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4-HYDROXY-2-QUINOLONES 131*. BROMINATION OF 3-ALLYL-4-HYDROXY-2-OXO-1,2-DIHYDRO-QUINOLINE

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The bromination of 3-allyl-4-hydroxy-2-oxo-1,2-dihydroquinoline by molecular bromine is accompanied by the closure of a five membered furan ring and gives the corresponding 2-bromomethyl-3,9-dihydro-2H-furo[2,3-b]quinolin-4-one.

Keywords: furo[2,3-*b*]quinolines, bromination, heterocyclization, X-ray structural analysis.

Addition of molecular bromine to the unsaturated bond of the allyl fragments in 1-allyl substituted 4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acids and their ethyl esters occurs almost instantly in the absence of any kind of catalyst and is accompanied by the closure of an oxazole ring [2]. 1-Allyl-4-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acid reacts similarly with bromine with the difference that the final reaction product is 2-bromomethyl-4-carboxy-5-methyl-1,2-dihydrooxazolo[3,2-*a*]quinolinium bromide [3] because the tautomeric 1,4-dihydro form cannot occur. Hydrogenation of the benzene part of the N-allylquinolone molecule in no way affects the path of this interesting reaction [4]. But in the case of the 1-allyl-4-hydroxy-2-oxo-1,2-dihydroquinolines and pyridines unsubstituted in position 3 only the 4-bromo-2-bromomethyl-1,2-dihydrooxazolo[3,2-*a*]quinolin- and pyridin-5-ones can be separated because the initially formed 4H-2-bromomethyloxazoles are again brominated by the bromine not taking part in the reaction much more readily than the starting N-allyl derivatives [5].

On the basis of the experiments carried out by us previously we can conclude that a necessary condition for formation of the 2-bromomethyloxazole ring annelated to the azaheterocycle is the presence in the molecule undergoing bromination of an N-allyl-1,2-dihydropyridin-2-one fragment. This does not exclude other nitrogen containing heterocycles containing a carbonyl or, possibly a hydroxyl group in the *ortho* position to the cyclic allyl substituted nitrogen atom undergoing a similar reaction but for now such a proposal has not been confirmed experimentally.

In this investigation we have studied the bromination of 3-allyl-4-hydroxy-2-oxo-1,2-dihydroquinoline (**1**).

* For Communication 130 see [1].

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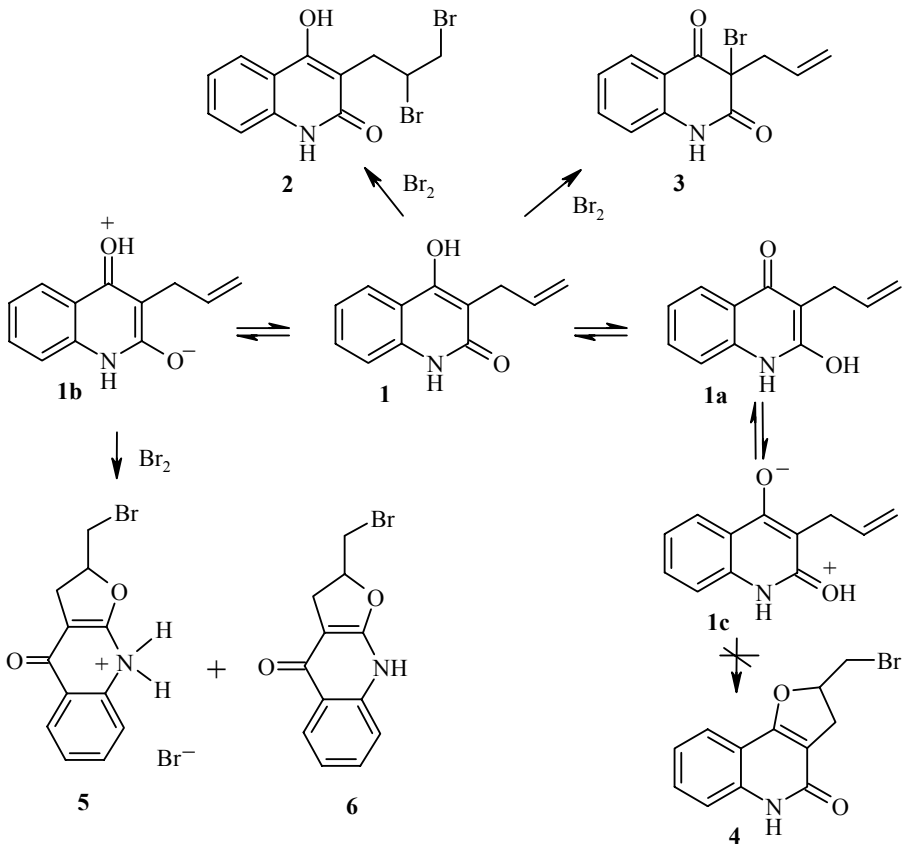


The main difference for this compound from those studied earlier is that the allyl residue is attached to a carbon rather than a nitrogen atom. Hence the reaction is not necessarily accompanied by heterocyclization and can present itself as a normal addition of bromine to the unsaturated allyl bond giving the 2,3-dibromopropyl derivative **2**. We also do not exclude a bromination of the quinolone ring at position 3 [6] characteristic of 3-alkyl-4-hydroxy-2-oxo-1,2-dihydroquinolines to give the 3-allyl-3-bromo-2,4-dioxo-1,2,3,4-tetrahydro-quinoline (**3**). However, if cyclization none the less occurs it leads to a furo- rather than oxazoloquinolone. However, since the allyl substituent is next to two potentially reactive centers (the 2-carbonyl and 4-hydroxy groups) it is possible for two isomeric forms (linear and angular) of the furoquinolin-4-ones to be formed. The actual direction in the case of cyclization will undoubtedly depend on which of the tautomeric forms of the starting allyl derivative **1** or **1a** (or more accurately their high nucleophilicity bipolar mesomeric forms **1b** or **1c**) proves to predominate. Such useful information is sometimes obtained by X-ray structural analysis [7, 8].

With this in mind we have carried out a detailed study of the structure of the starting 3-allylquinolone **1**. The data obtained in this way shows that the bicyclic fragment (plus atoms $O_{(1)}$, $O_{(2)}$, $C_{(10)}$) are planar to within 0.02 Å (Figure 1). The $–CH=CH_{(2)}$ fragment of the allyl substituent is placed perpendicularly to the bicycle plane (torsional angle $C_{(9)}–C_{(8)}–C_{(10)}–C_{(11)}$ 90.0(2)º) and virtually planar with the $C_{(8)}–C_{(10)}$ bond (torsional angle $C_{(8)}–C_{(10)}–C_{(11)}–C_{(12)}$ -2.9(3)º) despite the repulsion between a terminal CH_2 group hydrogen atom and the $C_{(8)}$ atom (intramolecular shortened contact $H_{(12a}\cdots C_{(8}$ 2.68 Å (sum of van der Waal radii 2.87 Å [9])). The hydroxyl group hydrogen is twisted towards the allyl substituent which leads to shortened intramolecular contacts $H_{(10a)}\cdots H_{(2O)}$ 2.08 (2.34) and $H_{(5)}\cdots O_{(2)}$ 2.42 Å (2.46 Å). The repulsion between the sterically close substituents causes an increase in the valence angles $O_{(2)}–C_{(7)}–C_{(8)}$ to 125.1(1) and $C_{(7)}–C_{(8)}–C_{(10)}$ to 123.3(1)º when compared with the angles $O_{(2)}–C_{(7)}–C_6$ 113.5(1) and $C_{(9)}–C_{(8)}–C_{(10)}$ 117.6(1)º.

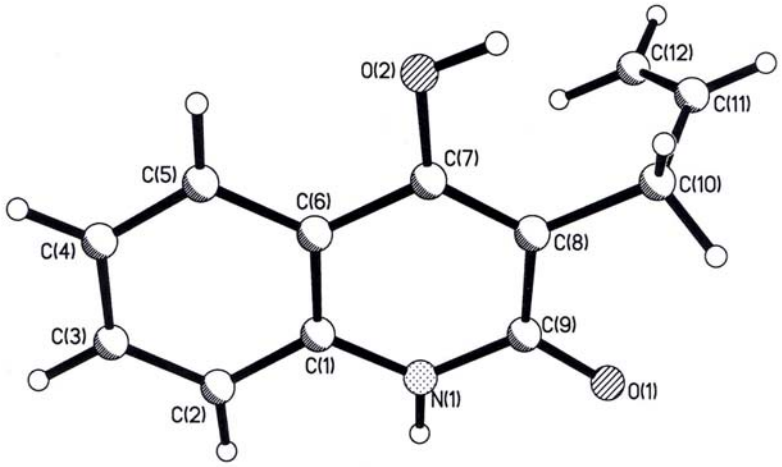


Fig. 1. Structure of the 3-allyl-substituted quinolone **1** with atomic numbering.

Lengthening of the $N_{(1)}$–$C_{(1)}$ 1.380(2) and $N_{(1)}$–$C_{(9)}$ 1.364(2) Å bonds are noted in the allylquinolone **1** when compared with their mean values [10] of 1.353 and 1.339 Å respectively. The $C_{(8)}$–$C_{(7)}$ 1.369(2) and $O_{(1)}$–$C_{(9)}$ 1.265(1) Å bonds are also lengthened when compared with their mean values of 1.326 and 1.210 Å respectively but the $C_{(8)}$–$C_{(9)}$ bond 1.441(2) Å is shortened (mean value 1.455 Å) and this points to a marked delocalization of electron density into the pyridine ring. This also encourages the formation of an intermolecular hydrogen bond $O_{(2)}$–$H_{(2O)}$···$O_{(1)}$ (-0.5+x, 0.5-y, 0.25 –z) H···O 1.84 Å, O–H···O 156º. However the length of the $O_{(2)}$–$C_{(7)}$ bond 1.345(2) Å proves comparable with its mean value of 1.333 Å. In contrast to the 4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acid derivatives [7, 8] the indicated features are in fact characteristic of 3-alkyl substituted derivatives and are repeatedly seen in compounds studied before [11, 12].

Hence, despite some structural grounds, it is not correct to propose a marked contribution of the bipolar 1,4-dihydro form **1b** to a resonance hybrid of the 3-allylquinolone **1**. Thus prediction of the route for the heterocyclization did not prove possible on the basis of the X-ray structural analysis of the starting compound

Similarly to the N-allyl substituted 1,2-dihydroquinolin-2-one, the $C_{(3)}$-allyl derivative **1** in glacial acetic acid gave an immediate decolorization of an added equimolar amount of bromine. The result was a technical product which chromato mass spectrometry showed to contain two substances **A** and **B** with molecular weight 280 amu each in the ratio 2: 1 and giving molecular ion peaks as doublets of approximately equal intensity and characteristic of monobromo compounds. This feature, on the one hand, allows us to exclude the 2,3-dibromo derivative **2** from the number of possible products from the reaction studied, even more unlikely because of the observation in the ^{1}H NMR spectrum of a diastereotopic CH_2Br group having the form of two double doublets and, on the other hand, serving as evidence for the change upon brominative heterocyclization since the NMR spectra of both compounds obtained clearly do not correspond to the C_3 allyl structure **3**.

Hence the analytical problem is significantly simplified and results only in the determination of which of the furoquinolines obtained is linear and which has an angular structure. The reaction mixture was separated by crystallization from ethanol. When the ^{1}H NMR spectra of the separated individual furoquinoline (the main **A** and minor **B**) isomers were studied it was found that they had common spin systems with some differences in the proton chemical shift values. Immediately after solution of sample **B** a series of spectral signals were broadened but, after heating for a short time and then cooling, gave sharp signals for all of the protons. Only the water signal remained broadened and this was likely associated with proton exchange. In the proton spectrum of substance **A** all of the signals were quite sharp. The signals for the NH group protons in both samples were

absent, evidently due to rapid deuterium exchange. By contrast, when measuring the carbon spectrum of product **B** a series of signals remained broadened to the extent that they almost failed to appear in the spectrum. No such anomaly was seen in the carbon spectrum of furoquinoline **A**.

For elucidation of the structure of the products obtained we have measured their heteronuclear 2D HMQC and HMBC spectra correlations. Use of the first method allows assignment of the signals of the proton bearing carbon atoms and the second gave the possibility of assigning the quaternary carbon atom signals via $^{1}H–^{13}C$ correlation through 2-3 chemical bonds. The Scheme below shows the assignment of signals for the furoquinoline **A** and the arrows show the HMBC correlations which served as the basis for assigning the quaternary carbon atom signals. All of the correlations found for this compound are presented in Table 1.

Key in establishing the structure of this compound is the correlation of the methine signal of the dihydrofuran ring which absorbs at 5.49 ppm with the low field carbon signals absorbing at 164.6 and 165.3 ppm. As follows from its correlation with the aromatic proton signals the first of these corresponds to the pyridine $C_{(4)}$ atom and the second to the $C_{(9a)}$ atom in the same ring. The signal with a chemical shift of 165.3 ppm has multi correlations with the signals for the aliphatic protons of the dihydrofuran ring. Looking at the formulae for the angular and linear structural isomers it can be seen that the signal for the furan CH proton in the angular isomer would be correlated with the same low field carbon signal (164.6 ppm) as the signals of the aromatic protons since, in this case, the given protons are removed by three chemical bonds from the relevant carbon atom. In fact, this correlation is not observed. On the other hand, in the alternative linear isomer the signal at 5.49 ppm must correlate with the $C_{(9a)}$ signal of the pyridine ring with which the aromatic signals do not correlate. Such a situation is actually seen in the main furoquinoline **A**. Hence we can deduce that it has the linear structure.

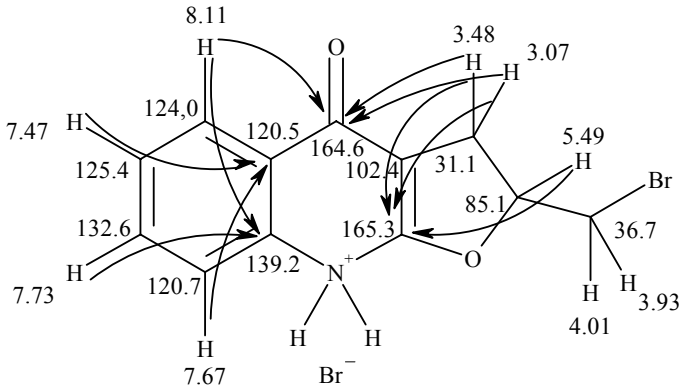
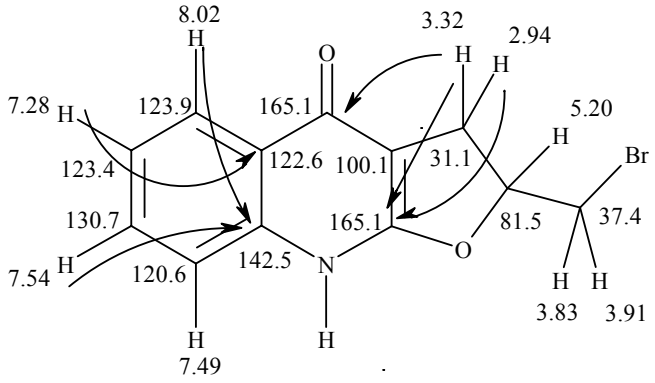


TABLE 1. Heteronuclear ^{1}H-^{13}C Correlations found for the Main Product **A** (Furoquinolone Hydrobromide **5**)

δ, ppm	HMQC	HMBC
8.11	124.0	164.6; 139.2; 132.6; 120.5
7.73	132.6	139.2; 124.0; 120.5
7.67	120.7	164.6; 125.4; 120.5
7.47	125.4	139.2; 132.6; 124.0; 120.5
5.49	85.1	165.3; 36.7
4.01	36.7	31.1; 85.1
3.93	36.7	31.1; 85.1
3.48	31.1	165.3; 164.6; 36.7; 120.5; 102.4; 85.1
3.07	31.1	165.3; 164.6; 36.7; 120.5; 102.4; 85.1

As noted above, in the carbon spectrum of the minor furoquinoline **B** many signals are broadened and it would be expected that a number of heteronuclear correlations would be lost in it. The scheme shows the assignment of signals in the proton and carbon spectra of this product and the correlations found in the HMBC spectrum are given. As in the previous example, the assignment of the signals for the protonated carbon atoms were made using the HMQC spectrum. A full list of the correlations found is given in Table 2.



Overall, the set of correlations obtained from the HMBC spectrum is similar to that for the preceding compound but a number of very important correlations are absent. Hence, in particular, a correlation of the low field carbon signal at 165.1 ppm (assigned to the two atoms $C_{(4)}$ and $C_{(9a)}$ together) with the CH proton signal of the dihydrofuran ring at 5.20 ppm is not observed. Hence an angular (or indeed linear) structure for compound **B** cannot be confirmed or contradicted in this case.

Since the furoquinolone **A** unambiguously has a linear structure it would be logical to characterize the minor isomer **B** as the angular 2-bromomethyl-3,5-dihydro-2H-furo[3,2-*c*]quinolin-4-one (**4**) by exclusion. However, as this conclusion is largely hypothetical we have used UV spectrophotometry to reach a more rigid proof as this provides a reliable distinction between linear and angular structures. It was unexpectedly found that the UV spectra of both compounds were virtually identical (Fig. 2) and this points to an essentially identical system of conjugated bonds, i.e. a linear 2-bromomethyl-3,9-dihydro-2H-furo[3,2-*b*]quinolin-4-one ring.

TABLE 2. Heteronuclear ^{1}H-^{13}C Correlations found for the Minor Product **B** (Furoquinolone Base **6**)

δ, ppm	HMQC	HMBC
8.02	123.9	142.5; 130.7
7.54	130.7	142.5; 123.9
7.49	120.6	123.4
7.28	123.4	130.7; 122.6
5.20	81.5	37.4
3.91	37.4	31.1; 81.5
3.83	37.4	31.1; 81.5
3.32	31.1	37.4; 165.1; 100.1; 81.5
2.94	31.1	37.4; 165.1; 100.1; 81.5

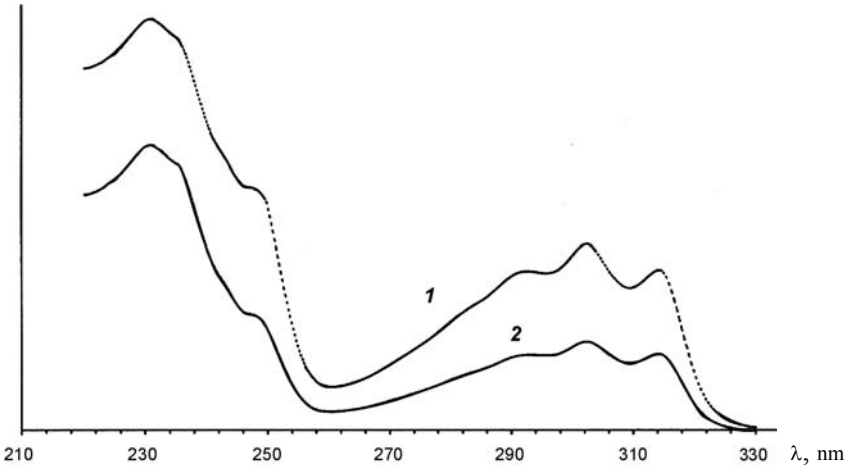


Fig. 2. The UV spectra in ethanol: 1 – furoquinolone **6**; 2 – its hydrobromide **5.**

From a correlation of the analytical results of all of the investigations above the limited differences in the properties of the furoquinolines **A** and **B** can only be explained through salt formation. In fact, an aqueous alcohol solution of the main material **A** gives a characteristic identification of bromide ions when treated with silver nitrate and this gives conclusive evidence that it is the 2-bromomethyl-3,9-dihydro-2H-furo-[3,2-*b*]quinolin-4-one hydrobromide (**5**). On the other hand, the minor isomer of this reaction **B** does not give such a reaction since it is the furoquinolone base **6** formed via the partial hydrolysis of hydrobromide **5** and a reverse reaction can be readily carried out by treatment with hydrobromic acid. It should be noted that such

TABLE 3. Bond Lengths (*l*) in the 3-Allyl Substituted Quinolone Structure **1**

Bond	*l*, Å	Bond	*l*, Å
$N_{(1)}$–$C_{(9)}$	1.364(2)	$N_{(1)}$–$C_{(1)}$	1.380(2)
$O_{(1)}$–$C_{(9)}$	1.265(2)	$O_{(2)}$–$C_{(7)}$	1.345(2)
$C_{(1)}$–$C_{(6)}$	1.398(2)	$C_{(1)}$–$C_{(2)}$	1.402(2)
$C_{(2)}$–$C_{(3)}$	1.376(2)	$C_{(3)}$–$C_{(4)}$	1.392(3)
$C_{(4)}$–$C_{(5)}$	1.371(3)	$C_{(5)}$–$C_{(6)}$	1.414(2)
$C_{(6)}$–$C_{(7)}$	1.451(2)	$C_{(7)}$–$C_{(8)}$	1.369(2)
$C_{(8)}$–$C_{(9)}$	1.441(2)	$C_{(8)}$–$C_{(10)}$	1.517(2)
$C_{(10)}$–$C_{(11)}$	1.484(3)	$C_{(11)}$–$C_{(12)}$	1.279(4)

TABLE 4. Valence Angles (ω) in the 3-Allyl Substituted Quinolone Structure **1**

Angle	ω, deg	Angle	ω, deg
$C_{(9)}$–$N_{(1)}$–$C_{(1)}$	124.3(1)	$N_{(1)}$–$C_{(1)}$–$C_{(6)}$	119.0(1)
$N_{(1)}$–$C_{(1)}$–$C_{(2)}$	120.2(1)	$C_{(6)}$–$C_{(1)}$–$C_{(2)}$	120.8(1)
$C_{(3)}$–$C_{(2)}$–$C_{(1)}$	119.3(2)	$C_{(2)}$–$C_{(3)}$–$C_{(4)}$	120.4(2)
$C_{(5)}$–$C_{(4)}$–$C_{(3)}$	121.2(2)	$C_{(4)}$–$C_{(5)}$–$C_{(6)}$	119.6(2)
$C_{(1)}$–$C_{(6)}$–$C_{(5)}$	118.7(1)	$C_{(1)}$–$C_{(6)}$–$C_{(7)}$	118.0(1)
$C_{(5)}$–$C_{(6)}$–$C_{(7)}$	123.3(1)	$O_{(2)}$–$C_{(7)}$–$C_{(8)}$	125.1(1)
$O_{(2)}$–$C_{(7)}$–$C_{(6)}$	113.5(1)	$C_{(8)}$–$C_{(7)}$–$C_{(6)}$	121.5(1)
$C_{(7)}$–$C_{(8)}$–$C_{(9)}$	119.1(1)	$C_{(7)}$–$C_{(8)}$–$C_{(10)}$	123.3(1)
$C_{(9)}$–$C_{(8)}$–$C_{(10)}$	117.6(1)	$O_{(1)}$–$C_{(9)}$–$N_{(1)}$	117.7(1)
$O_{(1)}$–$C_{(9)}$–$C_{(8)}$	124.2(1)	$N_{(1)}$–$C_{(9)}$–$C_{(8)}$	118.1(1)
$C_{(11)}$–$C_{(10)}$–$C_{(8)}$	114.8(2)	$C_{(12)}$–$C_{(11)}$–$C_{(10)}$	127.0(2)

structures are also not inconsistent with the mass spectrometric data which give very similar experimental spectra for the furoquinolones **5** and **6** only further confirming the fact (initially overlooked by us) that the mass spectra of amines with inorganic acids are usually identical to the spectra of the starting amines [13].

Hence bromination of 3-allyl-4-hydroxy-2-oxo-1,2-dihydroquinoline by molecular bromine is accompanied by heterocyclization to give tricyclic 2-bromomethyl-3,9-dihydro-2H-furo[2,3-*b*]quinolin-4-one molecular systems.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra for the furoquinolones **5** and **6**, 2D COSY ^{1}H NMR spectroscopy, and the heteronuclear HMQC and HMBC correlation spectra were measured on a Varian Mercury-400 instrument (400 and 100 MHz respectively). All of the 2D experiments were carried out with gradient selection of useful signals. The mixing times in the pulse sequences were $^1H_{CH}$ = 140 and $^{2-3}J_{CH}$ = 8 Hz. The number of increments in the COSY and HMQC spectra was 128 and in the HMBC 400. In all cases DMSO-d_6 was used as solvent and TMS as internal standard. Chromato mass spectra were recorded on an Agilent 1100 LC/MSD spectrometer capable of APCI (positive chemical ionization at atmospheric pressure). The chromato-mass spectrometric column parameters were: length 50 mm, diameter 4.6 mm, stationary phase ZORBAX Eclipse XDB-C18, solvent aqueous acetonitrile, gradient elution, rate of solvent elution 2.4 ml/min. UV Spectra were taken on a Specord M-40 instrument using ethanol as solvent.

3-Allyl-4-hydroxy-2-oxo-1,2-dihydroquinoline (1) was prepared by the method reported before [14]

2-Bromomethyl-3,9-dihydro-2H-furo[3,2-*b*]quinolin-4-one hydrobromide (5). A. Bromine (0.52 ml, 0.01 mol) was added with stirring to a solution of compound **1** (2.01 g, 0.01 mol) in acetic acid (15 ml) and was immediately decolorized. After several minutes a white precipitate began to appear. After 1 h the reaction mixture was diluted with cold water. The precipitated solid was filtered off, washed with cold water, dried, and crystallized from ethanol. The colorless crystals produced were separated and repeatedly crystallized from aqueous acetone to give the furoquinolone hydrobromide **5** (1.94 g, 53%) (precipitation of salt **5** from the mixture using anhydrous ether gave a yield of 96%); mp 228-230ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.11 (1H, d, *J* = 7.9, H-5); 7.73 (1H, t, *J* = 7.4, H-7); 7.67 (1H, d, *J* = 8.1, H-8); 7.47 (1H, t, *J* = 7.4, H-6); 5.49 (1H, m, CHO); 4.01 (1H, dd, *J* = 11.2, 3.9, CHBr); 3.93 (1H, dd, *J* = 11.2, 5.4, CHBr); 3.48 (1H, dd, *J* = 15.7, 10.3, H-3); 3.07 (1H, dd, *J* = 15.7, 6.1, H-3). ^{13}C NMR spectrum, δ, ppm: 165.3 ($C_{(9a)}$), 164.6 (C=O), 139.2 ($C_{(8a)}$), 132.6 ($C_{(7)}$), 125.4 ($C_{(6)}$), 124.0 ($C_{(5)}$), 120.7 ($C_{(80}$), 120.5 ($C_{(4a)}$), 102.4 ($C_{(3a)}$), 85.1 (CHO), 36.7 (CH_2Br), 31.3 ($C_{(3}$). Mass spectrum, *m/z** (I_{rel}, %): 280 $[M\text{-}HBr+H]^+$ (100), 200 $[M\text{-}HBr\text{-}Br+H]^+$ (5). Found, %: C 40.03; H 3.15; N 3.76. $C_{12}H_{10}BrNO_2$.HBr. Calculated, %: C 39.92; H 3.07; N 3.88.

B. A mixture of conc. HBr and ethanol (1: 10) was added to a solution of the furoquinolone **6** (2.8 g, 0.01 mol) to pH ~ 5 after which it was cooled in ice. The precipitated hydrobromide **5** was filtered off, washed with acetone, and dried. Yield 3.28 g (91%). A mixed sample with the hydrobromide **5** obtained by method **A** did not give a melting point depression. The ^{1}H NMR spectra of these compounds were identical.

2-Bromomethyl-3,9-dihydro-2H-furo[3,2-b]quinolin-4-one (6). The alcoholic filtrate obtained after removal of the salt **5** (see method A in the preceding example) was diluted with a five fold excess of cold water and left for several hours. The precipitate formed was filtered off and repeatedly crystallized from aqueous acetone to give the furoquinolone **6** (0.62 g, 22%); mp 191-193ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.02 (1H, d, *J* = 7.9, H-5); 7.54 (1H, t, *J* = 7.4, H-7); 7.49 (1H, d, *J* = 8.1, H-8); 7.28 (1H, t, *J* = 7.4, H-6); 5.20 (1H, m, CHO); 3.91 (1H, dd, *J* = 11.2, 4.3, CHBr); 3.83 (1H, dd, *J* = 11.2, 5.2, CHBr); 3.32 (1H, dd, *J* = 15.7, 9.5, H-3); 2.94 (1H, dd, *J* = 15.7, 6.2, H-3). ^{13}C NMR spectrum, δ, ppm: 165.1 ($C_{(9a)}$ + C=O), 142.5 ($C_{(8a)}$), 130.7 ($C_{(7)}$),

* For compounds **5** and **6** the *m/z* values are quoted for the ^{79}Br isotope.

123.9 ($C_{(5)}$), 123.4 (C_6), 122.6 ($C_{(4a)}$), 120.6 ($C_{(8)}$), 100.1 ($C_{(3a)}$), 81.5 (CHO), 37.4 (CH_2Br), 31.1 ($C_{(3)}$). Mass spectrum, *m/z* (I_{rel}, %): 280 $[M+H]^+$ (100), 200 $[M-Br+H]^+$ (5). Found, %: C 51.53; H 3.69; N 5.06. $C_{12}H_{10}BrNO_2$. Calculated, %: C 51.45; H 3.60; N 5.00.

X-ray structural investigation. Crystals of the 3-allyl substituted quinolone **1** are tetragonal (ethanol), at 20ºC: a = 10.551(1), c = 18.505(3) Å, V = 2059.9(4) Å^3, M_r = 201.22, Z = 8, space group $P4_32_12$, d_{calc} = 1.298 g/cm^3, μ(MoKα) = 0.089 mm^{-1}, F(000) = 848. The unit cell parameters and intensities of 18,451 reflections (3000 independent, R_{int} = 0.044) were measured on an Xcalibur-3 automatic four circle diffractometer (MoKα radiation, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ = 60º). The structure was solved by a direct method using the SHELXTL program package [15]. The positions of the hydrogen atoms were revealed from electron density difference synthesis and refined isotropically. The structure was refined *via* an F^2 full matrix least squares analysis in the anisotropic approximation for non-hydrogen atoms to wR_2 = 0.088 for 2978 reflections (R_1 = 0.039 for 1750 reflections with $F > 4\sigma(F)$, S = 0.859). The full crystallographic information has been placed in the Cambridge structural data bank (deposit reference CCDC 619708). The interatomic distances and valence angles are given in Tables 3 and 4.

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