ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 12, pp. 1509–1511. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © G.Yu. Ishmuratov, V.A. Vydrina, M.P. Yakovleva, G.V. Nasibullina, I.S. Nazarov, R.R. Muslukhov, A.G. Tolstikov, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 12, pp. 1538–1540.

Hydroboration–Oxidation of Ricinoleic Acid Ester Derivatives

G. Yu. Ishmuratov, V. A. Vydrina, M. P. Yakovleva, G. V. Nasibullina, I. S. Nazarov, R. R. Muslukhov, and A. G. Tolstikov

Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia
e-mail: insect@anrb.ru

Received May 26, 2012

Abstract—The chiral center in ricinoleic acid methyl ester (*ee* ~100%) strongly affects the regioselectivity of its hydroboration–oxidation, so that the resulting 1,3-diol dominates by 74% over the 1,4-isomer. Furthermore, new asymmetric centers are formed preferentially with (*S*)-configuration, up to 87% for 1,3-diols and up to 100% for 1,4-diols.

DOI: 10.1134/S1070428012120020

We previously showed [1] that the chiral center in unsaturated alcohols **I** and **II** (which may be regarded as ricinoleic acid derivatives) insignificantly affects the regioselectivity of their hydroboration–oxidation. Among isomeric 1,3- and 1,4-diols **III**, **IV** and **V**, **VI** thus obtained, the former prevail by 6 and 10%, respectively (Scheme 1). On the other hand, the new asymmetric center is formed preferentially with (*S*)-configuration, which was proved by subsequent cyclization of 1,3-diols **III** and **IV** (*de* 32 and 50%, respectively) into the corresponding stereoisomeric 1,3-dioxanes, and of 1,4-diols **V** and **VI** (*de* 40 and 22%, respectively) into 2,5-dialkyltetrahydrofurans.

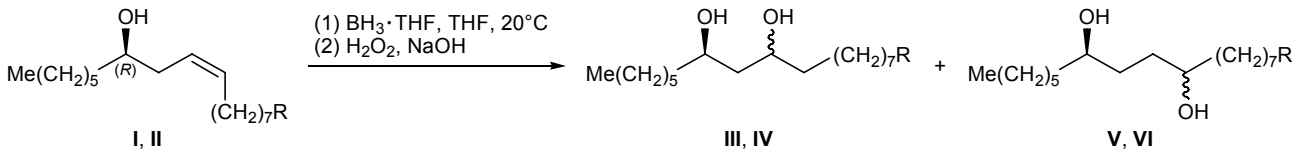
In continuation of our studies on the effect of the chiral center in (12*R*)-ricinoleic acid on the regio- and stereoselectivity of hydroboration–oxidation of the double bond, in the present work we examined the behavior of its esters, castor oil (containing ~90% of ricinoleic acid glyceride **VII**) and methyl ester **VIII**.

In the reaction of castor oil (**VII**) even with a double excess of $BH_3 \cdot THF$ (THF, 20°C) the double bond remained intact, whereas hydride reduction of the carboxy group gave unsaturated diol **II**. The low reactivity of triglyceride **VII** toward the complex $BH_3 \cdot THF$ may be rationalized by steric factors. Under more severe conditions (heating under reflux), triglyceride **VII** was converted in 85% yield into a mixture of regioisomeric 1,3- and 1,4-diols **IV** and **VI** at a ratio of 57 : 43 (according to the HPLC and ^1H NMR data), which are products of the reduction of the ester group and oxidation of the double bond (see table; Scheme 2).

Hydroboration of ricinoleic acid methyl ester (**VIII**) with excess $BH_3 \cdot THF$ at room temperature, followed by oxidation with hydrogen peroxide in alkaline solution, afforded a 87 : 13 mixture of triols **IV** and **VI** (see table). The same reaction carried out at elevated temperature was characterized by slightly lower regioselectivity, and the ratio of compounds **IV** and **VI** was 72 : 28 (Scheme 3).

Comparison of the NMR spectra of triols **IV** and **VI** with those of compounds **III–VI** obtained by hydroboration–oxidation of unsaturated alcohols **I** and **II** [2] showed that in all cases the major stereoisomer had (*S*)-configuration of the new chiral center. The data on the regio- and stereoselectivity of hydroboration–

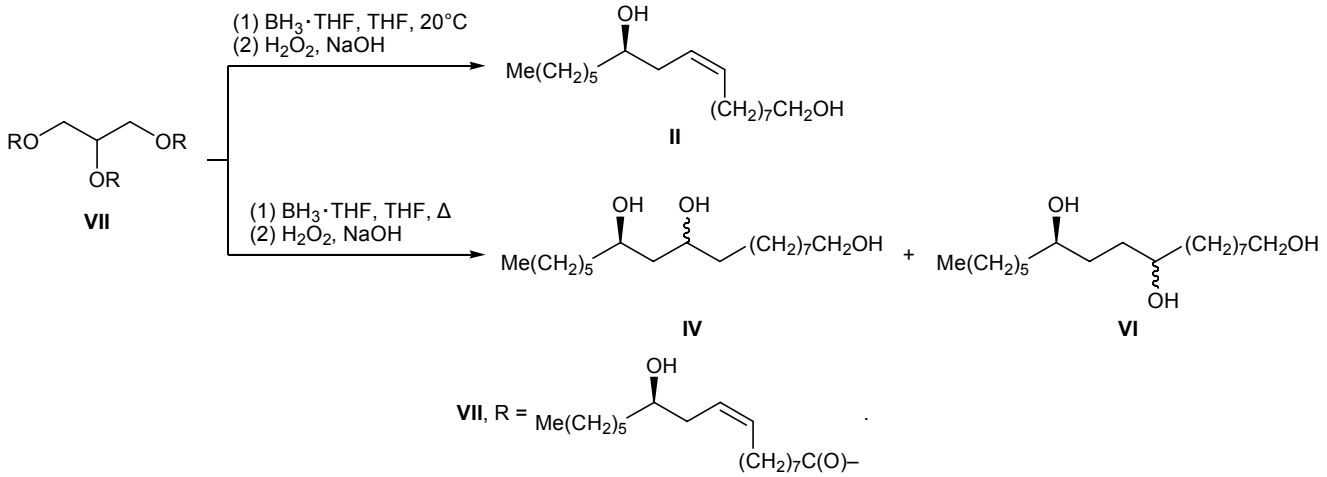
Scheme 1.



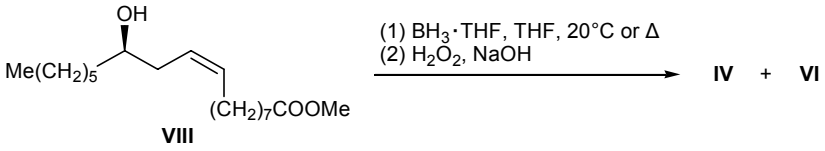
I, **II** **III**, **IV** **V**, **VI**

I, **III**, **V**, R = Me; **II**, **IV**, **VI**, R = $HOCH_2$.

Scheme 2.



Scheme 3.



oxidation of ricinoleic acid derivatives **VII** and **VIII** are given in table.

Thus ricinoleic acid methyl ester demonstrated the highest regio- and stereoselectivity in hydroboration–oxidation: the resulting 1,3-diol dominated over its 1,4-isomer by 74%, and the new asymmetric center had preferentially (*S*)-configuration (up to 87% for 1,3-diol and up to 100% for 1,4-diol).

EXPERIMENTAL

The IR spectra were recorded from films on a Specord M-82 instrument. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AMX-300 spectrometer at 300.13 and 75.47 MHz, respectively, using tetramethylsilane as internal reference. Signals in the NMR spectra were assigned using COSY H–H and COSY C–H two-dimensional correlation techniques. The ratios of diastereoisomers were determined from the NMR spectra recorded with a 10-s pulse delay. HPLC analyses were performed on a Du Pont liquid chromatograph (USA) equipped with a refractive index detector and a 300 × 3.9-mm stainless steel column packed with μ-Porasil Waters (5 μm); eluent hexane–propan-2-ol (92 : 8), room temperature. Silica gel (Sorbfil, Russia) was used for thin-layer chromatography. Column chromatography was performed on Macherey-Nagel silica gel (70–230 μm, Germany). The elemental compositions of all the isolated compounds were consistent with the calculated values.

(9*Z*,12*R*)-Octadec-9-ene-1,12-diol (II). A solution of 2.4 ml (15.0 mmol) of $BF_3 \cdot Et_2O$ in 8 ml of anhydrous tetrahydrofuran was added dropwise to a suspension of 2.0 g (2.1 mmol) of triglyceride **VII** and 0.55 g (14.4 mmol) of $NaBH_4$ in 45 ml of anhydrous THF (argon, 20°C). The mixture was kept for 24 h at room

Composition of the hydroboration–oxidation products of ricinoleic acid derivatives **VII** and **VIII**

Initial compound no.	Temperature, °C	Compound **IV**		Compound **VI**	
		fraction in the reaction mixture, %	isomer ratio (10*S*,12*R*)/(10*R*,12*R*)	fraction in the reaction mixture, %	isomer ratio (9*S*,12*R*)/(9*R*,12*R*)
VII	Δ	57	1.8 : 1.0	43	1.0 : 1.0
VIII	20	87	5.0 : 1.0	13	1.0 : 0
VIII	Δ	72	1.3 : 1.0	28	5.0 : 1.0

temperature and treated with 2.0 ml of water; after 10 min, 4.8 ml of 3 N NaOH and 4.8 ml of 30% H_2O_2 were added, and the mixture was stirred for 3 h. The mixture was then diluted with 200 ml of *tert*-butyl methyl ether, washed with brine, dried over Na_2SO_4, and evaporated, and the residue was subjected to flash chromatography to isolate 1.52 g (86%) of diol **II** whose ^1H and ^{13}C NMR spectra were identical to those reported in [2].

(10*RS*,12*R*)- and (9*RS*,12*R*)-Octadecane-1,10,12- and -1,9,12-triols IV and VI. *a*. A solution of 7.3 ml (45.7 mmol) of $BF_3 \cdot Et_2O$ in 24 ml of anhydrous THF was added dropwise to a suspension of 2.0 g (6.4 mmol) of methyl ester **VIII** and 1.68 g (43.9 mmol) of $NaBH_4$ in 137 ml of anhydrous THF (argon, 20°C), and the mixture was kept for 24 h at room temperature. The mixture was treated with 6.0 ml of water; after 10 min, 14.6 ml of 3 N NaOH and 14.6 ml of 30% H_2O_2 were added, and the mixture was stirred for 3 h, diluted with 200 ml of *tert*-butyl methyl ether, washed with brine, dried over Na_2SO_4, and evaporated. The residue was subjected to flash chromatography to isolate 1.90 g (98%) of a mixture of compounds **IV** and **VI** at a ratio of 87:13.

b. A solution of 7.3 ml (45.7 mmol) of $BF_3 \cdot Et_2O$ in 24 ml of anhydrous THF was added dropwise to a suspension of 2.0 g (6.4 mmol) of methyl ester **VIII** and 1.68 g (43.9 mmol) of $NaBH_4$ in 137 ml of anhydrous THF (argon, 20°C), and the mixture was heated for 5 h under reflux. The mixture was cooled and treated as described above in *a* to isolate 1.87 g (97%) of a mixture of compounds **IV** and **VI** at a ratio of 72:28.

c. A solution of 2.4 ml (15.0 mmol) of $BF_3 \cdot Et_2O$ in 8 ml of anhydrous THF was added dropwise to a suspension of 2.0 g (2.1 mmol) of triglyceride **VII** and 0.55 g (14.4 mmol) of $NaBH_4$ in 45 ml of anhydrous THF (argon, 20°C), and the mixture was heated for 5 h under reflux. The mixture was then treated with 2.0 ml of water and kept for 10 min, 4.8 ml of 3 N NaOH and 4.8 ml of 30% H_2O_2 were added, and the mixture was stirred for 3 h, diluted with 200 ml of *tert*-butyl methyl ether, washed with brine, dried over Na_2SO_4, and evaporated. The residue was subjected to flash chromatography to isolate 1.56 g (85%) of a mixture of compounds **IV** and **VI** at a ratio of 57:43.

(10*S*,12*R*)- and (10*R*,12*R*)-Octadecane-1,10,12-triols (IV). IR spectrum, ν, cm^{-1}: 3340 (OH), 1110 (C–O), 1050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (3H, CH_3, ^3J = 7.0 Hz), 1.20–1.45 m (20H, CH_2), 1.45–1.65 m (8H, 2-H, 9-H, 11-H, 13-H), 2.25 br.s (3H, OH), 3.65 t (2H, 1-H, ^3J = 6.5 Hz), 3.94 [4.05]* m (2H, 10-H, 12-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.16 q (C^{18}), 22.66 t (C^{17}), 25.62 t (C^8), 25.83 t (C^3, C^{14}), 29.39 t (C^7), 29.44 t (C^{15}), 29.55 t (C^5, C^6), 29.65 t (C^4), 31.90 t (C^2), 32.65 t (C^{16}), 37.57 t (C^9), 37.61 t (C^{13}), 42.40 t (C^{11}), 63.13 t (C^1), 69.56 d [69.53 d] (C^{10}, C^{12}).

(9*S*,12*R*)- and (9*R*,12*R*)-Octadecane-1,9,12-triols (VI). IR spectrum, ν, cm^{-1}: 3340 (OH), 1110 (C–O), 1050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (3H, CH_3, ^3J = 7.2 Hz), 1.20–1.45 m (18H, CH_2), 1.46 m (2H, 2-H), 1.45–1.70 m (8H, 8-H, 10-H, 11-H, 13-H), 2.25 br.s (3H, OH), 3.42 [3.47] m (2H, 9-H, 12-H), 3.64 t (2H, 1-H, ^3J = 6.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.14 q (C^{18}), 22.68 t (C^{17}), 25.76 t (C^7, C^{14}), 29.42 t (C^6, C^{15}), 29.62 t (C^3, C^4, C^5, C^6), 31.90 t (C^2), 32.84 t (C^{16}), 33.35 t (C^{10}), 34.08 t (C^{11}), 37.62 [37.57] t (C^{13}), 37.87 [37.82] t (C^8), 63.07 t (C^1), 72.38 d [72.02 d] (C^9, C^{12}).

REFERENCES

1. Muslukhov, R.R., Shayakhmetova, A.Kh., Yakovleva, M.P., Shitikova, O.V., Ishmuratov, G.Yu., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2008, vol. 44, p. 1130.
2. Mikhailov, B.M. and Bubnov, Yu.N., *Bororganicheskie soedineniya v organicheskom sinteze* (Organoboron Compounds in Organic Synthesis), Moscow: Nauka, 1977.

* The data for minor triol isomers (10*R*,12*R*)-**IV** and ((9*R*,12*R*)-**VI** are given in brackets.