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Eleuthesides and Their Analogs: III.* Reaction of Red-Al with γ,δ-Epoxy Nitriles

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Abstract—Oxiranyl-substituted cycloalkenecarbonitriles obtained by the Beckmann fragmentation of oximes derived from levoglucosenone adducts with 1,3-butadiene, isoprene, cyclohexadiene, and cyclopentadiene were subjected to Red-Al reduction with opening of the epoxide ring. The reactions with 1,3-butadiene, isoprene, and cyclohexadiene derivatives were accompanied by cyclopropane ring closure and reduction of the cyano group to aldehyde, whereas the cyclopentadiene derivative underwent hydrogenolysis of the oxirane fragment.

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We found previously [2] that reductive opening of the oxirane ring in epoxy nitrile I, including the reaction with Red-Al under anhydrous conditions, yields secondary alcohol II, the cyano group remaining unchanged. Treatment of I with Red-Al in the presence of water was accompanied by cyclopropane ring closure and reduction of the cyano group to aldehyde [2]. We have found no published data on the reduction of nitriles to aldehydes by the action of Red-Al.

Our attempts to obtain aldehyde from cyanoalkyl formate III having no oxirane fragment were unsuccessful. Treatment of III with Red-Al-H₂O (15:1) resulted in hydrolysis of the ester moiety, whereas the

reaction in the absence of water involved reductive dechlorination with formation of hydroxy nitrile II, i.e., the result was analogous to oxirane ring opening in compound I under anhydrous conditions (Scheme 1).

Presumably, the presence of a small amount of water favors the reaction to proceed toward formation of carbanion which initiates cyclopropanation or facilitates reduction of the cyano group. Furthermore, the formation of three-membered carbocycle may also activate the cyano group, leading to its reduction to aldehyde.

With a view to elucidate the reaction mechanism, epoxy nitrile I was treated with lithium diisopropyl-



* For communication II, see [1].



amide (LDA) to obtain in good yield hydroxy nitrile V. The hydroxy group in V was protected by treatment with *tert*-butyldimethylsilyl chloride (TBSCl), the resulting ether VI was reduced with Red-Al, and subsequent removal of the TBS protection afforded hydroxy aldehyde VII (Scheme 2). Thus, the first step in the reaction of I with Red-Al is cyclopropane ring closure, and in the second step excess Red-Al reduces the activated cyano group to aldehyde.

We tried to extend the scope of the discovered transformation of (1R,2R,6S)-2-methyl-6-[(2S)-oxiran-2-yl]cyclohex-3-ene-1-carbonitrile (I) into (1S,2R,6R,7S)-7-hydroxymethyl-2-methylbicyclo-[4.1.0]hept-3-ene-1-carbaldehyde (VII) [2] by the action of Red-Al with a view to obtain new synthetic blocks useful for the synthesis of eleutheside analogs. For this purpose we used Diels-Alder adducts VIII-XI derived from levoglucosenone and butadiene [3], isoprene [4], cyclopentadiene [5], and cyclohexadiene. The initial epoxy nitriles were synthesized according to a scheme analogous to that reported for the piperylene adduct [2]. The oximation of VIII-XI was more efficient as compared to the piperylene adduct, and oximes XII-XV were isolated in 95-98% yield (Scheme 3).

The second-order Beckmann rearrangement of oximes XII and XIV by the action of SOCl₂ afforded

chloro cyano formates XVI and XVIII in 83 and 62% yield, respectively. The yield of XVII from oxime XIII was appreciably lower, 49%. In addition, we isolated from the reaction mixture 7% of hydroxy formate XX. Chloro formate XIX was isolated in even poorer yield (32%), while the major product was γ -lactone XXI (40%). The oxirane ring in chloro formates XVI, XVII, and XIX was smoothly formed upon treatment with potassium hydroxide in aqueous ethanol (Scheme 4). Under analogous conditions, chloro formate XVIII gave rise to chlorohydrin XXV and γ -lactone **XXVI**, the latter being formed as a result of hydrolysis of the cyano group. Acid hydrolysis of XVIII (HCl/H₂O) afforded only 83% of chlorohydrin XXV, and the latter was converted into epoxide **XXVII** in 94% yield (cf. [2]).

From epoxy nitriles **XXII–XXIV** we obtained hydroxy aldehydes **XXVIII–XXX** (Scheme 5). In the reaction with **XXII**, we also succeeded in isolating from aqueous solution of the reaction mixture 36% of amino diol **XXXI**. Under analogous conditions, epoxy nitrile **XXVII** unexpectedly gave rise to nitrile **XXXII** as reductive deoxygenation product. It is known that closure of *endo*-cyclopropane ring in norbornene systems is fairly difficult [6]; therefore, the oxirane ring opening step is likely to be accompanied by hydrogenolysis (cf. [7]).



VIII, **XII**, **XVI**, R = H, *n* = 0; **IX**, **XIII**, **XVII**, R = Me, *n* = 0; **X**, **XIV**, **XVIII**, R = H, *n* = 1; **XI**, **XV**, **XIX**, R = H, *n* = 2.

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XXVIII, R = H, *n* = 0; **XXIX**, R = Me, *n* = 0; **XXX**, R = H, *n* = 2.

Thus, unlike the reduction-ring opening of the piperylene adduct by the action of Red-Al, the yields of the corresponding products from adducts **XXII**-**XXIV** derived from butadiene, isoprene, and cyclohexadiene are appreciably lower, whereas no cyclopropane derivative is formed from oxiranylnorbornene **XXVII**.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 and 75.47 MHz, respectively, and on a Bruker Avance III instrument (500 MHz for ¹H) using CDCl₃ as solvent unless otherwise stated. The IR spectra were measured on UR-20 and Specord M-80 instruments from films or mineral oil mulls. The mass spectra were obtained on a Hewlett Packard GC/MS system consisting of an HP 6890 chromatograph coupled with an HP 5973 mass-selective detector. Analytical thin-layer chromatography was performed on Sorbfil PTSKh-AF-A plates (*Sorbpolimer* closed corporation, Krasnodar, Russia). The melting points were measured on a Boetius PHMK 05 apparatus. The elemental compositions were determined on a Euro 2000 CHNS(O) analyzer. The optical rotations were measured with a Perkin Elmer 341 polarimeter. Commercial Red-Al (a 70% solution in toluene, Lancaster) was used.

(1*R*,2*R*,6*S*)-6-[(1*R*)-1-Hydroxyethyl]-2-methylcyclohex-3-ene-1-carbonitrile (II). A solution of 0.53 g (2.33 mmol) of compound III in 20.0 ml of THF was cooled to 0°C, 1.4 ml (4.66 mmol) of Red-Al was added under argon, and the mixture was stirred for 2 h at 0°C, treated with 6% aqueous HCl to dissolve the precipitate, and extracted with ethyl acetate (3× 20 ml). The extracts were combined and dried over MgSO₄, the solvent was distilled off on a rotary evaporator, and the residue was subjected to chromatography on silica gel. Yield 0.362 g (94%), oily substance, $[\alpha]_D^{20} = -81.59^\circ$ (*c* = 1.0, CHCl₃), *R*_f 0.5 (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3400, 3025, 2980, 2890, 2240, 1470, 1390, 1310, 1250,

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1100, 1010, 950, 890, 760. ¹H NMR spectrum, δ , ppm: 1.22 d (3H, CH₃, J = 7.2 Hz), 1.28 d (3H, 1'-CH₃, J = 6.2 Hz), 1.73 d.d.d.d (1H, 6-H, J = 9.5, 9.5, 5.5, 2.7 Hz), 1.94 m and 2.06 m (1H each, 5-H), 2.48 m (1H, 2-H), 3.46 d.d (1H, 1-H, J = 4.1, 3.8 Hz), 3.75 d.q (1H, 1'-H, J = 9.5, 6.2 Hz), 5.45 d (1H, 3-H, J = 10.1 Hz), 5.73 m (1H, 4-H). ¹³C NMR spectrum, δ_{C} , ppm: 18.89 (CH₃), 21.52 (CH₃), 25.05 (C⁵), 32.25 (C¹), 34.14 (C⁶), 43.61 (C²), 68.91 (C^{1'}), 119.0 (CN), 125.73 (C⁴), 129.80 (C³). Mass spectrum: m/z 166 [M + H]⁺. Found, %: C 73.45; H 9.62; N 7.76. C₁₀H₁₅NO. Calculated, %: C 72.69; H 9.15; N 8.48. *M* 165.2322.

(1R,2R,6S)-6-[(1S)-2-Chloro-1-hydroxyethyl]-2methylcyclohex-3-ene-1-carbonitrile (IV). A solution of 0.59 ml (1.98 mmol) of Red-Al in 10.0 ml of THF was cooled to 0°C, 0.003 ml (0.165 mmol) of water was added, the mixture was stirred for 1 h at room temperature, and a solution of 0.15 g (0.66 mmol) of compound III in 10.0 ml of THF was added. When the reaction was complete, the mixture was treated with 5% aqueous HCl to weakly acidic reaction and extracted with ethyl acetate $(3 \times 30 \text{ ml})$, the extracts were combined, dried over MgSO₄, and concentrated on a rotary evaporator, and the residue was subjected to chromatography on silica gel. Yield 0.130 g (99%), oily substance, $[\alpha]_{D}^{20} = -56.65^{\circ}$ (c = 1.0, CHCl₃), $R_{f} =$ 0.23 (petroleum ether-EtOAc, 3:1). ¹H NMR spectrum, δ , ppm: 1.21 d (3H, CH₃, J = 7.3 Hz), 2.03 m (3H, 5-H, 6-H), 2.50 m (1H, 2-H), 3.20-3.43 br.s (1H, OH), 3.43 d (1H, 1-H, J = 5.0 Hz), 3.58 d.d (1H, 2'-H₄, J = 11.9, 6.1 Hz, 3.80 m (2H, 1'-H, 2'-H_B), 5.48 d (1H, 3-H, J = 9.9 Hz), 5.72 d.d.d (1H, 4-H, J = 9.9, 7.1, 2.7 Hz). ¹³C NMR spectrum, δ_{C} , ppm: 18.91 (CH₃), 24.44 (C⁵), 29.64 (C²), 34.05 (C⁶), 39.62 (C¹), 48.54 $(C^{2'})$, 72.09 $(C^{1'})$, 118.62 (CN), 124.92 (C^{4}) , 130.14 (C³). Mass spectrum: m/z 200 $[M + H]^+$. Found, %: C 60.31; H 6.98; Cl 17.92; N 7.15. C₁₀H₁₄ClNO. Calculated, %: C 60.15; H 7.07; Cl 17.76; N 7.01. *M* 199.677.

(2*R*,6*R*,7*S*)-7-(Hydroxymethyl)-2-methylbicyclo-[4.1.0]hept-3-ene-1-carbonitrile (V). A solution of 0.21 ml (1.5 mmol) of diisopropylamine in 5.0 ml of THF was cooled to -1 to 0°C, 0.7 ml (1.6 mmol) of a 2.3 M solution of butyllithium in hexane was added under argon, the mixture was stirred for 20 min, and a solution of 0.2 g (1.2 mmol) of epoxy nitrile I in 10.0 ml of THF was added. When the reaction was complete (TLC), the mixture was treated with 3% aqueous HCl and extracted with ethyl acetate (3×10 ml). The extracts were combined, dried over MgSO₄, and concentrated on a rotary evaporator, and the residue was subjected to chromatography on silica gel. Yield 0.135 g (68%), oily substance, R_f 0.4 (petroleum ether–EtOAc, 1:1). IR spectrum, v, cm⁻¹: 3417, 2933, 2231, 1438, 1013, 717. ¹H NMR spectrum, δ , ppm: 1.22 d (3H, CH₃, J = 7.4 Hz), 1.89 m (1H, 6- H), 1.78 m (1H, 7-H), 2.28 br.d and 2.54 br.d (1H each, 5-H, J = 19.2 Hz), 2.85 m (1H, 2-H), 3.66 d.d (1H, 1'-H_A, J = 11.6, 7.9 Hz), 3.88 d.d (1H, 1'-H_B, J = 7.9, 6.4 Hz), 5.42 m (1H, 4-H), 5.62 br.d (1H, 3-H, J =9.0 Hz). ¹³C NMR spectrum, δ_C , ppm: 16.09 (C¹), 18.71 (C⁶), 19.48 (C⁵), 20.20 (CH₃), 28.83 (C⁷), 29.79 (C²), 56.52 (C^{1'}), 123.82 (C⁴), 128.19 (C³), 124.42 (CN). Found, %: C 73.49; H 8.03; N 8.60. C₁₀H₁₃NO. Calculated, %: C 73.59; H 8.03; N 8.58.

(2R,6R,7S)-7-(tert-Butyldimethylsilyloxy)-2methylbicyclo[4.1.0]hept-3-ene-1-carbonitrile (VI). Compound V, 0.116 g (0.7 mmol), was dissolved in 5.0 ml of methylene chloride, 0.121 g (0.84 mmol) of TBSCl and 0.116 g (1.7 mmol) of imidazole were added, and the mixture was stirred for 30 min. When the reaction was complete, the mixture was treated with water and extracted with methylene chloride $(3 \times 10 \text{ ml})$. The extracts were combined, dried over MgSO₄, and concentrated, and the residue was subjected to chromatography on silica gel. Yield 0.198 g (100%), oily substance, $[\alpha]_D^{20} = -27.6^\circ$ (c = 2.0, CHCl₃), $R_f 0.7$ (petroleum ether-EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3378, 2930, 2232, 1708, 1464, 1091, 837, 670. ¹H NMR spectrum, δ , ppm: 0.0 s (6H, SiCH₃), 0.87 s (9H, *t*-Bu), 1.18 d (3H, CH₃, *J* = 7.3 Hz), 1.68 m (1H, 7-H), 1.82 m (1H, 6-H), 2.24 br.d and 2.46 br.d (1H each, 5-H, J = 21.2 Hz), 2.82 m (1H, 2-H), 3.60 d.d (1H, 1'-H₄, J = 11.1, 7.8 Hz), 3.75 d.d (1H, 1'-H_B, J = 7.8, 6.5 Hz), 5.58 br.d (1H, 4-H, J =10.4 Hz), 5.90 br.d (1H, 3-H, J = 10.4 Hz). ¹³C NMR spectrum, δ_{C} , ppm: -5.45 (SiCH₃), 19.79 (C¹), 20.40 (C⁶), 20.56 (CH₃), 24.85 (C⁵), 25.57 [(CH₃)₃C], 29.88 (C²), 30.28 (C⁷), 57.62 (C¹), 124.08 (C⁴), 124.74 (CN) 129.68 (C³). Found, %: C 69.25; H 9.82; N 5.05; Si 10.12. C₁₆H₂₇NOSi. Calculated, %: C 69.26; H 9.81; N 5.05; Si 10.12.

(1*S*,2*R*,6*R*,7*S*)-7-Hydroxymethyl-2-methylbicyclo[4.1.0]hept-3-ene-1-carbaldehyde (VII). A solution of 0.13 g (0.47 mmol) of silyl ether VI in 10.0 ml of THF was cooled to 0°C, and 0.14 ml (0.7 mmol) of Red-Al was added to the solution under argon. When the reaction was complete (TLC), the mixture was treated with 6% aqueous HCl until the precipitate dissolved completely, and the product was extracted into ethyl acetate (3×20 ml). The extracts were combined, dried over MgSO₄, and concentrated on a rotary

evaporator, and the residue was subjected to hydrolysis in a mixture of 2.5 ml of THF, 0.25 ml of water, and 0.25 ml of concentrated aqueous HCl. When the reaction was complete (TLC), the mixture was neutralized with a saturated solution of NaHCO₃ and extracted with ethyl acetate $(3 \times 10 \text{ ml})$, the combined extracts were dried over MgSO₄ and concentrated, and the residue was purified by chromatography on silica gel. Yield 0.068 g (87%), colorless crystals, mp 85.7°C, $[\alpha]_D^{20} = -105.2^\circ$ (c = 1.0, CHCl₃), $R_f 0.3$ (petroleum ether-EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3400, 2970, 1640, 1700, 1370, 1070, 920. ¹H NMR spectrum, δ, ppm: 1.07 d.d.d (3H, CH_3 , J = 2.4, 2.7, 7.3 Hz), 1.72 d.d (1H, 6-H, J = 7.3, 9.7 Hz), 1.81 d.d.d (1H, 7-H, J = 6.1, 8.1, 9.7 Hz), 2.35 d.d (1H, 5-H₄, J = 4.7, 19.2 Hz), 2.50 d.d (1H, 5-H_B, J = 7.3, 19.2 Hz), 3.25 d.d.d (1H, 2-H, J = 2.4, 2.7, 7.3 Hz), 3.80 d.d $(1H, 8-H_B, J = 8.1, 11.2 Hz), 3.92 \text{ d.d.d} (1H, 8-H_B, J =$ 6.1, 8.1, 11.2 Hz), 5.50 d.d.d.d (1H, 4-H, J = 2.4, 4.7, 6.0, 10.3 Hz), 5.57 d.d.d (1H, 3-H, J = 2.4, 2.7, 3.0 Hz), 8.80 s (1H, CHO). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 19.27 (CH₃), 19.81 (C⁶), 20.47 (C⁵), 25.13 (C⁷), 27.69 (C²), 38.56 (C¹), 57.81 (C⁸), 122.96 (C⁴), 129.96 (C³), 201.80 (CHO). Found, %: C 72.26; H 8.49. C₁₀H₁₄O₂. Calculated, %: C 72.25; H 8.50.

(1S, 2S, 7R, 9R)-10, 12-Dioxatricyclo $[7.2.1.0^{2,7}]$ dodec-4-en-8-one syn-oxime (XII). Hydroxylamine hydrochloride, 6.5 g (93.9 mmol), was added under stirring to a solution of 5.0 g (27.6 mmol) of compound VIII in 50.0 ml of pyridine. The mixture was stirred for 30 min, ethyl acetate was added, and the mixture was washed with water. The product was extracted into ethyl acetate $(3 \times 10 \text{ ml})$, and the combined extracts were dried over MgSO4 and concentrated on a rotary evaporator. Yield 5.2 g (97%), colorless crystals, mp 118°C, $[\alpha]_D^{20} = +10.3^\circ$ (*c* = 1.0, CHCl₃), *R*_f = 0.5 (petroleum ether-EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3280, 2970, 2820, 1458, 964. ¹H NMR spectrum, δ, ppm: 1.95–2.06 m (2H, 6-H), 2.07–2.19 m (2H, 3-H), 2.36–2.54 m (1H, 2-H), 3.14 t (1H, 7-H, J= 6.2 Hz), 3.92 d.d (1H, exo-11-H, J = 7.0, 5.1 Hz), 4.08 d (1H, endo-11-H, J = 7.0 Hz), 4.41 d (1H, 1-H, J = 5.1 Hz), 5.62 m (2H, 4-H, 5-H), 6.50 s (1H, 9-H). ¹³C NMR spectrum, δ_{C} , ppm: 22.63 (C⁶), 23.50 (C³), $30.48 (C^7), 38.92 (C^2), 67.53 (C^{11}), 77.23 (C^1), 92.63$ (C^9) , 123.33 (C^4) , 124.81 (C^5) , 155.20 (C^8) . Mass spectrum: m/z 196 $[M + H]^+$. Found, %: C 61.91; H 9.00; N 6.50. C₁₀H₁₃NO₃. Calculated, %: C 61.53; H 6.71; N 7.18. M 195.2152.

(1S,2S,7R,9R)-4-Methyl-10,12-dioxatricyclo-[7.2.1.0^{2,7}]dodec-4-en-8-one *syn*-oxime (XIII) was

synthesized in a similar way from 1.9 g (9.0 mmol) of compound IX. Yield 1.9 g (95%), colorless crystals, mp 88°C, $[\alpha]_D^{20} = -13.0^\circ$ (*c* = 1.0, CHCl₃), $R_f = 0.57$ (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3417, 2968, 2927, 1726, 1444, 1170, 1114. ¹H NMR spectrum, δ, ppm: 1.60 s (3H, CH₃), 1.80 d.d (1H, 6-H, J = 17.3, 6.2 Hz), 2.00–2.30 m (2H, 2-H, 3-H), 2.30 d (1H, 3-H, J = 16.5 Hz), 2.46 m (1H, 6-H), 3.40 t (1H, 1)7-H, J = 6.2 Hz), 3.87 d.d (1H, exo-11-H, J = 7.2, 5.2 Hz), 4.38 d (1H, 1-H, J = 5.2 Hz), 4.40 d (1H, endo-11-H, J = 7.2 Hz), 5.29 br.s (1H, 5-H), 6.44 s (1H, 9-H), 7.92 br.s (1H, NOH). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 22.89 (C⁶), 23.60 (CH₃), 28.41 (C³), 29.97 (C^7) , 29.40 (C^2) , 67.53 (C^{11}) , 77.19 (C^1) , 92.61 (C^9) , 117.40 (C⁵), 131.58 (C⁴), 155.03 (C⁸). Mass spectrum: m/z 210 $[M + H]^+$. Found, %: C 63.42; H 9.28; N 6.20. C₁₁H₁₅NO₃. Calculated, %: C 63.41; H 9.31; N 6.16. *M* 209.2417.

(1S,2S,3S,6R,7R,9R)-10,12-Dioxatetracyclo- $[7.2.1.1^{3,6}.0^{2,7}]$ tridec-4-en-8-one *svn*-oxime (XIV) was synthesized in a similar way from 5.0 g (27.0 mmol) of X. Yield 5.2 g (97%), oily substance, $[\alpha]_{D}^{20} = -50^{\circ}$ (c = 0.58, CHCl₃), R_{f} 0.38 (petroleum ether-EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3433, 2860, 1750–1608, 1456. ¹H NMR spectrum, δ, ppm: 1.34 d $(1H, 13-H_4, J = 8.6 \text{ Hz}), 1.45 \text{ d.t} (1H, 13-H_B, J = 8.6),$ 1.8 Hz), 2.20 d.d (1H, 2-H, J = 9.4, 3.1 Hz), 2.94 br.s (1H, 3-H), 3.05 d.d (1H, 7-H, J = 9.4, 4.1 Hz),3.25 br.s (1H, 6-H), 3.72 d (1H, endo-11-H, J= 6.9 Hz), 3.78 d.d (1H, exo-11-H, J = 6.9, 5.0 Hz), 4.54 d (1H, 1-H, J = 5.0 Hz), 6.08 d.d (1H, 4-H, J =5.6, 2.0 Hz), 6.30 m (1H, 5-H), 6.28 s (1H, 9-H), 8.20 br.s (1H, NOH). ¹³C NMR spectrum, δ_C , ppm: $36.62 (C^2), 46.62 (C^3), 46.99 (C^7), 48.20 (C^6), 49.07$ (C¹³), 69.72 (C¹¹), 74.80 (C¹), 90.34 (C⁹), 134.36 (C⁴), 135.08 (C⁵), 154.70 (C⁸). Mass spectrum: m/z 208 $[M + H - CHO]^+$. Found, %: C 63.80; H 8.50; N 6.30. C₁₁H₁₃NO₃. Calculated, %: C 63.98; H 8.50; N 6.22. M 207.2259.

(1*S*,2*S*,3*S*,6*R*,7*R*,9*R*)-10,12-Dioxatetracyclo-[7.2.2.1^{1,9}.0^{2,7}]tetradec-4-en-8-one *syn*-oxime (XV) was synthesized in a similar way from 1.0 g (4.8 mmol) of XI. Yield 1.1 g (98%), colorless crystals, mp 119°C, $[\alpha]_D^{20} = -348.7^\circ$ (*c* = 1.0, CHCl₃), *R*_f 0.26 (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3264, 2941, 1724, 1377, 1175, 1117, 903, 688. ¹H NMR spectrum, δ , ppm: 1.20–1.40 m (2H, 13-H), 1.44–1.62 m (2H, 14-H), 1.84 d (1H, 2-H, *J* = 9.6 Hz), 2.59 m (1H, 3-H), 2.84 d.d (1H, 7-H, *J* = 9.6, 3.3 Hz), 3.05 m (1H, 6-H), 3.68 d (1H, *endo*-11-H, *J* = 7.0 Hz), 3.82 d.d (1H, *exo*-11-H, *J* = 7.0, 5.0 Hz), 4.42 d (1H, 1-H, J = 5.0 Hz), 6.12 d.d (1H, 4-H, J = 7.6, 7.0 Hz), 6.42 d.d (1H, 5-H, J = 7.6, 6.9 Hz), 6.27 s (1H, 9-H), 8.62 br.s (1H, NOH). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 22.78 (C¹³), 27.06 (C¹⁴), 35.35 (C²), 35.87 (C³), 37.64 (C⁶), 42.04 (C⁷), 67.70 (C¹¹), 77.02 (C¹), 91.04 (C⁹), 131.69 (C⁴), 133.64 (C⁵), 155.38 (C⁸). Mass spectrum: m/z 222 [M + H]⁺. Found, %: C 63.10; H 8.60; N 6.30. C₁₂H₁₅NO₃. Calculated, %: C 63.14; H 6.83; N 6.33. M 221.2524.

(1S)-2-Chloro-1-[(1S,6R)-6-cyanocyclohex-3-en-1-yl]ethyl formate (XVI). A solution of 1.8 ml (78.6 mmol) of thionyl chloride in 5.0 ml of methylene chloride was added to a solution of 5.1 g (26.2 mmol) of oxime XII in 30.0 ml of methylene chloride, cooled to 0°C. The mixture was stirred for 1 h at 0°C (TLC) and treated with a saturated aqueous solution of NaHCO₃ (until neutral reaction), the organic phase was separated, and the aqueous phase was extracted with methylene chloride $(3 \times 10 \text{ ml})$. The extracts were combined with the organic phase, dried over MgSO₄, and concentrated on a rotary evaporator. Yield 4.6 g (83%), colorless crystals, mp 46.6°C, $[\alpha]_{D}^{20} = -65.6^{\circ}$ (*c* = 0.5, CHCl₃), R_f 0.6 (petroleum ether-EtOAc, 3:1). IR spectrum, v, cm⁻¹: 1742, 1330. ¹H NMR spectrum, δ , ppm: 2.02-2.26 m (2H, CH₂), 2.31-2.48 m (3H, CH, CH₂), 3.16 d (1H, 6'-H, J = 2.0 Hz), 3.68 d.d (1H, 2-H_A, J =12.7, 3.1 Hz), 3.92 d.d (1H, 2-H⁻_B, J = 12.7, 2.6 Hz), 5.12 d.d (1H, 1-H, J = 9.6, 3.1 Hz), 5.71 br.s (1H, 4'-H), 5.80 br.s (1H, 3'-H), 8.14 s (1H, OCHO). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 24.10 (C^{2'}), 25.86 (C^{6'}), 28.23 (C^{5'}), 35.81 (C^{1'}), 43.57 (C²), 73.10 (C¹), 119.65 (CN), 123.25 (C^{3'}), 125.37 (C^{4'}), 159.94 (OCHO). Found, %: C 56.10; H 5.65; Cl 15.59; N 6.56. C₁₀H₁₂ClNO₂. Calculated, %: C 56.21; H 5.66; Cl 16.59; N 6.56.

Following an analogous procedure, from 4.3 g (20.0 mmol) of oxime XIII we obtained 2.3 g (49%) of formate XVII and 0.3 g (7%) of alcohol XX.

(1*S*)-2-Chloro-1-[(1*S*,6*R*)-3-methyl-6-cyanocyclohex-3-en-1-yl]ethyl formate (XVII). Colorless crystals, mp. 66°C, $[\alpha]_D^{20} = -47.8^\circ$ (c = 1.0, CHCl₃), R_f 0.6 (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 2920, 1728, 1433, 1163, 781, 756. ¹H NMR spectrum, δ , ppm: 1.67 s (3H, CH₃), 1.97 m (2H, CH₂), 2.34 m (3H, CH₂, CH), 3.8 m (1H, 6'-H), 3.67 d.d (1H, 2-H₄, J = 12.67, 3.1 Hz), 3.89 d.d (1H, 2-H_B, J = 12.67, 3.1 Hz), 5.08 d.t (1H, 1-H, J = 9.6, 3.1 Hz), 5.37 m (1H, 4'-H), 8.12 s (1H, OCHO). ¹³C NMR spectrum, δ_C , ppm: 23.09 (CH₃), 25.52 (C^{6'}), 28.06 (C^{2'}), 28.62 (C^{5'}), 36.06 (C^{1'}), 43.47(C²), 72.88 (C¹), 117.24 (C^{4'}), 119.64 (CN), 132.52 (C^{3'}), 159.77 (OCHO). Mass

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spectrum: m/z 245 $[M + H + H_2O]^+$. Found, %: C 58.00; H 6.22; Cl 15.60; N 6.15. $C_{11}H_{14}CINO_2$. Calculated, %: C 58.03; H 6.20; Cl 15.57; N 6.15. M 227.6871.

(1*S*)-2-Hydroxy-1-[(1*S*,6*R*)-3-methyl-6-cyanocyclohex-3-en-1-yl]ethyl formate (XX). Oily substance, $[\alpha]_D^{20} = -6.2^{\circ}$ (c = 1.0, CHCl₃), R_f 0.25 (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3464, 2914, 1724, 1176. ¹H NMR spectrum, δ , ppm: 1.72 s (3H, CH₃), 1.90–2.09 m (3H, CH₂, CH), 2.28–2.49 m (2H, CH₂), 3.50 t (1H, 6'-H, J = 2.4 Hz), 3.85 d.d (1H, 1-H, J = 6.5, 1.7 Hz), 4.14 d.d (1H, 2-H₄, J = 11.6, 6.5 Hz), 4.48 d.d (1H, 2-H_B, J = 11.6, 1.7 Hz), 5.43 br.s (1H, 4'-H), 8.16 s (1H, OCHO). ¹³C NMR spectrum, δ_C , ppm: 23.19 (CH₃), 25.73 (C^{6'}), 27.99 (C^{2'}), 29.31 (C^{3'}), 38.08 (C^{1'}), 65.51 (C²), 70.51 (C¹), 117.40 (C^{4'}), 120.6 (CN), 132.94 (C^{3'}), 161.13 (OCHO). Found, %: C 63.14; H 7.20; N 6.80. C₁₁H₁₅NO₃. Calculated, %: C 63.14; H 7.23; N 6.69.

(1S)-2-Chloro-1-[(1S,2S,3R,4R)-3-cyanobicyclo-[2.2.1]hept-5-en-2-yl]ethyl formate (XVIII) was synthesized in a similar way from 6.0 g (30.0 mmol) of oxime XIV. Yield 4.0 g (62%), colorless crystals, mp 45.5°C, $[\alpha]_{\rm D}^{20} = -42.6^{\circ}$ (c = 1.15, CHCl₃), $R_{\rm f}$ 0.6 (petroleum ether–EtOAc, 4:1). IR spectrum, v, cm^{-1} : 2891-2866, 2235, 1724, 1712, 1458, 1172, 1151. ¹H NMR spectrum, δ , ppm: 1.46 d.t (1H, 7'-H_A, J = 1.9, 9.4 Hz), 1.65 d.t (1H, 7'-H_B, J = 9.4, 1.6 Hz), 3.00 d.t (1H, 2'-H, J = 10.8, 9.1, 3.1 Hz), 3.08 br.s (1H, 4'-H), 3.15 d.d (1H, 3'-H, J = 9.1, 3.6 Hz), 3.30 br.s $(1H, 1'-H), 3.70 \text{ d.d} (1H, 2-H_A, J = 12.9, 1.9 \text{ Hz}),$ 4.01 d.d (1H, 2-H_B, J = 12.9, 2.2 Hz), 4.73 d.t (1H, 1-H, J = 10.8, 2.2, 1.9 Hz), 6.23 d.d (1H, 6'-H, J = 5.5, 2.8 Hz), 6.44 d.d (1H, 5'-H, J = 5.5, 3.0 Hz), 8.03 s (1H, OCHO). ¹³C NMR spectrum, δ_c , ppm: 31.33 (C^{3'}), 44.10 (C^{2'}), 44.21 (C^{4'}), 44.97 (C²), 46.50 (C^{1'}), 48.63 ($C^{7'}$), 73.36 (C^{1}), 120.01 (CN), 134.66 ($C^{6'}$), 136.41 (C^{5'}), 159.77 (OCHO). Mass spectrum: *m/z* 198 $[M + H - CHO]^+$. Found, %: C 58.50; H 6.00; Cl 15.17; N 6.16. C₁₁H₁₂ClNO₂. Calculated, %: C 58.54; H 5.36; Cl 15.17; N 6.21. M 225.6712.

Following an analogous procedure, from 0.734 g (3.1 mmol) of oxime **XV** we obtained 0.243 g (32%) of formate **XIX** and 0.244 g (40%) of lactone **XXI**.

(1*S*)-2-Chloro-1-[(1*S*,2*S*,3*R*,4*R*)-3-cyanobicyclo-[2.2.2]oct-5-en-2-yl]ethyl formate (XIX). Colorless crystals, mp 39°C, $[\alpha]_D^{20} = -82.1^\circ$ (*c* = 1.0, CHCl₃), R_f 0.5 (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 2800, 1714, 1458, 1139, 721, 372. ¹H NMR spectrum, δ , ppm: 1.32 m (2H, 7-H, 8-H), 1.58 m (2H, 7-H, 8-H), 2.56 t (1H, 2'-H, J = 9.2, 9.2 Hz), 2.63 m (1H, 1'-H), 3.0 m (1H, 4'-H), 3.02 m (1H, 3'-H), 3.73 d.d (1H, 2-H, J = 13.0, 2.9 Hz), 3.97 d.d (1H, 2-H, J = 13.0, 2.7 Hz), 4.87 (1H, 1-H), 6.30 t (1H, 5'-H, J = 7.1, 6.9 Hz), 6.40 t (1H, 6'-H, J = 7.1, 7.0 Hz), 8.00 s (1H, OCHO). ¹³C NMR spectrum, δ_{C} , ppm: 23.08 (C⁷), 25.20 (C⁸), 30.06 (C^{3'}), 32.57 (C^{4'}), 33.95 (C^{2'}), 41.17 (C^{1'}), 44.65 (C²), 74.09 (C¹), 120.67 (CN), 132.94 (C^{6'}), 133.22 (C^{5'}), 160.25 (OCHO). Mass spectrum: m/z 212 [M + H – CHO]⁺. Found, %: C 60.10; H 5.86; C1 14.60; N 5.89; C1 14.79; N 5.84. M 239.6978.

(1S,2S,3S,6R,7R)-5-Hydroxymethyl-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-en-5-one (XXI). Colorless crystals, mp 80°C, $[\alpha]_{D}^{20} = -10.5^{\circ}$ (c = 1.0, CHCl₃), $R_{\rm f}$ 0.1 (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3375, 2926, 1747, 1460, 1192, 719. ¹H NMR spectrum, δ, ppm: 1.23–1.36 m (2H, 10-H, 11-H), 1.48–1.60 m (2H, 10-H, 11-H), 2.55 d.d (1H, 2-H, J= 4.2, 3.3 Hz), 2.70 d.d (1H, 1-H, J = 7.0, 4.2 Hz), 2.80 d.d (1H, 6-H, J = 10.0, 2.4 Hz), 2.95 d.d (1H, 7-H, J = 7.0, 2.4 Hz), 3.10 br.s (1H, OH), 3.60 d.d (1H, $1'-H_A$, J = 12.3, 4.1 Hz), 3.80 d.d (1H, 1'-H_B, J = 12.3, 2.8 Hz), 4.08 m (1H, 3-H), 5.26 d.d (1H, 9-H, J = 7.1, 7.0 Hz), 6.31 d.d (1H, 8-H, J = 7.1, 7.0 Hz). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 23.33 (C¹⁰), 23.50 (C¹¹), 31.64 (C^7) , 32.98 (C^1) , 40.42 (C^2) , 46.26 (C^6) , 64.22 $(C^{1'})$, 85.33 (C³), 133.0 (C⁹), 134.11 (C⁸), 179.64 (C=O). Found, %: C 68.10; H 7.20. C₁₁H₁₄O₃. Calculated, %: C 68.02; H 7.27.

(1R,6S)-6-[(1R)-Oxiran-1-yl]cyclohex-3-ene-1carbonitrile (XXII). A solution of 4.5 g (21.1 mmol) of formate XVI and 4.8 g of potassium hydroxide in a mixture of 16.1 ml of water and 32.2 ml of ethanol was stirred for 30 min (TLC). The mixture was neutralized with 10% aqueous HCl to pH 7 and extracted with ethyl acetate $(3 \times 10 \text{ ml})$, the extracts were combined, washed with brine, dried over MgSO₄, and concentrated, and the residue was subjected to chromatography on silica gel. Yield 3.0 g (95%), colorless crystals, mp 18°C, $[\alpha]_{D}^{20} = -79.5^{\circ}$ (c = 1.0, CHCl₃), $R_{\rm f}$ 0.4 (petroleum ether–EtOAc, 7:1). IR spectrum, v, cm⁻¹: 2926, 2300, 1770, 1433, 921, 864, 673. ¹H NMR spectrum, δ, ppm: 1.55 m (1H, 6-H), 2.13–2.28 m (2H, CH₂), 2.42 m (2H, CH₂), 2.61 d.d (1H, 1-H, J = 4.7, 2.5 Hz), 2.86 d.d (1H, 2'-H_A, J = 10.8, 4.2 Hz), 3.0 d.d.d (1H, 2'-H_B, J = 10.8, 6.6, 2.8 Hz), 3.22 d.d (1H, 1'-H, J = 5.96, 2.8 Hz), 5.66 d.d (1H, 3-H, J = 3.96)10.3, 2.6 Hz), 5.78 d.d (1H, 4-H, J = 10.3, 2.3 Hz). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 23.86 (C⁵), 27.35 (C¹),

27.72 (C²), 38.41 (C⁶), 46.56 (C^{2'}), 52.98 (C^{1'}), 120.02 (CN), 122.98 (C³), 125.54 (C⁴). Mass spectrum: m/z 162 $[M + H]^+$. Found, %: C 72.40; H 7.43; N 9.39. C₉H₁₁NO. Calculated, %: C 72.46; H 7.43; N 9.39. *M* 149.1898.

(1R.6S)-4-Methyl-6-[(1R)-oxiran-1-yl]cyclohex-3-ene-1-carbonitrile (XXIII) was synthesized in a similar way from 2.3 g (10.0 mmol) of XVII. Yield 1.2 g (76%), colorless crystals, mp 16°C, $[\alpha]_D^{20} =$ -31.8° (c = 1.0, CHCl₃), $R_{\rm f}$ 0.53 (petroleum ether-EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3560, 2970, 2918, 2852, 1770, 1436, 871, 783. ¹H NMR spectrum, δ, ppm: 1.48-1.57 m (1H, 2-H₄), 1.68 s (3H, CH₃), 1.95 d.d (1H, 5-H_A, J = 17.7, 4.8 Hz), 2.10 m (1H, 2-H_B), 2.30–2.38 m (2H, 5-H_B, 2'-H_A), 2.57 d.d (1H, 6-H, J = 5.5, 2.5 Hz), 2.82 t (1H, 1-H, J = 4.2 Hz), 2.97 d.d.d (1H, 2'-H_B, J = 11.2, 7.2, 3.3 Hz), 3.15 d.d.d (1H, 1'-H, J = 7.2, 5.3, 2.9 Hz), 5.35 s (1H, 3-H).¹³C NMR spectrum, δ_{C} , ppm: 22.63 (CH₃), 23.53 (C⁵), 26.83 (C¹), 28.26 (C²), 38.38 (C⁶), 46.03 (C²), 52.58 $(C^{1'})$, 117.0 (C^{3}) , 119.84 (CN), 132.54 (C^{4}) . Mass spectrum: m/z 164 $[M + H]^+$. Found, %: C 73.09; H 8.00; N 8.58. C₁₀H₁₃NO. Calculated, %: C 73.59; H 8.03; N 8.58. *M* 163.2164.

(1S,2R,3S,4S)-3-[(1R)-Oxiran-1-yl]bicyclo[2.2.2]oct-5-ene-2-carbonitrile (XXIV) was synthesized in a similar way from 0.243 g (1.0 mmol) of XIX. Yield 0.133 g (63%), colorless crystals, mp 75°C, $\left[\alpha\right]_{\rm D}^{20}$ = -120.6° (c = 1.0, CHCl₃), \tilde{R}_{f} 0.33 (petroleum ether-EtOAc, 3:1). IR spectrum, v, cm⁻¹: 1458, 1377, 1174, 875, 725, 443. ¹H NMR spectrum, δ, ppm: 1.22– 1.38 m (2H, 7-H, 8-H), 1.47–1.52 m (2H, 7-H, 8-H), 1.72 t.d (1H, 3'-H, J = 9.7, 9.6, 1.6 Hz), 2.09 d.d.d $(1H, 1-H, J = 9.6, 3.2, 2.4 Hz), 2.56 d.d (1H, 2-H_4, J =$ 4.8, 2.4 Hz), 2.61 m (1H, 4'-H), 2.82 d.d (1H, 2-H_B) J = 4.8, 3.2 Hz), 2.99 d (1H, 1'-H, J = 2.6 Hz), 3.35 d.d (1H, 2'-H, J = 9.7, 2.6 Hz), 6.39 m (2H, 5'-H, 6'-H).¹³C NMR spectrum, δ_{C} , ppm: 23.60 (C^{8'}), 24.80 (C^{7'}), 31.59 (C^{2'}), 33.14 (C^{1'}), 35.54 (C^{3'}), 44.35 (C^{4'}), 47.14 (C^2) , 54.07 (C^1) , 120.45 (CN), 132.30 (C^5) , 134.24 (C^{6'}). Found, %: C 75.46; H 7.48; N 7.40. C₁₁H₁₃NO. Calculated, %: C 75.40; H 7.48; N 7.99.

Hydrolysis of compound XVIII. *a*. As described above for the hydrolysis of **XVI**, from 3.8 g (17.0 mmol) of formate **XVIII** we obtained 2.2 g of a mixture of chlorohydrin **XXV** (56%) and lactone **XXVI** (17%).

b. Compound **XVIII**, 0.2 g (1.0 mmol), was dissolved in 2.7 ml of THF, and 0.27 ml of water and 0.27 ml of concentrated aqueous HCl were added.

When the reaction was complete (TLC), the mixture was neutralized with a saturated aqueous solution of NaHCO₃ and extracted with ethyl acetate (3×10 ml), the combined extracts were dried over MgSO₄ and concentrated, and the residue was purified by chromatography on silica gel. Yield of **XXV** 0.144 g (83%).

(1*R*,2*R*,3*S*,4*S*)-3-[(1*S*)-2-Chloro-1-hydroxyethyl]bicyclo[2.2.1]hept-5-ene-2-carbonitrile (XXV). Oily substance, R_f 0.3 (petroleum ether-EtOAc, 3:1). ¹H NMR spectrum, δ , ppm: 1.60 d (1H, 7-H₄, J = 9.0 Hz), 1.39 d (1H, 7-H_B, J = 9.0 Hz), 2.55 d.t (1H, 3-H, J = 9.1, 9.1, 3.1 Hz), 2.92 br.s (1H, 4-H), 3.02 br.s (1H, OH), 3.16 d.d (1H, 2-H, J = 9.1, 3.2 Hz), 3.24 br.s $(1H, 1-H), 3.50 \text{ m} (1H, 2'-H_A), 3.58 \text{ d.d} (1H, 2'-H_B, J =$ 13.7, 3.3 Hz), 3.75 d.d.d (1H, 1'-H, J = 9.1, 3.6, 3.3 Hz), 6.18 m (1H, 5-H), 6.38 d.d (1H, 6-H, J = 5.4, 2.7 Hz). ¹³C NMR spectrum, δ_{C} , ppm: 32.07 (C²), 44.50 (C³), 46.40 (C¹), 47.90 (C⁴), 48.94 (C^{2'}), 49.51 (C'), 71.81 (C'), 121.18 (CN), 134.94 (C^6) , 136.15 (C⁵), 159.77 (OCHO). Found, %: C 60.70; H 6.19; Cl 17.90; N 7.10. C₁₀H₁₂ClNO. Calculated, %: C 60.76; H 6.12; Cl 17.94; N 7.09.

(1S,2S,3S,6R,7R)-3-Chloromethyl-4-oxatricyclo-[5.2.1.0^{2.6}]dec-8-en-5-one (XXVI). Colorless crystals, mp 56°C, $[\alpha]_{D}^{20} = -84.4^{\circ}$ (c = 1.0, CHCl₃), $R_{f} 0.2$ (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 2960, 2852, 1751, 1458, 1178, 1037, 966, 742. ¹H NMR spectrum, δ , ppm: 1.46 d (1H, 10-H_A, J= 8.4 Hz), 1.66 d (1H, 10-H_B, J = 8.4 Hz), 3.00 m (1H, 2-H), 3.15 m (1H, 7-H), 3.30 br.s (1H, 1-H), 3.33 m (1H, 6-H), 3.62 br.s and 3.64 br.s (1H each, 1'-H), 4.18 d.d.d (1H, 3-H, J = 7.1, 4.2, 2.9 Hz), 6.24 d.d (1H, 9-H, J = 5.5, 2.9 Hz), 6.32 d.d (1H, 8-H, J = 5.5, 2.9 Hz)2.9 Hz). ¹³C NMR spectrum, δ_{C} , ppm: 44.27 (C²), 45.25 (C¹), 45.65 (C⁷), 47.1 (C¹), 48.34 (C⁶), 51.38 $(C^{10}), 79.92 (C^3), 134.46 (C^9), 136.60 (C^8), 176.86$ (C=O). Mass spectrum: m/z 199 $[M + H]^+$. Found, %: C 60.45; H 5.60; Cl 17.85. C₁₀H₁₁ClO. Calculated, %: C 60.46; H 5.58; Cl 17.85. M 198.6458.

(1*R*,2*R*,3*S*,4*S*)-3-[(1*S*)-Oxiran-1-yl]bicyclo[2.2.1]hept-5-ene-2-carbonitrile (XXVII). A solution of 3.2 g (16.0 mmol) of chlorohydrin XXV in 30.0 ml of chloroform was cooled to 0°C, and a solution of sodium methoxide prepared from 0.37 g (16.0 mmol) of sodium and 17.8 ml of methanol was added. The mixture was stirred for 30 min (TLC), treated with water, and extracted with ethyl acetate (3×10 ml). The extract was dried over MgSO₄, the solvent was distilled off, and the residue was subjected to chromatography on silica gel. Yield 2.4 g (94%), colorless crystals, mp 96°C, $[\alpha]_{20}^{20} = -80.3^{\circ}$ (c = 1.9, CHCl₃), $R_{\rm f}$ 0.49 (petroleum ether–EtOAc, 3:1). IR spectrum, v, cm⁻¹: 3414, 2760, 2240, 1458, 1377, 1342, 875, 737. ¹H NMR spectrum, δ , ppm: 1.29 m (1H, 7-H_A), 1.55 d.t (1H, 7-H_B, J = 10.8, 2.0 Hz), 1.97 d.t (1H, 3-H, J = 9.0, 3.3, 2.6 Hz), 2.57 d.d (1H, 2'-H_A, J = 4.9, 2.6 Hz), 2,68 d.d.d (1H, 1'-H, J = 9.0, 4.0, 2.6 Hz), 2.78 d.d (1H, 2'-H_B, J = 4.0, 4.9 Hz), 2.98 br.s (1H, 4-H), 3.13 d.d (1H, 2-H, J = 9.0, 3.6 Hz), 3.26 br.s (1H, 1-H), 6.31 d.d (1H, 6-H, J = 5.6, 2.9 Hz), 6.37 d.d (1H, 5-H, J = 5.6, 3.1 Hz). ¹³C NMR spectrum, δ_{C} , ppm: 31.68 (C²), 45.22 (C³), 46.00 (C¹), 46.15 (C²), 46.96 (C⁴), 48.70 (C⁷), 51.98 (C^{1'}), 119.81 (CN), 134.51 (C⁶), 135.29 (C⁵). Mass spectrum: m/z 162 [M + H]⁺. Found, %: C 74.68; H 7.12; N 8.39. C₁₀H₁₁NO. Calculated, %: C 74.51; H 6.88; N 8.69. *M* 161.2005.

(15,6*R*,7*S*)-7-Hydroxymethylbicyclo[4.1.0]hept-3-ene-1-carbaldehyde (XXVIII). Red-Al, 0.59 ml (3.0 mmol), was dissolved at 0°C under argon in 7.0 ml of THF, 0.004 ml (1.5 mmol) of water was added, the mixture was stirred for 5 min, and a solution of 0.151 g (1.0 mmol) of compound XXII in 5.0 ml of THF was added dropwise. When the reaction was complete (TLC), the mixture was treated with 3% aqueous HCl to dissolve the precipitate, the product was extracted into ethyl acetate (3×2 ml), the combined extracts were dried over MgSO₄ and concentrated, and the residue was subjected to chromatography on silica gel to isolate 0.032 g (21%) of aldehyde XXVIII and 0.105 g (36%) of diol XXXI.

Aldehyde **XXVIII**. Oily substance, $[\alpha]_D^{20} = -54^{\circ}$ (*c* = 1.0, CHCl₃), *R*_f 0.2 (petroleum ether–EtOAc, 2:1). IR spectrum, v, cm⁻¹: 3400, 2889, 1776, 1697, 1147, 756, 665. ¹H NMR spectrum, δ , ppm: 0.87 m (1H, 7-H), 1.60 br.s (1H, OH), 1.75 m (1H, 6-H), 2.10 d.d (1H, 2-H_A, *J* = 9.6, 2.10 Hz), 2.28 br.d (1H, 5-H_B, *J* = 9.3 Hz), 2.55 d.d.d (1H, 5-H_A, *J* = 9.3, 1.5, 1.0 Hz), 3.10 d.t (1H, 2-H_B, *J* = 9.6 Hz), 3.67 d.d (1H, 1'-H_A, *J* = 11.5, 6.7 Hz), 3.75 d.d (1H, 1'-H_B, *J* = 11.5, 6.2 Hz), 5.09 d (1H, 4-H, *J* = 10.0, 1.0 Hz), 5.18 d.d (1H, 3-H, *J* = 10.0, 2.6 Hz), 8.81 s (1H, CHO). ¹³C NMR spectrum, δ_C , ppm: 18.35 (C²), 19.88 (C⁵), 29.20 (C⁷), 29.68 (C⁶), 31.96 (C¹), 57.76 (C^{1'}), 123.37 (C³), 123.71 (C⁴), 102.13 (CHO). Found, %: C 71.09; H 7.80. C₉H₁₂O₂. Calculated, %: C 71.03; H 7.95.

(1*S*,6*R*,7*S*)-7-Hydroxymethyl-4-methylbicyclo-[4.1.0]hept-3-ene-1-carbaldehyde (XXIX) was synthesized in a similar way from 0.5 g (3.1 mmol) of XXIII. Yield 0.107 g (21%), oily substance, $[\alpha]_D^{20} =$ -18.1° (*c* = 1.0, CHCl₃), *R*_f 0.25 (petroleum ether-EtOAc, 1:1). IR spectrum, v, cm⁻¹: 3446, 3396, 2962, 2922, 2854, 1701, 1685, 1438, 1055. ¹H NMR spectrum, δ , ppm: 2.08 s (3H, CH₃), 2.21 m (1H, 7-H), 2.22 m (1H, 6-H), 2.54 m (2H, 2-H_A, 5-H_B), 2.85 d.d (1H, 5-H_A), 3.52 d.d (1H, 2-H_B, J = 2.2 Hz), 4.05 d.d (1H, 1'-H_B, J = 11.5, 7.3 Hz), 4.13 d.d (1H, 1'-H_A, J = 11.5, 6.4 Hz), 5.65 d (1H, 3-H, J = 1.0 Hz), 9.25 s (1H, CHO). ¹³C NMR spectrum, δ_{C} , ppm: 19.06 (C²), 20.86 (CH₃), 23.16 (C⁶), 24.63 (C⁵), 29.25 (C⁷), 31.81 (C¹), 57.49 (C^{1'}), 118.11 (C³), 130.17 (C⁴), 201.89 (CHO). Mass spectrum: m/z 167 [M + H]⁺. Found, %: C 72.36; H 8.50. C₁₀H₁₄O₂. Calculated, %: C 72.26; H 8.49. M 166.217.

(1S,2S,3S,4R,5R)-3-(Hydroxymethyl)tricyclo-[3.2.2.0^{2,4}]non-6-ene-2-carbaldehyde (XXX) was synthesized in a similar way from 0.124 g (0.7 mmol) of **XXIV**. Yield 0.107 g (7%), oily substance, $[\alpha]_D^{20} =$ -20° (c = 0.3, CHCl₃), $R_{\rm f}$ 0.82 (petroleum ether-EtOAc, 6:1). IR spectrum, v, cm⁻¹: 2953, 2924, 1724, 1710, 1182, 1039, 754. ¹H NMR spectrum, δ, ppm: 1.20-1.32 m (2H, 8-H), 1.40-1.52 m (2H, 9-H), 1.70 m (1H, 6-H), 1.40 m (1H, 7-H), 2.20 m (1H, 5-H), 2.35 d (1H, 2-H, J = 7.0 Hz), 3.55 d.d (1H, 1'-H₄, J =11.4, 5.8 Hz), 3.75 d.d (1H, 1'-H_B, J = 11.4, 2.8 Hz), 6.23 t (1H, 4-H, J = 7.0, 6.9 Hz), 6.42 t (1H, 3-H, J = 7.0, 7.0 Hz), 9.98 s (1H, CHO). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 21.94 (C⁸), 26.74 (C⁹), 31.39 (C⁷), 33.52 (C⁶), $38.13 (C^5), 42.87 (C^1), 42.89 (C^2), 50.39 (C^{1'}), 134.19$ (C³), 135.88 (C⁴), 102.13 (CHO). Found, %: C 74.20; H 8.00. C₁₁H₁₄O₂. Calculated, %: C 74.13; H 7.92.

(1S)-1-[(1S,6S)-6-(Aminomethyl)cyclohex-3-en-1-vl]ethane-1,2-diol (XXXI). Colorless crystals, mp 126°C, $[\alpha]_{D}^{20} = +30.1^{\circ}$ (*c* = 1.0, EtOH), *R*_f 0.5 (EtOH). IR spectrum, v, cm⁻¹: 3329, 2855, 1637, 1467, 1394, 1055, 687. ¹H NMR spectrum (CD₃OD), δ , ppm: 2.06 m (3H, 5'-H, 6'-H), 2.41 m (2H, 2'-H), 2.62 d.d.d $(1H, 1'-H, J = 6.7, 5.9, 4.6 \text{ Hz}), 2.93 \text{ t} (1H, CH_2NH_2)$ J = 11.2, 11.2 Hz), 3.43 d.d (1H, CH₂NH₂, J = 11.2, 8.2 Hz), 3.75 d.d.d (1H, 1-H, J = 9.2, 4.6, 4.6 Hz), 3.85 d.d (1H, 2-H_A, J = 11.4, 9.2 Hz), 3.91 d.d (1H, $2-H_B$, J = 11.4, 4.6 Hz), 4.90 br.s (3H, NH₂, OH), 5.66 m (1H, 4'-H), 5.72 m (1H, 3'-H). ¹³C NMR spectrum, δ_{C} , ppm: 21.55 (C^{2'}), 24.76 (C^{5'}), 36.61 (C^{1'}), $37.15 (C^{6'}), 48.02 (CH_2NH_2), 60.25 (C^2), 68.52 (C^1),$ 125.49 (C^{3'}), 125.68 (C^{4'}). Found, %: C 63.10; H 10.00; N 8.28. C₉H₁₇NO₂. Calculated, %: C 63.13; H 10.01; N 8.18.

Following an analogous procedure, from 0.2 g (1.2 mmol) of compound **XXVII** we obtained 0.07 g (38%) of **XXXII** and 0.03 g (15%) of **XXXIII**.

(1S,2S,3S,4R)-3-Ethylbicyclo[2.2.1]hept-5-ene-2carbonitrile (XXXII). Oily substance, R_f 0.3 (petroleum ether–EtOAc, 2:1). IR spectrum, v, cm⁻¹: 3850, 2981, 2300, 1334, 864, 848, 725. ¹H NMR spectrum, δ , ppm: 1.68 (3H, CH₃, J = 7.5 Hz), 1.70 m (1H, 7-H₄), 2.14 d.d (1H, 1'-H₄, J = 4.7, 2.9 Hz), 2.38 d.d (1H, 7-H_B, J = 8.3, 1.5 Hz), 2.52 d.d (1H, 1'-H_B, J = 4.7, 6.5 Hz), 2.65 d.d.d (1H, 3-H, J = 6.5, 4.7, 2.9 Hz), 2.75 d.d (1H, 2-H, J = 4.7, 4.1 Hz), 3.10 br.d (1H, 4-H, J = 1.5 Hz), 3.25 br.s (1H, 1-H), 6.23 d (1H, 6-H, J = 5.7 Hz), 6.28 d (1H, 5-H, J = 5.7 Hz). ¹³C NMR spectrum, δ_{C} , ppm: 30.57 (CH₃), 45.50 (C²), 45.63 (C^{1'}), 47.97 (C³), 48.23 (C⁷), 49.13 (C¹), 52.76 (C⁴), 122.43 (CN), 134.92 (C⁵), 135.56 (C⁶). Found, %: C 81.56; H 8.90; N 9.51. C₁₀H₁₃N. Calculated, %: C 81.59; H 8.90; N 9.51.

(1*R*,2*R*,3*S*,4*R*)-3-[(1*R*)-1-Hydroxyethyl]bicyclo-[2.2.1]hept-5-ene-2-carbonitrile (XXXIII). Oily substance, R_f 0.17 (petroleum ether–EtOAc, 2:1). ¹H NMR spectrum, δ , ppm: 1.62 d (3H, CH₃, *J* = 6.2 Hz), 1.62 d.t (1H, 7-H₄, *J* = 9.0, 1.9, 1.9 Hz), 1.70 d.t (1H, 7-H_B, *J* = 9.0, 1.7, 1.7 Hz), 2.16 d.d (1H, 2-H, *J* = 4.6, 1.8 Hz), 2.32 d.d (1H, 3-H, *J* = 6.2, 4.6 Hz), 2.90 br.s (1H, 4-H), 3.15 d.d (1H, 1'-H, *J* = 6.2, 6.2 Hz), 3.24 br.s (1H, 1-H), 6.05 d.d (1H, 5-H, *J* = 5.6, 2.8 Hz), 6.17 d.d (1H, 6-H, *J* = 5.6, 3.0 Hz). Found, %: C 73.60; H 8.10; N 8.60. C₁₀H₁₃NO. Calculated, %: C 73.59; H 8.03; N 8.58.

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