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AMINO-DERIVATIVES OF USNINIC ACID

A. A. Tazetdinova, O. A. Luzina,* M. P. Polovinka, N. F. Salakhutdinov, and G. A. Tolstikov

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*Products from the reaction of usninic acid and 4-(3-aminopropyl)-2,6-di-*t*-butylphenol, 4-(2-aminoethyl)-2,6-di-*t*-butylphenol, antipyrine,* N,N*-diethylaminoethylamine,* p*-chloroaniline, and* p*-bromoaniline in addition to the quaternary ammonium salt (*E*)-2-(1-(6-acetyl-7,9-dihydroxy-8,9b-dimethyl-1,3-dioxo-1,9b-dihydrodibenzo[*b,d*]furan-2(3*H*)-ylidene)ethylamino)-*N,N*-diethyl-*N*-methylethaneammonium iodide were obtained.*

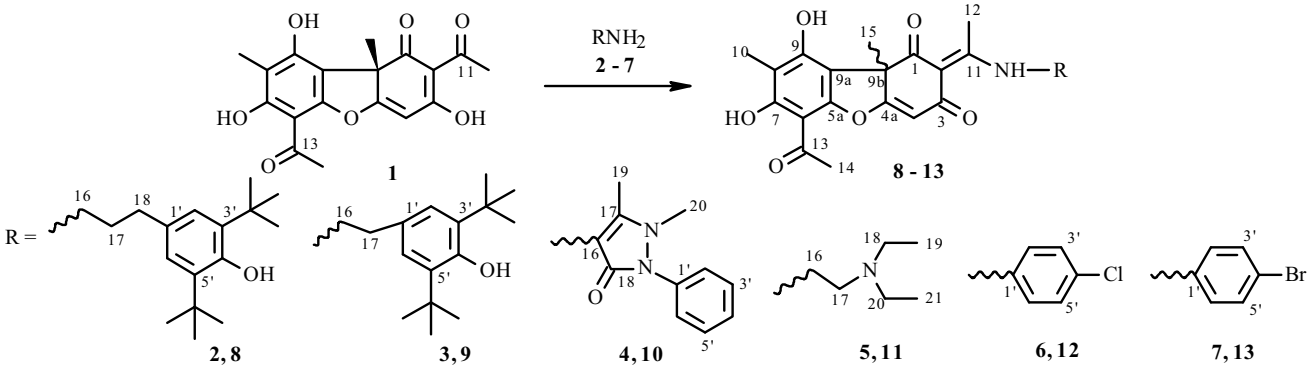
Key words: usninic acid, enamines, Schiff bases, quaternary ammonium salt.

Usninic acid (**1**) is a major secondary metabolite of several lichens and possesses antiviral, antibiotic, fungicidal, analgesic, antituberculosis, and other types of biological activity [1]. According to the literature [2], usninic acid can be used as a synergist of insecticides based on entomopathogenic microorganisms. Considering the biological activity and availability of usninic acid, it seemed advisable to expand the range of its synthetic transformations by including in the structure various pharmacophores that could lead to the production of new biologically active compounds.

It is known that introducing amine groups of various structure into organic compounds produces or increases the biological properties of the resulting compounds. Thus, it has been shown [3] that synthetic amino derivatives of **1** possess antitumor activity. Native amino derivatives of usninic acid that were isolated from the antarctic lichen *Stereocaulon alpinum* exhibited moderate antidiabetic activity [4].

It was observed previously that reaction of **1** with certain primary amines formed products from reaction of one or two carbonyls to form enamine derivatives [5]. Derivatives of usninic acid with hydrazines [6] and several amino acids [7] were produced.

Herein we present results from a study of the reactions of **1** with amines **2**–**7**, each of which contains a fragment with either its own biological activity or structural features allowing chemical modification of the products to continue.



Scheme 1

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, 630090, Novosibirsk, prosp. Akad. Lavrent′eva, 9, Russia, e-mail: luzina@nioch.nsc.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 672–675, November–December, 2009. Original article submitted June 2, 2009.

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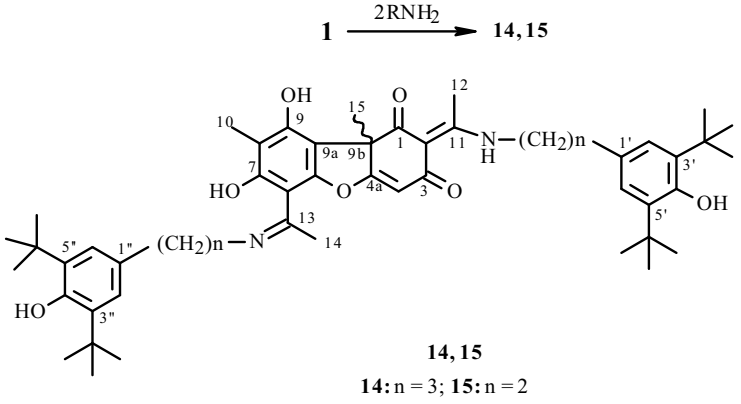
Amines **2** and **3** contained a sterically hindered phenol group that exhibits antioxidant properties [8]; amines **4** and **5**, fragments enhancing antibacterial activity [9]. They all contain tertiary N atoms predisposed to quaternization. Aromatic amines **6** and **7** have single halogen atoms in the aromatic ring. This can not only increase substantially the biological activity of the products [10] but also facilitate significantly the functionalization of the aromatic ring.

It was found that reaction of **1** with the aforementioned amines **2**–**7** taken in equimolar quantities produced enamine derivatives **8**–**13** (Scheme 1). The reactions were carried out in alcohol under reflux for 3 h. The products precipitated upon adding water to the cooled reaction mixture.



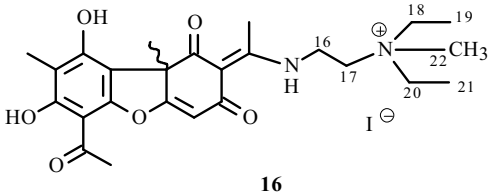
Scheme 2

Schiff bases **14** and **15** formed upon adding to the reaction three equivalents of **2** and **3** (Scheme 2). Amines **4**–**7** did not form similar compounds at the C^{13}=O carbonyl of usninic acid. Only enamines **10**–**13** were isolated from the reaction with an excess of **4**–**7** or after prolonged reflux (Scheme 1).

Compounds **14** and **15** appeared together with **8** and **9**, respectively, in the reaction mixture. Compounds **14** and **15** were isolated by column chromatography in 22 and 20% yields, respectively. The structures of **8**–**15** were established by NMR and IR spectroscopy and mass spectrometry. The configuration of the C^2–C^{11} double bond was assigned based on the literature [5].

It is known that a quaternized N atom both found in native alkaloids and produced by synthetic transformations of organic compounds imparts to a molecule several important and interesting biological activities. Thus, compounds containing this fragment exhibit myorelaxant [11], antitumor [12], spasmolytic [13], and several other activities.

Reaction of **11** with CH_3I produced quaternary ammonium salt **16** in 64% yield. The reaction occurred at room temperature in CH_2Cl_2 over 72 h. Amine **10** did not react with CH_3I even at elevated temperature.



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EXPERIMENTAL

PMR and ^{13}C NMR spectra in $CDCl_3$ and DMSO-d_6 were recorded on Bruker AM-400 (operating frequencies 400.13 and 100.61 MHz) and AV-300 (300.13 and 75.47 MHz, respectively) instruments. Solvent resonances (δ_H 7.24 ppm and δ_C 76.90 ppm for $CHCl_3$; δ_H 2.50 and δ_C 39.50 ppm for DMSO-d_6) were used as standards. IR spectra were recorded on a Vector 22 spectrometer (KBr); mass spectra (ionizing electron energy 70 eV), in a DFS high-resolution mass spectrometer. Usninic acid (**1**) was isolated from a mixture of lichens of the genus *Usnea* by the literature method [14]. The conversion of usninic acid was monitored using PMR spectra. Silica gel (Merck, 70–230 mesh) was used for column chromatography.

Amines 4-(3-aminopropyl)-2,6-di-*t*-butylphenol (**2**), 4-(3-aminoethyl)-2,6-di-*t*-butylphenol (**3**), 4-aminoantipyrine (**4**), *N*,*N*-diethylaminoethylamine (**5**), *p*-chloroaniline (**6**), and *p*-bromoaniline (**7**) were commercially available.

General Method for Reacting Usninic Acid (1) with an Equimolar Amount of Amines 2–7. Compound **1** (1 mmol) was treated with amine **2**–**7** (1.1 mmol), dissolved in ethanol (12 mL), refluxed on a water bath for 3 h, cooled, and treated with distilled water (10 mL). A white precipitate formed. The precipitate from the reaction with **2** and **6** was finely dispersed. Therefore, the reaction mixture was extracted with $CHCl_3$ (3×). The extracts were dried over anhydrous $MgSO_4$. The solvent was distilled in vacuo in a rotary evaporator. The precipitate from reaction with **3**, **4**, **5**, and **7** was filtered off, washed with water, and dried in air. This afforded **8**-**13**.

(*E*)-6-Acetyl-2-(1-(3,5-di-*t*-butyl-4-hydroxyphenpropylamino)ethylidene)-7,9-dihydroxy-8,9b-dimethyldibenzo[*b*,*d*]furan-1,3(2*H*,9b*H*)-dione (8). Yield 91%, mp 83–87°C. PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.43 (18H, s, H-Bu^t), 1.69 (3H, s, H-15), 2.03 (2H, m, H-17), 2.09 (3H, s, H-10), 2.58 (3H, s, H-12), 2.67 (3H, s, H-14), 2.68 (2H, t, J = 7.5, H-18), 3.46 (2H, dt, J = 7.2, 6.4, H-16), 5.10 (1H, s, OH-4′), 5.78 (1H, s, H-4), 6.96 (2H, s, H-2′, H-6′), 12.04 (s, OH-9), 13.36 and 13.53 (s and br.s, NH and OH-7).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.3 (C-10), 18.1 (C-12), 30.2 (6C-Bu^t), 30.5 (C-17), 31.0 (C-14), 31.8 (C-15), 32.5 and 34.2 (C-16, C-18), 43.1 (2C-Bu^t), 55.5 (C-9b), 101.3 (C-6), 102.4 (C-4), 102.4 (C-2), 105.9 (C-9a), 107.8 (C-8), 124.6 (C-2′ and C-6′), 130.4 (C-1′), 136.2 (C-5′ and C-3′), 152.2 (C-4′), 155.8 (C-5a), 158.3 (C-9), 163.4 (C-7), 173.9 (C-11), 174.7 (C-4a), 189.9 (C-3), 198.1 (C-1), 200.5 (C-13).

IR spectrum (ν, cm^{-1}): 3635, 3433, 2955, 1699, 1557, 1469, 1435, 1371, 1289, 1189, 1139, 1057. Found: *m*/*z* 589.3027 $[M]^+$ $C_{35}H_{43}O_7N$. Calcd: M = 589.3034.

(*E*)-6-Acetyl-2-(1-(3,5-di-*t*-butyl-4-hydroxyphenethylamino)ethylidene)-7,9-dihydroxy-8,9b-dimethyldibenzo[*b*,*d*]furan-1,3(2*H*,9b*H*)-dione (9). Yield 93%, mp 103–105°C. PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.42 (18H, s, H-Bu^t), 1.68 (3H, s, H-15), 2.08 (3H, s, H-10), 2.46 (3H, s, H-12), 2.66 (3H, s, H-14), 2.91 (2H, t, J = 7.1, H-17), 3.68 (2H, dt, J = 6.1, 7.1, H-16), 5.17 (1H, s, OH-4′), 5.78 (1H, s, H-4), 6.99 (2H, s, H-2′ and H-6′), 12.08 (1H, s, OH-9), 13.36 and 13.59 (1H and 1H, s and br.s, NH and OH-7).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.3 (C-10), 18.0 (C-12), 30.1 (6C-Bu^t), 31.1 (C-14), 31.8 (C-15), 34.2 (C-17), 35.4 (C-16), 45.9 (2C-Bu^t), 55.7 (C-9b), 101.5 (C-6), 102.4 (C-4), 102.9 (C-2), 106.0 (C-9a), 107.8 (C-8), 125.2 (C-2′ and C-6′), 127.5 (C-1′), 136.3 (C-5′ and C-3′), 155.7 (C-4′), 152.8 (C-5a), 158.2 (C-9), 163.3 (C-7), 174.0 (C-11), 174.7 (C-4a), 189.9 (C-3), 198.3 (C-1), 200.5 (C-13).

IR spectrum (ν, cm^{-1}): 3633, 2956, 1700, 1626, 1557, 1468, 1343, 1290, 1189, 1119, 1072. Found: *m*/*z* 575.2895 $[M]^+$ $C_{34}H_{41}O_7N$. Calcd: M = 575.2883.

(*E*)-6-Acetyl-2-(1-(1,5-dimethyl-3-oxo-2-phenethyl-2,3-dihydro-1*H*-pyrazol-4-ylamino)ethylidene)-7,9-dihydroxy-8,9b-dimethyldibenzo[*b*,*d*]furan-1,3(2*H*,9b*H*)-dione (10). Yield 72%, mp 195°C. PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.77 (3H, s, H-15), 2.11 (3H, s, H-10), 2.33 (3H, s, H-19), 2.72 (6H, s, H-12 and H-14), 3.24 (3H, s, H-20), 5.88 (1H, s, H-4), 7.42 and 7.52 (3H, m and 2H, m, H-arom), 11.83 (1H, s, OH-9), 13.38 (1H, s, OH-7), 14.31 (1H, br.s, NH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.0 (C-10), 10.4 (C-19), 20.0 (C-12), 30.8 (C-14), 30.4 (C-15), 35.2 (C-20), 57.1 (C-9b), 100.9 (C-6), 101.8 (C-4), 102.8 (C-2), 104.6 (C-16), 107.4 (C-9a), 107.7 (C-8), 124.3 (C-5′ and C-3′), 127.3 (C-4′), 129.1 (C-6′ and C-2′), 133.6 (C-7′), 149.0 (C-17), 155.3 (C-5a), 157.8 (C-9), 159.7 (C-18), 163.1 (C-7), 174.3 (C-11), 176.3 (C-4a), 190.6 (C-3), 198.2 (C-1), 200.2 (C-13).

IR spectrum (ν, cm^{-1}): 3436, 2924, 1706, 1545, 1362, 1272, 1133, 1069, 891. Found: *m*/*z* 529.1845 $[M]^+$ $C_{29}H_{27}O_7N_3$. Calcd: M = 529.1844.

(*E*)-6-Acetyl-2-(1-(2-(diethylamino)ethylidene)-7,9-dihydroxy-8,9b-dimethyldibenzo[*b*,*d*]furan-1,3(2*H*,9b*H*)-dione (11). Yield 88%, mp 68°C. PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.16 (6H, t, J = 7.1, H-19 and H-21), 1.73 (3H, s, H-15), 2.13 (3H, s, H-10), 2.67 (6H, s, H-12 and H-14), 2.69 (4H, q, J = 7.1, H-18 and H-20), 2.86 (2H, t, J = 6.0, H-17), 3.66 (2H, dt, J = 5.7, 6.0, H-16), 5.82 (1H, s, H-4), 12.01 (1H, br.s, OH-9), 13.36 and 13.39 (1H, s and 1H, s, NH, OH-7).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.3 (C-10), 11.5 (C-19 and C-21), 18.7 (C-12), 31.8 (C-14), 31.9 (C-15), 42.3 (C-16), 46.7 (C-18 and C-20), 50.8 (C-17), 59.0 (C-9b), 102.5 (C-4), 101.2 (C-6), 105.0 (C-2), 105.1 (C-9a), 107.7 (C-8), 155.8 (C-5a), 158.2 (C-9), 163.7 (C-7), 173.7 (C-11), 174.3 (C-4a), 191.5 (C-3), 197.9 (C-1), 200.6 (C-13).

IR spectrum (ν, cm^{-1}): 3387, 2926, 1701, 1627, 1555, 1370, 1287, 1061, 841. Found: *m*/*z* 442.2110 $[M]^+$ $C_{24}H_{30}O_6N_2$. Calcd: M = 442.2098.

(*E*)-6-Acetyl-2-(1-(4-chlorophenylamino)ethylidene)-7,9-dihydroxy-8,9b-dimethyldibenzo[*b*,*d*]furan-1,3(2*H*,9b*H*)-dione (12). Yield 87%, mp 110°C. PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.71 (3H, s, H-15), 2.05 (3H, s,

H-10), 2.54 (3H, s, H-12), 2.64 (3H, s, H-14), 5.83 (1H, s, H-4), 7.14 (2H, d, J = 8.5, H-2′ and H-6′), 7.43 (2H, d, J = 8.5, H-3′ and H-5′), 11.68 (1H, s, OH-9), 13.31 (1H, s, OH-7), 15.06 (1H, s, NH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.3 (C-10), 20.4 (C-12), 31.1 (C-14), 31.7 (C-15), 57.5 (C-9b), 101.2 (C-6), 102.0 (C-4), 102.7 (C-9a), 104.7 (C-2), 108.1 (C-8), 126.9 (C-2′ and C-6′), 129.7 (C-3′ and C-5′), 133.9 (C-4′), 134.5 (C-1′), 155.6 (C-5a), 157.9 (C-9), 163.4 (C-7), 173.7 (C-11), 174.7 (C-4a), 190.9 (C-3), 198.7 (C-1), 200.4 (C-13).

IR spectrum (ν, cm^{-1}): 3455, 2927, 1698, 1630, 1546, 1462, 1367, 1280, 1205, 1136, 1065, 844. Found: *m*/*z* 453.0966 $[M]^+$ $C_{24}H_{20}O_6NCl$. Calcd: M = 453.0971.

(*E*)-6-Acetyl-2-(1-(4-bromophenylamino)ethylidene)-7,9-dihydroxy-8,9b-dimethyldibenzo[*b*,*d*]furan-1,3(2*H*,9b*H*)-dione (13). Yield 87%, mp 170°C. PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.76 (3H, s, H-15), 2.11 (3H, s, H-10), 2.58 (3H, s, H-12), 2.69 (3H, s, H-14), 5.89 (1H, s, H-4), 7.11 (2H, d, J = 8.5, H-2′, H-6′), 7.61 (2H, d, J = 8.5, H-3′, H-5′), 11.74 (1H, s, OH-9), 13.38 (1H, s, OH-7), 15.10 (1H, s, NH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.3 (C-10), 20.4 (C-12), 31.1 (C-14), 31.7 (C-15), 57.5 (C-9b), 101.2 (C-6), 102.0 (C-4), 102.7 (C-9a), 104.7 (C-2), 108.1 (C-8), 126.9 (C-2′ and C-6′), 129.7 (C-3′ and C-5′), 133.9 (C-4′), 134.5 (C-1′), 155.6 (C-5a), 157.9 (C-9), 163.4 (C-7), 173.7 (C-11), 174.7 (C-4a), 190.9 (C-3), 198.7 (C-1), 200.4 (C-13).

IR spectrum (ν, cm^{-1}): 2925, 2725, 1698, 1634, 1543, 1462, 1365, 1276, 1206, 1137, 1065, 843. Found: *m*/*z* 497.04342 $[M]^+$ $C_{24}H_{20}O_6NBr$. Calcd: M = 497.04590.

General Method for Reacting Usninic Acid with a Three-fold Excess of Amines 2 and 3. Compound **1** (1 mmol) was treated with amines **2** and **3** (3 mmol), dissolved in alcohol (12 mL), refluxed on a water bath for 3 h, cooled, and treated with distilled water (10 mL). The white precipitate that formed was filtered off, washed with water, and dried in air. The reaction mixture was separated using column chromatography over silica gel with elution by $CHCl_3$ to afford **14** and **15**.

(*E*)-2-(1-3,5-Di-*t*-butyl-4-hydroxyphenylpropylamino)ethylidene)-6-((*E*)-1-(3,5-di-*t*-butyl-4-hydroxyphenpropylamino)-7,9-dihydroxy-8,9b-dimethyldibenzo[*b*,*d*]furan-1,3(2*H*,9b*H*)-dione (14). Yield 22%, mp 92–96°C. PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.42 (36H, s, H-Bu^t), 1.74 (3H, s, H-15), 1.83 (2H, m, H-17), 2.09 (2H, m, H-20), 2.10 (3H, s, H-10), 2.50 (2H, m, H-18 and 2H, m, H-21), 2.64 (3H, s, H-12), 2.67 (3H, s, H-14), 2.91 (2H, m, H-19), 3.29 (2H, m, H-16), 5.04 and 5.07 (1H, s and 1H, s, OH-4′ and OH-4″), 5.94 (1H, s, H-4), 6.92–6.96 (4H, m, H-arom), 11.22 (1H, br.s, OH-9), 13.32 (1H, br.s, OH-7), 17.97 (1H, br.s, NH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.9 (C-10), 17.5 (C-14), 18.0 (C-12), 30.1 (12C-Bu^t), 30.5, 31.3, 32.5, 32.9 (C-17, C-18, C-20, C-21), 31.9 (C-15), 34.1 (4C-Bu^t), 42.9 (C-16), 45.3 (C-19), 57.2 (C-9b), 98.9 (C-6), 101.3 (C-4), 101.9 (C-2), 106.0 (C-9a), 108.6 (C-8), 124.5 and 124.6 (C-2′, C-6′, C-2′, C-6′), 130.4 and 131.3 (C-1′ and C-1′), 135.7 and 135.9 (C-5′, C-3′ and C-5′, C-3′), 151.7 and 152.0 (C-4′ and C-4′), 155.2 (C-5a), 158.3 (C-9), 170.4 (C-7), 170.5 (C-13), 174.4 and 174.6 (C-4a and C-11), 189.9 (C-3), 198.6 (C-1).

IR spectrum (ν, cm^{-1}): 3639, 3431, 2955, 1697, 1623, 1558, 1466, 1436, 1369, 1235, 1189. Found: *m*/*z* 834.5161 $[M]^+$ $C_{52}H_{70}O_7N_2$. Calcd: M = 834.5178.

(*E*)-2-(1-3,5-Di-*t*-butyl-4-hydroxyphenethylamino)ethylidene)-6-((*E*)-1-(3,5-di-*t*-butyl-4-hydroxyphenethylamino)-7,9-dihydroxy-8,9b-dimethyldibenzo[*b*,*d*]furan-1,3(2*H*,9b*H*)-dione (15). Yield 20%, mp 85°C. PMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 1.40 and 1.42 (each 18H, s, H-Bu^t), 1.65 (3H, s, H-15), 2.12 (3H, s, H-10), 2.27 (3H, s, H-14), 2.46 (3H, s, H-12), 2.91 (2H, t, J = 7.2, H-19), 2.96 (2H, t, J = 7.0, H-17), 3.67 (2H, dt, J = 6.3, 7.0, H-16), 3.73 (2H, t, J = 7.2, H-18), 5.11 and 5.17 (1H, s, OH-4′ and OH-4′), 5.68 (1H, s, H-4), 6.99–7.01 (4H, m, H-arom), 11.43 (1H, br.s, OH-9), 13.56 (1H, br.s, OH-7), 17.97 (1H, br.s, NH).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.9 (C-10), 17.3 (C-14), 17.9 (C-12), 30.1 (12C-Bu^t), 32.0 (C-15), 34.1 (4C-Bu^t), 35.5 (C-17), 36.4 (C-19), 45.9 (C-16), 48.4 (C-18), 57.2 (C-9b), 99.0 (C-6), 101.3 (C-4), 102.0 (C-2), 106.1 (C-9a), 108.6 (C-8), 125.2 and 125.5 (C-2′, C-6′, C-2′, C-6′), 127.7 and 129.2 (C-1′ and C-1′), 135.9 and 136.3 (C-5′, C-3′ and C-5′, C-3′), 152.4 and 152.7 (C-4′ and C-4′), 155.1 (C-5a), 158.3 (C-9), 170.2 (C-7), 170.6 (C-13), 174.4 and 174.6 (C-4a and C-11), 189.9 (C-3), 198.6 (C-1).

IR spectrum (ν, cm^{-1}): 3639, 3433, 2957, 1697, 1623, 1558, 1466, 1436, 1370, 1235, 1189, 1076. Found: *m*/*z* 806.4856 $[M]^+$ $C_{50}H_{66}O_7N_2$. Calcd: M = 806.4865.

Reaction of 11 with Methyliodide. Amine **11** (1.1 mmol) in CH_2Cl_2 (10 mL) was treated with CH_3I (3 mmol) and stored for 3 d. The yellowish precipitate was filtered off, washed with $CHCl_3$, and dried in air to afford **16**.

(*E*)-2-(1-(6-Acetyl-7,9-dihydroxy-8,9b-dimethyl-1,3-dioxo-1,9b-dihydrodibenzo[*b*,*d*]furan-2(3*H*)-ylidene)ethylamino)-*N*,*N*-diethyl-*N*-methylethaneammonium Iodide (16). Yield 64%, mp 125°C. PMR spectrum (DMSO-d_6, δ, ppm, J/Hz): 1.22 (6H, t, J = 7.1, 3H-19 and 3H-21), 1.60 (3H, s, H-15), 1.90 (3H, s, H-10), 2.57 (3H, s, H-12), 2.64 (3H, s, H-14), 3.05 (3H, s, H-22), 3.38 (4H, q, J = 7.1, H-18 and H-20), 3.59 (2H, t, J = 6.0, H-17), 4.04 (2H, dt, J = 5.7, 6.0, H-16), 5.83 (1H, s, H-4), 12.06 (1H, s, OH-9), 12.97 and 13.32 (1H, s, NH and 1H, s, OH-7).

^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.6 (C-10), 7.7 (C-19 and C-21), 18.6 (C-12), 31.2 and 31.8 (C-14 and C-15), 37.2 (C-16), 47.1 (C-22), 56.4, 56.6, 57.5 (C-17, C-18, C-20), 59.0 (C-9b), 100.1 (C-6), 102.4 (C-4), 102.4 (C-2), 105.4 (C-9a), 106.6 (C-8), 155.8 (C-5a), 157.6 (C-9), 162.6 (C-7), 173.3 (C-11), 176.2 (C-4a), 189.0 (C-3), 197.7 (C-1), 201.1 (C-13).

IR spectrum (ν, cm^{-1}): 3440, 2976, 1700, 1629, 1556, 1369, 1288, 1060, 846.

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