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Effect of Molecular Structure on Optical Properties of Systems Containing Carbon Chirality Centers. XXIX. α-(3-Phenanthrylmercapte)-propionic Acids and Some of Their Derivatives

Wpływ budowy cząsteczkowej na własności optyczne układów z węglowymi centrami chiralności. XXIX. Kwasy α-3-(fenantrylomerkapto)-propionowe i ich niektóre pochodne

Влияние солекулярного строения на оптические свойства систем с углеродными центрами хиральности. XXIX. Кислоты α-3-(фенантрилмеркапто)-пропионовые и некоторые их производные

The problem of the effect of position isomerism of chirality center in aromatic nucleus on the optical properties of simple derivatives of aromatic compounds was studied in our laboratory in the group of diphenyl [1] dibenzofuran [2] and phenanthrene [3] on the example of their carboxymethylsulfinyl derivatives. On the basis of the results of our experiments we are able to show that characteristic rotational features exist in each system examined. A comparison of these features led us to the general conclusion that in the group of sulfinyl derivatives of the examined aromatic systems the molar rotations in the visible part of the spectra of sulfoxy compounds having analogous structures increase in the order: diphenyl derivatives → dibenzofuran derivatives → phenanthrene derivatives [2]. It is possible that this is caused by annelation of rings to the diphenyl system. The results of our studies encouraged us to investigate the compounds containing carbon chirality centers connected indirectly (through an

[*] Part XXVIII. Janczewski M., Zygo K., Polish. J. Chem., in press; Preliminary Communication, Janczewski M., Zygo K., Polish J. Chem., 52, 2501 (1978).

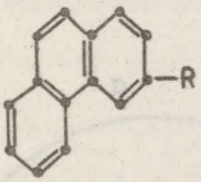
oxygen atom, a sulfur atom or methylene groups) or directly with arene fragments.

In the present communication we are reporting the results of our studies on the synthesis and principal optical and stereochemical properties of enantiomeric α-(3-phenanthrylmercapto)-propionic acids and some of their derivatives.

The starting compound was the already known 3-mercaptophenanthrene [3] (1) which was obtained in our laboratory in good yield through the reduction of 3-phenanth chloride [4] with stannous chloride in the acidic medium. We have obtained racemic α-(3-phenanthrylmercapto)-propionic acid (2) by condensation of 3-mercaptophenanthrene (1) with α-bromopropionic acid in alkaline solution. When mercaptoacid (2) was treated with an excess of 30 % hydrogen peroxide a good yield of sulfone 16 was obtained. (The IR spectra confirming the structures of both racemic acids 2 and 16 are shown in the experimental part). Mercaptoacid 2 was characterized as its amide (3), thioamide (4) and p-bromophenacyl (5) and p-nitrobenzyl (6) esters.

Racemic acid 2 was resolved by crystallization of diastereomeric salts with optically active bases. For this purpose, the neutral salts of cynchonidine and α-phenylethylamine were the most suitable. During fractional crystallization of the cynchonidine salt (from ethyl acetate), the first fractions contained the salt of the laevorotatory acid, whereas the dextrorotatory enantiomer could be separated from the racemate by crystallization (from benzene) of the salt with laevorotatory α-phenylethylamine.* Enantiomeric α-(3-phenanthrylmercapto)-propionic acids liberated in the usual way from the salts (7 and 10) showed a relatively high optical activity ($[\alpha]_D^{20} = \pm 125{,}0^\circ$ (acetone)) after purifying by crystallization from cyclohexane. It should be mentioned that enantiomeric acids 8 and 11 did not show a considerable resistance to racemization processes in the alkaline media. The optical purity of enantiomeric α-(3-phenanthrylmercapto)-propionic acids (8 and 11) was confirmed by studying the ^{1}HNMR spectra of racemic acid (Figs 2a and 2b), and laevorotatory enantiomer (Fig. 2c, 2d) methyl esters mixtures with tris-(3-trifluoroacetyl-d-camphorato)-europium (III) ($Eu(tfc)_3$) as a chiral shift reagent.

* It should be mentioned that the neutral cynchonidine salt can isolate from the racemate in the first fractions also dextrorotatory enantiomer through crystallization from acetone.



1: R=SH

2: R=SCH/CH$_3$/COOH

3: R=SCH/CH$_3$/CONH$_2$

4: R=SCH/CH$_3$/CSNH$_2$

5: R=SCH/CH$_3$/COOCH$_2$COC$_6$H$_4$Br

6: R=SCH/CH$_3$/COOCH$_2$C$_6$H$_4$NO$_2$

7: R=SCH/CH$_3$/COOH Cinch.

8: R=SCH/CH$_3$/COOH

9: R=SCH/CH$_3$/COOH Cinch.

10: R=SCH/CH$_3$/COOH α-Pheneth.

11: R=SCH/CH$_3$/COOH

12: R=SCH/CH$_3$/COOH

13: R=SCH/CH$_3$/CONH$_2$

14: R=SCH/CH$_3$/COOCH$_2$COC$_6$H$_4$Br

15: R=SCH/CH$_3$/COOCH$_2$C$_6$H$_4$NO$_2$

16: R=SO$_2$CH/CH$_3$/COOH

Cinch. = cinchonidine, α-Pheneth. = α-laevorotatory phenylethylamine.

Fig. 1. Structural patterns

The presented fragments of ^{1}HNMR spectrum of racemic acid methyl ester (Fig. 2a) and its mixture (Fig. 2b) with a chiral shift reagent demonstrate a diastereomeric differentiation of methine group protons. On the other hand, on the spectrum of laevorotatory acid methyl ester (Fig. 2c) and its mixture with Eu (tfc)$_3$ realized in the same conditions this effect is not observable. That proves laevorotatory acid being optically pure in the range of accuracy of the applied method (2-3 %).

After mixing the enantiomers (8 and 11) at an equimolar ratio and after crystallization racemic acid (2) was obtained. The comparison of some physical properties (m.p., solubility) of racemic acid (2) (the m.p. of racemate 2 was higher than that of the antipodes, $\Delta t = 28{,}5^{\circ}C$) with those of enantiomeric compounds 8 and 11 indicates that optically inactive system (2) is a true racemate. This conclusion was confirmed by thermal analysis of mixtures of enantiomers 8 and 11 carried out according to Reinboldt method [6] (Fig. 3).

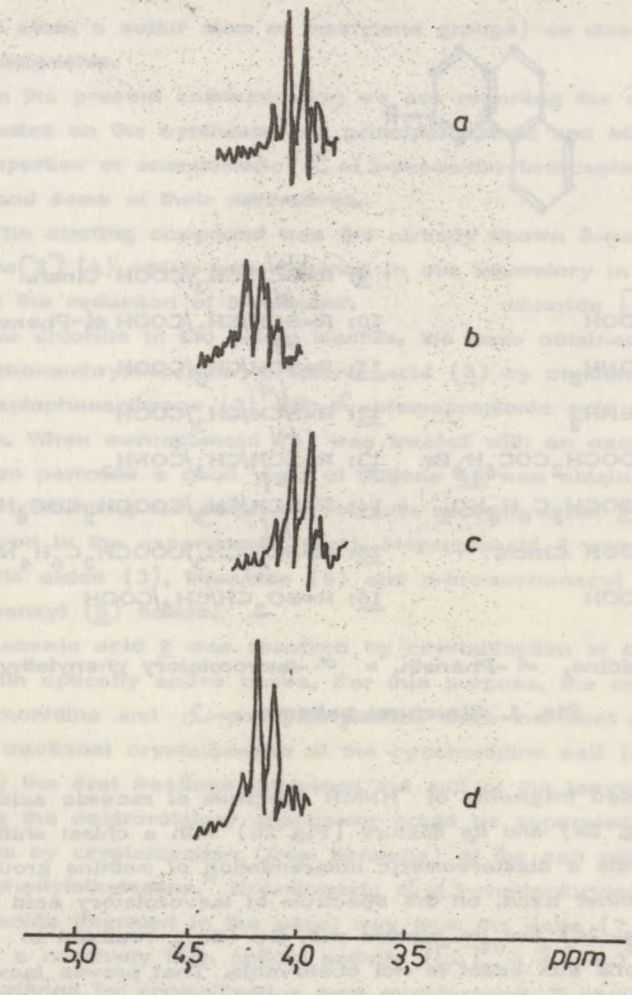


Fig. 2: a - ^{1}HNMR spectrum of methine group proton of racemic α-(3-phenanthrylmercapto)-propionic acid methyl ester; b - Methine group protons ^{1}HNMR spectrum of the mixture (1:1 - mole/mole) of racemic α-(3-phenanthrylmercapto)-propionic acid methyl ester and tris-(3-trifluoroacetyl-d-camphorato)-europium (III)($Eu(tfc)_3$); c - ^{1}HNMR spectrum of methine group proton of laevorotatory α-(3-phenanthrylmercapto)-propionic acid methyl ester; d - ^{1}HNMR spectrum of methine group proton of the mixture (1:1 - mole/mole) of laevorotatory α-(3-phenanthrylmercapto)-propionic acid methyl ester and tris-(3-trifluoroacetyl-d-camphorato)-europium (III)($Eu(tfc)_3$)

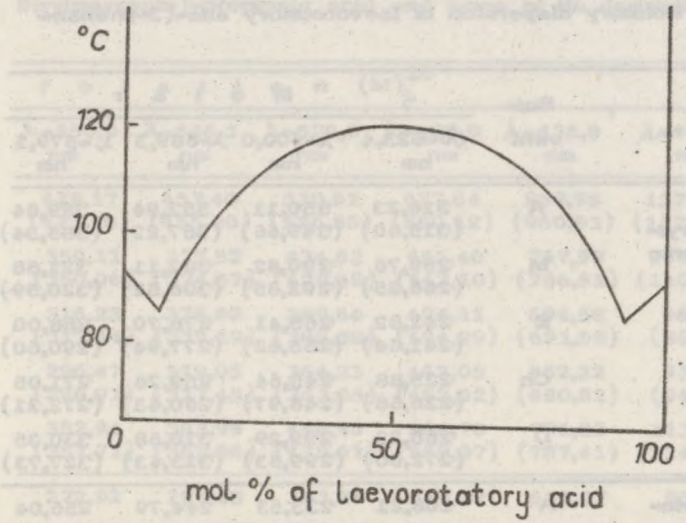


Fig. 3. Melting point curve of enantiomeric α-(3-phenanthrylmercapto)-propionic acids mixtures

As expected the m.p. curve (Fig. 3) had two eutectic points and the maximum corresponding to the m.p. of the racemic compound was situated symmetrically between the eutectic points.

In order to obtain more material for the comparative chiraloptical studies we have prepared amide (13), p-bromophenacyl ester (14) and p-nitrobenzyl ester (15) of acid 8. Since all the reactions were carried out under mild conditions, it can be assumed that racemization at the asymmetric carbon atom did not take place.

The results of measurements of molar rotations of laevorotatory acid 8 and its derivatives 13, 14 and 15 in the region $370 < \lambda < 623{,}4$ nm using methanol (M), dioxane (D), 96 % ethanol (E), acetone (A) and chloroform (Ch) as solvents are shown in Table 1.

A comparison of numerical values shown in this table indicates that the nature of the solvent has a considerable effect on the value of molar rotation. This dependence can be represented by the following suquences: a) for free acid A > D > M > E > Ch; b) for amide: A > M > E > D > Ch; c) for p-bromophenacyl and p-nitrobenzyl esters: A > D > M > E > Ch.

Tab. 1. Rotatory dispersion of laevorotatory alfa-(3-phenan-

Compound	Solvent	Molar			
		λ=623,4 nm	λ=600,0 nm	λ=589,3 nm	λ=579,1 nm
Laevorotatory alfa-(3-phenanthryl-mercapto)-propionic acid	A	316,23 (315,60)	350,11 (349,66)	352,94 (367,22)	389,64 (385,34)
	M	259,76 (266,25)	290,82 (292,85)	302,11 (306,52)	321,88 (320,59)
	E	242,82 (241,64)	265,41 (265,62)	276,70 (277,94)	288,00 (290,60)
	Ch	225,88 (226,68)	245,64 (248,97)	259,76 (260,43)	271,05 (272,21)
	D	268,23 (272,50)	299,29 (299,53)	310,58 (313,43)	330,35 (327,73)
Amide of laevorotatory alfa-(3-phenanthryl-mercapto)-propionic acid	A	208,21	233,53	244,79	256,04
	M	151,94	166,00	174,45	180,07
	E	123,80	135,06	140,68	146,31
	Ch	50,65	53,46	59,09	61,90
	D	92,85	120,99	123,80	129,43
p-Bromophenacyl ester of laevorotatory alfa--(3-phenanthrylmercap-to)-propionic acid	A	388,30	426,65	450,62	479,38
	M	364,33	397,89	421,86	441,03
	E	325,98	354,74	373,92	388,30
	Ch	292,42	321,19	335,57	345,16
	D	373,92	407,48	431,45	450,62
p-Nitrobenzyl ester of laevorotatory alfa--(3-phenanthrylmercap-to)-propionic acid	A	200,38	221,26	229,61	242,13
	M	133,59	150,29	158,64	166,99
	E	104,37	116,89	121,07	125,24
	Ch	100,19	108,54	116,89	121,07
	D	166,99	187,86	192,03	200,38

Solvents: A = acetone, M = methanol, E = ethanol,
Ch = chloroform, D = dioxane;
concentration = C=0,1 g/100 ccm

thylmercapto)-propionic acid and some of its derivatives

r o t a t i o n $(M)_{\lambda}^{20}$						
λ=560,0 nm	λ=546,1 nm	λ=520,0 nm	λ=480,0 nm	λ=435,8 nm	λ=400,0 nm	λ=380,0 nm
429,17 (423,48)	457,40 (455,20)	530,81 (526,86)	677,64 (680,12)	959,98 (960,93)	1375,04 (1373,55)	1823,97 -
350,11 (350,06)	375,52 (374,57)	434,82 (429,49)	553,40 (547,10)	767,99 (766,51)	1095,51 (1105,22)	1445,62 (1441,29)
316,23 (317,14)	338,82 (339,19)	389,64 (388,58)	494,11 (494,29)	694,58 (691,59)	988,22 (997,00)	1304,45 (1301,17)
296,47 (296,91)	319,05 (317,45)	364,23 (363,55)	463,05 (462,82)	552,22 (650,82)	937,40 (948,73)	1256,45 (1252,07)
352,94 (357,71)	383,99 (382,66)	440,46 (438,61)	564,70 (559,37)	796,22 (787,41)	1135,04 (1147,10)	1516,21 (1511,34)
272,92	295,43	343,26	447,37	633,07	936,94	1274,58
196,96	211,02	236,35	298,25	413,61	576,80	765,31
151,94	168,82	191,33	244,79	326,38	455,81	621,81
64,71	70,34	73,15	98,48	129,43	216,65	379,84
146,50	151,94	174,45	233,53	320,75	526,15	768,12
527,32	565,67	642,37	834,13	1179,28	1677,84	2229,14
484,18	522,53	594,44	757,43	1064,23	1514,85	1975,06
431,45	469,80	527,32	671,14	944,39	1342,26	1754,55
383,51	412,27	479,38	604,02	848,51	1217,64	1605,94
488,97	527,32	613,61	786,19	1102,58	1586,76	2080,53
267,18	283,88	333,97	434,16	626,20	939,30	1281,62
179,51	196,21	229,61	292,23	421,64	630,37	880,85
141,94	150,29	175,34	225,43	329,80	500,96	718,04
129,41	141,94	158,64	200,38	283,88	442,51	626,20
229,61	237,96	275,53	354,85	509,31	759,79	1039,49

An analysis of the data collected in the Table 1 shows that the curves representing the function $\frac{1}{\alpha}(\lambda^2)$ within the region $435 < \lambda < 620$ nm for acid 8, its amide 13 and esters 14 and 15 are almost straight lines. It should be stressed that within the region $435 < \lambda < 620$ nm the molar rotations of laevorotatory acid 8 in all the solvents used for measurements were lower than that of amide 13. On the basis of the above data and observations reported by Mattel [7] and Sjöberg [8] it is possible to determine the spatial configurations of optically active α-(3-phenanthrylmercapto)-propionic acids. According to the Swedish authors [7, 8] and our observations [9] laevorotatory α-(3-phenanthrylmercapto)-propionic acid (8) should have S (-) configuration dextrorotatory enantiomer (11), however, the spatial structure R(+). The conformation of this conclusion by another method was very desirable. The suggested correlation could be corroborated by the asymmetric transformation of laevorotatory α-bromopropionic acid to δ (+) α-(3-phenanthrylmercapto)-propionic acid. The starting material for this process was 3-mercaptophenanthrene and laevorotatory ($[\alpha]_D^{20} = -10{,}0^\circ$, acetone) α-bromopropionic acid having S (-)configuration [17, 18] obtained by resolution of racemic acid through the fractional crystallization of its neutral cinchonidine salt. The condensation product, i.e. δ(+) α-(3-phenanthrylmercapto)-propionic acid 12 had a specific rotation $[\alpha]_D^{20} = +30{,}0$ in acetone. Asymmetric transformation occurred according to S_{N2} mechanism with inversion of configuration on the asymmetric carbon atom [17]. Dextrorotatory acid 12 should, therefore, prove R(+) configuration which confirms the results obtained by the optical shift method according to Mattel [7] and Sjöberg [8]. The special structures can be represented by the following projection formulas (Fig. 4).

On the basis of the data collected in Tab. 1 ($380 < \lambda < 623{,}4$ nm) we have determined[*] the functions $[M](\lambda)$ for the dextrorotatory α-(3-phenanthrylmercapto)-propionic acid in the five solvents. These functions have the character of three-term equations which we cite below:

[*] The equations were determined by the method of the least squares using the algorithm of conjugated gradients for finding the functions of many variables (computer ODRA-1013).

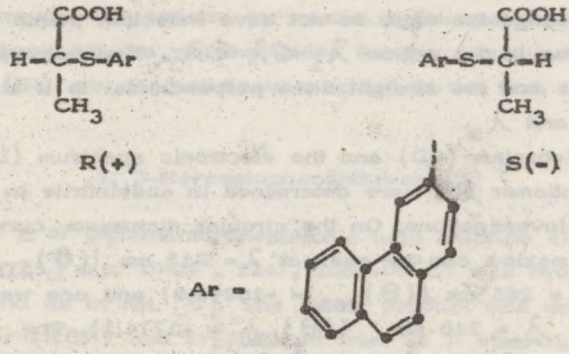


Fig. 4. Spatial configurations of optically active α-(3-phenanthryl-mercapto)-propionic acids

a) in methanol:

$$[M]_{\lambda}^{20} = \frac{1{,}3138743\times10^{9}}{\lambda^2-(216{,}00)^2} - \frac{2{,}3147058\times10^{9}}{\lambda^2-(240{,}00)^2} + \frac{1{,}0878799\times10^{9}}{\lambda^2-(265{,}00)^2}$$

b) in ethanol:

$$[M]_{\lambda}^{20} = \frac{1{,}2508947\times10^{9}}{\lambda^2-(216{,}00)^2} - \frac{2{,}1898239\times10^{9}}{\lambda^2-(240{,}00)^2} + \frac{1{,}0183635\times10^{9}}{\lambda^2-(265{,}00)^2}$$

c) in acetone:

$$[M]_{\lambda}^{20} = \frac{3{,}9668137\times10^{8}}{\lambda^2-(216{,}00)^2} - \frac{9{,}1531778\times10^{8}}{\lambda^2-(240{,}00)^2} + \frac{6{,}1158351\times10^{8}}{\lambda^2-(265{,}00)^2}$$

d) in dioxane:

$$[M]_{\lambda}^{20} = \frac{1{,}6372229\times10^{9}}{\lambda^2-(216{,}00)^2} - \frac{2{,}8634824\times10^{9}}{\lambda^2-(240{,}00)^2} + \frac{1{,}3166548\times10^{9}}{\lambda^2-(265{,}00)^2}$$

e) in chloroform:

$$[M]_{\lambda}^{20} = \frac{1{,}4450174\times10^{9}}{\lambda^2-(216{,}00)^2} - \frac{2{,}5117859\times10^{9}}{\lambda^2-(240{,}00)^2} + \frac{1{,}1427400\times10^{9}}{\lambda^2-(265{,}00)^2}$$

The molar rotation values calculated by means of the above equations are shown in brackets in Tab. 1. The agreement between the calculated values and the results of the experiments is good. The functions $[M](\lambda)$ describing in the rectangular system of coordinates (where λ is the independent variable), the optical pro-

perties of acid 11 change the sign, do not have inflection points and they have extrema in the region $\lambda_1 < \lambda < \lambda_3$. Their asymptotes are the λ axis and the straight lines perpendicular to it at the points λ_1, λ_2 and λ_3.

The circular dichroism (CD) and the electronic spectrum (UV) of laevorotatory enantiomer (8) were determined in acetonitrile in further stage of our investigations. On the circular dichroism curve two strong negative maxima can be seen at λ = 215 nm ($(\theta)_{215}$ = -8514,0) and at λ = 265 nm ($(\theta)_{265}$ = -10296,0) and one weak positive maximum at λ = 240 nm ($(\theta)_{240}$ = +1774,1). The electronic spectrum shows two stong absorption bands situated at λ = 212 nm (ε = 23044,0) and 257 nm (ε = 47889,0) as well as two considerably weaker ones at λ = 230 nm (ε = 17632,0) and 307 nm (ε =15142,0). It is significant that the characteristic points in CD ($\lambda_{\theta\,max}$) and UV ($\lambda_{\varepsilon\,max}$) spectra do not show any scattering on the axis of wave length λ. An analysis of the results of optical measurements leads to the conclusion that optically active α-(3-phenanthrylmercapto)-propionic acids have within the examined spectral range (in acetonitrile) three strong Cotton effects at λ = 215, 240 and 265 nm. It should be stressed that the effects mentioned are localized in the regions consistent with those which could be anticipated on the basis of the analysis of functions $[M](\lambda)$, the signs of these effects are consistent with those of rotational constants appearing in three term equations.

In the view of non-equivalence of positions 1, 2, 3, 4 and 9 in phenanthrene molecule, the determination of the effect of position isomerism of the chirality center in the nucleus on the optical rotation of isomeric α-(phenanthrylmercapto)-propionic acids and the comparison of their optical properties with those of the analogous diphenyl and dibenzofuran derivatives requires further stereochemical studies which we intend to continue. We will be able to draw more general conclusions from our studies after collecting more experimental data.

EXPERIMENTAL

The melting points are uncorrected. IR and UV spectra were obtained by means of Unicam SP-200 and SP-700 spectrophotometers. ORD spectra were obtained by means of Perkin-Elmer 241-MC spectro-

polarimeter and CD spectra by means of Roussel-Jouan III dichrograph. These spectra were obtained for the compounds suspended in Nujol (IR) and for solutions specified in the text.

1. 3-Mercaptophenanthrene (1)

26 g of 3-phenanthrenesulfonic acid chloride (mp. 108-109°, lit. [3, 10, 11] m.p. 108.5°, 114°, 108-109°C) was reduced to mercaptocompound as in ref. [3]. The crude product was dried in a vacuum desiccator (KOH) and crystallized from 96 % ethanol. Colorless plates (8 g), m.p. 112-113°C (lit. [3, 12] m.p. 112-113°C).

2. Racemic α-(3-phenantrylomercapto)-propionic acid (2)

12 g of 3-mercaptophenanthrene (1) and 12 g of rac. α-bromopropionic acid were converted into rac. acid 2 as in ref. [13]. The crude product (8.5 g) was dried at room teperature and crystalized from a mixture of benzene (25 ccm) and cyclohexane (25 ccm). Colorless needles (5 g); m.p. 120-121°C.

Analysis

For $C_{17}H_{14}O_2S$(282.35) - Calcd.: 72.3 % C, 5.6 % H;
found: 72.3 % C, 5.2 % H.

IR (cm^{-1}): 720 ν C-S; 750 δ C_{Ar}-H(subst. 1,2); 900, 1160 δ C_{Ar}-H (subst. 1, 2, 4); 990, 1060, 1140, 1195 δ C_{Ar}-H(subst. 1, 2 and 1, 2, 4); 825 δ C_{Ar}-H(subst. 1, 2, 4 and 1,2, 3, 4); 1460, 1510, 1590, 1610 ν C_{Ar} = C_{Ar}; 930 δ OH(COOH); 1230, 1290, 1420 δ OH and ν C-O(COOH); 1685 ν C=O(COOH).

3. Amide of racemic α-(3-phenanthrylmercapto)-propionic acid (3)

Rac. acid 2 (2,82 g) was converted into its amide under conditions described in ref. [13]. Air dried - crude product (2.6 g) was crystallized from benzene (90 ccm). Colorless plates (1.9 g), m.p. 154-155°C.

Analysis:

For $C_{17}H_{15}NOS$(281.36) - Calcd.: 4.9 % N;
found: 5.1 % N.

4. Thioamide of racemic α-(3-phenanthrylmercapto)-propionic acid (4)

Amide 3 (2.11 g) was converted into corresponding thioamide as in ref. [13] using 0.66 g of potassium polysulfide [14] and 0.74 g of phosphorus pentasulfide [15]. The reaction was carried out in the mixture of benzene (70 ccm) and xylene (70 ccm). The crude product (1.8 g) was crystallized from benzene (25 ccm). Colorless needles (0.9 g), m.p. 137-138°C.

Analysis

For $C_{17}H_{15}NS_2$ (297.43) - Calcd.: 4.7 % N;
found: 4.8 % N.

5. p-Bromophenacyl ester of racemic α-(3-phenanthryl-mercapto)-propionic acid (5)

Rac. acid 2 (2.82 g) was converted into its p-bromophenacyl ester 5 as in ref. [13] using 2.78 g p-bromophenacyl bromide. The estrification reaction was carried out for 1 h at 80°C in 85 % ethanol (130 ccm). The air dried crude product (3.5 g) was crystallized from methanol (300 ccm). Colorless plates (2.5 g), m.p. 121-122°C.

Analysis

For $C_{25}H_{19}BrO_3S$ (479.38) - Calcd.: 62.6 % C, 4.0 % H;
found: 62.9 % C, 4.3 % H.

6. p-Nitrobenzyl ester of rac. α-(3-phenanthrylmercapto)-propionic acid (6)

Rac. acid 2 (2.82 g) was converted into its p-nitrobenzyl ester 6 as in ref. [13] using 2.16 g p-nitrobenzyl bromide. The reaction was carried out for 1 h at 80°C in 82 % ethanol (105 ccm). The crude product (2 g) was crystallized from methanol (90 ccm). Colorless rods (1.5 g), m.p. 87.5-88.5°C.

Analysis

For: $C_{24}H_{19}NO_4S$ (417.46) Calcd.: 3.4 % N;
found: 3.1 % N.

7. Cinchonidine salt of laevorotatory α-(3-phenanthrylmercapto)-propionic acid (7)

Acid 2 (10 g, 0.035 mole) was mixed with 10.3 g (0.035 mole) of cinchonidine and dissolved in 70 ccm of boiling ethyl acetate. The hot solution was filtered and was allowed to stand at room temperature. After 24 h the first fraction of the salt was filtered off. Needles (14 g), m.p. 145-157°C, $[\alpha]_D^{20}$ = -71.0 (c=0.5, d=2, α=-0.710°) in methanol. After two crystallizations of the first fraction (I: 20.3 g; 70 ccm (solvent); 14.0 g, $[\alpha]_D^{20}$ = -71.0°; II: 14.0; 150; 8.0; -91.5; III: 8.0; 160; 5.0; -100.0; IV: 5.0; 110; 3.5; -100.0) the salt had physical properties which did not change during further purification. Colorless needles (3.5 g), m.p. 165-166°C, $[\alpha]_D^{20}$ = -100.0° (c=0.5, d=2, α=-1.00°) in methanol.

Analysis

For $C_{36}H_{36}N_2O_3S$(576.73) - Calcd.: 4.9 % N;
found: 4.9 % N.

8. Laevorotatory α-(3-phenanthrylmercapto)-propionic acid (8)

Powdered cinchonidine salt 7 (7 g) was converted into free acid. The product (2.5 g) was crystallized from cyclohexane (55 ccm). Colorless rods (1.8 g), m.p. 91.5-92.5°C, $[\alpha]_D^{20}$ = -125.0° (c=0.1, d=1, α = -0.125°) in acetone.

Analysis

For $C_{17}H_{14}O_2S$(282.35) - Calcd.: 72.3 % C, 5.0 % H;
found: 72.4 % C, 4.9 % H.

IR(cm^{-1}): 730 ν C-S; 740 δ C_{Ar}-H(subst. 1, 2); 865, 1160 δ C_{Ar}-H (subst. 1, 2, 4); 990, 1060, 1100, 1195 δ C_{Ar}-H(subst. 1, 2 and 1, 2, 4); 830 δ C_{Ar}-H (subst. 1, 2, 4 and 1, 2, 3, 4); 1460, 1505, 1595 ν C_{Ar}=C_{Ar}; 930 δ OH(COOH); 1235, 1280, 1420 δ OH and ν C=O(COOH); 1690 ν C=O(COOH).

9. Cinchonidine salt of dextrorotatory α-(3-phenanthrylmercapto)-propionic acid (9)

Rac. acid 2 (28.2 g; 0.1 mole) was mixed with 29.4 g (0.1 mole) of cinchonidine and was dissolved in 650 ccm of boiling acetone. The hot solution was filtered and was allowed to stand at room temperature. After 24 h the first fraction of the salt was

filtered off. Needles (38 g), m. p. 149-154°C, $[\alpha]_D^{20}$ = -60.0° (c=0.5, d=2, α =-0.60°) in methanol. After three crystalizations of the first fraction (I: 57.6 g; 250 ccm (solvent); 38.0 g; $[\alpha]_D^{20}$ = -60.0°; II: 38.0; 500; 30.0; -52.0; III: 30.0; 490; 22.5; -38.0; IV: 22.5; 400; 18.5; -35.0; V: 18.5; 360; 16.0; -35.0) the salt had the properties which did not change during futher purification. Needles (16.0 g), m.p. 164-165°C, $[\alpha]_D^{20}$ = -35.0° (c=0.5, d=2, α =-0.35°) in methanol.

Analysis

For $C_{36}H_{36}N_2O_3S$ (576.73) - Calcd.: 4.9 % N;
found: 5.1 % N.

10. Laevorotatory α-phenylethylamine salt of dextrorotatory α-(3-phenanthrylmercapto)-propionic acid (10)

Rac. acid 2 (5.6 g, 0.02 mole) was mixed with 2.4 g (0.02 mole) of laevorotatory ($[\alpha]_D^{20}$ = -40.0°; lit [16] $[\alpha]_D^{20}$ = -40.3°) -phenylethylamine and was dissolved in 385 ccm benzene. The hot solution was filtered and allowed to stand at room temperature. After 24 h the first fraction of the salt was filtered off. Needles (4.7 g); m.p. 154-162°C; $[\alpha]_D^{20}$ = +11.0° (c=0.1, d=1, α = +0.011°) in methanol. After four crystallizations (I: 8.0 g; 385 ccm (solvent); 4.7 g; $[\alpha]_D^{20}$ = +11.0°; II: 4.7; 280; 3.1; +25.0; III: 3.1; 255; 2.4; +33.0; IV: 2.4; 250; 1.8; +41.0; V: 1.8; 210; 1.4; +45.0) of the first fraction the salt had the properties which did not change during further purification. Needles (1.2 g); m.p. 165-166°C; $[\alpha]_D^{20}$ = +45.0° (c=0.1, d=1, α = +0.045°) in methanol.

Analysis

For $C_{25}H_{25}NO_2S$ (403.52) - Calcd.: 3.5 % N;
found: 3.2 % N.

11. Dextrorotatory α-(3-phenanthrylmercapto)-propionic acid (11)

a) Powdered cinohonidyne salt 9 (10.0 g) was converted into free acid. The product (4 g) was crystallized from cyclohexane (80 ccm). Needles (2.9 g); m.p. 91.5-92.5°, $[\alpha]_D^{20}$ = +125.0° (c=0.1, d=1, α = +0.125) in acetone.

Analysis

For $C_{17}H_{14}O_2S$(282.35) - Calcd.: 72.3 % C, 5.0 % H;
found: 72.3 % C, 4.8 % H.

b) Powdered α-phenylethylamine salt 10 (3.5 g) was converted into free acid. The product (2.5 g) was crystallized from cyclohexane (50 ccm). Rods (1.8 g); m.p. 91.5-92.5°C; $[\alpha]_D^{20}$ = +125.0° (c=0.1, d=1, α =+0.125°) in acetone.

Analysis

For $C_{17}H_{14}O_2S$(282.35) - Calcd.: 72.3 % C, 5.0 % H;
found: 72.1 % C, 5.0 % H.

12. δ (+) α-(3-phenanthrylmercapto)-propionic acid (12)
(asymmetric transformation)

3-Mercaptophenanthrene (2.10 g; 0.01 mole) was dissolved in 20 ccm of 5 % NaOH. The cooled to 5° solution was treated with a solution of 2 g (0.013 mole) of δ (-) α-bromopropionic acid ($[\alpha]_D^{20}$ = -10.0°; c=0.2, d=1, α =-0.05° in acetone) in 5 ccm of water preoviously neutralized with solid $NaHCO_3$. The solution was allowed to stand 2 h at room temperature. A fine crystalline precipitate soon separated. It was filtered off and dissolved in warm (80°C) water (80 ccm). The solution was filtered and acidified (congo) with 5 % HCl. A fine crystalline precipitate was filtered off (2.6 g), dried in a vacuum desiccator (H_2SO_4) and crystallized from a mixture of benzene (9 ccm) and cyclohexane (27 ccm). Needles (1.7 g); m.p. 112-115°; $[\alpha]_D^{20}$ = +30.0° (c=0.1, d=1, α = +0.030°) in acetone.

Analysis

For $C_{17}H_{14}O_2S$(282.35) - Calcd.: 72.3 % C, 5.0 % H;
found: 72.1 % C, 5.1 % H.

13. Amide of laevorotatory α-(3-phenanthrylmercapto)-propionic acid (13)

Acid 8 (2.82 g) was converted into its amide as in section 3. The crude product (2.3 g) was dried at room temperature and crystallized from benzene (160 ccm). Needles (1.6 g); m.p. 173-174°C, $[\alpha]_D^{20}$ = -87.0° (c=0.1, d=1, α =-0.087°) in acetone.

Analysis

For $C_{17}H_{15}NOS$(281.36) - Calcd.: 4.9 % N;
found: 5.2 % N.

14. p-Bromophenacyl ester of laevorotatory α-(3-phenanthrylmercapto)-propionic acid (14)

Acid 8 (2.82 g) and p-bromophenacyl bromide (2.78 g) were used to esterification which was carried out as in section 5 in 87 % ethanol (110 ccm). The crude product was dried at room temperature and crystallized from methanol (120 ccm). Needles (2.1 g); m. p. 107-108°, $[\alpha]_D^{20} = -94.0°$ (c=0.1, d=1, $\alpha = -0.094°$) in acetone.

Analysis

For $C_{25}H_{19}BrO_3S$(479.38) - Calcd.: 62.6 % C, 4.0 % H;
found: 62.8 % C, 4.1 % H.

15. p-Nitrobenzylester of laevorotatory α-(3-phenanthryl mercapto)-propionic acid (15)

Acid 8 (2.82 g) and p-nitrobenzyl bromide (2.16 g) were used to esterification which was carried out as in section 6 in 85 % ethanol (90 ccm). The crude product (2.8 g) was dried at room temperature and crystallized from methanol (90 ccm). Rods (1.7 g), m.p. 89-90°C, $[\alpha]_D^{20} = -55.0°$ (c=0.1, d=1, $\alpha = -0.055°$) in acetone.

Analysis

For: $C_{24}H_{19}NO_4S$(417.46) - Calcd.: 3.4 % N;
found: 3.2 % N.

16. Racemic α-(3-phenanthrylsulfonyl)-propionic acid (16)

Rac. acid 2 (2.82 g) was oxidized to its sulfonyl derivative as in ref. [13]. The crude product (2.3 g) was dried at room temperature and crystallized from benzene (380 ccm). Needles (1.9 g); m. p. 186-187°C.

Analysis

For: $C_{17}H_{14}O_4S$(314.35) - Calcd.: 64.9 % C, 4.5 % N;
found: 64.9 % C, 4.3 % N.

IR(cm^{-1}): 710 γ C-S; 745 δC_{Ar}-H(subst. 1, 2); 900, 1145 δC_{Ar}-H (subst. 1, 2, 4); 1000, 1070, 1090, 1200 δC_{Ar}-H(subst. 1, 2 and 1, 2, 4); 850 δC_{Ar}-H(subst. 1, 2, 4 and 1, 2, 3, 4); 1460, 1500, 1590, 1600 $\gamma C_{Ar}=C_{Ar}$; 1145 γsSO_2; 1315 $\gamma asSO_2$; 930 δ OH(COOH); 1230, 1280, 1415 δ OH i γCO(COOH); 1640 γCO(COOH).

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STRESZCZENIE

Opisano syntezę i podstawowe własności kwasów -(3-fenantrylomerkapto)-propionowych i -(3-fenantrylosulfonylo)-propionowych. Racemiczny merkaptokwas rozszczepiono w drodze krystalizacji frakcyjnej jego soli z cynchonidyną i lewoskrętną -fenyloetyloaminą z octanu etylu i benzenu na enancjomery. Poszczególnym enancjomerem przypisano bezwzględne konfiguracje przestrzenne. Zdefiniowano w widzialnej i nadfioletowej części widma dyspersję rotacji optycznej lewoskrętnego antymeru, jego amidu i estrów: p-nitrobenzylowego i p-bromofenacylowego. Wyznaczono trójczłonowe równania opisujące rotację optyczną prawoskrętnego enancjomeru w widzialnej i nadfioletowej części widma. Określono widma UV i CD w rejonie 200 300 nm lewoskrętnego antypodu i porównano ich wartości ekstremalne ze stałymi dyspersyjnymi występującymi w równaniach opisujących funkcje M ( ).

РЕЗЮМЕ

Описали синтез и основные свойства α-(3-фенантрилмеркапто)-пропионовых и α-(3-фенантрилсульфонил)- пропионовых кислот. Рацемическую меркаптокислоту расщепили путем фракционной кристаллизации ее солей с цинхонидином и левовращающим α-фенилэтиламином из этилацетата и бензола на энантиомеры. Отдельным энантиомерам приписали абсолютные пространственные конфигурации. Определили в видимом и ультрафиолетовой части спектра дисперсию оптической ротации левовращающего антимера, его амида и р-нитробензильного и р-бромфенацильного эфиров. Установили 3-членные уравнения, описывающие оптическую ротацию правовращающего энантиомера в видимой и ультрафиолетовой части спектра. Определили спектры UV и CD в пределах $200 < \lambda < 300$ nm левовращающего антипода и сравнили их экстремальные величины с дисперсионными постоянными, выступающими в уравнениях, описывающих функции $[M](\lambda)$.

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