SYNTHESIS OF TWO HEXAPRENOLS MODIFIED WITH RESPECT TO POSITION OF HYDROXY GROUP

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Studies on biosyntheses of polysaccharides and glycoproteins require a knowledge of influence of the structure of polyprenols [1], in particular the length and configuration of the chain, and also the positions of the hydroxyl group, on the membrane-active transport of monosaccharides [2-4]. The subject of the present article is the synthesis of hexaprenols (I) and (II), modified with respect to the position of the hydroxyl group.

From the previous results [5-7], it could be assumed that 2Z, 6E-configuration of (I) and 2E, 6Z geometry of (II) can be ensured by a directed aldol condensation at the stages of the creation of Δ^2- and Δ^6-bonds. The 10E, 14E, 18E-stereochemistry of (I) and (II) can be ensured by introducing into this condensation E, E, E-aldimine (III), which we have already described in [6] in connection with producing a Δ^6-bond. Therefore, the aldehyde component of the condensation, in which the Δ^6-bond is produced, should have structure (IV) for the synthesis of (I), and structure (V) for the preparation of (II) (scheme 1).

The simplest path for obtaining (IV) and (V) with a given configuration of the C=C bond was aldol condensation with the participation of aldimine (VI), a product of alkylation of N-cyclohexyl acetaldehyde imine by bromopropionaldehyde ethyleneacetal (scheme 2).

In fact, the condensation of (VI), deprotonated by means of i-Pr_2NLi, with acetaldehyde at −75°C, leads to a good yield of aldehydoacetal (VII), in which, according to the PMR data and in accordance with [5-7], the content of the E-isomer is above 85%. Since (VII) is unstable under distillation and chromatography conditions, without additional purification, it was quantitatively reduced to carbinol (VIII), a common precursor of (IV) and (V). As expected, treatment of (VIII) by pyridine sulfotrioxide, followed by reduction of the intermediate sulfo-ester by excess $LiAlH_4$ [8], give acetal (IX), which hydrolyzes to aldehyde (IV). Benzylation of (VIII) under conventional conditions with subsequent hydrolysis of the benzyloxyacetal (X) formed leads to aldehyde (V).

The condensation of (IV) and (V) with Li-(III) leads with preparative yields to E-acroleins (XI) and (XII), respectively (scheme 1). The stereoselectivity of the formation of (XI) is thus 97% and of (XII) 92% (PMR data). It should, however, be noted that storage of sample of (XII) in an argon atmosphere (~20°C, ~10 days) is accompanied by a decrease in the Z-isomer admixture to 1-2%. It is probable that the Z → E isomerization of aldehyde (XII), with a bulky substituent at C^3, proceeds more slowly than in the other cases that we studied. Reduction of (XI) gives the desired hexaprenol (I), while reduction of (XII) gives carbinol (XIII), which, as described above, was converted via the corresponding sulfo-ester, into benzyl ether (XIV), which is easily debenzylated into the desired hexaprenol (II).

The structure of all the above compounds was confirmed by elemental analysis and the total of all the physicochemical data. The results agree well with the previously discovered regularities. They conform, in particular, to the generality of the already discovered [6, 7] influence of functionalization of the Z-isoprenoid unit in the middle of the chain on the values of the chemical shifts (CS) of the carbon atoms composing this fragment. In ^{13}C NMR spectra of aldehydes (XI) and (XII), as in the spectra of disubstituted acroleins already studied, a triplet signal with δ ~ 24 ppm is observed under the conditions of selective heteronuclear $^{13}C-\{^1H\}$ resonance (SHR). Reduction of (XI) and (XII) by $NaBH_4$ into the corresponding carbinols (I) and (XIV) is accompanied by the disappearance of this signal and the appearance of a new triplet at δ ~ 28 ppm. It was shown [9] that these signals can be assigned to the C^8 atoms of the above compounds (Table 1).

Details of ^{13}C NMR spectra of disubstituted E-acroleins and their corresponding carbinols described in the present article and before [6, 7] will be discussed separately.

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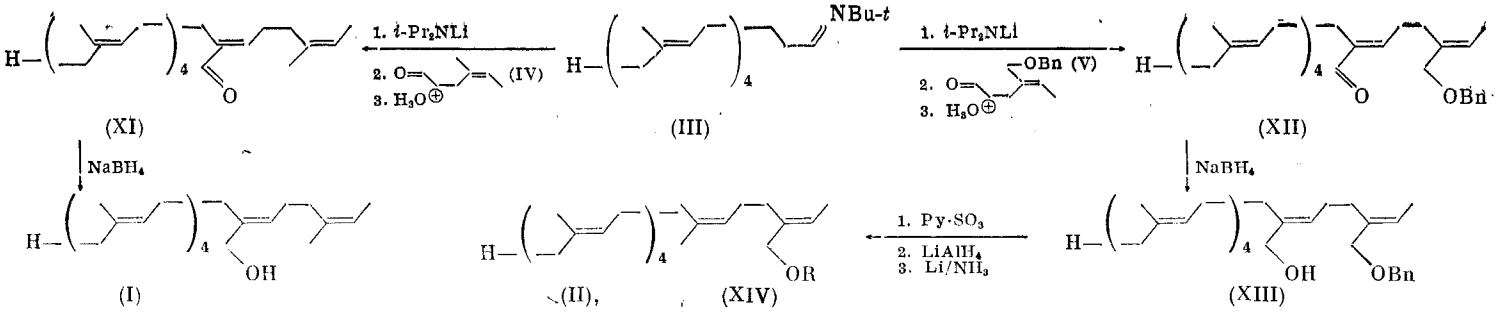
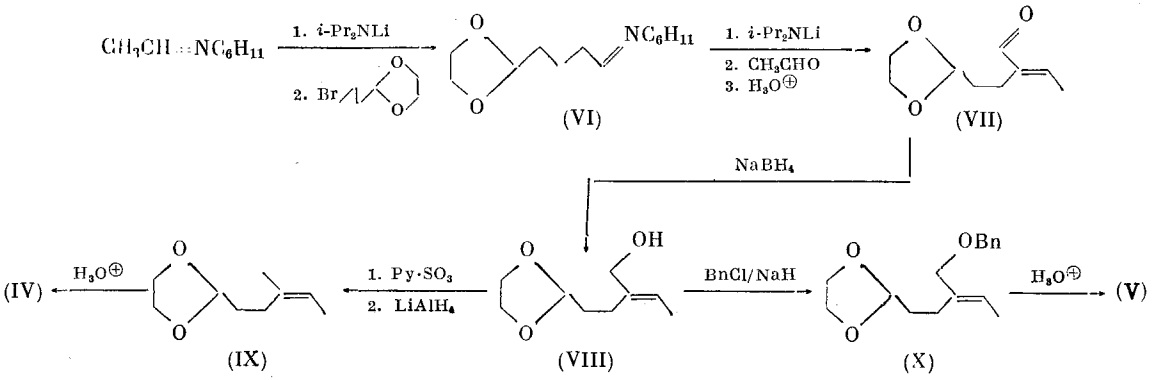
Scheme 1



(XI) (III) (XII) (I) (II), (XIV) (XIII)

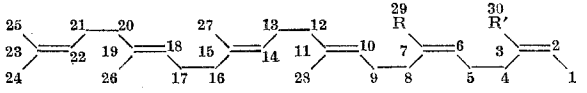
R = H (II), Bn(XIV); Bn—here and below designates $C_6H_5CH_2$

Scheme 2



(VI) (VII) (IX) (VIII) (X)

TABLE 1. ^{13}C NMR Spectra of Compounds (I), (II), (XI-XIV)



Fragment	Atom C^n	(XI) 29 R=CHO 30 R′=CH_3	(I) 29 R=CH_2OH 30 R′=CH_3	(XII) 29 R=CHO 30 31 R′=CH_2OCH_2Ph*	(XIII) 29 R=CH_2OH 30 31 R′=CH_2OCH_2Ph*	(XIV) 29 R=CH_3 30 31 R′=CH_2OCH_2Ph*	(II) 29 R=CH_3 30 R′=CH_2OH
CH_3	C^1	13,4	13,3	13,1	12,9	13,0	12,9
	$C^{26, 27, 28}$	16,1	16,0	15,95	15,8	16,0	16,0
	C^{25}	17,7	17,7	17,6	17,4	17,6	17,6
	C^{30}	23,2	23,4	–	–	–	–
	C^{24}	25,7	25,7	25,6	25,4	25,6	25,5
CH_2	C^3	24,4	28,3	24,25	28,06 †	32,0	31,9
	$C^{5, 9, 13, 17, 21}$	26,8–27,3	25,9–27,1	26,65–27,0	26.0–26,9	26,5–26,8	26,4–26,7
	C^4	30,4	31,4	27,55	27,83 †	28,3	28,1
	$C^{12, 16, 20}$	39,8	39,8	39,7	39,55	39,7	39,7
CH_2O	C^{30}	–	–	71,9	71,5	71,7	67,2
	C^{31}	–	–	74,6	74,4	74,65	–
HC=C	C^2	120,6	119,4	123,4–124,5	123,2	123,1	121,09
	$C^{10, 14, 18, 22}$	123,5–124,6	124,0–124,5		123,5–124,3	124,2–125,1	124,1–124,8
	C^6	154,35	126,8	153,95	126,2		
CH_3C=C	C^{23}	131,25	131,1	131,1	130,8	131,1	131,0
	C^3	134,3–136,2	134,8–135,6	136,0	136,6	137,1	139,7
	$C^{11, 15, 19}$			134,8–135,8	134,6–135,2	134,9–135,4	134,8–135,5
	C^7	143,6	139,15	143,6	139,1		
R	C^{29}	195,0	67,3	194,7	66,8	23,4	23,3

*In the spectra of compounds (XII)-(XIV) there is also a set of signals characteristic of the C_6H_5 group: 127.4, 127.6, 128.3, and 138.5.

†The signals thus marked may change places.

EXPERIMENTAL

The IR spectra obtained on an UR-20 spectrophotometer and the UV spectra of alcoholic solutions on Specord UV-VIS spectrophotometer. The PMR spectra were measured with reference to TMS on Varian DA-60-IL, Tesla BS-497 (100 MHz), and Bruker WM-250 spectrometers. The ^{13}C NMR spectra of compounds (I), (II), (XI)-(XIV) in solutions in $CDCl_3$ were run on a Bruker WM-250 spectrometer (62.89 MHz) (see Table 1). The mass spectra (MS) were obtained at an ionizing voltage of 70 eV on a Variant MAT CH-6 spectrometer. The preparative chromatography was carried out in a flash-variant on silica gel L (40-100 μ) from the firm Chemapol. The GLC analysis was carried out on an LKhM-8MD chromatograph on columns (2 m) with Apiezone and SE-30 on Chromosorb W.

N-Cyclohexyl 5,5-Ethylenedioxypentan-1-al-imine (VI). A 17.6 ml portion (100 mmoles) of hexametapol were added under argon to a stirred and cooled (−15°C) solution of 100 mmoles of i-Pr_2NLi in a mixture of 70 ml of hexane and 15 ml of THF. The mixture was heated to 0°C, held for 10 min, and a solution of 12.5 g (100 mmoles) of acetaldehyde cyclohexylimine [10] in 20 ml of THF was added in the course of 40 min. The mixture was held at 0°C for another 20 min, and then was cooled to −70°C, and a solution of 16.4 g (90 mmoles) of 3-bromopropionaldehyde ethylene acetal [11] in 30 ml of THF was added slowly. After 10 min, the mixture was heated to −40°C, held at −40°C for 6 h, then poured into ice water and, after the usual treatment, 25.05 g of a light-yellow oil were obtained which, by distillation, gave 12.4 g (62%) of (VI), bp 115°C (1 mm). IR spectrum (CCl_4, ν, cm^{-1}): 700, 750-820, 900, 960, 1040, 1140, 1210, 1410, 1450, 1550, 1670, 2860-2930. PMR spectrum (CCl_4, δ, ppm): 1.44 m (14H, CH_2), 2.18 m (2H, CH_2C^2), 2.83 m (1H, CHN), 3.77 m (4H, CH_2O), 4.71 t (1H, HC^5, J = 4 Hz), 7.58 t (1H, HC^1, J = 4.5 Hz).

4-Formylhex-4E-en-1-al Ethylene Acetal (VII). A solution of 6.82 g (30.3 mmoles) of (VI) in 10 ml of ether was added in the course of 40 min to a stirred and cooled (−10°C) solution of 30.3 mmoles of i-Pr_2NLi in a mixture of 24 ml of hexane and 10 ml of ether. The mixture was held for 45 min at 0° then cooled to −75°C, and a solution of a freshly distilled MeCHO in 5 ml of ether was added in the course of 15 min. The mixture was held at −75°C for 3 h, and then was poured into a cold acetate buffer solution at pH 4.5. The organic layer was separated, and subjected to usual treatment to yield 4.4 g of a yellow oil, distillation of which gave 2.3 g (45%) of (VII), bp 85°C (1.5 mm). IR spectrum (CCl_4, ν, cm^{-1}): 900, 940, 990, 1040, 1150, 1180, 1400, 1465, 1645, 1690, 1730, 2720, 2820-2960. UV spectrum: λ_{max} 229 nm (ε 15,400). PMR spectrum (CCl_4, δ, ppm): 1.6 m (2H, CH_2), 2.03 d (3H, CH_3, J = 7.5 Hz), 2.33 m (2H, $CH_2C{=}C$), 3.85 m (4H, CH_2O), 4.68 t (1H, HC^1, J = 4.5 Hz), 6.50 q (1H, HC=C, J = 7.5 Hz), 9.28 s (1H, E-CHO), 10.08 (0.03 H, Z-CHO). MS (m/z): 170 M^+, 169, 141, 97, 73, 29. Found, %: C 63.53, H 8.52. $C_9H_{14}O_3$. Calculated, %: C63.51, H 8.29.

4-Hydroxymethylhex-4E-en-1-al ethylene acetal (VIII) was obtained in a yield of 98% by reducing (VII) with $NaBH_4$ in 96% ethanol. In the reduction of unpurified (VII), obtained from undistilled (VI), after chromatography by a gradient elution from hexane to ether (up to 25% of the latter), the yield of (VIII) was 52% [based on 3-bromopropionaldehyde ethylene acetal used for the preparation of (VI)], bp 85-87°C (1.5 mm). IR spectrum (in thin layer, ν, cm^{-1}): 610, 740, 900, 940, 980, 1040, 1090, 1140, 1410, 1450, 2870-2960, 3500, 3620. PMR spectrum ($CDCl_3$, δ, ppm): 1.61 d (3H, CH_3, J = 7 Hz), 1.74 m (2H, HC^2), 2.2 m (2H, HC^3), 2.51 br.s (1H, OH), 3.82 m and 3.92 m (4H, CH_2O), 3.99 br.s (1H, CH_2OH), 4.82 t (1H, HC^1, J = 4.5 Hz), 5.49 q (1H, HC^5, J = 7 Hz). ^{13}C NMR spectrum (δ, ppm): 12.8 q* (CH_3), 21.9 t and 32.2 t (C^2 and C^3), 64.8 t (CH_2O), 67.0 t (CH_2OH), 104.2 d (C^1), 121.6 d (C^5), 139.0 s (C^4). MS (m/z): 172 M^+, 154, 70, 69. Found, %: C 62.68, H 9.36. $C_9H_{16}O_3$. Calculated, %: C 62.70, H 9.36.

4-Methylhex-4Z-en-1-al Ethylene Acetal (IX). A 10.54 g portion (65.5 mmoles) of $Py{\cdot}SO_3$ was added in the course of 10 min to a stirred (Ar) and cooled (0°C) solution of 7.47 g (43.7 mmoles) of (VIII) in 50 ml of THF. The mixture was held for 1 h at 0°C, then cooled to −30 °C, and a solution of 168 mmoles of $LiAlH_4$ in 330 ml of THF was added in the course of 1 h. The temperature was slowly raised to ~20°C and the mixture was allowed to stand for 4 days, with controlling the course of the reaction by TLC. The mixture was cooled to −10°C, and cautiously decomposed by ~2% NaOH. After the usual treatment, 5.01 g of a light-yellow oil were obtained, which were chromatographed on 100 g of SiH_2. By a gradient elution from hex-

*In the ^{13}C NMR spectra of compounds (VIII) and (X) the letters indicate the form of signal under the SHR conditions.

ane to ether (up to 5% of the latter), 4.70 g (68%) of (IX) was isolated, bath temperature 46°C (2 mm). IR spectrum (CCl_4, ν, cm^{-1}): 900, 945, 980, 1005, 1040, 1140, 1405, 1450, 1600, 2880-2990. PMR spectrum ($CDCl_3$, δ, ppm): 1.52 d (3H, CH_3C^5, J = 7 Hz), 1.63 s (3H, CH_3), 1.68 m (2H, HC^2), 2.09 m (2H, HC^3), 3.79 m and 3.92 m (4H, CH_2O), 4.79 t (1H, HC^1, J = 4.5 Hz), 5.17 q (1H, HC^5, J = 7 Hz). ^{13}C NMR spectrum (δ, ppm): 13.0 ($\underline{C}H_3C^5$), 23.1 ($\underline{C}H_3C^4$), 25.8 (C^2), 32.0 (C^3), 64.8 (CH_2O), 104.4 (C^1), 119.4 (C^5), 135.1 (C^4). MS (m/z): 156 M^+, 87.28. Found, %: C 69.12, H 10.39. $C_9H_{16}O_2$. Calculated, %: C 69.19, H 10.32.

4-Methylhex-4Z-en-1-al (IV). A solution of 4.7 g (30 mmoles) of (IX) in 90 ml of acetone, containing 0.2 ml of concentrated H_2SO_4 and 8 ml of H_2O was boiled until ~85% of (IV) accumulated in the reaction mixture (~10 h, GLC), then $NaHCO_3$ was added, the mixture was evaporated at 0°C, and extracted by pentane. The extract was washed with saturated solution of NaCl, dried over $MgSO_4$, and evaporated at 0°. The residue (2.54 g) was chromatographed on 100 g of SiO_2. A gradient elution from hexane to ether (up to 5% of the latter) gave, after the evaporation of solvent at 0°C, 1.17 g of strongly volatile (IV), bath temperature 83°C (15 mm). IR spectrum (CCl_4, ν, cm^{-1}): 520, 570, 660, 780, 820, 1030, 1050, 1100, 1380, 1410, 1450, 1725, 2720, 2820-2970. PMR spectrum ($CDCl_3$, δ, ppm): 1.60 d (3H, CH_3C^5, J = 7 Hz), 1.70 s (3H, CH_3C^4), 2.35 m and 2.52 m (4H, CH_2), 5.27 q (1H, HC^5, J = 7 Hz), 9.78 dist. t (1H, CHO). ^{13}C NMR spectrum (δ, ppm): 13.1 ($\underline{C}H_3C^5$), 22.9 ($\underline{C}H_3C^4$), 24.0 (C^3), 42.0 (C^2), 120.5 (C^5), 133.6 (C^4), 202.1 (C^1). MS (m/z): 112 M^+, 94, 68, 43. Found, %: C 74.62, H 10.53. $C_7H_{12}O$. Calculated, %: C 74.95, H 10.78.

7-Formyl-3,11,15,19,23-pentamethyltetraeicosa-2,6E,10E,14E,18E,22-hexane (XI). A solution of 0.91 g (99 mmoles) of diisopropylamine in 5 ml of ether was added to a solution of 10 mmoles of n-BuLi in 10 ml of hexane, stirred at −15°C (Ar). The mixture was held for 40 min at 0°C, and then cooled again to −15°C. A solution of 2.86 g (7 mmoles) of (III) [6] was added in the course of 20 min, and the mixture was held at 0°C for 1 h. It was then cooled to −70°C for 1.5 h, and a solution of 0.64 g (5.8 mmoles) of (IV) in 3 ml of ether was added. The mixture was held at −70°C for 1.5 h, then, after heating in the course of 1.5 h to ~20°C, it was held for another hour, transferred to a mixture of a solution of 2.72 g of $(COOH)_2 \cdot H_2O$ in 55 ml of H_2O and 50 ml of ether, stirred for 2 h, and the organic layer was separated. The subsequent usual treatment gave 3.25 g of an orange oil, which was chromatographed on 120 g of SiO_2. By gradient elution from hexane to ether (up to 2% of the latter), 1.03 g (42%) of (XI) was obtained, bath temperature 180°C (0.03 mm). IR spectrum ($CHCl_3$, ν, cm^{-1}): 840, 980, 1100, 1150, 1250, 1380, 1450, 1680, 2730, 2865-2970. UV spectrum (λ_{max}, nm (ε)): 232 (12,000). PMR spectrum ($CDCl_3$, δ, ppm): 1.60 br.s (15H, cis-CH_3), 1.69 s and 1.71 s (3H in each case, CH_3C^3 and trans-CH_3C^{22}), 2.05 m (14H, CH_2C=C), 2.25 m (4H, $HC^{4,8}$), 2.46 m (2H, HC^5), 5.12 br.s (5H, HC=C), 5.3 quartet (1H, HC^2, J = 7 Hz), 6.48 t (1H, HC^6, J = 7 Hz), 9.39 s (1H, CHO). MS (m/z): 423 $[M - 1]^+$, 273, 138, 69. Found, %: C 85.45, H 11.24. $C_{30}H_{48}O$. Calculated, %: C 84.84, H 11.39.

7-Hydroxymethyl-3,11,15,19,23-pentamethyltetraeicosa-2Z,6E,10E,14E,18E,22-hexane (I) was obtained by reduction of (XI) by $NaBH_4$ by a conventional procedure, and was then chromtographed on SiO_2 [gradient elution from hexane to ether (up to 5% of the latter), yield 68%, bp 225°C (0.05 mm)]. IR spectrum ($CHCl_3$, ν, cm^{-1}): 830, 1000, 1050, 1100, 1380, 1450, 2860-2960, 3610. PMR spectrum ($CDCl_3$, δ, ppm): 1.60 br.s (15 H, cis-CH_3), 1.70 br.s (6H, trans-CH_3), 2.05 br.m (20 H, CH_2), 4.02 br.s (2H, CH_2O), 5.10 m (4H, HC=C), 5.22 q (1H, HC^2, J = 7 Hz), 5.42 t (1H, HC^6, J = 7 Hz), MS (m/z): 426 M^+. Found, %: C 84.46, H 12.09. $C_{30}H_{50}O$. Calculated, %: C 84.44, H 11.81.

4-Benzyloxymethylhex-4E-en-1-al ethylene acetal (X) was obtained from (VIII) according to [12] and purified by chromatography on SiO_2 (gradient elution from hexane to ether, up to 15% of the latter), yield 79%, bath temperature 143°C (1.5 mm). IR spectrum (CCl_4, ν, cm^{-1}): 700, 720-810, 900, 940, 1070, 1100, 1140, 1360, 1400, 1460, 2880-2940. PMR spectrum ($CDCl_3$, δ, ppm): 1.65 d (3H, CH_3, J = 7 Hz), 1.75 m (2H, CH_2), 2.25 m (2H, CH_2C=C), 3.79 m and 3.89 m (4H, CH_2O), 3.90 s (2H, CH_2OBn), 4.43 s (2H, CH_2Ph), 4.82 t (1H, OCHO, J = 4.5 Hz), 5.53 q (1H, HC^5, J = 7 Hz), 7.32 m (5H, C_6H_5). ^{13}C NMR spectrum (δ, ppm): 12.9 q ($\underline{C}H_3C^5$), 22.35 t (C^2), 32.6 t (C^3), 64.8 t (CH_2O), 71.7 t (CH_2OBn), 74.5 t (CH_2Ph), 104.4 d ($\underline{C}^1$), 123.5 d (C^5), 127.35, 127.6, 128.2, and 138.7 (C_6H_5), 136.4 (C^4). Found, %: C 73.20, H 8.57. $C_{16}H_{22}O_3$. Calculated, %: C 73.25, H 8.45.

4-Benzyloxymethylhex-4E-en-1-al (V) was obtained by hydrolysis of (X), as described for (IV), and was purified by distillation, yield 60%, bp 134°C (1.5 mm). IR spectrum (CCl_4, ν, cm^{-1}): 700, 730, 820, 900, 940, 1070-1100, 1350, 1390, 1410, 1450, 1730, 2720, 2860, 2930, 3030. PMR spectrum ($CDCl_3$, δ, ppm): 1.7 d (3H, CH_3, J = 7 Hz), 2.5 m (4H, CH_2), 3.95 s (2H,

CH_2OBn), 4.47 s (2H, OCH_2Ph), 5.62 q (2H, HC^5, J = 7 Hz), 7.35 m (5H, Ph), 9.73 t (1H, CHO, J = 1.5 Hz). Found, %: C 76.68, H 8.73. $C_{14}H_{18}O_2$. Calculated, %: C 77.03, H 8.31.

7-Formyl-3-benzyloxymethyl-11,15,19,23-tetramethyltetraeicosa-2E,6E,10E,14E,18E,22-hexane (XII) was obtained in a similar way as (XI) by condensation of Li-derivative of (III) with aldehyde (V), yield 32%, bath temperature 215°C (0.04 mm). IR spectrum (CCl_4, ν, cm^{-1}): 700, 730-820, 910, 1070-1100, 1380, 1460, 1690, 2730, 2860, 2970. UV spectrum (λ_{max}, nm (ε)): 233 (10,200), 200 (43,000). PMR spectrum ($CDCl_3$, δ, ppm): 1.52 s (3H, CH_3C^{11}), 1.55 s (9H, cis-CH_3), 1.65 m (6H, trans-CH_3C^{23}, CH_3C^2), 2.05 m (14H, $CH_2C{=}C$), 2.25 m (4H, $HC^{4,8}$), 2.46 m (2H, HC^5), 3.90 br.s (2H, CH_2OBn), 4.40 s (2H, CH_2Ph), 5.05 m (4H, $HC{=}C$), 5.57 q (1H, HC^2, J = 7 Hz), 6.40 t (1H, HC^6, J = 7 Hz), 7.29 m (5H, C_6H_5), 9.29 br. s (1H, CHO). MS (m/z): 532, 531, 530 (M^+), 487, 439, 423, 354, 353. Found, %: C 83.69, H 10.28. $C_{37}H_{54}O_2$. Calculated, %: C 83.72, H 10.25.

7-Hydroxymethyl-3-benzyloxymethyl-11,15,19,23-tetramethyltetraeicosa-2E,6E,10,14E,18E,22-hexane (XIII) was obtained by reduction of (XII) by $NaBH_4$, yield 73%, bath temperature 220°C (0.015 mm). IR spectrum (CCl_4, ν, cm^{-1}): 700, 740-820, 910, 1000, 1030, 1070, 1100, 1380, 1460, 2860, 2920, 2960, 3620. PMR spectrum ($CDCl_3$, δ, ppm): 1.62 s (12H, cis-CH_3), 1.70 d (3H, CH_3C^2, J = 7 Hz), 1.71 s (3H, trans-CH_3C^{23}), 2.12 m (20H, $CH_2C{=}C$), 3.96 s (2H, CH_2OBn), 4.05 br.s (2H, CH_2OH), 4.49 s (2H, CH_2Ph), 5.15 m (4H, $HC{=}C$), 5.45 dist. t (1H, HC^6), 5.58 q (1H, HC^2, J = 7 Hz), 7.37 m (5H, C_6H_5). Found, %: C 83.44, H 10.42. $C_{37}H_{56}O_2$. Calculated, %: C 83.40, H 10.59.

3-Benzyloxymethyl-7,11,15,19,23-pentamethyltetraeicosa-2E,6Z,10E,14E,18E,22-hexane (XIV) was obtained by treating (XIII) with $Py{\cdot}SO_3$, followed by reduction of the sulfo-ester formed (without isolation) by $LiAlH_4$, as described for the preparation of (IX), yield 66%, bath temperature 198°C (0.015 mm). IR spectrum (CCl_4, ν, cm^{-1}): 700, 740-820, 1030, 1070, 1100, 1380, 1480, 2860, 2920, 2960. PMR spectrum ($CDCl_3$, δ, ppm): 1.68 s (12H, cis-CH_3), 1.73 d (3H, CH_3C^2, J = 7 Hz), 1.77 s (6H, trans-CH_3, 2.15 m (20H, CH_2), 4.02 s (2H, CH_2O), 4.53 s (2H, CH_2Ph), 5.21 m (5H, $HC{=}C$), 5.63 q (1H, HC^2, J = 7 Hz), 7.4 m (5H, C_6H_5). MS (m/z): 518 $[M + I]^+$, 449, 448, 427, 426, 411, 410, 409, 380, 312, 244. Found, %: C 86.38, H 10.88. $C_{37}H_{56}O$. Calculated, %: C 85.98, H 10.92.

3-Hydroxymethyl-7,11,15,19,23-pentamethyltetraeicosa-2E,6Z,10E,14E,18E,22-hexane (II). A mixture of 0.51 g (1 mmole) of (XIV), 0.01 g (1.43 mmole) of Li, 1 ml of ether, and ~100 ml of NH_3 was held for 3 h in a sealed ampule at −70°C, with vigorous shaking of the ampul every 10-15 min. The ampule was opened, its contents were treated with NH_4Cl and NH_3, and evaporated. After usual treatment, 0.46 g of a yellow oil was obtained, which was chromatographed on 30 g of SiO_2. Gradient elution from hexane to ether (up to 15% of the latter) gave 0.32 g [90%, based on reacted (XIV)] of (II), bath temperature 200°C (0.013 mm). IR spectrum (CCl_4, ν, cm^{-1}): 840, 1000, 1380, 1460, 1670, 2860, 2930, 2970, 3620. PMR spectrum ($CDCl_3$, δ, ppm): 1.63 s (12H, cis-CH_3), 1.65 d (3H, CH_3-C^2, J = 7 Hz), 1.7 s (6H, trans-CH_3), 1.83 s (1H, OH), 2.08 m (20H, CH_2), 4.03 s (2H, CH_2O), 5.15 m (5H, $HC{=}C$), 5.3 q (1H, HC^2, J = 7 Hz). MS (m/z): 427, 426, M^+, 407, 356, 288. Found, %: C 84.30, H 11.61. $C_{30}H_{50}O$. Calculated, %: C 84.44, H 11.81.

CONCLUSIONS

1. A highly stereospecific synthesis of two hexaprenols, modified with respect to the position of the hydroxy group, was carried out by the method of directed aldol condensation.

2. A highly stereoselective method has been developed for synthesizing of a common precursor of multipurpose syntones, -4-methylhex-4Z-en-al and 4-benzyloxyhex-4E-en-1-al.

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