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Wagner–Meerwein Rearrangement of Steviol 16α,17- and 15α,16-Epoxides

R. N. Khaibullin, I. Yu. Strobykina, V. E. Kataev, O. A. Lodochnikova, A. T. Gubaidullin, A. A. Balandina, and Sh. K. Latypov

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia
e-mail: kataev@iopc.ru

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Abstract—16α,17- and 15α,16-Epoxy derivatives of diterpenoid steviol having *ent*-kaurane structure were found for the first time to undergo Wagner–Meerwein rearrangement in alkaline medium or by the action of boron trifluoride–diethyl ether complex to give products with *ent*-beyerane structure. The geometric parameters of steviol 16α,17- and 15α,16-epoxides were determined by X-ray analysis.

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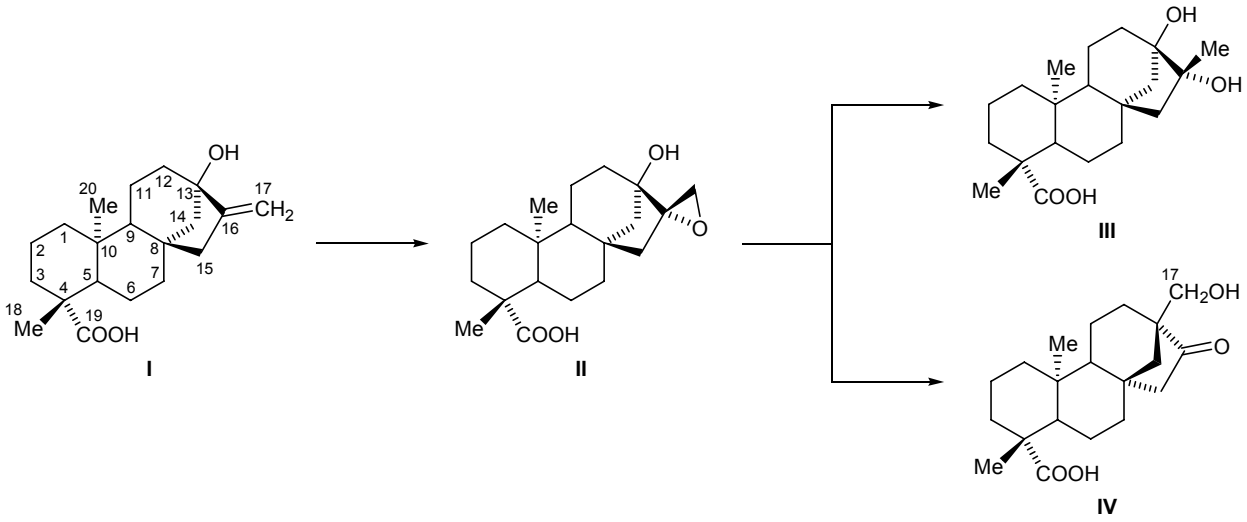
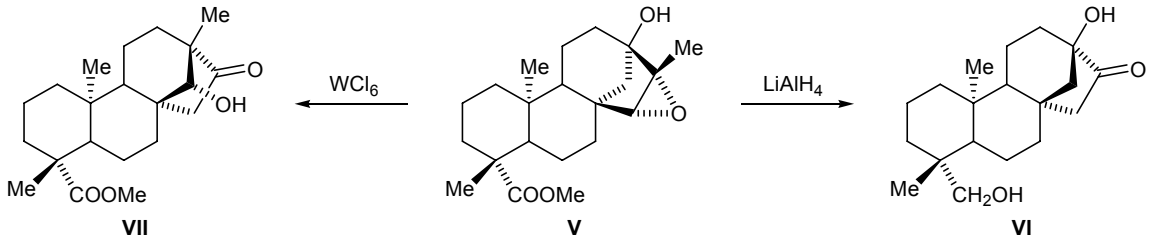
In the recent years, studies on biotransformations of diterpenoid steviol (**I**, 13-hydroxy-*ent*-kaur-16-en-19-oic acid) having *ent*-kaurane structure and its epoxy derivative **II** have been reported [1–4]. Epoxide hydrolases isolated from various microorganisms are universal biocatalysts for asymmetric hydrolysis of epoxides [4], and alcohols thus formed exhibit diverse biological activity, in particular hormone [3] and antihyperglycemic [2]. As concerns chemical modification of steviol epoxides **II** and **V**, their hydrolysis in the presence of mineral [5] and Lewis acids [6] and reduction with lithium tetrahydridoaluminate [6] were reported (Schemes 1, 2). In most cases, these reactions are accompanied by the Wagner–Meerwein rearrangement with formation of products having *ent*-beyerane (isosteviol) skeleton, i.e., compounds **IV** (Scheme 1) [5, 6], **VI**, and **VII** [6] (Scheme 2). In the present article we describe opening of the oxirane rings in steviol 16α,17- and 15α,16-epoxides **II** and **V** by the action of Lewis acid (boron trifluoride–diethyl ether complex $BF_3 \cdot Et_2O$).

Epoxide **II** was synthesized by oxidation of steviol (**I**) with *m*-chloroperoxybenzoic acid by analogy to the procedure reported in [7]. Compound **II** was assigned

Scheme 1.



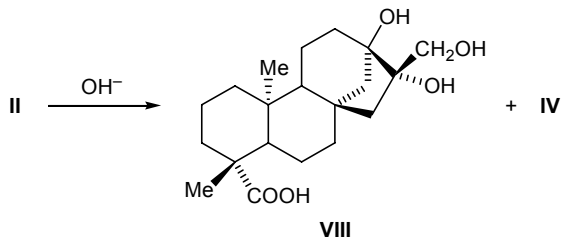
Scheme 2.



the 16α (or 16*S*) configuration on the basis of indirect data, namely taking into account the configuration of C^{16} in **III** [6]. We were the first to determine the molecular structure of **II** by X-ray analysis (Fig. 1). We showed that the oxidation of steviol **I** under the above conditions is completely stereoselective and that the only product is 16α,17-epoxide **II** having *S* configuration of C^{16}.

Alkaline hydrolysis of 16α,17-epoxide **II** on heating in 1.5% aqueous potassium hydroxide at the boiling point gave a mixture of two compounds which we failed to separate (Scheme 3). The absence of doublet signals at δ 2.78 and 2.92 ppm (which are typical of the methylene group in the oxirane ring of compound **II**) in the ^{1}H NMR spectrum of the product mixture indicated that the hydrolysis was complete. The formation of the expected product of oxirane ring opening, 13,16,17-trihydroxy-*ent*-kaur-19-oic acid, followed from the presence in the ^{1}H NMR spectrum of doublets at δ 3.63 and 3.81 ppm corresponding to methylene protons in the hydroxymethyl group on C^{16} and signals at δ 0.94 and 1.22 ppm due to protons in the *ent*-kaurane $C^{20}H_3$ and $C^{18}H_3$ methyl groups. The observed chemical shifts and spin–spin coupling constants in the ^{1}H NMR spectrum of the reaction mixture are consistent with those reported for 13α,16α,17-trihydroxy-*ent*-kaur-19-oic acid (**VIII**) which was synthesized by enzymatic hydrolysis of suavioside isolated from sweet leaves of *Rubus Suavissimus* [8].

Scheme 3.



The ^{1}H NMR spectrum also contained a doublet of doublets at δ 2.68 ppm, which is typical of the 15α-H proton in *ent*-beyerane skeleton [9], singlets at δ 0.81 and 1.26 ppm due to $C^{20}H_3$ and $C^{18}H_3$ groups in *ent*-beyerane [9], and doublets at δ 3.51 and 3.64 ppm, which belong to methylene protons of hydroxymethyl group. These data indicated that the second reaction product is 17-hydroxy-*ent*-16-oxobeyeran-l9-oic acid (**IV**), i.e., diterpenoid having *ent*-beyerane (isosteviol) structure. Compound **IV** was obtained previously [6] by acid hydrolysis of 16α,17-epoxide **II**. According to the ^{1}H NMR data, compounds **IV** and **VIII** were formed in equal amounts. The above assignment of signals from the $C^{20}H_3$, $C^{18}H_3$, and 15α-H protons is also consistent with the data reported in [6, 10]. However, there is ambiguity in the assignment of the doublet signal at δ 2.18 ppm (J = 13 Hz), which (as well as the doublet of doublets from 15α-H at δ 2.68 ppm) appears in a weaker field relative to most other proton signals of isosteviol skeleton. The signal at δ 2.18 ppm was previously assigned to 12-H [6, 10]. Later on, this assignment was shown to be invalid both experimentally and theoretically [9]. Nevertheless, erroneous assignment of ^{1}H NMR signals still may be encountered while analyzing the spectra of other metabolites of the *ent*-kaurane and *ent*-beyerane series (see, e.g., [11]). Probable reasons are considerable overlap of signals in the ^{1}H NMR spectra (which makes unambiguous correlation in the 2D ^{1}H–^{1}H COSY spectrum impossible)

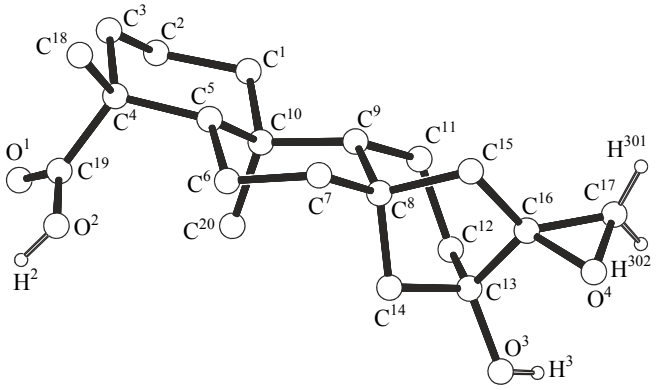


Fig. 1. Structure of the molecule of steviol 16α,17-epoxide (**II**) according to the X-ray diffraction data; selected hydrogen atoms are shown.

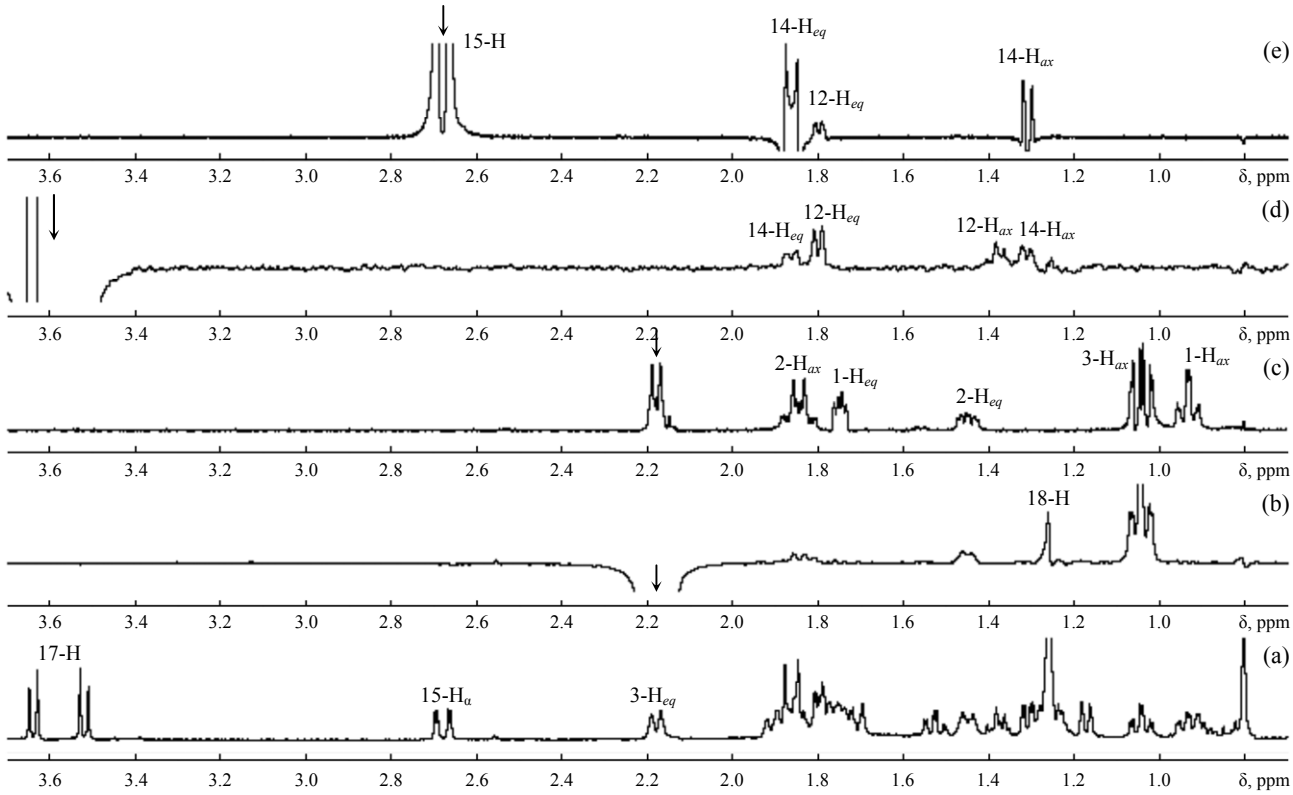


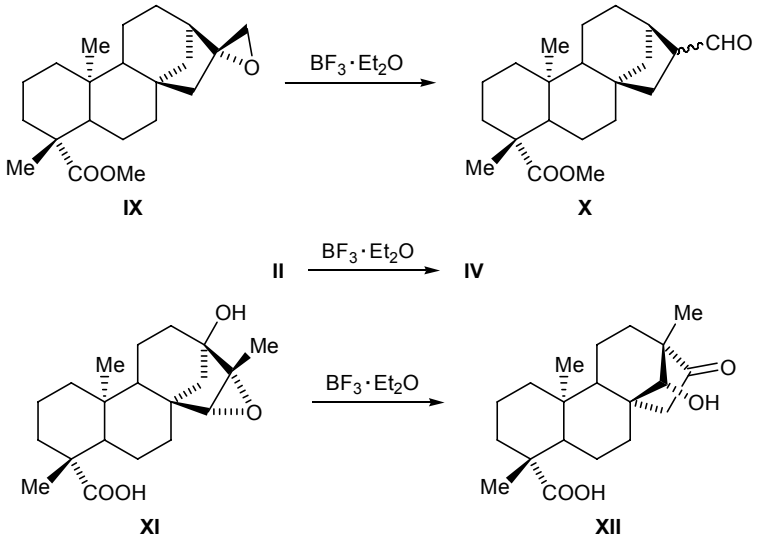
Fig. 2. Upfield region of the ^{1}H NMR spectra of compound **IV** (600 MHz, $CDCl_3$, 30°C). (a) ^{1}H NMR spectrum; (b, d) 1D DPFGNOE spectra; (c, e) 1D TOCSY spectra; irradiated protons are indicated with arrows.

and similarity of the resonance frequencies of the C^3 and C^{12} nuclei [9].

In this respect, compound **IV** isolated as individual substance provides one more chance to demonstrate without ambiguity that the conclusions drawn in [9] are valid, i.e., there was confusion in the assignment of the 3-H and 12-H signals. Analysis of the ^{1}H NMR spectra of compound **IV** allowed us to independently correlate the position of signals from 3-H and 12-H with clearly identifiable signals from the $C^{18}H_3$ and $C^{17}H_2OH$ protons. On the one hand, taking into account that the assignment of the $C^{18}H_3$ signal is beyond doubt, this signal can be used as reference. Nuclear Overhauser effect [12–14] observed on the $C^{18}H_3$ singlet upon irradiation at a frequency corresponding to proton resonating at δ 2.18 ppm (Fig. 2b) indicates spatial proximity of these protons. Therefore, the signal at δ 2.18 ppm should be assigned to only 3-H$_{eq}$. The 1D TOCSY spectrum [12–14] of compound **IV** with excitation of 3-H$_{eq}$ (Fig. 2c) made it possible to isolate coupled spin system consisting of protons in the **A** ring from overlapped signals in the ^{1}H NMR spectrum of **IV**. On the other hand, irradiation of the $C^{17}H_2$ protons in **IV**, which resonate in a weaker field (*AB* spin system, δ 3.64–3.51 ppm) relative to the other protons in the *ent*-beyerane skeleton, gives distinct NOEs on signals at δ 1.86, 1.80, 1.37, and 1.31 ppm (Fig. 2d). The latter should belong only to closely located protons, namely to 12-H or 14-H but not to 3-H. In this case, no response was observed on the doublet signal at δ 2.18 ppm; therefore, the corresponding proton is remote from the hydroxymethyl group, i.e., it cannot be a proton on C^{12}. According to the 1D TOCSY spectrum with excitation of the 15α-H proton, doublets of doublets at δ 1.86 and 1.31 ppm belong to $C^{14}H_2$ (Fig. 2e). Then the doublets of doublets at δ 1.80 and 1.37 ppm (Fig. 2d) correspond to resonance of protons on C^{12}, the first of these belonging to 12-H$_{eq}$. The same also follows from the appearance of the corresponding signal in the 1D TOCSY spectrum upon excitation of 15α-H (Fig. 2e).

Thus the doublet at δ 2.18 ppm was unambiguously assigned to 3-H$_{eq}$. Correct assignment of that signal is important, for it is characteristic not only of isosteviol derivatives having *ent*-beyerane structure (e.g., **IV**, **VI**, and **VII**) but also of metabolites of the *ent*-kaurane series having no other substituents in the **A** ring than the carboxy group on C^4.

Scheme 4.



In the IR spectrum of the product mixture we observed strong broadened absorption bands at 1698 cm^{-1} and in the region 2600–2700 cm^{-1}, which are typical of carboxy group; in addition, a band at 3436 cm^{-1} was present due to stretching vibrations of hydroxy group. The mass spectrum of the product mixture contained molecular ion peaks with *m*/*z* 334 and 352, which belong to *ent*-beyerane and *ent*-kaurane derivatives **IV** and **VIII**, respectively.

When alkaline hydrolysis of 16α,17-epoxide **II** was carried out under more severe conditions (heating for 12 h in 10% aqueous KOH in a sealed ampule), the fraction of product **IV** having *ent*-beyerane structure increased approximately twofold (according to the ^{1}H NMR data).

Well known rearrangement of epoxides into carbonyl compounds by the action of Lewis acids is widely used in organic synthesis [15–18]. When boron trifluoride–diethyl ether complex $BF_3 \cdot Et_2O$ is used as Lewis acid, fluorohydrins [17], unsaturated alcohols, or dienes [18] may be formed, depending on the substrate structure and reaction conditions. As concerns epoxy derivatives of the *ent*-kaurane series, steviol 15α,16-epoxide methyl ester (**V**) in the presence of WCl_6 underwent rearrangement into 14α-hydroxyisosteviol (**VII**) having *ent*-beyerane structure [6] (Scheme 2), while *ent*-kaurane 16α,17-epoxide **IX** in the presence of $BF_3 \cdot Et_2O$ gave rise to aldehyde **X** with *ent*-kaurane structure [19] (Scheme 4). We found that the direction of the latter reaction strongly depends on the presence (or absence) of a hydroxy group on C^{13}. The reactions of boron trifluoride–diethyl ether complex with steviol 16α,17- and 15α,16-epoxides **II** and **XI** having a hydroxy group on C^{13} (unlike *ent*-kaurenoic acid methyl ester **IX**) gave products with *ent*-beyerane structure, compounds **IV** and **XII** in quantitative yield (Scheme 4). The product obtained from 16α,17-epoxide was identical to previously described kaurenoid **IV** [5–7], whose formation may be rationalized by generation of carbocationic center on C^{16} as a result of electrophilic attack by Lewis acid and subsequent stabilization of the carbocation via 1,2-hydride shift (Wagner–Meerwein rearrangement).

The ^{1}H NMR spectrum of the product obtained from 15α,16-epoxide **XI** in the presence of boron trifluoride–diethyl ether complex lacked doublet at δ 2.72 ppm, corresponding to the 15β-H proton in the oxirane ring of **XI**, while a doublet at δ 3.38 ppm appeared. In keeping with the data of [6], the latter signal belongs to 14β-H in **XII**. These data indicated

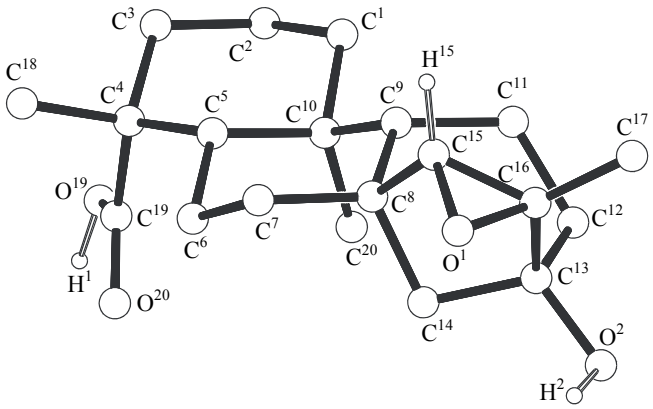


Fig. 3. Structure of the molecule of steviol 15α,16-epoxide (**XI**) according to the X-ray diffraction data; selected hydrogen atoms are shown.

that the conversion of **XI** was complete. The formation of compound **XII** might be expected, for opening of the 15α,16-oxirane ring in epoxide **XI** as a result of electrophilic attack by Lewis acid should generate more stable C^{16}-centered carbocation which promotes Wagner–Meerwein skeletal rearrangement leading to *ent*-beyerane structure **XII** with α-oriented hydroxy group on C^{14} (14*R*). In the ^{1}H NMR spectrum of **XII** we observed characteristic singlets at δ 0.82, 1.04, and 1.27 ppm due to protons in the $C^{20}H_3$, $C^{17}H_3$, and $C^{18}H_3$ methyl groups and a doublet of doublets at δ 2.53 ppm, which is typical of 15α-H in the *ent*-beyerane skeleton [9].

We were the first to determine the molecular structure of epoxide **XI** by X-ray analysis (Fig. 3). Compound **XI** was synthesized according to the procedure described in [6] by epoxidation of a mixture of steviol (**I**) and its Δ^{15}-isomer. The (15*R*,16*R*) configuration of the oxirane ring in **XI** corresponds to the 15α,16 configuration of methyl ester **V**, which was determined by ^{1}H NMR spectroscopy [6].

Thus we found for the first time that steviol 16α,17- and 15α,16-epoxides having *ent*-kaurane structure undergo Wagner–Meerwein rearrangement in alkaline medium or in the presence of boron trifluoride–diethyl ether complex to give products with *ent*-beyerane skeleton.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded at 30°C on a Bruker Avance-600 spectrometer at 600 MHz using $CDCl_3$ as solvent and reference ($CHCl_3$, δ 7.26 ppm). Nuclear Overhauser effects were measured using 1D DPFGNOE pulse sequence [14]. The IR spectra were recorded in the range from 400 to 3600 cm^{-1} on a UR-20 spectrometer and in the range from 400 to 4000 cm^{-1} on a Bruker Vector 22 instrument with Fourier transform. Crystalline samples were examined as dispersions in mineral oil or KBr pellets. The mass spectra (electron impact, 60 eV) were obtained on an MKh-1310 mass spectrometer at a resolution *R* of 10 000 with direct sample admission into the ion source (electron collector current 30 μA, ion source temperature 120°C, direct inlet probe temperature 120–250°C). Precise *m*/*z* values were determined using perfluorokerosene as reference.

Single crystals of compound **II** for X-ray analysis were obtained by crystallization from acetone, and single crystals of **XI**, by double recrystallization from acetone–hexane. The X-ray diffraction data for compound **II** were acquired on a SMART Apex II diffractometer [graphite monochromator, $\lambda(\mathrm{Mo}K_\alpha)$ = 0.71073 Å], and single crystals of **XI** were analyzed on a Kappa Apex diffractometer [graphite monochromator, $\lambda(\mathrm{Cu}K_\alpha)$ = 1.54184 Å, 293 K]. The structures were solved by the direct method. The positions and thermal parameters of non-hydrogen atoms were refined first in isotropic and then in anisotropic approximation by the full-matrix least-squares procedure. Hydrogen atoms were placed into positions calculated on the basis of geometry considerations and were refined using the riding model. All calculations were performed with the aid of SHELXL-97 software package [20]. The absolute configuration of molecules **II** and **XI** was set in accordance with the absolute configuration of (16*S*)-dihydrosteviol, which was determined by us previously [21] with a high accuracy. The complete sets of crystallographic data for structures **II** and **XI** were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 726865 and 726866, respectively).

Compound **II**. Monoclinic crystals; at 20°C: a = 11.5419(14), b = 7.6985(9), c = 11.761(2) Å; β = 119.100(2)°; V = 913.1(2) Å^3; Z = 2; d_{calc} = 1.216 g× cm^{-3}; space group $P2_1$; μ = 0.83 cm^{-1}. Total of 7719 reflection intensities were measured, 2107 of which were characterized by $I \geq 2\sigma(I)$. The final divergence factors were R = 0.035, R_W = 0.094.

Compound **XI**. Tetragonal crystals; at 20°C: a = 7.2837(2), b = 7.2837(2), c = 68.681(2) Å; V = 3643.7(2) Å^3; Z = 8; d_{calc} = 1.219 g/cm^3; space group $P4_32_12$; μ = 6.66 cm^{-1}. Total of 7123 reflection intensities were measured, 1985 of which were characterized by $I \geq 2\sigma(I)$. The final divergence factors were R = 0.039, R_W = 0.122.

Physicochemical studies of the synthesized compounds were performed at the Optical Spectroscopy, Mass Spectrometry, NMR, and X-Ray Analysis Departments of the Federal Collective Spectral and Analytical Center for Physicochemical Studies on the Structure, Properties, and Composition of Substances and Materials.

Silica gel (Chemapol) was used as sorbent for column chromatography. The reaction mixtures were analyzed by TLC on Silufol UV-254 plates.

Steviol 16α,17-epoxide (II, 16α,17-epoxy-13-hydroxy-*ent*-kauran-19-oic acid) was synthesized according to the procedure described in [7]. Yield 80%, mp 187–190°C; published data [7]: mp 207–210°C.

The spectral parameters of the product were consistent with those reported in [7].

Alkaline hydrolysis of steviol 16α,17-epoxide (II). Compound **II**, 0.09 g (0.27 mmol), was added to a solution of 0.07 g (1.25 mmol) of potassium hydroxide in 20 ml of water, the mixture was stirred for 12 h at 100°C, diluted with water (50 ml), and carefully acidified with acetic acid, and the white curd-like material was filtered off and recrystallized from methanol. We thus isolated 0.02 g of a white solid which was a mixture of compounds **IV** and **VIII**.

17-Hydroxy-16-oxo-*ent*-beyeran-19-oic acid (IV). IR spectrum, ν, cm^{-1}: 3400 (O–H), 1727 (C=O), 1698 (COOH). ^{1}H NMR spectrum, δ, ppm: 0.75–1.8 m (28H, isosteviol), 0.81 s (3H, $C^{20}H_3$), 1.26 s (3H, $C^{18}H_3$), 1.31 d.d (1H, 14-H_{ax}, J = 11.3, 3.7 Hz), 1.37 d (1H, 12-H_{ax}, J = 12.6 Hz), 1.80 d.d (1H, 12-H_{eq}, J = 11.4, 2.5 Hz), 1.86 d (1H, 14-H_{eq}, J = 18.8 Hz), 2.18 d (1H, 3-H_{eq}, J = 12.5 Hz), 2.68 d.d (1H, 15α-H, J = 18.8, 3.7 Hz), 3.51 d and 3.64 d (1H each, 17-H, J = 11.6 Hz). Mass spectrum: m/z 334 (I_{rel} 13%) $[M]^+$.

13α,16α,17-Trihydroxy-*ent*-kauran-19-oic acid (VIII). ^{1}H NMR spectrum, δ, ppm: 0.75–1.80 m (28H, steviol), 0.94 s (3H, $C^{20}H_3$), 1.22 s (3H, $C^{18}H_3$), 3.81 d and 3.63 d (1H each, 17-H, J = 11.3 Hz).

Reaction of steviol 16α,17-epoxide (II) with $BF_3 \cdot Et_2O$. Boron trifluoride–diethyl ether complex, 0.02 ml (0.16 mmol), was added to 80 mg (0.24 mmol) of steviol 16α,17-epoxide (**II**) in 10 ml of benzene, and the mixture was stirred for 30 min at 20°C. The mixture was then concentrated, treated with water, and extracted with diethyl ether. The extracts were dried over $MgSO_4$, and the solvent was distilled off to isolate compound **IV** as a colorless crystalline substance. Yield 80 mg (100%), mp 227–229°C; published data [5]: mp 230–232°C.

Steviol 15α,16-epoxide (XI, 15α,16-epoxy-13-hydroxy-*ent*-kauran-19-oic acid) was synthesized according to the procedure described in [6] by epoxidation of a mixture of steviol (**I**) and its Δ^{15}-isomer [22] and was isolated by double recrystallization from acetone–hexane. Yield 5%, mp 236–238°C. IR spectrum, ν, cm^{-1}: 3386 (O–H), 1691 (OC=O). ^{1}H NMR spectrum, δ, ppm: 0.70–1.60 m (28H, steviol), 0.93 s (3H, $C^{20}H_3$), 1.24 s (3H, $C^{18}H_3$), 1.38 s (3H, $C^{17}H_3$), 2.72 d (1H, 15-H, J = 1.0 Hz). Found, %: C 72.00; H 9.34. $C_{20}H_{30}O_4$. Calculated, %: C 71.82; H 9.04.

Reaction of epoxide XI with $BF_3 \cdot Et_2O$. Boron trifluoride–diethyl ether complex, 0.013 ml (0.1 mmol), was added to 40 mg (0.12 mmol) of steviol 15α,16-epoxide (**XI**) in 10 ml of benzene, and the mixture was stirred for 2 h at 20°C. The mixture was concentrated, treated with water, and extracted with diethyl ether. The extracts were dried over $MgSO_4$, and the solvent was distilled off to obtain 14α-hydroxy-16-oxo-*ent*-beyeran-19-oic acid (**XII**) as a colorless crystalline substance. Yield 40 mg (100%), mp 245–247°C (from acetone–hexane). IR spectrum, ν, cm^{-1}: 3469 (O–H), 1730 (C=O), 1694 (OC=O). ^{1}H NMR spectrum, δ, ppm: 0.70–2.00 m (30H, isosteviol), 0.82 s (3H, $C^{20}H_3$), 1.04 s (3H, $C^{18}H_3$), 1.27 s (3H, $C^{17}H_3$), 2.53 d.d (1H, 15α-H, J = 18.6, 1.4 Hz), 3.38 d (1H, 14-H, J = 1.3 Hz).

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