

ethanol) gave a peak of 280 $m\mu$ typical for indoles and it did not change after acidification. The nmr spectrum contained five peaks and was interpreted after integration as representative of eight aromatic hydrogens (τ 1.0–3.0), two pyrrole N-H, two N-NH₂, four CH₂, and two indole-2 hydrogens.

2-Hydrazino-8-quinolinol and Derivatives¹

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Hydrazones of carbonyl compounds and 2-hydrazino- and 2-(1-methylhydrazino)-8-quinolinols were prepared for antitumor tests. Those hydrazones from formyl-8-quinolinols might be of further interest as bifunctional chelating agents.^{2,3}

2-(1-Methylhydrazino)-8-quinolinol.—2-Chloro-8-quinolinol (1 g) and 0.39 g of methylhydrazine in 1-propanol as solvent were refluxed 24 hr. Evaporation of solvent, addition of 50 ml of water, and neutralization with K₂CO₃ precipitated the product, mp 106° after recrystallization from ligroin (80% yield). The ultraviolet spectra showed λ_{max} [$m\mu$ (log ϵ)]: EtOH, 250 s (4.27), 269 (4.52), 351 (3.56); 0.1 N HCl, 244 (4.23), 269 (4.48), 312 (3.48), 351 (3.71); 0.1 N NaOH, 279 (4.56), 318 s (3.18), 360 s (3.69).

Anal. Calcd for C₁₀H₁₁N₃O: C, 63.48; H, 5.80; N, 22.19. Found: C, 63.49; H, 5.70; N, 22.12.

Preparation of Hydrazones.—Equimolar amounts of the hydrazine and aldehyde or ketone were refluxed in ethanol for 0.5–5 hr to precipitate the hydrazones, generally yellow solids. Aldehydes reacted more quickly than ketones. Filtration of the products and recrystallization, generally from benzene, gave 80–95% yields of the compounds listed in Table I. Absorption spectra of some of these hydrazones were determined as follows for the carbonyl compound: λ_{max}^{EtOH} [$m\mu$ (log ϵ)]: 7-formyl-8-quinolinol, 249 (4.33), 290 s (4.27), 306 (4.40), 381 (4.37), 436 (3.69); 5-acetyl-8-quinolinol, 243 (4.51), 289 (4.46), 359 (4.12); 2-formylpyridine, 238 (4.19), 264 (4.17), 274 s (4.12), 318 s (4.34), 352 (4.45), 439 s (3.30).

TABLE I
HYDRAZONES FROM 2-HYDRAZINO-8-QUINOLINOL AND CARBONYL COMPOUNDS

Carbonyl compd	Mp, °C ^a	Formula	—% carbon—		—% hydrogen—		—% nitrogen—	
			Calcd	Found	Calcd	Found	Calcd	Found
5-Acetyl-8-quinolinol	218	C ₂₀ H ₁₈ N ₄ O ₂	69.75	69.60	4.68	4.75	16.26	16.10
5-Acetyl-2-methyl-8-quinolinol	207	C ₂₁ H ₁₈ N ₄ O ₂	70.38	70.45	5.06	5.20	15.63	15.83
4-Formyl-8-quinolinol	292	C ₁₉ H ₁₄ N ₄ O ₂	69.93	69.24	4.32	4.40	15.94	16.15
5-Formyl-2-methyl-8-quinolinol	233	C ₂₀ H ₁₆ N ₄ O ₂	69.75	69.57	4.68	4.84	16.26	16.11
7-Formyl-8-quinolinol	289	C ₁₉ H ₁₄ N ₄ O ₂	69.93	70.08	4.32	4.52	15.94	16.08
7-Formyl-2-methyl-8-quinolinol	277	C ₂₀ H ₁₆ N ₄ O ₂	69.75	69.53	4.68	4.83	16.26	16.14
7-Formyl-5-methyl-8-quinolinol	268	C ₂₀ H ₁₆ N ₄ O ₂	69.75	69.92	4.68	4.91	16.26	16.09
Salicylaldehyde	239	C ₁₀ H ₈ N ₄ O ₂	68.81	68.43	4.69	4.75	15.04	14.77
p-Dimethylaminobenzaldehyde	239	C ₁₃ H ₁₈ N ₄ O	70.58	70.30	5.92	6.14	18.28	17.98
Pentafluorobenzaldehyde	254	C ₁₃ H ₁₈ F ₅ N ₄ O	54.40	54.23	2.28	2.17	11.89	11.75
Phthalaldehydic acid	225	C ₁₇ H ₁₃ N ₄ O ₃	66.45	66.64	4.26	4.46	13.67	13.47
2-Formylpyridine	214	C ₁₅ H ₁₂ N ₄ O	68.17	68.19	4.57	4.66	21.19	21.32
3-Formylpyridinium methiodide	231	C ₁₆ H ₁₃ IN ₄ O					13.79	14.60
4-Antipyrinecarboxaldehyde	248	C ₂₁ H ₁₉ N ₃ O	67.55	67.33	5.13	5.17	18.74	18.53
Salicylaldehyde ^b	206	C ₁₇ H ₁₃ N ₃ O ₂	69.62	69.90	5.15	5.30	14.32	13.96

^a Upper end of a 1–2° range. ^b Hydrazone of 2-(1-methylhydrazino)-8-quinolinol.

Experimental Section⁴

2,8-Quinolinediol⁵ was tosylated and chlorinated with PCl₅–POCl₃ in agreement with the literature,⁶ although final hydrolysis with alkali to 2-chloro-8-quinolinol gave a product of substantially higher melting point (83–84°) than reported.

2-Hydrazino-8-quinolinol.—2-Chloro-8-quinolinol (5 g) was refluxed in 20 ml of 40% hydrazine for 4 hr. Solvent was removed under vacuum and 15 ml of water was added to precipitate the product. Recrystallization from 95% ethanol yielded a tan solid, mp 177–178° (81% yield).

Anal. Calcd for C₉H₉N₃O: C, 61.70; H, 5.17; N, 23.97. Found: C, 61.87; H, 5.09; N, 23.84.

Although reasonably stable as the solid, the hydrazine in solution decomposed in a few hours. The ultraviolet spectra in various solvents showed λ_{max} [$m\mu$ (log ϵ)]: EtOH, 245 (4.27), 263 (4.46), 280 s (4.04); 0.1 N HCl, 240 (4.12), 264 (4.40), 304 (3.87), 340 s (3.52); 0.1 N NaOH, 252 (4.36), 274 s (4.02), 330 (3.46), 356 s (3.41). The infrared spectra (KBr) showed bands at 3345, 3330, 1520, 1240, 820, and 738 cm⁻¹ (strongest bands).

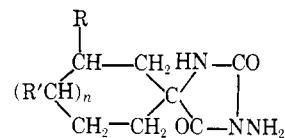
3-Aminospirhydantoin

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Some 3-amino-5,5-disubstituted hydantoin have a pronounced diuretic effect.² Such hydantoin have been prepared from the dihydrazide of α -substituted glycine-N-carboxylic acids,^{2–5} and



- I, $n = 0$; R = H IV, $n = 3$; R, R' = H
 II, $n = 1$; R, R' = H V, $n = 1$; R = CH₃; R' = H
 III, $n = 2$; R, R' = H VI, $n = 1$; R = H; R' = CH₃

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