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New Functionalization Opportunities for *peri*-Hydroxynaphthoyl and *peri*-Fused Heterocyclic Compounds

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Abstract—A capability was studied of hydrogenated α-pyrone heterocycle in 7-methoxy-4-(4-methoxy-phenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-2-one to undergo aminolysis under the treatment with hydrazine hydrate, primary and secondary aliphatic and aromatic amines. A new approach was developed to the preparation of *peri*-hydroxyketone of naphthalene series containing a specific functional substituent in the *ortho*-position with respect to hydroxy group. The effect was revealed of an acetyl group in the position *9* of 7-methoxy-4-(4-methoxyphenyl)-3,4-dihydro-2H-benzo[h]chromen-2-one on the reaction of this compound with aliphatic amines and hydrazine hydrate. 9-Methoxy-1-(4-methoxyphenyl)-6-methyl-3*H*-benzo[*de*]pyrido[3,2,1-if]cinnolin-3-one [9-methyl-6-methoxy-3-(4-methoxyphenyl)-10,10a-diazapyren-1-one] was obtained, a new bis-*peri*-fused heteroaromatic system.

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We formerly [1] developed a concept of building up a *peri*-hydroxycarbonyl moiety on the naphthalene framework based on an acid-catalyzed acylation (formylation) of 5-methoxy-1-naphthol esters. The cleavage of the ester group leads to the formation of the target *peri*-hydroxynaphthoyl compounds, versatile precursors for designing various *peri*-fused heterocyclic systems with a five-, six-, or seven-membered heteroring [2].

One of the ways to significantly extend the range of the research is the utilization of the potential of the functional substituents in the *ortho*-position to the hydroxy group of 5-methoxy-1-naphthol (**I**). The introduction of such substituents should affect the aromatic system through steric and electronic factors, and also influence the subsequent heterocyclization reactions. This study is a logical continuation of a research cycle on designing polynuclear heterocyclic compounds on a "matrix" of 1,5-naphthalenediol [3].

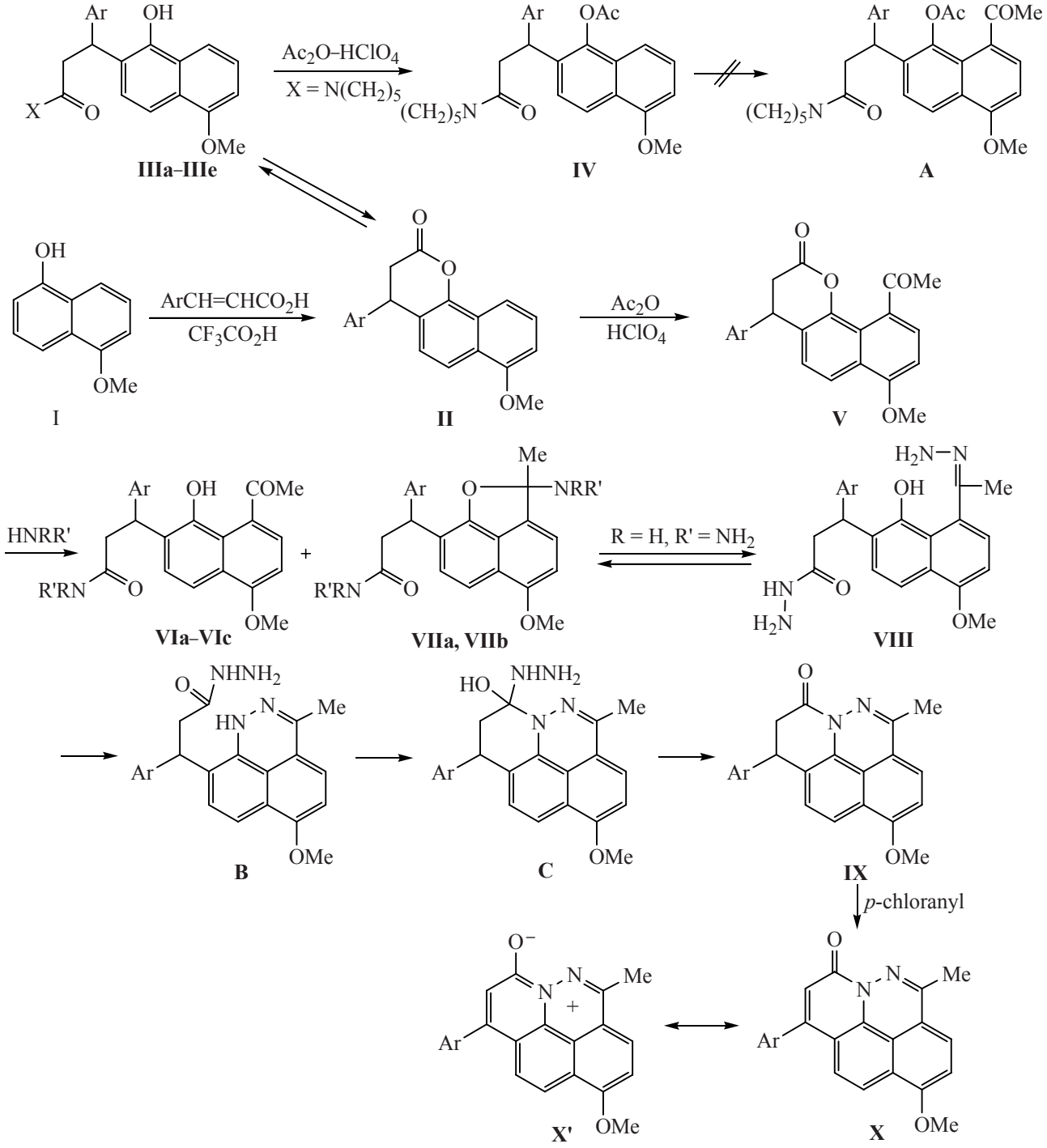
We chose in this study for initial compound easily available 4-(4-methoxyphenyl)-7-methoxy-3,4-dihydro-2*H*-benzo[*c*]chromen-2-one (**II**) (hereinafter dihydrobenzocoumarin) that we had previously described [3]. In this compound the part of an ester function is played by the dihydro-2-pyrone ring (Scheme 1).

The specific feature of this approach consists in the behavior at the cleavage of the ester fragment with nucleophilic reagents (alkali, metal alkylates, amines etc.): the expected derivatives of the corresponding carboxylic acid **III** do not eliminate but retain the specific substituent in the *ortho*-position to the hydroxy group. This fact essentially and peculiarly extends the functionalization opportunities of the *peri*-hydroxynaphthoyl compounds and consequently of preparation of new *peri*-fused heterocyles based thereon.

The experimental test of these suggestions showed that the corresponding acid and its methyl ester (**III**, X = OH, OMe) evidently formed at treating dihydrobenzocoumarin **II** with an alkali or sodium methylate respectively. However we failed to isolate these compounds for at the neutralization of the alkaline reagents with a weak acid like acetic acid the compounds underwent heterocyclization to give the initial dihydrobenzocoumarin (**II**).

The aminolysis or hydrazinolysis of dihydrobenzocoumarin **II** led to the opening of the heteroring and to the formation of fairly stable under common conditions naphtholes **IIIa–IIIe** containing in the *ortho*-position to the hydroxyl group a terminal amide or hydrazide function; therewith the ease of the process depended on the

Scheme 1.



III, X = NMe_2 (**a**), $NHCH_2CHMe_2$ (**b**), $N(CH_2)_5$ (**c**), NHC_6H_4Me-*p* (**d**), $NHNH_2$ (**e**); **VI**, NR'R = NMe_2 (**a**), $N(CH_2)_5$ (**b**), $N(CH_2)_4O$ (**c**); **VII**, NR'R = $N(CH_2)_5$ (**a**), $N(CH_2)_4O$ (**b**); Ar = *p*-$MeOC_6H_4$.

nucleophilicity of the amine and decreased from the primary and secondary aliphatic to primary aromatic ones. Amides **III** still underwent heterocyclization into dihydrobenzocoumarin **II** at boiling in acetic acid.

In the IR spectra of compounds **IIIa–IIIe** the band of the stretching vibrations of the carbonyl group is present in the range 1610–1635 cm^{-1}. The low value of this band is characteristic of amide carbonyl [4]. In the ^1H NMR

spectra of compounds **IIIa–IIIe** the proton signals of the fragment $CHCH_2$ should be noticed for due to the magnetic nonequivalence of the methylene group protons they appeared as multiplets with an individual shape for each definite compound.

We obtained a mass spectrum of one of the amides (compound **IIIb**) (Scheme 2), which demonstrated that the most stable ion radical Φ_1 (I_{rel} 100%) was a product of isobutylamine elimination. This result shows that under the conditions of the mass spectrum registration the heterocyclization **III** → **II** same as in the chemical experiment is the most favored process.

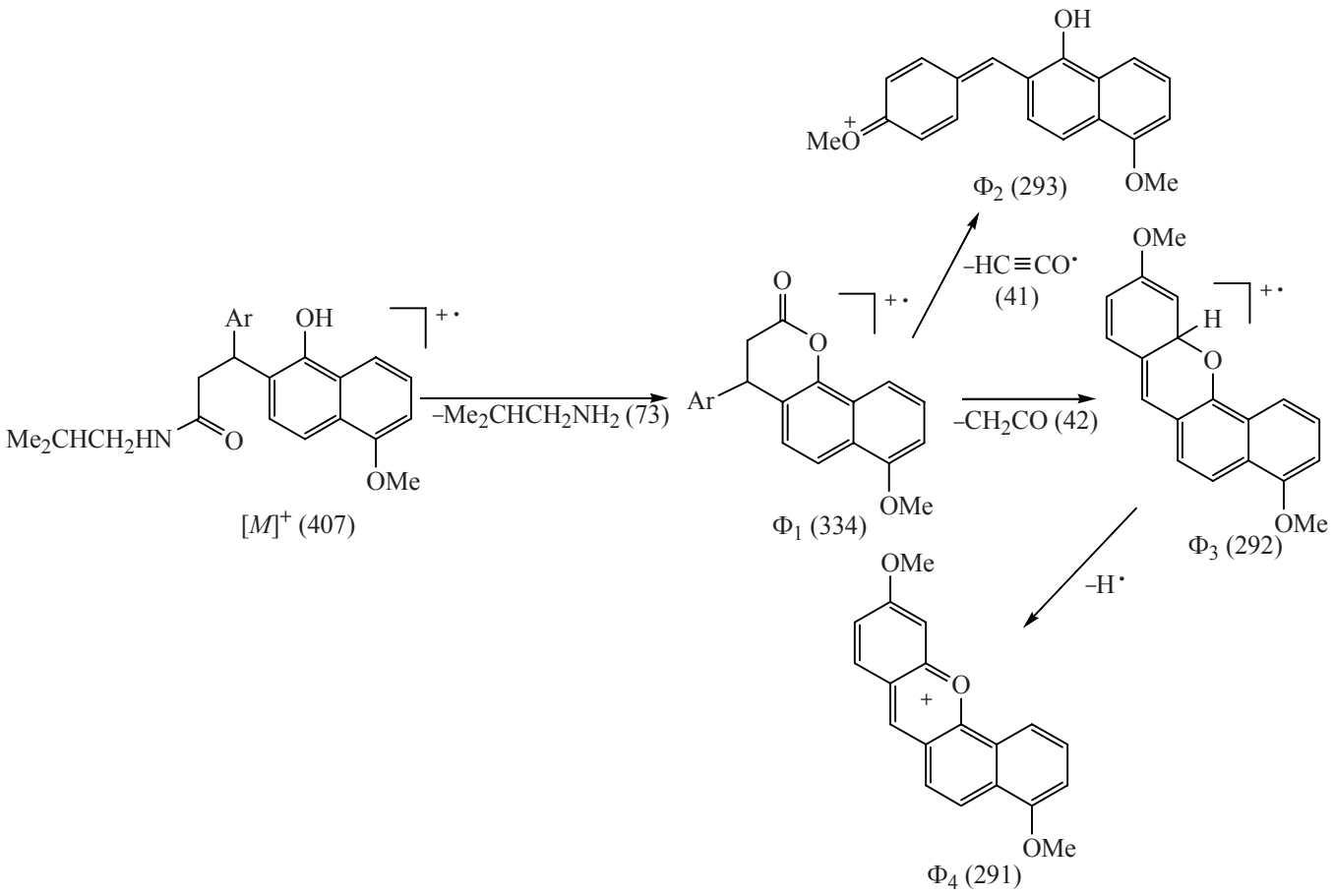
As follows from Scheme 2 the ion radical Φ_1 decomposed presumably by two routes: with the formation of a fragment ion Φ_2 owing to elimination of a free-radical species $HC{\equiv}CO^{\cdot}$, or of ions Φ_3 and Φ_4 by successive ejections of ketene CH_2CO, and then atomic hydrogen.

A priori two alternative ways exist of obtaining *peri*-hydroxynaphthoyl compounds with the mentioned functional substituent. One of these ways consists in the preliminary O- and C-acylation of amides **IIIa–IIIe** followed by the cleavage of the acyloxy group, and the other requires first to introduce the carbonyl function into the *peri*-position to the heterocyclic oxygen of dihydrobenzocoumarin (**II**) with subsequent aminolysis of the formed carbonyl derivatives.

The possibility to carry out the first opportunity was tested by the reaction of piperidine amide **IIIc** with acetic anhydride under the catalysis by perchloric acid. It turned out that in this case instead of expected *peri*-acetoxyketone **A** (Scheme 1) the reaction stopped at the stage of O-acylation giving acetyloxy derivative **IV** evidently due to the effect of the acetyloxy group "supported" by a bulky *ortho*-substituent hampering the approach of the acylating agent to the adjacent *peri*-position. The formation of compound **IV** with a structure of acetyloxyamide is confirmed by the IR spectrum containing a band of an ester group (1753 cm[1]) and lacking a band of ketone carbonyl in the region ~1680–1690 cm^{-1}.

The second way proved to be efficient: in reaction of dihydrobenzocoumarin **II** with acetic anhydride in the presence of catalytic quantity of perchloric acid we

Scheme 2.



obtained *peri*-acyloxyketone **V** whose aminolysis yielded the desired functionally-substituted *peri*-hydroxyketones **VIa–VIc** forming in come cases (in reaction with piperidine and morpholine) in a mixture with 2-amino derivatives of naphtho[1,8-*bc*]furan **VIIb** and **VIIc**. The latter result from the replacement of a hydroxyl group by an amine function in the reaction with amines of 2-hydroxynaphtho[1,8-*bc*]furans, cyclic tautomers of the corresponding *peri*-hydroxyketones **VI**.

In the ^{1}H NMR spectra of *peri*-hydroxyketones **VI** compared to the spectrum of *peri*-acetyldihydrobenzocoumarin (**V**) appeared a singlet from the proton of the hydroxy group in the region 10.7 ppm that disappeared at treating with deuterium oxide, and also the proton signals from amide substituent. IR spectra of *peri*-hydroxyketones **VI** are characterized by the appearance of the absorption band of the amide carbonyl, and also by a blue shift of the absorption band of the ketone carbonyl group caused by the intramolecular hydrogen bond between the *peri*-located carbonyl and hydroxy groups.

The presence of a chiral center in the position *2* of the furan ring of naphtho[1,8-*bc*]furans **VII** is the most probable reason of the splitting in two in the ^{1}H NMR spectrum of the methyl group signal and that of morpholine residue bonded to the asymmetrical carbon atom of the heteroring and also of proton signal of a methoxy group in the position *5* of naphtho[1,8-*bc*]furan fragment conjugated to this center.

The reaction of *peri*-acetyldihydrocoumarin **V** with hydrazine hydrate proceeded peculiarly. Based on elemental analusis, IR, ^{1}H NMR, and mass spectra we regard the compound obtained as N-acylated 1*H*-1,2-diazaphenalene* (dihydrodiazapyrenone **IX**).

The most probable mechanism of its formation might involve consecutive processes of prototropic opening of hemiaminal **VII** → **VIII**, heterocyclization of *peri*-hydroxyhydrazone into diazaphenalene **VIII** → **B****, closure of a six-membered heteroring **B** → **C**, and elimination of a hydrazine molecule **C** > **IX*****.

The probability of the succession of the stages of this transformation presented on Scheme 1 is confirmed by the results obtained in reactions of dihydrobenzocoumarin **II** with amines and hydrazine hydrate leading to the opening of the hydrogenated heteroring, and also by the previously found formation of hydrazones in the reaction of *peri*-hydroxyketones with hydrazine hydrate [7].

In the ^{1}H NMR spectrum of dihydrodiazapyrenone **IX** the proton signals are present in the same number and the same multiplicity as in the spectrum of its precursor *peri*-acetyldihydrobenzocoumarin **V** but their position in the NMR scale is another; together with the data of mass spectrometry and elemental analysis this sufficiently reliably confirms the assumed structure.

In the mass spectrum of this compound the molecular ion is the most stable (I_{rel} 100%); it ejects a methyl Me· forming a cation of probable structure Φ_1 (Scheme 3). The latter decomposes along two concurrent directions: with ejection of a CO molecule to give a fragment ion Φ_2, or by elimination of ketene CH_2CO to give cation Φ_3. Apparently, the ketene elimination is characteristic of the mass spectra of the whole series of compounds synthesized when they contain a fragment CH_2CO (Schemes 2 and 3).

Dihydrodiazapyrenone **IX** on heating with *p*-chloranil in *o*-dichlorobenzene suffered dehydrogenation and converted into a new, polynuclear heteroaromatic system of diazapyrenone **X**.

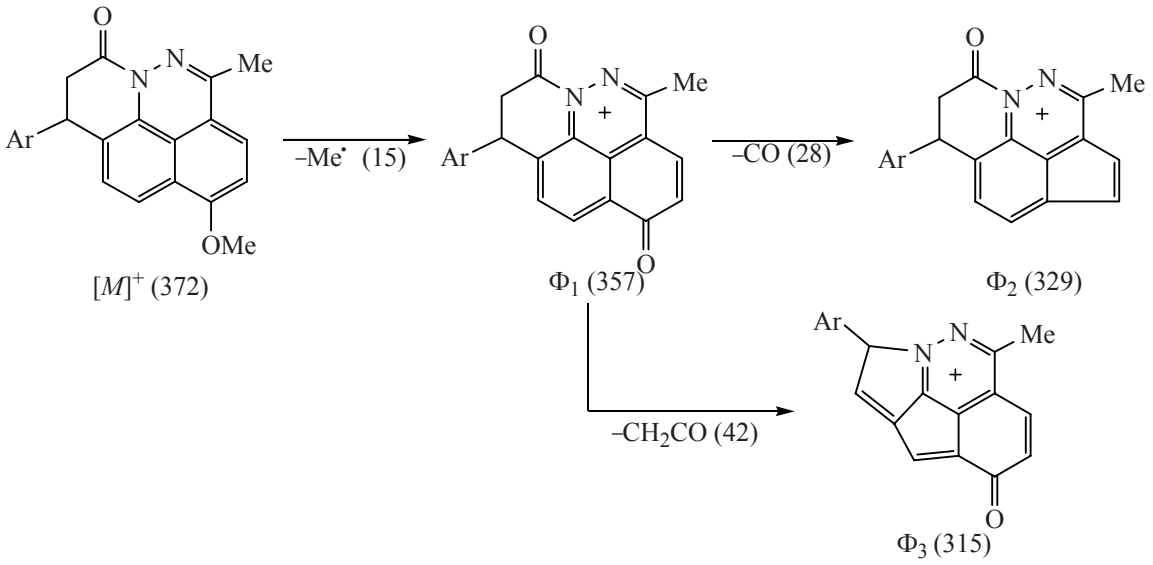
Interesting changes occur in the spectral characteristics due to the dehydrogenation of the saturated carbon-carbon bond during the formation of compound **X**. The involvement of the carbonyl group into overall π-electron ensemble as a result of a multiple bond formation led to the downfield shift ~0.5 ppm of the aromatic protons signals in the ^{1}H NMR spectrum of compound **X** as compared to the spectrum of compound **IX**. The downfield shift suffered also the protons of two methoxy and one methyl groups; therewith the latter signal sifted by 0.4 ppm. These fact may be attributed to the gain in the aromaticity of compound **X** (compared to compound **IX**) owing to a considerable contribution of a betaine structure **X'** (Scheme 1) containing in its structure two types of aromatic fragments: a 14-π-electron peripheral circuit, and a p-decet of the naphthalene or benzodiazine skeleton. Evidently, the "π-electron circuits" induced in these fragments by the external magnetic field in the probe of the NMR spectrometer are of the same direction and are mutually amplified forming a combined aromatic 16-π-electron ensemble involving p-electrons of seven peripheral and one internal double bonds. Analogous

* The ready occurrence of such heterocyclizations was noted in [7].

** Of 1*H*-1,2-diazaphenalenes, see [5], of diazapyrenes, see. [6].

*** This mechanism is also supported by the fact that hydrazide **III** (X = NH_2NH) on heating in acetic acid closed again into dihydrobenzocoumarin (**II**).

Scheme 3.



effects in the ^{1}H NMR spectra we observed at the conversion of the so-called "aceperidazines" to "aceperidazylenes". The latter formed by hydrogen molecule elimination from the bimethylene bridge of "aceperidazines" [8].

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 71IR from mulls in mineral oil. ^{1}H NMR spectra were registered on spectrometers Bruker Avance DPX-250 and Varian Unity-300 from solutions in $CDCl_3$. Mass spectra were measured on a Kratos instrument equipped with a direct admission of the sample into ion source, ionizing electrons energy 70 eV, controlling voltage 1.75 kV.

7-Methoxy-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-2-one (II) [3]. IR spectrum, ν, cm^{-1}: 1767 (OC=O), 1595. ^{1}H NMR spectrum, δ, ppm: 3.10 octet (2H, ArCHCH_2, ^1J 6.55, ^2J 6.17, ^3J 6.56, ^4J 6.55 Hz), 3.75 s (3H, OCH_3), 3.96 s (3H, OCH_3), 4.40 t (1H, ArCHCH$_2$, ^1J 6.56, ^2J 6.56 Hz), 6.78–6.89 m (3H, H_{Ar}, H^8), 7.02–7.09 m (3H, H_{Ar}, H^{10}), 7.47 t (1H, H^9, $^1J_{9,8}$ 8.10, $^2J_{9,10}$ 8.10 Hz), 7.86 d (1H, H^5, $J_{5,6}$ 8.49 Hz), 7.96 d (1H, H^6, $J_{6,5}$ 8.49 Hz).

3-(1-Hydroxy-5-methoxy-2-naphthyl)-3-(4-methoxyphenyl)-1-*N*,*N*-dimethylpropanamide (IIIa). To a cooled solution of 0.6 g (1.8 mmol) of dihydrobenzocoumarin **II** in ethanol was added 0.24 ml of dimethylamine. The mixture was kept at room temperature for 20 min, then poured into water, the precipitate was filtered off and recrystallized from ethanol. Yield 0.54 g (79%), colorless substance, mp 170–171°C. IR spectrum, ν, cm^{-1}: 1620 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.90 s (3H, NCH_3), 3.00 s (3H, NCH_3), 3.17 t (2H, H$^\alpha$CH$^\beta$, ^1J 2.69, ^2J 5.39 Hz), 3.75 s (3H, OCH_3), 3.90 s (3H, OCH_3), 5.12 d.d (1H, $CHCH_2$, ^1J 2.70, ^2J 5.39 Hz), 6.75 d (1H, H^6, $J_{6,7}$ 7.37 Hz), 6.82 d (2H, H_{Ar}, J 8.75 Hz), 6.84 d (1H, H^3, $J_{3,4}$ 8.75 Hz), 7.18 d (2H, H_{Ar}, J 8.42 Hz), 7.34 t (1H, H^7, $J_{7,6}$ 7.72, $J_{7,8}$ 8.48 Hz), 7.60 d (1H, H^4, $J_{4,3}$ 8.75 Hz), 7.97 d (1H, H^8, $J_{8,7}$ 8.48 Hz), 10.00 s (1H, OH). Found, %: C 73.38; H 6.63; N 3.26. $C_{23}H_{25}NO_4$. Calculated, %: C 73.4; H 6.62; N 3.25.

3-(1-Hydroxy-5-methoxy-2-naphthyl)-*N*-isobutyl-3-(4-methoxyphenyl)propanamide (IIIb) was similarly obtained from 0.6 g (1.8 mmol) of dihydrobenzocoumarin **II** and 0.13 ml of isobutylamine. Yield 0.55 g (73%), colorless crystals, mp 97°C. IR spectrum, ν, cm^{-1}: 3380 (NH), 1633 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.65 d [6H, $CH(CH_3)_2$, J 6.56 Hz], 1.55 septet [1H, $CH_2CH(CH_3)_2$, ^1J 6.56, ^2J 6.95 Hz], 2.70–3.20 m (4H, CH_2CHMe_2, CH_2CHAr), 3.70 s (3H, OCH_3), 3.90 s (3H, OCH_3), 5.10 d.d (1H, CH_2CHAr, ^1J 2.70, ^2J 8.10 Hz), 5.55 t (1H, NH, J 0.77 Hz), 6.75 d (1H, H^6, $J_{6,7}$ 7.70 Hz), 6.78 d (2H, H_{Ar}, J 8.48 Hz), 6.85 d (1H, H^3, $J_{3,4}$ 8.48 Hz), 7.08 d (2H, H_{Ar}, J 8.48 Hz), 7.35 t (1H, H^7, $J_{7,6}$ 7.72, $J_{7,8}$ 8.48 Hz), 7.64 d (1H, H^4, $J_{4,3}$ 8.48 Hz), 7.93 d (1H, H^8, $J_{8,7}$ 8.49 Hz), 10.00 s (1H, OH). Mass spectrum, *m/z* (I_{rel}, %): 407 (30) [M]$^+$, 334 (100), 306 (3), 291 (53), 277 (21), 261 (44), 248 (5), 234 (7), 227 (5), 218 (8), 200

(20), 189 (14), 178 (6), 167 (8), 152 (8), 146 (18), 135 (25), 115 (13), 108 (7), 101 (9), 88 (9), 82 (3), 72 (15), 57 (34), 41 (40). Found, %: C 73.67; H 7.09; N 3.55. $C_{25}H_{29}O_4N$. Calculated, %: C 73.7; H 7.12; N 3.51.

3-(1-Hydroxy-5-methoxy-2-naphthyl)-3-(4-methoxyphenyl)-1-piperidin-1-ylpropan-1-one (IIIc). A solution of 0.6 g (1.8 mmol) of dihydrobenzocoumarin **II** in 1 ml of piperidine was kept at room temperature for 20 min, then poured into water, the precipitate was filtered off and recrystallized from ethanol. Yield 0.48 g (64%), colorless crystals, mp 184°C. IR spectrum, ν, cm^{-1}: 1607 (NC=O). ^{1}H NMR spectrum, δ, ppm: 1.30–1.60 m [6H, $(CH_2)_3$], 3.15 t (ArCHCH_2, ^1J 4.24, ^2J 5.40 Hz), 3.30–3.65 m (4H, CH_2NCH_2), 3.75 s (3H, OCH_3), 3.95 s (3H, OCH_3), 5.13 d.d (1H, ArCHCH_2, ^1J 4.24, ^2J 4.63 Hz), 6.75 d (1H, H^6, $J_{6,7}$ 7.71 Hz), 6.80 d (2H, H_{Ar}, J 8.87 Hz), 6.90 d (1H, H^3, $J_{3,4}$ 8.87 Hz), 7.20 d (2H, H_{Ar}, J 8.87 Hz), 7.35 t (1H, H^7, $J_{7,6}$ 7.72, $J_{7,8}$ 8.48 Hz), 7.63 d (1H, H^4, $J_{4,3}$ 8.87 Hz), 7.97 d (1H, H^8, $J_{8,7}$ 8.48 Hz), 10.10 s (1H, OH). Found, %: C 74.89; H 7.09; N 2.75. $C_{26}H_{29}O_4N$. Calculated, %: C 74.91; H 7.13; N 2.69.

3-(1-Hydroxy-5-methoxy-2-naphthyl)-3-(4-methoxyphenyl)-*N*-(4-methylphenyl)-1-propanamide (IIId). To a cooled solution of 0.3 g (0.9 mmol) of dihydrobenzocoumarin **II** in benzene was added 0.96 g (0.9 mmol) of toluidine, 4 drops of triethylamine, and the mixture was boiled for 30 min. The formed solution was washed with water in a separating funnel. The organic layer was separated and dried with calcium chloride. Benzene was evaporated, and the residue was subjected to column chromatography on alumina (eluent chloroform). Yield 0.29 g (73%), colorless crystals, mp 175°C. IR spectrum, ν, cm^{-1}: 1633 (C=O), 1607. ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, *p*-$CH_3C_6H_4N$), 3.05 d.d (1H, HαCHβ, ^1J 4.63, ^2J 11.57 Hz), 3.35 d.d (1H, HαCHβ, ^1J 2.70, ^2J 16.20 Hz), 3.75 C (3H, OCH_3), 3.90 s (3H, OCH_3), 5.15 d.d (1H, ArCHCH_2, ^1J 2.70, ^2J 11.58 Hz), 6.75 d (1H, H^6, $J_{6,7}$ 8.10 Hz), 6.83 d (2H, H_{Ar}, $J_{6,7}$ 8.10 Hz), 6.92 d (1H, H^3, $J_{3,4}$ 8.87 Hz), 7.03 d (2H, H_{Ar}, J 8.48 Hz), 7.10–7.25 m (4H, *n*-MeC_6H_4N), 7.35 t (1H, H^7, $J_{7,6}$ 8.10, $J_{7,8}$ 8.48 Hz), 7.65 d (1H, H^4, $J_{4,3}$ 8.87 Hz), 7.93 d (1H, H^8, $J_{8,7}$ 8.48 Hz), 8.57 s (1H, NH), 10.10 C (1H, OH). Found, %: C 76.20; H 6.21; N 3.08. $C_{28}H_{27}O_4N$. Calculated, %: C 76.23; H 6.18; N 3.15.

3-(1-Hydroxy-5-methoxy-2-naphthyl)-3-(4-methoxyphenyl)propanohydrazide (IIIe) was obtained similarly to amide **IIIa** from 0.1 g (0.3 mmol) of dihydrobenzocoumarin **II** and 0.5 ml of hydrazine hydrate. Yield 0.08 g (74%), colorless crystals, mp 170°C. IR spectrum, ν, cm^{-1}: 3437 br ($NHNH_2$). ^{1}H NMR spectrum, δ, ppm: 2.83 d.d (1H, HαCHβ, ^1J 4.11, ^2J 11.37 Hz), 3.10 d.d (1H, HαCHβ, ^1J 3.48, ^2J 12.00 Hz), 3.75 s (3H, OCH_3), 3.95 s (3H, OCH_3), 3.85 br.s (2H, NH_2), 5.10 d.d (1H, CHCH_2, ^1J 3.48, ^2J 8.21 Hz), 6.78 d (1H, H^6, $J_{6,7}$ 7.89 Hz), 6.80 d (2H, H_{Ar}, J 8.53 Hz), 6.87 d (1H, H^3, $J_{3,4}$ 8.85 Hz), 7.37 t (1H, H^7, $J_{7,6}$ 7.89, $J_{7,8}$ 8.53 Hz), 7.65 d (1H, H^4, $J_{4,3}$ 8.85 Hz), 7.90 d (1H, H^8, $J_{8,7}$ 8.53 Hz), 8.42 br.s (1H, OH). Found, %: C 68.76; H 6.04; N 7.71. $C_{21}H_{22}O_4N_2$. Calculated, %: C 68.79; H 6.0; N 7.7.

3-(1-Acetyloxy-5-methoxy-2-naphthyl)-3-(4-methoxyphenyl)-1-(*N*-piperidin-1-yl)propan-1-one (IV). To a solution of 0.7 g (2.1 mmol) of amide **IIIc** in 6 ml of acetic anhydride was added in the cold 4 drops of 70% perchloric acid. The mixture was kept at room temperature for 40 min. The reaction mixture was poured into water, the precipitate was filtered off and dried. The product was isolated by column chromatography on silica gel (eluent chloroform). Yield 0.54 g (62%), light-yellow crystals, mp 95°C. IR spectrum, ν, cm^{-1}: 1753 (OCOMe), 1630 (NC=O). ^{1}H NMR spectrum, δ, ppm: 2.65 s (3H, COMe), 3.1 m (2H, CH_2), 3.75 s (3H, OMe), 4.0 s (3H, OMe), 4.4 m (1H, CH), 6.8–8.0 m ($8H_{arom}$). Found, %: C 73.20; H 6.42; N 2.87. $C_{28}H_{31}NO_5$. Calculated, %: C 72.86; H 6.77; N 3.03.

10-Acetyl-7-methoxy-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-2-one (V). To a solution of 0.7 g (2.1 mmol) of dihydrobenzocoumarin **II** in 6 ml of acetic anhydride was added in the cold 4 drops of 70% perchloric acid. The mixture was kept at room temperature for 40 min. The reaction mixture was poured into water, the precipitate was filtered off and dried. The product was isolated by column chromatography on silica gel (eluent chloroform). Yield 0.44 g (56%), light-yellow crystals, mp 95°C. IR spectrum, ν, cm^{-1}: 1767 ($OCOCH_2$), 1687 (MeC=O). ^{1}H NMR spectrum, δ, ppm: 2.60 s (3H, $COCH_3$), 3.07 d.d (2H, ArCHCH_2, ^1J 6.17, ^2J 7.33 Hz), 3.75 s (3H, OCH_3), 4.00 s (3H, OCH_3), 4.42 t (1H, ArCHCH_2, ^1J 6.56, ^2J 6.56 Hz), 6.80 d (1H, H^8, $J_{8,9}$ 8.10 Hz), 6.85 d (2H, H_{Ar}, J 8.48 Hz), 7.03 d (2H, H_{Ar}, J 8.48 Hz), 7.10 d (1H, H^5, $J_{5,6}$ 8.49 Hz), 7.34 d (1H, H^9, $J_{9,8}$ 8.10 Hz), 8.02 d (1H, H^6, $J_{6,5}$ 8.49 Hz). Found, %: C 73.40; H 5.64. $C_{23}H_{21}O_5$. Calculated, %: C 73.39; H 5.62.

3-(8-Acetyl-1-hydroxy-5-methoxynaphthyl-2)-3-(4-methoxyphenyl)-*N,N*-dimethylpropanamide (VIa). To a solution of 0.368 g (0.97 mmol) of 10-acetyldihydrobenzocoumarin (**V**) in ethanol was added 0.6 ml

of dimethylamine. The solution was kept for 30 min at 40°C. The reaction mixture was poured into water, the precipitate was filtered off and dried. The product was isolated by column chromatography on alumina (eluent chloroform). Yield 0.308 g (73%), colorless crystals, mp 160°C. IR spectrum, ν, cm^{-1}: 2725 (OH), 1687 (MeC=O), 1620 (NC=O). ^{1}H NMR spectrum, δ, ppm: 2.64 s (3H, $COCH_3$), 2.90 s (3H, CH_3NCH_3), 3.02 s (3H, CH_3NCH_3), 3.16 t (2H, $ArCHCH_2$, ^1J 3.04, ^2J 5.49 Hz), 3.78 s (3H, OCH_3), 3.96 s (3H, OCH_3), 5.14 d.d (1H, $ArCHCH_2$, ^1J 5.67, ^2J 5.75 Hz), 6.65 d (1H, H^6, $J_{6,7}$ 8.06 Hz), 6.82 d (2H, H_{Ar}, J 8.75 Hz), 7.07 d (1H, H^4, $J_{4,3}$ 8.79 Hz), 7.20 d (2H, H_{Ar}, J 8.68 Hz), 7.42 d (1H, H^7, $J_{7,6}$ 8.79 Hz), 7.65 d (1H, H^3, $J_{3,4}$ 8.75 Hz), 10.60 s (1H, OH). Found, %: C 68.83; H 6.47; N 6.4. $C_{25}H_{28}O_5N_2$. Calculated, %: C 68.81; H 6.42; N 6.42.

Reaction of 10-acetyl-7-methoxy-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-2-one (V) with piperidine. A solution of 0.6 g (1.6 mmol) of compound **V** in 3 ml of piperidine was kept at room temperature for 40 min. The reaction mixture was poured into water, the precipitate was filtered off and dried. The chromatography on alumina (eluent chloroform) provided two fractions. First fraction (R_f 0.35) was **3-{2-methyl-5-methoxy-2-(*N*-piperidin-1-yl)-2*H*-naphtho-[1,8-*bc*]furan-8-yl}-3-(4-methoxyphenyl)-1-(*N*-piperidin-1-yl)propan-1-one (VIIa).** Yield 0.076 g (9%), colorless crystals, mp 105–107°C. IR spectrum, ν, cm^{-1}: 1607 (NC=O). Found, %: C 74.97; H 7.63; N 5.3. $C_{33}H_{40}O_4N_2$. Calculated, %: C 74.96; H 7.63; N 5.31.

Second fraction (R_f 0.3) was **3-(8-acetyl-1-hydroxy-5-methoxynaphthyl-2)-3-(4-methoxyphenyl)-1-(*N*-piperidin-1-yl)propan-1-one (VIb).** Yield 0.45 g (61%), colorless crystals, mp130°C. IR spectrum, ν, cm^{-1}: 2727 (OH), 1687 (MeC=O), 1620 (NC=O). ^{1}H NMR spectrum, δ, ppm: 1.30–1.60 m [6H, $(CH_2)_3$], 2.62 s (3H, $COCH_3$), 3.15 t (2H, $ArCHCH_2$, ^1J 3.90, ^2J 5.02 Hz), 3.30–3.60 m [4H, $N(CH_2)_2$], 3.75 C (3H, OCH_3), 3.95 s (3H, OCH_3), 5.10 t (1H, $ArCHCH_2$, ^1J 6.18, ^2J 7.32 Hz), 6.67 d (1H, H^6 , $J_{6,7}$ 7.71 Hz), 6.80 d (2H, H_{Ar}, J 8.77 Hz), 7.05 d (1H, H^4, $J_{4,3}$ 8.87 Hz), 7.20 d (2H, H_{Ar}, J 8.87 Hz), 7.43 d (1H, H^7, $J_{7,6}$ 8.1 Hz), 7.70 d (1H, H^3, $J_{3,4}$ 8.88 Hz), 10.7 br.s (1H, OH). Found, %: C 72.71; H 6.95; N 3.04. $C_{28}H_{32}O_5N$. Calculated, %: C 72.73; H 6.93; N 3.02.

Reaction of 10-acetyl-7-methoxy-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-2-one (V) with morpholine. A solution of 0.116 g (0.31 mmol) of compound **V** in 3 ml of morpholine was heated at 40°C for 10 min. The reaction mixture was poured into water, the precipitate was filtered off and dried. The chromatography on alumina (eluent chloroform) provided two fractions. First fraction (R_f 0.35) was **3-(5-methoxy-2-methyl-2-morpholin-4-yl-2*H*-naphtho[1,8-*bc*]-furan-8-yl)-3-(4-methoxyphenyl)-1-morpholin-4-yl-1-propan-1-one (VIIb).** Yield 0.016 g (10%), colorless crystals, mp 95–100°C. IR spectrum, ν, cm^{-1}: 1620 (NC=O), 1500. ^{1}H NMR spectrum, δ, ppm: 1.80 d.s [3H, $CH_3C(N)O$], 2.50 br.s [2H, $O{=}CN(CH_2CH_2)_2O$], 2.75 br.s [2H, $O{=}CN(CH_2CH_2)_2O$], 3.05–3.70 m (14H, $ArCHCH_2$ and CH_{2morph}), 3.75 d.s (3H, 5-OCH_3), 3.95 s (3H, OCH_3), 4.70 m (1H, $ArCHCH_2$), 6.8 m (3H$_{arom}$), 7.08 m (1H$_{arom}$), 7.3 m (4H$_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 532 (45) $[M]^+$, 445 (45), 418 (100), 404 (50), 331 (40), 317 (35), 223 (15), 202 (10), 159 (15), 114 (15), 87 (20), 70 (23), 57 (45), 42 (20). Found, %: C 69.88; H 6.83; N 5.26. $C_{31}H_{36}N_2O_6$. Calculated, %: C 69.91; H 6.81; N 5.26.

Second fraction (R_f 0.3) was **3-(8-acetyl-1-hydroxy-5-methoxynaphthyl-2)-3-(4-methoxyphenyl)-1-morpholin-4-ylpropan-1-one (VIIc)**. Yield 0.096 g (67%), colorless crystals, mp 169–170°C. IR spectrum, ν, cm^{-1}: 2720 (OH), 1687 (C=O), 1600 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.70 s (3H, $COCH_3$), 3.15 t (2H, $ArCHCH_2$, ^1J 6.17, ^2J 8.87 Hz), 3.50 m [8H, $O(CH_2CH_2)_2N$], 3.72 s (3H, OCH_3), 3.95 s (3H, OCH_3), 5.10 d.d (1H, $ArCHCH_2$, ^1J 3.86, ^2J 5.40 Hz), 6.68 d (1H, H^6, $J_{6,7}$ 8.48 Hz), 6.83 d (2H, H_{Ar}, J 7.72 Hz), 7.15 d (1H, H^4, $J_{4,3}$ 8.88 Hz), 7.20 d (2H, H_{Ar}, J 7.70 Hz), 7.65 d (1H, H^7, $J_{7,6}$ 8.48 Hz), 7.75 d (1H, H^3, $J_{3,4}$ 8.90 Hz), 10.70 s (1H, OH). Found, %: C 69.96; H 6.31; N 3.02. $C_{27}H_9NO_6$. Calculated, %: C 69.8; H 6.1; N 3.02.

9-Methyl-6-methoxy-3-(4-methoxyphenyl)-2,3-dihydro-10,10a-diazapyren-1-one (IX). To a solution of 0.12 g (0.32 mmol) of *peri*-acetyldihydrobenzocoumarin (**V**) in ethanol was added 0.1 ml of hydrazine hydrate. The mixture was boiled for 30 min. The reaction mixture was poured into water, the precipitate was filtered off and dried. The obtained substance was dissolved in 2 ml of acetic acid and boiled for 1 h. The reaction mixture was poured into water, the precipitate was filtered off and dried. By chromatography on alumina (eluent chloroform) a fraction with R_f 0.4 was isolated. Yield 0.063 g (53%), yellow crystals, mp 205°C. IR spectrum, ν, cm^{-1}: 1687 (C=O), 1600. ^{1}H NMR spectrum, δ, ppm: 2.42 s (3H, $COCH_3$), 3.15 d.d (2H, $ArCHCH_2$, ^1J 1.35, ^2J 2.02, ^3J 7.08 Hz), 3.78 s (3H, OCH_3), 4.00 s (3H,

5-OCH_3), 4.24 t (1H, $ArCHCH_2$, ^1J 7.08, ^2J 7.07 Hz), 6.72 d (1H, H^4, $J_{4,3}$ 8.09 Hz), 6.82 d (2H, H_{Ar}, J 8.42 Hz), 7.04 d (1H, H^6, $J_{6,7}$ 8.42 Hz), 7.11 d (2H, H_{Ar}, J 8.76 Hz), 7.18 d (1H, H^3, $J_{3,4}$ 7.75 Hz), 7.59 d (1H, H^7, $J_{7,6}$ 8.42 Hz). Mass spectrum, *m/z* (I_{rel}, %): 372 $[M]^+$ (100), 357 (15), 329 (55), 315 (35), 300 (15), 299(10), 285 (5), 271 (10), 265 (5), 246 (5), 229 (5), 215 (5), 203 (10), 186 (10), 165 (20), 157 (18), 143 (5), 123 (5), 108 (7), 94 (5), 77 (5), 63 (8), 51 (5), 39 (5). Found, %: C 74.17; H 5.37; N 7.5. $C_{23}H_{20}N_2O_3$. Calculated, %: C 74.19; H, 5.37; N 7.53.

9-Methyl-6-methoxy-3-(4-methoxyphenyl)-10,10a-diazapyren-1-one (X). A mixture of 0.04 g (0.11 mmol) of diazadihydropyrenone **IX** and 0.025 g (0.1 mmol) of *p*-chloranil in 0.5 ml of *O*-dichlorobenzene was boiled for 15 min. The solvent was evaporated. By chromatography on alumina (eluent chloroform) a fraction with R_f 0.3 was isolated. Yield 0.027 g (68%), yellow crystals, mp 229–234°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1600. ^1H NMR spectrum, δ, ppm: 2.82 s (3H, $COCH_3$), 3.87 s (3H, OCH_3), 4.17 s (3H, 5-OCH_3), 7.07 d (2H, H_{Ar}, J 8.72 Hz), 7.08 s (1H, H^9), 7.29 d (1H, H^4, $J_{4,3}$ 8.35 Hz), 7.48 d (2H, H_{Ar}, J 8.72 Hz), 7.79 d (1H, H^6, $J_{6,7}$ *9.16 Hz), 7.81 d (1H,* H^3, $J_{3,4}$ 8.20 Hz), 7.91 d (1H, H^7, $J_{7,6}$ 9.15 Hz). Found, %: C 74.56; H 4.87; N 7.61. $C_{23}H_{18}O_3N_2$. Calculated, %: C 74.59; H 4.86; N 7.56.

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