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Oxidation of Terpenoid Diols with Chlorine Dioxide. Easy Preparation of α-Hydroxyketones

L. L. Frolova[a], A. V. Popov[a], L. V. Bezuglaya[a], I. N. Alekseev[a], P. A. Slepukhin[b], and A. V. Kuchin[a]

[a] *Institute of Chemistry, Komi Scientific Center, Ural Branch, Russian Academy of Sciences, ul. Pervomaiskaya 48, Syktyvkar, 167982 Russia*
e-mail: frolova-ll@chemi.komisc.ru

[b] *Postovskii Institute of Organic Synthesis, Ural Scientific Center, Russian Academy of Sciences, Yekaterinburg, Russia*

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Abstract—Oxidative dehydrogenation of vicinal diols of bornane and pinane type with chlorine dioxide in dimethylformamide has yielded α-hydroxyketones with high selectivity. 3α-Hydroxy-10β-pinane-4-one has been prepared for the first time with yield of 63–65%; the product structure has been confirmed by X-ray diffraction studies.

Keywords: terpenoid α-hydroxyketone, vicinal diol, oxidation, chlorine dioxide, selectivity

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Terpenoid α-hydroxyketones are important building blocks for total synthesis of natural products; furthermore, they are widely used in preparation of chiral catalysts of various asymmetric reactions [1, 2]. Isomeric α-ketols of bornane type can be prepared via a number of methods based on reduction of camphorquinone and its derivatives as well as oxidation of camphor enolates with electrophilic oxidants [3–6]. As far as α-ketols of pinane type are concerned, exclusively 2α-hydroxypinane-3-one has been available so far, due to its easy preparation procedure [7]. Three isomeric ketols of pinane type, bearing functional groups in positions 3 and 4 (4α-hydroxy-10α-pinane-3-one, 3β-hydroxy-10α-pinane-4-one, and 4β-hydroxy-10β-pinane-3-one), have been prepared with low yields of 0.5–15% via hydrolysis of acetates formed upon rearrangement of 2α-hydroxypinane-3-one in acetic anhydride [8]. Another isomeric ketol, 4α-hydroxy-10β-pinane-3-one has been prepared with yield of 10% via enol- and epoxyacetate of isopinocamphone [9] (Scheme 1).

In this work we report on easy and selective procedure to prepare α-hydroxyketones of bornane and pinane types using chlorine dioxide. The parent 2-exo,3-*exo*-bornanediol **I** and 3α,4β-pinanediol **II** were prepared via reduction of camphorquinone with $LiAlH_4$ in anhydrous diethyl ether (**I**) and hydroboration–oxidation of verbenone or *cis*-verbenol (**II**) [10, 11]. The diols oxidation was performed in pyridine or dimethylformamide DMF medium without any catalyst or in the presence of $VO(acac)_2$, $MoCl_5$, or $Mo(CO)_6$. Experimental results are collected in Tables 1–3.

Bornanediol **I** was extremely rapidly oxidized with chlorine dioxide in pyridine (Table 1): the conversion was practically 100% after 1 h. The major products were isomeric ketols, 3β-hydroxycamphor (**III**) and 2β-hydroxyepicamphor (**IV**), 74–80% in total, as

Scheme 1.

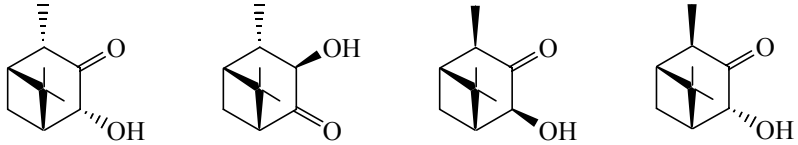


Table 1. Results of 2-exo,3-exo-bornanediol (**I**) oxidation at 20°C (3 wt % of the catalyst)

Solvent	Catalyst	Time, h	Conversion, %	Selectivity, %	**III** : **IV**[a]
Pyridine	–	1	100	74–80	1 : 1.0
″	–	3	100	49	1 : 1.0
″	$MoCl_5$	1	100	85	1 : 1.2
″	$VO(acac)_2$	1	100	87	1 : 1.4
DMF	–	1	26	100	1 : 1.2
″	–	3	100	95	1 : 1.2
″	$VO(acac)_2$	1	100	97	1 : 1.2
″	$MoCl_5$	1	100	99	1 : 1.1

[a] As determined by NMR.

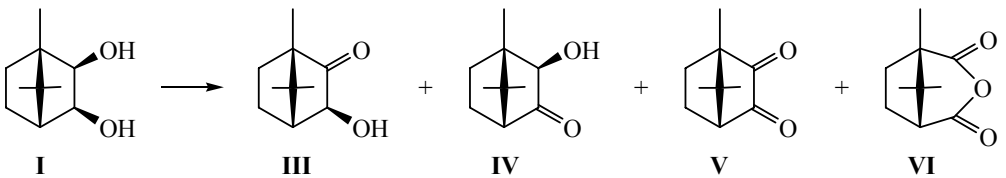
resulted from GLPC analysis. Besides those products, the reaction mixture contained 10–15% of camphorquinone (**V**) and 9–10% of camphor anhydride (**VI**) (Scheme 2). When the reaction was run longer (up to 3 h), the ketols content was down to 50%, and camphor anhydride yield was up to 40%, yield of camphor-quinone being almost the same (12–15%). The ratio of ketols **III** and **IV** in the mixture could not be determined due to equal R_t. However, the ratio was elucidated from NMR data. In the ^{13}C NMR spectrum, signals of similarly substituted atoms (CH, CH_2, CH_3) were of close intensity, thus revealing the 1 : 1 ratio of the ketols. The preparative yield of individual α-hydroxyketones after the column chromatography was of 37% (**IV**) and 31% (**III**), their spectral features coinciding with the reference data [12].

With $VO(acac)_2$ or $MoCl_5$ as catalyst, selectivity of the ketols formation was up to 85–87%, and the isomers ratio was somewhat shifted in favor of formation of *exo*-2-hydroxyepicamphor **IV**. When DMF was used as solvent instead of pyridine, the oxidation was significantly slowed down: conversion of the starting diol **I** was of 26% within 1 h. However, longer reaction run (3 h) or using the catalyst [$VO(acac)_2$ or $MoCl_5$] resulted in complete conversion of the diol with selectivity of 95–99% with respect to ketols. Under those conditions, only tiny amounts of camphorquinone and camphor anhydride were formed (Table 1).

Oxidation of 3α,4β-pinanediol **II** in pyridine without any catalyst or with $VO(acac)_2$ yielded a complex mixture of products that could be separated into the neutral and the acidic fractions via treatment with aqueous $NaHCO_3$ (5 wt %) (Table 2). In the neutral fraction, two isomeric ketols were identified: 3α-hydroxy-10β-pinane-4-one (**VII**) and 4β-hydroxy-10β-pinane-3-one (**VIII**), along with the chlorinated derivative, 2α-chloropinane-3,4-dione (**IX**). Of the acidic products, pinocamphor acid (**X**) was isolated, and *cis*-pinonic acid (**XI**) was identified.

Lower temperature of the diol **II** oxidation in pyridine favored formation of acids, especially of pinocamphor acid (its content being up from 4% to 26%). Molybdenum-containing catalysts decreased the diol **II** conversion to 35–54%, but selectivity of the α-ketols formation was up to 60–68%. In all the cases,

Scheme 2.



I **III** **IV** **V** **VI**

Table 2. Results of 3α,4β-pinanediol (**II**) oxidation in pyridine (1 h, 3 wt % of the catalyst)

Catalyst	*T*, °C	Conversion, %	Selectivity with respect to ketols, %	**VII** : **VIII**	Content (as determined from GLPC), %	
					VII + **VIII**	**IX**
–	20	86	54	3:1	47	16
–	0	100	47	4.5:1	47	2
$VO(acac)_2$	20	82	47	3:1	39	16
$Mo(CO)_6$	20	35	60	3.5:1	21	1
$MoCl_5$	20	54	68	2.6:1	37	4

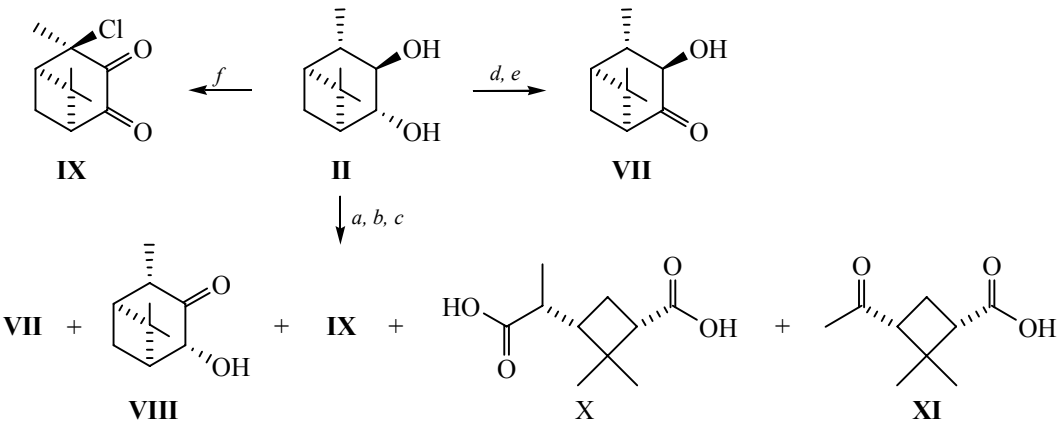
3α-hydroxy-10β-pinane-4-one was the major isomer. Despite the close values of R_f of **VII** and **VIII**, they could be separated by chromatography on SiO_2. Spectral features of **VIII** coincided with the published data [8] (Scheme 3).

IR spectrum of compound **X** contained characteristic bands of the acid hydroxyl stretching (2500–3400 cm^{-1}, broad) and of C=O stretching (1699 cm^{-1}). The ^{13}C NMR spectrum contained signals of 10 carbon atoms, including those belonging to two carboxyl groups and *gem*-dimethyl group; the ^1H NMR spectrum contained 9 signals of 16 protons, including those of CH_3CH group and pair of diastereotopic protons of the methylene group.

When DMF was used instead of pyridine, both without any catalyst or in the presence of $Mo(CO)_6$ or $MoCl_5$, α-hydroxyketone **VII** was practically the only reaction product, selectivity of its formation being independent of heating up to 40–45°C as well as cooling down to 0°C (Table 3). Compound **VII** was isolated via chromatography on SiO_2; mp 57–58°C and $[\alpha]_D^{22}$ +159.3° (after recrystallization from hexane–diethyl ether mixture). Configuration and structure of compound **VII** were elucidated by hetero- and homonuclear correlation NMR spectroscopy HMBC (H^3–C^4, H_e^7–C^4, H_n^7–C^4, H^5–C^4) and NOE (H^2–H_n^7, H^3–H^8, H^3–H^{10}, H^8–H^{10}).

Molecular structure of compound **VII** was explicitly confirmed by X-ray diffraction data (see figure). Heavy atoms were absent in the structure, therefore, it was not possible to elucidate the absolute configuration of the compound taking advantage of the anomalous scattering effect. In the crystal, molecules were packed in belts in parallel to the 0a axis; in the belts, the molecules were arranged via zigzag intermolecular hydrogen bonds of the OH···O type

Scheme 3.



a: ClO_2, Py; *b*: ClO_2, Py, Mo(II); *c*: ClO_2, Py, $VO(acac)_2$; *d*: ClO_2, DMF; *e*: ClO_2, DMF, Mo(II); *f*: ClO_2, DMF, $VO(acac)_2$.

Table 3. Results of 3α,4β-pinanediol (**II**) oxidation in DMF (1 h, 3 wt % of the catalyst)

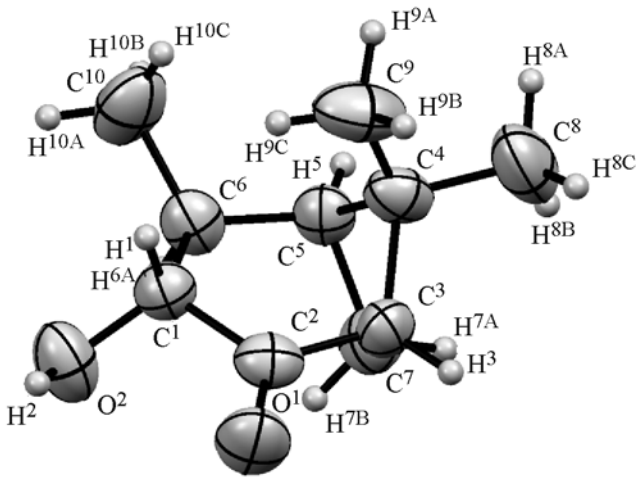
Catalyst	*T*, °C	Conversion, %	Selectivity with respect to ketol, %	Content (as determined from GLPC), %	
				VII	**IX**
–	20	100	88–92	82–90	–
–	0	78	92	71	–
–	40–45	100	87	87	–
$VO(acac)_2$	20	82	13	11	37
$VO(acac)_2$	40–45	100	–	–	68
$MoCl_5$	20	100	86	86	–
$Mo(CO)_6$	20	100	88	88	–

between hydroxyl and carbonyl groups on the adjacent molecules.

In the case of ClO_2–DMF—$VO(acac)_2$ oxidative system, the major product of the diol **II** oxidation was chlorinated diketone **IX**. With heating up to 40–45°C, its content in the mixture reached almost 70%.

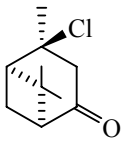
The chlorinated diketone **IX** was isolated by chromatography on SiO_2 in the form of yellow oily substance with $[\alpha]_D^{22}$ –53.3° (EtOH). In its IR spectrum, the absorption bands characteristic of hydroxyl groups were absent, however, the strong absorption bands were observed at 1730 and 698 cm^{-1}, assigned to stretching of C=O and C–Cl, respectively. In the ^{13}C NMR spectrum, signals assigned to keto groups were found, along with those of quaternary carbon atoms, a methylene, methyl, and methine groups. In the ^1H NMR spectrum, the doublet and quartet signals typical of CH_3CH group of the starting diol **II** were absent. *cis*-Positioning of the methyl group at C^{10} atom with respect to the *gem*-dimethyl group was confirmed by NOE interaction between the protons at C^{10} and C^8 atoms.

In the course of isolation of compound **IX**, about 5% of the fraction containing two chlorinated derivatives of *cis*-verbanone, 2α-chloropinane-4-one (**XII**) and 3α-chloro-10β-pinane-4-one (**XIII**) (3 : 2 ratio, GLPC and NMR results) was obtained. Those compounds were not identified in the products of the diol **II** oxidation in pyridine. Their traces (up to 2%) were found in the mixture when the reaction was performed in DMF; their content was up to 7.5% in the case of the ClO_2–DMF–$VO(acac)_2$ oxidative system 7.5%.

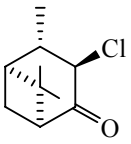


General view of 3α-hydroxy-10β-pinane-4-one (**VII**) molecule from XRD data.

NMR spectra of **XII** contained additional signals as compared to those of **IX**: signal of C^3 methylene group in the ^{13}C NMR spectrum and two signals of geminal protons at the same carbon atom (spin-spin coupling constant of 20 Hz) in the ^1H NMR spectrum. Presence of heteroatom at the quaternary C^2 atom was confirmed by its chemical shift (75.3 ppm). NMR spectra of compounds **VII** and **XIII** were in general similar, the signals of H^2, H^3, and H^5 protons being shifted downfield and the signals of C^3 and C^4 carbon fields being shifted upfield in the case of chlorinated derivative. *trans*-Positioning of chlorine with respect to gem-dimethyl group in compound **XIII** was confirmed by interaction of protons H^3–H^8.



XII



XIII

To summarize, composition of products of vicinal diols **I** and **II** oxidation with chlorine dioxide was majorly affected by nature of the solvent and the catalyst. Oxidative dehydrogenation in pyridine yielded diketones, acids, and chlorinated products. In DMF, both without any catalyst and in the presence of Mo-containing catalyst α-hydroxyketones were obtained with high selectivity. *exo*-Positioning of hydroxyl groups in bornane-2,3-diol affords equal accessibility of C–H bonds for the oxidants attack, and in most cases practically equimolar mixture of isomeric α-hydroxyketones **III** and **IV** was formed. In 3α,4β-pinanediol, the proton at C^4 atom was sterically hindered, and 3-hydroxypinane-4-one prevailed in the products, or even was the only isomer. In this work, 3α-hydroxy-10β-pinane-4-one was prepared for the first time with yield of 63–65% via oxidation of *trans*-pinane-3,4-diol with chlorine dioxide in DMF.

Attempts to prepare the α-hydroxyketone **VII** via oxidation of the diol **II** with *t*-BuOOH–$MoCl_5$ and *t*-BuOOH–$VO(acac)_2$ following the method described in [13] as well as via hydroboration followed with oxidation of organoborane with chromic acid failed.

EXPERIMENTAL

GLPC analysis was performed using the SHIMADZU GC-2010AF chromatograph (column HP1, flame-ionization detector, helium as carrier gas). IR spectra (thin film or KBr) were recorded with the IR Prestige 21 Shimadzu instrument. NMR spectra were registered with the Bruker AVANCE-II-300 instrument [300 (^1H) and 75 (^{13}C) MHz] in $CDCl_3$ or DMSO-d_6. The TP instrument was used to determine melting points. Optical rotation was measured with the P3002RS Kruss automated polarimeter (Germany).

Column chromatography was performed using the 60 silica gel (70–230 mesh, Alfa-Aesar). TLC analysis was carried out on Sorbfil plates with hexane or petroleum ether–diethyl ether as eluents and phosphormolybdic acid in EtOH (10%) or vanillin in EtOH (3%) as developed.

Chlorine dioxide was used in the form of aqueous solution (8–9 g/L, Mondi Syktyvkar LPK). The solvents were distilled prior to use. Terpenoid diols **I** (mp 254°C, $[\alpha]_D^{22}$ +19.4°) and **II** (mp 149–150°C, $[\alpha]_D^{22}$ +5.0°) were prepared as described elsewhere [10, 11].

X-ray diffraction studies were performed using the Xcalibur 3 diffractometer (CCD detector, MoK_α, λ 0.71073 Å, graphitic monochromator, 295(2) K, ω-scan]. The structure was solved via direct method and refined taking advantage of SHELXTL97 software package [14] and full-matrix least-squares method with respect to F^2 under anisotropic approximation for non-hydrogen atoms. Hydrogen atoms at C–H were added at the geometrically calculated positions and refined along with the dependent heat parameters in the rider model. Crystal: rhombic, space group $P2_12_12_1$, *a* 7.0945(10), *b* 11.410(3), *c* 11.831(3) Å, *V* 957.7(4), *Z* 4, d_{calc} 1.167 g/cm^3, μ 0.079 mm^{-1}, *F*(000) 368. At $3.35 < \theta < 28.29°$ of, 5031 reflections [1385 of them being independent; 556 of them with $I > 2\sigma(I)$ [were collected (R_{int} 0.0399), completeness for θ 28.29° was of 99.7%. The final refinement parameters were as follows: R_1 0.0318, wR_2 0.0492 [for reflections with $I > 2\sigma(I)$], R_1 0.0916, wR_2 0.0513 (for all reflections), *S* 1.000, $\Delta\rho_{\bar{e}}$(min/max) = 0.086/–0.113 ē Å^{-3}.

General procedure of terpenoid diols oxidation with ClO_2. Flow of aerated ClO_2 was bubbled through solution of 0.2 g of the starting compound (**I** or **II**) in 5 mL of pyridine or DMF, in the presence of catalyst or without catalyst. Reaction progress was monitored by TLC. The solvent was then distilled off, the reaction mixture was diluted with methyl-*tert*-butyl or diethyl ether, washed with 5 wt % aqueous H_2SO_4, water, and saturated aqueous NaCl, and dried over $MgSO_4$. After removal of ether, the reaction mixture was analyzed with GLPC and NMR spectroscopy. Reaction products were isolated by column chromatography on SiO_2.

***exo*-3-Hydroxycamphor (III).** Yield 31%, R_f 0.55 (petroleum ether–diethyl ether, 2 : 1), $[\alpha]_D^{22}$ –109.6° (*c* 0.2, EtOH). The spectral parameters coincided with the reference data [12].

***exo*-2-Hydroxyepicamphor (IV).** Yield 37%, R_f 0.59 (petroleum ether–diethyl ether, 2 : 1), $[\alpha]_D^{22}$ +114.4° (*c* 0.2, EtOH). The spectral parameters coincided with the reference data [12].

Camphorquinone (V) and camphor anhydride (VI). The spectral parameters coincided with the reference data [15].

3α-Hydroxy-10β-pinane-4-one (VII). Yield 63%, R_f 0.48 (hexane–diethyl ether, 1 : 2), $[\alpha]_D^{22}$ +159.3° (*c* 0.6 EtOH), mp 57–58°C. IR spectrum, ν, cm^{-1}: 3452 (OH), 2958, 1716 (C=O), 1467, 1379, 1328, 1247, 1080, 1045, 983, 933, 842, 804. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.95 s (3H, 8-CH_3), 1.20 d (3H, 10-CH_3, *J* 7.3), 1.31 d (1H, H^7, *J* 10.5), 1.32 s (3H, 9-CH_3), 1.93 d.d (1H, H^2, *J* 5.5, 7.3), 2.07 m (1H, H^1), 2.52 m (1H, H^5), 2.69 m (1H, H^7, *J* 10.5), 3.79 d (1H, H^3, *J* 5.5). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 212.33 (C^4), 76.27 (C^3), 58.08 (C^5), 47.41 (C^1), 43.33 (C^2), 40.00 (C^6), 29.75 (C^7), 27.29 (C^9), 25.11 (C^8), 19.79 (C^{10}).

4β-Hydroxy-10β-pinane-3-one (VIII). Yield 4%, R_f 0.52 (hexane–diethyl ether, 1 : 2). IR spectrum, ν, cm^{-1}: 3471 (OH), 2933, 1716 (C=O), 1466, 1373, 1180, 1111, 1028, 988, 839, 798. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.83 s (3H, 8-CH_3), 1.13 d (3H, 10-CH_3, *J* 7.2), 1.25 d (1H, H^7, *J* 10.5), 1.28 s (3H, 9-CH_3), 1.99 m and 2.15 m (2H, H^1, H^5), 2.56 m (1H, H^2, *J* 7.2), 4.00 m (1H, H^4). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 215.62 (C^4), 77.51 (C^4), 48.74 (C^2), 47.17 and 46.17 (C^1 and C^5), 31.75 (C^7), 27.78 (C^9), 23.01 (C^8), 16.34 (C^{10}).

2α-Chloropinane-3,4-dione (IX). Yield 40%, oily yellow substance, R_f 0.5 (hexane–diethyl ether, 1 : 1), $[\alpha]_D$– +53.3° (*c* 0.8 EtOH). IR spectrum, ν, cm^{-1}: 2962, 1730 (C=O), 1469, 1448, 1392, 1377, 1253, 1232, 1192, 1130, 1066, 1035, 1016, 987, 966, 937, 873, 839, 698, 680. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.91 s (3H, 8-CH_3), 1.44 s (3H, 9-CH_3), 1.82 s (3H, 10-CH_3), 2.21 d (1H, H^7, *J* 12), 2.93 d.d.d (1H, H^7, *J* 12, 6.1, 6.2, 12), 2.55 d.d (1H, H^1, *J* 6.1, 6.2), 2.86 d.d (1H, H^5, *J* 6.1, 6.2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 193.7 (C^3), 191.7 (C^4), 70.3 (C^2), 56.5, 52.5 (C^1 and C^5), 40.7 (C^6), 28.1 (C^7), 27.6 (C^8), 27.3 (C^9), 24.4 (C^{10}).

3-(1-Carboxyethyl)-2,2-dimethylcyclobutane carboxylic acid (pinocamphor acid) (X). Yield 20%, mp 176–178°C. IR spectrum, ν, cm^{-1}: 3462–2567 (OH), 1699 (C=O), 1460, 1421, 1371, 1305, 1282, 1246, 1213, 1159, 952, 925. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.93 s (3H, 9-CH_3), 0.95 d (3H, 6-CH_3, *J* 7), 1.13 s (3H, 10-CH_3), 1.73 d.d (1H, H^3, *J* 10.2, 10.4), 2.0 m (2H, H^2), 2.26 q. d (1H, H^5, *J* 7.0, 10.8), 2.60 d.d (1H, H^4, *J* 7.4, 10.8), 12.03 br.s (2H, H^7, H^8). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 177.6 (C^8), 174.0 (C^7), 45.4 (C^4), 44.9 (C^2), 42.4 (C^1), 40.4 (C^5), 30.2 (C^{10}), 23.5 (C^3), 17.8 (C^9), 15.2 (C^6).

3-Acetyl-2,2-dimethylcyclobutane carboxylic acid (*cis*-pinanoic acid) (XI). The spectral parameters coincided with the reference data [16].

2α-Chloropinane-4-one (XII). Combined yield of compounds **XII** and **XIII** 5%. R_f 0.58 (hexane–diethyl ether, 1 : 1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.86 s (3H, 8-CH_3), 1.36 s (3H, 9-CH_3), 1.71 s (3H, 10-CH_3), 1.75 d (1H, H^7, *J* 10), 2.13 m (1H, H^5), 2.40 m (1H, H^1), 2.62 m (1H, H^7), 2.63 d (1H, H^3, *J* 20), 2.81 d (1H, H^3, *J* 20). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 205.5 (C^4), 75.33 (C^2), 52.67 (C^1), 43.09 (C^3), 39.4 (C^6), 38.23 (C^5), 31.49 (C^7), 27.64 (C^{10}), 27.48 (C^9), 22.83 (C^8).

3α-Chloro-10β-pinane-4-one (XIII). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.01 s (3H, 8-CH_3), 1.26 d (3H, 10-CH_3, *J* 7), 1.34 s (3H, 9-CH_3), 1.41 d (1H, H^7, *J* 10), 2.17 m (1H, H^1), 2.43 m (1H, H^2), 2.69 m (1H, H^5), 2.79 m (1H, H^7), 4.66 d (1H, H^3, *J* 5.7). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 205.5 (C^4), 62.19 (C^3), 58.51 (C^5), 47.92 (C^1), 45.42 (C^2), 40.1 (C^6), 29.39 (C^7), 27.02 (C^9), 24.93 (C^8), 19.13 (C^{10}).

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