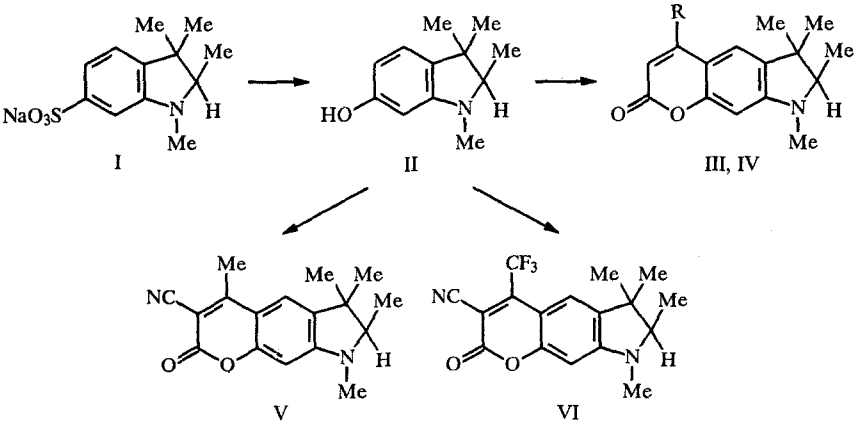
SUBSTITUTED 2-METHYL- AND 2-METHYLENINDOLINES. 5.* COUMARIN DYES DERIVED FROM 1,2,3,3-TETRAMETHYLINDOLINE

V. S. Tolmacheva, A. V. Kropachev, A. Ya. Il'chenko, A. A. Tolmachev, L. I. Shevchuk, and F. S. Babichev

Methods were developed to convert 1,2,3,3-tetramethyl-6-hydroxyindoline into coumarin dyes, in which the amino group is in the indoline system. The structure of the products was indicated by ^1H and ^{13}C NMR spectroscopy.

Derivatives of 7-aminocoumarins have been studied extensively as active laser media [3, 4]. However, only those derivatives, in which the amino group for extending the conjugation is introduced in various six-membered rings [5-8], have been investigated. 7-Aminocoumarins, in which the amino group is found in an indoline system, have not been reported.

In a previous communication [9], we described simple methods for the synthesis of sulfonic derivatives of 2-methyl- and 2-methylenindolines. Alkaline fusion [10] of the sodium salt of 1,2,3,3-tetramethylindoline-6-sulfonic acid I was obtained from 1,2,3,3-tetramethyl-6-hydroxyindoline II, which is the starting compound for the synthesis of coumarins III-VI.



III R=Me; IV R=CF_3

The condensation of phenol II with ethyl acetoacetate and ethyl trifluoroacetoacetate in acetic acid at reflux [11, 12] gave coumarins III and IV. Coumarins V and VI, containing a cyano group at C^3, were obtained by the condensation of phenol II with ethyl 3-chloro-2-cyano-2-butenoate and 1,1-dicyano-2-fluoromethyl-2-chloroethylene, respectively [8, 13].

The structures of II-VI were indicated by ^1H and ^{13}C NMR spectroscopy (Table 1). The assignment of the signals in the ^{13}C NMR spectra was carried out according to Soika [14].

*Communication 4, see ref. [1].

T. G. Shevchenko Kiev State University, 252017 Kiev; Institute of Organic Chemistry, Academy of Sciences of Ukraine, 252660 Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1614-1616, December, 1992. Original article submitted November 27, 1991.

 0009-3122/92/2812-1382$12.50

TABLE 1. Indices of II-VI

Compound	Chemical formula	Mp, °C	^1H and ^{13}C NMR spectra, ppm, J, Hz	IR spectrum, cm^{-1}	Absorption λ_{max}, nm ($\varepsilon \times 10^{-4}$)	Yield, %
II	$C_{12}H_{17}NO$	124...125	0,98 (3H, s, 3-CH_3); 1,23 (3H, s, 3-CH_3); 1,16 (3H, d, J = 6,6, 2-CH_3); 2,86 (1H, q, 2-H); 2,62 (3H, s, N–CH_3); 5,99 (1H, d, J = 1,6, 7-H); 6,17 (1H, d, d, J_{54} = 6,0, J_{57} = 1,6, 5-H); 6,83 (1H, d, J = 6,0, 4-H) 12,2 (2-CH_3); 23,1 (3-CH_3); 25,9 (3-CH_3); 33,9 (N–CH_3); 42,1 $C_{(3)}$; 72,6 $C_{(2)}$; 96,5 $C_{(7)}$; 105 $C_{(5)}$; 122,1 $C_{(4)}$; 131,7 $C_{(9)}$; 153,1 $C_{(8)}$; 155,8 $C_{(6)}$	—		70
III	$C_{16}H_{19}NO_2$	152...154	1,08 (3H, s, 6-CH_3); 1,32 (3-H, s, 6-CH_3); 1,19 (3H, d, J = 6,35, 7-CH_3); 3,18 (1H, q, 7-H); 2,78 (3H, s, N–CH_3); 2,36 (3H, d, J = 0,98, 4-CH_3); 5,95 (1H, q, 3-H); 7,08 (1H, s, 5-H); 6,28 (1H, s, 9-H); 12,5 (7-CH_3); 19,0 (6-CH_3); 23,3 (6-CH_3); 26,4 (4-CH_3); 32,2 (N–CH_3); 42,4 $C_{(6)}$; 71,5 $C_{(7)}$; 94,2 $C_{(9)}$; 109,9 $C_{(11)}$; 111,1 $C_{(3)}$; 116,9 $C_{(5)}$; 136,7 $C_{(13)}$; 153,5 $C_{(10)}$; 155,0 $C_{(12)}$; 163,4 (C=O)	1700 (C=O)	383 (1,57)	65
IV	$C_{16}H_{16}F_3NO_2$	132...134	1,10 (3H, s, 6-CH_3); 1,32 (3H, s, 6-CH_3); 1,20 (3H, d, J = 6,35, 7-CH_3); 3,29 (1H, q, 7-H); 6,38 (1H, s, 3-H); 6,29 (1H, s, 9-H)	1700 (C=O)	407 (2,01)	75
V	$C_{17}H_{18}N_2O_2$	222...224	1,14 (3H, s, 6-CH_3); 1,33 (3H, s, 6-CH_3); 1,22 (3H, d, J = 6,35, 7-CH_3); 3,42 (1H, q, 7-H); 2,89 (3H, s, N–CH_3); 2,64 (3H, s, 4-CH_3); 6,19 (1H, s, 9-H); 7,12 (1H, s, 5-H) 12,8 (7-CH_3); 18,1 (6-CH_3); 23,3 (6-CH_3); 27,3 (4-CH_3); 31,4 (N–CH_3); 42,2 $C_{(6)}$; 71,4 $C_{(7)}$; 92,9 $C_{(9)}$; 109,4 $C_{(11)}$; 118,3 $C_{(5)}$; 138,3 $C_{(13)}$; 157,7 $C_{(10)}$; 157,8 $C_{(12)}$; 161,4 (C=O)	1720 (C=O); 2200 (C=N)	425 (3,50)	87
VI	$C_{17}H_{15}F_3N_2O_2$	228...230	1,16 (3H, s, 6-CH_3); 1,33 (3H, s, 6-CH_3); 1,23 (3H, d, J = 6,35; 7-CH_3); 3,53 (1H, q, 7-H); 2,97 (3H, s, N–CH_3); 6,23 (1H, s, 9-H); 7,17 (1H, q, J_{CF} = 2,0, 5-H) 13,0 (7-CH_3); 23,2 (6-CH_3); 27,6 (6-CH_3); 31,3 (N–CH_3); 42,4 $C_{(6)}$; 71,4 $C_{(7)}$; 92,8 $C_{(9)}$; 112,9 $C_{(11)}$; 118,7 $C_{(5)}$, J_{CF} = 3,67; 139,4 $C_{(13)}$; 156,9 $C_{(10)}$; 158,9 $C_{(12)}$; 187,0 (C=O); 118,8 (C=N)	1730 (C=O); 2200 (C=N)	472 (3,15)	70

EXPERIMENTAL

The ^1H NMR spectra were taken on a Bruker WP-100SY spectrometer and the ^{13}C NMR spectra were taken on a Varian Gemini-200 spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the standard. The IR spectra were taken for KBr pellets on a UR-20 spectrometer.

The elemental data for C, H, and N corresponded to the calculated values.

1,2,3,3-Tetramethyl-6-hydroxyindoline (II). A sample of 16.23 g (0.406 mole) NaOH was fused in an iron cup with 5.0 ml water and 15.0 g (0.054 mole) sodium salt of 1,2,3,3-tetramethylindoline-6-sulfonic acid was added with good stirring at 270°C. Fusion was continued in a closed iron cup for 30 min at 300°C and for 1 h at 360°C. The melt was dissolved in water and the solution was acidified by adding a solution obtained by mixing one part water and one part concentrated hydrochloric acid. The mixture was made basic by adding 25% aqueous ammonia to pH 10 and extracted with chloroform. After removal of chloroform, the solid residue was treated with ether. The ethereal extracts were evaporated and the residue was triturated with hexane. An analytical sample was recrystallized from heptane.

4,6,6,7,8-Pentamethyl-6,7-dihydropyrrolo[3,2-*g*]coumarin (III). A solution of 0.2 g (1 mmole) 1,2,3,3-tetramethyl- mmole freshly distilled ethyl acetoacetate was heated in 50 ml glacial acetic acid at reflux for 7 h, poured into dilute hydrochloric acid, and left for 24 h. The precipitate formed was filtered off, washed with water, and dried. An analytical sample was obtained by recrystallization from heptane.

6,6,7,8-Tetramethyl-4-trifluoromethyl-6,7-dihydropyrrolo[3,2-*g*]coumarin (IV) was obtained analogously to coumarin III from II and ethyl trifluoroacetoacetate. An analytical sample was obtained by recrystallization from heptane.

4,6,6,7,8-Pentamethyl-3-cyano-6,7-dihydropyrrolo[3,2-*g*]coumarin (V). A sample of 0.4 g (2 mmoles) 1,2,3,3-tetrahydro-6-hydroxyindoline II and 0.17 g (1 mmole) ethyl 3-chloro-2-cyano-2-butenoate was heated at reflux in 50 ml glacial acetic acid for 30 min and poured into water. The dark yellow crystalline product was filtered off, washed with water, and dried. An analytical sample was recrystallized from 1:3 chloroform—heptane.

6,6,7,8-Tetramethyl-4-trifluoromethyl-3-cyano-6,7-dihydropyrrolo[3,2-*g*]coumarin (VI). A sample of 0.4 g (2 mmoles) 1,2,3,3-tetramethyl-6-hydroxyindoline II and 0.2 g (1 mmole) 1,1-dicyano-2-trifluoromethyl-2-chloroethylene were dissolved in 25 ml glacial acetic acid. Then, 5 ml water was added and the mixture was heated at reflux for 5 min. After cooling, the dark red crystalline product was filtered off, washed with water, and dried. An analytical sample was obtained by recrystallization from 1:3 chloroform—heptane.

REFERENCES

1. A. A. Tolmachev, V. S. Tolmacheva, L. I. Shevchuk, and F. S. Babichev, Khim. Geterotsikl. Soedin., No. 10, 1331 (1992).
2. I. I. Grandberg, L. K. Denisov, and O. A. Popova, Khim. Geterotsikl. Soedin., No. 2, 147 (1987).
3. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophors [in Russian], Khimiya, Moscow (1984), p. 145.
4. L. K. Denisov, N. A. Kozlov, and B. M. Uzhinov, Organic Compounds as Laser Active Media [in Russia], Series 4, No. 8, Élektronika Central Research Institute, Moscow (1980),
5. I. Z. Sokolova, N. Yu. Vasil'ev, L. I. Loboda, E. A. Sidorenko, O. I. Khochkina, A. Ya. Il'chenko, and A. V. Kropachev, Izv. Vyssh. Uchebn. Zaved. Fiz., No. 11, 79 (1986).
6. R. L. Atkins and D. E. Bliss, J. Org. Chem., **40**, No. 10, 1975 (1978).
7. R. A. Henry and P. R. Hamond, J. Heterocycl. Chem., **14**, No. 6, 1109 (1977).
8. A. V. Kropachev, A. Ya. Il'chenko, V. I. Popov, and L. M. Yagupol'skii, Ukr. Khim. Zh., **54**, No. 10, 1078 (1988).
9. V. S. Tolmacheva, A. A. Tolmachev, L. I. Shevchuk, and F. S. Babichev, Khim. Geterotsikl. Soedin., No. 11, 1567 (1989).
10. V. M. Rodionov, B. M. Bogoslovskii, and A. M. Fedorov, Laboratory Handbook on the Chemistry of Intermediates and Dyes [in Russian], Moscow (1948), p. 93.
11. H. von Pechman and G. Duisberg, Ber., **16**, 2119 (1883).
12. E. R. Blisser, A. R. Mitchell, and R. E. Smith, J. Org. Chem., **45**, No. 12, 2283 (1980).
13. A. Ya. Il'chenko, R. E. Koval'chuk, V. I. Krokhmyak, and L. M. Yagupol'skii, Zh. Org. Khim., 17, 2630 (1981).
14. S. A. Soika, J. Org. Chem., **40**, No. 8, 1175 (1975).