Studies on the Synthesis of Heterocyclic Compounds. XIII. The Synthesis of Macrocyclic Tetraesters From 1,2-Cyclohexane- and 2,3-Butanediols

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A new series of macrocyclic compounds containing 1,2-cyclohexanediols and 2,3-butandiol sub-unit have been prepared treating the stannolanic and stibolanic derivatives with diacyl chlorides. The structures of the compounds prepared have been determined by elemental analysis and spectroscopic data.

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In the previous papers on the synthesis and studies of heterocyclic compounds containing the O-M-X (M = P, As, Sb, Sn; X = O, S) bond, the excellent reactivity of some of these compounds with electrophilic derivatives [1,2] was observed. Successively, for reaction of 2-chloro-1,3,2-benzodioxastibole with diacyl chlorides, the exclusive formation of dimeric macrocycles containing catechol as a substituent in good yields and with a high degree of purity was obtained [3].

In the literature only a few cases on the synthesis of macrocyclic tetraesters with aliphatic substituents were reported.

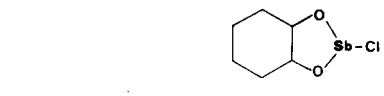
Suga and Matsuura have reported an oxidative process to form cyclic esters; thus, they have isolated a cyclic diester, by oxidizing the *trans*-1,2-cyclohexanediol with *t*-butyl chromate [4].

Bradshaw and his co-workers have reported other synthesis of macrocyclic esters which always contained only one substituent of a dicarboxylic acid [5-10].

However, dimeric macrocyclic esters containing the alkane or cycloalkane unit, like those shown here, have never been reported.

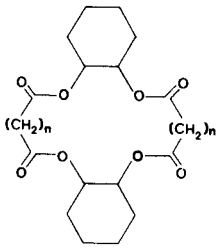
Although there are several methods for preparing macrocyclic esters, we here report a convenient and rapid method for their syntheses. The diastereomeric cyclohexanediols, neccessary for the synthesis of macrocyclic derivatives were conveniently prepared *via* the transformation of the mixture of diols in the corresponding stannolanes These stannolanic isomers are solid, stable and easily separable by fractional crystallization [11]. For the synthesis of the macrocyclic esters, both the 1,3,2-dioxastannolanic and the corresponding stibolanic derivatives were used; the latter were obtained by the exchange reaction of the dioxastannolanic compounds with antimony trichloride [1]. The stibolanic derivatives are insoluble in the common organic solvents and must be used immediately for the successive reactions in benzene suspension. Although the macrocyclic compounds were obtained with both derivatives, the stibolanic compounds have been preferred because the reaction times are remarkably shorter under homogeneous as well as in heterogeneous conditions; the yields also are slightly better and the antimony products obtained are more pure. In the light of the latest research by David and Tieffry [12], the greater reactivity of the stibolanic derivatives when compared to the tin derivatives can be attributed to the lower Sb-O bond energy than the stannolanic derivatives exhibit.

Scheme



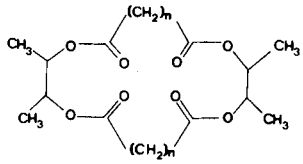
I trans

II cis



III a–e trans

IV a–e cis



Va–e

a) n=1; b) n=3; c) n=5; d) n=7; e) n=8

In this work we report the synthesis of the macrocyclics (IIIa-e, IVa-e and Va-e) prepared by action of malonyl, glutaryl, pimeloyl, azeloyl or sebacoyl chloride on the dioxastannolanic and dioxastibolanic derivatives (Scheme). In all the cases, the reactions were run by refluxing in a benzene solution or suspension.

The yields were in the range 36-18%. The structures proposed for the macrocyclics III, IV and V are consistent

with data from ir, nmr and ms spectra and elemental analyses.

The IIIa-e esters exhibited ir bands at 1740-1760 cm^{-1}, the IVa-e at 1730-1740 cm^{-1} and the Va-e at 1720-1740 cm^{-1}. The nmr spectra were particularly interesting. The spectra of the stereoisomers III and IV differ in the position of the C*H*-O-CO groups, which occur at δ 4.69-4.71 and δ 4.96-5.06 respectively. The CO-CH_2-CO groups of the compounds IIIa, IVa and Va exhibited peaks at δ 3.21, 3.35 and 3.36 respectively.

These chemical shifts are very near to those found by Bradshaw and his co-workers [11] in the macrocyclic ether-esters, and higher than those observed by us in the macrocycles containing the more rigid cathecol as a subunit [3]. Still, the methylene groups α to the carbonyl (O-CO-CH_2) and the inner methylene groups of the compounds III, IV and V (with n = 3,5,7,8) undergo only slight shifts. By means of the mass spectra of the compounds III, IV and V it has been possible to establish the dimeric structure of the obtained macrocycles; all spectra show a molecular ion in agreement with the proposed dimeric structures.

Spectrometric mass studies to determine the mechanistic aspect of fragmentation and a possible differentiation of *cis* and *trans* isomers are currently under investigation.

EXPERIMENTAL

The ir spectra were recorded on a Perkin-Elmer model 157 G spectrophotometer. The nmr spectra were determined on a Varian EM 360 L spectrometer and chemical shifts were measured in ppm (δ) using TMS as the internal standard. The mass spectra were run on a VGZAB-2F instrument operating at 70 eV (200 μA). Microanalyses for CHN were carried out on a Carlo Erba model 1106 Elemental Analyzer. Merck silica gel (70-230 mesh) were used for column chromatography; thin layer separation was carried out with Merck F_{254} silica gel and visualization was accomplished by Iodine. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. All products were identified by analytical and spectroscopic data.

Starting Materials.

The following compounds were prepared as described previously.

trans-2,2-Di-*n*-butyl-1,3,2-dioxacyclohexane stannolane [15], *cis*-2,2-di-*n*-butyl-1,3,2-dioxacyclohexanestannolane [15], *meso*-2,2-di-*n*-butyl-4,5-dimethyl-1,3,2-dioxastannolane [15], 2-chloro-4,5-dimethyl-1,3,2-dioxastibolane [1], *cis*-1,2-cyclohexandiol [17], azeloyl chloride [18] and pimeloyl chloride [18]. *Trans*-1,2-cyclohexandiol **Ia**, *meso*-2,3-butandiol, dibutyltin oxide, antimony trichloride, malonyl chloride, glutaryl chloride and sebacoyl chloride were used as received (EGA Chemie).

trans-2-Chloro-1,3,2-dioxacyclohexanestibolane (I).

Compound I was prepared as in the literature [1]. To a heated solution of *trans*-2,2-di-*n*-butyl-1,3,2-dioxacyclohexanestannolane (4.3 mmoles) in benzene (30 ml), antimony trichloride (4.3 mmoles) was added by stirring. The reaction mixture was refluxed for a night. The white precipitate was filtered, washed in hot benzene and dried giving I in quantitative yield, mp < 250° dec; ir (potassium bromide): 2940, 2860, 1450, 1420, 1350, 1290, 1230, 1190, 1130, 1070, 1040, 930, 860, 830, 720, 650 cm^{-1}; nmr (DMSO-d_6): δ 3.06 (m, 2H, 2 × C*H*-O-Sb) and 1.86-0.83 ppm (m, 8H, 4 × CH_2).

Anal. Calcd. for $C_6H_{10}ClO_2Sb$: C, 26.54; H, 3.68; Cl, 13.07. Found: C, 26.48; H, 3.70; Cl, 13.11.

cis-2-Chloro-1,3,2-dioxacyclohexanestibolane (II).

This compound was prepared as described above for I starting with *cis*-2,2-di-*n*-butyl-1,3,2-dioxacyclohexanestannolane (4.3 mmoles) and antimony trichloride (4.3 mmoles) in 30 ml of benzene to give II in quantitative yield, mp 232-235° dec; ir (potassium bromide): 2940, 2860, 1450, 1420, 1360, 1280, 1200, 1140, 1120, 1090, 1060, 1040, 980, 950, 910, 880, 850, 810, 770, 690, 650 cm^{-1}; nmr (DMSO-d_6): δ 3.4 (m, 2H, 2 × C*H*-O-Sb) and 1.78-1.03 ppm (m, 8H, 4 × CH_2).

Anal. Calcd. for $C_6H_{10}ClO_2Sb$: C, 26.54; H, 3.68; Cl, 13.07. Found: C, 26.60; H, 3.67; Cl, 13.05.

General Procedures for the Preparation of Macrocycles IIIa-e, IVa-e and Va-e.

Method A.

To a stirred hot suspension of *trans*-2-chloro-1,3,2-dioxacyclohexanestibolane I or *cis*-2-chloro-1,3,2-dioxacyclohexanestibolane II or 2-chloro-4,5-dimethyl-1,3,2-dioxastibolane, freshly prepared a solution of diacyl chloride in benzene was added dropwise. Afterwards the mixture became completely homogeneous (5-10 minutes) and was stirred under reflux for some hours. The benzene solution was then removed using a rotary evaporator to give a viscous residue which was purified by column chromatography on silica gel using benzene-ethyl acetate (5:1) as eluent, and the obtained solid was washed in diisopropyl ether. Specific details are given for each compound.

Method B.

To a stirred hot solution of *trans*-2,2-di-*n*-butyl-1,3,2-dioxacyclohexanestannolane or *cis*-2,2-di-*n*-butyl-1,3,2-dioxacyclohexanestannolane or *meso*-2,2-di-*n*-butyl-4,5-dimethyl-1,3,2-dioxastannolane in benzene, a solution of diacyl chloride in benzene was added dropwise. The resulting mixture was rapidly stirred under reflux for a day. After cooling, the benzene solution was then removed under reduced pressure and the residue was treated in petroleum-ether 40-70° (3 × 10 ml) to solubilize the dibutyltin dichloride. After decanting the petroleum-ether solution, the crude product was purified as in method A.

trans-Dicyclohexo[*b,i*]-1,4,8,11-tetraoxacyclotetradecane-5,7,12,14-tetraone (IIIa).

Method A.

Compound I (4.3 mmoles) and malonyl chloride (4.3 mmoles) were used. The crude reaction mixture was purified by column chromatography and washed in diisopropyl ether to give IIIa as white powder, yield 32%, mp 233-235°; ir (potassium bromide): 2960, 2870, 1740, 1450, 1430, 1360, 1325, 1290, 1260, 1160, 1070, 1050, 1040, 1010, 960, 920, 900, 840 cm^{-1}; nmr (deuteriochloroform): δ 1.03-1.95 (m, 16H, 8 × CH_2), 3.21 (s, 4H, 2 × CH_2-CO), 4.71 (m, 4H, 4 × C*H*); ms: m/e 368.

Anal. Calcd. for $C_{18}H_{24}O_8$: C, 58.69; H, 6.57. Found: C, 58.60; H, 6.59.

Method B.

Compound *trans*-2,2-di-*n*-butyl-1,3,2-dioxacyclohexanestannolane (4.3 mmoles) and malonyl chloride (4.3 mmoles) were used to give IIIa, yield 28%, mp 235°. The mixture mp with a sample obtained by method A was unaltered and spectral data (ir, nmr and ms) and elemental analyses were identical to those of the product obtained by method A.

trans-Dicyclohexo[*b,k*]-1,4,10,13-tetraoxacyclooctadecane-5,9,14,18-tetraone (IIIb).

Method A.

Compound I (4.3 mmoles) and glutaryl chloride (4.3 mmoles) were used. The crude product was purified by column chromatography and washed in diisopropyl ether to give IIIb as white powder, yield 35%, mp 220-222°; ir (potassium bromide): 2950, 2870, 1740, 1450, 1430, 1360, 1330, 1290, 1260, 1170, 1080, 1050, 1040, 1010, 960, 930, 900, 840 cm^{-1}; nmr (deuteriochloroform): δ 0.99-1.83 (m, 20H, 10 × CH_2), 2.26 (t, 8H, 4 × CH_2-CO), 4.72 (m, 4H, 4 × C*H*-O); ms: m/e 424.

Anal. Calcd. for $C_{22}H_{32}O_8$: C, 62.25; H, 7.60. Found: C, 62.24; H, 7.57.

Method B.

This compound was prepared as described for IIIa (method B) to give IIIb, yield 32%. The mixture mp with the sample isolated by method A was unaltered and the ir, nmr and ms spectra and elemental analyses were identical.

trans-Dicyclohexo[*b,m*]-1,4,12,15-tetraoxacyclodocosane-5,11,16,22-tetraone (IIIc).

Method A.

Compound I (4.3 mmoles) and pimeloyl chloride (4.3 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give IIIc as white powder, yield 27%, mp 210-212°; ir (potassium bromide): 2940, 2870, 1730, 1470, 1450, 1390, 1340, 1310, 1280, 1240, 1190, 1120, 1080, 1050, 1020, 990, 950, 920, 850 cm^{-1}; nmr (deuteriochloroform): δ 1.07-1.87 (m, 28H, 14 × CH_2), 2.22 (t, 8H, 4 × CH_2-CO), 4.72 (m, 4H, 4 × -CH-O); ms: m/e 480.

Anal. Calcd. for $C_{26}H_{40}O_8$: C, 64.98; H, 8.39. Found: C, 64.81; H. 8.36.

Method B.

Compound IIIc was prepared as in method B, described for IIIa, yield 22%; the mixture mp with the sample isolated by Method A was unaltered. Spectral data (ir, nmr and ms) and elemental analyses were identical to those of the product obtained by method A.

trans-Dicyclohexo[*b,o*]-1,4,14,17-tetraoxacyclohexacosane-5,13,18,26-tetraone (IIId).

Method A.

Compound I (4.3 mmoles) and azeloyl chloride (4.3 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in the diisopropyl ether to give IIId as white powder, yield 27%, mp 160-162°; ir (potassium bromide): 2940, 2860, 1730, 1470, 1450, 1360, 1290, 1260, 1230, 1180, 1110, 1100, 1040, 1010, 950, 930, 850, 730 cm^{-1}; nmr (deuteriochloroform): δ 1.09-1.73 (m, 36H, 18 × CH_2), 2.21 (t, 8H, 4 × CH_2-CO), 4.71 (m, 4H, 4 × CH-O); ms: m/e 536.

Anal. Calcd. for $C_{30}H_{48}O_8$: C, 67.13; H, 9.02. Found: C, 67.22; H, 9.05.

Method B.

IIId was prepared as in method B, described for IIIa, yield 17%, the mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

trans-Dicyclohexo[*b,p*]-1,4,15,18-tetraoxacyclooctacosane-5,14,19,28-tetraone (IIIe).

Method A.

Compound I (4.3 mmoles) and sebacoyl chloride (4.3 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give IIIe as white powder, yield 26%, mp 145-148°; ir (potassium bromide): 2930, 2860, 1730, 1470, 1420, 1390, 1380, 1315, 1280, 1260, 1230, 1190, 1175, 1125, 1110, 1060, 1035, 1010, 980, 915, 890, 770, 725 cm^{-1}; nmr (deuteriochloroform): δ 1.04-1.78 (m, 40H, 20 × CH_2), 2.19 (t, 8H, 4 × CH_2-CO), 4.69 (m, 4H, 4 × CH-O); ms: m/e 564.

Anal. Calcd. for $C_{32}H_{52}O_8$: C, 68.09; H, 9.22. Found: C, 68.29; H, 9.19.

Method B.

Compound IIIe was prepared as in method B, described for IIIa, yield 24%. The mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

cis-Dicyclohexo[*b,i*]-1,4,8,11-tetraoxacyclotetradecane-5,7,12,14-tetraone (IVa).

Method A.

Compound II (4.3 mmoles) and malonyl chloride (4.3 mmoles) were used. The crude reaction mixture was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give IVa as white powder, yield 36%, mp 189-191°; ir (potassium bromide): 2960, 2880, 1740, 1450, 1420, 1360, 1320, 1280, 1250, 1200, 1150, 1120, 1070, 1040, 1020, 1000, 970, 950, 930, 900, 870, 850, 800 cm^{-1}; nmr (deuteriochloroform): δ 1.05-1.86 (m, 16H, 8 × CH_2), 3.35 (s, 4H, 2 × CH_2-CO), 5.1 (m, 4H, 4 × CH-O); ms: m/e 368.

Anal. Calcd. for $C_{18}H_{24}O_8$: C, 58.69; H, 6.57. Found: C, 58.49; H, 6.55.

Method B.

Compound *cis*-2,2-di-*n*-butyl-1,3,2-dioxacyclohexanestannolane (4.3 mmoles) and malonyl chloride (4.3 mmoles) were used to give IVa, yield 29%, mp 190°. The mixture mp with a sample obtained by method A was unaltered. Spectral data (ir, nmr and ms) and elemental analyses were identical with those of the product obtained by method A.

cis-Dicyclohexo[*b,k*]-1,4,10,13-tetraoxacyclooctadecane-5,9,14,18-tetraone (IVb).

Method A.

Compound II (4.3 mmoles) and glutaryl chloride (4.3 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give IVb as white powder, yield 27%, mp 144-146°; ir (potassium bromide): 2940, 2860, 1730, 1450, 1420, 1380, 1350, 1320, 1280, 1220, 1190, 1150, 1120, 1070, 1060, 1010, 980, 950, 930, 900, 870, 850, 750 cm^{-1}; nmr (deuteriochloroform): δ 1.11-1.85 (m, 20H, 10 × CH_2), 2.24 (t, 8H, 4 × CH_2-CO), 4.97 (m, 4H, 4 × CH-O); ms: m/e 424.

Anal. Calcd. for $C_{22}H_{32}O_8$: C, 62.25; H, 7.60. Found: C, 62.32; H, 7.63.

Method B.

Compound IVb was prepared as in method B, described for IVa, yield 26%. The mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

cis-Dicyclohexo[*b,m*]-1,4,12,15-tetraoxacyclodocosane-5,11,16,22-tetraone (IVc).

Method A.

Compound II (4.3 mmoles) and pimeloyl choride (4.3 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give IVc as white powder, yield 33%, mp 143-145°; ir (potassium bromide): 2950, 2860, 1760, 1450, 1420, 1370, 1350, 1260, 1180, 1120, 1070, 1050, 1030, 950, 910, 850, 820, 760 cm^{-1}; nmr (deuteriochloroform): δ 1.05-1.95 (m, 28H, 14 × CH_2), 2.30 (t, 8H, 4 × CH_2-CO), 5.06 (m, 4H, 4 × CH-O); ms: m/e 480.

Anal. Calcd. for $C_{26}H_{40}O_8$: C, 64.98; H, 8.39. Found: C, 64.83; H, 8.36.

Method B.

Compound IVc was prepared as in method B, described for IVa, yield 31%. The mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

cis-Dicyclohexo[*b,o*]-1,4,14,17-tetraoxacyclohexacosane-5,13,18,26-tetraone (IVd).

Method A.

Compound II (4.3 mmoles) and azeloyl chloride (4.3 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give IVd as white powder, yield 31%, mp 134-136°; ir (potassium bromide): 2940, 2860, 1740, 1450, 1420, 1370, 1350, 1250, 1170, 1120, 1100, 1070, 1050, 1020, 1000, 950, 910, 850, 800, 750 cm^{-1}; nmr (deuteriochloroform): δ 1.04-2.06 (m, 36H, 18 × CH_2), 2.28 (t, 8H, 4 × CH_2-CO), 5.05 (m, 4H, 4 × CH-O); ms: m/e 536.

Anal. Calcd. for $C_{30}H_{48}O_8$: C, 67.13; H, 9.02. Found: C, 67.26; H, 9.03.

Method B.

Compound IVd was prepared as in method B, described for IVa, yield 26%. The mixture mp with the sample isolated by method A was unalter-

ed and spectral data were identical.

cis-Dicyclohexo[*b,p*]-1,4,15,18-tetraoxacyclooctacosane-5,14,19,28-tetraone (IVe).

Method A.

The compound II (4.3 mmoles) and sebacoyl chloride (4.3 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give IVe as white powder, yield 32%, mp 93-95°; ir (potassium bromide): 2940, 2860, 1740, 1450, 1420, 1370, 1350, 1250, 1170, 1120, 1100, 1050, 1020, 950, 910, 850, 750 cm^{-1}; nmr (deuteriochloroform): δ 1.03-1.95 (m, 40H, 20 × CH_2), 2.24 (t, 8H, 4 × CH_2-CO), 4.97 (m, 4H, 4 × C*H*-O); ms: m/e 564.

Anal. Calcd. for $C_{32}H_{52}O_8$: C, 68.09; H, 9.22. Found: C, 68.33; H, 9.25.

Method B.

Compound IVe was prepared as in method B, described for IVa, yield 29%. The mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

meso-2,3,9,10-Tetramethyl-1,4,8,11-tetraoxacyclotetradecane-5,7,12,14-tetraone (Va).

Method A.

The 2-chloro-4,5-dimethyl-1,3,2-dioxastibolane (6.1 mmoles) and malonyl chloride (6.1 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give Va as white solid, yield 18%, mp 173-175°; ir (potassium bromide): 2980, 2860, 1720, 1450, 1420, 1380, 1350, 1310, 1260, 1230, 1150, 1120, 1100, 1050, 1030, 960, 890, 810, 770 cm^{-1}; nmr (deuteriochloroform): δ 1.22 (d, 12H, 4 × CH_3-CH-O), 3.36 (s, 4 H, CH_2-CO), 4.96 (m, 4H, 4 × CH_3C*H*-O); ms: m/e 316.

Anal. Calcd. for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.28; H, 6.40.

Method B.

The *meso*-2,2-di-*n*-butyl-4,5-dimethyl-1,3,2-dioxastannolane (4.6 mmoles) and malonyl chloride (4.6 mmoles) were used, yield 14%. The mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

meso-2,3,11,12-Tetramethyl-1,4,10,13-tetraoxacyclooctadecane-5,9,14,18-tetraone (Vb).

Method A.

The 2-chloro-4,5-dimethyl-1,3-2-dioxastibolane (6.1 mmoles) and glutaryl chloride (6.1 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give Vb, as white solid, yield 29%, mp 156-158°; ir (potassium bromide): 2940, 2860, 1740, 1450, 1420, 1380, 1340, 1250, 1160, 1100, 1090, 1060, 1020, 980, 760 cm^{-1}; nmr (deuteriochloroform): δ 1.20 (d, 12H, 4 × CH_3-CH-O), 1.76-2.10 (m, 4H, 2 × CH_2-CH_2-CO), 2.28 (t, 8H, 4 × CH_2-CO), 4.92 (m, 4H, 4 × CH_3-C*H*-O); ms: m/e 372.

Anal. Calcd. for $C_{18}H_{28}O_8$: C, 58.05; H, 7.58. Found: C, 58.22; H, 7.60.

Method B.

Compound Vb was prepared as in method B, described for Va, yield 26%. The mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

meso-2,3,13,14-Tetramethyl-1,4,12,15-tetraoxacyclodocosano-5,11,16,22-tetraone (Vc).

Method A.

The 2-chloro-4,5-dimethyl-1,3,2-dioxastibolane (6.1 mmoles) and pimeloym chloride (6.1 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give Vc as white solid, yield 23%, mp 135-136°; ir (potassium bromide): 2940, 2860, 1720, 1480, 1440, 1420, 1360, 1310, 1280, 1240, 1150, 1090, 930, 740 cm^{-1}; nmr (deuteriochloroform): δ 1.20 (d, 12H, 4 × CH_3-CH-O), 1.38-1.96 (m, 12H, 6 × CH_2-CH_2-CO), 2.28 (t, 8H, 4 × CH_2-CO), 4.95 (m, 4H, 4 × CH_3-C*H*-O); ms: m/e 428.

Anal. Calcd. for $C_{22}H_{36}O_8$: C, 61.66; H, 8.47. Found: C, 61.42; H, 8.50.

Method B.

Compound Vc was prepared as in method B, described for Va, yield 20%. The mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

meso-2,3,15,16-Tetramethyl-1,4,14,17-tetraoxacyclohexacosano-5,13,18,-26-tetraone (Vd).

Method A.

The 2-chloro-4,5-dimethyl-1,3,2-dioxastibolane (6.1 mmoles) and azeloyl chloride (6.1 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give Vd as white solid, yield 28%, mp 118-120°; ir (potassium bromide): 2940, 2860, 1740, 1460, 1420, 1390, 1340, 1250, 1180, 1130, 1090, 1020, 950, 730 cm^{-1}; nmr (deuteriochloroform): δ 1.10-1.94 (m, 32H, 10 × CH_2-CH_2-CO and 4 × CH_3-CH-O), 2.28 (t, 8H, 4 × CH_2-CO), 4.92 (m, 4H, 4 × CH_3-C*H*-O); ms: m/e 484.

Anal. Calcd. for $C_{26}H_{44}O_8$: C, 64.44; H, 9.15. Found: C, 64.69; H, 9.18.

Method B.

Compound Vd was prepared as in method B, described for Va, yield 17%. The mixture mp with the sample isolated by method A was unaltered and spectral data were identical.

meso-2,3,16,17-Tetramethyl-1,4,15,18-tetraoxacyclooctacosano-5,14,19,28-tetraone (Ve).

Method A.

The 2-chloro-4,5-dimethyl-1,3,2-dioxastibolane (6.1 mmoles) and sebacoyl chloride (6.1 mmoles) were used. The crude product was purified by column chromatography and the obtained solid was washed in diisopropyl ether to give Ve as white solid, yield 32%, mp 116-118°; ir (potassium bromide): 2940, 2860, 1730, 1470, 1420, 1390, 1340, 1310, 1280, 1260, 1230, 1170, 1120, 1090, 1050, 950, 730 cm^{-1}; nmr (deuteriochloroform): δ 1.03-1.96 (m, 36H, 12 × CH_2-CH_2-CO and 4 × CH_3-CH_2-CO), 2.30 (t, 8H, 4 × CH_2-CO), 4.91 (m, 4H, 4 × CH_3-C*H*-O): ms: m/e 512.

Anal. Calcd. for $C_{28}H_{48}O_8$: C, 65.59; H, 9.44. Found: C, 65.41; H, 9.47.

Method B.

Compound Ve was prepared as in method B, described for Va, yield 31%. The mixture mp with the sample isolated by Method A was unaltered and spectral data were identical.

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