

## Tertiary Acetylene Alcohols Prepared from 1-Octadecyne\*

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**Abstract**—Synthesis of tertiary acetylene alcohols was developed based on 1-octadecyne treatment with butyllithium followed by reaction of 1-octadecynyllithium with aliphatic, aromatic, alicyclic, and terpene ketones.

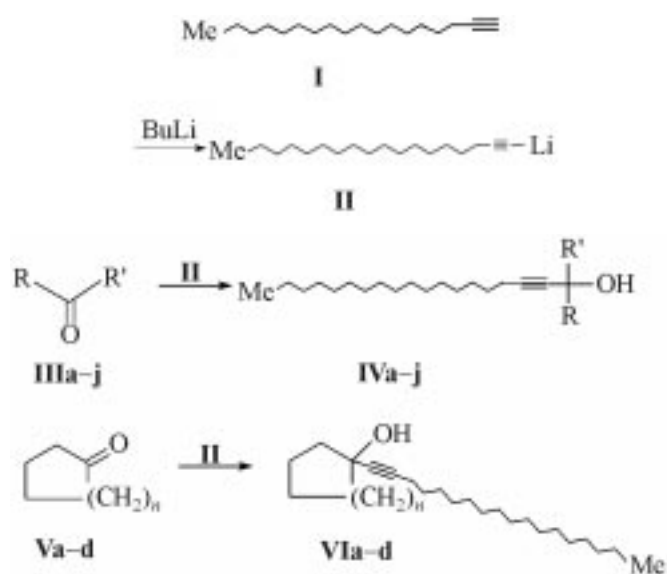
Derivatives of alcohols with a long hydrocarbon backbone possess amphiphilic properties and are used as thin film materials and surfactants [1]. The acetylene alcohols were established besides to process high biological activity [2].

The target of this study was preparation of tertiary acetylene alcohols **IVa–j**, **VIa–d**, **VIII**, **Xa, b**, **XII**, **XIVa, b**, **XVI**, **XVIII** by reaction between 1-octadecynyllithium (**II**) obtained by treating 1-octadecyne (**I**) with butyllithium and aliphatic **IIIa–f**, aromatic **IIIg–j**, alicyclic **Va–d** ketones, acetylferrocene (**VII**), *R*-(–) and *S*-(+)-carvone (**IXa, b**), isocamphanone

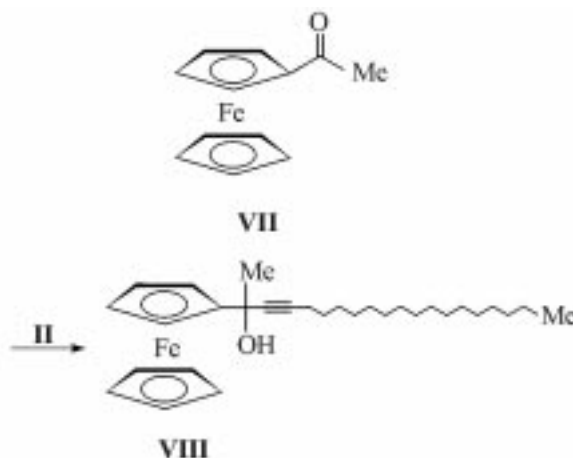
(**XI**), (1*R*,4*R*)-(+)– and (1*S*,4*S*)-(–)-camphor (**XIIIa, b**), (1*S*)-(+)–fenchone (**XV**), and isofenchone (**XVII**).

It was established that with terpene ketones **IXa, b**, **XI**, **XIIIa, b**, **XV**, **XVII** the reaction proceeded stereospecifically affording a single isomer of alcohol. Basing on the previous detailed investigation of <sup>13</sup>C NMR spectra of model acetylene alcohols prepared from such ketones [3, 4] we assigned to compound **XII** a structure with the *endo*-position of hydroxy group and to compounds **XIVa, b**, **XVI**, **XVIII** with the *exo*-position of this group. Tertiary acetylene alcohols **IVa–j**, **VIa–d**, **VIII**, **Xa, b**, **XII**, **XIVa, b**, **XVI**, **XVIII** after purification by column chromatography on Al<sub>2</sub>O<sub>3</sub> were isolated in preparative yield of 62–75%.

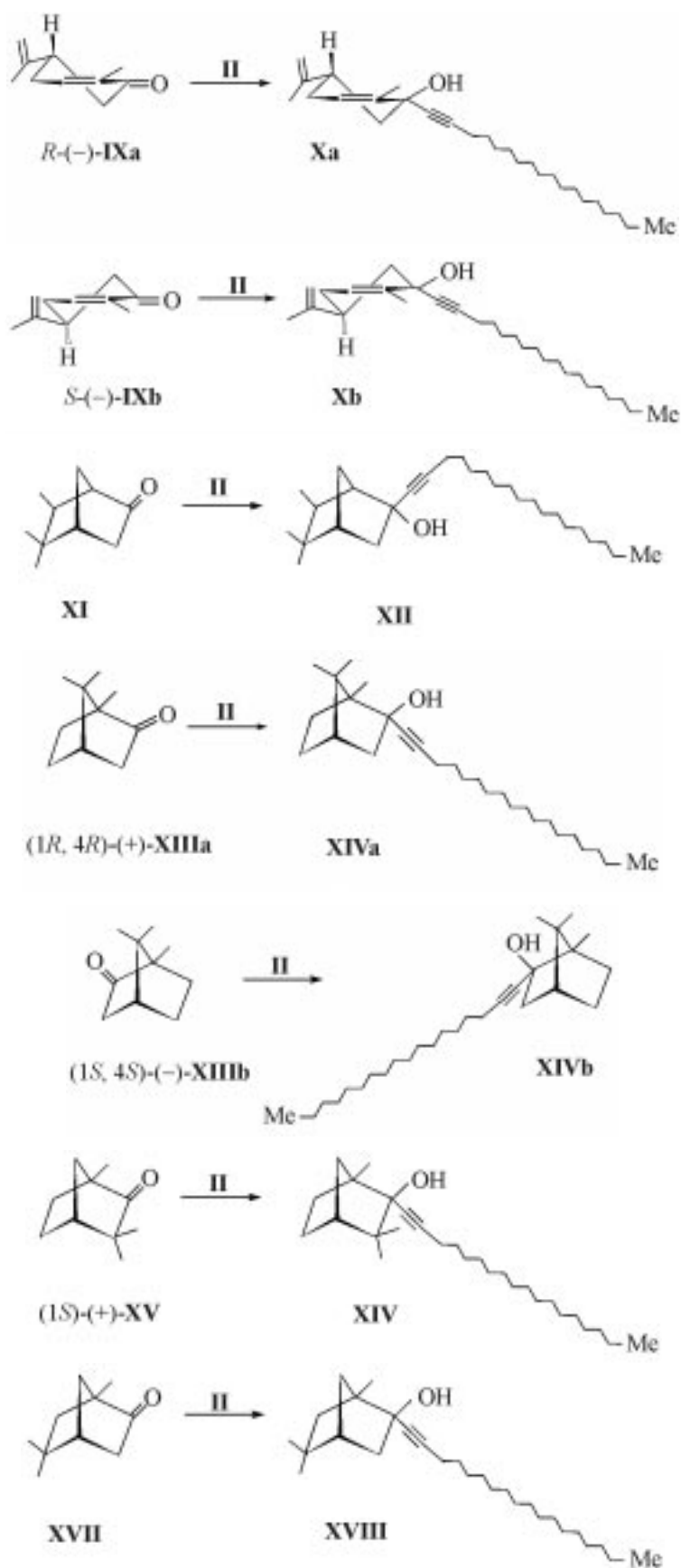
The composition and structure of compounds synthesized was established from elemental analyses, IR, UV, and <sup>1</sup>H NMR spectra presented in Tables 1–3. In the IR spectra of compounds obtained the absorption bands of carbonyl groups characteristic of initial ketones in 1700 cm<sup>–1</sup> region disappear, and the absorption bands of O–H and C–O bonds are observed in the range 3330–3475 and 920–1070 cm<sup>–1</sup>



**III, IV**, R = R' = Me (**a**); R = R' = CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (**b**); R = Me; R' = Et (**c**), *t*-Bu (**d**), (CH<sub>2</sub>)<sub>5</sub>Me (**e**), (CH<sub>2</sub>)<sub>2</sub>CH=CH<sub>2</sub> (**f**), Ph (**g**), α-C<sub>10</sub>H<sub>7</sub> (**h**), β-C<sub>10</sub>H<sub>7</sub> (**i**); R = Ph, R' = C<sub>6</sub>H<sub>4</sub>-OMe-*p* (**j**); **V, VI**, *n* = 1 (**a**), 2 (**b**), 3 (**c**), 8 (**d**).



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**Table 1.** Yields, physical properties, and elemental analyses of compounds **IVa-j**, **VIa-d**, **VIII**, **Xa, b**, **XII**, **XIVa, b**, **XVI**, **XVIII**

Compd. no.	Yield, %	$d_{20}^{20}$	$d_D^{20}$	Found, %		Formula	Calculated, %		<i>M</i>	
				C	H		C	H	found	calculated
<b>IVa</b> <sup>a</sup>	69	–	–	81.93	13.10	C <sub>21</sub> H <sub>40</sub> O	81.75	13.07	296.3	308.5
<b>IVb</b>	68	0.8119	1.4640	82.51	13.43	C <sub>25</sub> H <sub>48</sub> O	82.35	13.27	350.1	364.7
<b>IVc</b>	62	0.8409	1.4640	82.11	13.31	C <sub>22</sub> H <sub>42</sub> O	81.92	13.12	306.7	322.6
<b>IVd</b>	73	0.8185	1.4655	82.54	13.46	C <sub>24</sub> H <sub>46</sub> O	82.21	13.22	338.8	350.6
<b>IVe</b>	72	0.8229	1.4640	82.71	13.44	C <sub>26</sub> H <sub>50</sub> O	82.47	13.31	366.2	378.7
<b>IVf</b>	62	0.8356	1.4710	82.93	12.79	C <sub>24</sub> H <sub>44</sub> O	82.69	12.72	330.4	348.6
<b>IVg</b>	68	0.9446	1.4965	84.56	11.51	C <sub>26</sub> H <sub>42</sub> O	84.26	11.42	355.8	370.6
<b>IVh</b>	73	0.9451	1.5375	86.04	10.83	C <sub>30</sub> H <sub>44</sub> O	85.65	10.54	398.1	420.7
<b>IVi</b>	71	0.8154	1.5325	85.94	10.77	C <sub>30</sub> H <sub>44</sub> O	85.65	10.54	408.5	420.7
<b>IVj</b>	75	0.9121	1.5285	83.38	10.24	C <sub>32</sub> H <sub>46</sub> O <sub>2</sub>	83.06	10.02	449.6	462.7
<b>VIa</b> <sup>a</sup>	68	–	–	82.81	12.83	C <sub>23</sub> H <sub>42</sub> O	82.57	12.65	306.9	334.6
<b>VIb</b> <sup>a</sup>	72	–	–	82.85	12.79	C <sub>24</sub> H <sub>44</sub> O	82.69	12.72	330.4	348.6
<b>VIc</b> <sup>a</sup>	66	–	–	83.07	12.91	C <sub>25</sub> H <sub>46</sub> O	82.80	12.79	349.1	362.6
<b>VI d</b> <sup>a</sup>	71	–	–	83.64	13.23	C <sub>30</sub> H <sub>56</sub> O	83.26	13.04	419.0	432.8
<b>VIII</b> <sup>b</sup>	69	0.8963	1.5325	75.48	9.91	C <sub>30</sub> H <sub>46</sub> FeO	75.30	9.69	460.3	478.5
<b>Xa</b>	65	0.8787	1.4935	84.11	12.15	C <sub>28</sub> H <sub>48</sub> O	83.93	12.07	389.4	400.7
<b>Xb</b>	69	0.8589	1.4885	84.06	12.21	C <sub>28</sub> H <sub>48</sub> O	83.93	12.07	388.7	400.7
<b>XII</b>	68	0.9216	1.4830	83.91	12.65	C <sub>28</sub> H <sub>50</sub> O	83.51	12.51	390.3	402.7
<b>XIVa</b>	70	0.9046	1.4870	83.81	12.71	C <sub>28</sub> H <sub>50</sub> O	83.51	12.51	389.4	402.7
<b>XIVb</b>	66	0.906	1.4880	83.78	12.73	C <sub>28</sub> H <sub>50</sub> O	83.51	12.51	391.6	402.7
<b>XVI</b>	68	0.8492	1.4840	83.96	12.81	C <sub>28</sub> H <sub>50</sub> O	83.51	12.51	388.0	402.7
<b>XVIII</b>	67	0.8863	1.4855	83.71	12.75	C <sub>28</sub> H <sub>50</sub> O	83.51	12.51	390.5	402.7

<sup>a</sup> mp, °C: 24–25 (**IVa**), 28–29 (**VIa**), 34–35 (**VIb**), 24–25 (**VIc**), 33–34 (**VI d**). <sup>b</sup> Found, %: Fe 10.98. Calculated, %: 11.67.

respectively. Characteristic absorption bands of triple bonds vibrations appear at 2225–2245 cm<sup>-1</sup> (Table 3). In the UV spectra of the alcohols a band at 201–225 nm is present whose intensity varies within wide limits depending on the type of groups attached to OH (Table 3). The highest molecular extinction (80000) is observed for naphthalene derivatives **IVh**, **i**.

In the <sup>1</sup>H NMR spectra of compounds synthesized alongside the signals from proton-containing moieties present in the initial ketones the resonances from octadecyne rest are observed and a broadened singlet of OH group at 1.79–2.72 ppm; the latter in the spectra of compounds **VIa–d**, **Xa, b**, **XII**, **XIVa, b**, **XVI**, **XVIII** is overlapped with multiplets of the octadecyne and alicyclic fragments. Since the ketones reacted with octadecynyllithium exactly at the carbonyl group and the other centers of the initial ketones remained intact, the attribution of methyl group signals to *exo*- and *endo*-positions in the rings of compounds **XII**, **XIVa, b**, **XVI**, **XVIII** was carried out by analogy to the known data for derivatives of isocamphanone, camphor, fenchone, and

isofenchone: the upfield signal was assigned to a methyl located in the *endo*-position to the ring, and the downfield signal corresponded to the methyl in the *exo*-position [5]. The integral intensities are consistent with the assumed assignments (Table 2).

Tertiary acetylene alcohols prepared from carvone, camphor, and fenchone **IXa, b**, **XIIIa, b**, **XV** are optically active,  $[\alpha]_D^{20}$ : –107 (**Xa**), +112 (**Xb**), +23 (**XIVa**), –18 (**XIVb**), –9° (**XVI**).

Compounds **IVa–j**, **VIa–d**, **VIII**, **Xa, b**, **XII**, **XIVa, b**, **XVI**, **XVIII** are stable at storage in the dark in sealed ampoules. The tertiary alcohols from cyclopentanone and acetylferrocene **VIa**, **VIII** are sensitive to heating and over 60–80°C suffer dehydration to yield the corresponding enynes as we have formerly shown on the other alicyclic acetylene alcohols [6]. In the IR spectra of compounds **VIa**, **VIII** appears a characteristic absorption band of vibrations from the conjugated C=C bond at 1620±5 cm<sup>-1</sup>, and in the <sup>1</sup>H NMR spectra a signal of olefin proton is present at 5.8 ppm.

**Table 2.**  $^1\text{H}$  NMR spectra of compounds **IVa-j**, **VIa-d**, **VIII**, **Xa, b**, **XII**, **XIVa, b**, **XVI**, **XVIII**

Compd. no.	$^1\text{H}$ NMR spectra, $\delta$ , ppm
<b>IVa</b>	0.88 t (3H, Me), 1.15–1.70 m [28H, $(\text{CH}_2)_{14}$ ], 1.50 s (6H, $\text{Me}_2\text{C}$ ), 1.94 s (1H, OH), 2.17 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>IVb</b>	0.80–1.03 m (9H, 3Me), 1.15–1.70 m [36H, 2 $(\text{CH}_2)_2$ and $(\text{CH}_2)_{14}$ ], 1.81 s (1H, OH), 2.19 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>IVc</b>	0.87 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 1.02 t (3H, $\text{MeCH}_2$ ), 1.20–1.80 m [28H, $(\text{CH}_2)_{14}$ ], 1.44 s (3H, $\text{MeCC}\equiv\text{C}$ ), 1.66 q (2H, $\text{CH}_2\text{Me}$ ), 1.89 s (1H, OH), 2.18 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>IVd</b>	0.88 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 1.03 s (9H, $\text{Me}_3\text{C}$ ), 1.20–1.60 m [28H, $(\text{CH}_2)_{14}$ ], 1.41 s (3H, $\text{MeCC}\equiv\text{C}$ ), 1.79 s (1H, OH), 2.19 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>IVe</b>	0.90 t (6H, $2\text{MeCH}_2$ ), 1.15–1.70 m [38H, $(\text{CH}_2)_5$ and $(\text{CH}_2)_{14}$ ], 1.45 s (3H, $\text{MeCC}\equiv\text{C}$ ), 2.04 s (1H, OH), 2.17 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>IVf</b>	0.90 t (3H, Me), 1.15–2.45 m [32H, $(\text{CH}_2)_2$ and $(\text{CH}_2)_{14}$ ], 1.47 s (3H, $\text{MeCC}\equiv\text{C}$ ), 1.97 s (1H, OH), 2.20 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 4.90–5.18 m (2H, $\text{C}=\text{CH}_2$ ), 5.68–6.10 m (1H, $\text{CH}=\text{C}$ )
<b>IVg</b>	0.89 t (3H, Me), 1.15–1.65 m [28H, $(\text{CH}_2)_{14}$ ], 1.73 s (3H, $\text{MeCC}\equiv\text{C}$ ), 2.28 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.33 s (1H, OH), 7.25–7.73 m (5H, Ph)
<b>IVh</b>	0.89 t (3H, Me), 1.10–1.70 m [28H, $(\text{CH}_2)_{14}$ ], 2.02 s (3H, $\text{MeCC}\equiv\text{C}$ ), 2.25 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.55 s (1H, OH), 7.35–7.95 m, 8.65–8.85 m (7H, $\text{C}_{10}\text{H}_7$ )
<b>IVi</b>	0.89 t (3H, Me), 1.15–1.70 m [28H, $(\text{CH}_2)_{14}$ ], 1.81 s (3H, $\text{MeCC}\equiv\text{C}$ ), 2.31 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.46 s (1H, OH), 7.38–8.15 m (7H, $\text{C}_{10}\text{H}_7$ )
<b>IVj</b>	0.89 t (3H, Me), 1.15–1.70 m [28H, $(\text{CH}_2)_{14}$ ], 2.31 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.72 s (1H, OH), 3.76 s (3H, MeO), 6.74–7.62 m (9H, $\text{C}_6\text{H}_4$ and Ph)
<b>VIa</b>	0.89 t (3H, Me), 1.10–2.05 m [37H, OH, $(\text{CH}_2)_4$ and $(\text{CH}_2)_{14}$ ], 2.20 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>VIb</b>	0.88 t (3H, Me), 1.10–2.00 m [39H, OH, $(\text{CH}_2)_5$ and $(\text{CH}_2)_{14}$ ], 2.21 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>VIc</b>	0.89 t (3H, Me), 1.15–2.05 m [41H, OH, $(\text{CH}_2)_6$ and $(\text{CH}_2)_{14}$ ], 2.20 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>VI d</b>	0.89 t (3H, Me), 1.10–2.00 m [51H, OH, $(\text{CH}_2)_{11}$ and $(\text{CH}_2)_{14}$ ], 2.19 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>VIII</b>	0.88 t (3H, Me), 1.15–1.65 m [28H, $(\text{CH}_2)_{14}$ ], 1.68 s (3H, $\text{MeCC}\equiv\text{C}$ ), 2.29 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.45 s (1H, OH), 4.07–4.37 m (4H, $\text{C}_5\text{H}_4$ ), 4.21 s (5H, $\text{C}_5\text{H}_5$ )
<b>Xa</b>	0.89 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 1.10–2.70 m [34H, OH, CH, 2 $\text{CH}_2$ and $(\text{CH}_2)_{14}$ ], 1.73 s and 1.85 s (6H, 2 $\text{MeC}=\text{C}$ ), 2.22 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 4.74 s (2H, $\text{C}=\text{CH}_2$ ), 5.46 br.s (1H, $\text{MeCH}=\text{C}$ )
<b>Xb</b>	0.88 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 1.15–2.70 m [34H, OH, CH, 2 $\text{CH}_2$ and $(\text{CH}_2)_{14}$ ], 1.74 s and 1.86 s (6H, 2 $\text{MeC}=\text{C}$ ), 2.22 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 4.74 s (2H, $\text{C}=\text{CH}_2$ ), 5.46 br.s (1H, $\text{MeCH}=\text{C}$ )
<b>XII</b>	0.86 d (3H, $\text{C}^6\text{Me}$ , $J$ 7.0 Hz), 0.89 s (3H, $\text{C}^5\text{Me-endo}$ ), 0.90 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 1.02 s (3H, $\text{C}^5\text{Me-exo}$ ), 1.10–2.15 m [36H, OH, 3CH, 2 $\text{CH}_2$ and $(\text{CH}_2)_{14}$ ], 2.18 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>XIVa</b>	0.86 s (3H, $\text{C}^1\text{Me}$ ), 0.93 s (3H, $\text{C}^7\text{Me-endo}$ ), 0.94 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 1.06 s (3H, $\text{C}^7\text{Me-exo}$ ), 1.16–2.15 m [36H, OH, CH, $\text{CH}_2$ , $(\text{CH}_2)_2$ and $(\text{CH}_2)_{14}$ ], 2.19 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>XIVb</b>	0.87 s (3H, $\text{C}^1\text{Me}$ ), 0.93 s (3H, $\text{C}^7\text{Me-endo}$ ), 0.94 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 1.05 s (3H, $\text{C}^7\text{Me-exo}$ ), 1.10–2.00 m [36H, OH, CH, $\text{CH}_2$ , $(\text{CH}_2)_2$ and $(\text{CH}_2)_{14}$ ], 2.20 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>XVI</b>	0.92 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 0.94 s (3H, $\text{C}^1\text{Me}$ ), 1.00–1.84 m [36H, OH, CH, $\text{CH}_2$ , $(\text{CH}_2)_2$ and $(\text{CH}_2)_{14}$ ], 1.11 s (3H, $\text{C}^3\text{Me-endo}$ ), 1.17 s (3H, $\text{C}^3\text{Me-exo}$ ), 2.22 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )
<b>XVIII</b>	0.85 s (3H, $\text{C}^1\text{Me}$ ), 0.93 s (3H, $\text{C}^5\text{Me-endo}$ ), 0.94 t [3H, $\text{Me}(\text{CH}_2)_{15}$ ], 1.13 s (3H, $\text{C}^5\text{Me-exo}$ ), 1.15–2.15 m [36H, OH, CH, 3 $\text{CH}_2$ and $(\text{CH}_2)_{14}$ ], 2.20 t (2H, $\text{CH}_2\text{C}\equiv\text{C}$ )

## EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord 75IR from thin films.  $^1\text{H}$  NMR spectra were registered on spectrometer Tesla BS-567A in  $\text{CDCl}_3$  solutions, internal reference TMS. UV spectra were measured on Specord UV Vis instrument from solu-

tions of concentration  $1 \times 10^{-3}$  M (**IVa-e**, **VIa-d**, **XII**, **XIVa, b**, **XVI**, **XVIII**),  $1 \times 10^{-4}$  M (**IVf, g, j**, **VIII**), and  $1 \times 10^{-5}$  M (**IVh, i**) in methanol. The specific rotation of compounds **Xa, b**, **XIVa, b**, **XVI** was measured on SM-2 device from solutions of ~3.5% concentration in methanol. Molecular weight of compounds was determined by cryoscopy in benzene. The

**Table 3.** IR and UV spectra of compounds **IVa-j**, **VIa-d**, **VIII**, **Xa, b**, **XII**, **XIVa, b**, **XVI**, **XVIII**

Compd. no.	IR spectrum, $\nu$ , $\text{cm}^{-1}$	UV spectrum, $\lambda_{\text{max}}$ ( $\epsilon$ )
<b>IVa</b>	3360 (OH), 2980, 2960, 2925, 2855 (CH alkyl), 2240 (C≡C), 1470 (CH <sub>2</sub> ), 950 (C–O)	208 (300), 232 (170)
<b>IVb</b>	3420 (OH), 2960, 2925, 2875, 2855 (CH alkyl), 2235 (C≡C), 1470 (CH <sub>2</sub> ), 1010 (C–O)	204 (300), 230 (200)
<b>IVc</b>	3375 (OH), 2960, 2925, 2855 (CH alkyl), 2240 (C≡C), 1470 (CH <sub>2</sub> ), 920 (C–O)	203 (250), 234 (170)
<b>IVd</b>	3475 (OH), 2970, 2925, 2855 (CH alkyl), 2240 (C≡C), 1470 (CH <sub>2</sub> ), 1005 (C–O)	203 (300), 231 (150)
<b>IVe</b>	3380 (OH), 2960, 2875, 2860 (CH alkyl), 2240 (C≡C), 1470 (CH <sub>2</sub> ), 1025 (C–O)	204 (250), 235 (230)
<b>IVf</b>	3405 (OH), 3080 (=CH), 2960, 2880, 2810 (CH alkyl), 2240 (C≡C), 1645 (C=C), 1470 (CH <sub>2</sub> ), 1025 (C–O)	201 (800), 240 (900)
<b>IVg</b>	3380(OH), 3090, 3060, 3030 (CH arom), 2980, 2960, 2925, 2855 (CH alkyl), 2240 (C≡C), 1600, 1490 ( arom), 1470 (CH <sub>2</sub> ), 1025 (C–O), 765, 700 (CH arom)	206 (7000)
<b>IVh</b>	3425 (OH), 3055 (CH arom), 2955, 2925, 2855 (CH alkyl), 2240 (C≡C), 1595, 1505 (CH arom), 1470 (CH <sub>2</sub> ), 1025 (C–O), 805, 780 (CH arom)	221 (80000)
<b>IVi</b>	3425 (OH), 3060 (CH arom), 2980, 2955, 2930, 2855 (CH alkyl), 2245 (C≡C), 1600, 1505 (CH arom), 1470 (CH <sub>2</sub> ), 1025 (C–O), 855, 820, 750, 725 (CH arom)	225 (80000)
<b>IVj</b>	3470(OH), 3090, 3070, 3040, 3005 (CH arom), 2925, 2855 (CH alkyl), 2230 (C≡C), 1605, 1585, 1505 (CH arom), 1470 (CH <sub>2</sub> ), 1040 (C–O–Me), 1055 (C–OH), 830, 755, 725, 700 (CH arom)	203 (17000), 230 (9000)
<b>VIa</b>	3330 (OH), 2960, 2980, 2855, (CH alkyl), 2230 (C≡C), 1470 (CH <sub>2</sub> ), 1000 (C–O)	203 (300), 258 (500)
<b>VIb</b>	3360 (OH), 2925, 2855 (CH alkyl), 2230 (C≡C), 1470 (CH <sub>2</sub> ), 1070 (C–O)	203 (250), 220 (170)
<b>VIc</b>	3375 (OH), 2980, 2855 (CH alkyl), 2240 (C≡C), 1470 (CH <sub>2</sub> ), 1025 (C–O)	208 (300), 232 (170)
<b>VI d</b>	3450 (OH), 2955, 2980, 2960, 2850 (CH alkyl), 2235 (C≡C), 1470 (CH <sub>2</sub> ), 1005 (C–O)	204 (250), 222 (130)
<b>VIII</b>	3450(OH), 3100 (CH Cp), 2980, 2955, 2925, 2855 (CH alkyl), 2245 (C≡C), 1470 (CH <sub>2</sub> ), 1025 (C–O), 820 (CH Cp)	207 (24000)
<b>Xa</b>	3425 (OH), 3080, 3025 (=CH), 2925, 2855 (CH alkyl), 2225 (C≡C), 1645 (C=C), 1470 (CH <sub>2</sub> ), 1025 (C–O)	204 (7000)
<b>Xb</b>	3425 (OH), 3080, 3025 (=CH), 2925, 2855 (CH alkyl), 2225 (C≡C), 1645 C=C), 1470 (CH <sub>2</sub> ), 1025 (C–O)	204 (6000)
<b>XII</b>	3440 (OH), 2955, 2925, 2855 (CH alkyl), 2240 (C≡C), 1470 (CH <sub>2</sub> ), 1025 (C–O)	203 (200)
<b>XIVa</b>	3475 (OH), 2955, 2925, 2850 (CH alkyl), 2225 (C≡C), 1470 (CH <sub>2</sub> ), 1060 (C–O)	204 (600), 261 (800)
<b>XIVb</b>	3455 (OH), 2955, 2925, 2855 (CH alkyl), 2230 (C≡C), 1470 (CH <sub>2</sub> ), 1065 (C–O)	204 (600), 259 (700)
<b>XVI</b>	3475 (OH), 2960, 2930, 2875, 2855 (CH alkyl), 2230 (C≡C), 1470 (CH <sub>2</sub> ), 1050 (C–O)	204 (250), 227 (100)
<b>XVIII</b>	3470 (OH), 2955, 2930, 2855 (CH alkyl), 2235 (C≡C), 1470 (CH <sub>2</sub> ), 1050 (C–O)	204 (500), 251 (300)

compounds synthesized were pure to 95–98% as shown by <sup>1</sup>H NMR spectra and TLC (development by iodine vapor). To column chromatography was applied neutral Al<sub>2</sub>O<sub>3</sub> L 40/250  $\mu$  of II grade Brockmann activity. 1-Octadecyne was prepared by procedure from [7], butyllithium by method [8].

**2-Hydroxy-2-methyl-3-eicosyne (IVa)**, **4-hydroxy-4-propyl-5-docosyne (IVb)**, **3-hydroxy-3-methyl-4-heneicosyne (IVc)**, **3-hydroxy-2,2,3-trimethyl-4-heneicosyne (IVd)**, **7-hydroxy-7-methyl-8-pentaicosyne (IVe)**, **5-hydroxy-5-methyl-trieicos-1-en-6-yne (IVf)**, **2-hydroxy-2-phenyl-3-eicosyne (IVg)**, **2-hydroxy-2-(1-naphthyl)-3-eicosyne (IVh)**, **2-hydroxy-2-(2-naphthyl)-3-eicosyne (IVi)**, **1-hydroxy-1-phenyl-1-(4-methoxyphenyl)-2-nonadecyne (IVj)**, **1-hydroxy-1-octadecynylcyclopentane (VIa)**, **1-hydroxy-1-octadecynylcyclohexane (VIb)**, **1-hydroxy-1-octadecynylcycloheptane (VIc)**, **1-hydroxy-1-octadecynylcyclododecane (VI d)**, **2-hydroxy-2-ferrocenyl-3-eicosyne (VIII)**, **(5R)-(-)-1-hydroxy-5-isopropenyl-2-methyl-1-octadecynyl-2-cyclohexene (Xa)**, **(5S)-(+)-1-hydroxy-5-isopropenyl-2-methyl-1-octadecynyl-2-cyclohexene (Xb)**, **2-endo-hydroxy-2-exo-octadecynyl-5,5,6-trimethylbicyclo[2.2.1]heptane (XII)**, **(1R,2R,4R)-(+)-2-exo-hydroxy-2-endo-octadecynyl-1,7,7-trimethylbicyclo[2.2.1]heptane (XIVa)**, **(1S,2S,4S)-(-)-2-exo-hydroxy-2-endo-octadecynyl-1,7,7-trimethylbicyclo-**

[2.2.1]heptane (XIVb), (1S)-(-)-2-*exo*-hydroxy-2-*endo*-octadecynyl-1,3,3-trimethylbicyclo[2.2.1]heptane (XVI), 2-*exo*-hydroxy-2-*endo*-octadecynyl-1,5,5-trimethylbicyclo[2.2.1]heptane (XVIII). General procedure. To a solution of 0.013 mol of 1-octadecyne (**I**) in 20 ml of anhydrous tetrahydrofuran cooled to  $-40 \div -20^\circ\text{C}$  was added under an argon flow within 0.5 h 0.011 mol of butyllithium in hexane solution. The mixture was stirred for 1 h, and then 0.01 mol of ketones **IIIa-j**, **Va-d**, **VII**, **IXa, b**, **XI**, **XIIIa, b**, **XV**, **XVII** was added thereto, the mixture was warmed to  $20\text{--}23^\circ\text{C}$  within 1–2 h, the reaction mixture was stirred for 3–4 h more and left standing for 18 h. The lithium alcoholates formed were quenched with 100 ml of water, and alcohols **IVa-j**, **VIa-d**, **VIII**, **Xa, b**, **XII**, **XIVa, b**, **XV**, **XVIII** were extracted into hexane, the extract was dried with  $\text{CaCl}_2$ , the solvent was removed, the residue was kept under reduced pressure and then applied to a column packed with  $\text{Al}_2\text{O}_3$  ( $h$  15 cm,  $d$  2 cm). Unreacted 1-octadecyne was eluted with 150 ml of hexane, compounds **IVa-j**, **VIa-d**, **VIII**, **Xa, b**, **XII**, **XIVa, b**, **XV**, **XVIII** were eluted with a mixture of 200 ml of hexane and 50 ml of ethyl ether, and the solvent was removed.

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