SYNTHESIS AND INVESTIGATION OF 2-(2-QUINOLYL)-5,6-BENZOCINCHONINIC ACID AND ITS DERIVATIVES

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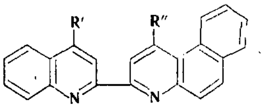
2-(2-Quinolyl)- and 2-(4-phenyl-2-quinolyl)-5,6-benzocinchoninic acids were synthesized, and their derivatives were obtained and decarboxylated. The UV and IR spectra of the compounds were studied, and it was found that all of the new compounds form colored Cu(I) complexes.

The possibility of the formation of bonded heterocyclic systems from quinoline and benzoquinoline rings by the reaction of formylquinaldine with carbonyl compounds and β-naphthylamines was demonstrated by one of us in [1]. A characteristic property of such systems is their ability to form colored Cu(I) complexes.

The aim of the present investigation was the synthesis of 2-(2-quinolyl)- and 2-(4-phenyl-2-quinolyl)-5,6-benzocinchoninic acids, decarboxylation of them, and conversion to acid chlorides, esters, amides, and anilides.



I-XII

The acids were synthesized by condensation of the appropriate formylquinaldine with β-naphthylamine and pyruvic acid. Data characterizing the substances obtained are presented in Table 1.

Decarboxylation of acids I (R' = H, R" = COOH) and VII (R' = Ph, R" = COOH) gave VI (R' = R" = H) and XII (R' = Ph, R" = H), which were identical to 2-(2-quinolyl)- and 2-(4-phenyl-2-quinolyl)-5,6-benzoquinolines obtained by condensation of azomethines of formylquinaldine with formalin [1,2].

The disappearance of the absorption band at 1730 cm^{-1} of the carbonyl group of the carboxyl grouping in the IR spectra after decarboxylation confirms structures VI and XII. Three absorption bands, apparently associates with $\pi-\pi*$ transitions, appear in the UV spectra of alcohol solutions of the synthesized compounds (Table 2). The introduction of a phenyl group into the 4 position of the quinoline ring leads to a bathochromic shift and increases the absorption intensity, particularly in the short-wave portion of the spectrum.

Some conclusions regarding the unsaturated character of the double bond of the carbonyl group in the compounds obtained can be drawn on the basis of the IR spectra (Table 2). Depending on the character of R in the $R-\overset{\overset{O}{\|}}{C}-X$ grouping, $\nu_{(CO)}$ increases on passing from the diethylamino group to chlorine; this attests to an increase in the unsaturated character of the bond.

An investigation of the reaction of the synthesized substances with Cu(I) ions demonstrated that they form alcohol-soluble, red-violet complexes, the intensity of the coloration of which depends on the structure and increases when a phenyl group is introduced into the 4 position of the quinoline ring.

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TABLE 1. 2-(2-Quinolyl)-5,6-benzocinchoninic Acid and Its Derivatives

Comp.	R′	R″	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
I	H	COOH	259—260	$C_{23}H_{14}N_2O_2$	78,8	4,1	7,7	78,8	4,0	8,0	30
II	H	COCl	247—249	$C_{23}H_{13}N_2OCl$	74,8	3,6	7,4	74,9	3,5	7,6	96
III	H	$CON(C_2H_5)_2$	188	$C_{27}H_{23}N_3O$	80,0	5,6	10,0	79,9	5,7	10,1	65
IV	H	$COOC_5H_{11}$	119—120	$C_{28}H_{24}N_2O_2$	80,1	5,6	6,5	80,0	5,7	6,6	60
V	H	$CONHC_6H_5$	325—326	$C_{29}H_{19}N_3O$	82,2	4,4	9,7	82,1	4,5	9,8	70
VI	H	H	212	$C_{22}H_{14}N_2$	86,3	4,5	9,0	86,2	4,7	9,1	40
VII	C_6H_5	COOH	271—272	$C_{29}H_{18}N_2O_2$	81,5	4,4	6,3	81,7	4,2	6,3	38
VIII	C_6H_5	COCl	251—253	$C_{29}H_{17}N_2OCl$	76,0	3,7	6,1	76,1	3,8	6,3	95
IX	C_6H_5	$CON(C_2H_5)_2$	219	$C_{33}H_{27}N_3O$	82,4	5,5	8,6	82,3	5,6	8,5	70
X	C_6H_5	$COOC_5H_{11}$	191—192	$C_{34}H_{28}N_2O_2$	82,4	5,5	5,5	82,2	5,7	5,4	64
XI	C_6H_5	$CONHC_6H_5$	338—339	$C_{35}H_{23}N_3O$	83,6	4,4	8,2	83,8	4,6	8,3	76
XII	C_6H_5	H	228—230	$C_{28}H_{18}N_2$	88,0	5,0	7,1	87,9	4,8	7,3	43

TABLE 2. Spectral Characteristics of the Reagents and Their Cu(I) Complexes

Comp.	UV spectra	IR spectra	Cu(I) complex, solution in isoamyl alcohol	
№	λ_{max}, nm (lg ε)	ν_{CO}, cm^{-1}	λ_{max}	lg ε
I	276(4,73) 326(4,35), 366(3,91)	1730	535	3,86
II	—	1760	—	—
III	280(4,66), 328(4,39), 369(3,89)	1634	538	3,87
IV	282(4,67), 327(4,44), 370(3,97)	1759	542	3,89
V	280(4,75), 327(4,45), 368(3,99)	1688	538	3,92
VI	280(4,62), 327(4,35), 365(3,96)	—	535	3,86
VII	281(4,81), 330(4,37), 368(3,99)	1730	538	3,97
VIII	—	1760	—	—
IX	280(4,82), 328(4,45), 369(4,00)	1635	540	3,98
X	285(4,70), 331(4,37), 370(3,91)	1761	548	3,98
XI	283(4,76), 330(4,39), 370(3,93)	1688	550	4,01
XII	285(4,69), 330(4,35), 365(4,07)	—	540	3,97

EXPERIMENTAL

The UV spectra were recorded with an SF-4A spectrophotometer. The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. The spectra of solutions of the Cu(I) complexes in isoamyl alcohol were recorded with an SF-4A spectrophotometer. The general method of the preparation of alcohol solutions of the complexes consisted in vigorous stirring of an alcohol solution of the complexing agent with an aqueous solution containing copper nitrate, acetate buffer (pH 6.4), and hydroxylamine hydrochloride.

2-(2-Quinolyl)-5,6-benzocinchoninic Acid (I). A 1.57-g (0.01 mole) sample of formylquinaldine and 1.43 g (0.01 mole) of β-naphthylamine were dissolved in 25 ml of ethanol, a solution of 1.76 g (0.02 mole) of pyruvic acid in 2 ml of ethanol and 1 ml of concentrated hydrochloric acid was added, and the mixture was refluxed with stirring for 1.5 h and cooled. The resulting precipitate was separated and introduced into 250 ml of water. The solution was made alkaline with potassium hydroxide and heated until all of the solid dissolved. The hot solution was filtered, and the filtrate was acidified with acetic acid. The precipitated I was washed with water and reprecipitated once more. Crystallization from dimethylformamide gave I as a white crystalline powder.

2-(2-Quinolyl)-5,6-benzocinchoninyl Chloride (II). A 3.50-g (0.01 mole) sample of I was refluxed with 80 ml of thionyl chloride. The excess thionyl chloride was removed by distillation, initially at normal pressure and then in vacuo. The residual yellow powdered II was suitable for subsequent transformations without additional purification. Crystallization from anhydrous benzene gave long yellow prisms.

2-(2-Quinolyl)-5,6-benzocinchoninic Acid Diethylamide (III). A 3.69-g (0.02 mole) sample of II was refluxed with 40 ml of anhydrous diethylamine for 2 h. The mixture was cooled, and the precipitate was separated and washed with hot water and an ammonia–methanol mixture (1 : 1). Crystallization from dimethylformamide gave III as a white crystalline powder.

Isoamyl 2-(2-Quinolyl)-5,6-benzocinchoninate (IV). A 3.69-g (0.01 mole) sample of II was refluxed for 1.5 h with 20 ml of anhydrous isoamyl alcohol. The dark solution was cooled and treated with 50% aqueous methanol until precipitation was complete. The precipitate was removed by filtration, washed with warm methanol, and crystallized from dimethylformamide to give IV as a white crystalline powder.

2-(2-Quinolyl)-5,6-benzocinchoninic Acid Anilide (V). A 3.69-g (0.01 mole) sample of II was refluxed for 1.5 h with 40 ml of aniline. The mixture was cooled, and the precipitate was separated and washed with hot water and an ammonia–methanol mixture (1 : 1). Crystallization from dimethylformamide gave V as a white powder.

2-(2-Quinolyl)-5,6-benzoquinolyl (VI). A 3.68-g (0.01 mole) sample of I was heated in an infusible test tube at 260-270° for 30 min. The test tube was cooled after the evolution of carbon dioxide gas bubbles ceased and the mass had been converted to a homogeneous melt. The solidified melt was pulverized and crystallized from isoamyl alcohol or dimethylformamide to give VI as a white crystalline powder.

2-(4-Phenyl-2-quinolyl)-5,6-benzocinchoninic Acid (VII). As in the preparation of I, 2.3 g (0.01 mole) of 4-phenylformylquinaldine and 1.43 g (0.01 mole) of β-naphthylamine gave VII as a white crystalline powder (from dimethylformamide).

The preparation of acid chloride VIII, diethylamide IX, isoamyl ester X, and anilide XI and decarboxylation with conversion to XII were accomplished via the methods presented above for derivatives of I.

LITERATURE CITED

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