SYNTHESIS OF 4-NITRO-3,3,7-TRIMETHYL-2-(2-HYDROXYSTYRYL)INDOLENINES

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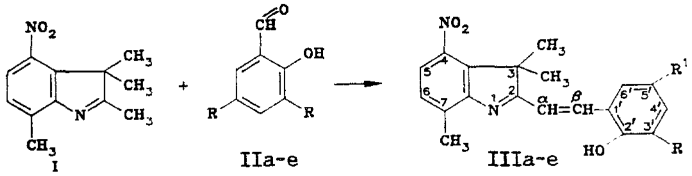
The previously unknown hydroxystyrylindolenines have been synthesized by the direct condensation of 4-nitro-2,3,3,7-tetramethylindolenine with substituted salicylaldehydes. The structure of the prepared compounds has been confirmed by spectroscopic investigation.

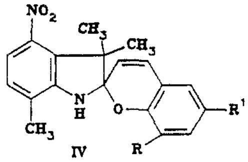
It is known that the hydrogen halide salts of 2,3,3-trimethyl- and 5-nitro-2,3,3-trimethylindolenines [1] and also 2,3,3-trimethylindolenine [2] react with aromatic aldehydes at the 2-methyl group to form styryl-substituted indolenines. In this work we have synthesized the novel styrylindolenines IIIa-e by condensation of 4-nitro-2,3,3,7-tetramethylindolenine I with substituted salicylaldehydes II:



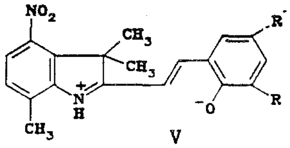
I IIa-e IIIa-e

II, IIIa $R=OCH_3$, $R^1=NO_2$; b $R=H$, $R^1=NO_2$; c $R=Br$, $R^1=NO_2$; d $R=NO_2$, $R^1=OCH_3$; e $R=NO_2$, $R^1=H$

The presence of the hydroxy group ortho to the ethylene fragment can also suggest the spiro IV or merocyanin V structures:



IV



V

Choice of the hydroxystyrylindolenine structure III can be made on the basis of NMR, UV, and mass spectral analysis.

In the NMR spectra of IIIa-e (Table 1) the signal for the protons of the 3-methyl groups appears as a singlet at 1.6-1.7 ppm. The absence of the closed ring (structure IV) was confirmed by the 16 Hz trans spin-spin coupling for the vinyl protons (contrast the value of 10 Hz [3] expected for the cis double bond in the spiro compound IV). The presence in the spectrum of the phenolic forms IIId, e having a fixed, intramolecular OH...O type hydrogen bond with an ortho-nitro group supports structural type III.

The long wavelength maximum for III in the region 350-370 nm also excludes a merocyanin (absorption expected at 500-600 nm [4]) and the spiro form (expected at 250-300 nm). The absence of solvatochromic and photochromic effects also excludes the spiro and merocyanin structures.

In the mass spectra of IIIa-e, one of the most intense fragment peaks is that formed by elimination of the hydroxy group from the molecular ion. A peak is also seen at 204* which apparently corresponds to the 4-nitro-7-methyl-3,3-dimethylindolenine fragment.

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*Here and further values of m/z are given for ion peaks.

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TABLE 1. Parameters for 4-Nitro-3,3,7-trimethyl-2-(2-hydroxystyryl)indolenines IIIa-e

Compound	Empirical formula	mp, °C	J, Hz*			δ, ppm**								Yield, %***
			trans α-H, β-H	ortho 5-H, 6-H	meta 6'-H, 4'-H	3-CH₃	5-H	6-H	7-CH₃	α-H	β-H	6'-H	4'-H	
IIIa	$C_{20}H_{19}N_3O_6$	255...260	15,5	8,4	2,4	1,65	7,93	7,30	2,71	7,25	8,15	8,24	7,72	6
IIIb	$C_{19}H_{17}N_3O_5$	232...233	15,8	8,4	2,4	1,69	7,99	7,37	2,75	7,15	8,37	8,49	8,02	3
IIIc	$C_{19}H_{16}BrN_3O_5$	287...288	15,9	8,4	2,4	1,65	7,95	7,31	2,72	7,25	8,11	8,49	8,40	7
IIId	$C_{20}H_{19}N_3O_6$	228...230	16,2	8,4	2,4	1,67	7,93	7,30	2,73	7,20	8,19	7,40	7,58	3
IIIe	$C_{19}H_{17}N_3O_5$	229...230	16,4	8,4	2,4	1,67	7,99	7,37	2,73	7,18	8,22	7,84	8,02	7

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*Compound IIIb: $J_{3'4'} = 8.6$ Hz; signal 3'-H at 6.90 ppm; compound IIIe: $J_{3'4'} \approx J_{5'6'} = 8.5$ Hz; signal 5'-H at 7.03 ppm.

**For IIIa-c signal 2'-OH is broadened and not seen; for IIId δ = 11.14 (2'-OH), for IIIe δ = 11.41 ppm (2'-OH).

***Based on starting hydrazine.

All of the above data allows us to assign styrylindolenine structures to IIIa-e (Table 1).

EXPERIMENTAL

NMR spectra were measured on a CFT-20 spectrometer (80 MHz) in $CDCl_3$ solvent. Mass spectra were recorded on an MX-1303 instrument.

Elemental analytical data for C, H, N, and Br for the synthesized compounds agreed with that calculated.

5-Nitro-2-methylphenylhydrazine was obtained in 37% yield by diazotization of 5-nitro-2-methylaniline with subsequent reduction of the diazonium salt by method [5], mp 155°C (from ethanol).

4-Nitro-3,3,7-trimethyl-2-(2-hydroxy-3-methoxy-5-nitrostyryl)indolenine (IIIa). A solution of 5-nitro-2-methylphenylhydrazine (4.3 g, 12 mmole) in absolute ethanol (70 ml) was stirred with methyl-isopropyl ketone (2.15 g, 25 mmole) with cooling by water. The reaction mixture was allowed to stand overnight, the alcohol distilled off, the residue treated with glacial acetic acid (50 ml), and the mixture heated on a water bath for 2 h. The product was treated with concentrated HCl (15 ml) to separate the indole and the indolenine and heated for a further 1 h. The solution was cooled, poured into water (100 ml), and the organic components extracted with ether. The aqueous layer was neutralized with sodium carbonate, extracted with ether, dried with anhydrous magnesium sulfate and evaporated. The starting I was heated in situ for 1 h at ≈ 100°C with a solution of 3-methoxy-5-nitrosalicylaldehyde (0.85 g, 4 mmole) in absolute ethanol (40 ml). A solid did not form on cooling hence the solution was evaporated to one third bulk. After two days light green crystals of IIIa (0.58 g) precipitated. Mass spectrum: 397 $[M]^+$, 380 $[M - 17]^+$, 193 $[M - 204]^+$.

Compounds IIIb-e were obtained similarly.

Compounds IIIa-e did not possess solvatochromic or photochromic properties.

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