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REACTION OF (+)-USNINIC ACID AND SEVERAL OF ITS DERIVATIVES WITH DIAZOMETHANE

D. N. Sokolov,* O. A. Luzina, D. V. Korchagina, M. P. Polovinka, and N. F. Salakhutdinov

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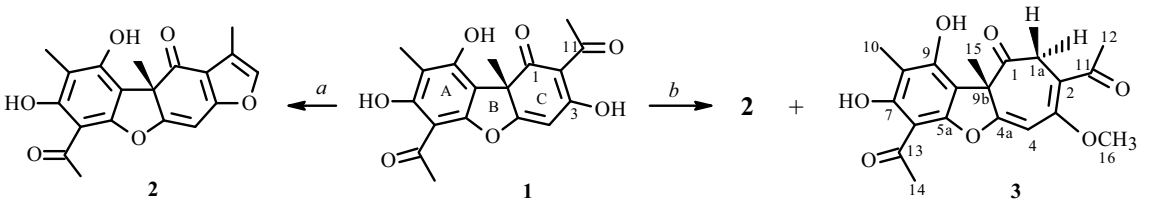
New derivatives of (+)*-usninic acid including products of ring expansion, methylation of enol and phenol hydroxyls, and formation of an oxirane ring in addition to products with pyran and furan rings annelated to ring A of* (+)*-usninic acid were prepared by reaction of* (+)*-usninic acid and its pyrazole derivatives with diazomethane.*

Keywords: (+)-usninic acid, diazomethane, methylation.

Usninic acid is a unique and available domestic plant metabolite that exhibits many types of biological activity [1]. Optically active usninic acid with optical rotations of opposite signs and high optical purities is isolated from various lichen species in adequate quantities. However, its difficultly predicted and highly varied reactivity prevents its broad use in synthetic practice. The resorcinol system of ring A in both usninic acid and its derivatives is very labile under basic conditions and complicates the reactions. Therefore, the phenol and hydroxyl groups must be protected under such conditions to impart stability. One of the available methods is methylation of the phenol hydroxyls with diazomethane, a common reagent for preparing methylated alcohols, phenols, and carboxylic acids. All hydroxyls of usninic acid are known to be involved in the formation of intramolecular H-bonds [2]. This limits significantly the ability to methylate them with diazomethane [3]. In fact, the preparation of methylated (+)-usninic acid (**1**) via its reaction with diazomethane at 4°C was reported [4]. However, only compound **2**, which contained a furan ring annelated to ring C, was isolated in small yield (14%) from the multi-component product mixture (Scheme 1).



a. CH_2N_2, CH_2Cl_2, 4°C; *b*. CH_2N_2, $CHCl_3$, –35°C

Scheme 1

We investigated the reaction of (+)-usninic acid (**1**) with diazomethane at lower temperature and studied the reactions of several of its derivatives with diazomethane under various conditions.

Treatment of **1** with an ether solution of diazomethane for 5 h at –35°C (Scheme 1) gave a violent reaction and formed a complicated product mixture from which **2** and **3** were isolated in 8 and 7% yields. One of the products was already known **2**. The other formed as a result of methylation of the enol hydroxyl and expansion of ring C (**3**).

Products of methylation of the phenol hydroxyls were not isolated before [4] or by us. Reactions with catalysts used for methylation of hydroxyl-containing compounds by diazomethane [5] produced either starting **1** [$BF_3 \cdot Et_2O$, $Pd(OAc)_2$] or

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, 630090, Novosibirsk, Prosp. Akad. Lavrent′eva, 9, Russia, e-mail: dsokolov@nioch.nsc.ru . Translated from Khimiya Prirodnykh Soedinenii, No. 5, September–October, 2011, pp. 623–627. Original article submitted February 1, 2011.

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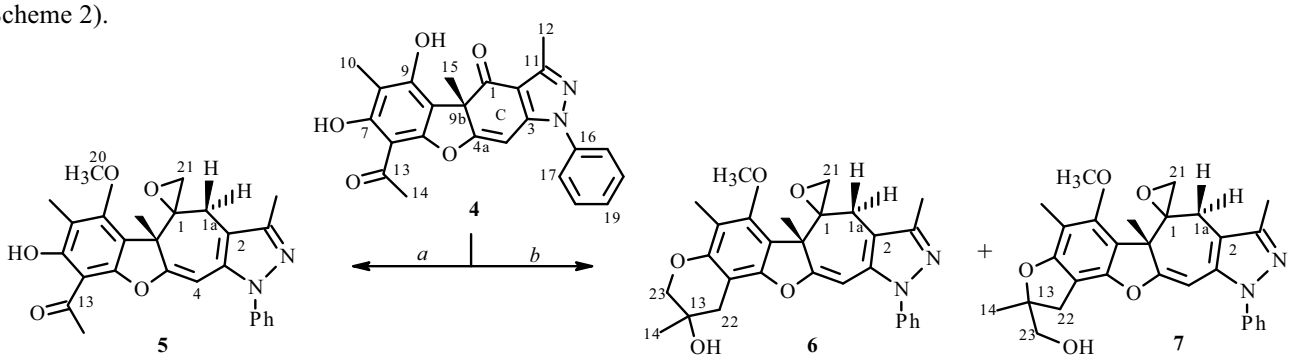
did not affect the course of the reaction [$Co(BF_4)_2 \cdot 6H_2O$]. Thus, neither lowering the temperature nor using catalysts could produce derivatives methylated at the phenol hydroxyls. The reaction occurred non-selectively with transformation of ring C of usninic acid.

Reaction with diazomethane at room temperature of (+)-usninic acid derivative **4** led to methylation of phenol hydroxyl C_9–OH and expansion of ring C to form an oxirane ring from the carbonyl (C_1=O). Compound **5** was formed as the main product and existed according to NMR spectra as a single stereoisomer. It was isolated in 55% yield after chromatography (Scheme 2).



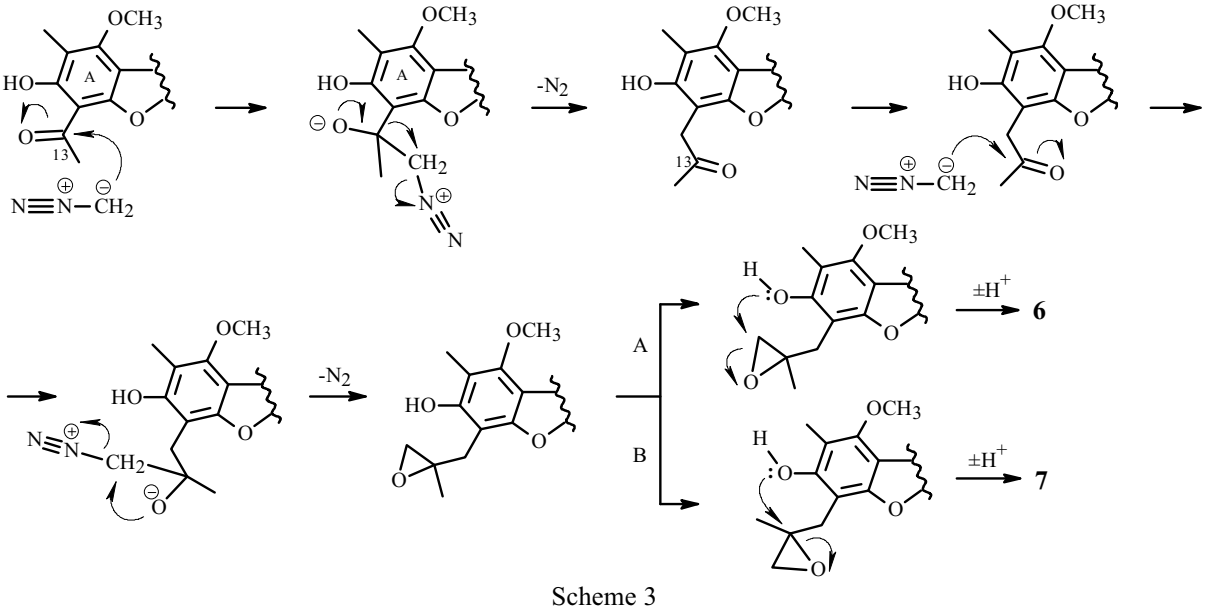
a. CH_2N_2, $CHCl_3$, 20°C; *b*. CH_2N_2, $CHCl_3/CH_3OH$, 20°C

Scheme 2

The formation of homologs and/or oxiranes from carbonyl compounds by the action of diazomethane is known to depend on the substrate structure and the conditions. These reactions can be suppressed or initiated by varying the solvent or using different reagents [6, 7]. In particular, adding methanol to the reaction mixture affects the reaction of diazomethane with carbonyl compounds.

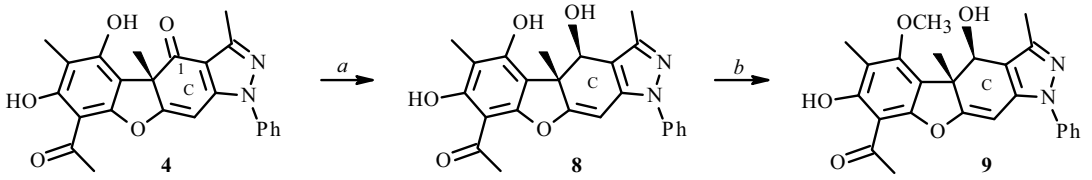
The reaction of **4** with diazomethane in the presence of MeOH formed compounds **6** and **7** as the main products (isolated as a 3:2 mixture according to the PMR spectrum) in overall yield of about 50% (Scheme 2). Besides methylation of the C_9–OH phenol hydroxyl, expansion of ring C, and formation of an oxirane from the carbonyl (C_1=O), the acetophenone fragment of **4** reacted with diazomethane to form annelated pyran and furan rings in **6** and **7**, respectively. We also isolated **6** and **7** as single stereoisomers.

The formation of the pyran and furan rings in **6** and **7** could be explained by assuming the following series of transformations (Scheme 3). A CH_2 group is incorporated initially between the carbonyl (C_{13}=O) and aromatic ring A. Then, the carbonyl (C_{13}=O) reacts with diazomethane to form an oxirane ring [8] that is opened as the result of attack by an internal nucleophile, the hydroxyl O atom, with subsequent heterocyclization and formation of **6** (pathway A) and **7** (pathway B).



Scheme 3

Reduction of the carbonyl (C_1=O) in ring C of **4** by $NaBH_4$ in THF produced **8** in 96% yield (Scheme 4). The configuration of the C-1 center in **8** was proposed based on literature data for the reaction mechanism of carbonyl compounds with $NaBH_4$ [9]. Diazomethane reacted with **8** to form monomethylated **9** (Scheme 4). As assumed, transformations of substrate ring C did not occur in this instance. The methylation occurred selectively with formation of the 9-*O*-methylated derivative. However, transformations involving the carbonyl (C_{13}=O) also were not observed. Compound **9** was the main reaction product in both $CHCl_3$ and MeOH in yields of 80 and 69%, respectively.



a. $NaBH_4$, THF, –20°C; *b*. CH_2N_2, $CHCl_3$, 20°C

Scheme 4

Thus, we investigated the reaction of **1** and several of its derivatives with diazomethane. Compound **1** reacted violently with diazomethane even at low temperature to form a complicated product mixture. One of the reaction pathways was expansion of ring C. Carrying out the reaction with diazomethane and a modified phenylhydrazine derivative of **1** (compound **4**) resulted in expansion of ring C, formation of an oxirane ring involving the C_1=O carbonyl, and methylation of the C_9–OH phenol hydroxyl. Adding MeOH to the reaction mixture enhanced the reaction of the C_{13}=O carbonyl with diazomethane and formed **6** and **7**. Reaction of the pyrazole derivative (compound **8**) reduced at the C_1=O carbonyl with diazomethane gave selectively the methylation product of the C_9–OH phenol hydroxyl (**9**) in good yield.

EXPERIMENTAL

PMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AV-400 (operating frequency 400.13 MHz for ^1H and 100.61 MHz for ^{13}C) and DRX-500 (operating frequency 500.13 MHz for ^1H and 125.76 MHz for ^{13}C) spectrometers. The internal standards were the signals of residual $CHCl_3$ (δ_H 7.24 ppm) and the solvent (δ_C 76.90 ppm). The structures of the compounds were elucidated by NMR methods based on analyses of PMR spectra using ^1H–^1H double resonance and two-dimensional (2D) homonuclear ^1H–^1H correlation spectra (^1H–^1H COSY) in addition to analyses of ^{13}C NMR spectra using 2D heteronuclear ^{13}C–^1H correlation spectroscopy COSY ($^1J_{C,H}$ = 160 Hz) and COLOC ($^{2,3}J_{C,H}$ = 10 Hz). The single resonance spectra were recorded in order to determine the direct $^1J_{C,H}$ SSCC. Multiplicities of resonances in ^{13}C NMR spectra were determined from spectra recorded in J-modulation mode (JMOD). Mass spectra (ionizing-electron energy 70 eV) were measured in a DFS Thermo Scientific high-resolution mass spectrometer. Melting points were determined on a Kofler stage.

(+)-Usninic acid (**1**) {$[\alpha]_D$ +478° (*c* 0.1, $CHCl_3$)} was isolated from a mixture of *Usnea* lichen species by the literature method [10]. Compound **2** was synthesized by the literature method [11]; *N*-methyl-*N*-nitrosourea and diazomethane, as before [12]. We used commercially available $NaBH_4$ and Merck silica gel (60–200 μm) for column chromatography.

The numbering of atoms in the compounds is given for assigning resonances in NMR spectra and does not always agree with the atomic numbering in the nomenclature.

Reaction of 1 with Diazomethane. A solution of **1** (344 mg, 1 mmol) in $CHCl_3$ (5 mL) was placed into a thermostat at –35°C. A solution of diazomethane prepared from *N*-methyl-*N*-nitrosourea (2 g) was added carefully with stirring. The mixture was left at this temperature until **1** was fully converted (about 4–5 h, TLC monitoring) and treated with acetic acid (10%) in Et_2O until the evolution of gas bubbles ceased. The solvent was removed. The products were chromatographed over a column of silica gel (60–200 μm) with elution by $CHCl_3$.

(*S*)-1,1′-(1,3-Dihydroxy-7-methoxy-2,10a-dimethyl-10-oxo-10,10a-dihydro-9*H*-cyclohepta[*b*]benzofuran-4,8-diyl)diethanone (3). Yield 26 mg (7%), mp 77–79°C.

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.58 (3H, s, H-15), 2.05 (3H, s, H-10), 2.47 (3H, s, H-12), 2.66 (3H, s, H-14), 2.81 (1H, dd, ^2J = 13.0, $J_{1a\beta,4}$ = 0.8, H-1a*β*), 3.93 (3H, s, OCH_3-16), 4.20 (1H, d, ^2J = 13.0, H-1a*α*), 6.62 (1H, d, $J_{4,1a\beta}$ = 0.8, H-4), 9.55 (1H, s, OH-9), 13.32 (1H, s ,OH-7).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.28 (q, C-10), 25.38 (q, C-15), 31.18 (q, C-14), 32.09 (q, C-12), 41.07 (t, C-1a), 57.89 (q, C-16), 61.33 (s, C-9b), 97.82 (d, C-4), 101.10 (s, C-6), 103.84 (s, C-9a), 108.26 (s, C-2), 108.87 (s, C-8),

154.46 (s, C-5a), 157.58 (s, C-9), 162.32 (s, C-3), 163.60 (s, C-7), 169.14 (s, C-4a), 195.38 (s, C-11), 200.52 (s, C-13), 217.21 (s, C-1).

Found: *m*/*z* 372.1197 $[M]^+$, $C_{20}H_{20}O_7$; calcd: M = 372.1204.

A comparison of PMR spectra of starting **1** and **3** that was prepared from it showed that the spectrum of the latter lacked a resonance for the OH at ~18 ppm and exhibited a resonance for a MeO group at 3.93 ppm. This indicated that the C-3 OH group was methylated. The similarity of the chemical shifts of the resonances for ring A atoms of **1** and **3** and the appearance of resonances for CH_2 in the PMR and ^{13}C NMR spectra of **3** were consistent with an unchanged aromatic ring and expansion of ring C in **3**. Correlation couplings obtained from 2D spectra confirmed the proposed structure.

Reaction of 4 with $NaBH_4$. A solution of **4** (416 mg, 1 mmol) in THF (20 mL) was cooled to –20°C, treated with a suspension of $NaBH_4$ (50 mg) in THF (5 mL), and stirred at this temperature for 2 h. The reaction mixture was treated with dilute HCl until the pH was ~5, brought to room temperature, treated with CH_2Cl_2 (30 mL), washed twice with H_2O, and dried over calcined $MgSO_4$. The solvent was removed. The products were chromatographed over a column of silica gel (60–200 μm) with elution by $CHCl_3$.

1-((4*S*,4a*R*)-4,5,7-Trihydroxy-3,4a,6-trimethyl-1-phenyl-4,4a-dihydro-1*H*-benzofuro[3,2-*f*]indazol-8-yl)ethanone (8). Yield 401 mg (96%), mp 155°C, $[\alpha]_D$ +152° (*c* 0.1, $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 1068, 1288, 1369, 1441, 1627, 3188, 3392.

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.35 (3H, s, H-15), 2.03 (3H, s, H-10), 2.32 (3H, s, H-12), 2.61 (3H, s, H-14), 5.26 (1H, br.s, OH-1), 5.33 (1H, d, J = 6, H-1), 5.87 (1H, s, H-4), 7.31–7.42 (5H, m, H-arom), 9.25 (1H, s, 9-OH), 13.31 (1H, s, 7-OH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 6.97 (C-10), 12.25 (C-12), 15.93 (C-15), 30.79 (C-14), 50.90 (C-9b), 74.30 (C-1), 88.99 (C-4), 101.03 (C-6), 106.56 (C-9a), 107.66 (C-8), 111.35 (C-2), 123.23 (C-17), 127.39 (C-19), 129.01 (C-18), 137.75 (C-16), 138.10 (C-3), 146.22 (C-11), 156.84 (C-9), 157.26 (C-5a), 162.58 (C-7), 167.26 (C-4a), 200.58 (C-13).

Found: *m*/*z* 418.1521 $[M]^+$, $C_{24}H_{22}O_5N_2$; calcd: M = 418.1523.

Reaction of 4 and 8 with Diazomethane (General Method). A solution of **4** (416 mg, 1 mmol) (418 mg, 1 mmol of **8**) in $CHCl_3$ (5 mL) was treated carefully with stirring with a solution of diazomethane prepared from *N*-methyl-*N*-nitrosourea (2 g) and left at room temperature until evolution of gas bubbles ceased completely. The solvent was removed. The products were chromatographed over a column of silica gel (60–200 μm) with elution by $CHCl_3$ to afford **5** (**9**). Analogously from **4** using a $CHCl_3$:MeOH mixture (1:1) as the solvent, **6** and **7** were obtained in overall yield 249 mg (50%).

1-((5a*S*)-8-Hydroxy-6-methoxy-3,5a,7-trimethyl-1-phenyl-4,5a-dihydro-1*H*-spiro[benzofuro[3′,2′:5,6]cyclopenta[1,2-*c*]pyrazol-5,2′-oxiran]-9-yl)ethanone (5). Yield 252 mg (55%), mp 112–114°C, $[\alpha]_D$ +69° (*c* 0.3, $CHCl_3$).

PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.73 (3H, s, H-15), 2.11 (3H, s, H-10), 2.14 (1H, dd, ^2J = 4.7, $J_{21,1a\alpha}$ = 2.0, H-21), 2.24 (3H, s, H-12), 2.39 (1H, d, ^2J = 17.0, H-1a*β*), 2.44 (1H, d, ^2J = 4.7, H′-21), 2.61 (3H, s, H-14), 3.66 (1H, dd, ^2J = 17.0, $J_{1a\alpha,21}$ = 2.0, H-1a*α*), 3.93 (3H, s, OCH_3-20), 6.10 (1H, s, H-4), 7.34–7.38 (1H, m, H-19), 7.42–7.50 (4H, m, H-17, H-18), 13.30 (1H, s, 7-OH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 9.66 (q, C-10), 11.57 (q, C-12), 17.95 (q, C-15), 30.17 (t, C-1a), 31.44 (q, C-14), 50.84 (t, C-21), 52.07 (s, C-9b), 58.15 (s, C-1), 61.63 (q, C-20), 9.195 (d, C-4), 102.86 (s, C-6), 111.30 (s, C-9a), 111.35 (s, C-3), 112.75 (s, C-8), 125.19 (d, 2C-17), 127.43 (d, C-19), 129.06 (d, 2C-18), 133.33 (s, C-2), 139.37 (s, C-16), 147.90 (s, C-11), 156.49 (s, C-5a), 163.13 (s, C-9), 163.61 (s, C-7), 163.78 (s, C-4a), 201.62 (s, C-13).

Found: *m*/*z* 458.1835 $[M]^+$, $C_{27}H_{26}O_5N_2$; calcd: M = 458.1836.

A comparison of PMR spectra of starting **4** and **5** that was prepared from it showed that the spectrum of the latter lacked a resonance for the OH at ~11 ppm and exhibited a resonance for a MeO group at 3.93 ppm. This indicated that the C-9 hydroxyl group was methylated. The resonance of the C_1=O carbonyl disappeared in the ^{13}C NMR spectrum of **5** and two resonances for methylenes at 30.17 and 50.84 ppm and one resonance for a quaternary C atom at 58.15 appeared. The chemical shifts of the resonances for the last two C atoms and the direct ^{13}C–^1H SSCC of the CH_2 fragment at 50.84 ppm ($^1J_{C,H}$ = 174.7) that was obtained from the single resonance spectrum were consistent with these C atoms being in an epoxide ring. The SSCC between one of the protons in the CH_2 group of the epoxide ring at 2.14 ppm and one of the CH_2 protons at 3.66 ppm ($J_{H,H}$ = 2.0) that was observed in the PMR spectra could be explained by a through-space W-interaction, from which it follows that the oxirane ring and the CH_2 group were located in neighboring positions.

1-((4*S*,4a*R*)-4,7-Dihydroxy-5-methoxy-3,4a,6-trimethyl-1-phenyl-4,4a-dihydro-1*H*-benzofuro[3,2-*f*]indazol-8-yl)ethanone (9). Yield 345 mg (80%), mp 78°C, $[\alpha]_D$ +218° (*c* 0.3, $CHCl_3$).

PMR spectrum ($CDCl_3$, δ, ppm): 1.48 (3H, s, H-15), 2.13 (3H, s, H-10), 2.44 (3H, s, H-12), 2.67 (3H, s, H-14), 3.94 (3H, s, H-20), 3.97 (1H, s, 1-OH), 5.40 (1H, s, H-1), 5.96 (1H, s, H-4), 7.30–7.51 (5H, m, H-arom), 13.26 (1H, s, 7-OH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 8.94 (C-10), 12.49 (C-12), 17.77 (C-15), 31.30 (C-14), 52.00 (C-9b), 61.49 (C-20), 74.21 (C-1), 89.93 (C-4), 103.92 (C-6), 111.96 (C-2), 112.05 (C-9a), 114.77 (C-8), 122.66 (C-17), 126.55 (C-19), 128.83 (C-18), 136.01 (C-16), 138.86 (C-3), 147.52 (C-11), 157.63 (C-5a), 159.36 (C-9), 162.86 (C-7), 166.71 (C-4a), 201.59 (C-13).

Found: *m*/*z* 432.1678 $[M]^+$, $C_{25}H_{24}O_5N_2$; calcd: M = 432.16797.

(6b*S*)-6-Methoxy-2,5,6b,9-tetramethyl-11-phenyl-1,2,3,6b,8,11-hexahydrospiro[chromeno[6″,5″:4′,5′]furo[3′,2′:5,6]cyclohepta[1,2-*c*]pyrazol-7,2′-oxiran]-2-ol (6). PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.30 (3H, s, H-14), 1.70 (3H, s, H-15), 2.08 (3H, s, H-10), 2.13 (1H, dd, ^2J= 4.8, $J_{21,1a\alpha}$ = 1.8, H-21), 2.21 (3H, s, H-12), 2.36 (1H, d, ^2J = 17.1, H-1aβ), 2.41 (1H, d, ^2J = 4.8, H′-21), 2.61 (1H, d, ^2J = 16.5, H-22a), 2.68 (1H, dd, ^2J = 16.5, $J_{22e,23e}$ = 2.2, H-22e), 3.64 (1H, dd, ^2J = 17.1, $J_{1a\alpha,21}$ = 1.8, H-1aα), 3.77 (1H, d, ^2J = 10.8, H-23a), 3.84 (3H, s, H-20), 3.92 (1H, dd, ^2J = 10.8, $J_{23e,22e}$ = 2, H-23e), 6.00 (1H, s, H-4), 7.29–7.35 (1H, m, H-19), 7.39–7.46 (4H, m, H-17, H-18).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 9.80 (q, C-10), 11.54 (q, C-12), 18.21 (q, C-15), 24.67 (q, C-14), 30.21 (t, C-1a), 33.49 (t, C-22), 50.97 (t, C-21), 53.17 (s, C-9b), 58.09 (s, C-1), 61.43 (q, C-20), 64.94 (s, C-13), 73.81 (t, C-23), 90.72 (d, C-4), 99.05 (s, C-6), 110.93 (s, C-3), 112.41 (s, C-9a), 112.76 (s, C-8), 125.13 (d, 2C-17), 127.22 (d, C-19), 128.91 (d, 2C-18), 133.95 (s, C-2), 139.35 (s, C-16), 147.74 (s, C-11), 152.79 (s, C-7), 153.57 (s, C-5a), 155.48 (s, C-9), 164.72 (s, C-4a).

((5b*S*)-5-Methoxy-2,4,5b,8-tetramethyl-10-phenyl-2,5b,7,10-tetrahydro-1*H*-spiro[furo[2″,3″:6′,7′]benzofuro[3′,2′:5,6]cyclohepta[1,2-*c*]pyrazol-6,2′-oxiran]-2-yl)methanol (7). PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.39 (3H, s, H-14), 1.70 (3H, s, H-15), 2.06 (3H, s, H-10), 2.14 (1H, dd, ^2J = 4.8, $J_{21,1a\alpha}$ = 2.2, H-21), 2.21 (3H, s, H-12), 2.36 (1H, d, ^2J = 17.1, H-1aβ), 2.41 (1H, d, ^2J = 4.8, H′-21), 2.77 (1H, d, ^2J = 15.2, H-22), 3.13 (1H, d, ^2J = 15.2, H′-22), 3.55 (1H, d, ^2J = 11.8, H-23), 3.62 (1H, d, ^2J = 11.8, H′-23), 3.64 (1H, br.d, ^2J = 17.1, H-1aα), 3.85 (3H, s, H-20), 5.99 (1H, s, H-4), 7.29–7.35 (1H, m, H-19), 7.39–7.46 (4H, m, H-17, H-18).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 9.97 (q, C-10), 11.54 (q, C-12), 18.16 (q, C-15), 23.30 (q, C-14), 30.23 (t, C-1a), 34.73 (t, C-23), 50.91 (t, C-21), 52.73 (s, C-9b), 58.08 (s, C-1), 61.27 (q, C-20), 67.93 (t, C-22), 89.80 (s, C-13), 90.72 (d, C-4), 102.40 (s, C-6), 107.15 (s, C-8), 111.04 (s, C-3), 112.28 (s, C-9a), 125.08 (d, 2C-17), 127.20 (d, C-19), 128.91 (d, 2C-18), 133.93 (s, C-2), 139.35 (s, C-16), 147.73 (s, C-11), 150.78 (s, C-5a), 156.98 (s, C-9), 160.20 (s, C-7), 165.05 (s, C-4a).

Resonances in NMR spectra of **6** and **7** had chemical shifts that were rather similar. The greatest differences in the chemical shifts in the ^{13}C NMR spectra were observed for C-5a–C-8 of the resorcinol ring and C-13, C-22, and C-23. The presence and positions of hydroxyls in the formed pyran (**6**) and furan (**7**) rings were confirmed by the ^{13}C NMR spectrum for a solution of their mixture in $CDCl_3$ with added D_2O. Strong-field shifts of the singlet at 64.94 ppm (Δδ = 0.12 ppm) and the triplet at 67.97 ppm (Δδ = 0.15 ppm) that were assigned to C-13 in **6** and C-23 in **7**, respectively, occurred upon exchange of the hydroxyl proton by deuterium because of the isotope effect.

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