HETEROANALOGUES OF 1-TRIACONTANOL

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A synthesis of twelve heteroanalogues *II*–*XIII* of the plant growth stimulator 1-triacontanol (*I*), derived from the parent alcohol by a replacement of 1–4 methylene units by heteroatoms O, S, NH and/or by a replacement of 1–2 ethylene units by —CO—O—, —CO—NH— or —CH(O)—CH— groups is reported. Spectral and gas-chromatographic properties (Kováts retention indices) of the compounds are described.

As a part of our interest[1–4] in compounds with potential plant-growth regulating activity we have prepared a series of heteroanalogues of 1-triacontanol arising, formally, from the parent alcohol *I* by a replacement of 1–4 methylene units by heteroatoms O, S, NH and/or by a replacement of 1–2 ethylene units by —CO—O—, —CO—NH— or —CH(O)—CH— groups (Scheme 1). All these compounds are isosteric with 1-triacontanol and possess the structural features which according to Ries[5] are requisite for the plant-growth stimulating[6,7] activity of *I*, *i.e.*, 30 atom long straight chaing and the terminal hydroxyl group. Easily accessible derivatives of octadecanoic and 10-undecenoic acids (Scheme 2) were employed as versatile building blocks for synthesis of the heteroanalogues *II*–*XIII*. Base-catalysed reaction of 1-octadecanol (*XIVa*) with 11-bromoundecyl ethyl acetaldehyde acetal (*XV*), followed by acidic hydrolysis, afforded 12-oxa-1-triacontanol (*II*). The analogous reaction of 1-octadecanthiol (*XIVb*) with *XV* yielded 12-thia-1-triacontanol (*III*). The reaction of 1-octadecyl methanesulphonate (*XIVc*) with ethylene glycol gave rise to 3-oxa-1-heneicosanol (*XVI*) which on successive treatment with *p*-toluenesulphonyl chloride and 1,8-octanediol provided 9,12-dioxa-1-triacontanol (*V*). Similarly, 3,6,9,12-tetraoxa-1-triacontanol (*VI*) was obtained by a one-step reaction from 1-octadecyl bromide (*XIVd*) and tetraethylene glycol.

The heteroanalogues with —CO—O— grouping, *VIII* and *IX*, were prepared from octadecanoyl chloride by a treatment with 1,11-undecanediol and tetraethylene glycol, respectively. The amidic analogue *X* was obtained, *via* a mixed anhydride, from octadecanoic acid by a treatment with 11-amino-1-undecanol (*XVII*). The

other analogue with amidic grouping, *XI*, was prepared from 1-octadecyl methanesulphonate (*XIVc*) by reaction with N-(6-hydroxyhexyl)phthalimide (*XVIII*) followed successively by hydrazinolysis of the resulting elongated phthalimide *XIX* and a treatment with 4-hydroxybutyrolactone.

$CH_3(CH_2)_{29}OH$ *I*

$CH_3(CH_2)_{17}O(CH_2)_{11}OH$ *II*

$CH_3(CH_2)_{17}S(CH_2)_{11}OH$ *III*

$CH_3(CH_2)_{17}NH(CH_2)_{11}OH$ *IV*

$CH_3(CH_2)_{17}(OCH_2CH_2)_2(CH_2)_6OH$ *V*

$CH_3(CH_2)_{17}(OCH_2CH_2)_4OH$ *VI*

$CH_3(CH_2)_{17}O(CH_2)_6NH(CH_2)_4OH$ *VII*

$CH_3(CH_2)_{16}CO.O(CH_2)_{11}OH$ *VIII*

$CH_3(CH_2)_{16}CO.(OCH_2CH_2)_4OH$ *IX*

$CH_3(CH_2)_{16}CO.NH(CH_2)_{11}OH$ *X*

$CH_3(CH_2)_{17}O(CH_2)_6NH.CO(CH_2)_3OH$ *XI*

$CH_3(CH_2)_{18}CH(O)CH(CH_2)_9OH$ *XII* (*trans*-10,11)

$CH_3(CH_2)_7CH(O)CH(CH_2)_9CH(O)CH(CH_2)_9OH$ *XIII* (*trans*-10,11-*trans*-21,22)

SCHEME 1

$CH_3(CH_2)_{17}X$

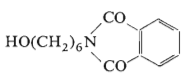
XIVa: X = OH *XIVc*: X = OSO_2CH_3

XIVb: X = SH *XIVd*: X = Br

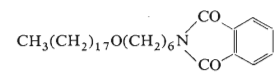
$Br(CH_2)_{11}OCH(CH_3)OC_2H_5$ *XV*

$CH_3(CH_2)_{17}OCH_2CH_2OH$ *XVI*

$NH_2(CH_2)_{11}OH$ *XVII*



XVIII



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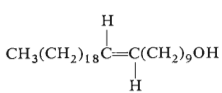
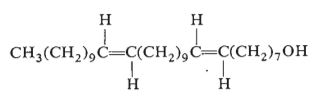


XX



XXI

SCHEME 2

The aza- and oxaza-analogues *IV* and *VII* were synthetized from the corresponding amides *X* and *XI*, respectively, by reduction with $LiAlH_4$. The epoxy-analogues *XII* and *XIII* were obtained from the corresponding unsaturated alcohols *XX* and *XXI* by reaction with peracetic acid.

Structure of the analogues *II*–*XIII* was confirmed by ^1H NMR, IR and mass-spectroscopy. Purity of the products was checked by thin-layer and gas-chromatography. The gas-chromatographic properties of the free alcohols *I*–*XIII*, and also of their trimethylsilyl derivatives have been determined and the results summarized in form of the Kováts retention indices.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. The IR spectra were recorded with Perkin–Elmer Model 580 spectrophotometer. The mass spectra were measured on a double focusing A.E.I. MS 902 apparatus with a direct inlet at 140–170°C and 70 eV. ^1H NMR spectra were recorded with Tesla BS 467 (60 Mc) spectrometer at 30°C using tetramethylsilane as the internal standard. The gas chromatography was carried out on the Packard 427 apparatus equipped with a dual system of columns and flame ionization detectors and with Packard 610 recorder. Thin-layer chromatography was performed on Silicagel GF_{254}, Type 60 (Merck).

Materials: 1-Octadecanol, octadecanoic acid and 10-undecenoic acid were commercial products. 1-Octadecanthiol[8,9], 1-octadecyl bromide[10,11], octadecanoyl chloride[12], 1-octadecyl methanesulphonate[13], 11-bromo-1-undecanol[14–16], 1,8-octanediol[17], 1,11-undecanediol[18], 11-amino-1-undecanol[19], 6-amino-1-hexanol[19], (*E*)-10-triaconten-1-ol[1], and (10*E*,21*E*)-10,21-triacontadien-1-ol[1] were prepared by the described procedure.

11-Bromoundecyl Ethyl Acetaldehyde Acetal (*XV*)

Prepared from 11-bromo-1-undecanol by the same procedure as we reported previously[1] for preparation of ethyl 10-undecynyl acetaldehyde acetal. Yield 97%; purity 97% (gas chromatography).

3-Oxa-1-heneicosanol (*XVI*)

Potassium tert-butoxide (8·4 g; 75 mmol) was added to ethylene glycol (44·5 g; 720 mmol) and the basic solution was treated under stirring with 1-octadecyl methanesulphonate (8·7 g; 25 mmol). After heating at 80°C for 5 h the mixture was diluted with water and extracted with ether. The ethereal extract was washed with water and dried over Na_2SO_4. The solvent was taken down, the crude product purified on a column of silicagel (chloroform) and crystallized from methanol (yield 83%); m.p. 49–50°C. For $C_{20}H_{42}O_2$ (314·6) calculated: 76·37% C, 13·46% H; found: 76·51% C, 13·48% H. Mass spectrum: (*m/e*) M^+ 314. I.R. ($CHCl_3$, cm^{-1}): 3 605, 3 475ν(OH), 1 121ν(C—O—C), 1 059δ(OH). *p*-Toluenesulphonate: prepared in 67% yield by a standard procedure.

N-(7-Oxapentacosyl)phthalimide (*XIX*)

To a stirred solution of potassium tert-butoxide (13·4 mmol) in tert-butanol (25 ml) was successi-

vely added N-(6-hydroxyhexyl)phthalimide (3·3 g; 13·4 mmol) and 1-octadecyl methanesulphonate (4·66 g; 13·4 mmol). After heating under reflux for 5 h the product which deposited on cooling was sucked off, washed with water and light petroleum (yield 41%) and crystallized from ethanol, m.p. 65–66°C. For $C_{32}H_{53}NO_3$ (499·8) calculated: 76·91% C, 10·69% H, 2·80% N; found: 76·78% C, 10·65% H, 2·51% N. Mass spectrum: (*m/e*) M^+ 499. I.R. ($CHCl_3$, cm^{-1}): 1 773, 1 711ν(C=O), 1 106, 1 060ν(C—O—C). 7-Oxapentacosylamine: prepared from the phthalimide *XIX* by hydrazinolysis under standard condition.

TABLE I
Alcohols *II*–*XIII*

Alcohol	Yield, %	M.p., °C (solvent)	Formula (mol.weight)	Calculated/Found		
				% C	% H	% N
II	31	70–71 (methanol)	$C_{29}H_{60}O_2$ (440·8)	79·02 79·12	13·72 13·46	— —
III	90	75–76 (methanol)	$C_{29}H_{60}OS$[a] (456·9)	76·24 76·08	13·24 13·16	— —
IV	85	74–75 (ethanol)	$C_{29}H_{61}NO$ (439·8)	79·20 78·96	13·98 13·63	3·18 3·10
V	38	57–58 (methanol)	$C_{28}H_{58}O_3$ (442·8)	75·96 76·00	13·20 13·22	— —
VI	55	41–42 (light petroleum)	$C_{26}H_{54}O_5$ (446·7)	69·91 70·21	12·18 12·32	— —
VII	50	46–48 (light petroleum–ethyl acetate)	$C_{28}H_{59}NO_2$ (441·8)	76·12 75·96	13·46 13·30	3·17 2·95
VIII	56	64–65 (light petroleum–ethyl acetate)	$C_{29}H_{58}O_3$ (454·8)	76·59 76·62	12·86 12·94	— —
IX	61	39–40 (light petroleum)	$C_{26}H_{52}O_6$ (460·7)	67·79 67·69	11·38 11·35	— —
X	82	104–105 (ethanol)	$C_{29}H_{59}NO_2$ (453·8)	76·76 76·60	13·10 13·00	3·09 3·28
XI	55	91–92 (ethanol)	$C_{28}H_{57}NO_3$ (455·8)	73·79 73·60	12·61 12·75	3·07 2·81
XII	81	80–81 (methanol)	$C_{30}H_{60}O_2$ (452·8)	79·58 79·76	13·36 13·39	— —
XIII	90	73–74 (methanol)	$C_{30}H_{58}O_3$ (466·8)	77·19 77·18	12·52 12·62	— —

[a] Calculated: 7·02% S; found: 7·26% S.

TABLE II

Alcohols *II*—*XIII*: spectral data

Alcohol	($M^{\ddagger}$) *m/e*	I.R. *ν*, cm^{-1}	^1H NMR ($CDCl_3$) *δ*, ppm
II	440	(CCl_4): 3 625, 3 450 *ν*(OH), 1 106 *ν*(C—O—C), 1 050 *δ*(OH)	0·88 (dist. t, 3 H, —CH_3); 1·28 (bs, 45 H, —CH_2— and OH); 1·56 (m, 6 H, —CH_2CH_2O—); 3·38 (t, $J = 6$ Hz, 4 H, —CH_2O—); 3·63 (t, $J = 6$ Hz, 2 H, —CH_2OH)
III	456	($CHCl_3$): 3 625 *ν*(OH), 610 *ν*(C—S)	($CDCl_3$—C_6D_6): 0·87 (dist. t, 3 H, —CH_3); 1·16 (bs, 1 H, OH); 1·26 (bs, 44 H, —CH_2—); 1·40—1·70 (m, 6 H, —CH_2CH_2S— and —CH_2CH_2OH; 2·44 (t, $J = 6$ Hz, 4 H, —CH_2S—); 3·48 (t, $J = 6$ Hz, 2 H, —CH_2OH)
IV	439	($CHCl_3$, KBr): 3 622 *ν*(OH), 3 170 *ν*(N—H), 1 118 *ν*(C—N), 1 052 *δ*(OH)	0·88 (dist. t, 3 H, —CH_3); 1·26 (bs, 48 H, —CH_2—); 1·69 (bs, 2 H, —CH_2CH_2O—); 1·93 (bs, 1 H, OH); 2·55 (m, 4 H, —CH_2N—); 3·58 (m, 2 H, —CH_2OH)
V	442	(CCl_4): 3 638, 3 485 *ν*(OH), 1 120 *ν*(C—O—C), 1 055 *δ*(O—H)	0·87 (dist. t, 3 H, —CH_3); 1·25 (bs, 44 H, —CH_2—); 3·33—3·75 (m, 10 H, —OCH_2—)
VI	446	(CCl_4): 3 605, 3 485 *ν*(OH), 1 120 *ν*(C—O—C)	0·80 (dist., t, 3 H, —CH_3); 0·92 (s, 1 H, OH); 1·20 (bs, 32 H, —CH_2—); 3·50 (bs, 18 H, —CH_2O—)
VII	441	($CHCl_3$): 3 620 *ν*(OH), 3 120 *ν*(OH...N), 1 108 *ν*(C—O—C)	0·85 (dist, t, CH_3); 1·23 (bs, 38 H, —CH_2—); 1·44—1·67 (m, 6 H, —CH_2CH_2O—); 2·62 (m, 4 H, —CH_2N—); 3·27 (bs, 1 H, —NH...O—); 3·33—3·67 (m, 6 H, —CH_2O—)
VIII	454	(CCl_4): 3 638, 3 520 *ν*(OH), 1 737 *ν*(C=O), 1 173 *ν*(C—O)	0·83 (dist. t, 3 H, —CH_3); 1·18 (bs, 49 H, —CH_2— and OH); 2·25 (m, 2 H, —CH_2COO—); 3·60 (m, 2 H, —CH_2OH); 4·04 (m, 2 H, —CH_2OCO—)

TABLE II
(*Continued*)

Alcohol	($M^{+\cdot}$) *m/e*	I.R. *ν*, cm^{-1}	^1H NMR ($CDCl_3$) *δ*, ppm
IX	460	(CCl_4): 3 605, 3 490 *ν*(OH), 1 740 *ν*(C=O), 1 173 *ν*(C—O), 1 140, 1 118 *ν*(C—O—C)	0·83 (dist. t, 3 H, —CH_3); 1·21 (bs, 31 H, —CH_2— and OH); 2·08—2·67 (m, 2 H, —CH_2COO—); 3·62 (bs, 14 H, —CH_2O—); 4·08—4·34 (m, 2 H, —CH_2OCO—)
X	453	(KBr): 3 420 *ν*(OH) and *ν*(NH), 1 635 *ν*(C=O), 1 540 *δ*(NH), 1 059 *δ*(OH)	($CDCl_3$—C_5D_5N): 0·87 (dist. t, 3 H, —CH_3); 1·27 (bs, 48 H, —CH_2—); 2·07—2·45 (m, 2 H, —CH_2CONH—); 3·18—3·55 (m, 2 H, —CH_2NH. .CO—); 3·57—4·02 (m, 2 H, —CH_2O—)
XI	455	($CHCl_3$): 3 622 *ν*(OH), 3 448 *ν*(NH), 1 657 *ν*(C=O), 1 525 *δ*(NH), 1 108 *ν*(C—O—C)	0·88 (dist, t, —CH_3); 1·25 (bs, 42 H, —CH_2—); 1·95 (s, 1 H, OH); 2·18 to 2·47 (m, 2 H, —CH_2CONH—); 3·03—3·52 (m, 6 H, —CH_2O— and —CH_2NHCO—); 3·67 (t, J = 6 Hz, 2 H, —CH_2OH); 5·59 (bs, 1 H, —CONH—)
XII	452	(KBr): 3 290 *ν*(OH), 1 430, 1 260 and 875 *ν*(C—O—C), 729 and 719 *ϱ*$(CH_2)_n$	0·88 (dist. t, 3 H, —CH_3); 1·25 (bs, 52 H, —CH_2—); 2·50—2·77 (m, 2 H, —CH(O)); 3·50—3·83 (m, 2 H, —CH_2OH)
XIII	466	(KBr): 3 290 *ν*(OH), 1 428, 1 256, 874 *ν*(C—O—C), 728 and 719 *ϱ*$(CH_2)_n$	0·87 (dist. t, 3 H, —CH_3); 1·20—1·67 (m, 48 H, —CH_2—); 2·50—2·78 (m, 4 H, —CH(O)); 3·50—3·80 (m, 2 H, —CH_2OH)

12-Oxa-1-triacontanol (*II*)

1-Octadecanol (1·89 g; 7 mmol) was treated under nitrogen with 0·5M solution of potassium tert-butoxide in tert-butanol (14 ml; 7 mmol). 11-Bromoundecyl ethyl acetaldehyde acetal (2·26 g; 7 mmol) was added dropwise to the stirred solution and heated at 70°C for 3 h. After dilution with water the mixture was extracted with ether, the ethereal layer was washed with water and dried over K_2CO_3. The solvent was taken down and the residue was separated on alumina (60 g; activity II; chloroform–diethyl ether) affording the starting alcohol (1·2 g; 65%) and acetal of *II* (2·4 g). Upon hydrolysis with methanolic solution (100 ml) of *p*-toluenesulphonic acid (0·6 g) at reflux temperature (1 h) the latter compound furnished the title product. Yield, elemental analysis and physical properties are in Tables I and II.

12-Thia-1-triacontanol (*III*)

1-Octadecanthiol (2·03 g; 7·1 mmol) in ethanol (30 ml) was successively treated with 1·1M solution of sodium ethoxide in ethanol (6·3 ml; 6·9 mmol) and with 11-bromoundecyl ethyl acetaldehyde acetal (2·21 g; 6·9 mmol) in ethanol (10 ml) under nitrogen. After stirring at 45°C for 4 h the mixture was treated with *p*-toluenesulphonic acid (1 g) and kept under reflux for 1 h. The product which deposited on cooling was purified by crystallization; *cf.* Tables I and II.

12-Aza-1-triacontanol (*IV*)

Amide *X* (1·6 g; 3·5 mmol) was dissolved in hot tetrahydrofuran (20 ml) and added under stirring to a suspension of lithium aluminium hydride (0·35 g; 9·2 mmol) in boiling tetrahydrofuran (20 ml). After additional reflux (8 h) the mixture was decomposed by a standard procedure and filtered over silica. The filtrate was taken to dryness and the residue was purified by crystallization; *cf.* Tables I and II.

9,12-Dioxa-1-triacontanol (*V*)

3-Oxa-1-heneicosyl *p*-toluenesulphonate (3·2 g; 6·84 mmol) was treated with 1,8-octanediol (3·6 g; 24·7 mmol) dissolved in 0·3M-t-C_4H_9OK–t-C_4H_9OH solution (22·8 ml; 6·84 mmol). After stirring at reflux temperature for 7 h the mixture was diluted with water (200 ml) and extracted with light petroleum. The extract was washed with brine and dried over K_2CO_3, the solvent was taken down, the residue separated on a column of silicagel [ethyl acetate–chloroform (5 : 95)] and the product crystallized; *cf.* Tables I and II.

3,6,9,12-Tetraoxa-1-triacontanol (*VI*)

1-Octadecyl bromide (3 g; 9 mmol) was treated with tetraethylene glycol (25 ml) dissolved in 0·4M-t-C_4H_9OK–t-C_4H_9OH solution (25 ml; 10 mmol). After 4 h stirring at reflux temperature the mixture was diluted with water (200 ml) and extracted with light petroleum. The extract was washed with water and dried over Na_2SO_4. The solvent was taken down and the residue was purified by crystallization; *cf.* Tables I and II.

5-Aza-12-oxa-1-triacontanol (*VII*)

Amide *XI* (0·45 g; 1 mmol) was treated with a slurry of lithium aluminium hydride (0·12 g; 3 mmol) in tetrahydrofuran under reflux. After stirring for 6 h at the reflux temperature the mixture was decomposed by a usual procedure, the product was purified on a column of silicagel (ethanol–diethylamine) and crystallized; *cf.* Tables *I* and *II*.

11-Hydroxyundecyl Octadecanoate (*VIII*)

The solution of 1,11-undecanediol (1·88 g; 10 mmol) in benzene (80 ml) was added dropwise to a stirred solution of octadecanoyl chloride (1·51 g; 5 mmol) in benzene (20 ml). After heating

TABLE III

Kováts retention indices *I* of the alcohols *I*—*XIII* (OH) and of their trimethylsilyl derivatives (OTMS)

Compound	Temperature °C	SE-30[a]		OV-17[a]	
		OH	OTMS	OH	OTMS
I	270	3 291·9 ± 1·1	3 350·0 ± 1·1	3 414·9 ± 1·4	3 340·1 ± 1·0
	290	—	—	3 418·1 ± 1·4	3 334·4 ± 2·0
II	270	3 234·0 ± 1·6	3 288·5 ± 0·7	3 408·0 ± 1·3	3 329·8 ± 1·1
	290	—	—	3 413·7 ± 0·8	3 326·4 ± 1·6
III	270	3 494·6 ± 2·2	3 542·6 ± 1·8	—	3 637·4 ± 0·4
	290	—	—	3 725·4 ± 0·9	3 638·6 ± 0·3
IV	270	3 341·4 ± 0·4	3 392·4 ± 1·6	3 521·3 ± 1·5	3 442·6 ± 1·6
	290	—	—	3 527·6 ± 1·1	3 440·9 ± 0·8
V	270	3 199·4 ± 2·7	3 251·5 ± 1·6	3 422·2 ± 1·2	3 340·5 ± 0·9
	290	—	—	3 428·6 ± 1·1	3 338·6 ± 1·3
VI	270	3 123·7 ± 1·3	3 206·4 ± 1·5	3 416·3 ± 1·0	3 388·0 ± 1·6
	290	—	—	3 421·8 ± 0·1	3 384·7 ± 1·9
VII	270	3 041·1 ± 1·9	3 336·3 ± 1·0	3 176·0 ± 0·6	3 438·2 ± 0·4
	290	—	—	3 188·1 ± 1·8	3 436·7 ± 1·5
VIII	270	3 345·1 ± 0·3	3 396·9 ± 0·9	3 578·4 ± 0·5	3 491·9 ± 0·9
	290	—	—	3 581·4 ± 1·0	3 489·1 ± 0·9
IX	270	3 219·0 ± 1·6	3 293·3 ± 1·0	3 560·2 ± 0·5	3 522·3 ± 0·9
	290	—	—	3 565·8 ± 0·4	3 519·0 ± 2·0
X	270	3 616·9 ± 1·7	3 656·8 ± 1·2	—	—
	290	—	—	3 958·2 ± 2·5	3 858·1 ± 1·3
XI	270	3 267·5 ± 1·4	3 586·7 ± 1·3	3 572·4 ± 1·8	—
	290	—	—	3 581·6 ± 0·8	3 830·1 ± 2·8
XII	270	3 447·8 ± 2·5	3 492·1 ± 1·1	3 659·4 ± 0·7	3 574·1 ± 2·0
	290	—	—	3 661·2 ± 1·4	3 571·1 ± 1·2
XIII	270	3 599·1 ± 2·4	3 639·9 ± 2·8	—	—
	290	—	—	3 905·6 ± 0·4	3 812·8 ± 1·4

[a] Mean values of *I* calculated from at least three measurements; the error is expressed as an estimate of standard deviation.

at reflux for 2·5 g benzene was distilled off *in vacuo* and the residue was separated on a column of silicagel. The product was eluted with chloroform–ethyl acetate (95 : 5) mixture and crystallized; *cf.* Tables I and II.

11-Hydroxy-3,6,9-trioxaundecyl Octadecanoate (*IX*)

To a solution of tetraethylene glycol (9·7 g; 50 mmol) in benzene (100 ml) was added octadecanoyl chloride (3 g; 10 mmol) dissolved in benzene (40 ml). After standing for 2 h at room temperature and occasional shaking the mixture was poured into water, the organic layer was separated and dried over $MgSO_4$. Benzene was distilled off *in vacuo*, the residue was separated on a column of silicagel [chloroform–ethyl acetate (95 : 5)] and the product crystallized; *cf.* Tables I and II.

N-(11-Hydroxyundecyl)octadecanamide (*X*)

To a stirred solution of octadecanoic acid (2·84 g; 10 mmol) in chloroform (40 ml) was successively added triethylamine (1·4 ml; 10 mmol), pyridine (0·8 ml; 10 mmol) and pivaloyl chloride (1·22 g; 10 mmol) in chloroform (10 ml). The mixture was treated with a solution of 11-amino-1-undecanol (1·87 g; 10 mmol) in chloroform (20 ml) and the resulting suspension was stirred at room temperature overnight. The solvent was taken down on aspirator, the crude product was washed with water, sucked off and crystallized; *cf.* Tables I and II.

TABLE IV

Differences ∂I between the Kováts retention indices of the trimethylsilylated and free alcohols *I*—*XIII* at 270°C and/or at 290°C (data in parentheses)

Compound	∂I	
	SE-30	OV-17
I	+ 58·1 (—[a])	— 74·8 (— 83·7)
II	+ 54·5 (—[a])	— 78·2 (— 87·3)
III	+ 48·0 (—[a])	—[a] (— 86·8)
IV	+ 51·0 (—[a])	— 78·7 (— 86·7)
V	+ 52·1 (—[a])	— 81·7 (— 90·0)
VI	+ 82·7 (—[a])	— 28·3 (— 37·1)
VII	+295·2 (—[a])	+262·2 (+248·6)
VIII	+ 51·8 (—[a])	— 86·5 (— 92·3)
IX	+ 74·3 (—[a])	— 37·9 (— 46·8)
X	+ 39·9 (—[a])	—[a] (—100·1)
XI	+319·2 (—[a])	—[a] (+248·5)
XII	+ 44·3 (—[a])	— 85·3 (— 90·1)
XIII	+ 40·8 (—[a])	—[a] (— 92·8)

[a] Not determined.

N(7-Oxapentacosyl)-4-hydroxybutyramide (*XI*)

A mixture of 7-oxa-1-pentacosylamine (1 g; 2·7 mmol), 4-hydroxybutyrolactone (1·5 ml; 19·7 mmol) and toluene (30 ml) was heated under reflux for 20 h. The product which deposited on cooling was washed with toluene and crystallized; *cf.* Tables I and II.

trans-10,11-Epoxy-1-triacontanol (*XII*)

A 38% solution of peracetic acid (0·5 ml; 2·5 mmol) was added to a stirred mixture of (*E*)-10-triaconten-1-ol (250 mg; 0·57 mmol), anhydrous sodium carbonate (2 g) and dichloromethane (40 ml). After stirring for 4 h at room temperature the mixture was treated with sodium sulphite (0·5 g), washed with water and solution of sodium bicarbonate, dried over $MgSO_4$ and the solvent was taken down. The crude product was purified by crystallization; *cf.* Tables I and II.

trans-10,11-*trans*-21,22-Diepoxy-1-triacontanol (*XIII*)

Prepared analogously from (10*E*,21*E*)-10,21-triacontadien-1-ol and peracetic acid; *cf.* Tables I and II.

Trimethylsilylation of the Alcohols *II*—*XIII*

Performed analogously as we described earlier[1]. N,O-bis(trimethylsilyl)trifluoroacetamide containing 1% of trimethylchlorsilane (Regis) was employed as the silylating agent.

Gas Chromatography

Glass columns (0·24 × 185 cm) packed with 3% OV-17 on GAS-CHROM Q were identical with those described previously[1] ($N = 3\,300$, $t'_R = 17{\cdot}1$ min (85·3 mm) for n-$C_{34}H_{70}$; $t'_R = 17{\cdot}8$ min (89·2 mm) for 1-triacontanol. New glass columns (0·24 × 185 cm) packed with 3% SE-30 on GAS-CHROM Q (80—100 mesh) were prepared from the same pretested G.C. packing (lot SP-1323) as we employed in the previous study[1]. $N = 3\,200$, $t'_R = 13{\cdot}1$ min (65·4 mm) for n-$C_{34}H_{70}$; $t'_R = 10{\cdot}1$ min (50·3 mm) for 1-triacontanol. The Kováts retention indices were in most instances determined under the conditions reported in ref.[1] (column temperature 270°C; injector temperature 280°C). Since retention times of the heteroanalogues *III*, *X*, *XI* and *XIII* on OV-17 would be too long under these conditions, the Kováts indices of all the alcohols *I*—*XIII* and their trimethylsilyl derivatives were determined on the OV-17 column also at a higher temperature (column temperature 290°C; injector temperature 300°C).

The Kováts retention indices of the free and trimethylsilylated alcohols *I*—*XIII* are summarized in Table III. The differences between the indices determined for the corresponding trimethylsilylated and free alcohols are compared in Table IV. Anomalous behaviour of the analogues *VII* and *XI* is apparent from Table IV showing that the observed values ∂I for the two systems are exceptionally high. Intramolecular hydrogen bonding (seven-membered ring) or disilylation of the free alcohols *VII* and *XI* is probably the responsible factor.

Other anomalies have been also noted in course of the measurement. Thus free alcohols *IV*, *IX*, *XI* and *XIII* showed on OV-17 tailing peaks. The alcohol *IX* showed on SE-30 a visible peak only under conditions of oversampling. The alcohol *XI* underwent a partial fragmentation (formation of an additional peak with the Kováts indices 2 748·8 ± 2·3 on SE-30 and 2 890·3 ± ± 1·5 on OV-17).

The analyses were carried out in the Analytical Department of this Institute (Dr J. Horáček, head). The infrared spectra were recorded and evaluated by Dr S. Vašíčková. The ^{1}H NMR *spectra were recorded by Dr M. Synáčková. The mass spectra were recorded by Dr A. Trka.*

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