ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 1, pp. 102–114. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.E. Shul'ts, D.S. Oleinikov, I.V. Nechepurenko, M.M. Shakirov, G.A. Tolstikov, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 1, pp. 108–119.

Synthetic Transformations of Higher Terpenoids: XVIII.* Synthesis of Optically Active 9,10-Anthraquinone Derivatives

E. E. Shul'ts, D. S. Oleinikov, I. V. Nechepurenko, M. M. Shakirov, and G. A. Tolstikov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: schultz@nioch.nsc.ru

Received February 18, 2008

Abstract—Retro-Diels–Alder decomposition of dodecahydro-*endo*-4b,12-ethenochrysene-1,4-diones obtained from a tricyclic diterpenoid, levopimaric acid, gave optically active 5-[2-(6-vinyl-2,6-dimethyl-2-carboxycyclohexyl)ethyl]-7-isopropyl-1,4-naphthoquinones which reacted with silyloxybutadienes to produce the corresponding 6- and 7-hydroxyanthraquinones, 5-furyl-7-hydroxytetrahydroanthraquinones, or 5-furyl-7-oxohexahydroanthraquinones. Condensation of the naphthoquinone derivatives with 5-isopropenyl-2,3-dihydrothiophene 1,1-dioxide resulted in the formation of 6,11-dioxodihydro- and 6,11-dioxohexahydroanthra[2,1-*b*]thiophene 3,3-dioxides. 6- and 7-Hydroxyanthraquinones were also obtained by reaction of dodecahydro-*endo*-4b,12-ethenochrysene-1,4-diones with Danishevsky diene, followed by cleavage of the polycyclic adducts. The cycloaddition of 5-[2-(-2-carboxy-2,6-dimethyl-6-vinylcyclohexyl)ethyl]-7-isopropyl-1,4-naphthoquinones in the presence of Lewis acids was characterized by increased regioselectivity.

DOI: 10.1134/S1070428009010138

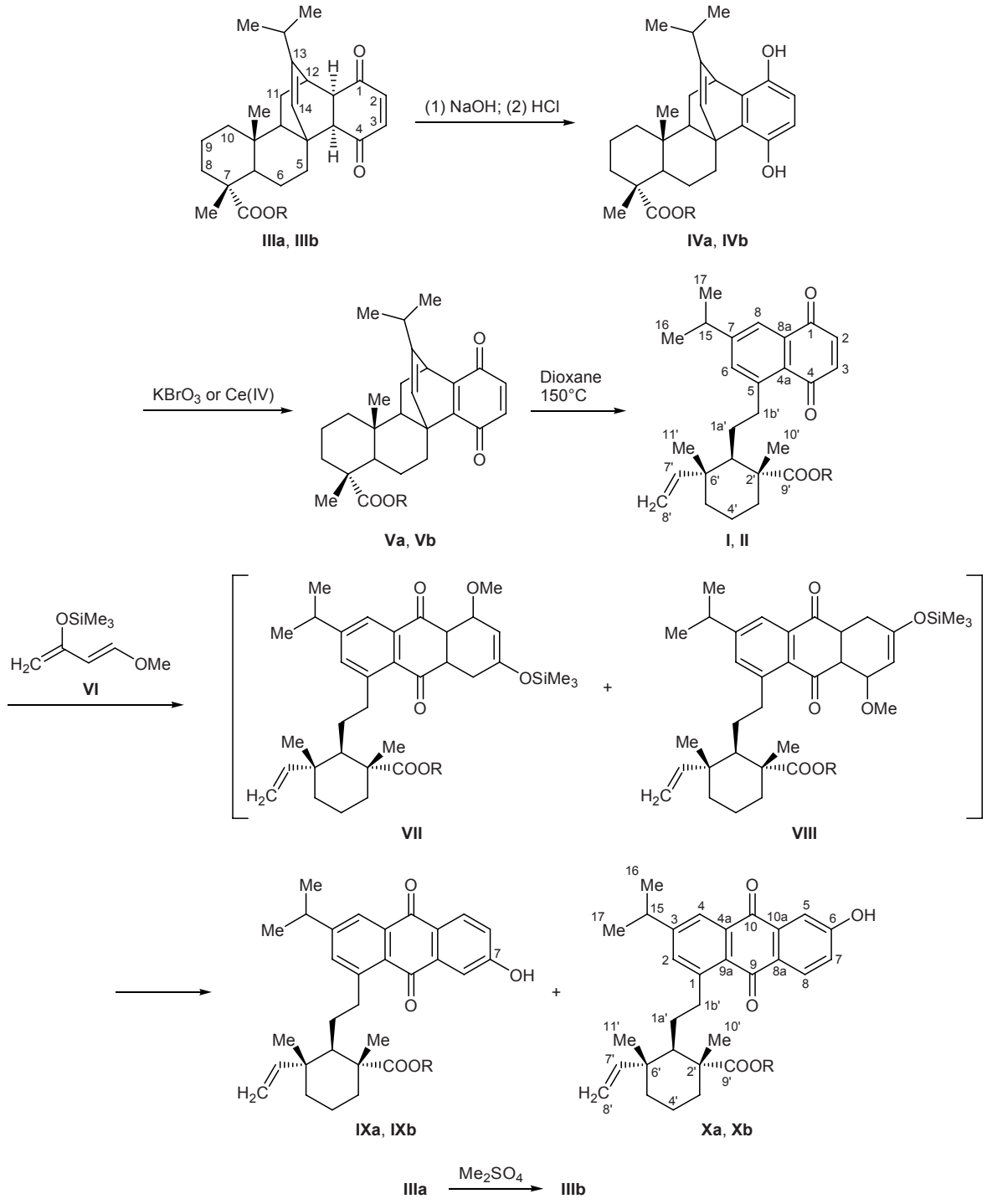
It is well known that functionally substituted 9,10-anthraquinones are very promising as pharmacologically active substances [2–4]. A widely used procedure for the synthesis of such compounds is based on [4+2]-cycloaddition of various dienes to naphthoquinones. We previously described preparation of a series of 9,10-anthraquinone derivatives by transformations of levopimaric acid adducts with 1,4-quinones [5]. In the present article we report on the Diels–Alder reactions of quinones **I** and **II** which were obtained by transformations of levopimaric acid adduct with 1,4-benzoquinone (compound **IIIa**) [6]. Treatment of acid **IIIa** with dimethyl sulfate gave diketo ester **IIIb**. Compounds **IIIa** and **IIIb** were treated with 5% aqueous sodium hydroxide and then with hydrochloric acid; hydroquinones **IVa** and **IVb** were oxidized with silver oxide or cerium ammonium nitrate to polycyclic quinones **Va** and **Vb**, and the latter were subjected to retro-Diels–Alder decomposition in dioxane to obtain naphthoquinone terpenoids **I** and **II** (Scheme 1). The overall yield of quinones **I** and **II**, calculated on levopimaric acid present in pine pitch, was 68–75%.

The behavior of the newly synthesized quinones in [4+2]-cycloaddition was studied using siloxybutadienes and 5-isopropenyl-2,3-dihydrothiophene 1,1-dioxide as diene component. Naphthoquinones **I** and **II** reacted with 1-methoxy-3-trimethylsiloxybuta-1,3-diene (**VI**, Danishefsky diene) [7] in acetonitrile, and subsequent decomposition of primary adducts **VII** and **VIII** by treatment with trifluoroacetic acid gave regioisomeric 7- and 6-hydroxyanthraquinones **IXa**/**Xa** (yield 49%) and **IXb**/**Xb** (65%), respectively. The reaction with methyl ester **II** was more selective: the ratio of compounds **IXb** and **Xb** was 3:1 against 2:1 (**IXa**/**Xa**) in the reaction with acid **I**. The regioselectivity of this reaction increased in the presence of $ZnCl_2$; in this case, the acidolysis products were pure 7-hydroxyanthraquinones **IXa** (yield 55%) and **IXb** (yield 61%).

Likewise, chrysenequinones **Va** and **Vb** reacted with diene **VI** in the presence of $ZnCl_2$ in regioselective fashion to give 2-hydroxybenzo[*b*]chrysenedione derivatives **XIa** and **XIb** in 62 and 77% yield, respectively. Analogous thermal reaction of **Va** in the absence of zinc(II) chloride (acetonitrile, 80°C) resulted in the

* For communication XVII, see [1].

Scheme 1.

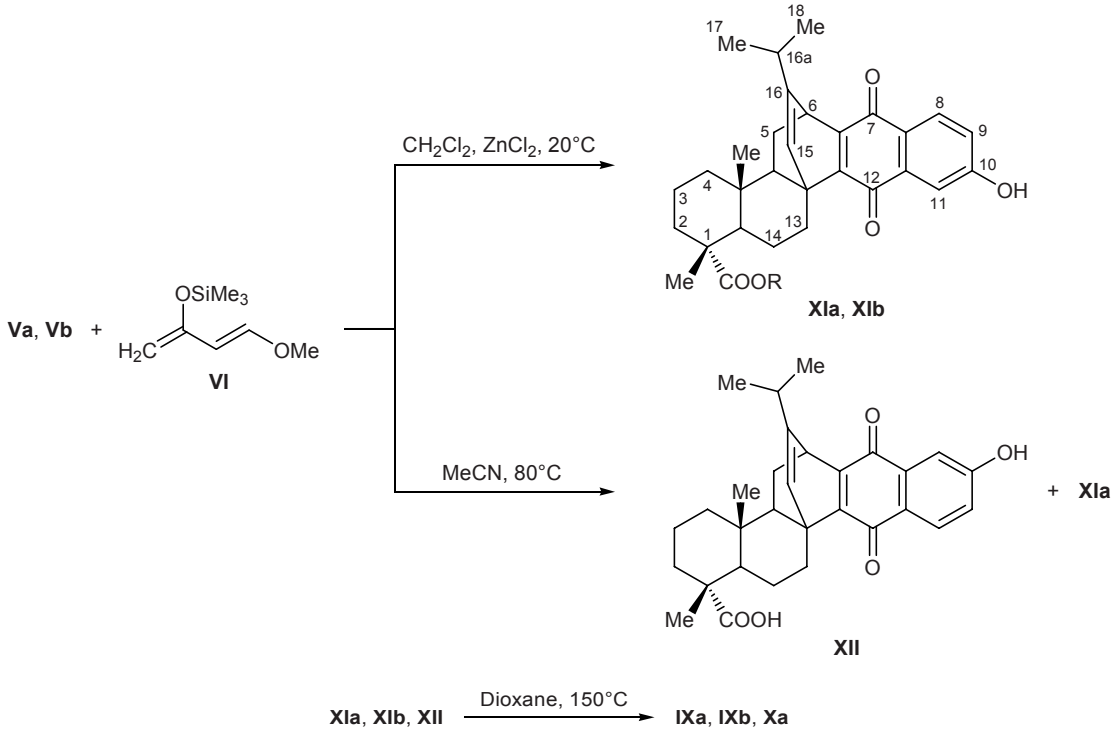


I, R = H; **II**, R = Me; **III**–**V**, **IX**–**XI**, R = H (**a**); Me (**b**).

formation of a mixture of regioisomers **XIa** and **XII** at a ratio of 4 : 1 (overall yield 58%); here, the 10-hydroxy-substituted adduct prevailed (Scheme 2).

Pure 7-hydroxyanthraquinones **IXa** and **IXb** were obtained in quantitative yield by heating polycyclic quinones **XIa** and **XIb** in dioxane at 150°C (in a sealed ampule). Analogous retro-Diels–Alder reaction of quinone mixture **XIa**/**XII** afforded regioisomeric hydroxyanthraquinones **IXa** and **Xa** which were separated by column chromatography.

Scheme 2.



R = H (**a**), Me (**b**).

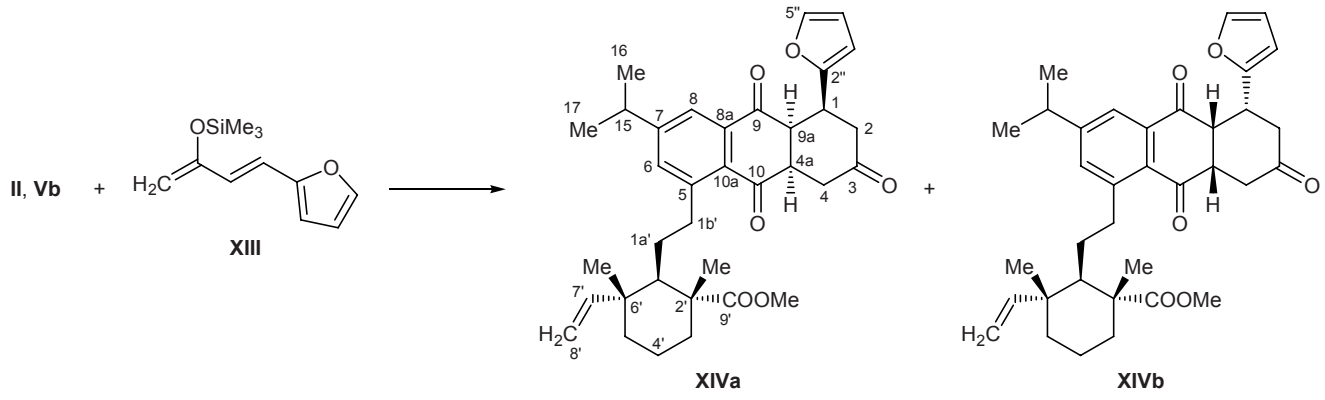
Comparison of the described two synthetic routes (*a* and *b*, see below) to hydroxyanthraquinones starting from levopimaric acid shows that the latter is more effective from the viewpoint of the yield. The primary Diels–Alder adducts can be hydrolyzed by treatment with both water (catalytic reaction) and trifluoroacetic acid.

Path *a*: Levopimaric acid → chrysenequinone → naphthoquinone → hydroxyanthraquinone;

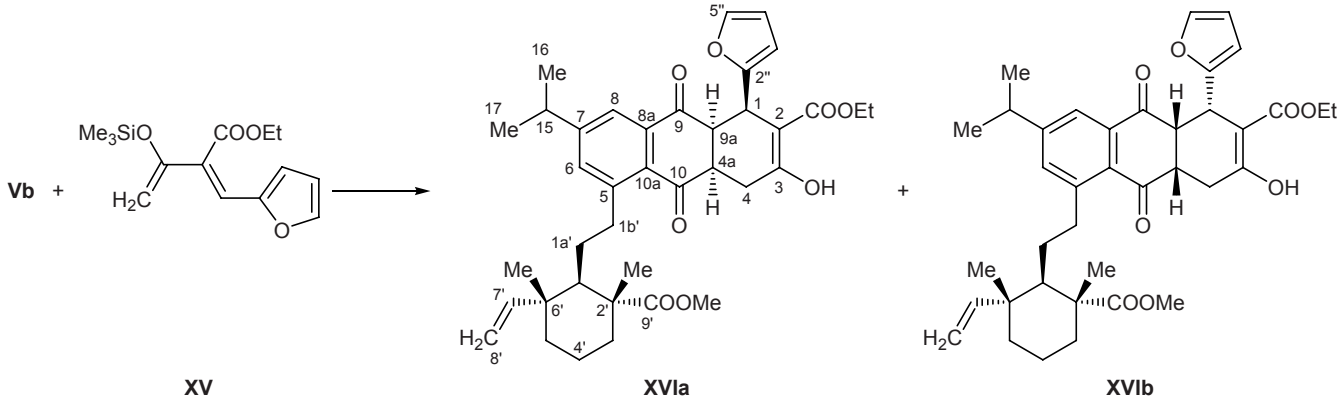
Path *b*: Levopimaric acid → chrysenequinone → benzo[*b*]chrysenedione → hydroxyanthraquinone.

By reaction of chrysenequinone **Vb** with 1-(2-furyl)-3-trimethylsiloxybuta-1,3-diene (**XIII**) [8] on heating in dioxane we obtained products of retro-Diels–Alder decomposition, a mixture of stereoisomeric 3-oxohexahydroanthraquinones **XIVa** and **XIVb** (yield 36%; Scheme 3). The same compounds were formed in the reaction of diene **XIII** with substituted naphthoquinone **II**. Ethyl 2-furfurylidene-3-trimethylsiloxybut-3-enoate (**XV**) [9] reacted with polycyclic quinone **Vb** at a ratio of 1.1:1 to give 43% of stereoisomeric 3-hydroxytetrahydroanthraquinones **XVIa** and **XVIb** (in addition, 11% of naphthoquinone **II** was isolated),

Scheme 3.



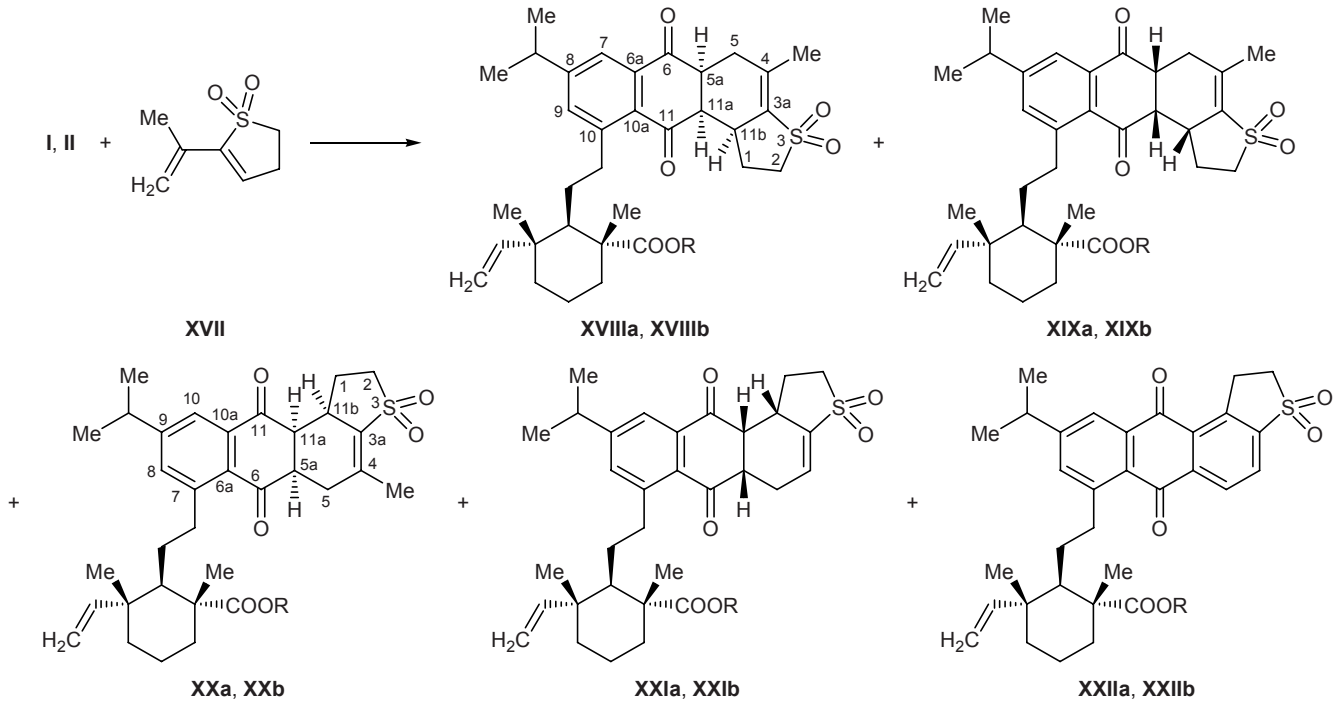
Scheme 4.



while the yield of **XVIa**/**XVIb** increased to 80% in the presence of 2 equiv of the diene (Scheme 4). Unfortunately, we failed to isolate individual stereoisomers in these experiments. The stereochemical results of the reactions of siloxydienes **XIII** and **XV** with naphthoquinone **II** and chrysenequinone (**Vb**), i.e., the formation of equimolar amounts of stereoisomeric adducts, indicates that the first step is cleavage of polycyclic quinone **Vb** to naphthoquinone **II**. Unlike chrysenedione, naphthoquinone **II** contains no substituents capable of affecting the stereoselectivity of cycloaddition.

With a view to obtain sulfur-containing 9,10-anthraquinone derivatives, 5-isopropenyl-2,3-dihydrothiophene 1,1-dioxide (**XVII**) [10] was brought into Diels–Alder reaction with naphthoquinones **I** and **II**. As might be expected, the reaction under thermal conditions (acetonitrile, reflux) was not selective. In both cases, equimolar mixtures of stereoisomeric 6,11-dioxohexahydroanthra[2,1-*b*]thiophene dioxides **XVIIIa**, **XIXa**, **XXa**, and **XXIa** and **XVIIIb**, **XIXb**, **XXb**, and **XXIb** were obtained in 61 and 66% yield from quinones **I** and **II**, respectively. When the reactions with the same reactants were carried out in the presence of a catalyst ($BF_3 \cdot Et_2O$, CH_2Cl_2, 20°C), the overall yield of the above stereoisomeric adducts increased to 75 (**I**) and 70% (**II**). In addition, the fraction of regioisomers

Scheme 5.



R = H (**a**), Me (**b**).

XXa and **XXIa** or **XXb** and **XXIb** was greater, and dehydrogenated derivatives **XXIIa** and **XXIIb** were formed. The catalytic reaction of diene **XVII** with quinone **I** was more selective (**XVIIIa**/**XIXa**/**XXa**/**XXIa**/**XXIIa** ratio 1:1:2:2:1.4) than the reaction with methyl ester **II** (**XVIIIb**/**XIXb**/**XXb**/**XXIb**/**XXIIb** ratio 1:1:1.5:1.5:1; Scheme 5). Regioisomeric adducts **XVIIIa**/**XIXa**, **XXa**/**XXIa**, **XVIIIb**/**XIXb**, and **XXb**/**XXIb**, as well as 6,11-dioxoanthra[2,1-*b*]thiophene 1,1-dioxides **XXIIa** and **XXIIb** were isolated by column chromatography on silica gel.

The structure of the newly synthesized compounds was confirmed by spectral data. In the ^{1}H and ^{13}C NMR spectra of diastereoisomeric 1-(2-furyl)octahydroanthraquinones **XIVa**/**XIVb**, 1-(2-furyl)hexahydroanthraquinones **XVIa**/**XVIb**, and 6,11-dioxohexahydroanthra[2,1-*b*]thiophene 1,1-dioxides **XVIII–XXI** signals from methyl protons and carbon atoms and those in the A ring were doubled, and the difference in the chemical shifts was 0.02–0.30 ppm. The ratio of diastereoisomers was determined on the basis of the ^{1}H NMR spectra from signal intensity ratios of some characteristic proton signals. The ratios of diastereoisomeric 6,11-dioxohexahydroanthra[2,1-*b*]thiophene 1,1-dioxides **XVIIIa**–**XIXa** and **XVIIIb**–**XIXb** and 6,11-dioxoanthra[2,1-*b*]thiophene 1,1-dioxides **XXIIa** and **XXIIb** were determined from the intensities of singlets from protons in the methyl groups on C^4 [δ, ppm: 2.02 (**XVIIIb**), 2.05 (**XIXb**), 2.17 (**XXb**), 2.18 (**XXIb**), 2.70 (**XXIIb**)] and C$^{6'}$ [δ, ppm: 0.98 (**XVIIIb**, **XIXb**), 1.07 (**XXb**, **XXIb**, **XXII**)]. The ratio of diastereoisomers **XIVa** and **XIVb** (1:1) was determined from the 6′-CH_3 (δ 0.98, 1.05 ppm) and MeO signal intensities (δ 3.67, 3.70 ppm). While determining the ratio of isomers **XVIa** and **XVIb** (1:1), intensities of the 6′-CH_3 (δ 0.97, 1.03 ppm), CH_3O (δ 3.65, 3.69 ppm), 1-H (δ 3.86, 3.91 ppm, d), and 2-$OCH_2C\mathbf{H}_3$ (t) proton signals were compared.

The position of the hydroxy group on C^7 in anthraquinones **IXa** and **IXb** or on C^6 in molecules **Xa** and **Xb** was assigned by analysis of multiplicities of the C^9 and C^{10} carbonyl carbon signals in the ^{13}C NMR spectra. The C^{10} signal in the spectrum of **IXa** (δ_C 182.64 ppm) was a doublet of doublets due to coupling with 4-H and 5-H (J = 3.8 Hz in both cases). Simultaneously, the 5-H signal (δ 7.84 ppm) in the ^{1}H NMR spectrum appeared as a doublet ($J_{5,6}$ = 6.8 Hz). The C^9 nuclei resonated at δ_C 185.08 ppm as a doublet due to coupling with 8-H (J = 3.3 Hz), and the latter displayed in the ^{1}H NMR spectrum a doublet with a coupling constant $J_{8,6}$ of 1.5 Hz.

In the proton-coupled ^{13}C NMR spectrum of quinone **Xa**, the C^{10} signal (δ_C 183.75 ppm) is a doublet of doublets due to couplings with 4-H and 5-H. The 5-H proton resonates in the ^{1}H NMR spectrum at δ 7.80 ppm as a doublet ($J_{5,7}$ = 1.5 Hz). The C^9 signal is located at δ_C 185.98 ppm; it is split into a doublet due to coupling with 8-H (J = 3.5 Hz); the latter gives a doublet with $J_{8,7}$ = 7.0 Hz in the ^{1}H NMR spectrum. Analogous analysis of the ^{1}H and ^{13}C NMR spectra allowed us to unambiguously assign the structure of polycyclic quinones **XI**, **XIb**, and **XII**.

Signals from the C^9 and C^{10} carbonyl carbon atoms were assigned, and mutual orientation of the fyryl substituent and terpenoid fragment in **XIVa**/**XIVb** and **XVIa**/**XVIb** and of the terpenoid and sulfolane fragments in 6,11-dioxohexahydroanthra[2,1-*b*]thiophene 1,1-dioxides **XVIIIa**–**XXIa** were determined, using the two-dimensional ^{1}H–^{13}C correlation technique (COLOC) (because of signal doubling due to the presence of diastereoisomers and impossibility of reliably determining coupling constants J_{CH} from routine proton-coupled ^{13}C NMR spectra). The C^9 carbonyl carbon atom (δ_C 195.0 ppm for **XVIa** and **XVIb**) was found to interact with 8-H (δ 7.79 ppm), 1-H (δ 3.86 ppm), and 10a-H (δ 3.75 ppm), while the C^{10} carbonyl carbon nucleus (δ_C 198.2 ppm) was coupled with 4-H (δ 2.58 and 2.32 ppm for **XVIa** and **XVIb**, respectively). These data indicated that the furyl and 2-(cyclohexylethyl) substituents are attached to C^1 and C^5, respectively. In the ^{1}H–^{13}C COLOC spectra of regioisomeric thienoanthraquinones **XVIIIa** and **XIXa** we observed cross peaks between the C^{11} carbonyl carbon atom (δ_C 197.85 and 197.99 ppm, respectively), on the one hand, and aromatic 6-H proton (δ 7.79 ppm) and protons on C^5, on the other (the C^5 signal appeared as a doublet in the JMOD ^{13}C NMR spectrum). The C^{10} carbonyl carbon atom (δ_C 196.02 and 196.09 ppm for **XVIIIa** and **XIXa**, respectively) showed in the COLOC spectrum a cross peak with 10a-H and 10b-H (the corresponding carbon atoms resonated as doublets in the JMOD ^{13}C NMR spectrum). This pattern indicated that the terpenoid fragment is attached to the C^9 atom.

EXPERIMENTAL

The NMR spectra were recorded from solutions in $CDCl_3$ on Bruker AC-200 (200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C), AV-300 (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C), AM-400 (400.13 MHz for ^{1}H and 100.78 MHz for ^{13}C), and DRX-500 spectrometers

(500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C). Signals in the NMR spectra were assigned using various proton–proton and carbon–proton shift correlation techniques (COSY, COLOC).** The molecular weights and elemental compositions were determined from the high-resolution mass spectra (electron impact, 70 eV) which were obtained on a Finnigan MAT-8200 mass spectrometer (ion souce temperature 270–300°C). The IR spectra were measured on a Vector-22 instrument from samples prepared as KBr pellets. The UV spectra were recorded from solutions in ethanol ($c = 10^{-4}$ M) on an HP 8453 UV-Vis spectrophotometer. The melting points were determined on a Kofler hot stage. The optical rotations ($[\alpha]_D^{20}$ values) were measured on Polamat A and Polar 3005 polarimeters from solutions in chloroform or ethanol at room temperature (20–25°C). The progress of reactions was monitored by TLC on Silufol UV-254 plates. The products were isolated by column chromatography on silica gel (0.035–0.070 mm, ACROS Organic).

Pine pitch from *Pinus sylvestris L.* containing ~20% of levopimaric acid (according to the HPLC data and GC–MS data for the methylation products) was used. 2-(3-Trimethylsiloxybuta-1,3-dien-1-yl)furan (**XIII**) [8], ethyl 2-furfurylidene-3-trimethylsiloxybut-3-enoate (**XV**) [9], and 5-isopropenyl-2,3-dihydrothiophene 1,1-dioxide (**XVII**) [10] were synthesized by known methods.

20-Isopropyl-5,9-dimethyl-14,17-dioxopentacyclo[10.6.2.0^{1,10}.0^{4,9}.0^{13,18}]icosa-15,19-diene-5-carboxylic acid (IIIa, 4b,12-etheno-13-isopropyl-7,10a-dimethyl-1,4-dioxo-4,4a,5,6,6a,7,8,9,10,10a,10b,11,12,12a-tetradecahydro-1*H*-chrysene-7-carboxylic acid). A solution of 5.9 g of 1,4-benzoquinone in 50 ml of freshly distilled acetonitrile was added to a solution of 110 g of pine pitch in 100 ml of acetonitrile, and the mixture was left to stand for 7 days at room temperature in the dark. The solvent was distilled off, 50 ml of ethanol was added to the residue, and 30 ml of diethyl ether was added to the resulting solution. The precipitate was filtered off, and washed with cold diethyl ether. Yield 13.6 g (82%, calculated on levopimaric acid), yellow crystals, mp 208–210°C; published data: mp 212–214°C [6], 192°C [11]; $[\alpha]_D^{20} = -168°$ (c = 10.1, $CHCl_3$).

Methyl 20-isopropyl-5,9-dimethyl-14,17-dioxopentacyclo[10.6.2.0^{1,10}.0^{4,9}.0^{13,18}]icosa-15,19-diene-5-carboxylate (IIIb, methyl 4b,12-eteno-13-isopropyl-7,10a-dimethyl-1,4-dioxo-4,4a,5,6,6a,7,8,9,10,10a,10b,11,12,12a-tetradecahydro-1*H*-chrysene-7-carboxylate). Acid **IIIa**, 10.25 g (25 mmol), was dissolved in 150 ml of acetone, 4.14 g (30 mmol) of potassium carbonate and 2.84 ml (30 mmol) of dimethyl sulfate were added, and the mixture was heated for 20 h under reflux, filtered, and evaporated. The residue was treated with 50 ml of water and extracted with chloroform, the extract was washed with water and evaporated, and the residue was recrystallized from methanol–petroleum ether (1:5). Yield 8.02 g (76%), mp 167–168°C; published data [6]: mp 163°C; $[\alpha]_D^{20} = -118°$ (c = 4.5, $CHCl_3$). Mass spectrum, m/z (I_{otn}, %): 424 (5), 365 (3), 316 (100), 187 (22), 146 (45). Found: m/z 424.26195 $[M]^+$. $C_{27}H_{32}O_4$. Calculated: M 424.26134.

14,17-Dihydroxy-20-isopropyl-5,9-dimethylpentacyclo[10.6.2.0^{1,10}.0^{4,9}.0^{13,18}]icosa-13(18),14,16,19-tetraene-5-carboxylic acid (IVa, 4b,12-etheno-1,4-dihydroxy-13-isopropyl-7,10a-dimethyl-4b,5,6,6a,7,8,9,10,10a,10b,11,12-dodecahydrochrysene-7-carboxylic acid). Compound **IIIa**, 4.26 g (10.2 mmol), was added under stirring to 2.3 ml of a 5% solution of sodium hydroxide, preliminarily purged with argon. The mixture was kept for 30 min and acidified with 20 ml of 3% hydrochloric acid to pH 6. The precipitate was filtered off, thoroughly washed with water, and dried first in air and then at 90°C (2 h). Yield 4.0 g (95%), mp 208–210°C, $[\alpha]_D = -108°$ (c = 2.3, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3420, 1690, 1480, 1260. UV spectrum: λ_{max} 296 nm (log ε 3.53). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, 10a-CH_3), 0.76–0.86 m (3H, 10b-H, 11-H), 0.98 d and 1.03 d [3H each, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 1.15 s (3H, 7-CH_3), 1.18–1.35 m (4H, 6-H, 9-H, 10-H), 1.62–1.93 m (6H, 5-H, 6a-H, 8-H, 9-H, 10-H), 2.30 m (1H, 15-H), 2.87 m (1H, 5-H), 4.02 s (1H, 12-H), 5.63 s (1H, 14-H), 6.45 d (1H, 2-H, J = 8.9 Hz), 6.51 d (1H, 3-H, J = 8.9 Hz), 8.32 s (2H, OH), 10.08 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 16.44 (C^{18}), 16.59 (C^{19}), 17.00 (C^9), 20.14 and 20.32 (C^{16}, C^{17}), 22.19 (C^6), 27.86 (C^{11}), 31.88 (C^{15}), 34.00 (C^5), 35.97 (C^{10a}), 36.50 (C^{10}), 38.31 (C^{12}), 38.47 (C^8), 46.82 (C^{4b}), 47.57 (C^7), 49.47 (C^{6a}), 54.49 (C^{10b}), 112.91 (C^3), 114.75 (C^2), 128.44 (C^{14}), 134.95 (C^{4a}), 134.95 (C^{1a}), 142.67 (C^4), 144.45 (C^1), 151.52 (C^{13}), 184.99 (C^{20}). Found, %: C 76.4; H 8.0. $C_{26}H_{34}O_4$. Calculated, %: C 76.06; H 8.35.

Methyl 14,17-dihydroxy-20-isopropyl-5,9-dimethylpentacyclo[10.6.2.0^{1,10}.0^{4,9}.0^{13,18}]icosa-13(18),14,16,19-tetraene-5-carboxylate (IVb, methyl 4b,12-etheno-1,4-dihydroxy-13-isopropyl-7,10a-dimethyl-4b,5,6,6a,7,8,9,10,10a,10b,11,12-dodecahy-

** For atom numbering, see Schemes 1–5.

drochrysene-7-carboxylate). Compound **IIIb**, 0.42 g (1 mmol), was dissolved in 30 ml of ethanol, 3 ml of a 5% solution of sodium hydroxide was added under stirring, and the mixture was kept for 40 min and acidified with 3% hydrochloric acid. The precipitate was filtered off, washed with water, dried, and recrystallized from ethyl acetate. Yield 0.34 g (80%), mp 185–187°C, $[\alpha]_D^{20}$ = –106° (*c* = 1.5, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 0.67 s (3H, 10a-CH_3), 0.76–0.86 m (3H, 10b-H, 11-H), 0.97 d and 1.0 d [3H each, $CH(CH_3)_2$, *J* = 6.9 Hz], 1.15 s (3H, 7-CH_3), 1.18–1.46 m (4H, 6-H, 9-H, 10-H), 1.62–1.98 m (6H, 5-H, 6a-H, 8-H, 9-H, 10-H), 2.30 m (1H, 15-H), 2.80 m (1H, 5-H), 3.66 s (3H, OCH_3), 4.08 s (1H, 12-H) 5.62 s (1H, 14-H), 6.30 d (1H, 2-H, *J* = 8.0 Hz), 6.38 d (1H, 3-H, *J* = 8.0 Hz), 8.0 s (2H, OH). Found, %: C 76.9; H 8.1. $C_{27}H_{36}O_4$. Calculated, %: C 76.38; H 8.55.

Oxidation of hydroquinones IVa and IVb (*general procedure***).** *a*. Compound **IVa** or **IVb**, 4.9 mmol, was dissolved in 40 ml of ethanol, 4.9 mmol of freshly prepared silver oxide was added under stirring, and the mixture was stirred at room temperature (silver deposited on the walls of the flask). When the reaction was complete (5–8 h, TLC), the precipitate was filtered off, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel using chloroform as eluent. Yield of chrysenequinones **Va** and **Vb** 92 and 87%, respectively.

b. Compound **IVa** or **IVb**, 1.3 mmol, was dissolved in 40 ml of anhydrous acetonitrile, 1.3 mmol of ammonium cerium(IV) nitrate was added, and the mixture was stirred for 5–6 h, poured into 70 ml of water, and extracted with chloroform (3×20 ml). The combined extracts were washed with water and a saturated solution of sodium chloride (2×20 ml), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel using chloroform as eluent to isolate 84% of compound **Va** or 89% of **Vb**.

20-Isopropyl-5,9-dimethyl-14,17-dioxopentacyclo[10.6.2.0^{1,10}.0^{4,9}.0^{13,18}]icosa-13(18),15,19-triene-5-carboxylic acid (Va, 4b,12-etheno-13-isopropyl-7,10a-dimethyl-1,4-dioxo-4b,5,6,6a,7,8,9,10,-10a,10b,11,12-dodecahydrochrysene-7-carboxylic acid. mp 140–145° C (from diethyl ether–hexane), $[\alpha]_D^{20}$ = –12.6° (*c* = 4.5, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 0.83 s (3H, 10a-CH_3), 1.15 d and 1.19 d [3H each, $CH(CH_3)_2$, *J* = 7.0 Hz], 1.30 s (3H, 7-CH_3), 1.00–1.97 m (12H, 6-H, 6a-H, 8-H, 9-H, 10-H, 10b-H, 11-H), 2.35 m (1H, 5-H), 2.49 m (1H, 15-H), 2.96 m (1H, 5-H), 4.24 br.s (1H, 12-H), 5.71 s (1H, 14-H), 6.55 d and 6.71 d (1H each, 2-H, 3-H, *J* = 8.2 Hz), 10.18 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 16.29 (C^{18}), 16.44 (C^{19}), 17.05 (C^9), 20.50 and 20.23 (C^{16}, C^{17}), 21.78 (C^6), 27.08 (C^{11}), 31.56 (C^5), 33.92 (C^{15}), 36.44 (C^{10a}), 36.58 (C^{10}), 38.47 (C^{12}), 39.35 (C^8), 46.83 (C^{4b}), 47.17 (C^7), 49.17 (C^{6a}), 54.85 (C^{10b}), 127.13 (C^{14}), 133.50 (C^3), 137.44 (C^2), 150.63 (C^{4a}), 151.11 (C^{13}), 152.72 (C^{1a}), 183.90 (C^1), 184.90 (C^4), 184.99 (C^{20}). Found, %: C 76.65; H 7.80. $C_{26}H_{32}O_4$. Calculated, %: C 76.44; H 7.90.

The spectral parameters of compound **Vb** were consistent with those reported in [12].

Thermolysis of chrysenequinones Va and Vb (*general procedure***).** A solution of 2.3 mmol of compound **Va** or **Vb** in 15 ml of dioxane was heated in a sealed ampule under argon for 10 h at 130°C. The ampule was then cooled and opened, the mixture was diluted with chloroform and filtered, the filtrate was evaporated, and the residue was subjected to chromatography on silica gel using chloroform as eluent. A fraction containing compound **I** or **II** was evaporated, the residue was dissolved in diethyl ether, and the product was precipitated with hexane.

(1*R*,3*R*)-2-[2-(3-Isopropyl-5,8-dioxo-5,8-dihydronaphthalen-1-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylic acid (I). Yield 97%, mp 86–100°C, $[\alpha]_D$ = –21.4° (*c* = 0.3, EtOH). IR spectrum, ν, cm^{-1}: 3430, 1695, 1660, 1280. UV spectrum, λ_{max}, nm (log ε): 252 (4.28), 345 (3.62). ^{1}H NMR spectrum, δ, ppm: 1.01 s (3H, 6′-CH_3), 1.22 d and 1.25 d (3H each, $C^{16}H_3$, $C^{17}H_3$, *J* = 7.0 Hz), 1.35 s (3H, 2′-CH_3), 1.48–1.61 m (6H, 1a′-H, 3′-H, 4′-H, 5′-H), 1.73–2.08 m (3H, 1′-H, 3′-H, 5′-H), 2.62 m (2H, 1b′-H), 2.77 m (1H, 15-H), 4.89 m and 4.94 m (1H each, 8′-H), 5.70 m (1H, 7′-H), 7.41 d (1H, 8-H, *J* = 1.8 Hz), 6.81 d and 6.90 d (1H each, 2-H, 3-H, *J* = 8.2 Hz), 6.77 d (1H, 6-H, *J* = 1.8 Hz), 12.07 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 17.20 ($C^{4'}$), 17.43 ($C^{11'}$), 23.16 and 23.28 (C^{16}, C^{17}), 23.48 ($C^{10'}$), 29.32 ($C^{1a'}$), 34.08 (C^{15}), 34.91 ($C^{1b'}$), 37.02 ($C^{3'}$), 38.72 ($C^{6'}$), 39.91 ($C^{5'}$), 45.35 ($C^{2'}$), 47.20 ($C^{1'}$), 110.91 ($C^{8'}$), 123.29 (C^8), 126.8 (C^{4a}), 131.12 (C^{1a}), 133.4 (C^6), 136.3 and 136.7 (C^2, C^3), 140.36 (C^5), 150.36 ($C^{7'}$), 153.76 (C^7), 184.1 (C^1), 183.6 ($C^{9'}$), 186.0 (C^4). Mass spectrum, *m/z* (I_{rel}, %): 408 (33), 362 (100), 214 (38), 43 (36). Found: *m/z* 408.23001 $[M]^+$. $C_{26}N_{32}O_4$. Calculated: *M* 408.23004.

Methyl (1*R*,3*R*)-2-[2-(3-isopropyl-5,8-dioxo-5,8-dihydronaphthalen-1-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylate (II). Yield 98%, mp 116–

118°C, $[\alpha]_D^{20}$ = –8.6° (*c* = 4.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 1.02 s (CH_3), 1.25 d and 1.29 d (3H each, $C^{16}H_3$, $C^{17}H_3$, *J* = 6.9 Hz), 1.33 s (3H, CH_3), 1.38–1.66 m (6H, 1a′-H, 3′-H, 4′-H, 5′-H), 1.73–1.85 m (3H, 1′-H, 3′-H, 5′-H), 2.76–2.89 m (2H, 1b′-H), 2.97 m (1H, 15-H), 3.70 s (3H, OCH_3), 4.87–4.99 m (2H, 8′-H), 5.72–5.81 m (1H, 7′-H), 6.84 d and 6.88 d (1H each, 2-H, 3-H, *J* = 8.0 Hz), 7.34 d (1H, 8-H, *J* = 1.9 Hz), 7.87 d (1H, 6-H, *J* = 1.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.77 ($C^{4'}$), 18.49 ($C^{11'}$), 23.17 and 23.25 (C^{16}, C^{17}), 24.52 ($C^{10'}$), 29.27 ($C^{1a'}$), 34.18 (C^{15}), 34.92 ($C^{1b'}$), 37.26 ($C^{3'}$), 38.65 ($C^{6'}$), 39.98 ($C^{5'}$), 45.77 ($C^{2'}$), 47.86 ($C^{1'}$), 55.20 (CH_3), 111.21 ($C^{8'}$), 123.29 (C^8), 126.82 (C^{4a}), 131.41 (C^{1a}), 133.45 (C^6), 136.23 (C^2), 136.67 (C^3), 140.41 (C^5), 150.72 ($C^{7'}$), 153.76 (C^7), 179.21 s ($C^{9'}$), 184.62 s (C^1), 186.09 s (C^4). Found, %: C 76.3; H 8.2. $C_{27}H_{34}O_4$. Calculated, %: C 76.74; H 8.11.

Diels–Alder reaction of Danishefsky diene (VI) with quinones I, II, Va, and Vb. *a*. Diene **VI**, 0.49 g (0.6 ml, 2.82 mmol) was added under argon to a solution of 0.54 g (1.32 mmol) of quinone **I** in 20 ml of acetonitrile. The mixture was heated for 16 h under reflux, the solvent was evaporated under reduced pressure, the residue, 1.05 g, was dissolved in 12 ml of methylene chloride–methanol (3:1), two drops of trifluoroacetic acid were added, and the mixture was kept for 1 h. The solvent was removed under reduced pressure, the residue was dissolved in 50 ml of methylene chloride, the solution was washed first with water and then with a saturated solution of sodium chloride and dried over $MgSO_4$, the solvent was removed, and the residue was separated by column chromatography on silica gel using chloroform and chloroform–ethanol (10:1) as eluents. Two fractions were isolated. The first of these contained 0.09 g of compound **IXa**, and the second, 0.13 g of a mixture of 2- and 3-hydroxyanthraquinones **IXa** and **Xa** (overall yield 49%). The second fraction was ground with petroleum ether, and the precipitate, 0.1 g of a mixture of anthraquinones **IXa** and **Xa** at a ratio of 2.2:1 (mp 157–160°C), was filtered off. Repeated chromatographic separation using benzene–diethyl ether (1:1) as eluent, followed by recrystallization from ethyl acetate, gave 0.05 g of compound **Xa**. Following the above procedure, from 1.05 g of quinone **II** and 0.9 g of diene **VI** we obtained 0.58 g (65%) of anthraquinone mixture **IXb**/**Xb**. By column chromatography on silica gel we isolated 0.22 g of **IXb** (eluent chloroform) and 0.12 g of **Xb** (benzene–diethyl ether, 1:1). Following the above procedure with 0.55 g of quinone **Va** and 0.55 g of diene **VI**, after double chromatographic separation [(1) chloroform, chloroform–ethanol, 10:1; (2) benzene–diethyl ether], we isolated 0.27 g (58%) of a mixture of anthraquinones **XIa** and **XII** at a ratio of 4:1. Recrystallization of that mixture from diethyl–acetonitrile gave a finely crystalline product containing the same compounds at the same ratio; we also failed to separate regioisomers **XIa** and **XII** by subsequent recrystallization from petroleum ether–diethyl ether.

b. Zinc(II) chloride, 0.37 g (2.71 mmol), was dispersed in 20 ml of anhydrous tetrahydrofuran, and a solution of 1.0 g (2.45 mmol) of quinone **I** in 5 ml of THF and 1.27 g (1.6 ml, 7.4 mmol) of diene **VI** were added in succession under argon. The mixture was kept for 30 h at room temperature with occasional stirring, poured into 30 ml of water, stirred for 30 min, and extracted with 100 ml of methylene chloride. The extract was washed with water and a saturated solution of sodium chloride and dried over magnesium sulfate. The solvent was distilled off, and the oily residue, 1.07 g, was subjected to chromatography on silica gel to isolate 0.46 g (55%) of 2-hydroxyanthraquinone **IXa**. Likewise, from 0.5 g of quinone **II** and 0.46 g of diene **VI** we obtained 0.28 g (65%) of 2-hydroxyanthraquinone **IXb**. In the reaction of 0.35 g of quinone **Va** with 0.42 g of diene **VI** we isolated 0.18 g (62%) of benzo[*b*]chrysenequinone **XIa**, and the reaction of 0.65 g of compound **Vb** with 0.62 g of diene **VI** gave 0.42 g (77%) of quinone **XIb**.

(1*R*,3*R*)-2-[2-(7-Hydroxy-3-isopropyl-9,10-dioxo-9,10-dihydroanthracen-1-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylic acid (IXa). mp 183–185°C (from chloroform), $[\alpha]_D^{20}$ = –32.6° (*c* = 3.8, $CHCl_3$). UV spectrum, λ_{max}, nm (log ε): 269 (3.15), 342 (2.34). ^{1}H NMR spectrum, δ, ppm: 1.12 s (3H, 6′-CH_3), 1.21 d and 1.25 d (3H each, $C^{16}H_3$, $C^{17}H_3$, *J* = 7.0 Hz), 1.19–1.42 m (4H, 1a′-H, 4′-H, 5′-H), 1.30 s (3H, 2′-CH_3), 1.56–1.78 m (3H, 1a′-H, 3′-H, 5′-H), 1.87–2.18 m (2H, 1′-H, 3′-H), 2.58 m (2H, 1b′-H), 2.85 m (1H, 15-H), 4.81–4.91 m (2H, 8′-H), 5.65–5.75 m (1H, 7′-H), 6.90 d.d (1H, 6-H, *J* = 6.8, 1.5 Hz), 7.28 d (1H, 4-H, *J* = 1.9 Hz), 7.41 d (1H, 8-H, *J* = 1.5 Hz), 7.62 d (1H, 2-H, *J* = 1.9 Hz), 7.84 d (1H, 5-H, *J* = 6.8 Hz), 8.80 br.s (1H, OH), 12.21 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 18.03 ($C^{4'}$), 18.20 and 18.78 ($C^{10'}$, $C^{11'}$), 23.30 and 23.36 (C^{16}, C^{17}), 29.32 ($C^{1a'}$), 34.08 (C^{15}), 35.19 ($C^{1b'}$), 37.48 ($C^{3'}$), 40.69 ($C^{5'}$), 42.41 ($C^{6'}$), 46.04 ($C^{2'}$), 47.35 ($C^{1'}$), 111.05 ($C^{8'}$), 112.97 (C^8), 120.93 (C^6), 124.00 (C^4), 125.56 (C^{10a}), 128.96 (C^{9a}), 129.63 (C^5), 130.95 (C^2), 134.21 (C^{4a}),

136.75 (C^{8a}), 140.76 (C^{1}), 150.96 ($C^{8'}$), 154.69 (C^{3}), 162.07 (C^{7}), 182.64 (C^{10}), 184.91 (COOH), 185.08 (C^{9}). Mass spectrum: *m*/*z* 474.23992 $[M]^+$. $C_{30}H_{34}O_5$. Calculated: *M* 474.24061.

(1*R*,3*R*)-2-[2-(6-Hydroxy-3-isopropyl-9,10-dioxo-9,10-dihydroanthracen-1-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylic acid (X). $[\alpha]_D^{20}$ = –42.2° (*c* = 5.5, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3300, 3271, 1692, 671, 1670, 1583, 1302, 1076, 898, 858, 758, 724. UV spectrum, λ_{max}, nm (logε): 215 (4.39), 271 (4.53), 347 (3.75). ^1H NMR spectrum, δ, ppm: 1.12 s (3H, 6′-CH_3), 1.25 d and 1.28 d (3H each, $C^{16}H_3$, $C^{17}H_3$, *J* = 7.0 Hz), 1.30 s (3H, 2′-CH_3), 1.39–1.70 m (6H, 1a′-H, 4′-H, 5′-H), 1.91 m (1H, 3′-H), 2.18 m (2H, 1′-H, 3′-H), 2.72 m (2H, 1b′-H), 2.85 m (1H, 15-H), 4.86 m and 4.92 m (1H each, 8′-H), 5.65–5.75 m (1H, 7′-H), 6.82 d (1H, 7-H, *J* = 7.0, 1.5 Hz), 7.28 d (1H, 4-H, *J* = 1.8 Hz), 7.68 d (1H, 2-H, *J* = 1.8 Hz), 7.80 d (1H, 5-H, *J* = 1.5 Hz), 7.84 d (1H, 8-H, *J* = 7.0 Hz), 8.9 br.s (1H, OH), 10.30 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 18.23 ($C^{4'}$), 18.28 and 18.91 ($C^{10'}$, $C^{11'}$), 23.23 and 23.36 (C^{16}, C^{17}), 29.82 ($C^{1a'}$), 33.16 (C^{15}), 34.12 ($C^{1b'}$), 35.89 ($C^{3'}$), 38.52 ($C^{5'}$), 39.91 ($C^{6'}$), 45.94 ($C^{2'}$), 47.85 ($C^{1'}$), 111.65 ($C^{8'}$), 113.39 (C^{5}), 121.09 (C^{7}), 124.78 (C^{4}), 125.62 (C^{8a}), 129.12 (C^{2}), 129.83 (C^{8}), 130.95 (C^{9a}), 133.51 (C^{4a}), 136.25 (C^{10a}), 139.12 (C^{1}), 151.06 ($C^{8'}$), 154.91 (C^{3}), 161.92 (C^{6}), 183.75 (C^{10}), 185.00 (COOH), 185.98 (C^{9}). Mass spectrum: *m*/*z* 474.24033 $[M]^+$. $C_{30}H_{34}O_5$. Calculated: *M* 474.24061.

Methyl (1*R*,3*R*)-2-[2-(7-hydroxy-3-isopropyl-9,10-dioxo-9,10-dihydroanthracen-1-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylate (IXb). mp 148–151°C (from ethyl acetate), $[\alpha]_D^{20}$ = –29.5° (*c* = 5.3, $CHCl_3$). UV spectrum, λ_{max}, nm (logε): 214 (3.22), 271 (3.33), 342 (2.60), 464 (1.72). IR spectrum, ν, cm^{-1}: 3372 (OH); 1669, 1724 (C=O). ^1H NMR spectrum, δ, ppm: 1.21 d and 1.24 d (3H each, $C^{16}H_3$, $C^{17}H_3$, *J* = 7 Hz), 1.12 s and 1.30 s (3H each, 2′-CH_3, 6′-CH_3), 1.47–1.62 m (5H, 1a′-H, 4′-H, 5′-H), 1.78–1.92 m (2H, 5′-H, 3′-H), 2.10 m (2H, 1′-H, 3′-H), 2.76 m (2H, 1b′-H), 2.92 m (1H, 15-H), 3.67 s (3H, OCH_3), 4.81–4.90 m (2H, 8′-H), 5.79 m (1H, 7′-H), 7.08 d.d (1H, 6-H, *J* = 6.8, 1.5 Hz), 7.37 d (1H, 4-H, *J* = 1.8 Hz), 7.57 d (1H, 8-H, *J* = 1.5 Hz), 8.03 d (1H, 5-H, *J* = 6.8 Hz), 8.10 d (1H, 2-H, *J* = 1.8 Hz), 8.88 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 18.03 ($C^{4'}$), 18.12 and 19.08 ($C^{10'}$, $C^{11'}$), 23.30 (C^{16}, C^{17}), 29.32 ($C^{1a'}$), 33.42 (C^{15}), 34.50 ($C^{1b'}$), 35.79 ($C^{3'}$), 39.69 ($C^{5'}$), 40.09 ($C^{6'}$), 45.84 ($C^{2'}$), 47.56 ($C^{1'}$), 51.95 (OMe), 111.10 ($C^{8'}$), 112.95 (C^{8}), 120.80 (C^{6}), 123.98 (C^{4}), 125.56 (C^{10a}), 129.48 (C^{2}), 129.65 (C^{5}), 130.19 (C^{9a}), 134.93 (C^{4a}), 136.87 (C^{8a}), 140.78 (C^{1}), 150.91 ($C^{7'}$), 153.70 (C^{3}), 162.0 (C^{2}), 177.05 (C=O), 182.64 (C^{10}), 185.08 (C^{9}). Mass spectrum: *m*/*z* 488.25821 $[M]^+$. $C_{31}H_{36}O_5$. Calculated: *M* 488.25626.

Methyl (1*R*,3*R*)-2-[2-(6-hydroxy-3-isopropyl-9,10-dioxo-9,10-dihydroanthracen-1-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylate (Xa). mp 162–165°C (from ethyl acetate), $[\alpha]_D^{20}$ = –34.1° (*c* = 7.3, $CHCl_3$). UV spectrum, λ_{max}, nm (logε): 214 (3.22), 271 (3.33), 342 (2.60), 464 (1.72). ^1H NMR spectrum, δ, ppm: 1.21 d and 1.26 d (3H each, $C^{16}H_3$, $C^{17}H_3$, *J* = 7 Hz), 1.12 s and 1.33 s (3H each, 2′-CH_3, 6′-CH_3), 1.37–1.62 m (5H, 1a′-H, 4′-H, 5′-H), 1.80 m (2H, 3′-H, 5′-H), 1.88–2.12 m (2H, 1′-H, 3′-H), 2.93 m (2H, 1b′-H), 2.96 m (1H, 15-H), 3.67 s (3H, OCH_3), 4.81–4.90 m (2H, 8′-H), 5.79 m (1H, 7′-H), 7.08 d.d (1H, 7-H, *J* = 6.8, 1.3 Hz), 7.35 d (1H, 4-H, *J* = 1.8 Hz), 7.47 d (1H, 5-H, *J* = 1.3 Hz), 7.96 d (1H, 2-H, *J* = 1.8 Hz), 8.08 d (1H, 8-H, *J* = 6.8 Hz), 8.80 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 18.12 ($C^{4'}$), 18.21 and 18.96 ($C^{10'}$, $C^{11'}$), 23.18 and 13.29 (C^{16}, C^{17}), 29.99 ($C^{1a'}$), 33.26 (C^{15}), 35.08 ($C^{1b'}$), 37.51 ($C^{3'}$), 40.01 ($C^{5'}$), 41.16 ($C^{6'}$), 46.02 ($C^{2'}$), 47.05 ($C^{1'}$), 51.95 (OCH_3), 111.10 ($C^{8'}$), 112.09 (C^{5}), 120.12 (C^{7}), 124.08 (C^{4}), 125.26 (C^{8a}), 129.41 (C^{2}), 129.76 (C^{5}), 130.39 (C^{9a}), 135.09 (C^{4a}), 136.42 (C^{10a}), 141.09 (C^{1}), 150.68 ($C^{7'}$), 152.72 (C^{3}), 161.68 (C^{6}), 176.88 (C=O), 183.34 (C^{10}), 184.98 (C^{9}). Mass spectrum: *m*/*z* 488.25821 $[M]^+$. $C_{31}H_{36}O_5$. Calculated: *M* 488.25626.

8-Hydroxy-24-isopropyl-5,9-dimethyl-14,21-dioxohexacyclo[10.6.2.$0^{1,10}$.$0^{4,9}$.$0^{13,22}$.$0^{15,20}$]tetracosa-13(22),15,17,19-tetraene-5-carboxylic acid (XIa, 6,12b-etheno-10-hydroxy-16-isopropyl-1,4-dimethyl-7,12-dioxo-1,1a,2,3,4,4a,4b,5,6,7,12,12b,13,14-tetradecahydrobenzo[*b*]chrysene-1-carboxylic acid). mp 142–144°C (from ethyl acetate), $[\alpha]_D^{20}$ = –28.6° (*c* = 3.0, $CHCl_3$). ^1H NMR spectrum, δ, ppm: 0.68 (3H, 4a-CH_3), 0.97 d and 1.02 d (3H each, $C^{17}H_3$, $C^{18}H_3$, *J* = 7 Hz), 1.17 s (3H, 1-CH_3), 1.11–1.52 m (9H, 2-H, 3-H, 4-H, 4a-H, 5-H, 14-H), 1.70–2.12 m (4H, 3-H, 4-H, 13-H, 14a-H), 2.47 m (1H, 16a-H), 2.58 m (1H, 13-H), 3.88 m (1H, 6-H), 5.58 s (1H, 15-H), 7.03 d.d (1H, 8-H, *J* = 8.0, 1.6 Hz), 7.39 s (1H, 11-H, *J* = 1.6 Hz), 7.87 d (1H, 8-H, *J* = 8.0 Hz), 8.80 br.s (1H, OH), 11.85 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 15.03 (4a-CH_3), 16.12 (1-CH_3), 17.28 (C^{3}), 21.38 and 21.62 (C^{17}, C^{18}), 21.92 (C^{14}), 27.85 (C^{5}), 32.20 (C^{16a}), 32.48 (C^{12b}), 36.48 (C^{13}), 37.62 (C^{6}),

39.04 (C^2), 39.33 (C^{4a}), 47.95 (C^1), 49.95 (C^{4b}), 49.39 (C^4), 54.40 (C^{14a}), 112.59 (C^{11}), 118.98 (C^9), 124.98 (C^{7a}), 126.95 (C^{15}), 128.26 (C^8), 135.18 (C^{11a}), 151.23 (C^{6a}), 152.96 (C^{16}), 154.89 (C^{12a}), 161.75 (C^{10}), 181.62 (C^7), 183.11 (C^{12}), 184.82 (C=O). Mass spectrum: *m*/*z* 474.23990 $[M]^+$. $C_{30}H_{34}O_5$. Calculated: *M* 474.24061.

Methyl 8-hydroxy-24-isopropyl-5,9-dimethyl-14,21-dioxohexacyclo[10.6.2.0^{1,10}.0^{4,9}.0^{13,22}.0^{15,20}]-tetracosa-13(22),15,17,19-tetraene-5-carboxylate (XIb, methyl 6,12b-etheno-10-hydroxy-16-isopropyl-1,4-dimethyl-7,12-dioxo-1,1a,2,3,4,4a,4b,5,6,7,-12,12b,13,14-tetradecahydrobenzo[*b*]chrysene-1-carboxylate). mp 125–127°C (from diethyl ether), $[\alpha]_D^{20}$ = –21.6° (*c* = 4.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3371 (OH); 1726, 1698 (C=O). UV spectrum, λ_{max}, nm (log ε): 270 (3.20), 346 (2.25). ^{1}H NMR spectrum, δ, ppm: 0.68 (3H, 4a-CH_3), 0.98 d and 1.02 d (3H each, $C^{17}H_3$, $C^{18}H_3$, *J* = 7 Hz), 1.16 s (3H, 1-CH_3), 1.03–1.50 m (9H, 2-H, 3-H, 4-H, 4a-H, 5-H, 14-H), 1.70–2.12 m (4H, 3-H, 4-H, 13-H, 14a-H), 2.46 m (1H, 16a-H), 2.52 m (1H, 13-H), 3.93 m (1H, 6-H), 3.70 s (3H, OCH_3), 5.59 s (1H, 15-H), 7.05 d (1H, 8-H, *J* = 8.0 Hz), 7.49 s (1H, 11-H, *J* = 1.5 Hz), 7.92 d.d (1H, 9-H, *J* = 8.0, 1.5 Hz), 8.80 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 15.25 (4a-CH_3), 16.03 (1-CH_3), 17.64 (C^3), 21.15 and 21.48 (C^{17}, C^{18}), 21.38 (C^{14}), 27.62 (C^5), 32.02 (C^{16a}), 32.61 (C^{12b}), 36.31 (C^{13}), 37.28 (C^6), 38.64 (C^2), 39.40 (C^{4a}), 47.28 (C^1), 49.62 (C^{4b}), 49.93 (C^4), 52.50 (OCH_3), 54.92 (C^{14a}), 113.28 (C^{11}), 119.46 (C^9), 124.83 (C^{7a}), 127.12 (C^{15}), 128.01 (C^8), 135.78 (C^{11a}), 151.07 (C^{6a}), 152.19 (C^{16}), 155.81 (C^{12a}), 161.38 (C^{10}), 179.85 (C=O), 181.16 (C^7), 183.08 (C^{12}). Mass spectrum: *m*/*z* 488.25821 $[M]^+$. $C_{31}H_{36}O_5$. Calculated: *M* 488.25626.

Retro-Diels–Alder decomposition of compounds XIa/XII and XIb. *a*. A solution of 0.24 g of adduct **XIb** in 20 ml of dioxane was heated for 8 h in a sealed ampule in the presence of molecular sieves. The solvent was distilled off under reduced pressure, the residue was ground with diethyl ether, and the precipitate of anthraquinone **IXb** was filtered off. Yield 0.22 g, mp 148–152°C.

b. A solution of 0.45 g of regioisomer mixture **XIa**/**XII** in 30 ml of dioxane was heated for 9 h in a sealed ampule in the presence of molecular sieves. The solvent was distilled off under reduced pressure, and the residue, 0.46 g, was subjected to chromatography on silica gel. Elution with chloroform gave 0.06 g of 6-hydroxyanthraquinone **Xa**, and the subsequent elution with chloroform–ethanol (20 : 1) gave 0.28 g of 7-hydroxyanthraquinone **IXa**.

Diels–Alder reactions of quinones II and Vb with dienes XIII and XV (*general procedure***).** Diene **XIII** or **XIV**, 1.1–2 equiv, was added to a solution of 1.25 mmol of quinone **II** or **Vb** in 30 ml of anhydrous dioxane, and the mixture was heated for 23–33 h under argon in a sealed ampule. The ampule was cooled and opened, the solvent was evaporated under reduced pressure, and oily products were isolated by column chromatography on silica gel using petroleum ether–diethyl ether (3 : 1) and diethyl ether for **XIVa** and **XIVb** and chloroform and chloroform–methanol (100 : 1) for **XVIa** and **XVIb**.

Methyl (1*R*,3*R*)-2-{2-[5-(furan-2-yl)-3-isopropyl-7,9,10-trioxo-5,6,7,8,8a,9,10,10a-octahydroanthracen-1-yl]ethyl}-1,3-dimethyl-3-vinylcyclohexane-1-carboxylate (XIVa/XIVb) (mixture of diastereoisomers**).** ^{1}H NMR spectrum, δ, ppm: 0.98 s and 1.05 s (3H, CH_3), 1.19 d and 1.22 d (3H each, $C^{16}H_3$, $C^{17}H_3$, *J* = 7 Hz), 1.27 s (3H, CH_3), 1.40–1.63 m (5H, 1a′-H, 4′-H, 5′-H), 1.80–2.13 m (4H, 1′-H, 3′-H, 5′-H), 2.19–2.32 m and 2.45–2.52 m (2H each, 2-H, 4-H), 2.60 m (2H, 1b′-H), 2.77 m (1H, 15-H), 3.62 m (1H, 4a-H), 3.67 s and 3.70 s (3H, OCH_3), 3.83 m (1H, 1-H), 4.12 m (1H, 9a-H), 4.89 m (2H, 8′-H), 5.72 m (1H, 7′-H), 6.05 m and 6.10 m (1H, 3″-H), 6.35 d.d (1H, 4″-H, *J* = 3.2, 2.6 Hz), 7.44 d (1H, 6-H, *J* = 1.4 Hz), 7.48 d.d (1H, 5″-H, *J* = 2.6, 1.2 Hz), 7.78 d (1H, 8-H, *J* = 1.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.02 ($C^{4'}$), 18.61 and 19.32 (6′-CH_3), 20.01 (2′-CH_3), 23.72 (C^{16}, C^{17}), 28.31 and 28.72 (C^1), 30.11 ($C^{1a'}$), 33.81 (C^{15}), 35.12 ($C^{1b'}$), 36.51 and 36.93 (C^{4a}), 38.03 ($C^{3'}$), 39.22 ($C^{5'}$), 40.31 and 40.52 (C^4), 41.81 ($C^{6'}$), 43.08 and 43.31 (C^2), 44.71 ($C^{2'}$), 47.81 ($C^{1'}$), 50.42 and 50.61 (C^{9a}), 52.11 (CH_3), 107.67 ($C^{3''}$), 111.08 ($C^{4''}$), 112.13 ($C^{8'}$), 123.91 (C^8), 128.26 (C^6), 132.51 (C^{10a}), 134.34 (C^{8a}), 140.71 (C^5), 141.52 ($C^{5''}$), 151.61 ($C^{7'}$), 152.22 ($C^{2''}$), 153.81 (C^7), 179.22 (C=O), 196.45 (C^9), 198.11 (C^{10}), 205.31 (C^3). Found, %: C 75.2; H 8.0. $C_{35}H_{42}O_6$. Calculated, %: C 75.24; H 7.58.

Ethyl (1*R*,3*R*)-1-(furan-2-yl)-3-hydroxy-7-isopropyl-5-[2-(2-methoxycarbonyl-2,6-dimethyl-2-vinylcyclohexyl)ethyl]-9,10-dioxo-1,4,4a,9,9a,10-hexahydroanthracene-2-carboxylate (XVIa/XVIb) (mixture of diastereoisomers**).** $[\alpha]_D$ = –3.0° (*c* = 5.21, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3429, 1694, 1598, 1235. UV spectrum, λ_{max}, nm (log ε): 235 (4.37); in the presence of NaOH: 235 (4.29), 461 (3.36), 612 (2.92). ^{1}H NMR spectrum, δ, ppm: 0.97 and 1.03 (3H, CH_3), 1.16 d and 1.18 d (3H each, $C^{16}H_3$, $C^{17}H_3$, *J* = 7 Hz), 1.26 s (3H, CH_3), 1.25 t and 1.28 t (3H, CH_3, *J* =

7 Hz), 1.42–1.58 m (5H, 1a′-H, 4′-H, 5′-H), 1.88–2.13 m (4H, 1′-H, 3′-H, 5′-H), 2.32 m and 2.58 m (1H each, 4-H), 2.68 m (2H, 1b′-H), 2.75 (1H, 15-H), 3.39 m (1H, 4a-H), 3.65 s and 3.69 s (3H, OCH_3), 3.75 m (1H, 9a-H), 3.86 d and 3.91 d (1H, 1-H, J = 4 Hz), 4.14 q and 4.19 q (2H, C**H**$_2$CH$_3$), 4.83 m and 4.91 m (1H each, 8′-H), 5.75 m (1H, 7′-H), 5.94 d (1H, 3″-H, J = 2.5 Hz), 6.33 d.d (1H, 4″-H, J = 2.5, 3.2 Hz), 7.39 d (1H, 6-H, J = 1.6 Hz), 7.47 d (1H, 5″-H, J = 3.2 Hz), 7.79 (1H, 8-H, J = 1.6 Hz), 12.43 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 13.85 and 13.95 (CH_3); 17.83 and 17.88 (6′-CH_3); 18.44 and 18.72 (2′-CH_3); 19.0 ($C^{4'}$); 23.16, 23.25, 23.31, and 23.33 (C^{16}, C^{17}); 26.47 and 26.98 (C^{1}); 28.97 and 29.05 (C^{4}); 30.1 ($C^{1a'}$); 31.5 (C^{15}); 34.1 ($C^{1b'}$); 36.7 ($C^{3'}$); 39.1 ($C^{5'}$); 40.3 ($C^{6'}$); 44.8 ($C^{2'}$); 44.9 and 45.1 (C^{4a}); 46.6 ($C^{1'}$); 47.5 and 47.7 (C^{9a}); 51.7 and 51.8 (OCH_3); 60.5 and 60.6 (OCH_2); 97.23 (C^{2}); 106.7 ($C^{2''}$); 110.6 ($C^{3''}$); 111.7 ($C^{8'}$); 123.20 and 123.25 (C^{8}); 128.35 (C^{10a}); 131.2 (C^{6}); 135.6 (C^{8a}); 138.2 (C^{5}); 141.5 ($C^{5'}$); 146.8 (C^{7}); 150.7 ($C^{7'}$); 151.8 ($C^{1''}$); 154.8 (C^{7}); 169.2 and 169.3 (C^{3}); 171.6, 171.8, and 179.2 (C=O); 195.05 and 195.07 (C^{9}); 198.15 and 198.23 (C^{10}). Found, %: C 72.0; H 7.3. $C_{38}H_{46}O_8$. Calculated, %: C 72.36; H 7.35.

Diels–Alder reactions of naphthoquinones I and II with diene XVII. *a*. A solution of 2.4 mmol (0.96 g) of compound **I** and 2.1 mmol (0.4 g) of diene **XVII** in 20 ml of acetonitrile was heated for 10–12 h under reflux (TLC). The mixture was cooled, the precipitate was filtered off, the filtrate was evaporated, and the residue was separated by column chromatography on silica gel using chloroform and chloroform–ethanol (100:1, 50:1, 20:1) as eluents. Three fractions were isolated. The first two fractions were subjected to repeated chromatography to isolate 0.42 g (31%) of adducts **XXa** and **XXIa** (mixture of stereoisomers), and from the third fraction we isolated a mixture of diastereoisomers **XVIIIa** and **XIXa**. Treatment of that mixture with diethyl ether gave an amorphous material consisting of compounds **XVIIIa** and **XIXa** at a ratio of 1:1; yield 0.41 g (30%).

b. An ampule was charged with a solution of 0.8 mmol (0.30 g) of compound **I** in 20 ml of methylene chloride, 0.8 mmol (0.11 g) of boron trifluoride–diethyl ether complex was added, and 0.84 mmol (0.16 g) of diene **XVII** was then added under argon. The ampule was sealed, kept for 2 weeks at 20°C, and opened, and the mixture was poured into 100 ml of water and extracted with methylene chloride (3× 20 ml). The combined extracts were washed with water and dried over magnesium sulfate, the drying agent was filtered off, the filtrate was evaporated, and the residue was subjected to column chromatography on silica gel using benzene–diethyl ether (100:1 to 1:1) as eluent. Repeated chromatographic treatment of the first fraction using chloroform and chloroform–ethanol as eluents gave adducts **XVIIIa**/**XIXa**, **XXa**/**XXIa**, and **XXIIa** which were additionally purified by reprecipitation from acetonitrile. We thus isolated 0.093 g (20%) of a mixture of diastereoisomers **XVIIIa** and **XIXa** at a ratio of 1:1, 0.18 g (40%) of a mixture of diastereoisomers **XXa** and **XXIa** at a ratio of 1:1, and 0.07 g (15%) of pure 6,11-dioxodihydroanthra[2,1-*b*]thiophene 3,3-dioxide **XXIIa**.

Analogous thermal reaction (method *a*) of 2.3 mmol (0.98 g) of quinone **II** with 2.1 mmol (0.4 g) of diene **XVII** in acetonitrile gave equimolar mixtures of diastereoisomeric adducts **XVIIIb** and **XIXb**, yield 0.46 g (33%), and **XXb** and **XXIb**, yield 0.46 g (33%). In the reaction of 3 mmol (1.26 g) of compound **II** and 3 mmol (0.57 g) of diene **XVII** according to procedure *b* we isolated 0.46 (26%) of diastereoisomer mixture **XVIIIb**/**XIXb** (1:1), 0.72 g (39%) of diastereoisomer mixture **XXb**/**XXIb**, and 0.24 (13%) of pure compound **XXIIb**. Treatment of **XXb**/**XXIb** with petroleum ether gave an amorphous substance with mp 89–91°C (1:1 mixture of diastereoisomers). The physical constants and spectral parameters of 6,11-dioxodihydroanthra[2,1-*b*]thiophene dioxides **XXIIa** and **XXIIb** coincided with those reported in [5].

2-[2-(8-Isopropyl-4-methyl-3,3-dioxido-6,11-dioxo-1,2,5,5a,6,11,11a,11b-octahydroanthra[2,1-*b*]-thiophen-10-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylic acid (XVIIIa/XIXa, mixture of diastereoisomers, 1:1**).** mp 119–125°C. ^{1}H NMR spectrum, δ, ppm: 0.98 (3H, CH_3), 1.16 d and 1.18 d (3H each, $C^{16}H_3$, $C^{17}H_3$, J = 7 Hz), 1.28 s (3H, CH_3), 1.40–1.52 m (5H, 1a′-H, 4′-H, 5′-H), 1.75–2.13 m (7H, 1-H, 1′-H, 3′-H, 5-H, 5′-H), 2.03 d and 2.07 d (3H, CH_3, $J \approx$ 2 Hz), 2.25–2.55 m (4H, 1b′-H, 5′-H, 11b-H), 2.85 (1H, 15-H), 3.08 m and 3.28 m (1H each, 2-H), 3.66 m (1H, 5a-H), 3.78 m (1H, 11a-H), 4.88 m and 4.91 m (1H each, 8′-H), 5.79 m (1H, 7′-H), 7.32 d (1H, 9-H, J = 1.6 Hz), 7.79 (1H, 6-H, J = 1.6 Hz), 10.08 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 16.22 (CH_3), 17.26 ($C^{4'}$), 17.79 (CH_3), 18.19 (CH_3), 21.91 (C^{1}), 23.17 and 23.28 (4-CH_3), 29.32 (C^{5}), 30.14 and 30.37 ($C^{1a'}$), 32.92 and 32.48 (C^{11b}), 34.10 (C^{15}), 36.18 ($C^{1b'}$), 37.40 ($C^{1a'}$), 37.80 ($C^{3'}$), 38.42 ($C^{5'}$), 40.40 ($C^{6'}$), 45.11 ($C^{2'}$), 46.34 ($C^{1'}$), 50.14 (C^{2}), 50.31 and 50.42 (C^{5a}), 53.24 and 53.38 (C^{11a}), 110.89 ($C^{8'}$), 123.17 (C^{7}), 131.45 (C^{10a}), 132.26 (C^{9}), 134.59 (C^{6a}), 133.25 and 133.47

(C^{3a}), 138.96 (C^{10}), 139.36 and 139.52 (C^{4}), 150.78 ($C^{7'}$), 155.20 (C^{8}), 184.28 (C=O), 196.02 and 196.09 s (C^{11}), 197.85 and 197.99 (C^{6}). Found, %: C 63.91; H 6.70; S 4.32. $C_{33}H_{42}O_6S \cdot 1/2CHCl_3 \cdot 1/2Et_2O$. Calculated, %: C 64.3; H 7.2; S 4.8.

2-[2-(9-Isopropyl-4-methyl-3,3-dioxido-6,11-dioxo-1,2,5,5a,6,11,11a,11b-octahydroanthra[2,1-*b*]thiophen-7-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylic acid (XXa/XXIa, mixture of diastereoisomers, 1:1**).** mp 108–112°C. ^{1}H NMR spectrum, δ, ppm: 1.06 (3H, CH_3), 1.16 d and 1.18 d (3H each, $C^{16}H_3$, $C^{17}H_3$, J = 7 Hz), 1.28 s and 1.30 s (3H, CH_3), 1.46–1.54 m (5H, 1a′-H, 4′-H, 5′-H), 1.71–2.20 m (7H, 1-H, 1′-H, 3′-H, 5′-H), 2.15 d and 2.18 d (3H, CH_3, J = 2.0 Hz), 2.23–2.59 m (4H, 1b′-H, 5-H, 11b-H), 2.85 (1H, 15-H), 3.08 m and 3.22 m (1H each, 2-H), 3.68 m (1H, 5a-H), 3.76 m (1H, 11a-H), 4.83 m and 4.94 m (1H each, 8′-H), 5.82 m (1H, 7′-H), 7.30 d (1H, 7-H, J = 1.6 Hz), 7.77 d (1H, 9-H, J = 1.6 Hz), 10.17 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 16.34 (CH_3), 17.39 (CH_3), 17.87 ($C^{4'}$), 18.19 (CH_3), 22.08 (C^{1}), 22.96 (CH_3), 22.98 (CH_3), 29.49 (C^{5}), 30.07 ($C^{1a'}$), 32.07 and 32.45 (C^{11b}), 33.58 (C^{15}), 36.07 ($C^{1b'}$), 37.60 ($C^{3'}$), 38.60 ($C^{5'}$), 40.52 ($C^{6'}$), 46.01 ($C^{2'}$), 46.12 ($C^{1'}$), 50.19 (C^{2}), 50.42 and 50.68 (C^{5a}), 52.80 and 52.92 (C^{11a}), 110.53 ($C^{8'}$), 123.56 (C^{9}), 132.11 (C^{7}), 132.47 (C^{6a}), 133.38 and 133.56 (C^{3a}), 134.70 (C^{9a}), 138.79 (C^{6}), 139.54 (C^{4}), 151.12 ($C^{7'}$), 154.98 (C^{8}), 185.18 (C=O), 195.52 (C^{10}), 196.52 (C^{11}). Found, %: C 69.5; H 6.9; S 5.3. $C_{33}H_{42}O_6S$. Calculated, %: C 69.93; H 7.47; S 5.66.

Methyl 2-[2-(8-isopropyl-4-methyl-3,3-dioxido-6,11-dioxo-1,2,5,5a,6,11,11a,11b-octahydroanthra-[2,1-*b*]thiophen-10-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylate (XVIIIb/XIXb, mixture of diastereoisomers**).** ^{1}H NMR spectrum, δ, ppm: 0.98 s and 1.01 s (3H, CH_3), 1.18 d and 1.21 d (3H each, $C^{16}H_3$, $C^{17}H_3$, J = 7 Hz), 1.28 s and 1.30 s (3H, CH_3), 1.38–1.61 m (5H, 1a′-H, 4′-H, 5′-H), 1.75–2.13 m (7H, 1-H, 1′-H, 3′-H, 5-H, 5′-H), 2.02 d and 2.05 d (3H, CH_3, J = 1.8 Hz), 2.25–2.55 m (4H, 1b′-H, 5-H, 11b-H), 2.85 (1H, 15-H), 3.08 m and 3.28 m (1H each, 2-H), 3.66 m (1H, 5a-H), 3.78 m (1H, 10a-H), 3.68 s and 3.69 s (3H, OCH_3), 4.88 m and 4.91 m (1H each, 8′-H), 5.79 m (1H, 7′-H), 7.28 d (1H, 9-H, J = 1.6 Hz), 7.77 (1H, 7-H, J = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.32 (CH_3), 17.34 (CH_3), 17.79 ($C^{4'}$), 21.79 (CH_3), 21.93 (C^{1}), 22.69 and 22.68 (4-CH_3), 27.30 (C^{1}), 29.32 (C^{5}), 30.14 and 30.37 ($C^{1a'}$), 32.32 (C^{10b}), 33.81 (C^{15}), 35.71 ($C^{1b'}$), 37.80 ($C^{3'}$), 38.41 ($C^{5'}$), 41.02 ($C^{6'}$), 44.12 ($C^{2'}$), 46.83 ($C^{1'}$), 50.03 (C^{2}), 50.35 and 50.45 (C^{5a}), 51.42 (OCH_3), 53.18 and 53.39 (C^{10a}), 111.12 ($C^{8'}$), 123.37 (C^{6}), 131.52 (C^{9a}), 132.12 (C^{8}), 133.25 and 133.47 (C^{3a}), 134.59 (C^{6a}), 139.19 (C^{9}), 139.68 and 139.92 (C^{4}), 151.07 ($C^{7'}$), 155.08 (C^{7}), 179.19 (C=O), 196.02 and 196.09 (C^{10}), 197.85 and 197.99 (C^{11}). Found, %: C 69.8; H 6.9; S 5.4. $C_{34}H_{44}O_6S$. Calculated, %: C 70.31; H 7.64; S 5.52.

Methyl 2-[2-(9-isopropyl-4-methyl-3,3-dioxido-6,11-dioxo-1,2,5,5a,6,11,11a,11b-octahydroanthra-[2,1-*b*]thiophen-7-yl)ethyl]-1,3-dimethyl-3-vinylcyclohexane-1-carboxylate (XXb/XXIb, mixture of diastereoisomers**).** UV spectrum, λ_{max}, nm (log ε): 236 (4.42), 264 (4.06), 311 (3.53). IR spectrum, ν, cm^{-1}: 1722, 1690 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.98 s and 1.01 s (3H, CH_3), 1.22 d and 1.24 d (3H each, $C^{16}H_3$, $C^{17}H_3$, J = 7 Hz), 1.29 s (3H, CH_3), 1.39–1.60 m (5H, 1a′-H, 4′-H, 5′-H), 1.74–2.16 m (7H, 1-H, 1′-H, 3′-H, 5-H, 5′-H), 2.17 d and 2.18 d (3H, CH_3, $J \approx$ 2 Hz), 2.30–2.53 m (4H, 1a′-H, 1b′-H, 5-H, 11b-H), 2.85 (1H, 15-H), 3.10 m and 3.28 m (1H each, 2-H), 3.69 s and 3.71 s (3H, OCH_3), 3.69 m (1H, 5a-H), 3.73 m (1H, 11a-H), 4.86 m and 4.92 m (1H each, 8′-H), 5.76 m (1H, 7′-H), 7.30 d (1H, 7-H, J = 1.6 Hz), 7.75 s (1H, 9-H, J = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.39 (CH_3), 17.21 (CH_3), 17.53 ($C^{4'}$), 18.19 (CH_3), 22.08 (C^{1}), 23.26 (CH_3), 23.32 (CH_3), 29.49 (C^{5}), 30.07 ($C^{1a'}$), 32.07 and 32.45 (C^{11b}), 33.58 (C^{15}), 36.07 ($C^{1b'}$), 37.72 ($C^{3'}$), 39.01 ($C^{5'}$), 40.52 ($C^{6'}$), 46.53 ($C^{2'}$), 47.18 ($C^{1'}$), 50.51 (C^{2}), 50.42, 51.06 (C^{5a}), 51.49 (OCH_3), 52.80 and 52.92 (C^{11a}), 110.53 ($C^{8'}$), 123.13 (C^{10}), 131.96 (C^{8}), 132.47 (C^{6a}), 133.38 and 133.56 (C^{3a}), 134.70 (C^{10a}), 138.79 (C^{7}), 139.54 (C^{4}), 151.12 ($C^{7'}$), 154.98 (C^{9}), 185.18 (C=O), 195.52 (C^{11}), 196.72 (C^{6}). Mass spectrum, m/z (I_{rel}, %): 580 (18), 576 (27), 520 (69), 516 (37), 398 (31), 383 (34), 209 (30), 149 (95), 135 (30), 109 (37), 95 (55), 93 (49), 91 (34), 81 (100). Found, %: C 69.8; H 6.9; S 5.3. $C_{34}H_{44}O_6S$. Calculated, %: C 70.31; H 7.64; S 5.52.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 06-03-32150).

REFERENCES

1. Kharitonov, Yu.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2008, vol. 44, p. 516.
2. Thomson, R.H., *Naturally Occurring Quinones IV. Recent Advances*, London: Chapman & Hall, 1997, p. 309.

3. Gorelik, M.V., *Khimiya antrakhinonov i ikh proizvodnykh* (Chemistry of Anthraquinones and Their Derivatives), Moscow: Khimiya, 1983.
4. Gauze, G.F.B. and Dudnik, Yu.V., *Protivoopukholevye antibiotiki* (Antitumor Antibiotics), Moscow: Meditsina, 1987.
5. Tolstikov, G.A., Shul'ts, E.E., Mukhametzyanova, T.Sh.., Baikova, I.P., and Spirikhin, L.V., *Zh. Org. Khim*., 1993, vol. 29, p. 698.
6. Herz, W., Blackstone, R.C., and Nair, M.G., *J. Org. Chem*., 1967, vol. 32, p. 2992.
7. Danishefsky, S., Kitahara, T., Yan, C.F., and Morris, J., *J. Am. Chem. Soc*., 1979, vol. 101, p. 6996; Brownbridge, P., *Synthesis*, 1983, p. 85.
8. Tolstikov, G.A., Shul'ts, E.E., Safarova, G.M., Spirikhin, L.V., and Panasenko, A.A., *Zh. Org. Khim*., 1990, vol. 26, p. 1283.
9. Shul'ts, E.E., Petrova, T.N., Rybalova, T.V., Gatilov, Yu.V., and Tolstikov, G.A., *Russ. J. Org. Chem*., 1998, vol. 34, p. 845.
10. Argyle, C.S., Mason, K.G., Smith, M.A., and Stern, E.S., *J. Chem. Soc. C*, 1967, p. 2176.
11. Ruzicka, L. and Kaufmann, S., *Helv. Chim. Acta*, 1941, vol. 24, p. 1425.
12. Tret'yakova, E.V., Flekhter, O.B., Galin, F.Z., Shul'ts, E.E., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2005, vol. 41, p. 828.