Synthesis of Optically Active Tricyclic Ethers by Reactions of (−)-β-Pinene with Phenols in Organized Media

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The reactions of (−)-β-pinene (**1**) with some methyl- and hydroxy-substituted phenols on Hβ-zeolite yield optically active products – tricyclic terpenyl phenyl ethers – in contrast to reactions in homogeneous media, which occur with loss of optical activity. The formation of these products is promoted by the presence of *meta*-substituents in the phenol molecule.

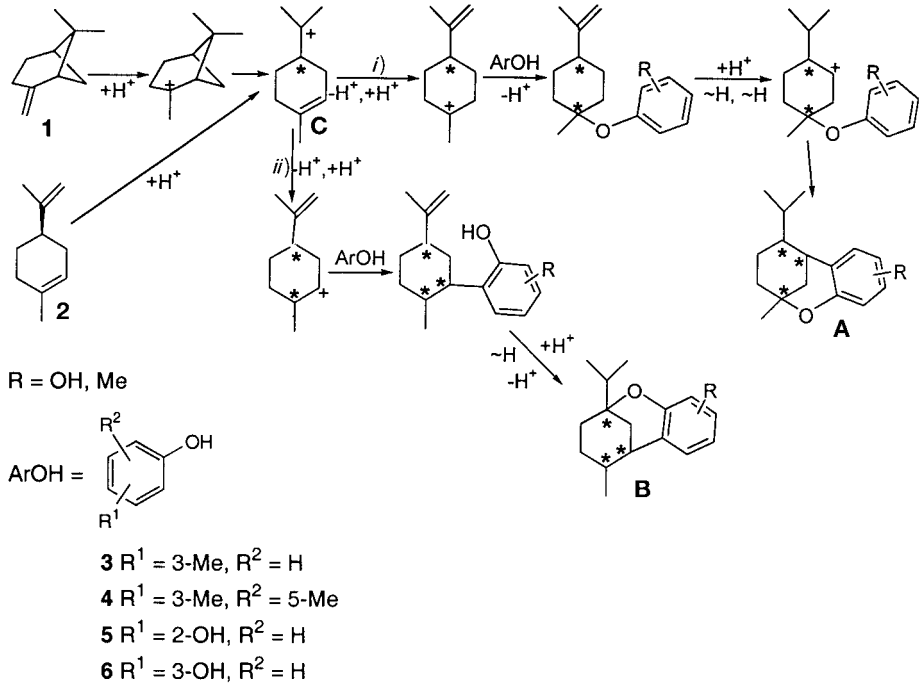
Introduction. – The use of organized media (clays, zeolites) [1][2] in some known processes involving natural compounds improves the ecological characteristics of these reactions. The conformational flexibility and polyfunctionality of the compounds additionally opens up prospects for realizing unusual transformations, expanding the applications of recyclable raw materials in fine organic synthesis. In organized media, the rate ratio between different competing reactions changes compared to that in homogeneous media under the action of statistical and concentration factors and/or due to a relative change in the activation barriers to possible transformations. This leads not only to unusual products, but also, which is not less important, to deceleration of undesirable racemization and to products with preserved optical activity, which are rarely formed in homogeneous media.

Previously [3–5], we investigated alkylations of various methyl- and hydroxy-substituted phenols by natural terpenes, *i.e.*, camphene and caryophyllene, in organized media (β-zeolite, room temperature). It was shown that the reaction is either *C*- or *O*-alkylation forming terpenylphenols or terpenyl phenyl ethers, respectively, depending on the structure of the phenols and on the solvent used. The reaction of a widespread bicyclic monoterpene, (−)-β-pinene (**1**) with phenols on β-zeolite forms both *C*- and *O*-alkylation products – optically active isomeric tricyclic ethers.

Results and Discussion. – Alkylation of various Me- and OH-substituted phenols, *i.e.*, *m*-cresol (**3**), 3,5-dimethylphenol (**4**), and resorcinol (**6**), by optically active (−)-β-pinene (**1**) yielded optically active isomeric tricyclic ethers – compounds of type **A** and **B** – on the hypothetical pathways *i* and *ii* (see *Scheme*).

It is known that formation of **A**- and **B**-type products is possible when phenols interact with various terpenes: limonene [6][7], α-pinene [7], mircene [8], α-phellandrene [8], or terpene alcohols [7][8]. It should be noted, however, that the products were racemates. Recrystallization and chromatography of the reaction mixtures with optically inactive sorbents gave optically active products [8] that differ in the value of the optical rotation for products from different fractions or (in one case) in

Scheme



i), *ii*) See text.

the sign of the optical rotation for different fractions of the same product. The detection of optical activity in the latter case may be explained by contamination of the product with the starting limonene (α-phellandrene) or its isomerization products. Thus, the use of homogeneous acids and a cation-exchange resin for syntheses of tricyclic ethers from the above-mentioned terpenes or their derivatives and phenols evidently leads to racemates. An organized medium (β-zeolite) possibly prevents undesirable quick racemization by way of a hydride shift in cation **C** [9], the extent of the preserved optical activity depending on the method of generation of cation **C** (see *Scheme*). For example, if the starting terpene is (+)-limonene (**2**), the reaction with 3,5-dimethylphenol (**4**) gives the same product **10** (see *Fig.*) as in this case of (−)-β-pinene (**1**), confirming the suggested mechanism; in this case, the yield of the product with a dominant enantiomer increases from 21 to 46%, and $[\alpha]_{580}^{20}$ decreases from −9.7 to −0.6 (*Table 1*). The rate-determining role of the concentration of ion **C** is manifested in the diastereoisomer-forming reactions of the latter with phenols but not in the hydride shift. Probably, the limiting step of the reactions of (−)-β-pinene with phenols is the formation of cation **C**, resulting from ring opening accompanied by C−C bond cleavage in the pinyl cation. Therefore, the presence of a large amount of limonene in the reaction mixture leads to a faster double-bond protonation to produce cation **C** than in the case of (−)-β-pinene, and, hence, to a higher yield of the product with lower enantiomeric purity.

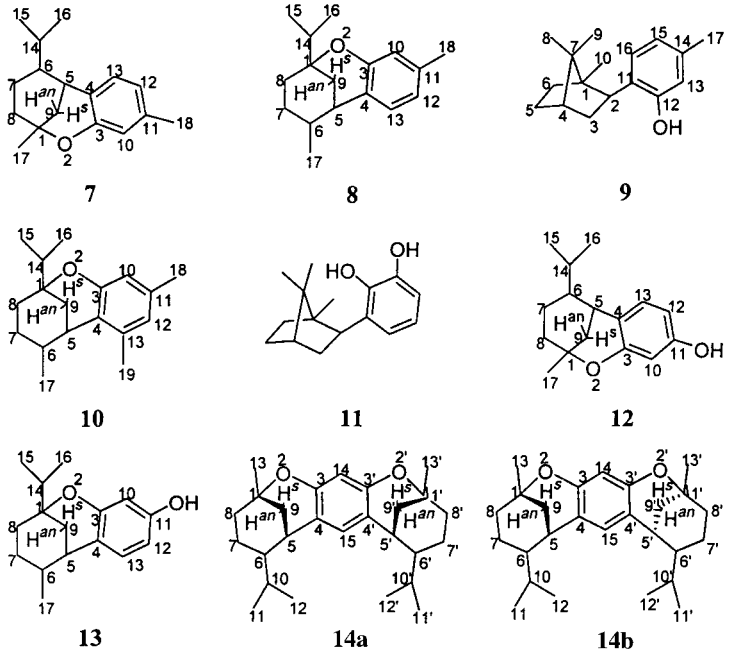


Figure. *Products formed from (−)-β-pinene* (**1**) *and phenols* **3**–**6** *in the presence of β-zeolite*[1])

Reactions of *m*-cresol (**3**) and pyrocatechol (**5**) with (−)-*β*-pinene (**1**) yield optically active products **9** and **11**, respectively, having an isobornyl structure, besides **7** and **8** in the case of **3** (*Table 1*). Previously [3][4], we obtained analogous products in reactions of camphene with the corresponding phenols on *β*-zeolite, but they were racemates because of rapid racemization of camphene.

Table 1. *Experimental Conditions*

(−)-*β*-Pinene [mg]	Phenol ([mg])	Solvent ([ml])	Catalyst ([mg])	Product, type of product ([mg])	Yield [%]	$[\alpha]_{580}^{20}$ (*c* [g/100 ml])	Elemental composition, M^+	
							Found	Calc.
404	**3** (160)	CH_2Cl_2 (5)	HB-2 (500)	**7**, **A** (42)	12	−5.7 (1.8)	$C_{17}H_{24}O$, 244.18281	$C_{17}H_{24}O$, 244.18270
				8, **B** (82)	23	0 (2.9)	$C_{17}H_{24}O$, 244.18232	$C_{17}H_{24}O$, 244.18270
				9, – (8.5)	2	+15.4 (0.5)	$C_{17}H_{24}O$, 244.18232	$C_{17}H_{24}O$, 244.18270
119	**4** (53)	CH_2Cl_2 (5)	HB-2 (150)	**10**, **B** (24)	21	−9.7 (1.4)	$C_{18}H_{26}O$, 258.19818	$C_{18}H_{26}O$, 258.19835
124	**5** (50)	CH_2Cl_2 (6)	HB-2 (150)	**11**, – (22)	19	−6.0 (1.3)	$C_{16}H_{22}O_2$, 246.16169	$C_{16}H_{22}O_2$, 246.16197
420	**6** (170)	CH_2Cl_2 (6)	HB-2 (500)	**12**, **A** (57)	15	+22.4 (4.6)	$C_{16}H_{22}O_2$, 246.16144	$C_{16}H_{22}O_2$, 246.16197
				13, **B** (42)	11	+27.9 (4.9)	$C_{16}H_{22}O_2$, 246.16144	$C_{16}H_{22}O_2$, 246.16197
				14, – (33)	6	−4.0 (2.0)	$C_{26}H_{38}O_2$, 382.28697	$C_{26}H_{38}O_2$, 382.28716

[1]) Arbitrary numbering; for systematic names, see *Exper. Part.*

In addition to **A**- and **B**-type products **12** and **13**, the reaction of resorcinol (**6**) with (−)-β-pinene (**1**) gave dialkylation products – a mixture of diastereoisomeric pentacyclic diethers **14a**,**b** in a 1:1 ratio (by ^{1}H- and ^{13}C-NMR, arom. H), formed by addition of a second (−)-β-pinene molecule by mechanism *i*. Compound **14a** apparently differs from **14b** in the relative position of the methano bridges in the bicyclic moieties with respect to the plane of the central aromatic ring. Note that there were no products of addition of a second (−)-β-pinene molecule to compound **A** (mechanism *ii*) or products of addition of a second (−)-β-pinene molecule to the monoalkylated compound formed by mechanism *ii*, although, as mentioned above, both types of monoalkylation product, *i.e.*, **12** and **13**, were obtained with resorcinol (**6**).

We have also performed reactions of (−)-β-pinene (**1**) with other phenols. It appeared, however, that the reactions of *o*-cresol (=2-methylphenol) and phenol lead to complex mixtures of terpenylphenols and terpenyl phenyl ethers, whereas, in the case of hydroquinone (benzene-1,4-diol), phloroglucinol (= benzene-1,3,5-triol), and tyrosol (=4-hydroxybenzeneethanol), the yields and the degree of conversion were low. Thus the presence of *meta*-substituents in the phenol molecule apparently promotes the formation of tricyclic terpenyl phenyl ethers.

All new compounds were characterized by their ^{1}H- and ^{13}C-NMR and mass spectra.

To assign the C(10) and C(12) signals in the ^{13}C-NMR spectra of **7**, **8**, **10**, **12**, and **13**, we used the data on the additional effects of Me or OH and OR groups on the aromatic ring; the shift parameters were taken from [10]. The effect of the 4-substituent may be ignored because it is the same for both C(10) and C(12), and the effect of the alkyl substituents in the *meta*-position is negligible [10]. For **8**, the assignment is supported by selective resonance spectra with separate decoupling for H−C(10) and H−C(12). In the ^{1}H-NMR spectrum of **10**, signal assignment for H−C(10) and H−C(12) was made based on ^{13}C,^{1}H 2D-COSY data.

Experimental Part

General. β-Zeolite was obtained as described [11], SiO_2/Al_2O_3 *ca.* 40, $d \approx 8$ Å, Na_2O 0.04%, Al_2O_3 5.14%, SiO_2 81.57% it was calcined for 2 h at 500° before use. The starting (−)-β-pinene (99%; $[\alpha]_{580}^{20} = -22$) was purchased from *Fluka* (No. 80608) and (+)-(*R*)-limonene (97%, $[\alpha]_{580}^{20} = +123$) from *Aldrich* (No. 18316-4). Column chromatography (CC): Al_2O_3 column, *Poland*, 2nd degree of activity according to *Brockman*. Specific rotation: polarimeter *Polamat A*, $CHCl_3$ solns. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM-400* (400.13 and 100.61 MHz, resp. spectrometer; $CCl_4/(CD_3)_2CO$ *ca.* 4:1 (*v*/*v*) solns. with $(CD_3)_2CO$ as internal standard (δ(H) 2.04, δ(C) 29.80); structure assignments by means of geminal, vicinal, and long-range J(H,H) from ^{1}H,^{1}H double-resonance, ^{13}C-NMR and 2D ^{13}C,^{1}H heteronuclear correlation spectra (COSY-experiment conditions optimized for ^1J(C,H) = 135 Hz); δ(C) assignments by selective and off-resonance proton irradiation and by differential spectra modulated with far spin-spin interaction ^{13}C,^{1}H (LRJMD-experiment conditions optimized for J(C,H) = 10 Hz); for ^{13}C-NMR spectra, see *Table 2*. HR-MS: *Finnigan 8200*.

Standard Procedure. A soln. of the reagents in a solvent is added dropwise with stirring to a suspension of a solid catalyst in a solvent. The mixture is allowed to continue stirring and then is filtered off on a porous glass filter, the solid washed with Et_2O, the filtrate evaporated, and the residue kept for 20 min at 60°/10 Torr. The products were separated by CC. All product yields were calculated based on phenol. For the particular experimental conditions, see *Table 1*.

*3,4,5,6-Tetrahydro-5-isopropyl-2,9-dimethyl-2,6-methano-2*H*-1-benzoxocin* (**7**). ^{1}H-NMR[1]): 0.95, 1.06 (2*d*, J = 6.5, Me(15), Me(16)); 1.14 (*dm*, J = 6,14) = 10, 1 H−C(6)); 1.29 (*s*, Me(17)); 1.40 – 1.59 (*m*, 2 H−C(7), 1 H−C(8), 1 H$_s$−C(9)); 1.69 (*m*, 1 H−C(8)); 1.79 (*dqq*, J = 10, J(14,15) = 6.5, J(14,16) = 6.5, 1 H−C(14)); 1.82 (*dd*, J(9*an*,9*s*) = 13, J(9*an*,5) = 3, H$_{an}$−C(9)); 2.24 (*s*, Me(18)); 2.95 (*ddd*, J(5,6) = 3, J(9*s*,5) = 3, J = 3, 1 H−C(5)); 6.46 (*dd*, J(12,13) = 7, J(12,10) = 1.5, 1 H−C(12)); 6.47 (br. *s*, 1 H−C(10)); 6.71 (*d*, J = 7, 1 H−C(13)). MS: 244 (93, M^+), 201 (22), 176 (57), 174 (63), 161 (27), 159 (100), 145 (15), 121 (53), 91 (10), 28 (30).

Table 2. *^{13}C-NMR Data for Compounds* **7**–**10**, **12**, *and* **13**[1]). Chemical shifts in ppm[a]).

	7	**8**	**9**	**10**	**12**	**13**
C(1)	73.91 (*s*)	78.45 (*s*)	49.88 (*s*)	77.89 (*s*)	73.93 (*s*)	78.43 (*s*)
C(2)	–	–	44.85 (*d*)	–	–	–
C(3)	156.61 (*s*)	156.54 (*s*)	34.03 (*t*)	156.66 (*s*)	156.60[a]) (*s*)	156.75[a]) (*s*)
C(4)	124.16 (*s*)	124.94 (*s*)	45.94 (*d*)	123.03 (*s*)	118.40 (*s*)	119.22 (*s*)
C(5)	34.43 (*d*)	38.68 (*d*)	27.86 (*t*)	34.81 (*d*)	34.06 (*d*)	38.29 (*d*)
C(6)	47.57 (*d*)	35.03 (*d*)	39.81 (*t*)	32.34 (*d*)	47.67 (*d*)	35.10 (*d*)
C(7)	20.12 (*t*)	24.05 (*t*)	48.05 (*s*)	24.47 (*t*)	20.08 (*t*)	23.98 (*t*)
C(8)	35.43 (*t*)	29.63 (*t*)	21.84[a]) (*q*)	29.44 (*t*)	35.36 (*t*)	29.55 (*t*)
C(9)	31.05 (*t*)	25.21 (*t*)	20.57[a]) (*q*)	25.28 (*t*)	31.25 (*t*)	25.28 (*t*)
C(10)	115.89 (*d*)	115.90 (*d*)	12.50 (*q*)	114.07 (*d*)	102.16 (*d*)	102.15 (*d*)
C(11)	136.51 (*s*)	136.68 (*s*)	126.69 (*s*)	135.90 (*s*)	157.36[a]) (*s*)	157.29[a]) (*s*)
C(12)	119.93 (*d*)	119.99 (*d*)	155.62 (*s*)	121.93 (*d*)	106.89 (*d*)	106.86 (*d*)
C(13)	127.80 (*d*)	127.73 (*d*)	115.72 (*d*)	134.40 (*s*)	128.28 (*d*)	128.15 (*d*)
C(14)	26.51 (*d*)	37.94 (*d*)	135.41 (*s*)	37.90 (*d*)	26.47 (*d*)	37.88 (*d*)
C(15)	22.37[a]) (*q*)	17.37[a]) (*q*)	120.21 (*d*)	17.29 (*q*)	22.38[b]) (*q*)	17.34[b]) (*q*)
C(16)	21.57[a]) (*q*)	17.34[a]) (*q*)	127.87 (*d*)	17.29 (*q*)	21.51[b]) (*q*)	17.28[b]) (*q*)
C(17)	29.73 (*q*)	18.09 (*q*)	21.08 (*q*)	18.04 (*q*)	29.70 (*q*)	17.94 (*q*)
C(18)	21.41 (*q*)	21.45 (*q*)	–	21.25[a]) (*q*)	–	–
C(19)				18.26[a]) (*q*)		

[a])[b]) Assignments may be interchanged.

*3,4,5,6-Tetrahydro-2-isopropyl-5,9-dimethyl-2,6-methano-2*H*-1-benzoxocin* (**8**). ^{1}H-NMR[1]): 0.98, 1.00 (2*d*, *J* = 7, Me(15), Me(16)); 1.13 (*d*, *J*(17,6) = 7, Me(17)); 1.17 (*m*, H_e−C(7)); 1.53 (*dm*, *J*(9*s*,9*an*) = 13, H_s−C(9)); 1.56–1.68 (*m*, H_a−C(7), 2 H−C(8)); 1.76 (*sept.*, *J* = 7, 1 H−C(14)); 1.87 (*m*, 1 H−C(6)); 1.89 (*dd*, *J* = 13, *J*(9*an*,5) = 3, H_{an}−C(9)); 2.25 (*s*, Me(18)); 2.63 (*m*, *J*(5,6) = 3, *J*(5,9*s*) = 3, *J* = 3, 1 H−C(5)); 6.47 (*dd*, *J*(12,13) = 7.5, *J*(12,10) = 1.5, 1 H−C(12)); 6.51 (*d*, *J* = 1.5, 1 H−C(10)); 6.74 (*d*, *J* = 7.5, 1 H−C(13)). MS: 244 (62, M^+), 201 (100), 187 (11), 159 (60), 148 (39), 145 (12), 121 (29), 28 (20).

5-Methyl-2-(1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)phenol (**9**). ^{1}H-NMR[1]): 0.73 (*s*, Me(10)); 0.81, 0.87 (2*s*, Me(8), Me(9)); 1.31 (*ddd*, *J*(5*endo*,5*exo*) = 12, *J*(5*endo*,6*endo*) = 9, *J*(5*endo*,6*exo*) = 6, H_{endo}−C(5)); 1.47, 1.52 (2*m*, 2 H−C(6)); 1.53 (*dd*, *J*(3*endo*,3*exo*) = 12, *J*(3*endo*,2*endo*) = 9, H_{endo}−C(3)); 1.77 (*dd*, *J*(4,3*exo*) = 4, *J*(4,5*exo*) = 4, 1 H−C(4)); 1.80 (*m*, H_{exo}−C(5)); 2.20 (*s*, Me(17)); 2.13 (*dddd*, *J* = 12, *J*(3*exo*,2*endo*) = 8, *J*(3*exo*,4) = 4, *J*(3*exo*,5*exo*) = 3.5, H_{exo}−C(3)); 3.15 (*dd*, *J* = 9, *J* = 8, H_{endo}−C(2)); 6.46 (*d*, *J*(13,15) = 1.5, 1 H−C(13)); 6.49 (*dd*, *J*(15,16) = 8, *J* = 1.5, 1 H−C(15)); 6.55 (*s*, OH); 7.01 (*d*, *J* = 8, 1 H−C(16)). MS: 244 (25, M^+), 229 (14), 159 (8), 149 (9), 134 (100), 121 (24), 95 (10), 28 (7).

*3,4,5,6-Tetrahydro-2-isopropyl-5,7,9-trimethyl-2,6-methano-2*H*-1-benzoxocin* (**10**). ^{1}H-NMR[1]): 0.96, 0.98 (2*d*, *J* = 7, Me(15), Me(16)); 1.13 (*d*, *J*(17,6) = 7, Me(17)); 1.19 (*dm*, *J*(7e,7a) = 13, *J*(7e,8a) = 4, *J*(7e,6) = 2, *J*(7e,8e) = 2, H_e−C(7)); 1.45 (*ddd*, *J*(9*s*,9*an*) = 13, *J*(9*s*,5) = 3, *J*(9*s*,8*e*) = 3, H_s−C(9)); 1.59 (*m*, H_a−C(7)); 1.60 (*m*, H_e−C(8)); 1.68 (*m*, H_a−C(8)); 1.74 (*sept.*, *J* = 7, 1 H−C(14)); 1.86 (*m*, 1 H−C(6)); 1.92 (*dd*, *J* = 13, *J*(9*an*,5) = 3, H_a−C(9)); 2.16, 2.18 (2*s*, Me(18), Me(19)); 2.78 (*ddd*, *J*(5,6) = 3, *J* = 3, 3, 1 H−C(5)); 6.33 (br. *s*, 1 H−C(12)); 6.35 (br. *s*, 1 H−C(10)). MS: 258 (100, M^+), 215 (66), 201 (18), 173 (85), 162 (37), 159 (26), 135 (34), 91 (9), 32 (14), 28 (54).

*3,4,5,6-Tetrahydro-5-isopropyl-2-methyl-2,6-methano-2*H*-1-benzoxocin-9-ol* (**12**). ^{1}H-NMR[1]): 0.93, 1.04 (2*d*, *J* = 6.5, Me(15), Me(16)); 1.10 (*dm*, *J*(6,14) = 10, 1 H−C(6)); 1.27 (*s*, Me(17)); 1.37–1.53 (*m*, 2 H−C(7), 1 H−C(8)); 1.53 (*dm*, *J*(9*s*,9*an* = 13, H_s−C(9)); 1.65 (*m*, 1 H−C(8)); 1.77 (*dqq*, *J*(14,6) = 10, *J*(14,15) = 6.5, *J*(14,16) = 6.5, 1 H−C(14)); 1.80 (*dd*, *J* = 13, *J*(9*an*,5) = 3, H_{an}−C(9)); 2.89 (*ddd*, *J*(5,6) = 3, *J*(5,9*s*) = 3, *J* = 3, 1 H−C(5)); 6.11 (*d*, *J*(10,12) = 2.5, 1 H−C(10)); 6.14 (*dd*, *J*(12,13) = 8, *J* = 2.5, 1 H−C(12)); 6.62 (*d*, *J* = 8, 1 H−C(13)); 7.15 (*s*, OH). MS: 246 (62, M^+), 231 (8), 203 (20), 178 (37), 176 (29), 163 (21), 161 (100), 147 (11), 123 (36), 28 (9).

*3,4,5,6-Tetrahydro-2-isopropyl-5-methyl-2,6-methano-2*H*-1-benzoxocin-9-ol* (**13**). ^{1}H-NMR: 0.96, 0.97 (2*d*, *J* = 7, Me(15), Me(16)); 1.10 (*d*, *J* = 7, Me(17)); 1.14 (*m*, H_e−C(7)); 1.51 (*dm*, *J*(9*s*,9*an*) = 13, H_s−C(9));

1.56–1.68 (*m*, H_a–C(7), 2 H–C(8)); 1.74 (*sept.*, *J* = 7, 1 H–C(14)); 1.82 (*m*, 1 H–C(6)); 1.86 (*dd*, *J* = 13, *J*(9*an*,5) = 3, H_{an}–C(9)); 2.57 (*ddd*, *J*(5,6) = 3, *J*(5,9*s*) = 3, *J* = 3, 1 H–C(5)); 6.14 (*m*, 1 H–C(10), 1 H–C(12)); 6.64 (*d*, *J* = 9, 1 H–C(13)); 7.15 (*s*, OH). MS: 246 (63, M^+), 203 (100), 163 (13), 161 (51), 150 (54), 147 (13), 123 (23), 41 (9), 28 (9).

*3,4,5,6,9,10,11,12-Octahydro-5,9-diisopropyl-2,12-dimethyl-2,6 : 8,12-dimethano-2*H,*8*H-*benzo[1,2*-b : *4,5*-b′*]bisoxocin* (**14a**,**b**). ^{1}H-NMR: 0.94, 0.95, 1.05, 1.06 (4*d*, *J* = 6.5, 2 Me(11), 2 Me(11′), 2 Me(12), 2 Me(12′)); 1.12 (*dm*, *J* = 10, 2 H–C(6), 2 H–C(6′)); 1.26, 1.27 (2*s*, 2 Me(13), 2 Me(13′)); 1.66 (*m*, 2 H–C(8), 2 H–C(8′)); 1.78 (*m*, 2 H–C(10), 2 H–C(10′)); 1.80 (*dd*, *J* = 13, 3, 2 H_{an}–C(9), 2 H_{an}–C(9′)); 2.87 (*m*, 2 H–C(5), 2 H–C(5′)); 6.01, 6.02 (2*s*, 2 H–C(14)); 6.36, 6.37 (2*s*, 2 H–C(15)); 1.37–1.58 (*m*, other protons). ^{13}C-NMR: 73.72 (*s*, 2 C(1), 2 C(1′)); 155.83 (*s*, 2 C(3), 2 C(3′)); 118.23, 118.36 (2*s*, 2 C(4), 2 C(4′)); 34.05, 34.16 (2*d*, 2 C(5), 2 C(5′)); 47.64, 47.80 (2*d*, 2 C(6), 2 C(6′)); 20.13, 20.24 (2*t*, 2 C(7), 2 C(7′)); 35.35, 35.37 (2*t*, 2 C(8), 2 C(8′)); 31.29, 31.38 (2*t*, 2 C(9), 2 C(9′)); 26.46, 26.47 (2*d*, 2 C(10), 2 C(10′)); 21.46, 21.51, 22.36, 22.43 (4*q*, 2 C(11), 2 C(11′), 2 C(12), 2 C(12′)); 29.75, 29.76 (2*q*, 2 C(13), 2 C(13′)); 101.32, 101.40 (2*d*, 2 C(14)); 126.38, 126.57 (2*d*, 2 C(15)). MS: 382 (82, M^+), 367 (10), 314 (28), 297 (100), 85 (7), 83 (11), 28 (10). Molecular mass (*Knauer* vapor-pressure osmometer): *M* 390 g/mol.

3-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl)benzene-1,2-diol [4] (**11**). MS: 246 (10, M^+), 137 (88), 110 (13), 95 (29), 81 (100), 67 (17), 41 (11), 28 (8).

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