 (28 H, m), 2.01 (3 H, s), 2.08 (3 H, s), 2.11 (3 H, s), 4.16 and 4.33 (2 H, *AB*X, CH_2O), 4.23 (1 H, m, CHN), 5.08 (1 H, m, CHO), and 5.48 (1 H, d, *J* 9 Hz, NH); after irradiation at δ_H 5.08, the *AB*X system at δ_H 4.15 and 4.33 collapsed to an AB quartet (*J* 11 Hz), and the multiplet at δ_H 4.23 was simplified; δ_C ([$^2H_6$]acetone) 73.2, 63.5, 49.4, 32.6, 32.2, 31.7, 30.8, 30.7, 30.5, 30.4, 29.8, 28.8, 27.8, 23.3, 23.0, 21.0, 20.8, and 14.3; *m/z*, 427 (M^+ 2), 284 (25), 283 (100), 242 (16), 241 (83), and 97 (14) (Found: C, 67.5; H, 10.7; N, 3.2. $C_{24}H_{45}NO_5$ requires C, 67.41; H, 10.61; N, 3.28%).

3-*Trichloroacetamido-octadec*-1-*ene* (**12**).—A solution of the imidate (**5**) (8.2 g, 20 mmol) in decahydronaphthalene (100 ml) was refluxed for 12 h. After chromatography of the crude reaction mixture on silica gel, with cyclohexane as eluant, the amide (**12**) was obtained (7.4 g, 90%) as a clear oil; $\nu_{max.}$ 3 300, 1 690, 1 520, and 920 cm^{-1}; $\delta_H(CDCl_3)$ 0.9 (3 H, t), 1.25 (26 H, m), 1.5—1.9 (2 H, m), 4.1—4.8 (1 H, m) 4.9—6.1 (3 H, m), and 6.5 (1 H, br s, NH); $\delta_C(CDCl_3)$ 161.2, 136.9, 115.9, 53.5, 36.5, 31.9, 29.7, 29.4, 28.7, 25.4, 22.7, and 14.1.

cis- *and* trans-5-*Iodomethyl*-4-*pentadecyl*-2-*trichloromethyl*-4,5-*dihydro-oxazole* (**13a** *and* **b**).—To a solution of the amide (**12**) (6.2 g, 15 mmol) in $CHCl_3$ (200 ml) was added NIS (3.6 g, 16 mmol). The mixture was stirred for 12 h at room temperature, then 10% aqueous $Na_2S_2O_3$ was added; the organic layer was separated and the solvent was removed under reduced pressure. The residue was chromatographed through silica gel with cyclohexane as eluant, to give the oxazole (**13**) (7.2 g, 90%) as a *cis*:*trans* mixture in the ratio 45:55; $\nu_{max.}$ 1 660 cm^{-1}. *cis*-Isomer (**13a**): $\delta_H(CDCl_3)$ 0.9 (3 H, t), 1.3 (26 H, m), 1.6—1.8 (2 H, m), 3.3 (2 H, d, *J* 7 Hz), 3.8—4.3 (1 H, m), and 4.8—5.35 (1 H, dt, *J* 7 and 9 Hz); $\delta_C(CDCl_3)$ 160.2, 85.7, 68.1, 30.3, 29.7, 22.7, 14.1, and −1.4. trans-*Isomer* (**13b**): $\delta_H(CDCl_3)$ 0.9 (3 H, t), 1.3 (26 H, m), 1.6—1.8 (2 H, m), 3.35 (2 H, d, *J* 7 Hz), 3.8—4.3 (1 H, m,), and 4.4—4.7 (1 H, dt, *J* 7 and 6 Hz); $\delta_C(CDCl_3)$ 160.2, 85.7, 72.1, 36.8, 30.0, 29.7, 27.5, 22.7, 14.1, and 5.7 (Found: C, 36.0; H, 5.2; N, 2.2. $C_{20}H_{35}Cl_3INO$ requires C, 36.09; H, 5.30; N, 2.10%).

erythro-3-*Amino*-1-*iodo-octadecan*-2-*ol Hydrochloride* (**14**).—A solution of the *cis*-oxazole (**13a**) (5.4 g, 10 mmol) in MeOH (20 ml) was treated with 2M-HCl (10 ml) for 2 h at room temperature. The solvent was then removed under reduced pressure, the residue was washed with AcOEt to remove the trichloroacetic acid, and the salt (**14**) was obtained (3.6 g, 80%) as an oil; $\nu_{max.}$ 3 340 cm^{-1}; $\delta_H(CD_3OD)$ 0.9 (3 H, t), 1.3 (26 H, m), 1.9—2.1 (2 H, m), 3.1—3.8 (4 H, m), and 4.85 (4 H, br s, OH and NH_3^+); $\delta_C[(CD_3)_2SO]$ 70.4, 51.9, 31.2, 29.8, 28.6, 28.3, 26.2, 22.4, 13.9, and 8.7.

Alternative Preparation of erythro-3-*Acetamido*-1,2-*diacetoxyoctadecane* (**11**).—To a solution of the salt (**14**) (2.2 g, 5 mmol) in benzene (15 ml) was added Amberlyst A 26 (AcO^- form) (5 g; ~3.8 mequiv. g^{-1}) and the mixture was refluxed for 12 h. After filtration of the resin and removal of the solvent under reduced pressure, the residue was directly acetylated with acetic anhydride (0.5 ml) in pyridine (4 ml) for 18 h at room temperature. The organic phase was then evaporated under reduced pressure and the residue was chromatographed on silica gel with cyclohexane–AcOEt (1:1) as eluant, to give the triacetate (**11**) (1.3 g, 60%) as a low melting solid.

erythro-3-*Amino*-2-*iodo-octadecan*-1-*ol Hydrochloride* (**15**).—To a solution of the oxazine (**6**) (5.4 g, 10 mmol) in acetone (20 ml) was added 2M-HCl (10 ml) and the mixture was stirred at room temperature for 2 h. The solvent was then stripped off under reduced pressure and the residue was washed with AcOEt to remove trichloroacetic acid. The salt (**15**) was obtained in quantitative yield as a low melting solid; $\nu_{max.}$ 3 380 cm^{-1}; $\delta_H(CD_3OD)$ 0.9 (3 H, t), 1.3 (26 H, m), 1.8—2.2 (2 H, m), 3.2—3.4 (2 H, m), 3.8—4.0 (2 H, m), and 4.2 (4 H, br s, OH and NH_3^+); $\delta_C[(CD_3)_2SO]$ 61.4, 58.0, 56.1, 31.2, 29.9, 28.7, 28.6, 28.1, 26.1, 22.0, and 13.8.

erythro-2-*Acetamido*-1,3-*diacetoxyoctadecane* (erythro-*Sphinganine Triacetate*) (**1**).—To a solution of the salt (**15**) (3.6 g, 8 mmol) in dry benzene (20 ml) was added Amberlyst A 26 (AcO^- form) (8 g; ~3.8 mequiv. g^{-1}) and the suspension was refluxed for 12 h. The resin was then filtered off and the solvent was removed under reduced pressure, to give a mixture of the amides (**16**) and (**17**) ($\nu_{max.}$ 1 660 and 1 510 cm^{-1}) which were directly acetylated with acetic anhydride (1 ml) in pyridine (5 ml). After 18 h at room temperature, the organic phase was stripped off under reduced pressure and the residue was chromatographed through silica gel with cyclohexane–AcOEt (8:2) as eluant; the title triacetate (**1**) (1.4 g, 42%) was obtained as a white solid, m.p. 89—91 °C (lit.,[4d] 90—92 °C); $\nu_{max.}$ and δ_H data are as reported in the preceding paper; $\delta_C(CDCl_3)$ 73.6, 63.4, 51.0, 31.7, 29.8, 29.7, 29.5, 29.4, 28.9, 28.5, 25.9, 23.3, 22.9, 20.9, 20.7, and 14.1; *m/z*, 427 (M^+, 1), 308 (9), 295 (15), 188 (8), 145 (61), 85 (90), and 84 (100).

Further elution with cyclohexane–AcOEt (8:2) as eluant gave *erythro*-3-acetamido-1,2-diacetoxyoctadecane (**11**) (0.6 g, 18%) as a low melting solid.

trans-2-*Hydroxymethyl*-3-*pentadecylaziridine* (**18**).—To a solution of the salt (**15**) (4.5 g, 10 mmol) in dry benzene (15 ml) was added Amberlyst A 26 (CO_3^{2-} form) (10 g; ~3.8 mequiv. g^{-1}) and the suspension was refluxed for 1 h. The resin was then filtered off and the solvent was removed under reduced pressure to give the trans-*aziridine* (**18**) (2.55 g, 90%) as an oil; $\nu_{max.}$ 3 350 cm^{-1}; $\delta_H(CD_3OD)$ 0.9 (3 H, t), 1.3 (28 H, m), 1.8 (2 H, m), 3.55 (2 H, m), and 4.8 (2 H, br s, OH and NH); δ_C([$^2H_5$]pyridine) 63.4, 39.2, 34.0, 32.1, 30.0, 29.6, 28.2, 22.9, and 14.2 (Found: C, 76.4; H, 13.2; N, 4.9. $C_{18}H_{37}NO$ requires C, 76.26; H, 13.16; N, 4.94%).

Alternative Route to erythro-2-*Acetamido*-1,3-*diacetoxyoctadecane* (erythro-*Sphinganine Triacetate*) (**1**)—.To a solution of the aziridine (**18**) (1.4 g, 5 mmol) in MeOH (10 ml) was added 2M-HCl (2 ml) and the solvent was removed under reduced pressure. The residue was then dissolved in benzene (15 ml), Amberlyst A 26 (AcO^- form) (5 g; ~3.8 mequiv. g^{-1}) was added, and the suspension was refluxed for 12 h. The resin was filtered off and the residue was treated with acetic anhydride (1 ml) in pyridine (3 ml) at room temperature for 18 h. After removal of the organic solvents, the crude product was separated by chromatography through silica gel with cyclohexane–ethyl acetate (8:2) as eluant, to give the title triacetate (**1**) (0.96 g, 45%) as a white solid, m.p. 90—91 °C (lit.,[4d] 90—92 °C); further elution gave the regioisomer (**11**) (0.38 g, 18%) as an oil.

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