BENZINDOLES

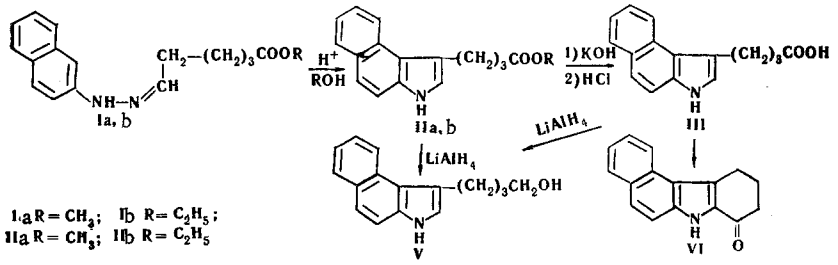
II.* SYNTHESIS OF γ-(4,5-BENZINDOL-3-YL)BUTYRIC ACID AND ITS DERIVATIVES

L. B. Shagalov, V. N. Eraksina, K. F. Turchin, and N. N. Suvorov

UDC 547.294'759.3:543.422.4.6:541.67

The synthesis of γ-(4,5-benzindol-3-yl)butyric acid and a number of its derivatives has been effected. It has been shown that the Fischer cyclization of the β-naphthylhydrazones of δ-formylvaleric acid is accompanied by the formation of parasitic compounds identified as esters of ω,ω-di[3-(γ-alkoxycarbonylpropyl)-4,5-benzindol-2-yl] caproic acids. The yield of the latter increases with an increase in the strength of the acid used as the cyclizing agent.

In order to continue investigations performed previously [1-4] on the connection between structure and biological action in substituted γ-(indol-3-yl)butyric acid and to determine the influence of substituents in the aromatic nucleus of the initial arylhydrazones on the ease of occurrence of the Fischer reaction, we have performed the synthesis of γ-(4,5-benzindol-3-yl)butyric acid in accordance with the following scheme:



The cyclization of the hydrazono ethyl ester Ib under the action of a solution of orthophosphoric acid in ethanol takes place with insignificant resinification. In the purification of the technical reaction product, two substances were isolated: A with mp 104.5-105°C (64%) and B with mp 151-152°C (5.2%).

Substance A was identified as ethyl γ-(4,5-benzindol-3-yl)butyrate (IIb). It saponified smoothly to form the acid III; on treatment with hydrazine hydrate it gave the hydrazide IV, and it was reduced by lithium hydride to γ-(4,5-benzindol-3-yl)butanol (V). In an addition to elementary analysis, both the ester IIb and the products of its transformation III-V were characterized by their UV, IR, and NMR spectra, which do not contradict the structures given for these compounds. We also performed the conversion of the acid III into 1,2,3,4-tetrahydro-5,6-benzocarbazol-1-one (VI) as a possible [1, 5] by-product of the reaction. However, we were unable to detect this compound in the reaction mixture.

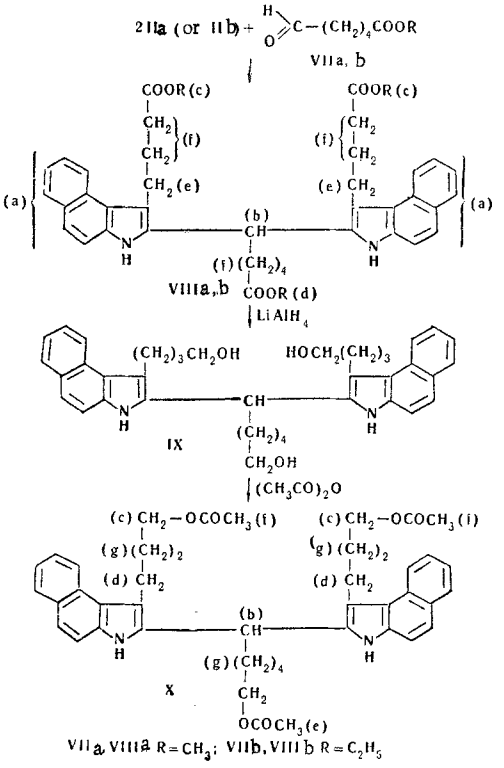
It appeared of great interest to investigate the structure of substance B, since in all the syntheses of benzindoles by the Fischer reaction described in the literature [6-9] the presence of unidentified by-products has been reported.

*For Communication I see [14].

Mendeleev Moscow Chemical and Technological Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 7, pp. 945-950, July, 1970. Original article submitted February 21, 1969.

Chalmers and Lions [9] have put forward the hypothesis that in the cyclization of β-napthylhydrazones the closure of the ring can take place not only in the α but also in the β position with the formation of 5,6-benzo derivatives of indole in addition to the 4,5-derivatives. However, in view of modern ideas on the mechanism of the Fischer reaction and information on the chemistry of β-substituted napthalenes, we rejected the possibility of this direction of the reaction in our case. The structure VIIIb appeared to us to be considerably more likely for compound B, the formation of which can be regarded as the result of the reaction of two molecules of the indole derivative IIb with a molecule of the initial aldehydo ester VII.

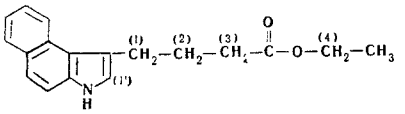
The results of spectroscopic studies were also in harmony with this hypothesis. Thus, the IR spectrum of substance B proved to be extremely similar to that of the ester IIb, differing from it only by the presence of a second carbonyl band, and in a comparison of the UV spectra of these compounds only a slight shift in the maxima in the long-wave direction for substance B was found.



There is information in the literature on the possibility of the formation of structures of type VIII under the conditions of the Fischer reaction. Bauer [10], in the cyclization of the p-nitrophenylhydrazone of proprionaldehyde, and Shaw and Wooley [11], working with the p-nitrophenylhydrazone of butyraldehyde, isolated by-products which, on the basis of elementary analysis, were ascribed the structure of the corresponding di(3-alkyl-5-nitroindol-2-yl)alkanes. Noland and Robinson [12] have shown that 3-alkylindoles react with benzaldehyde to form di(3-alkylindol-2-yl)phenylmethanes and have drawn attention to similarity of the UV spectra of the compounds obtained and those of the initial indoles.

The alcoholysis of p-benzyloxyphenylhydrazone of the aldehydo ester VII was observed by Suvorov and Murasheva in an attempt to subject it to Fischer cyclization [13]. We further assumed that the yield of compound B should rise when phosphoric acid was replaced as cyclizing agent by a stronger acid. In actual fact, in the cyclization of Ib by the action of a solution of sulfosalicylic acid (SSA) in ethanol, the yield of by-product rose to 22% and that of the ester IIb fell to 17%. When this reaction was carried out in methanol, the yield of the methyl ester IIa was likewise only 23% and that of the by-product C was 45%. Substances C and B had different melting points, but their IR and UV spectra were practically identical. Consequently it was natural to assume that the structure of C is analogous to that of substance B and corresponds to VIIIa. We also obtained the ester IIa from Ia in methanol. The two samples were identical and on saponification with alcoholic alkali were converted smoothly into the acid III.

TABLE 1. Chemical Shifts of the Protons of Compound IIb



Type of H atoms	CH_3	CH_2-(1)	CH_2-(2)	CH_2-(3)	CH_2-(4)	CH (1')	CH aromat.
δ, ppm	1,22	3,14	2,19	2,45	4,12	6,95	7,30—8,45

TABLE 2. Chemical Shifts of the Protons of Substance C (VIIIa)

Type of H atoms	Aromatic protons	Triplet	OCH_3	OCH_3	CH_2	Signals in the strong field
δ, ppm	7,31—8,32	4,67	3,67	3,59	3,11	1,25—2,55
No. of protons, obtained from the ratio of intensities	12	1	6	3	4	16
Assignment of the protons*	a	b	c	d	e	f

*See scheme on page 609.

TABLE 3. Chemical Shifts of the Protons of Compound X

Type of H atoms	Aromatic protons	Triplet	$O-CH_2$	$Ar-CH_2$	$O-CO-CH_3$	$O-CO-CH_3$	CH_2 (in the strong field)
δ, ppm	7,21—8,26	4,63	4,02	3,07	1,98	1,85	1,15—2,25
No. of protons calculated for structure X	12	1	6	4	3	6	16
Assignment of the protons	a	b	c	d	e	f	g

To prove that substances B and C corresponded to the structure VIII, we reduced them with lithium aluminum hydride to the triol IX and acetylated the latter with acetic anhydride to form the triacetyl derivative X. The esters IIa and IIb, and also substances B, C, and X, were studied by the NMR method. The values of the chemical shifts so obtained for compounds IIb, C, and X and the intensities calculated from the spectra of substances C and X are given in Tables 1-3.

A comparison of the NMR spectra of the esters IIa and IIb with the spectra of B, C, and X permitted the following conclusions.

1. The signals of the protons belonging to the naphthalene nucleus practically coincide in all the compounds studied. At the same time, the signal of the proton in the α position of the indole ring (CH-1), which has the form of a doublet in the spectra of the esters IIa and b because of spin-spin coupling with the proton of the NH group, is absent from the spectra of compounds B, C, and X. This shows, in the first place, that all the compounds mentioned have similar cyclic structures and, in the second place, that compounds B, C, and X have a substituent in position 2 of the indole nucleus.

2. In the spectrum of compound B there are two combinations of peaks corresponding to the protons of an ethoxycarbonyl group (with a ratio of the intensities of 1 : 2). In the spectrum of compound C, obtained when the reaction was carried out in methanol, the protons of the methoxycarbonyl group are likewise represented by two peaks (δ = 3.59 and 3.67) with the same intensity ratio. It is natural to conclude from this that all similar compounds contain three ethoxycarbonyl or methoxycarbonyl groups, as the case may be, of which two are equivalent to one another and differ from the third.

3. In the region of the signals corresponding to aliphatic protons in the spectra of compounds B, C, and X there is a triplet with δ = 4.67 for B, 4.69 for C, and 4.63 for X, the intensity of which is $1/12$-$1/14$ of the total intensity of the aromatic protons.

In the strong-field region of these compounds, apart from signals analogous to the signals of methylene groups 1, 2, and 3 of the esters II, there are broad lines arising because of the superposition of strongly split multiplets. These lines partially overlap with the signals of the protons of methylene groups 2 and 3, and therefore their relative intensity can be determined only as the sum with the signals of these protons The number of protons obtained from the ratio of the intensities agrees well with the proposed structures VIIIa and X.

Determinations of the number of ethoxy groups and the molecular weight performed mass spectrometrically for substance B also gave results corresponding to those calculated for the proposed structure.

The possibility of the formation of VIIIa, b by the reaction of the esters IIa, b with the initial aldehydo esters VIIa, b was shown by heating the latter in alcoholic solutions of SSA. When the Fischer reaction was performed under the action of SSA, we likewise succeeded in isolating from the reaction mixture β-naphthylhydrazine sulfosalicylate with a yield approximately corresponding to the yield of by-products.

EXPERIMENTAL

The IR spectra were taken on a UR-10 spectrophotometer, and the UV spectra on an SF-4M spectrophotometer. The NMR spectra were obtained on a JNM-4H 100 spectrometer with a working frequency of 100 MHz. Deuterochloroform was used as solvent and tetramethylsilane as standard.

The molecular weights were measured on an MKh-1303 mass spectrometer fitted with a system for the introduction of the sample into the ion source close to the ionization chamber at energies of about 30-40 and 70 eV and temperatures of 120-160°C.

Methyl δ-Formylvalerate. This was obtained in a similar manner to ethyl δ-formylvalerate [15] using absolute methanol. Yield 40%. Bp 93-95°C (14 mm). Found %: C 58.25; H 8.19. $C_7H_{12}O_3$. Calculated %: C 58.31; H 8.32. 2,4-Dinitrophenylhydrazone. mp 101.5-102.5°C. Found %: C 48.03; H 4.90; N 17.45. $C_{13}H_{16}N_4O_6$. Calculated %: C 48.25; H 4.94; N 17.33.

β-Naphthylhydrazone of Ethyl δ-Formylvalerate (Ib). A solution of 8.87 g (56 mmoles) of β-naphthyl hydrazine and 8.87 g (56 mmoles) of ethyl δ-formylvalerate in 160 ml of absolute methanol was boiled for 45 min, evaporated to 30 ml, and cooled to −5°C. The precipitate was filtered off. Yield 12.5 g (75%), mp 63-64°C (from methanol). UV spectrum: λ_{max}, nm: 255, 304, 348; log ε 4.43, 4.13, 3.58 (in ethanol). IR spectrum, ν_{max}, cm^{-1}: 3320 (N−H); 1718 (C=O); 1610 (C=N). Found %: C 72.29; H 7.39; N 9.43. $C_{18}H_{22}N_2O_2$. Calculated %: C 72.50; H 7.40; N 9.40.

Cyclization of the β-Naphthylhydrazone of Ethyl δ-Formylvalerate. a. By the Action of Orthophosphoric Acid in Ethanol. A mixture of 2.4 g (8 mmoles) of IIb and 2.2 g of crystalline orthophosphoric acid in 25 ml of absolute ethanol was boiled for 4 h, cooled, and poured onto ice. The precipitate was separated off and dried, dissolved in 50 ml of benzene, and chromatographed on Al_2O_3. Elution was performed with benzene. The benzene was distilled off from the first fraction (six 50-ml portions) and the residue was recrystallized from heptane−chloroform (3:1). This yielded 1.29 g (64%) of ethyl γ-(4,5-benzindol-3-yl)butyrate (IIb) with mp 104.5-105°C. It gave a blue coloration with Ehrlich's reagent. R_f* 0.76 (ether); 0.49 [benzene−methanol (30:1)]; 0.57 [benzene−ether (1:1)]; 0.39 (chloroform). UV spectrum: λ_{max}, nm: 228, 255, 308, 320; log ε 4.48, 4.40, 3.88, 3.88 (in ethanol). IR spectrum: ν_{max}, cm^{-1}: 3320 (N−H), 1715 (C=O). Found %: C 76.94; H 6.91. $C_{18}H_{19}NO_2$. Calculated %: C 76.90; H 6.76.

The second fraction (the subsequent nine 50-ml portions) yielded similarly 0.12 g (5.2%) of ethyl ω,ω-di[3-(3'-ethoxycarbonylpropyl)-4,5-benzindol-2-yl]caproate (VIIIb). mp 151-152°C. R 0.41 [benzene−ether (1:1)]; 0.58 (ether). UV spectrum, λ_{max}, nm: 228, 256, 322, 338; log ε 4.42, 4,36, 3.88, 4.00 (in ethanol). IR spectrum, ν_{max}, cm^{-1}: 3335, 3410 (N−H), 1730, 1715 (C=O). Found %: C 75.18; H 7.23; N 3.97; OC_2H_5 18.69; mol. wt. 702. $C_{44}H_{50}N_2O_6$. Calculated %: C 75.19; H 7.17; N 3.98; OC_2H_5 19.37; mol. wt. 702.9.

b. By the Action of SSA in Methanol. A solution of 3 g (10 mmoles) of Ib and 6 g of SSA (27 mmoles) in 60 ml of absolute methanol was boiled for 4 h. After 24 h standing at room temperature, the crystals were filtered off and carefully washed with water. This gave 1.15 g (45%) of methyl ω,ω-di[3-(3'-methoxy-

*Here and below, the R_f values are given for alumina of activity grade 2. The spots were revealed with iodine.

carbonylpropyl)-4,5-benzindol-2-yl]caproate (VIIIa), mp 180-181°C (from methanol). R_f 0.50 (ether); 0.22 [benzene–ether (1:1)]. UV spectrum: λ_{max}, nm: 230, 257, 322, 338; log ε 4.20, 4.15, 3.95, 3.98 (in ethanol). IR spectrum: ν_{max}, cm^{-1}: 3370, 3335 (N–H), 1735, 1715 (C=O). Found %: C 74.43; H 6.67; N 4.10; OCH_3 14.12. $C_{41}H_{44}N_2O_6$. Calculated %: C 74.53; H 6.56; N 4.25; OCH_3 14.05.

The mother liquor was poured onto ice, and the precipitate was filtered off. This gave 0.65 g (23.3%) of methyl γ-(4,5-benzindol-3-yl)butyrate (IIa), mp 136°C (from methanol). R_f 0.51 [benzene–ether (1:1)]. UV spectrum: λ_{max}, nm: 228, 255, 308, 320; log ε 4.50, 4.44, 390, 3.90 (in ethanol). IR spectrum: ν_{max}, cm^{-1}: 3340 (N–H), 1728 (C=O). Found %: C 76.57; H 6.53; N 5.20. $C_{17}H_{17}NO_2$. Calculated %: C 76.38; H 6.41; N 5.24.

c. By the Action of SSA in Ethanol. A solution of 8.4 g (28 mmoles) of Ib and 16.8 g (77 mmoles) of SSA in 170 ml of ethanol was boiled for 5 h. Then it was evaporated to half volume, cooled, and poured onto ice. The precipitate was evaporated off, dried, and treated with ether. This gave 1.55 g (19.4%) of β-naphthyldrazine sulfosalicylate, mp 236°C (from water). UV spectrum, λ_{max}, nm: 240, 296-304, 344; log ε 4.54, 4.07, 3.46 (in ethanol). IR spectrum, ν_{max}, cm^{-1}: 3470-3430, 1675, 1615, 1580. Found %: C 54.31; H 4.10; N 7.30; S 8.40. $C_{17}H_{16}N_2O_6S$. Calculated %: C 54.25; H 4.28; N 7.44; S 8.52. It gave no depression of the melting point with an authentic sample of β-naphthylhydrazine sulfosalicylate.

The ethereal extract was evaporated and the residue was treated with methanol. The insoluble part was filtered off, giving 1.76 g (21.8%) of ethyl ω,ω-di[3-(3'-ethoxycarbonylpropyl-4,5-benzindol-2-yl]-caproate (VIIIb); mp 151-152°C (from methanol). It gave no depression of the melting point with the sample obtained by cyclization in the presence of phosphoric acid.

The residue after the evaporation of the methanol was boiled with petroleum ether (bp 100-110°C), giving 1.35 g (17%) of ethyl γ-(4,5-benzindol-3-yl)butyrate (IIb), mp 98-100°C.

Methyl γ-(4,5-Benzindol-3-yl)butyrate (IIa). A mixture of 1.55 g (10.8 mmoles) of methyl γ-formylvalerate and 1.7 g (10.8 mmoles) of β-naphthylhydrazine in 15 ml of dry methanol was boiled for 30 min, and then 15 ml of dry benzene was added and the solvents were distilled off in vacuum. The residue was dissolved in 25 ml of ethyl cellosolve and boiled with 2.17 g of crystalline orthophosphoric acid for 1 h 30 min. After the usual working up, 2.52 g (88%) of crude product with mp 116-118°C was isolated. It was recrystallized from a mixture of chloroform and petroleum ether. mp 134-134.5°C. It gave no depression of the melting point with the sample obtained previously. Found %: N 5.53. $C_{17}H_{17}NO_2$. Calculated %: N 5.24.

Hydrazide of γ-(4,5-Benzindol-3-yl)butyric Acid (IV). A solution of 1 g (3.56 mmoles) of IIb and 2 ml of hydrazine hydrate in 6 ml of ethanol was boiled for 3 h. The precipitate that deposited after cooling was separated off. Yield 0.93 g, mp 205.5-206°C. Found %: C 72.0; H 6.45; N 15.5. $C_{16}H_{17}N_3O$. Calculated %: C 72.0; H 6.37; N 15.7.

γ-(4,5-Benzindol-3-yl)butyric Acid (III). 1.5 g (5.35 mmoles) of IIb was boiled for 30 min in 20 ml of a 5% ethanolic solution of KOH, and the mixture was cooled, poured into water, and acidified with dilute HCl. Yield 1.17 g (86%), mp 177.5-178.5°C (from aqueous methanol). Found %: C 75.61; H 6.04; N 5.55. $C_{16}H_{15}NO_2$. Calculated %: C 75.80; H 5.92; N 5.53.

Compound III was obtained similarly by the hydrolysis of IIa, mp 177-178°C.

1,2,3,4-Tetrahydro-5,6-benzocarbazol-1-one (VI). A mixture of 0.6 g (2.37 mmoles) of III and 2.5 g (17.6 mmoles) of phosphorous pentoxide in 20 ml of p-xylene was boiled for 1 h. Then it was cooled and carefully decomposed with a 10% aqueous solution of NaOH. The xylene layer was separated off and the aqueous layer was extracted with ether. Evaporation of the solvents yielded 0.34 g (60.5%) of a red substance with mp 204°C (from toluene). R_f 0.61 (benzene); 0.45 [benzene–ether (1:1)]. UV spectrum: λ_{max}, nm: 238, 262, 282, 328, 340-342; log ε 4.53, 3.97, 4.16, 4.30, 4.33 (in ethanol). IR spectrum, ν_{max}, cm^{-1}: 3260 (N–H), 1645 (C=O), 1620 (C=C arom.). Found %: C 81.67; H 5.67; N 5.99. $C_{16}H_{13}NO$. Calculated %: C 81.68; H 5.57; N 5.95.

δ-(4,5-Benzindol-4-yl)butanol (V). a. A solution of 1 g (3.95 mmoles) of III in 120 ml of absolute ether was added to a stirred suspension of 0.15 g (3.95 mmoles) of lithium aluminum hydride in 25 ml of absolute ether. The mixture was heated for 1 h, carefully decomposed with water, and made alkaline. The ethereal layer was separated off and dried, and the solvent was distilled off. The yield of V was 0.65 g

(60%), mp 110-111°C (from a mixture of benzene and petroleum ether), R_f 0.35 [chloroform–ethyl acetate (4:1)]. UV spectrum: λ_{max}, nm: 228, 253, 309, 319; log ε 4.48, 4.47, 3.89, 3.90 (in ethanol). IR spectrum, ν_{max}, cm^{-1}: 3430, 3410 (O–H, N–H). Found %: C 81.28; H 6.03. $C_{16}H_{17}NO$. Calculated %: C 81.68; H 5.57.

b. A solution of 0.7 g (2.5 mmoles) of IIb in 50 ml of absolute ether was added dropwise to a suspension of 0.3 g (7.9 mmoles) of lithium aluminum hydride in 25 ml of absolute ether, and the mixture was stirred and heated in the water bath for another 2 h. Then it was decomposed with water and dilute HCl, the ethereal layer was dried, and the solvent was distilled off. The yield of V was 0.36 g (61.2%), mp 110°C.

ω,ω-Di[3-(4'-hydroxybutyl)-4,5-benzindol-2-yl]hexanol (IX). At room temperature a solution of 0.6 g (0.85 mmole) of VIIIb in 15 ml of tetrahydrofuran was added dropwise to a suspension of 0.3 g (7.9 mmoles) of lithium aluminum hydride in 15 ml of absolute tetrahydrofuran. The mixture was stirred for another 3 h and was carefully decomposed with 0.25 ml of water, 0.25 ml of 15% NaOH solution, and again with 0.75 ml of water. The precipitate of hydroxides was filtered off, and the mother liquor was evaporated in vacuum. On prolonged standing and trituration with petroleum ether, 0.57 g (98%) of light yellow crystals of IX were obtained with mp 116-117°C, R_f 0.20 [benzene–methanol (9:1)]. UV spectrum, λ_{max}, nm: 230, 256, 324, 338; log ε 4.38, 4.30, 3.92, 3.96 (in ethanol). Found %: N 4.85. $C_{38}H_{44}N_2O_3$. Calculated %: N 4.86.

The reduced product was boiled with 5 ml of acetic anhydride for 45 min. Then the mixture was cooled and poured into water, and the white crystals of O-acetyl derivative X were filtered off. Yield 0.60 g. mp 127°C (from ethanol). Found %: C 75.47; H 7.22; N 4.09. $C_{44}H_{50}N_2O_6$. Calculated %: C 75.19; H 7.17; N 3.98.

Condensation of Methyl γ-(4,5-Benzindol-3-yl)butyrate (IIa) with Ethyl γ-Formylvalerate. A solution of 0.12 g (0.45 mmole) of IIa in 30 ml of methanol was treated with 0.2 g (0.92 mmole) of SSA and, with heating, a solution of 0.06 g (0.38 mmole) of ethyl ω-formylvalerate in 15 ml of ethanol was slowly added. The mixture was heated for 5 h. The excess of solvent was distilled off in vacuum, and 0.05 g of the unchanged initial ester with bp 136°C was recovered. The mother liquor was poured into water and the precipitate was separated off. This yielded 0.02 g (38%) of methyl ω,ω-[3-(3'-methoxycarbonylpropyl)-4,5-benzindol-2-yl]caproate (VIIIa), mp 181°C (from methanol), giving no depression of the melting point with the sample obtained above. R_f 0.22 [benzene–ether (1:1)]. IR spectrum, ν_{max}, cm^{-1}: 3334, 3370, 1734, 1715.

Similarly, by the condensation of 0.85 g (3 mmoles) of IIb with 0.25 g (15.8 mmoles) of ethyl γ-formylvalerate, 0.49 g (46%) of ethyl ω,ω-di[3-(3'-ethoxycarbonylpropyl)-4,5-benzindol-2-yl]caproate (VIIIb) was obtained with mp 152°C and giving no depression of the melting point with the sample obtained above. IR spectrum, ν_{max}, cm^{-1}: 3335, 3400 (N–H), 1730, 1715 (C=O). Found %: C 75.33; H 6.86; N 4.26. $C_{44}H_{50}N_2O_6$. Calculated %: C 75.19; H 7.17; N 3.98.

LITERATURE CITED

1. N. N. Suvorov and V. K. Antonov, Dokl. Akad. Nauk SSSR, 84, 971 (1952).
2. N. N. Suvorov, V. K. Antonov, and E. M. Rokhlin, Dokl. Akad. Nauk SSSR, 91, 1345 (1953).
3. N. N. Suvorov, V. P. Mamaev, and L. B. Shagalov, Dokl. Akad. Nauk SSSR, 93, 835 (1953).
4. L. B. Shagalov, N. P. Sorokina, and N. N. Suvorov, ZhOKh, 34, 1592 (1964).
5. R. Jackson and R. Manske, J. Am. Chem. Soc., 52, 5029 (1930).
6. V. V. Feofilaktov, ZhOKh, 17, 993 (1947).
7. V. V. Feofilaktov, and N. K. Semenova, ZhOKh, 23, 644 (1953).
8. S. Birghero and O. Finsterle, Gazz., 85, 65 (1955); C. A., 50, 4883 (1956).
9. A. Chalmers and F. Lions, Proc. Roy. Soc. N. S. Wales, 67, 178 (1933); C. A., 28, 765 (1934).
10. H. Bauer and E. Strauss, Ber., 65, 308 (1932).
11. E. Shaw and D. Wooley, J. Am. Chem. Soc., 75, 1877 (1953).
12. W. Noland and D. Robinson, Tetrahedron, 3, 68 (1958).
13. N. N. Suvorov and V. S. Murasheva, ZhOKh, 30, 3112 (1962).
14. N. N. Suvorov, V. A. Porotikova, and V. N. Erakasina, KhGS [Chemistry of Heterocyclic Compounds], 6, 24 (1970).
15. E. Boer, J. Am. Chem. Soc., 64, 1416 (1942).