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Alkylation of 2,4-Dimethylphenol with (+)-α- and (–)-β-Pinenes in the Presence of Aluminum Xylenolate

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Abstract—Alkylation of 2,4-dimethylphenol with (+)-α- and (–)-β-pinenes in the presence of aluminum 2,4-dimethylphenoxide generated *in situ* led to the formation of mixtures of products, from which optically active compounds were isolated. The structure of 2-bornyl-4,6-dimethylphenol was determined by X-ray analysis; its (+)- and (–)-enantiomers were assigned (1*R*,2*R*,4*S*) and (1*S*,2*S*,4*R*) configurations, respectively.

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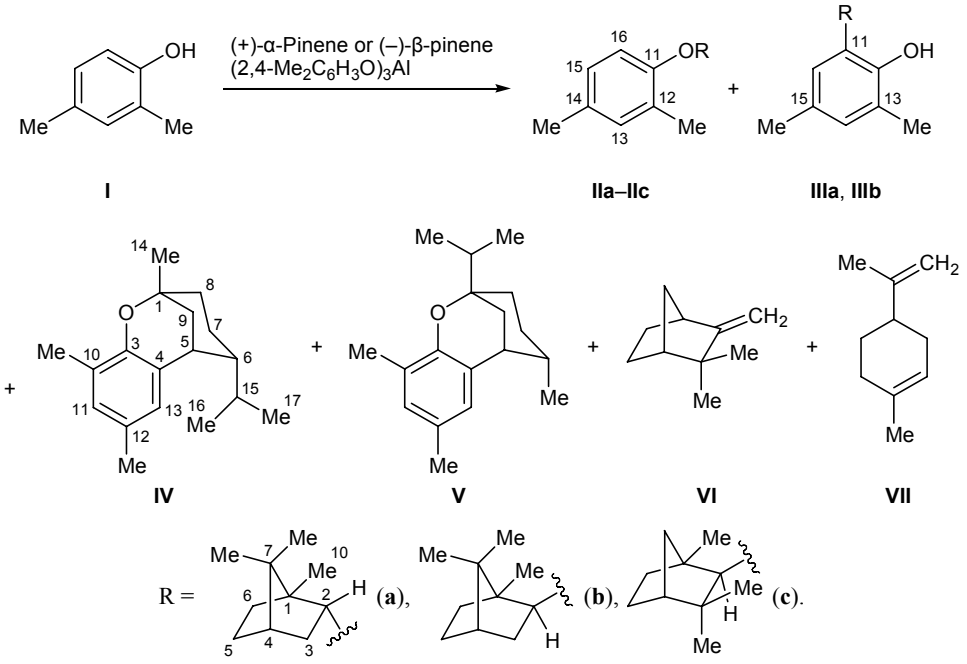
Phenols and cresols with an isobornyl substituents exhibit biological activity, in particular antioxidant, hemorheological, membrane-protecting, and anti-inflammatory [1–4]. In some Western Europe countries the liquid spray formulation Bornilene (Abiogen Pharma) containing 2-isobornyl-4,5-dimethylphenol (Xibornol) as active component is used for the treatment of throat diseases [5]. The problem of obtaining enantiomerically enriched and enantiomerically pure compounds remains topical since different enantiomers may show different biological effects [6].

We previously reported on the alkylation of phenol with excess α- or β-pinene, which led to the formation of optically active C- and O-bornyl derivatives [7, 8].

Scheme 1.



Alkylation of 2,4-dimethylphenol with (+)-α-pinene and (–)-β-pinene

Terpene	Product composition, %							
	IIa	**IIb, IIc**	**IIIa**	**IIIb**	**IV**	**V**	**VI**	**VII**
(+)-α-Pinene	28	3	23	6	3	2	22	13
(–)-β-Pinene	26	2	22	6	17	7	11	9

In the present work we extended this reaction to other phenolic compounds and studied the alkylation of 2,4-dimethylphenol (**I**) with (+)-α-pinene and (–)-β-pinene (Scheme 1).

The reactions were carried out by heating the reactants for 7 h at 200°C using 2 equiv of the terpene component and aluminum 2,4-dimethylphenoxide generated *in situ* as catalyst. The reaction of 2,4-dimethylphenol (**I**) with (+)-α-pinene afforded mainly O-alkylation products, 28% of 2,4-dimethylphenyl bornyl ether (+)-**IIa** and a small amount of an inseparable mixture of isobornyl and fenchyl ethers **IIb** and **IIc**, and C-alkylation products (–)-**IIIa** and **IIIb** with bornyl and isobornyl substituents (see table). In addition, a small amount of chroman derivatives **IV** and **V**, camphene (**VI**), and limonene (**VII**) were isolated in an overall yield 35%. Compounds **VI** and **VII** are likely to be formed via rearrangement and opening of the four-membered pinene ring at fairly high temperature in the presence of Lewis acid [7, 9, 10]. The alkylation of xylenol **I** with (–)-β-pinene gave an analogous set of products, but the yield of chroman derivatives **IV** and **V** was higher, and of terpenes **VI** and **VII**, lower (see table); furthermore, unlike the reaction with (+)-α-pinene, 2,4-dimethylphenyl bornyl ether (–)-**IIa** and 2-bornyl-4,6-dimethylphenol (+)-**IIIa** had the opposite configuration.

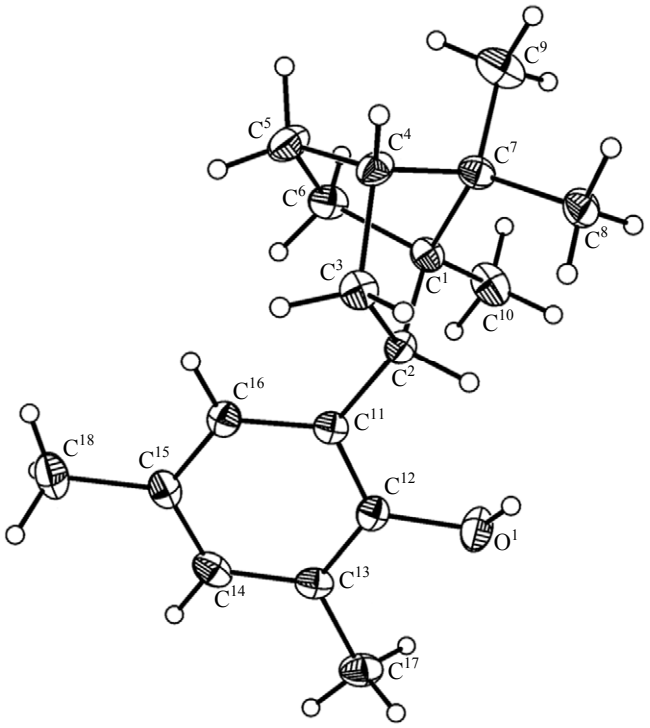


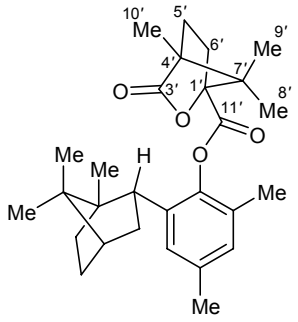
Fig. 1. Structure of the molecule of 2,4-dimethyl-6-{(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}phenol (+)-(**IIIa**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

The structure of the isolated compounds was determined by NMR spectroscopy. Because of similar chromatographic mobilities it was difficult to isolate pure compounds **IIb**, **IIc**, **IIIb**, **IV**, and **V**, and they were identified and quantitated in the product mixtures by ^{1}H NMR spectroscopy. The spectrum of a mixture of ethers **IIb** and **IIc** displayed signals typical of isobornyl ether **IIb**: three singlets at δ 0.95, 1.06, and 1.14 ppm from methyl protons on C^8, C^9, and C^{10}, a multiplet at δ ~4.1 ppm from 2-H, and two multiplets at δ ~6.6 and ~6.9 ppm from aromatic protons; fenchyl ether **IIc** was identified by the presence in the spectrum of a characteristic multiplet signal of 2-H at δ 3.86 ppm. Compound **IIIb** was identified in a mixture with **IIIa** by comparing with the spectral parameters of isobornyl phenols described previously [11]. Cyclic ether **V** was identified in a mixture with compound **IV**. The ^{1}H NMR spectrum of that mixture contained a multiplet signal at δ ~2.7 ppm, which is typical of **V**. The identification of **IV** and **V** was based on comparison with the spectra of structurally related compounds obtained from 3,5-dimethylphenol and β-pinene [12]. The ^{1}H NMR spectra of camphene (**VI**) and limonene (**VII**) coincided with those of authentic samples.

According to the chiral HPLC data, the *ee* values of ethers (+)- and (–)-**IIa** were 80 and 93%, respectively, and of phenols (+)- and (–)-**IIIa**, more than 99 and 75%, respectively.

The structure of compound (+)-**IIIa** isolated as a crystalline substance with high enantiomeric purity

was determined by X-ray analysis. The symmetry-independent part of its unit cell contained one molecule of (+)-**IIIa** (Fig. 1). Orientation of the bornyl fragment with respect to the aromatic ring can be described by the torsion angle $C^{16}C^{11}C^{2}C^{3}$ equal to 37.0(2)°. Molecules (+)-**IIIa** in crystal form dimers through weak intermolecular hydrogen bond O–H···O [H···O 2.20, O···O 2.996(2) Å, ∠OHO 155°], which leads to disordering of the hydroxy proton. The absolute configuration of molecule (+)-**IIIa** was estimated as (1*R*,2*R*,4*S*) using Cu radiation, though the error in the determination of the Flack parameter was fairly large [0.1(3)] since the molecule contains only one oxygen atom.



(+)-**VIII**

The configuration of chiral centers in compound (+)-**IIIa** was confirmed by the X-ray diffraction data for ester (+)-**VIII** which was synthesized by acylation of (+)-**IIIa** with (1*S*)-camphanoyl chloride. The symmetry-independent part of a unit cell of (+)-**VIII** in crystal also comprises one molecule (Fig. 2). The $C^{1'}$–$C^{10'}$ fragment is oriented with respect to the $O^{1}C^{11'}O^{2}$ group in such a way that the $C^{4'}C^{7'}C^{1'}$ plane is almost orthogonal to the $O^{1}C^{11'}O^{2}$ plane [the dihedral angle is 86.8(2)°] and the torsion angles $O^{1}C^{11'}C^{1'}C^{6'}$ and $O^{2}C^{11'}C^{1'}O^{3}$ are 36.0(4) and –26.2(4)°, respectively. The $O^{1}C^{11'}O^{2}$ group is also orthogonal to the

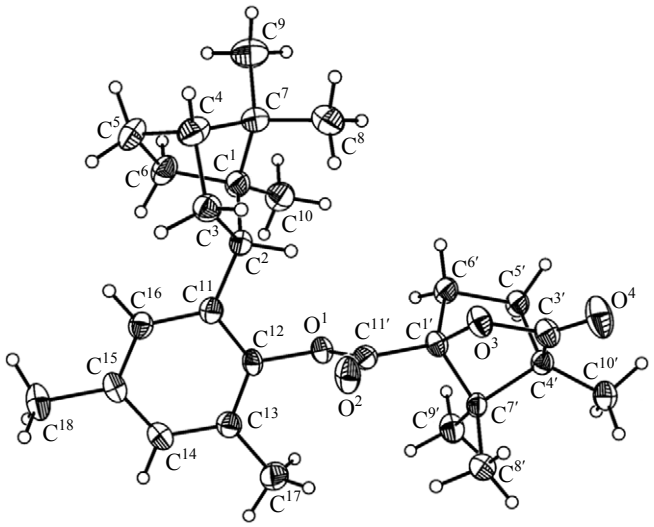
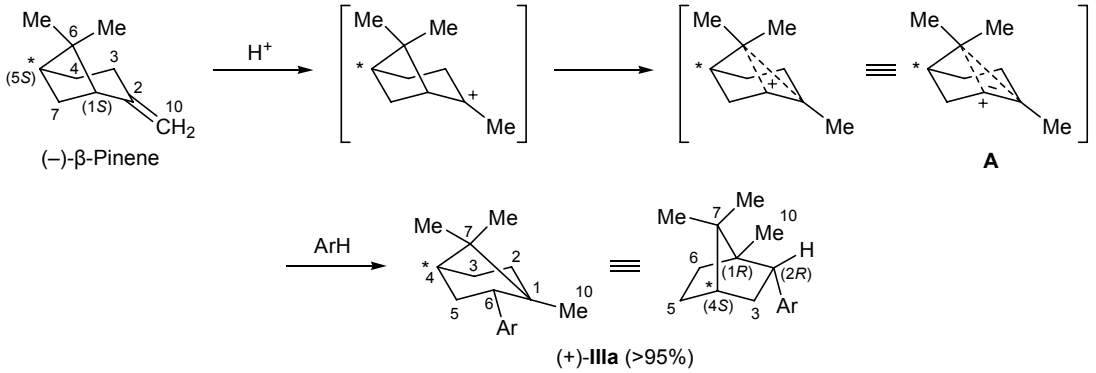


Fig. 2. Structure of the molecule of 2,4-dimethyl-6-{(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}phenyl (1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (+)-(**VIII**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

aromatic ring [torsion angle $C^{11'}O^{1}C^{12}C^{11}$ 83.0(3)°], presumably for steric reasons. Analogous structure was found previously for 2,6-diisobornyl-4-formylphenyl camphanate [13]. The torsion angle $C^{16}C^{11}C^{2}C^{3}$ which characterize orientation of the bornyl fragment with respect to the benzene ring is 39.1(4)°; this value is close to those found by us previously in (+)-2-bornylphenol and its aminomethyl derivatives [14]. By analogy with isobornylphenols studied in [2, 15–17], we can presume that the observed orientation is largely determined by intramolecular factors. The chiral centers in the bornyl fragment of (+)-**VIII** were assigned (1*R*,2*R*,4*S*) absolute configuration on the basis of the known configuration of the chiral centers in the camphane moiety.

Scheme 2.

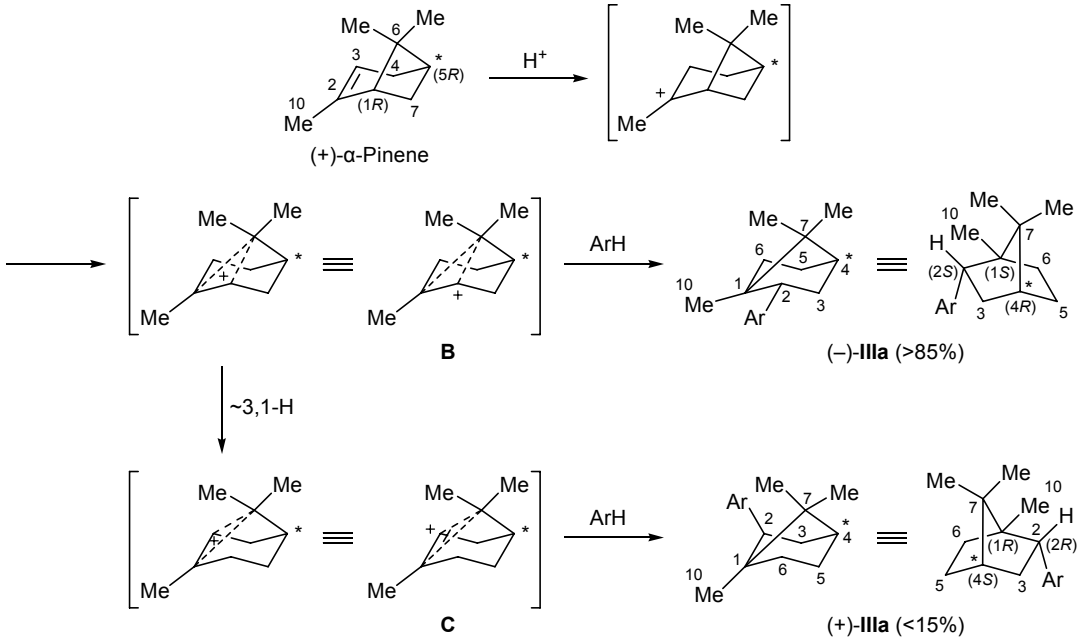


(–)-β-Pinene

(+)-**IIIa** (>95%)

Ar = 2-HO-3,5-$Me_2C_6H_2$.

Scheme 3.



Ar = 2-HO-3,5-$Me_2C_6H_2$.

The steric structure of (+)-**VIII** confirms our assumption [14] that C-alkylation of phenols with (−)-β-pinene involves Wagner–Meierwein rearrangement through carbocation **A** (Scheme 2), where the original configuration of C^5 is retained. Presumably, C-alkylation of 2,4-dimethylphenol (**I**) with (+)-α-pinene with formation of compound (–)-**IIIa** having (1*S*,2*S*,4*R*) configuration is mediated by carbocation **B**. Some amount (≤15%) of the opposite enantiomer (+)-**IIIa** may be formed through carbocation **C** (Scheme 3) (In Schemes 2 and 3 the initial terpene and alkylation products have their own atom numbering; the C^5 atom of pinenes is marked with an asterisk).

Taking into account that the reactions of phenol [14] and 2,4-xylenol with (–)-β-pinene yields C-alkylation products containing a (1*R*,2*R*,4*S*)-bornyl fragment, analogous mechanism may be proposed for the reactions with other phenols (cresols, xylenols, naphthols). (1*S*,2*S*,4*R*)-Bornylphenols are obtained from (+)-α-pinene, and enantiomeric (1*R*,2*R*,4*S*)-bornylphenols, from (–)-β-pinene.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Shimadzu IR Prestige 21 spectrometer. The ^1H and ^{13}C NMR spectra were measured from solutions in $CDCl_3$ on a Bruker Avance II 300 spectrometer at 300.17 and 75.48 MHz, respectively, using the residual proton and carbon signals of the solvent as reference ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.00 ppm). Signals were assigned with the aid of *J*-modulation technique (^{13}C NMR) (for atom numbering, see Scheme 1). The melting points were determined on a Kofler hot stage and were not corrected. The optical rotations were measured on a PolAAr 3001 automated digital polarimeter (λ 589 nm).

The progress of reactions was monitored by TLC on Sorbfil plates. Compounds **I**–**VII** were detected by treatment with a solution of vanillin in alcohol, followed by heating to 100–150°C; spots of **VIII** were developed with a solution of Bromocresol Purple, followed by heating to 100−120°C. HPLC analyses were carried out on an Agilent 1100 chromatograph (UV detector, λ 219 nm; 20°C); the *ee* values of (+)-**IIa**, (–)-**IIa**, (+)-**IIIa**, and (–)-**IIIa** were determined using a Chiralcel OD-H column [Daicel, 25 cm× 4.6 mm, grain size 5 μm; eluent hexane (**IIa**) or hexane–propan-2-ol, 99:1 (**IIIa**), flow rate 1.0 mL/min]. Product mixtures were separated by column chromatography on silica gel (70–230 mesh, Alfa Aesar; wet packing) using petroleum ether–diethyl ether as eluent.

Petroleum ether with bp 65–70°C and diethyl ether of analytical grade were used. 2,4-Dimethylphenol, (+)-α-pinene, (–)-β-pinene, (1*S*)-camphanoyl chloride, triethylamine (Sigma–Aldrich), and 4-dimethylamino-

pyridine (Acros Organics) were used without additional purification. Aluminum 2,4-dimethylphenoxide was generated *in situ*.

Single crystals of (+)-**IIIa** and (+)-**VIII** suitable for X-ray analysis were obtained by slow evaporation of their solutions in hexane–diethyl ether. The X-ray diffraction data were acquired on a Bruker Smart Apex2 CCD diffractometer [graphite monochromator, ω-scanning, CuK_α radiation (λ = 1.54178 Å) for (+)-**IIIa**; MoK_α radiation (λ = 0.71073 Å) for (+)-**VIII**]. The initial arrays of reflection intensities were processed using SAINT and SADABS programs built in APEX2 software package [18]. The structures were solved by the direct method and were refined against F^2_{hkl} by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms using SHELXTL [19]. The coordinates of atoms and their temperature factors for structures (+)-**IIIa** and (+)-**VIII** were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 982664 and 982665).

Alkylation of 2,4-dimethylphenol with α- and β-pinenes. 2,4-Dimethylphenol (**I**), 2.0 g (16.4 mmol), was heated to 180°C, 13.5 mg (0.5 mmol) of aluminum turnings was added in portions, the mixture was stirred until it became homogeneous and cooled to 40°C, 4.35 g (31.9 mmol) of (+)-α-pinene or (–)-β-pinene was added, and the mixture was heated for 7 h at 200°C. When the reaction was complete, the mixture was cooled and diluted with diethyl ether, dilute aqueous HCl was added to decompose the catalyst, a 5% solution of sodium hydroxide was then added to convert unreacted 2,4-dimethylphenol into phenoxide, and the mixture was washed with water until neutral reaction. The organic extract was dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was separated by column chromatography using petroleum ether–diethyl ether as eluent.

1,7,7-Trimethyl-2-*endo*-(2,4-dimethylphenoxy)-bicyclo[2.2.1]heptane (IIa). Colorless oily liquid. Enantiomer (+)-**IIa** [from (+)-α-pinene]: $[\alpha]_D^{25}$ = +61.1° (*c* = 3.4, $CHCl_3$), *ee* 80%, retention time 5.36 min; enantiomer (−)-**IIa** [from (–)-β-pinene], $[\alpha]_D^{24}$ = –86.4° (*c* = 0.41, $CHCl_3$), *ee* 93%, retention time 6.25 min. IR spectrum, ν, cm^{-1}: 2951, 2876, 1502 (C–H), 1254 (=C–O), 1136 (C−O). ^{1}H NMR spectrum, δ, ppm: 0.99–1.02 m (9H, C^8H_3, C^9H_3, $C^{10}H_3$), 1.15–1.20 m (1H, 3-H), 1.33–1.38 m (2H, 5-H, 6-H), 1.78–1.82 m (2H, 4-H, 6-H), 2.30–2.44 m (2H, 3-H, 5-H), 2.26 s (3H, 14-Me), 2.29 s (3H, 12-Me), 4.30–4.33 m (1H, 2-H), 6.60–6.63 m (1H, 13-H), 6.94–6.99 m (2H, 15-H, 16-H). ^{13}C NMR spectrum, δ_C, ppm: 13.82 (C^{10}), 16.44 (14-Me), 19.00 (C^9), 19.74 (C^8), 20.41 (12-Me), 27.00 (C^5), 27.99 (C^6), 37.07 (C^3), 45.29 (C^4), 47.48 (C^1), 49.71 (C^7), 82.65 (C^2), 111.89 (C^{16}), 126.76 (C^{15}), 126.95 (C^{14}), 128.80 (C^{12}), 131.38 (C^{13}), 154.95 (C^{11}). Found, %: C 83.49; H 10.48. $C_{18}H_{26}O$. Calculated, %: C 83.67; H 10.14.

2,4-Dimethyl-6-{(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}phenol (+)-(IIIa) and 2,4-dimethyl-6-{(1*S*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl}phenol (–)-(IIIa). Colorless or light yellow crystals, mp 119–121°C. Enantiomer (+)-**IIIa** [from (–)-β-pinene]: $[\alpha]_D^{24}$ = +35.2° (*c* = 0.46, $CHCl_3$), *ee* >99%, retention time 6.35 min; enantiomer (−)-**IIIa** [from (+)-α-pinene]: $[\alpha]_D^{24}$ = –26.9 (*c* = 1.5, $CHCl_3$), *ee* 75%, retention time 7.28 min. IR spectrum, ν, cm^{-1}: 3603, 3587 (OH); 1196 (C–O); 2953, 2879, 1479 (C–H). ^{1}H NMR spectrum, δ, ppm: 0.84 s (3H, $C^{10}H_3$), 0.99 s (3H, C^9H_3), 1.14 s (3H, C^8H_3), 1.16–1.25 m (1H, 6-H), 1.41–1.63 m (3H, 3-H, 5-H, 6-H), 1.78–1.87 m (2H, 4-H, 5-H), 2.19–2.28 m (1H, 3-H), 2.28 s (3H, 15-Me), 2.31 s (3H, 13-Me), 3.47–3.54 m (1H, 2-H), 4.53 s (1H, OH), 6.84 s (1H, 16-H), 6.95 s (1H, 14-H). ^{13}C NMR spectrum, δ_C, ppm: 15.02 (C^{10}), 16.32 (13-Me), 18.74 (C^9), 19.88 (C^8), 20.96 (15-Me), 28.38 (C^5), 28.86 (C^6), 34.90 (C^3), 41.68 (C^2), 45.59 (C^4), 50.36 (C^1), 50.48 (C^7), 123.01 (C^{13}), 127.55 (C^{15}), 127.87 (C^{16}), 128.54 (C^{11}), 128.97 (C^{14}), 150.51 (C^{12}). Found, %: C 84.01; H 9.92. $C_{18}H_{26}O$. Calculated, %: C 83.67; H 10.14.

Enantiomer (+)-**IIIa**. $C_{18}H_{26}O$. Monoclinic crystal system. Unit cell parameters (120 K): *a* = 19.7564(3), *b* = 7.38690(10), *c* = 13.3708(4) Å; β = 130.399(1)°; *V* = 1486.02(5) $Å^3$; *Z* = 4; space group *C*2; d_{calc} = 1.155 g/cm^3; μ = 0.522 mm^{-1}. Total of 10353 reflections intensities were measured (θ_{max} = 67°) from a 0.22×0.18×0.18-mm single crystal; the structure was refined using 2522 independent reflections (R_{int} = 0.0176). Final divergence factors: wR_2 = 0.0809 (all reflections), R_1 = 0.0306 [2520 reflections with $I > 2\sigma(I)$]; goodness of fit 1.059; Flack parameter 0.1(3).

2,4-Dimethyl-6-(1,7,7-trimethylbicyclo[2.2.1]-hept-2-*exo*-yl)phenol (IIIb) was isolated in a mixture with compound **IIIa** as a semicrystalline material. ^{1}H NMR spectrum, δ, ppm: 0.80 s (3H, $C^{10}H_3$), 0.86 s and 0.91 s (3H each, C^8H_3, C^9H_3); 1.29–1.52 m, 1.53–1.74 m, and 1.77–1.94 m (2H each, 3-H, 4-H, 5-H, 6-H), 2.12–2.33 m (1H, 3-H), 2.22 s (3H, 13-Me), 2.26 s (3H, 15-Me), 3.06 t (1H, 2-H, *J* = 8.8 Hz), 4.51 s (1H, OH), 6.79 s and 6.97 s (1H each, 14-H, 16-H). ^{13}C NMR spectrum, δ_C, ppm: 12.39 (C^{10}), 16.13 (13-Me), 20.31 (C^9), 20.90 (15-Me), 21.42 (C^8), 27.55

(C^5), 34.17 (C^6), 40.08 (C^3), 45.55 (C^2), 45.80 (C^4), 48.08 (C^1), 49.64 (C^7), 122.34 and 128.39 (C^{11}, C^{13}, C^{15}), 126.43 and 128.61 (C^{14}, C^{16}), 150.74 (C^{12}).

5-Isopropyl-2,6-methano-2,8,10-trimethyl-3,4,5,6-tetrahydro-2*H*-1-benzoxocine (IV). Light brown oily liquid. IR spectrum, ν, cm^{-1}: 1217 (=C–O); 1155 (C–O); 2945, 2870, 1479 (C–H). ^{1}H NMR spectrum, δ, ppm: 1.00 d (3H, $C^{17}H_3$, J = 6.6 Hz), 1.12 d (3H, $C^{16}H_3$, J = 6.6 Hz), 1.39 s (3H, $C^{14}H_3$), 1.52–1.94 m (8H, 6-H, 7-H, 8-H, 9-H, 15-H), 2.20 s (3H, 10-Me), 2.29 s (3H, 12-Me), 3.03 m (1H, 5-H), 6.68 s (1H, 13-H), 6.83 s (1H, 11-H). ^{13}C NMR spectrum, δ_C, ppm: 15.97 (10-Me), 20.10 (C^7), 20.41 (12-Me), 21.31 (C^{17}), 22.07 (C^{16}), 26.33 (C^{15}), 29.50 (C^{14}), 30.76 (C^9), 34.76 (C^5), 35.48 (C^8), 47.45 (C^6), 74.13 (C^1), 123.66 (C^{10}), 126.02 (C^{13}), 126.73 (C^{12}), 127.17 (C^4), 129.11 (C^{11}), 152.59 (C^3). Found, %: C 83.49; H 10.48. $C_{18}H_{26}O$. Calculated, %: C 83.77; H 10.10.

2-Isopropyl-2,6-metano-5,8,10-trimethyl-3,4,5,6-tetrahydro-2*H*-1-benzoxocine (V) was isolated in a mixture with compound **IV**. ^{1}H NMR spectrum, δ, ppm: 0.85 d (3H, $C^{17}H_3$, J = 5.0 Hz), 1.00 d (3H, $C^{16}H_3$, J = 5.0 Hz), 1.18 d (3H, $C^{14}H_3$, J = 7.0 Hz), 1.61–2.02 m (8H, 6-H, 7-H, 8-H, 9-H, 15-H), 2.23 s (3H, 10-Me), 2.31 s (3H, 12-Me), 2.71 m (1H, 5-H), 6.79 s (1H, 13-H), 6.95 s (1H, 11-H).

2,4-Dimethyl-6-{(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}phenyl (1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (+)-(VIII). Compound (+)-**IIIa**, 0.194 g (0.75 mmol), was dissolved in 5 mL of toluene, 0.203 g (0.94 mmol) of (1*S*)-camphanoyl chloride, 0.105 mL (0.94 mmol) of triethylamine, and 9 mg (0.075 mmol) of 4-dimethylaminopyridine were added, and the mixture was heated for 2 h under reflux with stirring in a stream of argon. The mixture was evaporated and filtered from quaternary ammonium salt, and the residue was purified by column chromatography. Yield 0.301 g (91%), colorless crystals, mp 192–194°C, $[\alpha]_D^{23}$ = +30.7° (c = 0.39, $CHCl_3$). IR spectrum, ν, cm^{-1}: 2953, 2878, 1474 (C–H); 1796, 1761 (C=O); 1261 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.73 s (3H, $C^{10}H_3$), 0.92 s and 1.00 s (3H each, C^8H_3, C^9H_3); 1.13 s, 1.16 s, and 1.18 s (3H each, $C^{8'}H_3$, $C^{9'}H_3$, $C^{10'}H_3$); 1.28–1.64 m (3H) and 1.69–2.05 m (5H) (4-H, 5-H, 5′-H, 6-H, 6′-H), 2.07–2.32 m (2H, 3-H, 6-H), 2.12 s (3H, 13-Me), 2.34 s (3H, 15-Me), 2.45–2.63 m (1H, 3-H), 3.15 br.m (1H, 2-H), 6.92 s and 7.02 s (1H each, 14-H, 16-H). ^{13}C NMR spectrum, δ_C, ppm: 9.62 ($C^{10'}$), 14.58 (C^{10}); 16.84, 17.07, 17.27 ($C^{8'}$, $C^{9'}$, 13-Me); 18.77 and 19.75 (C^8, C^9), 21.23 (15-Me), 28.35 (C^5), 28.85 (C^3), 29.01 and 31.67 ($C^{5'}$, $C^{6'}$), 35.08 (C^6), 41.91 (C^4), 45.44 (C^2), 50.36 and 50.42 (C^1, C^7), 54.10 and 54.84 ($C^{4'}$, $C^{7'}$), 90.85 ($C^{1'}$), 128.35 and 129.47 (C^{14}, C^{16}), 134.89 (C^{11}), 146.09 (C^{12}), 166.02 and 177.83 ($C^{3'}$, $C^{11'}$). Found, %: C 76.39; H 8.88. $C_{28}H_{38}O_4$. Calculated, %: C 76.68; H 8.73.

Rhombic crystals; unit cell parameters (120 K): a = 7.8057(7), b = 7.9220(7), c = 39.851(4) Å; V = 2464.3(4) $Å^3$; Z = 4; space group $P2_12_12_1$; d_{calc} = 1.182 g/cm^3; μ = 0.077 mm^{-1}. Total of 35501 reflection intensities were measured (θ_{max} = 28.3°) from a 0.18×0.12×0.02-mm single crystal; the structure was refined using 3517 independent reflections (R_{int} = 0.1056); final divergence factors wR_2 = 0.1206 (all reflections), R_1 = 0.0509 [2292 reflections with $I > 2\sigma(I)$]; goodness of fit 1.102.

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