Pinacol Rearrangement of 3,4-Dihydro-3,4-dihydroxyquinolin-2(1*H*)-ones: An Alternative Pathway to Viridicatin Alkaloids and Their Analogs

by **Ondřej Rudolf**[a]), **Michal Rouchal**[a]), **Antonín Lyčka**[b])[c]), and **Antonín Klásek***[a])

[a]) Department of Chemistry, Faculty of Technology, Tomas Bata University, CZ-762 72 Zlín (e-mail: klasek@ft.utb.cz)

[b]) Research Institute for Organic Syntheses (VUOS), Rybitví 296, CZ-533 54 Pardubice 20

[c]) University of Hradec Králové, Faculty of Science, CZ-500 03 Hradec Králové 3

Dedicated to Prof. *Vojeslav Štěrba* on the occasion of his 90th birthday

3-Alkyl/aryl-3-hydroxyquinoline-2,4-diones were reduced with $NaBH_4$ to give *cis*-3-alkyl/aryl-3,4-dihydro-3,4-dihydroxyquinolin-2(1*H*)-ones. These compounds were subjected to pinacol rearrangement by treatment with concentrated H_2SO_4, resulting in 4-alkyl/aryl-3-hydroxyquinolin-2(1*H*)-ones. When a benzyl (Bn) group was present in position 3 of the starting compound, its elimination occurred during the rearrangement, and the corresponding 3-hydroxyquinolin-2(1*H*)-one was formed. The reaction mechanisms are discussed for all transformations. All compounds were characterized by IR, ^{1}H- and ^{13}C-NMR spectroscopy, as well as mass spectrometry.

Introduction. – 3-Hydroxyquinoline-2,4-diones **2** are known as metabolites of some *Pseudomonas* species [1][2]. These compounds are available by several pathways: the photooxidation of 4-hydroxyquinolin-2(1*H*)-ones **1** [3], the oxidation of 4-hydroxyquinolin-2(1*H*)-ones with peroxy acids [1][4], or the reaction of the quinisatines and/or their hydrates and aminals with phenols [5][6]. We studied, the reaction of **2** with ethyl (triphenylphosphoranylidene)acetate to give (*E*)-4-[(ethoxycarbonyl)methylidene]-3-hydroxy-1,2,3,4-tetrahydroquinolin-2-ones and 2,3a,4,5-tetrahydrofuro[2,3-*c*]quinoline-2,4-diones was studied [7][8]. The same reaction with 3,5,8-trisubstituted starting compounds afforded, *via* a molecular rearrangement of **2**, 1,3-dihydro-3-phenylacetoxy-2*H*-indol-2-ones [9]. 3-Acyloxy-1,3-dihydro-2*H*-indole-2-ones and isomeric 4-acyl-1,4-dihydro-3,1-benzoxazin-2-ones were obtained by the double rearrangement of **2** in boiling xylene in the presence of 4-(dimethylamino)-pyridine (DMAP) or Ph_3P as a catalyst [10], or by the thermally induced rearrangement of **2** in boiling cyclohexylbenzene [11]. The rearrangement of compounds **2** also proceeded in aqueous KOH with the formation of 2-hydroxyindoxyls and/or dioxindoles [12].

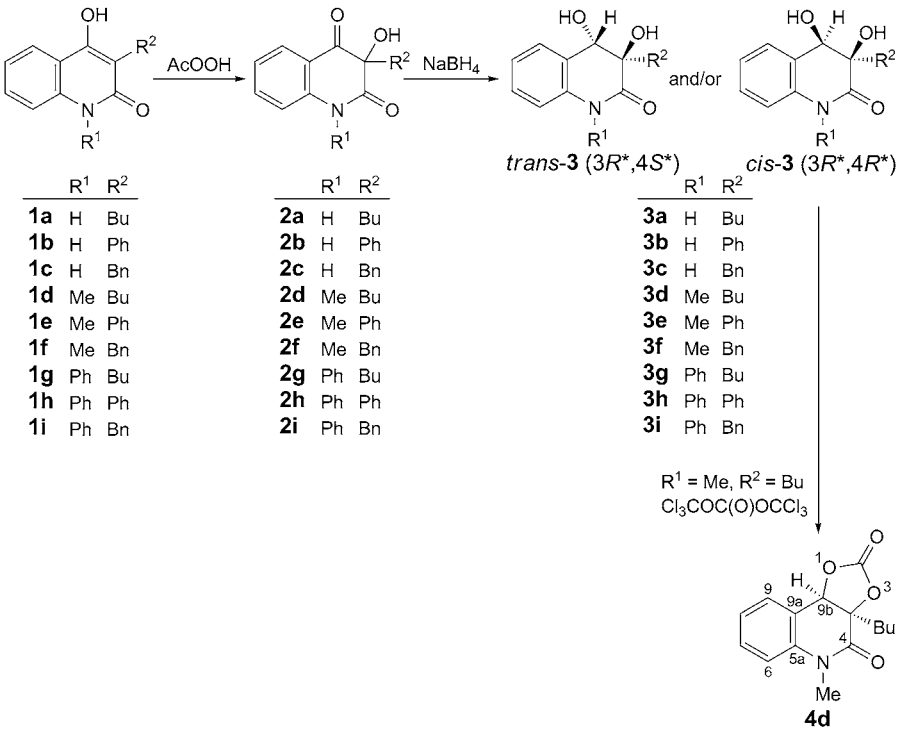
Our results revealed that 3-hydroxyquinoline-2,4-diones **2** are very reactive compounds, prone to the molecular rearrangements that result in the formation of new heterocyclic compounds. The chemistry of **2** inspired us to attempt at their reduction to the corresponding diols, which should also be suitable compounds to study molecular rearrangements. Herein, we report the validity of that presumption, and that

novel and interesting compounds, including quinoline alkaloids, can be prepared in this way.

Results and Discussion. – We have found only two examples of the reduction of 3-hydroxyquinoline-2,4-diones **2** in the literature. *Podesva et al.* [13] prepared 6-chloro-3,4-dihydro-3,4-dihydroxy-1-methyl-3-phenylquinolin-2(1*H*)-one by the reduction of the corresponding 3-hydroxyquinoline-2,4-dione with $NaBH_4$, and *Kappe et al.* [5] prepared 3,4-dihydro-3,4-dihydroxy-3-(pyridin-2-yl)methylquinolin-2(1*H*)-one by the hydrogenation of the corresponding 3-hydroxyquinoline-2,4-dione in the presence of a Pd/C catalyst. In both cases, the configuration of the product was not described. For our experiments, we chose $NaBH_4$ as the reducing agent. The starting 3-hydroxyquinoline-2,4-diones **2a**–**2i** were prepared by oxidation of the corresponding 4-hydroxyquinolin-2(1*H*)-ones **1** with AcOOH according to a well-known protocol [7]. To determine the influence of the R^2 substituent on the transformation of compounds **2**, we chose Bu, Ph, and Bn groups. The H-atom, and the Me and Ph groups were selected as the R^1 substituent.

The results of the reduction of compounds **2** with $NaBH_4$ are compiled in *Table 1*. In principle, four stereoisomers, *i.e.*, two pairs of diastereoisomers, *trans*-**3** and *cis*-**3**, should form from the reduction (*Scheme 1*). However, all the reduction products **3a**–**3i**

Scheme 1



	R^1	R^2
1a	H	Bu
1b	H	Ph
1c	H	Bn
1d	Me	Bu
1e	Me	Ph
1f	Me	Bn
1g	Ph	Bu
1h	Ph	Ph
1i	Ph	Bn

	R^1	R^2
2a	H	Bu
2b	H	Ph
2c	H	Bn
2d	Me	Bu
2e	Me	Ph
2f	Me	Bn
2g	Ph	Bu
2h	Ph	Ph
2i	Ph	Bn

	R^1	R^2
3a	H	Bu
3b	H	Ph
3c	H	Bn
3d	Me	Bu
3e	Me	Ph
3f	Me	Bn
3g	Ph	Bu
3h	Ph	Ph
3i	Ph	Bn

Table 1. *The Results of the Reduction of Compounds* **2a**–**2i**

Entry	Starting compound	R^1	R^2	Product (Yield [%])[a])
1	**2a**	H	Bu	*cis*-**3a** (79)
2	**2b**	H	Ph	*cis*-**3b** (88)
3	**2c**	H	Bn	*cis*-**3c** (74)
4	**2d**	Me	Bu	*cis*-**3d** (64)
5	**2e**	Me	Ph	*cis*-**3e** (77)
6	**2f**	Me	Bn	*cis*-**3f** (75)
7	**2g**	Ph	Bu	*cis*-**3g** (83)
8	**2h**	Ph	Ph	*cis*-**3h** (93)
9	**2i**	Ph	Bn	*cis*-**3i** (83)

[a]) The yields of pure recrystallized compounds are given.

exhibited only one TLC spot in several solvent systems. In the NMR spectra of the reaction products (*Table 2*), only one set of signals was observed, indicating that the reaction proceeded with high diastereoselectivity to give only one of the possible two diastereoisomers.

The assignment of the ^{1}H- and ^{13}C-NMR chemical shifts of compounds **3** followed from the analysis of 1D- and 2D-NMR (COSY, NOESY, HMQC, and gs-HMBC) experiments. The differentiation of the resonance of the OH group was based on the presenece of a ^3J(C(4)H,C(4)OH) coupling, with a value of 4.8 ± 0.5 Hz in the ^{1}H-NMR spectra, while the OH group at C(3) appeared as a *singlet*. The NOESY spectra of compounds **3** were recorded with the aim of determining the mutual orientation of the substituents at C(3) and C(4). The results strongly supported a through-space proximity of both OH groups, as well as the proximity of H–C(4) with suitable H-atoms of the R^2 substituent due to the appearance of appropriate cross-peaks in the NOESY spectra. However, because the compounds **3** were not completely rigid, the dynamic behavior of the substituents on C(3) and C(4) (certain rotamers) resulted in some additional cross-peaks. The ^{1}H and ^{13}C chemical shifts of compounds **3** are collected in *Table 2*.

Thus, it was possible to differentiate between the possible diastereoisomers *trans* and *cis* with NMR spectra. However, we decided to prepare a cyclic carbonate of one of the reaction products by its reaction with triphosgene (= bis(trichloromethyl) carbonate). From *cis*-**3d**, carbonate **4d** was prepared, which is convincingly indicative of the *cis*-configuration of the OH groups in **3d**. In the ^{1}H-NMR spectrum of **4d**, no OH group signals appeared, while a new resonance was detected in the ^{13}C-NMR spectrum of this compound, ascribed to a C(3)–O–C(=O)–O–C(4) fragment, resonating at 153.2 ppm (*Table 2*).

The ESI-MS experiments of compounds *cis*-**3** were carried out in the positive-ion mode. Typically, signals at *m*/*z* corresponding to $[M+H]^+$, as well as $[M+Na]^+$ and $[M+K]^+$ were observed for all of the examined structures (except the $[M+H]^+$ ion for *cis*-**3b**). These signals were accompanied by several types of higher associates, namely the singly charged Na^+ adduct of the dimer $[2M+Na]^+$ and the doubly charged Ca^{2+} adduct of the trimer $[3M+Ca]^{2+}$. In addition, the doubly charged Ca^{2+} adduct of the dimer $[2M+Ca]^{2+}$ was determined in the first-order ESI mass spectra of *cis*-**3c**, *cis*-**3f**,

Table 2. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds cis-***3** *and* **4d** (δ in ppm)

Position	*cis*-**3a**		*cis*-**3b**		*cis*-**3c**		*cis*-**3d**		*cis*-**3e**		*cis*-**3f**		*cis*-**3g**		*cis*-**3h**		*cis*-**3i**		**4d**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	172.6	–	171.1	–	171.6	–	171.8	–	171.7	–	170.9	–	171.9	–	171.6	–	171.0	–	153.2
3	–	74.8	–	77.2	–	74.6	–	74.8	–	77.5	–	74.9	–	75.3	–	77.6	–	75.1	–	–
3-OH	5.59	–	6.02	–	5.30	–	5.16	–	6.10	–	5.33	–	5.36	–	6.28	–	5.62	–	–	–
3a											–	–	–	–	–	–	–	–	–	83.2
4	4.62	71.8	4.92	73.1	4.31	70.8	4.62	71.0	4.95	72.1	4.35	70.2	4.81	71.2	5.17	72.4	4.50	70.4	–	164.9
4-OH	5.09	–	5.93	–	5.69	–	5.67	–	6.07	–	5.81	–	5.81	–	6.19	–	5.96	–	–	–
4a	–	127.4	–	127.4	–	126.9	–	128.7	–	128.6	–	128.2	–	128.4	–	128.5	–	128.0	–	–
5	7.38	126.8	7.30	125.9	7.23	126.0	7.45	126.5	7.34	125.3	7.32	127.6	7.49	127.1	7.42	125.9	7.38	126.2	–	–
5a	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	137.8
6	7.01	122.1	7.00	122.6	6.98	122.0	7.11	122.8	7.07	123.2	7.08	122.7	7.09	122.9	7.05	123.3	7.05	122.8	7.40	116.6
7	7.21	128.0	7.23	128.1	7.21	128.2	7.32	128.2	7.32	128.1	7.34	128.4	7.14	128.2	7.14	127.9	7.14	128.1	7.53	129.4
8	6.86	114.5	6.97	114.7	6.89	114.7	7.13	114.3	7.20	114.4	7.10	114.4	6.21	115.6	6.29	115.7	6.23	115.9	7.29	124.1
8a	–	135.9	–	138.9	–	136.5	–	138.1	–	138.7	–	138.4	–	139.1	–	138.7	–	139.5	–	–
9	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	7.40	121.7
9a	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	121.9
9b	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	6.19	78.4
Substituent at N(1)																				
1	10.15	–	10.59	–	10.23	–	3.32	29.6	3.46	29.9	3.31	29.6	–	138.7	–	138.7	–	138.8	3.37	29.8
2,6	–	–	–	–	–	–	–	–	–	–	–	–	7.24	129.2	7.25	129.1	7.24	129.1	–	–
3,5	–	–	–	–	–	–	–	–	–	–	–	–	7.60	130.0	7.64	130.1	7.60	129.9	–	–
4	–	–	–	–	–	–	–	–	–	–	–	–	7.50	127.9	7.55	128.5	7.50	128.0	–	–
Substituent at C(3)																				
1	1.70	30.1	–	135.6	3.05	36.6	1.68	30.4	–	137.7	3.02	37.3	1.81	30.3	–	138.4	3.13	37.2	1.52	28.5
	1.39	–	–	–	2.97	–	1.39	–	–	–	2.96	–	1.56	–	–	–	3.07	–	1.30	–
2	1.41	24.6	7.37	127.5	–	137.0	1.39	24.6	7.24	127.7	–	136.8	1.50	24.7	7.47	127.8	–	136.8	1.34	24.6
	1.18	–	–	–	–	–	1.18	–	–	–	–	–	1.26	–	–	–	–	–	1.17	–
3,7	1.22	22.9	7.21	127.2	7.27	130.9	1.21	22.8	7.17	127.1	7.18	130.8	1.26	22.9	7.40	127.3	7.31	130.9	1.17	22.0
4,6	0.86	14.2	7.21	127.2	7.27	127.6	0.84	14.1	7.17	127.3	7.25	127.5	0.89	14.2	7.25	127.4	7.61	127.7	0.78	13.7
5	–	–	–	–	7.27	127.8	–	–	–	–	7.22	127.6	–	–	–	–	7.26	127.7	–	–

and *cis*-**3i** bearing a Bn group at C(3). The fragmentation (MS/MS) of the $[M+H]^+$ ion under collision-induced dissociation (CID) conditions led in all cases to the loss of a H_2O molecule. Further fragmentation (MS^3) of the $[M+H-H_2O]^+$ ion was considerably affected by the R^2 substituent at C(3). In the MS^3 of compounds *cis*-**3a**, *cis*-**3d**, and *cis*-**3g** ($R^2=Bu$), three signals originating from consecutive losses of CO and two $CH_2{=}CH_2$ molecules were observed. When a Ph group was present at C(3) (*cis*-**3b**, *cis*-**3e**, and *cis*-**3h**), only the loss of CO (*m*/*z* 28) occurred. Finally, in the MS^3 of compounds *cis*-**3c**, *cis*-**3f**, and *cis*-**3i** ($R^2=Bn$), two signals, assigned to $[M+H-H_2O-CO]^+$ and Bn^+ (*m*/*z* 91), were observed.

Only two compounds **3** were reported in the literature [5][13], but neither their configuration nor biological activity were. However, from *Penicilium janczewskii*, two diastereoisomeric alkaloids were isolated, differing from *cis*-**3b** only by the presence of the 4-methoxyphenyl group at C(4) and the H-atom at C(3). These alkaloids showed low-to-moderate cytotoxic activities against various human tumor cell lines, but significantly stronger cytotoxicities against SKOV-3 cells (human ovary adenocarcinoma) [14].

Compounds *cis*-**3** are vicinal diols that are easily liable to the pinacol rearrangement [15–17] under acid catalysis. To perform the rearrangement of compounds *cis*-**3**, we used concentrated H_2SO_4.

The rearrangement of diols *cis*-**3a**, *cis*-**3b**, *cis*-**3d**, *cis*-**3e**, *cis*-**3g**, and *cis*-**3h** took place quickly and, with the exception of *cis*-**3g**, only a single product was obtained (*Table 3*). The IR spectrum of the products exhibited strong absorption bands characteristic of a OH group in the region of 3251–3436 cm^{-1}, and an amide group in the region of 1643–1685 cm^{-1}, but it did not exhibit any absorption bands in the aldehyde or ketone region.

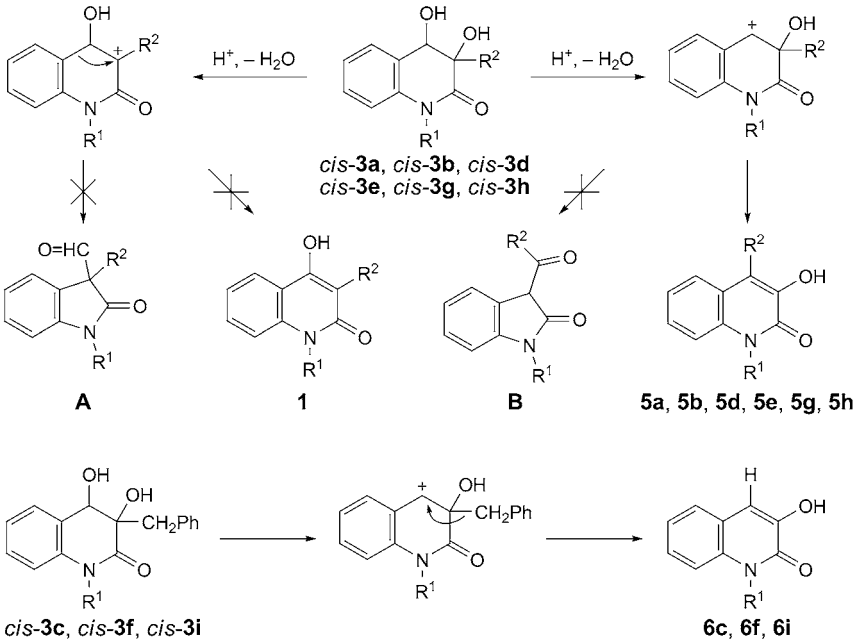
Table 3. *The Results of the Rearrangement of Compounds cis*-**3**

Entry	Starting compound	R^1	R^2	Product (Yield [%])[a]
1	*cis*-**3a**	H	Bu	**5a** (71)
2	*cis*-**3b**	H	Ph	**5b** (85)
3	*cis*-**3c**	H	Bn	**6c** (59)
4	*cis*-**3d**	Me	Bu	**5d** (72)
5	*cis*-**3e**	Me	Ph	**5e** (93)
6	*cis*-**3f**	Me	Bn	**6f** (63)
7	*cis*-**3g**	Ph	Bu	**5g** (61), **1g** (9)[b]
8	*cis*-**3h**	Ph	Ph	**5h** (65)
9	*cis*-**3i**	Ph	Bn	**6i** (58)

[a]) The yields of pure recrystallized compounds. [b]) Identical in all respects to the authentic sample.

Four compounds may be produced during the rearrangement of compounds *cis*-**3** (*Scheme 2*). The structures **A**, **B**, and **1** can be excluded, because they are not in accordance with the IR spectra of the products. The remaining structure **5** is, therefore, plausible as the structure of the products of the pinacol rearrangement of compounds *cis*-**3**. This result indicates that the elimination of H_2O from C(4) of the protonated *cis*-**3** results in the formation of a secondary carbocation securing the aromatic ring, which

Scheme 2



contributes to the delocalization of the positive charge (benzylic cation). The following 1,2-shift of the alkyl or aryl group from C(3) provides a tertiary carbocation which, after the deprotonation, gives compound **5**. It is interesting that also compounds *cis*-**3b**, **3e**, and **3h** with Ph substituents at C(3), which should be able to create a carbocation at C(3), also react to give products **5**. From this viewpoint, it is surprising that the isomeric side product **1g** was isolated in addition to **5g** from the reaction of *cis*-**3g** with H_2SO_4. The NMR data of compounds **5** are compiled in *Table 4*. In the case of compounds *cis*-**3c**, *cis*-**3f**, and *cis*-**3i**, the products of molecular rearrangement did not exhibit the Bn signals in their NMR spectra and were identified as debenzylated compounds **6**. The formation of **6** can be explained as the result of the stabilization of the intermediate carbocation by removal of the Bn group (*Scheme 2*). The NMR data of compounds **6** are given in *Table 4*.

In the positive-ion-mode first-order ESI-MS of compounds **5**, we observed five significant peaks for each structure. These peaks were assigned to the $[M+H]^+$ ion, Na^+ and K^+ adducts of the molecular ion, Na^+ adduct of the dimer, and doubly charged Ca^{2+} adduct of the trimer $[3M+Ca]^{2+}$. In the first-order ESI-MS of compounds **6**, the peaks mentioned above were accompanied by those of two additional ions, namely of the K^+ adduct of the dimer $[2M+K]^+$ and a peak at *m*/*z* corresponding to the doubly charged Ca^{2+} adduct of the tetramer $[4M+Ca]^{2+}$. Moreover, in the case of compounds **6c** and **6f**, the $[3M+K]^+$ ion peak was also detected. It should be noted that the peak at *m*/*z* 91 (Bn^+), which was formed during the fragmentation (MS^3) of compounds *cis*-**3c**, *cis*-**3f**, and *cis*-**3i**, and was also observed at low intensity in the first-order MS of these

Table 4. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **5** *and* **6** (δ in ppm)

Position	**5a**		**5b**		**5d**		**5e**		**5g**		**5h**		**6c**		**6f**		**6i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(H)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	158.0	–	158.4	–	157.7	–	158.2	–	157.7	–	158.2	–	158.7	–	158.4	–	158.4
3	–	133.4	–	133.3	–	134.5	–	134.4	–	135.7	–	133.8	–	146.3	–	145.3	–	145.7
3-OH	9.08	–	9.25	–	9.10	–	9.25	–	9.24	–	9.38	–	9.48	–	9.30	–	9.20	–
4	–	124.0	–	124.1	–	122.8	–	123.1	–	123.8	–	123.9	7.14	112.6	7.16	111.8	7.29	112.7
4a	–	120.6	–	121.0	–	121.0	–	121.5	–	121.0	–	121.5	–	120.8	–	121.2	–	121.1
5	7.66	123.1	7.12	124.4	7.74	123.5	7.17	125.0	7.79	123.6	7.20	125.0	7.53	125.9	7.60	126.7	7.64	126.6
6	7.24	122.3	7.12	122.3	7.33	122.7	7.22	122.6	7.30	122.8	7.18	122.7	7.17	122.2	7.26	122.6	7.23	122.7
7	7.34	126.3	7.38	126.6	7.48	126.8	7.49	127.0	7.27	126.7	7.28	126.7	7.32	126.4	7.46	126.8	7.26	126.5
8	7.34	115.5	7.38	115.4	7.53	114.9	7.61	114.9	6.54	115.6	6.61	115.6	7.32	114.8	7.50	114.5	6.49	115.1
8a	–	142.7	–	142.6	–	141.9	–	141.7	–	142.2	–	142.1	–	133.6	–	134.8	–	136.1
Substituent at N(1)																		
1	12.03	–	12.28	–	3.75	30.1	3.83	30.1	–	137.7	–	135.7	12.04	–	3.74	29.9	–	137.7
2,6	–	–	–	–	–	–	–	–	7.39	129.1	7.46	130.0	–	–	–	–	7.39	129.0
3,5	–	–	–	–	–	–	–	–	7.68	130.2	7.62	128.6	–	–	–	–	7.68	130.2
4	–	–	–	–	–	–	–	–	7.61	128.9	7.53	127.9	–	–	–	–	7.60	129.0
Substituent at C(3)																		
1	2.84	24.1	–	133.8	2.86	24.1	–	133.8	2.94	24.3	–	137.6	–	–	–	–	–	–
2,6	1.55	30.5	7.38	130.0	1.55	30.6	7.37	130.0	1.60	30.6	7.49	128.6	–	–	–	–	–	–
3,5	1.39	22.4	7.56	128.5	1.42	22.4	7.56	128.5	1.48	22.5	7.73	130.7	–	–	–	–	–	–
4	0.96	14.0	7.49	128.4	0.95	14.0	7.49	127.8	0.99	14.0	7.66	129.1	–	–	–	–	–	–

structures (see *Exper. Part*), was completely absent in the ESI-MS of compounds **6**. These results were in accordance with other structural analyses, indicating that structures **6c**, **6f**, and **6i** are debenzylated products due to the rearrangement of corresponding compounds *cis*-**3**.

In nature, compounds **5** bearing a Ph group at C(4) occur frequently as secondary metabolites of fungi belonging to the genus *Penicillium* [18]. Two of the well-known quinolin-2-ones of fungal origin are viridicatin (**5b**) and viridicatol (viridicatin bearing a OH group at C(3) of the Ph substituent). These compounds showed significant biological activities [19], *e.g.*, inhibition of the glycine binding site associated with the NMDA receptor [20], inhibition of human immunodeficiency virus (HIV) induced by tumor necrosis factor (TNF-α) [21], and antibacterial activities owing to their action as maxi-K channel openers [22]. Additionally, compounds **6** exhibit biological activities, *e.g.*, **6c** causes reduction of lymphocyte MT-4 cells, and inhibits activity of reverse transcriptase ribonuclease H of HIV-1 and D-amino acid oxidase [23], and **6f** inhibits activity of D-amino acid oxidase [23]. 3-Butyl derivatives **5a**, **5d**, and **5g** have not been described in the literature yet, but a 4-Me analog of **5a** exhibited biological effects similar to those of compounds **6c** and **6f** [23].

4-Alkyl/aryl-3-hydroxyquinolin-2(1*H*)-ones or their 4-unsubstituted analogs were most frequently prepared by the reaction of isatins with aryldiazomethanes or diazoalkanes [24–26], or by *Friedländer*-type condensations [27]. The best hitherto known method for the preparation of 4-arylquinolin-2(1*H*)-one derivatives appears to be the *Knoevenagel* condensation of cyanoacetanilides with aromatic aldehydes, followed by oxidative cyclization [19].

Conclusions. – In summary, we have demonstrated an efficient approach to the synthesis of 4-alkyl/aryl-3-hydroxyquinolin-2(1*H*)-ones **5** or **6**, starting from the easily accessible 3-hydroxyquinoline-2,4-diones **2**. The $NaBH_4$ reduction of **2** proceeds with high diastereoselectivity to give *cis*-3,4-dihydro-3,4-dihydroxyquinolin-2(1*H*)-ones, *cis*-**3**, as the sole products. The subsequent pinacol rearrangement of *cis*-**3** to **5** or **6** opens the way to prepare a broad-spectrum of both 4-alkyl- or 4-aryl substituted compounds **5** and 4-unsubstituted compounds **6**. The described transformations are very interesting from the viewpoint of theory and, owing to the simple reaction protocol, open a path to the synthesis of new compounds of types **3**, **5**, and **6**. Because compounds **3**, **5**, and **6** exhibit significant biological activities, the new compounds described in this article could also be interesting structures for studies in this direction.

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Experimental Part

1. *General.* TLC: *Alugram®-SIL-G/UV$_{254}$* foils (*Macherey–Nagel*); elution with benzene/AcOEt 4:1, $CHCl_3$/EtOH 9:1 and/or 19:1, $CHCl_3$/AcOEt 7:3, and THF/AcOH 4:1. Column chromatography (CC): silica gel (SiO_2; *Merck*, grade *60*, 70–230 mesh); elution with $CHCl_3$, then $CHCl_3$/EtOH 99:1 → 8:2 or benzene, and then benzene/AcOEt 99:1 → 8:2. M.p.: *Kofler* block or *Gallencamp* apparatus. IR Spectra: *Nicolet iS10* spectrophotometer; KBr; in cm^{-1}. NMR Spectra: *Bruker Avance* spectrometer at 500.13

(^{1}H) and 125.76 MHz (^{13}C), and *Bruker Avance II 400* spectrometer at 400.13 (^{1}H) and 100.56 (^{13}C); (D_6)DMSO soln.; δ in ppm rel. to Me_4Si as internal standard; J in Hz; manufacturer's software for all 2D experiments (gradient-selected gs-COSY, gs-NOESY, gs-HMQC, and gs-HMBC). EI-MS (pos.): *Shimadzu QP-2010* instrument within m/z 50–600, using direct inlet probe (DI); analysis of samples in CH_2Cl_2 (30 µg/ml), 10 µl of the soln. was evaporated in DI cuvette at 50; ion-source temp., 200°; the energy of electrons, 70 eV; only signals exceeding rel. abundance of 5% are listed. ESI-MS (pos. as well as neg.): *amaZon X* ion-trap mass spectrometer (*Bruker Daltonics*, DE-Bremen) equipped with an ESI source; individual samples infused into the ion source as MeOH/H_2O 1:1 (v/v) solns. *via* a syringe pump at a constant flow rate of 4 µl/min; other instrumental conditions: m/z range, 50–1500; electrospray voltage, ±4.2 kV; drying gas temp., 220; drying gas flow, 6.0 dm^3/min; nebulizer pressure, 55.16 kPa; cap. exit, ±140 V; N_2 used as nebulizing as well as drying gas. Elemental analysis (C, H, N): *Flash EA 1112* elemental analyzer (*Thermo Fisher Scientific*).

2. *General Procedure for the Preparation of Compounds* cis-**3** (=(3*R**,4*R**)-**3**). $NaBH_4$ (85 mg, 2.5 mmol) was added in four portions during 5 min to the stirred soln. of compound **2** (2 mmol) in MeOH (10 ml) at r.t. After 20 min, crushed ice (up to 20 g), conc. HCl (0.25 ml), and H_2O (4 ml) were added successively to the mixture under cooling with crushed ice. Deposited product was filtered off, washed with H_2O, and recrystallized from an appropriate solvent. In the case of *cis*-**3i**, the deposited product was of a gummy character; therefore, the mixture was extracted with $CHCl_3$. The dried (Na_2SO_4) extract was evaporated to dryness, and the residue was recrystallized from the benzene/hexane mixture. The yields are given in *Table 1*, for NMR spectra of compounds *cis*-**3**, see *Table 2*.

cis-*3-Butyl-3,4-dihydro-3,4-dihydroxyquinolin-2(1*H*)-one* (*cis*-**3a**). Prepared from **2a** in 79% yield. White solid. M.p. 160–170° and then 176–190° (MeOH). IR: 3434, 3218, 3072, 2950, 2927, 2869, 1673, 1637, 1596, 1486, 1436, 1386, 1238, 1226, 1162, 1126, 1079, 1058, 873, 848, 761, 694, 671, 518. EI-MS: 235 (7, M^+), 132 (21), 123 (8), 122 (100), 94 (12), 93 (9), 77 (12), 57 (7). ESI-MS (pos.): 493.3 (24, [2 M + Na]$^+$), 372.8 (87, [3 M + Ca]$^{2+}$), 274.2 (11, [M + K]$^+$), 258.2 (100, [M + Na]$^+$), 236.2 (13, [M + H]$^+$), 218.2 (15, [M + H − H_2O]$^+$). Anal. calc. for $C_{13}H_{17}NO_3$ (235.28): C 66.36, H 7.28, N 5.95; found: C 66.42, H 7.27, N 5.95.

cis-*3,4-Dihydro-3,4-dihydroxy-3-phenylquinolin-2(1*H*)-one* (*cis*-**3b**). Prepared from **2b** in 88% yield. White solid. M.p. 236–242° (EtOH). IR: 3432, 3355, 3199, 3062, 1671, 1637, 1594, 1488, 1448, 1432, 1374, 1332, 1270, 1238, 1203, 1176, 1099, 1079, 1045, 1024, 971, 943, 914, 873, 846, 794, 767, 750, 709, 692, 674, 570, 536. EI-MS: 255 (7, M^+), 132 (10), 123 (8), 122 (100), 94 (13), 93 (9), 77 (37), 71 (6), 57 (6), 51 (9). ESI-MS (pos): 533.2 (14, [2M + Na]$^+$), 294.2 (85, [M + K]$^+$), 278.2 (100, [M + Na]$^+$), 238.2 (7, [M + H − H_2O]$^+$). Anal. calc. for $C_{15}H_{13}NO_3$ (255.27): C 70.58, H 5.13, N 5.49; found: C 70.64, H 5.15, N 5.45.

cis-*3-Benzyl-3,4-dihydro-3,4-dihydroxyquinolin-2(1*H*)-one* (*cis*-**3c**). Prepared from **2c** in 74% yield. White solid. M.p. 230–233° (MeOH). IR: 3419, 3303, 3218, 2915, 1666, 1633, 1596, 1488, 1454, 1432, 1394, 1299, 1282, 1241, 1207, 1112, 1070, 1022, 944, 916, 877, 848, 833, 761, 738, 721, 696, 671, 659, 632, 586, 503. EI-MS: 269 (21, M^+), 251 (20), 178 (17), 177 (5), 161 (10), 160 (24), 149 (7), 133 (10), 132 (69), 123 (8), 122 (100), 121 (8), 120 (6), 105 (7), 104 (12), 94 (14), 93 (20), 92 (16), 91 (65), 78 (8), 77 (30), 76 (5), 65 (24), 51 (11). ESI-MS (pos.): 561.2 (5, [2M + Na]$^+$), 423.7 (9, [3M + Ca]$^{2+}$), 308.2 (48, [M + K]$^+$), 292.2 (100, [M + Na]$^+$), 289.2 (43, [2M + Ca]$^{2+}$), 270.2 (19, [M + H]$^+$), 252.2 (4, [M + H − H_2O]$^+$), 91.3 (3, [Bn]$^+$). Anal. calc. for $C_{16}H_{15}NO_3$ (269.30): C 71.36, H 5.61, N 5.20; found: C 71.27, H 5.63, N 5.18.

cis-*3-Butyl-3,4-dihydro-3,4-dihydroxy-1-methylquinolin-2(1*H*)-one* (*cis*-**3d**). Prepared from **2d** in 64% yield. White solid. M.p. 100–103° (benzene/hexane). IR: 3457, 3394, 2950, 2925, 2857, 1666, 1604, 1477, 1359, 1288, 1178, 1132, 1110, 1079, 1047, 943, 842, 755, 696, 640, 609, 553. EI-MS: 249 (10, M^+), 164 (30), 147 (13), 146 (100), 136 (35), 135 (8), 118 (32), 106 (16), 91 (14), 77 (12), 57 (6), 41 (9). ESI-MS (pos.): 537.3 (5, [2M + K]$^+$), 521.3 (22, [2M + Na]$^+$), 393.8 (100, [3M + Ca]$^{2+}$), 288.2 (10, [M + K]$^+$), 272.2 (50, [M + Na]$^+$), 250.2 (8, [M + H]$^+$), 232.2 (4, [M + H − H_2O]$^+$). Anal. calc. for $C_{14}H_{19}NO_3$ (249.31): C 67.45, H 7.68, N 5.62; found: C 67.53, H 7.70, N 5.68.

cis-*3,4-Dihydro-3,4-dihydroxy-1-methyl-3-phenylquinolin-2(1*H*)-one* (*cis*-**3e**). Prepared from **2e** in 77% yield. White solid. M.p. 198–200° (benzene). IR: 3475, 3399, 1660, 1606, 1592, 1467, 1380, 1290, 1213, 1110, 1074, 1047, 1025, 970, 850, 790, 755, 742, 703, 680, 649, 624, 576. EI-MS: 269 (11, M^+), 165 (7), 164 (43), 147 (8), 146 (78), 137 (9), 136 (100), 135 (11), 119 (6), 118 (68), 117 (6), 107 (8), 106 (38), 105 (38), 93 (8), 91 (24), 78 (12), 77 (68), 65 (7), 51 (17). ESI-MS (pos.): 561.2 (18, [2M + Na]$^+$), 423.7 (68,

$[3M + Ca]^{2+}$), 308.2 (17, $[M + K]^+$), 292.2 (100, $[M + Na]^+$), 270.2 (5, $[M + H]^+$), 252.2 (24, $[M + H - H_2O]^+$), 224.2 (23, $[252 - CO]^+$). Anal. calc. for $C_{16}H_{15}NO_3$ (269.29): C 71.36, H 5.61, N 5.20; found: C 71.50, H 5.59, N 5.18).

cis-*3-Benzyl-3,4-dihydro-3,4-dihydroxy-1-methylquinolin-2(1*H*)-one* (*cis*-**3f**). Prepared from **2f** in 75% yield. White solid. M.p. 144–147° (benzene). IR: 3396, 3021, 1643, 1604, 1473, 1415, 1380, 1305, 1213, 1157, 1122, 1066, 1045, 1006, 916, 873, 786, 754, 732, 698, 673, 646, 584. EI-MS: 283 (21, M^+), 265 (9), 236 (17), 192 (39), 191 (5), 175 (9), 174 (45), 164 (15), 147 (14), 146 (100), 136 (17), 135 (7), 118 (30), 106 (18), 91 (63), 78 (7), 77 (22), 65 (16), 51 (9). ESI-MS (pos.): 589.2 (7, $[2M + Na]^+$), 444.7 (20, $[3M + Ca]^{2+}$), 322.2 (30, $[M + K]^+$), 306.2 (100, $[M + Na]^+$), 303.2 (58, $[2M + Ca]^{2+}$), 284.2 (23, $[M + H]^+$), 91.3 (4, $[Bn]^+$). Anal. calc. for $C_{17}H_{17}NO_3$ (283.32): C 72.07, H 6.05, N 4.94; found: C 72.03, H 6.05), N 4.98.

cis-*3-Butyl-3,4-dihydro-3,4-dihydroxy-1-phenylquinolin-2(1*H*)-one* (*cis*-**3g**). Prepared from **2g** in 83% yield. White solid. M.p. 165–169° (benzene/hexane). IR: 3475, 3440, 3062, 2954, 1677, 1604, 1492, 1459, 1346, 1299, 1282, 1265, 1186, 1147, 1079, 1058, 1004, 944, 871, 856, 763, 696, 646, 559. EI-MS: 311 (16, M^+), 238 (9), 237 (7), 227 (6), 226 (42), 209 (17), 208 (100), 198 (24), 197 (18), 196 (11), 181 (12), 180 (80), 168 (25), 167 (14), 93 (6), 77 (22), 65 (6), 57 (16), 51 (9), 43 (11), 41 (17). ESI-MS (pos.): 645.3 (12, $[2M + Na]^+$), 627.3 (9, $[2M + Na - H_2O]^+$), 486.8 (40, $[3M + Ca]^{2+}$), 677.8 (16, $[2M + Ca - H_2O]^{2+}$), 350.2 (19, $[M + K]^+$), 234.3 (100, $[M + Na]^+$), 216.2 (32, $[M + Na - H_2O]^+$), 312.3 (19, $[M + H]^+$), 294.3 (77, $[M + H - H_2O]^+$), 266.3 (4, $[294 - CO]^+$). Anal. calc. for $C_{19}H_{21}NO_3$ (311.38): C 73.29, H 6.80, N 4.50; found: C 73.35, H 6.79, N 4.30.

cis-*3,4-Dihydro-3,4-dihydroxy-1,3-diphenylquinolin-2(1*H*)-one* (*cis*-**3h**). Prepared from **2h** in 93% yield. White solid. M.p. 197–200° (benzene/hexane). IR: 3469, 3311, 2852, 1675, 1606, 1494, 1459, 1347, 1267, 1184, 1120, 1074, 1027, 1000, 944, 854, 761, 725, 700, 688, 649, 588. EI-MS: 331 (13, M^+), 303 (5), 227 (7), 226 (43), 209 (11), 208 (66), 199 (8), 198 (56), 197 (30), 196 (17), 181 (15), 180 (100), 169 (7), 168 (44), 167 (19), 152 (8), 106 (9), 105 (45), 93 (9), 78 (9), 77 (78), 65 (10), 51 (23). ESI-MS (pos.): 685.3 (7, $[2M + Na]^+$), 516.8 (6, $[3M + Ca]^{2+}$), 370.2 (33, $[M + K]^+$), 354.2 (100, $[M + Na]^+$), 332.3 (3, $[M + H]^+$), 314.3 (6, $[M + H - H_2O]^+$), 286.3 (5, $[314 - CO]^+$). Anal. calc. for $C_{21}H_{17}NO_3$ (331.36): C 76.12, H 5.17, N 4.23; found: C 76.26, H 5.28), N 3.95.

cis-*3-Benzyl-3,4-dihydro-3,4-dihydroxy-1-phenylquinolin-2(1*H*)-one* (*cis*-**3i**). Prepared from **2i** in 83% yield. White solid. M.p. 148–152° (benzene/hexane). IR: 3461, 3062, 1687, 1602, 1494, 1459, 1351, 1299, 1236, 1199, 1128, 1108, 1022, 960, 875, 862, 761, 730, 696, 647, 599. EI-MS: 346 (8), 345 (32, M^+), 327 (7), 298 (20), 255 (8), 254 (49), 237 (10), 236 (48), 226 (29), 209 (18), 208 (100), 198 (15), 197 (16), 196 (13), 181 (13), 180 (97), 179 (8), 168 (31), 167 (19), 152 (10), 105 (15), 92 (12), 91 (55), 78 (7), 77 (38), 66 (6), 65 (21), 51 (16). ESI-MS (pos.): 713.2 (5, $[2M + Na]^+$), 537.8 (7, $[3M + Ca]^{2+}$), 384.2 (43, $[M + K]^+$), 368.2 (100, $[M + Na]^+$), 365.2 (41, $[2M + Ca]^{2+}$), 346.3 (10, $[M + H]^+$), 328.3 (5, $[M + H - H_2O]^+$), 91.3 (3, $[Bn]^+$). Anal. calc. for $C_{22}H_{19}NO_3$ (345.39): C 76.50, H 5.54, N 4.06; found: C 76.54, H 5.55, N 3.88.

3. *Synthesis of 3a-Butyl-5,9b-dihydro-5-methyl[1,3]dioxolo[4,5-*c*]quinoline-2,4(3a*H*)-dione* (**4d**). Triphosgene (= bis(trichloromethyl) carbonate; 43 mg, 0.073 mmol) was added at r.t. in several portions during 1 h to the well-stirred soln. of *cis*-**3d** (99 mg, 0.4 mmol), Et_3N (0.138 ml, 0.1 mmol), and DMAP (= 4-(dimethylamino)pyridine; 20 mg, 0.18 mmol) in benzene (10 ml). The soln was stirred at r.t. for 1 h and then heated at reflux for 4 h. After cooling, the soln was filtered, and the filtrate was evaporated to dryness. H_2O (15 ml) was added to the residue, and the suspension was extracted with benzene (3 × 20 ml). Collected extracts were dried (Na_2SO_4), evaporated, and the residue was separated by CC (SiO_2). Compound **4d** was obtained in 34% yield. White solid. M.p. 150–151° (benzene/hexane). IR: 2956, 2871, 1818, 1700, 1616, 1585, 1496, 1465, 1379, 1344, 1232, 1188, 1165, 1109, 1070, 1008, 979, 935, 918, 777, 763, 679, 638, 532. NMR Spectra: see *Table 2*. EI-MS: 276 (10), 275 (60, M^+), 247 (11), 205 (15), 203 (11), 189 (8), 188 (15), 175 (33), 174 (19), 161 (10), 160 (43), 149 (23), 148 (10), 147 (51), 135 (15), 134 (16), 133 (8), 132 (23), 130 (13), 125 (10), 120 (13), 119 (31), 118 (100), 117 (27), 113 (10), 111 (12), 107 (9), 106 (9), 104 (10), 99 (11), 97 (17), 95 (9), 91 (55),90 (13), 89 12), 85 (32), 83 (26), 81 (13), 78 (11), 77 (40), 76 (10), 71 (40), 70 (16), 69 (25), 65 (16), 57 (81), 56 (13), 55 (41), 51 (19), 44 (42), 43 71), 42 (23), 41 (77). ESI-MS (pos.): 573.2 (25, $[2M + Na]^+$), 314.2 (33, $[M + K]^+$), 298.2 (100, $[M + Na]^+$), 276.2 (12, $[M + H]^+$), 254.2 (6, $[M + Na - CO_2]^+$), 232.2 (5, $[M + H - CO_2]^+$). Anal. calc. for $C_{15}H_{17}NO_4$ (275.30): C 65.44, H 6.22, N 5.09; found: C 65.58, H 6.28, N 5.09.

4. *General Procedure for the Rearrangement of Compounds cis-***3**. Under intensive stirring, the starting compound *cis*-**3** (0.75 mmol) was dissolved at 0° in conc. H_2SO_4 (2 ml), and stirring was continued for 1 h at r.t. The mixture was blended with crushed ice (15 g), the deposited precipitate was filtered with suction, washed with H_2O (10 ml), then with a 3% soln. of $NaHCO_3$ (4 ml) and H_2O, and recrystallized from an appropriate solvent. In the case of *cis*-**3i**, the crude mixture after blending with crushed ice was extracted with $CHCl_3$. The dried (Na_2SO_4) extract was evaporated to dryness and worked-up by CC (SiO_2). The yields are given in *Table 3*, for NMR spectra of compounds **5** and **6**, see *Table 4*.

*4-Butyl-3-hydroxyquinolin-2(1*H*)-one* (**5a**). Prepared from *cis*-**3a** in 71% yield. White solid. M.p. 179–188° (benzene). IR: 3436, 3291, 2956, 2871, 1646, 1625, 1569, 1506, 1405, 1288, 1259, 1218, 1114, 952, 904, 755, 715, 682, 626, 565. EI-MS: 217 (M^+, 20), 188 (13), 176 (11), 175 (100), 174 (14), 146 (19), 129 (8), 128 (22), 117 (10), 115 (8), 91 (7), 90 (7), 77 (13), 43 (7), 41 (9). ESI-MS (pos.): 457.3 (19, $[2M+Na]^+$), 345.8 (45, $[3M+Ca]^{2+}$), 256.2 (21, $[M+K]^+$), 240.2 (81, $[M+Na]^+$), 218.2 (100, $[M+H]^+$). Anal. calc. for $C_{13}H_{15}NO_2$ (217.26): C 71.87, H 6.96, N 6.45; found: C 72.12, H 6.94, N 6.51.

*3-Hydroxy-4-phenylquinolin-2(1*H*)-one* (**5b**). Prepared from *cis*-**3b** in 85% yield. White solid. M.p. 270–271° (benzene). For **5b** (*viridicatin*), m.p. of 266–269° was reported [19]. IR: 3357, 3058, 2994, 2869, 1658, 1635, 1575, 1506, 1409, 1351, 1309, 1292, 1226, 1157, 952, 883, 759, 717, 698, 673, 611, 595. EI-MS: 238 (14), 237 (91, M^+), 236 (100), 191 (6), 190 (22), 180 (23), 165 (7), 152 (14), 118 (10), 95 (8), 90 (8), 77 (18), 76 (16), 57 (11), 43 (12). ESI-MS (pos.): 497.2 (25, $[2M+Na]^+$), 375.7 (56, $[3M+Ca]^{2+}$), 276.2 (36, $[M+K]^+$), 260.2 (100, $[M+Na]^+$), 238.2 (40, $[M+H]^+$). Anal. calc. for $C_{15}H_{11}NO_2$ (237.25): C 75.94, H 4.67, N 5.90; found: C 76.02, H 4.71, N 5.83.

*4-Butyl-3-hydroxy-1-methylquinolin-2(1*H*)-one* (**5d**). Prepared from *cis*-**3d** in 72% yield. White solid. M.p. 118–121° (benzene/hexane). IR: 3284, 2958, 2925, 2852, 1644, 1616, 1600, 1506, 1467, 1459, 1415, 1400, 1328, 1249, 1168, 1120, 1049, 954, 848, 781, 744, 682, 646, 599. EI-MS: 231 (22, M^+), 202 (11), 190 (13), 189 (100), 188 (12), 161 (10), 160 (39), 149 (38), 132 (12), 131 (7), 130 (15), 117 (20), 115 (12), 113 (13), 111 (16), 109 (10), 99 (16), 98 (11), 97 (27), 95 (16), 91 (12), 71 (54), 69 (52), 67 (18), 57 (91), 55 (45), 43 (92), 41 (69). ESI-MS (pos.): 485.2 (18, $[2M+Na]^+$), 366.8 (78, $[3M+Ca]^{2+}$), 270.2 (10, $[M+K]^+$), 254.2 (100, $[M+Na]^+$), 232.3 (55, $[M+H]^+$). Anal. calc. for $C_{14}H_{17}NO_2$ (231.29): C 72.70, H 7.41, N 6.06; found: C 72.62, H 7.44, N 6.05.

*3-Hydroxy-1-methyl-4-phenylquinolin-2(1*H*)-one* (**5e**). Prepared from *cis*-**3e** in 93% yield. White solid. M.p. 212–215° (benzene: [19]: 190–191°). IR: 3262, 3064, 2940, 1642, 1623, 1600, 1498, 1463, 1417, 1394, 1346, 1328, 1272, 1162, 1118, 948, 912, 782, 754, 742, 700, 673, 644, 559. EI-MS: 252 (15), 251 (91, M^+), *250* (100), 194 (18), 165 (13), 152 (11), 126 (6), 89 (6), 77 (12), 76 (9), 51 (5). ESI-MS (pos.): 525.2 (21, $[2M+Na]^+$), 396.8 (51, $[3M+Ca]^{2+}$), 290.2 (28, $[M+K]^+$), 274.2 (100, $[M+Na]^+$), 252.2 (53, $[M+H]^+$). Anal. calc. for $C_{16}H_{13}NO_2$ (251.28): C 76.48, H 5.21, N 5.57; found: C 76.45, H 5.21, N 5.74.

*4-Butyl-3-hydroxy-1-phenylquinolin-2(1*H*)-one* (**5g**). Prepared from *cis*-**3g** in 61% yield besides **1g**. White solid. M.p. 167–170° (benzene). IR: 3311, 2960, 2854, 1643, 1622, 1599, 1591, 1562, 1500, 1489, 1458, 1396, 1323, 1302, 1232, 1199, 1176, 1162, 1112, 1068, 1047, 978, 962, 901, 827, 781, 733, 752, 694, 661, 631, 511. EI-MS: 293 (17, M^+), 278 (8), 264 (22), 252 (17), 251 (100), 250 (47), 222 (9), 196 (10), 195 (7), 168 (6), 167 (13), 77 (18), 69 (5), 55 (7), 51 (7), 43 (10), 41 (12). ESI-MS (pos.): 609.3 (18, $[2M+Na]^+$), 459.8 (13, $[3M+Ca]^{2+}$), 332.2 (29, $[M+K]^+$), 316.3 (81, $[M+Na]^+$), 294.3 (100, $[M+H]^+$). Anal. calc. for $C_{19}H_{19}NO_2$ (293.36): C 77.79, H 6.53, N 4.77; found: C 77.64, H 6.53, N 4.40.

*3-Hydroxy-1,4-diphenylquinolin-2(1*H*)-one* (**5h**). Prepared from *cis*-**3h** in 65% yield. White solid. M.p. 254–257° (benzene). IR: 3291, 3062, 1637, 1623, 1602, 1592, 1492, 1455, 1392, 1322, 1272, 1191, 1126, 1068, 985, 954, 823, 755, 744, 694, 659, 615, 516. EI-MS: 314 (21), 313 (100, M^+), 312 (98), 256 (16), 254 (15), 179 (9), 178 (6), 152 (9), 151 (5), 127 (10), 77 (19), 51 (11). ESI-MS (pos.): 649.2 (10, $[2M+Na]^+$), 489.7 (10, $[3M+Ca]^{2+}$), 352.2 (14, $[M+K]^+$), 336.2 (100, $[M+Na]^+$), 314.2 (25, $[M+H]^+$). Anal. calc. for $C_{21}H_{15}NO_2$ (313.35): C 80.49, H 4.82, N 4.47; found: C 80.35m, H 4.80, N 4.42.

*3-Hydroxyquinolin-2(1*H*)-one* (**6c**). Prepared from *cis*-**3c** in 59% yield. White solid. M.p. 263–270° (benzene). For **6c**, m.p. 261–263° was reported [28]. IR: 3276, 3166, 3056, 3000, 1654, 1625, 1612, 1575, 1504, 1400, 1349, 1290, 1274, 1249, 1184, 1126, 939, 906, 862, 755, 736, 701, 603, 551. ESI-MS (pos.): 522.2 (8, $[3M+K]^+$), 361.2 (10, $[2M+K]^+$), 345.1 (48, $[2M+Na]^+$), 342.2 (35, $[4M+Ca]^{2+}$), 261.7 (80, $[3M+$

$Ca]^{2+}$), 200.1 (6, $[M+K]^+$), 184.1 (100, $[M+Na]^+$), 162.2 (33, $[M+H]^+$). Anal. calc. for $C_9H_7NO_2$ (161.16): C 67.07, H 4.38, N 8.69; found: C 66.88, H 4.55, N 8.62.

*3-Hydroxy-1-methylquinolin-2(1*H*)-one* (**6f**). Prepared from *cis*-**3f** in 63% yield. White solid. M.p. 168–179°, then 187–189° (benzene/cyclohexane: [29]: 186°). IR: 3251, 3037, 1654, 1617, 1600, 1504, 1465, 1421, 1334, 1299, 1245, 1182, 1116, 1041, 933, 883, 777, 752, 738, 727, 682, 532. EI-MS: 175 (65, M^+), 167 (10), 155 (7), 149 (22), 147 (36), 146 (12), 141 (10), 127 (15), 125 (18), 123 (14), 122 (9), 118 (22), 113 (32), 111 (29), 109 (16), 99 (22), 97 (35), 95 (21), 91 (11), 90 (6), 85 (52), 83 (43), 81 (25), 77 (15), 71 (87), 70 (19), 69 (43), 67 (12), 57 (100), 56 (29), 55 (34), 43 (51), 41 (19). ESI-MS (pos.): 564.2 (27, $[3M+K]^+$), 389.2 (74, $[2M+K]^+$), 373.2 (38, $[2M+Na]^+$), 370.1 (13, $[4M+Ca]^{2+}$), 282.7 (90, $[3M+Ca]^{2+}$), 214.1 (14, $[M+K]^+$), 198.2 (69, $[M+Na]^+$), 176.2 (100, $[M+H]^+$). Anal. calc. for $C_{10}H_9NO_2$ (175.18): C 68.56, H 5.18, N 8.00; found: C 68.36, H 5.23, N 7.89.

*3-Hydroxy-1-phenylquinolin-2(1*H*)-one* (**6i**). Prepared from *cis*-**3i** in 58% yield. White solid. M.p. 184–185° (benzene/hexane). IR: 3255, 3029, 1650, 1631, 1600, 1488, 1459, 1411, 1317, 1290, 1234, 1184, 1124, 1074, 944, 904, 881, 777, 761, 752, 696, 667, 613. ESI-MS (pos.): 513.2 (5, $[2M+K]^+$), 497.2 (40, $[2M+Na]^+$), 494.1 (6, $[4M+Ca]^{2+}$), 375.7 (19, $[3M+Ca]^{2+}$), 276.2 (7, $[M+K]^+$), 260.2 (100, $[M+Na]^+$), 238.2 (36, $[M+H]^+$). Anal. calc. for $C_{15}H_{11}NO_2$ (237.25): C 75.94, H 4.67, N 5.90; found: C 75.80, H 4.70, N 5.71.

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