

## UNSATURATED ANALOGUES OF 1-TRIACONTANOL

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A simple regio- and stereoselective synthesis of unsaturated analogues of the plant growth stimulator 1-triacontanol from  $\omega$ -alkyn-1-ols is reported. Starting from the easily accessible 10-undecyn-1-ol, eight  $n$ - $C_{30}$  alcohols containing  $-C\equiv C-$ , (*E*)  $-C=C-$  or (*Z*)  $-C=C-$  group in the position 21 and/or 10 have been prepared. Spectral and gas-chromatographic properties (Kováts retention indices) of the novel compounds are described.

1-Triacontanol (*Ia*) was reported to be a potent plant growth stimulator<sup>1,2</sup>. The effect of several analogues of *Ia* differing in chain length ( $C_{16-32}$ ), position and identity of the functional group was also examined<sup>3</sup>. However, none of the analogues caused an increase in plant growth; instead, inhibition of the stimulating effect of *Ia* was observed. The  $C_{30}$  straight chain as well as presence of the terminal hydroxyl group thus appear to be specific for the growth-promoting activity of *Ia*.

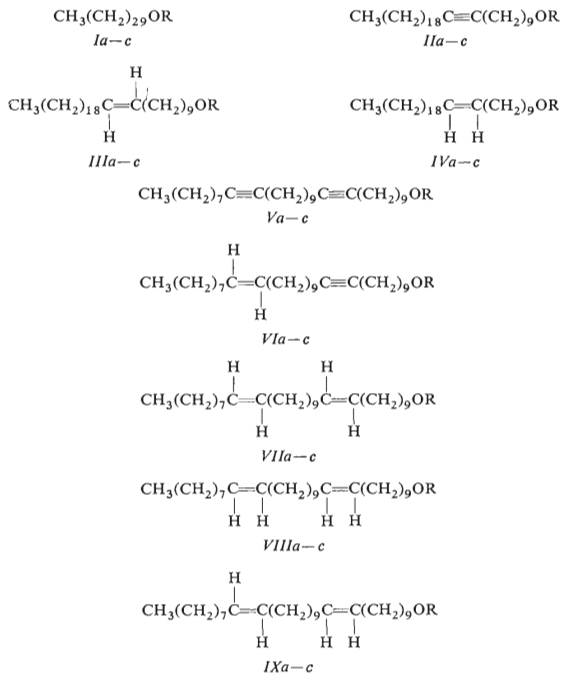
In this paper we report synthesis\* of eight unsaturated analogues of *Ia*, *Ila*–*IXa* (Scheme 1). All these novel compounds possess the requisite  $C_{30}$  chain length and the terminal hydroxyl group.

Ethyl 10-undecynyl acetaldehyde acetal (*X*), easily available<sup>5,6</sup> from the commercial 10-undecenoic acid has been employed as a convenient synthon for *Ila*–*IXa* (Scheme 2). Alkylation of the lithium salt of *X* in hexamethylphosphoric triamide (procedure *A*) or of the sodium salt of *X* in xylene in presence of catalytic amounts of 18-crown-6-ether (procedure *B*) with 1-bromononadecane (*XIb*) yielded 10-triacontyn-1-ol (*Ila*). Analogous alkylation with 19-bromo-9-nonadecyne (*XIIb*) and 19-bromo-9*E*-nonadecene (*XIIIb*) afforded the acetylenic alcohols *Va* and *VIa*, respectively.

The required bromides *XIb*–*XIIIb* were prepared, *via* the corresponding alcohols *XIa*–*XIIIa*, also from the synthon *X*. Alkylation of the sodium salt of *X* with 1-bromooctane by the procedure *B* afforded 10-nonadecyn-1-ol (*XIIa*) which upon reduction yielded the alcohols *XIa* or *XIIIa*.

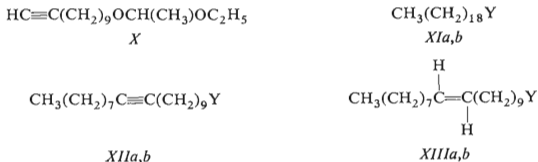
The *E*-isomeric olefinic alcohols *IIIa*, *VIIa* and *XIIIa* were prepared from the corresponding acetylenic precursors *Ila*, *Va* and *XIIa*, respectively, by a treatment,

\* The synthesis is a subject of a recent patent application; ref.<sup>4</sup>.



In formulae I–IX: a, R = H; b, R = Si(CH<sub>3</sub>)<sub>3</sub>; c, R = COCH<sub>3</sub>.

## SCHEME 1



In formulae XI–XIII: a, Y = OH; b, Y = Br.

## SCHEME 2

with  $\text{LiAlH}_4$  in diglyme<sup>7</sup> under reflux. The *Z*-isomeric alcohols *Iva*, *VIIIa* and *IXa* were obtained from the alcohols *Ila*, *Va* and *VIa*, respectively, by hydrogenation over P2 nickel catalyst<sup>8</sup> in ethanol in presence of ethylenediamine.

Hydrogenation of the acetylenic alcohols *Ila* and *Va* over the Adams catalyst in ethanol afforded 1-triacontanol (*Ia*) which according to gas chromatography did not contain lower homologues. This makes from *X* also a convenient synthon<sup>9</sup> (alternative synthons are described in refs.<sup>10-17</sup>) for the parent alcohol *Ia*, owing to the inhibitory effect<sup>3</sup> of the lower homologues upon the growth stimulating activity of 1-triacontanol.

Isomeric purity of the unsaturated alcohols *Ila*–*IXa* was examined by IR spectrometry and also by gas chromatography. The gas-chromatographic behaviour of the  $\text{C}_{30}$  alcohols *Ia*–*IXa* and their trimethylsilyl (*Ib*–*IXb*) and acetyl (*Ic*–*IXc*) derivatives was investigated in a more detail and the results were summarized in form of the Kováts retention indices.

## EXPERIMENTAL<sup>1</sup>

Melting points were determined on a Kofler block and are uncorrected. The IR spectra (in  $\text{CS}_2$ ; 0.04–0.22M solutions) were recorded with Perkin-Elmer Model 580 spectrophotometer. The mass spectra were measured on a double focusing A.E.I. MS 902 apparatus. Samples were introduced *via* direct inlet at 140–170°C at 70 eV. <sup>1</sup>H 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 using the Packard 610 recorder. Thin layer chromatography was performed on Silicagel GF<sub>254</sub>, type 60 (Merck).

10-Undecenoic acid and *n*-octyl bromide were commercial products (Koch-Light). 10-Undecyenoic acid<sup>5</sup> and 10-undecyn-1-ol<sup>6</sup> were prepared by described procedures.

### Ethyl 10-Undecynyl Acetaldehyde Acetal (*X*)

Ethyl vinyl ether (21.6 g; 0.3 mol) was added dropwise (15 min) to a stirred solution (0°C) of 10-undecyn-1-ol (16.8 g; 0.1 mol) and *p*-toluenesulphonic acid (50 mg) in diethyl ether (170 ml). After additional stirring for 2 h at 0°C the solution was washed with 4% aqueous solution of KOH and dried over  $\text{K}_2\text{CO}_3$ . Evaporation of the solvent on aspirator afforded 23.4 g (98%) of the required product which according to gas chromatography contained less than 2% of impurities.

### Acetylenic Alcohols *Ila*, *Va*, *VIa* and *XIIa*

*Procedure A:* To a stirred solution of the acetal *X* (3.4 g; 14.2 mmol) in hexamethylphosphoric triamide (10 ml) was added under cooling (0°C) and a nitrogen atmosphere *n*-butyllithium (14.2 mmol) in *n*-hexane (10.1 ml). The solution was stirred for 30 min at 0°C and *n*-hexane was distilled off at 2.7 kPa. To the residue was added under cooling (0°C) and a nitrogen atmosphere solution of the appropriate bromide (12.7 mmol) in tetrahydrofuran (8 ml) in course of 15 min. The mixture was stirred for 12 h at room temperature, diluted with brine and the product was extracted with several portions of light petroleum. The combined extracts were washed with brine, dried over  $\text{MgSO}_4$  and taken down. The residue (6.5 g) was dissolved in methanol (80 ml),

TABLE I  
Acetylenic alcohols *Ila*, *Va*, *Vla* and *XIIa*

Compound	Yield, % (procedure)	M.p., °C (methanol)	Formula (mol. weight)	Calculated/Found	
				% C	% H
<i>Ila</i>	69 ( <i>A</i> )	70–71	C <sub>30</sub> H <sub>58</sub> O (434·8)	82·87	13·45
	81 ( <i>B</i> )			82·58	13·27
<i>Va</i>	64 ( <i>A</i> )	55–56	C <sub>30</sub> H <sub>54</sub> O (430·8)	83·65	12·64
	69 ( <i>B</i> )			83·67	12·50
<i>Vla</i>	55 ( <i>A</i> )	55–56	C <sub>30</sub> H <sub>56</sub> O (432·8)	83·26 83·28	13·04 12·82
<i>XIIa</i>	52 ( <i>A</i> )	38–39	C <sub>19</sub> H <sub>36</sub> O (280·5)	81·36	12·94
	87 ( <i>B</i> )			81·51	12·83

TABLE II  
Alkynols *Ila*, *Va*, *Vla* and *XIIa*: spectral data

Alkynol	IR (CCl <sub>4</sub> ) ν(OH), cm <sup>-1</sup>	M <sup>+</sup> , <i>m/e</i>	<sup>1</sup> H NMR (CCl <sub>4</sub> ) δ, ppm
<i>Ila</i>	3 640	434	<sup>a</sup> 0·87 (dist. t, 3 H, CH <sub>3</sub> ); 1·25 (bs, 48 H, CH <sub>2</sub> ); 1·97–2·33 (m, 4 H, ≡C–CH <sub>2</sub> ); 3·48–3·77 (m, 2 H, CH <sub>2</sub> OH)
<i>Va</i>	3 635, 3 350	430	0·88 (dist. t, 3 H, CH <sub>3</sub> ); 1·31 (bs, 40 H, CH <sub>2</sub> ); 1·86–2·26 (m, 8 H, ≡C–CH <sub>2</sub> ); 3·39–3·68 (m, 2 H, CH <sub>2</sub> OH)
<i>Vla</i>	3 625, 3 350 <sup>b</sup>	432	0·86 (dist. t, 3 H, CH <sub>3</sub> ); 1·25 (bs, 40 H, CH <sub>2</sub> ); 1·75–2·20 (m, 8 H, =CH–CH <sub>2</sub> and ≡C–CH <sub>2</sub> ); 3·38–3·70 (m, 2 H, CH <sub>2</sub> OH); 5·20–5·42 (m, 2 H, –CH=)
<i>XIIa</i>	3 635	280	0·87 (dist. t, 3 H, CH <sub>3</sub> ); 1·30 (bs, 26 H, CH <sub>2</sub> ); 1·97–2·23 (m, 4 H, ≡C–CH <sub>2</sub> ); 2·42 (s, 1 H, OH); 3·33–3·67 (m, 2 H, CH <sub>2</sub> OH)

<sup>a</sup> In CDCl<sub>3</sub>. <sup>b</sup> In CS<sub>2</sub>.

acidified with *p*-toluenesulphonic acid (1 g) and the solution was heated under reflux for 1.5 h. The crude product which deposited on cooling was purified by crystallization from methanol and identified by elemental analysis (Table I) and spectral data (Table II).

**Procedure B:** A stirred mixture of the acetal *X* (9.8 g; 41 mmol), 50% suspension of sodium amide in toluene (3.2 g; 41 mmol), 18-crown-6-ether (0.21 g; 0.8 mmol) and xylene (140 ml) was heated under reflux for 40 min (evolution of NH<sub>3</sub> ceased after 15 min). To the boiling mixture was added dropwise a solution of the appropriate bromide (41 mmol) in xylene (40 ml) and heating was continued for another 8 h. After cooling the mixture was treated with brine, the organic layer was separated, washed successively with a dilute hydrochloric acid (1 : 5) and with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was distilled off *in vacuo* and the residue was treated with a methanolic solution (150 ml) of *p*-toluenesulphonic acid (2 g) under reflux for 1 h. The product was isolated analogously as in the procedure *A* (Tables I and II).

Reduction of the Acetylenic Alcohols *Ila*, *Va* and *XIIa*  
with LiAlH<sub>4</sub> in Diglyme: Synthesis of the (*E*)-Isomers *IIIa*, *VIIa* and *XIIIa*

The appropriate alkynol (14 mmol) was added to a slurry of LiAlH<sub>4</sub> (1.5 g; 40 mmol) in a mixture of tetrahydrofuran (6 ml) and diethylene glycol dimethyl ether (26 ml). The reaction flask was placed into a bath and the bath temperature was gradually raised (140°C) until about 4 ml

TABLE III  
(*E*)- and (*Z*)-Olefinic alcohols

Compound	Yield %	M.p., °C	% <i>E</i> (% <i>Z</i> ) <sup>a</sup>	Formula (mol.weight)	Calculated/Found	
					% C	% H
<i>IIIa</i>	74	73–74 <sup>b</sup>	95 (— <sup>c</sup> )	C <sub>30</sub> H <sub>60</sub> O (436.8)	82.49 82.38	13.85 13.89
<i>VIIa</i>	61	64 <sup>b</sup>	90 (— <sup>c</sup> )	C <sub>30</sub> H <sub>58</sub> O (434.8)	82.87 83.18	13.45 13.35
<i>XIIIa</i>	87	40 <sup>d</sup>	99 (— <sup>c</sup> )	C <sub>19</sub> H <sub>38</sub> O (282.5)	80.78 80.74	13.56 13.46
<i>IVa</i>	85	58 <sup>b</sup>	<1 (>99)	C <sub>30</sub> H <sub>60</sub> O (436.8)	82.49 82.72	13.85 14.10
<i>VIIIa</i>	95	— <sup>e</sup>	1 (99)	C <sub>30</sub> H <sub>58</sub> O (434.8)	82.87 83.14	13.45 13.52
<i>IXa</i>	96	40–41 <sup>b</sup>	49 (51)	C <sub>30</sub> H <sub>58</sub> O (434.8)	82.87 83.18	13.45 13.61

<sup>a</sup> Overall isomer purity estimated by IR spectrometry; *cf.* Experimental. <sup>b</sup> Crystallized from methanol. <sup>c</sup> Not determined. <sup>d</sup> Crystallized from light petroleum. <sup>e</sup> A viscous oil.

of a low boiling distillate (b.p. 64°C) was collected. The mixture was then kept under reflux for 10 h and decomposed after cooling with ice-water, dilute hydrochloric acid (1 : 1) and extracted with dichloromethane. The combined extracts were washed with water and dried over CaSO<sub>4</sub>. The solvent was distilled off *in vacuo* and the residue was crystallized from methanol or from light petroleum and identified by elemental analysis (Table III), and spectral data (Table IV).

Hydrogenation of the Acetylenic Alcohols *Ila*, *Va* and *Vla* over the P2 Nickel Catalyst: Synthesis of the (*Z*)-Isomers *Iva*, *VIIIa* and *IXa*

Solution of the appropriate acetylenic alcohol (2.7 mmol) in diethyl ether (30 ml) was added to a suspension of P-2 nickel catalyst<sup>8</sup> (10 mmol) in ethanol (80 ml) containing ethylenediamine (2 ml; 30 mmol) and hydrogenated at atmospheric pressure and room temperature until consumption of hydrogen ceased. The catalyst was sucked off through a layer of silica, the filtrate was diluted with water and extracted repeatedly with ether. The combined extracts were dried

TABLE IV  
(*E*)- and (*Z*)-Alkenols: spectral data

Alkenol	I.R. (CS <sub>2</sub> ) ν(OH), cm <sup>-1</sup>	M <sup>+</sup> , <i>m/e</i>	<sup>1</sup> H NMR <sup>a</sup> δ, ppm
<i>IIIa</i>	3 630	436	0.86 (dist. t, 3 H, CH <sub>3</sub> ); 1.26 (bs, 48 H, CH <sub>2</sub> ); 1.83–2.08 (m, 4 H, =CH—CH <sub>2</sub> ); 3.60 (t, <i>J</i> = 6 Hz, 2 H, CH <sub>2</sub> OH); 5.26–5.40 (m, 2 H, =CH—)
<i>VIIa</i>	3 628, 3 350	434	0.85 (dist. t, 3 H, CH <sub>3</sub> ); 1.25 (bs, 40 H, CH <sub>2</sub> ); 1.73–2.10 (m, 8 H, =CH—CH <sub>2</sub> ); 3.32–3.65 (m, 2 H, CH <sub>2</sub> OH); 5.17–5.43 (m, 4 H, =CH—)
<i>XIIIa</i>	3 630	282	0.86 (dist. t, 3 H, CH <sub>3</sub> ); 1.25 (bs, 26 H, CH <sub>2</sub> ); 1.73–2.13 (m, 4 H, =CH—CH <sub>2</sub> ); 2.50 (s, 1 H, OH); 3.35–3.65 (m, 2 H, CH <sub>2</sub> OH); 5.20–5.43 (m, 2 H, =CH—)
<i>IVa</i>	3 630	436	0.86 (dist. t, 3 H, CH <sub>3</sub> ); 1.26 (bs, 48 H, CH <sub>2</sub> ); 1.88–2.12 (m, 4 H, =CH—CH <sub>2</sub> ); 3.60 (t, <i>J</i> = 7 Hz, 2 H, CH <sub>2</sub> OH); 5.29 (m, 2 H, =CH—)
<i>VIIIa</i>	3 625, 3 345	434	0.88 (dist. t, 3 H, CH <sub>3</sub> ); 1.28 (bs, 40 H, CH <sub>2</sub> ); 1.75–2.25 (m, 8 H, =CH—CH <sub>2</sub> ); 3.52–3.82 (m, 2 H, CH <sub>2</sub> OH); 5.37 (m, 4 H, =CH—)
<i>IXa</i>	3 628, 3 350	434	0.87 (dist. t, 3 H, CH <sub>3</sub> ); 1.27 (bs, 40 H, CH <sub>2</sub> ); 1.75–2.25 (m, 8 H, =CH—CH <sub>2</sub> ); 3.63 (m, 2 H, CH <sub>2</sub> OH); 5.23–5.53 (m, 4 H, =CH—)

<sup>a</sup> In CDCl<sub>3</sub> (*IIIa*, *IVa*, *VIIIa* and *IXa*) or in CCl<sub>4</sub> (*VIIa* and *XIIIa*).

over  $\text{CaSO}_4$  and taken down *in vacuo*. The product was crystallized from methanol and identified by elemental analysis (Table III) and spectral data (Table IV).

Hydrogenation of the Acetylenic Alcohols *Ila* and *Va* over the Adams Catalyst:  
Synthesis of 1-Triacontanol (*Ia*)

The magnetically stirred solution of *Ila* (0.5 g; 1.1 mmol) in ethanol (50 ml) was hydrogenated in presence of  $\text{PtO}_2$  (0.05 g) at atmospheric pressure under reflux (2 h). The solution was treated with charcoal, filtered and taken down on aspirator. Yield 0.45 g (90%), m.p. 87–88°C (ethanol; lit.<sup>9-17</sup> 86.3–88.5°C). For  $\text{C}_{30}\text{H}_{62}\text{O}$  (438.8) calculated: 82.11% C, 14.24% H; found: 82.39% C, 14.38% H. Mass spectrum:  $M^+$  438. Analogous results were obtained by hydrogenation of the diynol *Va* under the same conditions.

Alkyl Bromides *XIb*–*XIIIb*

To a stirred solution of triphenylphosphine (11.1 g; 42 mmol) in dioxane (45 ml) was added bromine (6.8 g; 42 mmol) at 20°C, followed by pyridine (7.1 ml) at 15°C and by the appropriate alcohol (*XIa*–*XIIIa*; 35 mmol) in dioxane (20 ml) at 10°C. After stirring at room temperature for 3 h the mixture was poured into ice-water (1.5 l) and extracted several times with light petroleum (500 ml). The combined extract was washed with water, 1M hydrochloric acid, water and dried ( $\text{Na}_2\text{SO}_4$ ). The solution was taken down on aspirator, the residue was transferred into a column of neutral alumina (70 g; activity II) and the product was eluted with light petroleum and distilled. Yields, boiling points and elemental analyses are summarized in Table V.

Trimethylsilylation of the Alcohols *Ia*–*IXa*

The appropriate alcohol (4 mg) was dissolved in chloroform (0.3 ml) and treated with N,O-bis(trimethylsilyl)trifluoroacetamide (0.1 ml) in a sealed tube for 1 h at 80°C. A sample of the reaction mixture was directly injected into gas-chromatographic column.

TABLE V  
Alkyl bromides *XIb*–*XIIIb*

Compound	Yield, %	B.p., °C/Pa	Formula (mol. weight)	Calculated/Found		
				% C	% H	% Br
<i>XIb</i>	75	144/133	$\text{C}_{19}\text{H}_{39}\text{Br}$ (347.4)	65.69	11.31	23.00
				65.80	11.46	22.74
<i>XIIb</i>	73	145/133	$\text{C}_{19}\text{H}_{35}\text{Br}$ (343.4)	66.46	10.27	23.27
				66.20	10.27	23.49
<i>XIIIb</i>	71	146/66	$\text{C}_{19}\text{H}_{37}\text{Br}$ (345.4)	66.07	10.80	23.13
				66.01	10.97	22.86

TABLE VI  
Kováts retention indices *I* of the alcohols (OH), acetates (OAc) and trimethylsilyl ethers (OTMS) *I*—*IX* at 270°C

Com- pound	SE-30			OV-17			POLY-S 179		
	OH	OAc	OTMS	OH	OAc	OTMS	OH	OAc	OTMS
<i>I</i>	3 288.6 ± 0.5	3 399.4 ± 1.3	3 346.8 ± 0.9	3 412.6 ± 0.9	3 511.9 ± 0.4	3 340.4 ± 0.5	3 726.7 ± 0.6	3 724.4 ± 0.6	3 321.8 ± 2.6
<i>II</i>	3 276.3 ± 0.4	3 381.9 ± 1.2	3 329.8 ± 0.8	3 492.7 ± 1.4	3 589.2 ± 0.4	3 416.1 ± 0.9	3 890.4 ± 1.3	3 873.4 ± 1.1	3 455.3 ± 1.9
<i>III</i>	3 263.9 ± 0.1	3 371.2 ± 0.7	3 319.5 ± 0.2	3 414.4 ± 1.5	3 510.1 ± 0.8	3 339.2 ± 1.4	3 755.7 ± 2.3	3 748.2 ± 1.3	3 337.9 ± 2.3
<i>IV</i>	3 257.6 ± 0.8	3 362.5 ± 0.9	3 309.5 ± 1.4	3 407.4 ± 0.9	3 502.7 ± 0.1	3 330.8 ± 1.9	3 754.6 ± 1.5	3 745.8 ± 1.5	3 336.9 ± 1.7
<i>V</i>	3 274.2 ± 1.0	3 379.7 ± 0.6	3 327.3 ± 1.6	3 589.5 ± 0.2	3 682.0 ± 0.9	3 506.0 ± 1.9	4 071.9 ± 1.2	4 053.3 ± 2.2	3 610.2 ± 1.0
<i>VI</i>	3 257.7 ± 0.6	3 362.1 ± 1.1	3 309.5 ± 0.5	3 501.0 ± 0.3	3 595.9 ± 0.1	3 422.8 ± 1.0	3 919.3 ± 0.2	3 904.7 ± 1.1	3 481.3 ± 0.5
<i>VII</i>	3 242.5 ± 1.4	3 351.5 ± 0.5	3 300.6 ± 0.8	3 420.2 ± 0.1	3 518.0 ± 0.3	3 346.0 ± 1.1	3 783.1 ± 0.6	3 785.8 ± 0.7	3 365.3 ± 1.4
<i>VIII</i>	3 232.8 ± 0.2	3 338.9 ± 0.3	3 286.8 ± 0.4	3 410.3 ± 0.4	3 505.9 ± 0.6	3 333.4 ± 2.2	3 783.6 ± 1.4	3 783.5 ± 0.5	3 362.1 ± 0.8
<i>IX</i>	3 235.8 ± 0.3	3 342.2 ± 0.8	3 290.5 ± 1.1	3 413.8 ± 0.1	3 510.2 ± 0.3	3 338.6 ± 0.6	3 782.7 ± 0.8	3 774.0 ± 0.8	3 361.1 ± 1.8



Acetylation of the Alcohols *Ia*—*IXa*

A mixture of the appropriate alcohol (0.2 mmol), pyridine (3 ml) and acetic anhydride (3 ml) was heated at 70–80°C for 1 h. The mixture was diluted with water and extracted with pentane. The combined extract was washed successively with a dilute hydrochloric acid (1 : 1) and water, dried (MgSO<sub>4</sub>) and taken down.

## Analytical Methods

**Infrared spectrometry:** Isomer purity in the resulting olefinic alcohols *IIIa*, *IVa*, *VIIa*—*IXa* and *XIIIa* was estimated by a comparison of the molar extinction coefficients of the bands due to the out-of-plane bending vibration  $\gamma(=CH)$  at 967 cm<sup>-1</sup> and  $\gamma(=CH)$  at 716 cm<sup>-1</sup> with the corresponding ones determined in (*E*)- and (*Z*)-5-decenes, respectively. Incomplete separation of the bands  $\gamma(=CH)$  at 716 cm<sup>-1</sup> and  $\rho(CH_2)$  at 722 cm<sup>-1</sup> (deformation bending) was solved by a comparison of the molar extinction coefficient of  $\rho(CH_2)_n$  in the individual olefinic alcohols with those found in the corresponding alkynols *Ila* or *Va*.

**Gas chromatography:** Glass columns (0.24 × 185 cm) packed with 3% SE-30 on GAS-CHROM Q (80–100 mesh; pretested G.C. packing, lot SP-1323, effective theoretical plate number  $N = 2450$ , adjusted retention time  $t'_R = 9.5$  min (47.5 mm) for n-C<sub>34</sub>H<sub>70</sub>;  $t'_R = 7.2$  min (36.2 mm) for *Ia*), 3% OV-17 on GAS-CHROM Q (100–120 mesh;  $N = 3200$ ,  $t'_R = 18.2$  min (91.2 mm) for n-C<sub>34</sub>H<sub>70</sub>;  $t'_R = 18.5$  min (92.6 mm) for *Ia*), and 3% POLY-S 179 on GAS-CHROM Q (100–120 mesh;  $N$  value was not determined owing to asymmetry and tailing of n-alkanes,  $t'_R = 4.6$  min (23 or 46 mm) for n-C<sub>36</sub>H<sub>74</sub>;  $t'_R = 6.0$  min (30 mm) for *Ia*). All phases, supports and standard n-alkanes were purchased from Science Applied Laboratory U.S.A., except for n-C<sub>38</sub>H<sub>78</sub> (Alltech Associates, U.S.A.). A mixture containing predominantly odd n-alkanes (C<sub>29</sub>—C<sub>39</sub>) were isolated from the cuticular wax of leaves of *Hoya carnosa* R. Br.<sup>19</sup>. Free alcohols *Ia*—*IXa*, their trimethylsilyl (*Ib*—*IXb*) and acetyl (*Ic*—*IXc*) derivatives have been injected in 1% w/v concentration in CHCl<sub>3</sub>. The volumes of individual samples (together with a pair of n-alkanes) did not exceed 1.5  $\mu$ l. The "solvent flush" method<sup>20</sup> has been used. The Kováts retention indices<sup>21,22</sup>  $I$  were determined at column temperature 270°C (detector temperature 270°C; injector (with glass insert) temperature 280°C; N<sub>2</sub> flow rate 40 ml/min; chart speed 5 mm/min except for the derivatives *Ib*—*IXb* on POLY-S 179 (10 mm/min)). Mean values  $I$  summarized in Table VI were calculated from at least three measurements; the error is expressed as an estimate of standard deviation.

*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 <sup>1</sup>H NMR spectra were recorded by Dr M. Synáčeková. The mass spectra were recorded by Dr A. Trka.*

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