Tetrahedron Vol. 40, No. 19, pp. 3677 to 3694, 1984
Printed in the U.S.A.

0040-4020/84 $3.00+.00
Pergamon Press Ltd.

SYNTHESIS OF ξ-PYRROMYCINONE, 7-DEOXYAURAMYCINONE, AND 7-DEOXYAKLAVINONE VIA KETOESTER CYCLIZATION [1]

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(*Received in Germany* 26 *June* 1984)

Abstract: 7,10-O-Dimethyl-ξ-pyrromycinone (8) and the not naturally occurring 7-deoxyanthracyclinones 6 and 7 are prepared via base induced cyclization of the ketoesters 3 - 5, and stereoselectively hydroxylated to the 2,4-cis diols 8 and 5.

Because of their important antitumor potential, the ever increasing number of Streptomyces produced anthracyclines has stimulated intense synthetic investigations [2]. The underlying tetracyclic aglycone (anthracyclinone) is differentiated considerably by the nature of the substituents on the aromatic as well as the hydroaromatic part of the molecule [3,4]. Previously, we proposed a two part classification of the anthracyclinones on a biogenetic basis: Type B possesses an ester group at the benzylic position, but Type A does not [5]. The Ollis group first reported that pyrromycinone 3 (Type B) is biosynthesized through a cyclization of a polyketide precursor [6]. Type A, i.e. daunomycinone, is consequentely produced from B through decarboxylation and further transformation [7]. Their different synthetic pathways also support the Type A/Type B classification.

A while ago we developed a synthetic model that was somewhat similar to the biosynthetic pathway [5]. The key step was the base catalyzed cyclization of the ketoester, II, to the 4-deoxyanthracyclinone, I, which was subsequently hydroxylated at C-4 to afford anthracyclinones such as 1 - 5 (Scheme 1). This model found application in the ε-rhodomycinone [8] and aklavinone (2) [9] syntheses, and other authors have modified it for the aklavinone [10,11], and recently, the first pyrromycinone [12] syntheses.

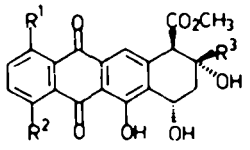
Following the ketoester cyclization model, the second synthesis of pyrromycinone 3, and the syntheses of the naturally not occurring 7-deoxy compounds 4 and 5 derived from auramycinone (1) [13], and aklavinone (2) are reported.

Production of Starting Materials

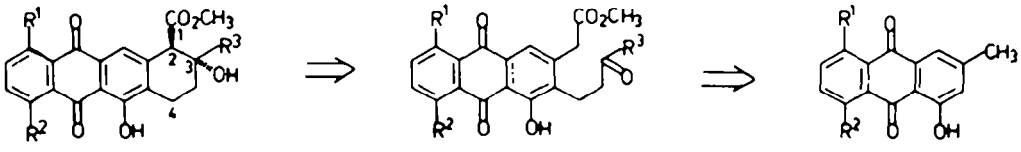
The formation of the A-ring by successive Marschalk reactions in the ε-rhodomycinone synthesis was made possible by the presence of para hydroxy groups in ring B;

*) The numbering system used in this paper follows the Chemical Abstracts/IUPAC rules instead of those of Brockmann [3].

Scheme 1



	R^1	R^2	R^3
1	H	OH	CH_3
2	H	OH	C_2H_5
3	OH	OH	C_2H_5
4	H	H	CH_3
5	H	H	C_2H_5

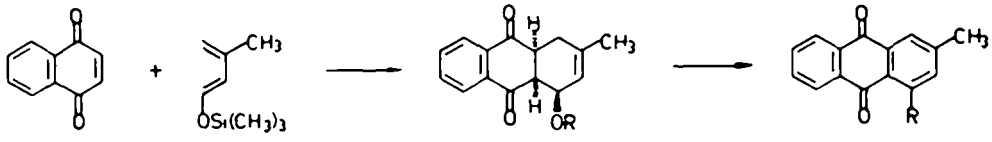


I II III

however, the presence of only one phenol group in ring B in both pyrromycinone and aklavinone made it necessary to modify this pathway. Thus, we started with the 3-methylanthraquinones of the general formula III. The further synthetic plan called for the addition of a functionalized side chain ortho to the phenol and the carboxylation of the methyl group to an acetic acid derivative.

The formation of the 1-hydroxy-3-methyl-9,10-anthraquinone (10) followed the procedure earlier described for the chrysophanol synthesis [14]. The Diels-Alder reaction of naphthoquinone (6) with 3-methyl-1-trimethylsiloxy-1,3-butadiene (7) at room temperature gave 8a.

Scheme 2



6 7

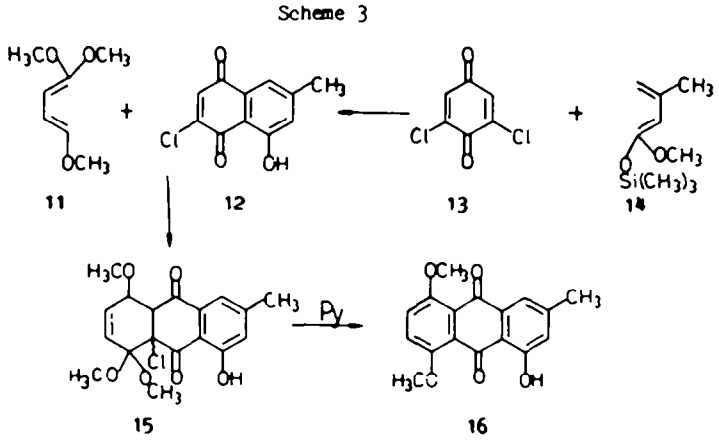
	R
8a	$SiMe_3$
8b	H

	R
9	H
10a	OH
10b	OPiv

Piv = $COC(CH_3)_3$

The relative stereochemistry of 8a was assigned by comparison with an analogous compound whose configuration had been determined by X-ray analysis [15]. The silyl ether 8a was cleaved to the allyl alcohol 8b with dilute HCl and then oxidized to pachybasin (10a)[16] with pyridinium chlorochromate (PCC) in 65 % overall yield. Some of the elimination product 9 was also formed. The elimination to 9 could almost be avoided by directly oxidizing the silyl ether 8a in the presence of two mols of acetic acid (71 % overall yield). Sufficient quantities (10 gram scale) of the analogous dimethyl ether 16 (5,8-O-dimethyl-helminthosporin) were prepared by a modification of the Cameron procedure [17]. The Diels-Alder reaction of the 1,1,4-trimethoxy-1,3-butadiene (11) [18] with 2-chloro-8-hydroxy-6-methyl-1,4-naphthoquinone (12) [19] yielded the intermediate product 15. Aromatization with pyridine to the desired dimethyl ether followed in 70 % overall yield. It has to be stressed, that for the subsequent attachment of a side chain at C-2 under the Marschalk [20] conditions, both phenol groups at C-5 and C-8 of the helminthosporin must be protected.

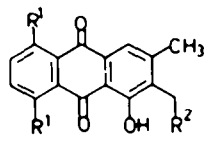
Scheme 3



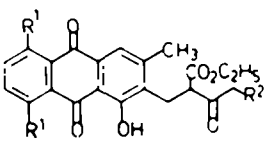
With the anthraquinone models 10 and 16 at hand, the carboxylation of the methyl group could be investigated. First, however, the attachment of the side chains at C-2 shall be described briefly. The resulting syntheses followed earlier investigations and methods closely [21].

The anthraquinones 10 and 15 were dissolved in a mixture of THF/MeOH/aq.NaOH, reduced to the corresponding hydroquinones with sodium dithionite, and then hydroxymethylated with formaldehyde ortho to the phenol. To prevent the elimination of the benzylic alcohol under the Marschalk conditions, the reaction was carried out at 5°. The often observed formation of dimers could be avoided by rapid reoxidation of the hydroanthraquinones in a dilute H_2O_2 solution. The resulting benzylalcohols 17 and 18 were obtained in 70-80 % yields and subsequently converted quantitatively to the chlorides 19 and 20 with thionyl chloride. After reacting the chlorides with acetoacetic acid to give 21 or with 3-oxovaleric acid ethylester to yield 22 and 23, the ketones 24 - 26 were prepared almost quantitatively by saponification and decarboxylation of the ketoesters 21 - 23.

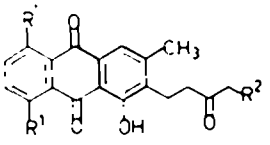
Scheme 4



	R^1	R^2
17	H	OH
18	OCH_3	OH
19	H	Cl
20	OCH_3	Cl



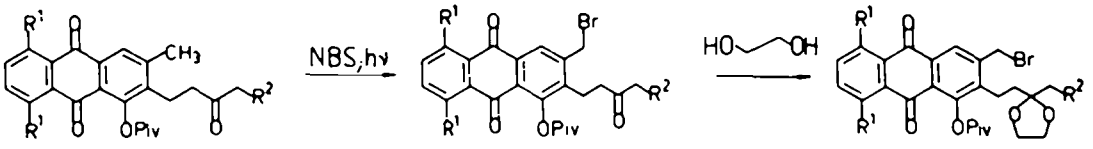
	R^1	R^2
21	H	H
22	H	CH_3
23	OCH_3	CH_3



	R^1	R^2
24	H	H
25	H	CH_3
26	OCH_3	CH_3

In order to selectively brominate the methyl group at C-2, the benzylic position of the C-4 side chain was sterically shielded by converting the phenols 24 - 26 to the pivaloates 27 - 29. For the acylation of the sterically hindered and hydrogen bonded phenol groups, the addition of equivalent amounts of 4-dimethylamino pyridine [22] was necessary.

Scheme 5



	R^1	R^2
27	H	H
28	H	CH_3
29	OCH_3	CH_3

	R^1	R^2
30	H	H
31	H	CH_3
32	OCH_3	CH_3

	R^1	R^2
33	H	H
34	OCH_3	CH_3

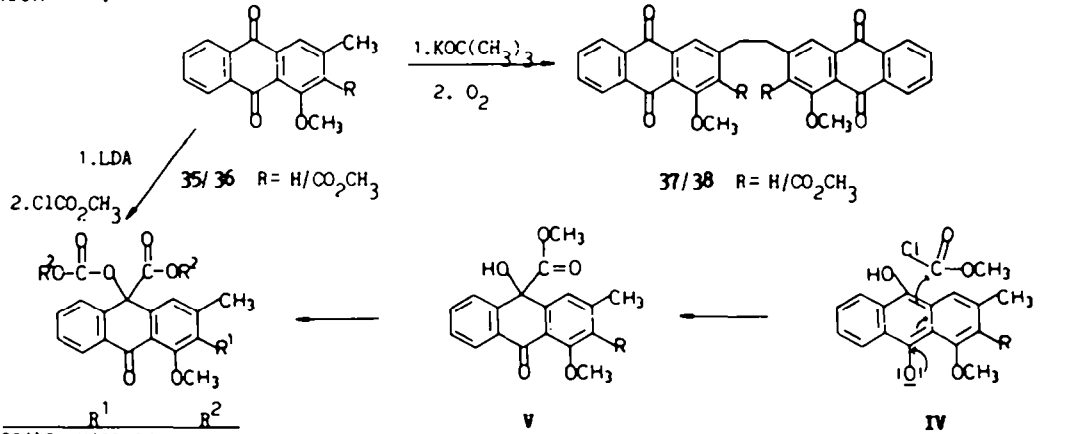
Light induced bromination of the pivaloates with N-bromosuccinimide gave the desired monobromides 30 - 32 in 70 to 80 % yields. The ketone was then protected by ketalization with ethylene glycol giving 33 and 34. The shift of the equilibrium in favor of the ketal was effected by the addition of methyl orthoformate and removal by distillation of the methyl formate under weak vacuum as it was formed [23].

Carboxylation of the Methyl Group

With the anthraquinones 10 and 16 and likewise bromides 30 - 34 at our disposal, the elongation of the methyl group by one C atom to an acetic acid derivative could be investigated. The bromides could easily be converted to the corresponding aldehydes and carboxylic acids (see below). The description of the carboxylation proceeds (independent from the success of the respective reactions) systematically corresponding to the oxidation state of the C-3 group ($-CH_3$, $-CH_2Br$, CHO, COOH).

1. Direct Carboxylation of the Methyl Anthraquinones 35 and 36.

The shortest path to chain elongation appeared to be the direct carboxylation of a carbanion derived from the methyl anthraquinone. Through deprotonation of the benzyl position with strong base, it should be possible to generate the carbanion. In theory, partial charge delocalization through the quinone carbonyls could stabilize it and allow reaction with electrophiles [24]. After methylating the phenol 10, 35 was choosen as a model compound. Dissolving 35 in THF, followed by the addition of potassium tert-butoxide immediately produced a deep red color. However, after the workup, the single, almost quanitative, reaction product was the dimer 37. This result was unchanged by the addition of electrophiles such as chloroformate or diethyl carbonate to the reaction. The possible mechanism of this noteworthy condensation is assumed to be the dimerization of the intermediate radical anion [25].



	R^1	R^2
39/40	H/CO_2CH_3	CH_3
41/42	H/CO_2CH_3	C_2H_5

Scheme 6

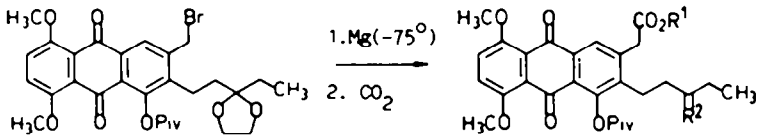
A totally different result was obtained from the reaction of 35 with lithium diisopropyl amide as well as sodium naphthalenide and quenching with chloroformate or diethylcarbonate. The surprising result was the isolation of the anthrones 39 and 41 as the main products. The addition at C-10 was proven by proton NMR, as a relatively high field shift of the C-2, C-4, and C-5 protons were observed due to the absence of the carbonyl group at C-10. What is the mechanistic explanation of this unexpected formation of the anthrones 39 and 41? We propose that the anthraquinone was reduced in an initial step to the hydroquinone, because LDA is known to reduce carbonyls through a single electron transfer [26] as well as in the manner of a Meerwein-Ponndorf-Verley reaction [27]. The anthrahydroquinone IV reacts as shown with chloroformate giving the intermediate V, which under the reaction conditions is acylated to 39 or 41.

The ideas concerning the formation of the anthrone derivatives 39 and 41 were supported by the reaction of preformed hydroquinones of chrysazine [28] and other anthraquinones with α,ß-unsaturated carbonyl compounds to yield similar adducts[29] This interesting reaction sequence was investigated further with the analogous anthraquinone carboxylic ester 36 [30] under similar conditions. We assumed that the additional ester group could promote formation of the carbanion. However, like 35, subjection of 36 to potassium tert-butoxide yielded the dimer 38, and the anthrones 40 and 42 were also generated by LDA treatment and quenching with chloroformate and diethyl carbonate respectively. Apparently, direct carboxylation of the methyl anthraquinones under these experimental conditions cannot be realized. Even the analogous xanthon systems can only be carboxylated with 4 % yield [31]. For these reasons, we turned to the benzyl bromides as synthetic precursors

2. Chain Elongation from the Benzyl Bromides

The initially obvious pathway was the exchange of the benzylic bromide, as in 33 and 34, with cyanide. This investigation employed four more model compounds and was conducted under practically all published variations, but without generation of the benzylic cyanide in a preparatively useful yield [32]. However, the stabilized carbanion of malonitrile was smoothly alkylated with bromides as 42. Thus, the reaction of acyl and carboxyl anion equivalents was studied. Neither the method of Bestmann (reactions of the corresponding phosphonium bromide with chloroformate) [33] nor the reactions with the anions of N,N-diethylaminoacetonitrile [34] or dimethoxyacetonitrile [35] were favorable. On the other hand, the successful carboxylation of the bromide 34 through a Grignard reagent to the carboxylic acid 43 gave a 25 % yield.

Scheme 7



34

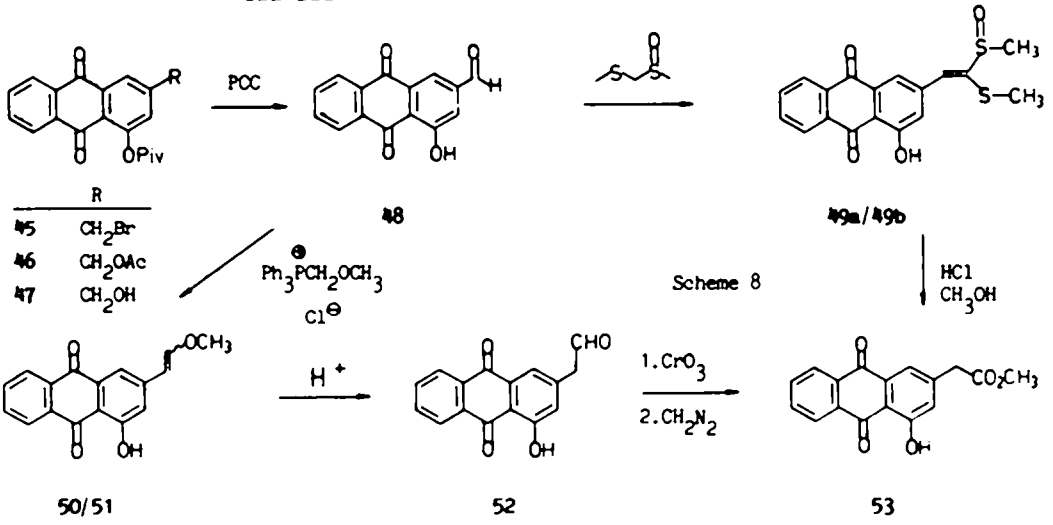
	R^1	R^2
43	H	OCH_2CH_2O
44	CH_3	O

Since the metalation under normal conditions and even with the highly activated magnesium of Rieke [36] failed, we decided to employ the methods of Kündig [37] and Oppolzer [38]. In this process a specially constructed rotary evaporator was used

to condense the metal into -196° THF under high vacuum. The magnesium slurries prepared in this manner reacted with the benzyl bromide 34 in a few minutes even at -75° as shown by thin layer chromatography.*) Our experience showed that by evaporating the metal under a high vacuum, we generated the most active and cleanest form of magnesium [39]. The subsequent reaction of the Grignard reagent with CO_2 (-75° - 0°) gave a mixture of products, from which the polar carboxylic acid 43 was isolated in 25 % yield. The yield of this reaction could probably be considerably increased by diluting the reaction solution to avoid competitive dimer formation. By cleavage of the ketal and esterification, the ketoester 44 was obtained. Prior saponification yielded the keto ester 75 which was identical to a sample synthesized from another pathway (see below).

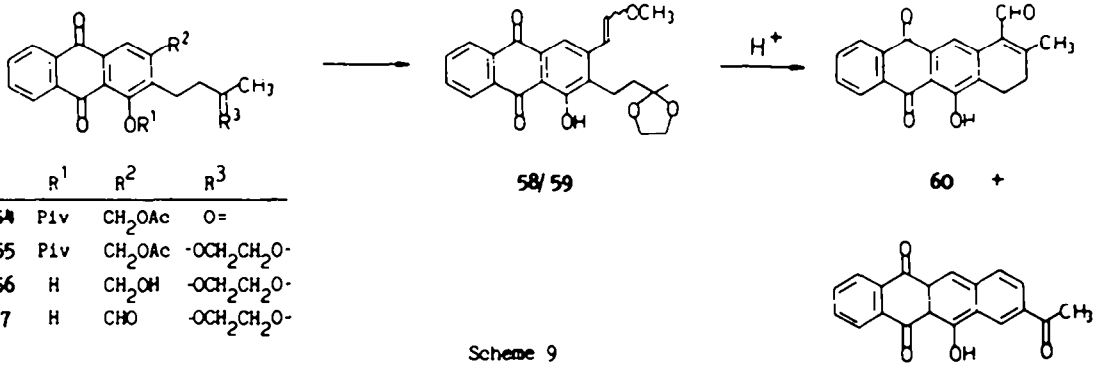
3. Homologization of the Aldehydes 48 and 57

The literature contains numerous examples of aldehyde homologizations from which we tested some of the interesting possibilities. The aldehydes 48 and 57 were generated in good yields from their corresponding benzyl bromides 45 and 30 by acetolysis to 46 and 54. Subsequent ketalization of 54 to 55 preceeded saponification of both acetates 46 and 55 to 47 and 56 followed by PCC oxidation to the aldehyde 48 and 57. The next step converted the model aldehyde 48 to the cis/trans-olefin 49a/49b using the methyl-methylthiomethyl sulfoxide introduced by Ogura [40]. The resulting cis and trans olefins 49a and 49b could be distinguished by TLC but were not separated for the next reaction. The ester 53 was directly obtained by methanolysis of 49a/49b in the presence of HCl in 25 % overall yield.



The ester 53 can be obtained just as easily by the Wittig reaction of 48 with methoxymethyltriphenylphosphonium chloride. Especially suitable for the Wittig reaction was the deprotonation of the phosphonium salt with potassium carbonate in the presence of 18-crown-6 as described by Boden [41]. The isomeric olefin mixture 50/51 that was generated in 70 % yield could be separated by preparative TLC. The homologous enol ether was subsequently cleaved with acid, and, after immediate oxidation with chromic (VI) oxide and esterification with diazomethane, yielded the ester 53. Hence, both procedures appeared suitable for use on the substituted aldehyde 57.

+) We thank Dr. Kündig and Prof. Oppolzer for providing the necessary apparatus, and W. Pachinger for his excellent practical help conducting the Grignard reaction.



	R^1	R^2	R^3
54	Piv	CH_2OAc	O=
55	Piv	CH_2OAc	$-OCH_2CH_2O-$
56	H	CH_2OH	$-OCH_2CH_2O-$
57	H	CHO	$-OCH_2CH_2O-$

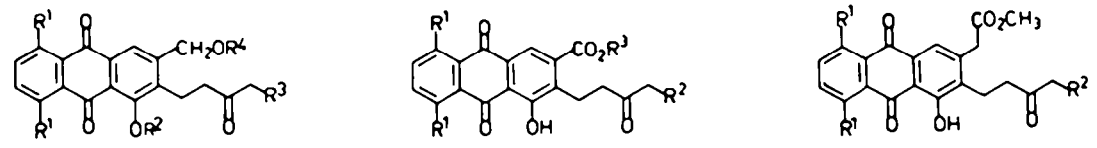
58/59 60 + 61

Scheme 9

However, the reaction of 57 with the Ogura reagent gave only a complex mixture of products leaving only the Wittig reaction pathway open. Fortunately, the E/Z-olefin 58/59 mixture was prepared with methoxymethyl triphenylphosphonium chloride in a good yield from 57. Acid enol ether cleavage under very mild conditions yielded a mixture of the cyclization products 60 and 61. Although olefins similar to 60 have be transformed to the anthracyclines in the aklavinone series [42], the intended ketoester cyclization was not realized.

4. Arndt-Eistert Homologization

Finally, we have investigated the Arndt-Eistert homologization of the acids 67, 69, and 71, that were easily obtained from the corresponding alcohols 62, 64, and 66 by Jones oxidation. The acids were characterized in form of the corresponding methyl ethers 68, 70, and 72. The Arndt-Eistert reaction was first successfully applied in anthracyclinone chemistry by Boeckman [11] and also used in our aklavinone synthesis [9].



	R^1	R^2	R^3	R^4
62	H	H	H	H
63	H	Piv	CH_3	$COCH_3$
64	H	H	CH_3	H
65	OCH_3	Piv	CH_3	$COCH_3$
66	OCH_3	H	CH_3	H

	R^1	R^2	R^3
67	H	H	H
68	H	H	CH_3
69	H	CH_3	H
70	H	CH_3	CH_3
71	OCH_3	CH_3	H
72	OCH_3	CH_3	CH_3

	R^1	R^2
73	H	H
74	H	CH_3
75	OCH_3	CH_3

Scheme 10

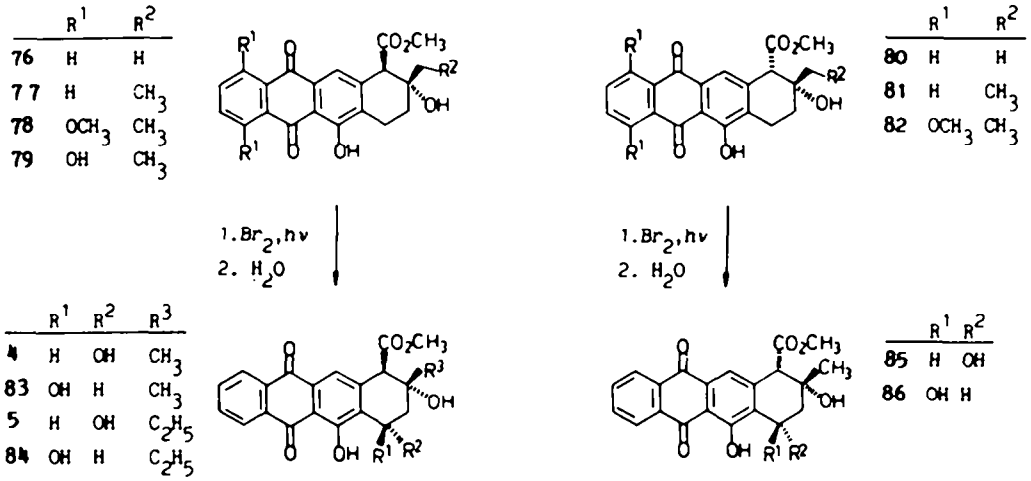
In fact, the anthraquinone carboxylic acids 67 and 69 could be transformed to the acetic acid derivatives 73 and 74 in 35 and 39 % overall yield respectively using the multistep procedure described earlier [9,11]. However, the pyrromycinone precursor 75 was only obtained in 11 % yield. The keto ester 75 was shown to be identical with the product isolated from the Grignard carboxylation (see above), which provided a much shorter route to the desired anthracyclinone precursor 75.

5. Keto Ester Cyclization and Hydroxylation

The central step of our synthetic strategy was the base induced aldol cyclization of the keto esters 73-75, which has been shown to proceed almost quantitatively

for similar substrates under appropriate reaction conditions [5,8-12]. Of major interest was, however, the ratio of the diastereomeric ß-hydroxy esters corresponding to the natural (i.e. 76 - 78) or not natural configuration (i.e. 80 - 82). In our hands good results could be obtained using a mixture of pyridine and methanol as solvent and triton B as catalyst in kinetically controlled reactions at -15°. Thus, 76 and 80 were isolated in a ratio of 2.0 : 1 and stereoselectivity was further improved for 74 and 75 to afford the anthracyclines with ethyl side chains 77 and 78 as well as 78 and 82 in a ratio of 3.6 : 1 and 3.3 : 1 respectively. This result is in agreement with similar findings of Boeckman, who recommended the usage of protic solvents for the aldol cyclization [11]. The ratio of the epimers is approximately the same employing magnesium methoxide as catalyst [12]. In contrast to the results of Hauser and Mal [12] the isomers 78 and 82 could readily be separated by TLC (CH_2Cl_2/2 % CH_3OH) and characterized in pure form. Cleavage of the methyl ethers of 78 afforded the racemic ξ-pyrromycinone (79), which has already been hydroxylated to give (±)- ε-pyrromycinone (3) [12].

Scheme 11



Hydroxylation of 76, 77 and also of the non naturally configurated 80 was effected via light induced bromination and solvolysis of the labile intermediate bromides with THF/water. The ratio of the epimeric 2,4-cis- and 2,4-trans-diols (i.e. 4/83 and 5/84) was found to be 7.5 : 1 and 8 : 1 respectively. In contrast, the 2,4-trans-diol 86 was the major product obtained from the cis ß-hydroxy ester 80 (85/86 = 6 : 1). This reversal of the stereochemical outcome is probably due to a different conformation of the cis-ß-hydroxy ester 80 and chelation of the tertiary hydroxy group with the neighbouring ester carbonyl [9].

Experimental

For general remarks see lit. [9].

1-Hydroxy-3-methyl-9,10-anthraquinone (10a). A solution of 20.00 g (0.12 mol) of 1,4-naphthoquinone (6) and 24.00 g (0.15 mol) of 3-methyl-1-trimethylsiloxy-1,3-butadiene (7) [14] in 800 mL CH_2Cl_2 was stirred for 24 h at 20°. 57.50 g (0.27 mol) of PCC and 7.20 g (0.12 mol) acetic acid were added portionwise (2 h) and the mixture was stirred vigorously for another 3 h. The mixture was filtered (Na_2SO_4) and purified by column chromatography (4 x 40 cm, CH_2Cl_2) to afford after crystallization from ether 21.40 g (71 %) of pachybasin (10a); mp 178-180°; (lit.[16] mp 178°). IR: 1671, 1636, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 211 sh, 224 (4.32), 245 (4.41), 253 (4.43), 258 (4.42), 277 sh, 326 (3.47), 383 sh, 402 (3.77), 422 nm sh. - ^1H NMR (90 MHz): δ = 2.45 (s; 3H, CH_3), 7.03 (s; 1H, 2-H), 7.80 (s; 1H, 4-H), 7.70 (m; 2H, 6-, 7-H), 8.20 (m; 2H, 5-, 8-H), 12.48 (s; 1H, OH).

3-Methyl-1-(2,2-dimethylpropionyloxy)-9,10-anthraquinone (10b). A solution of 1.90g (7.98 mmol) of 10a, 1.86 g (16 mmol) of pivalic acid chloride and 100 mg of 4-dimethylaminopyridine in 20 mL of dry pyridine was stirred for 12 h. The mixture was poured into ice cold HCl and the precipitate isolated by filtration. Crystallization from ether afforded 2.47 g (96 %) of pivaloyl ester 10b; mp 161-162°. - IR: 1745, 1672, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 205 (4.44), 223 (4.44), 236 sh, 243 (4.56), 253 (4.57), 258 (4.56), 280 sh, 325 (3.66), 403 (3.93). - ^1H NMR (90 MHz): δ = 1.44 (s; 9H, $C(CH_3)_3$), 2.44 (s; 3H, CH_3), 7.10 (d, $J_{2,4}$ = 2 Hz; 1H, 2-H), 7.67 (m; 2H, 6-, 7-H), 8.00 (d, $J_{2,4}$ = 2 Hz; 1H, 4-H), 8.16 (m; 2H, 5-H, 8-H).

1-Hydroxy-5,8-dimethoxy-3-methyl-9,10-anthraquinone (16). A solution of 5.00 g (22 mmol) of 3-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone (12) [19] in 150 mL of CH_2Cl_2 was treated with 3.20 g (22 mmol) of 1,1,4-trimethoxy-1,3-butadiene (11)[18]. After 48 h stirring at 20° the solvent was evaporated at reduced pressure and the adduct 15 was precipitated with petroleum ether. 15 was dissolved in a minimum amount of pyridine (15 mL) and refluxed for 20 min. The residue was treated with cold diluted HCl and extracted with CH_2Cl_2. The product was purified by filtration through a short column of silica gel (CH_2Cl_2) to afford 4.60 g (70 %) of 5,8-di-O-methyl-helminthosporin; mp 215° (lit.[17] 215°).

1-Hydroxy-2-hydroxymethyl-3-methyl-9,10-anthraquinone (17). A solution of 6.00 g (25 mmol) of 10a in a mixture of 1 L of methanol and 80 mL of aqueous 1N NaOH was treated under N_2 at 40-50° with a solution of 6.00 g sodium dithionite in 150 mL of water. The solution was cooled to 5° and 22 mL of 35 % formaldehyde were added all at once. After 4-5 h stirring at 4-5° (TLC control) the solution was poured into 1.5 L of cold water, which contained 50 mL of 1N NaOH and 10 mL of 50 % H_2O_2. The mixture was acidified with HCl and extracted three times with each 300 mL of CH_2Cl_2 and the organic phase was washed with water and the solvent evaporated under reduced pressure. The residue was crystallized from 30 mL of CH_2Cl_2 to afford 5.13 g (76 %) of 17; mp 214-216° (recrystallized from CH_2Cl_2). - IR: 3470, 3440, 1670, 1635, 1590 cm^{-1}. - ^1H NMR (400 MHz): δ = 2.51 (t; J = 6.2 Hz; 1H, OH), 2.55 (s; 3H, CH_3), 4.88 (d,J = 6.2 Hz; 2H, CH_2O), 7.69 (s; 1H, 4-H), 7.85 (m, 2H, 6-, 7-H), 8.35 (m; 2H, 5-, 8-H), 13.18 (s; 1H, OH).

1-Hydroxy-2-hydroxymethyl-5,8-dimethoxy-3-methyl-9,10-anthraquinone (18). 4.00 g (13.4 mmol) of anthraquinone 16 were hydroxymethylated as described for 17 to yield 2.64 g (60 %) of 18, mp 217-219°. - IR: 3495, 1660, 1630, 1565, 1490, 1405, 1275, 1255, 1195, 1010, 815 cm^{-1}. - UV: λ_{max}(lg ε) = 230 (4.65), 259 (4.27), 280 sh (4.03), 451 nm (4.06). - ^1H NMR (400 MHz): δ = 2.52 (s; 3H, CH_3), 2.57 (t,J = 6 Hz; 1H, CH_2OH), 4.00 (s; 3H, OCH_3), 4.03 (s; 3H, OCH_3), 4.86 (d,J = 7 Hz; 2H, CH_2OH), AB-signal 7.35 a. 7.38 (J = 9 Hz; 6-H, 7-H), 7.54 (s; 1H, 4-H), 13.29 (s; 1H, OH).- MS (380°C): m/e = 328 (100 %, M+), 313 (87), 298 (26), 284 (17), 267 (21), 253 (16), 239 (13), 225 (7), 211 (7), 197 (6), 181 (10), 165 (15), 152 (16), 139 (15), 127 (10), 115 (10), 77 (9). - Calcd. for $C_{18}H_{16}O_6$: C,65.85 H, 4.91; Found: C,65.66 H,4.73.

2-Chloromethyl-1-hydroxy-3-methyl-9,10-anthraquinone (19). - A suspension of 4.30g (16 mmol) of hydroxymethyl-anthraquinone 17 in 100 mL of dry CH_2Cl_2 was treated with 4 mL of thionyl chloride and 0.1 mL of DMF and stirred for 2 h at 20°. The solvent and excess thionyl chloride were evaporated at reduced pressure and the residue was washed with 10 mL petroleum ether. Yield 4.58 g (99 %); mp 192°. - IR: 1672, 1633, 1590 cm^{-1}. - UV: λ_{max}(lg ε) = 205 (4.36), 227 (4.34), 230 sh, 246 (4.49), 256 (4.46), 260 (4.46), 283 sh, 330 (3.53), 395 sh, 410 (3.86), 425 nm sh. - ^1H NMR (90 MHz): δ = 2.54 (s; 3H, CH_3), 4.76 (s; 2H, CH_2Cl), 7.60 (s; 1H, 4-H), 7.73 (m; 2H, 6-H, 7-H), 8.24 (m; 2H, 5-H, 8-H), 13.12 (s; 1H, OH). -

2-Chloromethyl-1-hydroxy-5,8-dimethoxy-3-methyl-9,10-anthraquinone (20). 2.30 g (7.0 mmol) benzylalcohol 18 were chlorinated with 3 mL of thionyl chloride as described for 19 to afford 2.30 g of 20 (97 %); mp 228°. - ^1H NMR (90 MHz): δ = 2.52 (s; 3H, CH_3), 3.97 (s; 3H, OCH_3), 3.99 (s; 3H, OCH_3), 4.76 (s; 2H, CH_2Cl), 7.32 (s; 2H, 6-H, 7-H), 7.49 (s; 1H, 4-H), 13.24 (s; 1H, OH). - Calcd. for $C_{18}H_{15}O_5Cl$: C,62.35 H,4.36; Found: C,62.07 H, 4.24.

Ethyl-2-(9,10-dihydro-1-hydroxy-3-methyl-9,10-dioxo-2-anthrylmethyl)-3-oxobutanoate (21). A solution of 5.82 g (20.3 mmol) of benzyl chloride 19 was added under nitrogen to a solution of sodium ethyl acetoacetate (prepared from 1.87 g Na and 13.20 g (0.1 mol) ethyl acetoacetate) in 300 mL of dry ethanol. After stirring 0.5 h at 20° the mixture was poured into 1 L of ice cold 0.2 N HCl and extracted three times with each 250 mL of ether. The combined organic phases were washed with 200 mL of water, dried over Na_2SO_4, evaporated to dryness, and crystallized from ether/petroleum ether to afford 7.70 g (96 %) of ß-ketoester 21; mp 191°. - IR: 1725, 1711, 1672, 1632, 1591 cm^{-1}. - UV: λ_{max}(lg ε) = 206 (4.35), 228 (4.32), 246 (4.48), 263 (4.50), 328 (3.59), 407 nm (3.86). - ^1H NMR (90 MHz): δ = 1.22 (t, J = 7 Hz; 3H, CH_2CH_3), 2.31 (s; 3H, $COCH_3$), 2.52 (s; 3H, CH_3), 3.29 (d,J = 7 Hz; 2H, Benzyl-H), 4.17 (q; 2H, CH_2CH_3), 4.19 (t; 1H, $CHCH_2$), 7.62 (s; 1H, 4-H), 7.80 (m; 2H, 6-H, 7-H), 8.29 (m; 2H, 5-H, 8-H), 13.14 (s; 1H, OH). - Calcd. for

$C_{22}H_{20}O_6$: C,69.47 H,5.30; Found: C,69.66 H,5.17.

Ethyl-2-(9,10-dihydro-1-hydroxy-3-methyl-9,10-dioxo-2-anthryl-methyl)-3-oxopentanoate (22). 7.20 g (50 mmol) of ethyl-3-oxopentanoate were alkylated with 4.20 g (14.7 mmol) of chloride 19 as described for 21; yield 5.55 g (96 %); mp 138°. - IR: 1731, 1712, 1672, 1628, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 207 (4.26), 228 sh, 245 (4.45), 263 (4.49), 408 nm (3.83). - ^1H NMR (90 MHz): δ = 1.02 (t,J = 7.5 Hz; 3H, $COCH_2CH_3$), 1.18 (t,J = 7.5 Hz; 3H, OCH_2CH_3), 2.48 (s; 2H, benzyl -H), 252 (q, J = 7.5 Hz; 2H, $COCH_2CH_3$), 3.27 (d,J = 7.5 Hz; 2H, benzyl-H), 4.13 (q; 2H, CO_2-CH_2CH_3), 4.19 (t,J = 7.5 Hz; 1H, CH_2CH_3), 7.56 (s; 1H, 4-H), 7.76 (m; 2H, 6-H, 7-H), 8.22 (m; 2H, 5-H, 8-H), 13.02 (s; 1H, OH). - Calcd. for $C_{23}H_{22}O_6$: C,70.04 H,5.62; Found: C,68.88 H,5.60.

Ethyl-2-(9,10-dihydro-1-hydroxy-5,8-dimethoxy-3-methyl-9,10-dioxo-2-anthryl-methyl)-3-oxopentanoate (23). The alkylation of ethyl-3-oxopentanoate (4.30 g, 30 mmol) with 3.37 g (10.7 mmol) of chloride 20 was performed as described for 21; yield 4.70g (95 %) ß-ketoester 23; mp 167-169°. - IR: 1738, 1710, 1662, 1624, 1582 cm-1. - UV: λ_{max} (lg ε) = 231 (4.55), 261 (4.35), 280 sh, 450 nm (4.08). - ^1H NMR (400 MHz): δ = 1.05 (t,J = 7.5 Hz; 3H, CH_2CH_3), 1.20 (t,J = 7.5 Hz; 3H, $CO_2CH_2CH_3$), 2.48 (s; 3H, CH_3), 2.55 (m; 2H, CH_2), 3.28 (dd, 2H, CH_2), 4.02 (s; 3H, OCH_3), 4.05 (s; 3H, OCH_3), 4.13 (q,J = 7.5 Hz; 2H, CO_2CH_2), 4.19 (t, 1H, CH), 7.37 (q; 2H, 6-H, 7-H), 7.51 (s; 1H, 4-H), 13.21 (s; 1H, OH).

Saponification and decarboxylation of the ß-ketoesters 21-23. A suspension of 10-20 mmoles of 21-23 in 200-400 mL of ethanol was treated under nitrogen with 200-400 mL 1 N NaOH and stirred for 12 h (TLC-control). The solution was acidified with 250-500 mL of 1 N HCl and extracted three times with each 200 mL of ethyl acetate. The combined organic phases were dried over Na_2SO_4, evaporated to dryness, and heated for 20 min at 150°. The residue was dissolved in CH_2Cl_2 and filtered through a short (4 x 10 cm) column of silica gel (CH_2Cl_2). The eluate was evaporated and the residue crystallized from 20-30 mL of ether.

1-Hydroxy-3-methyl-2-(3-oxobutyl)-9,10-anthraquinone (24). 6.16 g of 21 afforded 4.79 g (96 %) of 24; mp 203 °. - IR: 1705, 1668, 1628, 1590 cm^{-1}. - UV: λ_{max}(lg ε) = 208 (4.20), 232 sh, 246 (4.46), 263 (4.48), 280 sh, 326 (3.52), 391 sh, 410 (3.83), 432 nm sh. - ^1H NMR (90 MHz): δ = 2.22 (s; 3H, $COCH_3$), 2.46 (s; 3H, CH_3), 258-3.13 (m; 4H, 2 CH_2), 7.65 (s; 1H, 4-H), 7.81 (m; 2H, Aromaten-H), 8.30 (m; 2H, Aromaten-H), 13.02 (s; 1H, OH). - Calcd. for: $C_{19}H_{16}O_4$: C,74.01 H,5.23; Found: C,74.09 H,5.19.

1-Hydroxy-3-methyl-2-(3-oxopentyl)-9,10-anthraquinone (25). 5.80 g of 22 afforded 4.55 g (96 %) of ketone 25; mp 179°. - IR and UV see 24. - ^1H NMR (90 MHz): δ = 1.07 (t,J = 7.5 Hz; 3H, CH_2CH_3), 2.44 (s; 3H, benzyl-CH_3), 2.45 (q; 2H, CH_2CH_3), 2.62-3.16 (m; 4H, 2 CH_2), 7.60 (s; 1H, 4-H), 7.76 (m; 2H, 6-H, 7-H), 8.27 (m; 2H, 5-H, 8-H), 13.00 (s; 1H, OH). - Calcd. for: $C_{20}H_{18}O_4$: C,74.52 H,5.63; Found: C,74.07 H,5.12.

1-Hydroxy-5,8-dimethoxy-3-methyl-2-(3-oxopentyl)-9,10-anthraquinone (26). 4.70 g (10.3 mmol) of 23 afforded 3.80 g (96 %) of ketone 26; mp 182°. - IR: 1708, 1668, 1626, 1580 cm^{-1}. - UV: λ_{max} (lg ε) = 210 sh, 231 (4.62), 261 (4.35), 280 sh, 451 nm (4.08). - ^1H NMR (400 MHz): δ = 1.10 (t; 3H, CH_2CH_3), 2.45 (s; 3H, CH_3), 248 (q,J = 7.5 Hz; 2H, CH_2CH_3), 2.71 (t,J = 8.1 Hz, 2H, CH_2), 3.05 (t,J = 8.1 Hz; 2H, CH_2), 4.01 (s; 3H, OCH_3), 4.06 (s; 3H, OCH_3), 7.37 (q; 2H, 3-H, 4-H), 7.51 (s; 1H, 4-H), 13.08 (s; 1H, OH). - Calcd for: $C_{22}H_{22}O_6$: C,69.10 H,5.80; Found: C,68.57 H 5.71.

3-Methyl-1-(2,2-dimethylpropionyloxy)-2-(3-oxobutyl)-9,10-anthraquinone (27). According to the procedure given for 10b 4.80 g phenol 24 using 4.5 g 4-(dimethyl-amino)-pyridine were transformed to 5.50 g (96 %) pivaloate 27; mp 137-139°. - IR: 1749, 1710, 1672, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 209 (4.33), 258 (4.68), 275 sh, 333 nm (3.76). - ^1H NMR (90 MHz):δ = 1.50 (s; 9H, $C(CH_3)_3$), 2.16 (s; 3H, $COCH_3$), 2.49 (s; 3H, CH_3), 2.56-3.22 (m; 4H, 2 CH_2), 7.71 (m; 2H, 6-H, 7-H), 8.06 (s; 1H, 4-H), 8.20 (s; 2H, 5-H, 8-H). - Calcd. for: $C_{24}H_{24}O_5$: C,73.45 H,6.17; Found: C,73.51 H,5.98.

3-Methyl-1-(2,2-dimethylpropionyloxy)-2-(3-oxopentyl)-9,10-anthraquinone (28). 4.35g (10 mmol) of 25 were transformed according to the procedure given for 10b; 95 % of 28 (using 4.00 g of catalyst); mp 152-154°. - IR and UV see 24. - ^1H NMR (90 MHz): δ = 1.07 (t,J = 7.5 Hz; 3H, CH_2CH_3), 1.49 (s; 9H, $C(CH_3)_3$), 2.29-3.13 (m; 4H, $2CH_2$), 2.49 (s; 2H, CH_3, $COCH_2CH_3$), 7.71 (m; 2H, 6-H, 7-H), 8.04 (s; 1H, 4-H), 8.20 (m; 2H, 5-H, 8-H). - Calcd. for: $C_{25}H_{26}O_5$: C,73.87 H,6.45; Found: C.74.04 H,6.34.

5,8-Dimethoxy-1-(2,2-dimethyl-1-propionyloxy)-3-methyl-2-(3-oxopentyl)-9,10-anthraquinone (29). 3.55 g (9.3 mmol) phenol 26 were transformed to 4.16 g (96 %) 29 mp 146-148° (procedure see 10b). - IR: 1750, 1710, 1673, 1597 cm^{-1}. - UV: λ_{max}(lg ε) = 221 (4.50), 260 (4.52), 332 (3.48), 421 nm (3.81). - ^1H NMR (300 MHz): δ = 1.07 (t; 3H, CH_2CH_3), 1.45 (s; 9H, $C(CH_3)_3$), 2.42 (q,J = 7.5 Hz; 2H, CH_2CH_3), 2.43 (s; 3H, CH_3), 3.88 and 3.96 (2 s; 6H, 2 OCH_3), 7.24 (q; 2H, 6-H, 7-H), 7.82 (s; 1H, 4-H). - Calcd. for: $C_{27}H_{30}O_7$: C,69.51 H,6.48; Found: C,69.55 H,6.44.

3-Bromomethyl-1-(2,2-dimethylpropionyloxy)-2-(3-oxobutyl)-9,10-anthraquinone (30). A mixture of 5.20 g (13.3 mmol) methylanthraquinone 27, 3.07 g (17.3 mmol) of N-bromosuccinimide in 250 mL of CCl_4 was irridiated for 30 min at 80° with a 300 watt daylight lamp. The solution was cooled to ca. 30°, filtered, and evaporated at reduced pressure. The residue was taken up in CH_2Cl_2 and purified by column chromatography on silica gel (4 x 40 cm, CH_2Cl_2). After a forerun of less polar di- and tribromides the fraction of medium polarity was evaporated and crystallized from ether/petroleum ether to afford 4.26 g (68 %) of bromide 30; mp 147° (decomps.). - IR: 1753, 1710, 1671, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 213 (4.45), 260 (4.68), 277 sh, 337 nm (3.80). - ^1H NMR (90 MHz): δ = 1.49 (s; 9H, $C(CH_3)_3$), 2.16 (s; 3H, $COCH_3$), 2.71-3.22 (m; 4H, 2 CH_2), 4.64 (s; 2H, CH_2Br), 7.73 (m; 2H, 6-H, 7-H), 818 (m; 2H, 5-H, 8-H), 8.20 (s; 1H, 4-H). - Calcd. for: $C_{24}H_{23}BrO_5$: C,61.15 H,4.92; Found: C,61.02 H,4.91.

3-Bromomethyl-1-(2,2-dimethylpropionyloxy)-2-(3-oxopentyl)-9,10-anthraquinone (31). 4.90 g (12.1 mmol) of 28 were brominated with 2.79 g (15.7 mmol) of N-bromosuccinimide as described for 30 yielding 3.92 g (67 %) of 31; mp 146-148°. - IR and UV see 30.- ^1H NMR (90 MHz): δ 1.04 (t,J = 7.5 Hz; 3H, CH_3), 1.47 (s; 9H, $C(CH_3)_3$), 2.27-3.26 (m; 4H 2 CH_2), 4.64 (s; 2H, CH_2Br), 7.73 (m; 2H, 6-H, 7-H), 8.19 (m; 2H, 5-H, 8-H), 8.21 (s; 1H, 4-H). - Calcd for: $C_{25}H_{25}BrO_5$: C,61.86 H,5.19; Found: C,62.20 H,5.21.

3-Bromomethyl-5,8-dimethoxy-1-(2,2-dimethylpropionyloxy)-2-(3-oxopentyl)-9,10-anthraquinone (32). 3.90 g of 29 were brominated as described for 30 to yield 3.05 g (67 %) of bromide 32; mp 146°. - IR: 1753, 1718, 1673, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 224 (4.54), 260 (4.53), 332 (3.49), 425 nm (3.81). - ^1H NMR (400 MHz): δ = 1.09 (t; 3H, CH_2CH_3), 1.46 (s; 9H, $C(CH_3)_3$), 2.43 (q,J = 7.5 Hz; 2H, CH_2CH_3), 2.69-3.15 (m; 4H, 2 CH_2), 3.90 and 3.97 (2 s; 6H, 2 OCH_3), 4.62 (s; 2H, CH_2Br), 7.26 (q; 2H, 6-H, 7-H), 8.01 (s; 1H, 4-H). - Calcd.for $C_{27}H_{29}BrO_7$: C,59.46 H,5.36; Found: C,59.38 H,5.41.

3-Bromomethyl-1-(2,2-dimethylpropionyloxy)-9,10-anthraquinone (45). 1.80 g (7.56 mmol) 10b were brominated with 1.39 g (7.81 mmol of N-bromosuccinimid) as described for 30 to afford 1.24 g (41 %) of monobromide 45; mp 154°. - IR: 1740, 1677, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 212 (4.42), 256 (4.66), 273 sh, 333 nm (3.77). - ^1H NMR (90 MHz): δ = 1.50 (s; 9H, $C(CH_3)_3$), 4.53 (s; 2H, CH_2Br), 7.38 (d,$J_{2,4}$ = 2.1 Hz; 1H, 2-H), 7.73 (m; 2H, 6-H, 7-H), 8.22 (m; 2H, 5-H, 8-H), 8.24 (d,$J_{2,4}$ = 2.1 Hz; 1H, 4-H). -

3-Bromomethyl-1-(2,2-dimethylpropionyloxy)-2-(3,3-ethylendioxybutyl)-9,10-anthraquinone (33). To a solution of 3.87 g bromoketone 30 in 150 mL of benzene were added 3 mL of ethyleneglycol, 6 mL of trimethylorthoformate and 40 mg of p-toluene sulfonic acid. The mixture was then heated to 50° and the methyl formate was removed under reduced pressure (ca. 50-100 mm Hg). Each h an additional 10 mg of acid was added. After 5 h the solution was washed with aqueous $NaHCO_3$, dried over Na_2SO_4 and evaporated at reduced pressure. The residue was crystallized from ether to give 4.02 g (95 %) of acetal 33; mp 110° (for the general procedure see 23)). - IR: 1750, 1672, 1586 cm^{-1}. - UV: λ_{max} (lg ε) = 213 (4.44), 260 (4.23), 278 (4.21), 336 nm (3.80). - ^1H NMR (300 MHz): δ = 1.39 (s; 3H, CH_3), 1.55 (s; 9H, $C(CH_3)_3$), 1.95 (m; 2H, CH_2), 2.72-3.03 (2 dd, J_{gem} = 12.5 Hz, J = 5.0 Hz; CH_2CH_2, AB-H), 4.03 (s; 4H, OCH_2CH_2O), 4.63 (q; 2H, CH_2Br), 7.75 (m; 2H, 5-H, 8-H), 8.23 (m; 2H, 6-H, 7-H), 8.26 (s; 1H, 4-H). - Calcd.for: $C_{26}H_{27}BrO_6$: C,60.59 H,5.28; Found: C,60.55 H,5.28.

3-Bromomethyl-5,8-dimethoxy-1-(2,2-dimethylpropionyloxy)-2-(3,3-ethylendioxypentyl)-9,10-anthraquinone (34). 1.10 g (30 mmol) bromoketone 32 were transformed to the acetal according to the procedure given for 33; yield 1.11 g (93 %), mp 127-129°. - IR: 1753, 1674, 1596, 1587, 1558 cm^{-1}. - ^1H NMR (90 MHz): δ = 0.92 (t; 3H, CH_3), 1.50 (s; 9H, $C(CH_3)_3$), 1.60-2.02 (m; 2H, CH_2), 3.92 (s; 3H, OCH_3), 3.97 (s; 3H, OCH_3), 4.02 (s; 4H, OCH_2CH_2O), 4.60 (s; 2H, 6-, 7-H), 8.01 (s; 1H, 4-H).

1-Methoxy-3-methyl-9,10-anthraquinone (35). A solution of 2.25 g (9.4 mmol) of phenol 10a in 50 mL of dry THF was treated with 13.8 g (0.1 mol) of K_2CO_3, 150 mg of 18-crown-6 and 1.25 g (9.9 mmol) of dimethylsulfate. After stirring for 17 h at 20° 150 mL of CH_2Cl_2 were added and the suspension filtered. The solution was washed with water, dried over Na_2SO_4, and evaporated at reduced pressure. The residue crystallized from petroleum ether; 2.32 g (98 %); mp 188-189°. - IR: 1670, 1660, 1600, 1588, 1460, 1450, 710 cm^{-1}. - ^1H NMR (90 MHz): δ = 2.47 (s; 3H, CH_3), 4.00 (s; 3H, OCH_3), 7.10 (s; 1H, 2-H), 7.71 (m; 3H, 4,6-,7-H), 8.19 (m; 2H, 5-, 8-H).

3,3'-Ethylenbis(1-methoxy-9,10-anthraquinone) (37). A solution of 52 mg (0.2 mmol) of 35 in dry THF was treated at 20° under nitrogen with 53 mg (0.4 mmol) of potassium tert-butoxide. The solution turned dark red immediately and was poured on cold 1N HCl after 5 min. The precipitate was filtered off and recrystallized from CH_2Cl_2 to afford 51 mg (98 %) of the dimer 37; mp 253°. - IR: 1670, 1660, 1600, 1590, 1460, 1450, 1330, 1270, 705 cm^{-1}. - ^1H NMR (400 MHz): δ = 3.16 (s; 3H, CH_3), 4.02 (s; 3H, OCH_3), 7.14, (s; 1H, 2-H), 7.83 (m; 3H, 4-, 6-, 7-H), 8.24 (m; 2H, 5-, 8-H). - MS (280 °C): m/e = 502 (M^+, 100 %), 487 (53), 251 (34), 180 (32), 163 (50), 149 (47), 121 (34), 105 (55), 91 (53).

Methyl-10-(9,10-dihydro-1-methoxy-10-methoxycarbonyl-3-methyl-9-oxo-anthryl)-carbonate (39). To a solution of 49 mg (0.2 mmol) of 35 in 5 mL of dry THF was added at 0° under N_2 1 mL of a 0.2 N solution of LDA in THF. The red mixture was stirred for 15 min and then quenched by addition to 0.5 mL of methyl chloroformate. The solvent was distilled off at reduced pressure, the residue taken up in 10 mL of CH_2Cl_2, washed with water, dried over Na_2SO_4, and filtered through a short column of silica gel (CH_2Cl_2). The eluate was evaporated to dryness and the residue crystallized from petroleum ether to afford 35 mg (48 %) of ester 39; mp 177-178°. A similar treatment of 35 (48 mg) with sodium naphthalenide gave 32 mg (44 %) of 39.- IR: 1772, 1758, 1635, 1440, 1265, 1230 cm^{-1}. - ^1H NMR: δ = 2.49 (s; 3H, CH_3), 3.96 (s; 3H, OCH_3), 3.97 (s; 3H, OCH_3), 3.98 (s; 3H, OCH_3), 6.61 (s; 1H, 2-H), 7.44 (m; 3H, 4-, 6-, 7-H), 7.94 (m; 1H, 5-H), 8.14 (m; 1H, 8-H). - MS (110 °C): m/e = 370 (M^+, 84), 326 (4), 311 (37), 295 (14), 279 (5), 267 (100), 252 (42), 236 (54), 223 (49), 208 (35), 207 (35), 193 (29), 178 (34), 165 (54), 152 (35), 139 (13), 127 (7), 115 (14), 105 (13), 91 (16), 84 (37), 76 (18), 59 (34), 45 (44).

Ethyl-10-(9,10-dihydro-1-methoxy-10-ethoxycarbonyl-3-methyl-9-oxo-anthryl)-carbonate (41). A solution of 53 mg (0.2 mmol) of 35 in 5 mL of dry THF was treated with LDA as described above (see 39), and quenched with diethyl carbonate. Workup as usual afforded 42 mg (53 %) of 41; mp 163-165°. - IR: 1769, 1749, 1630, 1560, 1531, 1360 cm^{-1}. - ^1H NMR: δ = 1.42 (t, J = 6.5 Hz; 6H, CH_2CH_3), 2.49 (s; 3H, CH_3), 4.38 (q, J = 6.5 Hz; 2H, CH_2CH_3), 4.39 (q, J = 6.5 Hz; 2H, CH_2CH_3), 6.61 (s; 1H, 2-H), 7.44 (m; 3H, 4-, 6-, 7-H), 7.94 (m; 1H, 5-H), 8.14 (m; 1H, 8-H). - MS (150 °C): m/e = 398 (M^+, 19), 281 (10), 253 (100), 238 (20), 223 (14), 181 (7), 165 (12), 152 (8). - Calcd. for: $C_{22}H_{22}O_7$: C,66.29 H,5.58; Found: C,65.97 H,5.49.

3,3'-Ethylenbis(1-methoxy-2-carboxymethyl-9,10-anthraquinone (38). A solution of 49 mg (0.16 mmol) of ester 36 [30] in 5 mL THF was treated with potassium tert-butoxide as described for 37. Yield of 38 14.7 mg (31 %); mp 241-243°. - IR: 1733, 1675, 1587, 1450, 710 cm^{-1}. - ^1H NMR: δ = 3.06 (s; 4H, $ArCH_2CH_2Ar$), 4.00 (s; 12H, OCH_3, CO_2CH_3), 7.78 (m; 4H, 6-, 7-H), 7.97 (s; 2H, 4-H), 8.24 (m; 4H, 5-, 8-H). - MS (215 °C): m/e 618 (M^+, 100 %), 586 (69), 573 (29), 554 (93), 539 (88), 526 (73), 511 (38), 495 (23), 483 (20), 467 (20), 459 (14), 309 (57), 293 (34), 277 (45), 264 (47), 250 (42), 235 (29), 221 (31), 208 (28), 193 (39), 180 (29), 165 (41), 151 (33), 105 (20).

Methyl-10-(9,10-dihydro-1-methoxy-2,10-bis-methoxycarbonyl-3-methyl-9-oxo-anthryl)-carbonate (40). 42 mg of ester 36 [30] were treated with LDA as described for 39. Yield 32.4 mg (54 %) of 40; mp 153-154°. - IR: 1770, 1763, 1740, 1628, 1435 cm^{-1}. - UV: λ_{max} (lg ε) = 224 (4.16), 259 (5.01), 336 (3.49), 359 (3.77), 377 (3.86), 397 (3.81) nm. - ^1H NMR: δ = 2.46 (s; 3H, CH_3), 3.92 (s; 3H, OCH_3), 3.96 (s; 3H, OCH_3), 3.97 (s; 3H, OCH_3), 4.00 (s; 3H, OCH_3), 7.56 (m; 3H, 4-, 6-, 7-H), 8.00 (m; 1H, 5-H), 8.20 (m; 1H, 8-H).

Ethyl-10-(9,10-dihydro-1-methoxy-2-methoxycarbonyl-10-ethoxycarbonyl-3-methyl-9-oxo-anthryl)-carbonate (42). 54 mg of ester 36 were treated with LDA as described for 39 and quenched with diethyl carbonate to yield 45 mg (58 %) of anthrone 42; mp 148°. - IR and UV see 40. - ^1H NMR: δ = 1.33 (t, J = 6.50 Hz; 3H, CH_2CH_3), 1.42 (t, J = 6.50 Hz; 3H, CH_2CH_3), 2.43 (s; 3H, CH_3), 3.94 (s; 6H, CO_2CH_3, OCH_3), 4.33 (q, J = 6.50 Hz; 2H, CH_2CH_3), 4.41 (q, J = 6.50 Hz; 2H, CH_2CH_3), 7.52 (m; 3H, 4-, 6-, 7-H), 7.97 (m; 1H, 5-H), 8.18 (m; 1H, 8-H). - MS (150 °C): m/e = 456 (M^+, 17 %), 425 (3), 412 (2), 384 (7), 339 (8), 311 (48), 279 (100), 265 (99), 222 (26), 207 (8), 194 (17), 181 (13), 165 (34), 152 (28). - Calcd. for: $C_{24}H_{25}O_9$: C,63.14 H, 5.30; Found: C,63.34 H,5.28.

Grignardation and carboxylation of 34. 3-(3,3-Ethylendioxypentyl)-5,8-dimethoxy-4-(2,2-dimethylpropionyloxy)-9,10-anthraquinone acetic acid (43). A suspension of 2 mmol of magnesium in 5 mL of THF was prepared under an atmosphere of argon as described in the lit. [37] and a solution of 294 mg benzyl bromide 34 in 5 mL of THF was added dropwise at -78° within 5 min. A stream of dry CO_2 was then bubbled through the suspension at -78° for 10min. The cooling bath was removed and the mixture was hydrolyzed at 0° with 10 mL of saturated aqueous NH_4Cl. The mixture was extracted with CH_2Cl_2 and the organic phase was extracted twice with 5 mL of $NaHCO_3$ solution. The aqueous phase was acidified with diluted HCl and again extracted with CH_2Cl_2 to afford after removal of the solvent 69 mg (25 %) of the acid 43.

Methyl [5,8-dimethoxy-4-(2,2-dimethoxypropionyloxy)-3-(3-oxopentyl)-9,10-anthraquinone-2-yl] acetate (44). The acid 43 was dissolved in 2 mL of CH_3OH and treated with 0.05 mL of conc. HCl to cleave the acetal. After 2 h at 20° the solvent was evaporated at reduced pressure, the residue dissolved in 2 mL of CH_2Cl_2 and treated with 1 mL of etheral diazomethane. Removal of the solvent and crystallization from ether/petroleum ether afforded 63 mg (92 %) of ester 44; mp 97-100°. - ^1H NMR (300 MHz): δ = 1.06 (t; 3H, CH_3), 1.45 (s; 9H, $C(CH_3)_3$), 2.41 (q, J = 7.5 Hz; 2H, CH_2), 2.54-3.08 (m; 4H, 2 CH_2), 3.71 (d; 3H, CO_2CH_3), 3.84 (s; 2H, CH_2), 3.90, 3.97 (2 s; 2 x 3H, 2 OCH_3), 7.26 (q; 2H, 6-, 7-H), 7.89 (s; 1H, 1-H).

Acetolysis of the benzyl bromides 30, 31, and 32 to the acetates 54, 63, and 65. A solution of 2 mmol of the bromides 30, 31, or 32 and 3.00 g of dry sodium acetate in 100 mL of acetic acid were stirred for 3 h at 100°. The cold solution was poured

into 500 mL of ice water and extracted twice with each 200 mL of CH_2Cl_2. The combined organic phases were washed three times with water and once with aqueous $NaHCO_3$ solution. The solution was dried over Na_2SO_4, evaporated to dryness, and the residue crystallized from ether.

3-(Acetoxymethyl)-1-(2,2-dimethylpropionyloxy)-2-(3-oxobutyl)-9,10-anthraquinone (54). 4.00 g (8.48 mmol) 30 were transformed to 3.67 g (96 %) 54 mp 112°. - IR: 1745, 1710, 1672, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 209 (4.39), 257 (4.68), 274 sh, 332 nm (3.79). - ^1H NMR (400 MHz): δ = 1.51 (s; 9H, $C(CH_3)_3$), 2.17 (s; 3H, $COCH_3$), 2.18 (s; 3H, acetate), 2.61-3.09 (m; 4H, 2 CH_2), 5.29 (q; 2H, CH_2O), 7.77 (m; 6-H, 7-H), 8.24 (m; 2H, 5-H, 8-H), 8.28 (s; 1H, 4-H). - Calcd.for $C_{26}H_{26}O_7$: C,69.32 H,5.82; Found: C,69.26 H,5.43.

3-(Acetoxymethyl)-1-(2,2-dimethylpropionyloxy)-2-(3-oxopentyl)-9,10-anthraquinone (63). 2.50 g (5.2 mmol) 31 were transformed to 2.30 g (96 %) of 63; mp 130°. - IR and UV see 54. - ^1H NMR (400 MHz): δ = 1.09 (t, J = 7.5 Hz; 3H, CH_3), 1.49 (s; 9H, $C(CH_3)_3$), 2.17 (s; 3H, acetate), 2.42 (q; 2H, CH_2CH_3), 2.58-3.11 (m; 4H, 2 CH_2), 5.29 (q; 2H, CH_2O), 7.77 (m; 2H, 6-H, 7-H), 8.24 (m; 2H, 5-H, 8-H), 8.27 (s; 1H, 4-H). - Calcd.for: $C_{27}H_{28}O_7$: C,69.81 H,6.08; Found: C,69.48 H,5.86.

3-(Acetoxymethyl)-5,8-dimethoxy-1-(2,2-dimethylpropionyloxy)-2-(oxopentyl)-9,10-anthraquinone (65). 2.90 g (5.3 mmol) 32 were transformed to 2.65 g (95 %) of acetate 65; mp 193°. - IR: 1760, 1732, 1712, 1672, 1598 cm^{-1}. - UV: λ_{max} (lg ε) = 222 (4.48), 255 (4.47), 325 (3.45), 420 nm (3.79). - ^1H NMR (300 MHz): δ = 1.07 (t; 3H, CH_2CH_3), 1.45 (s; 9H, $C(CH_3)_3$), 2.14 (s; 3H, $COCH_3$), 2.41 (q; J = 7.5 Hz; 2H, CH_2CH_3), 3.89 and 3.97 (2 s; 6H, 2 OCH_3), 5.22 (d; 2H, CH_2OAc), 7.25 (d; 2H, 6-H, 7-H), 8.11 (s; 1H, 4-H). - Calcd.for $C_{29}H_{32}O_9$: C,66.40 H,6.15; Found: C,66.12 H,6.19.

9,10-Dihydro-4-hydroxy-9,10-dioxo-2-anthracenecarbaldehyde (48). A solution of 615 g (2.44 mmol) of acetate 46 in 30 mL of THF was treated with 60 mL of 3 N NaOH and stirred for 3 h under N_2. The mixture was poured into cold HCl and extracted twice with each 200 mL of CH_2Cl_2). The solvent was removed at reduced pressure and the residue suspended in 100 mL of dry CH_2Cl_2 and treated portionwise with 1.10 g of PCC. After stirring 3 h at 20° the solution was filtered through a short (3 x 15 cm) column of silica gel (CH_2Cl_2). The unpolar fraction was evaporated to dryness and crystallized from ether to afford 394 mg (64 %) of 48; mp 214-216°. - IR: 1708, 1667, 1638, 1586 cm^{-1}. - UV: λ_{max} (lg ε) = 206 (4.32), 219 (4.32), 252 (4.47), 276 sh, 325 (3.51), 401 nm (3.80). - ^1H NMR (90 MHz): δ = 7.81 (d, J = 2.1 Hz; 1H), 7.89 (m; 2H), 8.36 (m; 3H), 10.13 (s; 1H, ArCHO), 12.61 (s; 1H, 1-OH). - Calcd.for $C_{15}H_8O_4$: C,71.43 H,3.20; Found: C,71.36 H,3.03.

Methyl [4-hydroxy-9,10-anthraquinone-2-yl] acetate 53 via the sulfoxides 49a/49b. A mixture of 50 mg aldehyde 48, 30 mg methyl-methylthiomethyl sulfoxide, and 0.1 mL of triton B (40 % in CH_3OH) was refluxed under N_2 in 20 mL of THF for 4 h. The solvent was removed at reduced pressure to give the mixture 49a/49b of crude sulfoxides. The residue was dissolved in 20 mL of dry CH_3OH and a stream of HCl was bubbled through the solution for 20 min. The mixture was poured into ice water and extracted with 50 mL of CH_2Cl_2. The organic phase was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography on silica gel (2 x 5 cm) to afford 13 mg (22 %) of ester 53; mp 147°. - IR: 1730, 1668, 1638, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 206 (4.23), 223 (4.23), 253 (4.38), 277 sh, 328 (3.47), 403 nm (3.73). - ^1H NMR (90 MHz): δ = 3.67 (s; 2H, CH_2), 3.76 (s; 3H, CH_3), 7.20 (d, J = 2 Hz; 1H, 2-H), 7.67 (d, J = 2 Hz; 1H, 4-H), 7.76 (m; 2H, 6-, 7-H), 8.22 (m; 2H, 5-, 8-H), 12.47 (s; 1H, OH). - Calcd.for $C_{17}H_{12}O_5$: C,68.29 H,4.08; Found: C,68.76 H,3.85.

Ester 53 via the Wittig reaction (50/51 → 52 → 53). A solution of 200 mg of E/Z-vinyl ether 50/51 in 25 mL acetone was treated with 1 mL of 30 % H_2SO_4 and refluxed for 3 h. The solution was diluted with 100 mL of H_2O and extracted with 200 mL of CH_2Cl_2. The solvent was removed at reduced pressure, the residue dissolved in 25 mL of acetone, and 300 mg of CrO_3 and 1 drop of conz. H_2SO_4 were added. After 3 h stirring at 20° 100 mL of water were added and the solution extracted with 150 mL of CH_2Cl_2. The organic phase was washed with water, dried over Na_2SO_4, treated with 5 mL of etheral diazomethane, and evaporated. The residue was separated by TLC to afford 93 mg (44 %) of ester 53 from the polar fraction.

E- and Z-1-Hydroxy-3-(2-methoxyethenyl)-9,10-anthraquinone (50/51). A mixture of 340 mg (1.35 mmol) of aldehyde 48, 900 mg (2.63 mmol) of methoxymethylphosphonium chloride, 1.20 g K_2CO_3, and 20 mg 18-crown-6 in 50 mL of dry THF was refluxed for 2 h. The mixture was acidified with cold HCl, extracted twice with 200 mL of CH_2Cl_2 and washed with 200 mL of H_2O. The dried (Na_2SO_4) solution was evaporated to dryness to give 268 mg (71 %) of the mixture of E and Z olefins 50 and 51 which were separated by preparative TLC (silica gel, CH_2Cl_2).

E-Isomer 50: Polar zone, 126 mg; mp 198°. - IR: 1675, 1630, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 209 (4.43), 250 (4.45), 297 (4.43), 429 nm (3.98). - ^1H NMR (90 MHz): δ = 3.78 (s; 3H, OCH_3), 5.83 (d, J = 12 Hz; 1H, olefin-H), 7.03 (d, J = 2 Hz; 1H, 2-H), 7.36 (d, J = 12 Hz; 1H), 7.69 (d, J = 2 Hz; 1H, 4-H), 7.77 (m; 2H), 8.28 (m; 2H), 12.63 (s; 1H, OH). - Calcd.for $C_{17}H_{12}O_4$: C,72.85 H,4.32; Found: C,72.84 H,4.33.

Z-Isomer 51: Less polar zone, 124 mg; mp 195°. - IR: 1670, 1645, 1625-, 1588 cm^{-1}. UV: λ_{max} (lg ε) = 211 (4.44), 252 (4.46), 296 (4.28), 424 nm (3.87). - ^1H NMR (90 MHz): δ = 3.89 (s; 3H, OCH_3), 5.31 and 6.38 (2 d,J = 6.5 Hz; 2H, $CH{=}CHOCH_3$), 7.57 (d,J = 2 Hz; 1H, 2-H), 7.76 (m; 2H, Aromaten-H), 7.89 (d,J = 2 Hz; 1H, 4-H), 8.28 (m; 2H, Aromaten-H), 12.60 (s; 1H, OH).

3-(Acetoxymethyl)-1-(2,2-dimethylpropionyloxy)-2-(3,3-ethylenedioxybutyl)-9,10-anthraquinone (55). 3.57 g (7.92 mmol) of ketone 54 were transformed to 3.72 g (95 %) of the acetal 55 as described for 33; mp 110°. - IR: 1745, 1730, 1673, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 210 (4.40), 257 (4.69), 277 (4.17), 333 nm (3.79). ^1H NMR (90 MHz): δ = 1.33 (s; 3H, CH_3C), 1.53 (s; 9H, $C(CH_3)_3$), 1.71-2.04 (m; 2H, CH_2C), 2.18 (s; 3H, $COCH_3$), 2.60-2.93 (m; 2H), 3.98 (s; 4H), 5.27 (s; 2H, CH_2O), 7.73 (m; 2H, 6-H, 7-H), 8.20 (m; 2H, 5-H, 8-H).

2-(3,3-Ethylenedioxybutyl)-1-hydroxy-3-hydroxymethyl-9,10-anthrachinone (56). Saponification of 3.56 (7.12 mmol) benzyl acetate 55 was effected as described for 47 to yield 2.49 g (95 %) of benzyl alcohol 56; mp 153°. - IR: 3450, 1665, 1633, 1592 cm^{-1}. - UV: λ_{max} (lg ε) = 207 (4.20), 230 sh, 246 (4.48), 257 (4.47), 262 (4.47), 278 sh, 328 (3.50), 392 sh, 413 (3.85), 437 nm sh. - ^1H NMR (90 MHz): δ = 1.42 (s; 3H, CH_3), 1.97 (m; 2H, $ArCH_2CH_2C$), 2.86 (m; 2H, $ArCH_2CH_2$), 4.02 (s; OCH_2CH_2O), 4.84 (s; 2H, CH_2OH), 7.79 (m; 2H, 6-H, 7-H), 7.88 (s; 1H, 4-H), 8.28 (m; 2H, 5-H, 8-H), 12.93 (s; 1H, 1-OH). - Calcd for $C_{21}H_{20}O_6$: C,68.47 H,5.47; Found: C,68.51 H,5.34.

3-(3,3-Ethylenedioxybutyl)-9,10-dihydro-4-hydroxy-9,10-dioxo-anthracenecarbaldehyde (57). Oxidation of 2.39 g (6.49 mmol) of alcohol 56 was effected as described for 48 (3 g PCC) to afford 1.69 g (71 %) of the aldehyde 57; mp 163°. - IR: 1692, 1670, 1634, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 203 (4.38), 229 sh, 245 (4.54), 262 (4.57), 280 sh, 327 (3.61), 390 sh, 410 (3.92), 425 nm sh. - ^1H NMR (90 MHz): δ = 1.44 (s; 3H, CH_3), 1.87-2.11 (m; 2H, CH_2C), 3.20-3.42 (m; 2H, $ArCH_2$), 4.00 (s; 4H, OCH_2CH_2O), 7.76-7.93 (m; 2H, 6-, 7-H), 8.20 (s; 1H, 1-H), 8.21-8.42 (m; 2H, 5-H, 8-H), 10.41 (s; 1H, CHO), 13.08 (s; 1H, OH). - Calcd. for $C_{21}H_{18}O_6$: C,68.84 H,4.95; Found: C,68.40 H,4.74.

E/Z-2-(3,3-Ethylenedioxybutyl)-1-hydroxy-3-(2-methoxyethenyl)-9,10-anthraquinone 58/59. 1.35 g of the aldehyde 57 were transformed to the olefins 58/59 as described for 50/51 to afford 1.02 g (70 %) of a 1 : 1 E/Z mixture. - ^1H NMR (90 MHz): δ = 1.42 (s; 6H, 2 CH_3), 1.87 and 2.91 (2 m; 8H, 4 CH_2), 3.79 and 3.88 (2s; 6H, 2 OCH_3), 4.02 (s; 8H, 2 OCH_2CH_2O), 5.48 (d,J = 7.6 Hz; 1H, Olefin-H), 6.11 (d,J = 13 Hz; 1H), 6.41 (d,J = 7.6 Hz; 1 H, Olefin-H), 7.29 (d,J = 13 Hz; 1H, Olefin-H), 7.76 (m; 4H), 7.80 (s; 1H, 4-H), 8.27 (m; 4H), 8.44 (s; 1H, 4-H), 13.24 and 13.26 (2s; 2H, 2 OH).

9-Acetyl-11-hydroxy-5,12-naphthacenedione (61). 50 mg of 58/59 were treated with H_2SO_4 in acetone as described for 52/53. The resulting mixture was separated by TLC. From the less polar zone 3 mg (7.5 %) of 61 were isolated; mp 215°. - IR: 1685, 1670, 1622, 1589 cm^{-1}. - UV: λ_{max} (lg ε) = 206 (4.25), 255 (4.65), 285 sh, 305 (4.19), 438 nm (3.98). - ^1H NMR (250 MHz): δ = 2.85 (s; 3H, $ArCOCH_3$), 7.57 (d,J = 8.6 Hz; 1H, 7-H), 7.84 (dd; 2H, Aromaten-H), 8.38 (dd; 2H, Aromaten-H), 8.64 (d,J = 8.6 Hz; 1H, 8-H), 9.20 and 11.05 (2s; 2H, Aromaten-H), 14.39 (s; 1H, OH). - MS (170 °C): m/e = 317 (22 %, M^+ + 1), 316 (100, M^+), 301 (93, M^+ - CH_3), 288 (86, M^+ - CO), 273 (32, M^+ - $COCH_3$), 259 (18). - High resolution mass spectrum: Calcd. for $C_{20}H_{12}O_4$: 316.0735; Found: 316.0735.

3,4,6,11-Tetrahydro-5-hydroxy-2-methyl-6,11-dioxonaphthacene-carbaldehyde (60). From the polar zone of the TLC separation (see 61) were obtained 23 mg (58 %) of the aldehyde 60; mp 195°. - IR: 1682, 1673, 1630, 1591 cm^{-1}. - UV: λ_{max} (lg ε) = 210 (4.38), 250 sh, 260 (4.47), 275 sh, 325 (3.61), 395 sh, 417 (3.93), 437 nm sh. - ^1H NMR (400 MHz): δ = 2.48 (s; 3H, CH_3), 2.57 and 294 (2 t,J = 7.9 Hz; 4H, 2 CH_2), 7.84 and 8.24 (2 m; 4H), 8.38 (s; 1H, 12-H), 10.41 (s; 1H, CHO), 12.94 (s; 1H, OH). - MS (160 °C): m/e = 319 (57 %, M^+ + 1), 318 (96, M^+), 290 (100, M^+ - CO), 289 (95, M^+ - CHO), 275 (99, M^+ - CO -CH_3), 261 (41). - High resolution mass spectrum: Calcd.for $C_{20}H_{14}O_4$: 318.0892; Found: 318.0892.

1-Hydroxy-3-hydroxymethyl-2-(3-oxopentyl)-9,10-anthraquinone (64). 1.90 g (4.1 mmol) of acetate 63 were treated with aqueous NaOH as described for 47 to give 1.33 g (96 %) of benzyl alcohol 64; mp 165-167°. - IR: 1705, 1662, 1632 cm^{-1}. - UV: λ_{max} (lg ε) = 206 (4.22), 228 sh, 246 (4.48), 257 (4.47), 410 nm (3.85). - ^1H NMR (400 MHz): δ = 1.06 (t,J = 7,4 Hz; 3H, CH_2CH_3), 2.45 (q; 2H, CH_2CH_3), 2.95 (t,J = 7.2 Hz; 2H, CH_2), 2.98 (t,J = 5.8 Hz; 1H, OH), 3.08 (t,J = 7.2 Hz; 2H, CH_2), 4.85 (d,J = 5.8 Hz; 2H, CH_2OH), 7.83 (m; 2H, 6-H, 7-H), 7.92 (s; 1H, 4-H), 8.29 (m; 2H, 5-H, 8-H), 13.06 (s; 1H, 1-OH). - Calcd.for $C_{20}H_{18}O_5$: C,70.99 H,5.36; Found: C,70.66 H,5.33.

1-Hydroxy-3-hydroxymethyl-5,8-dimethoxy-2-(3-oxopentyl)-9,10-anthraquinone (66). 2.50 g (4.8 mmol) of acetate 65 were treated with 1N NaOH (see 48) to afford 1.86 g (96 %) of 66; mp 152-154°. - IR: 3490, 1660, 1623 cm^{-1}. - UV: λ_{max} (lg ε) = 210 sh, 230 (4.57), 258 (4.30), 265 sh, 450 nm (3.99). - ^1H NMR (400 MHz): δ = 1.04 (t;3H, CH_3), 2.43 (q,J = 7.5 Hz; 2H, CH_2CH_3), 3.89 and 4.05 (2t,J = 7.0 Hz; 4H, 2 CH_2),737

(q; 2H, 6-H, 7-H), 7.77 (s; 1H, 4-H), 13.10 (s; 1H, 1-OH). - Calcd. for $C_{22}H_{22}O_7$: C,66.32 H,5.57; Found: C,66.17 H,5.59.

Methyl [4-hydroxy-3-(3-oxobutyl)-anthraquinone-2-yl]carboxylate (68). A solution of 1.70 g (5.2 mmol) of benzyl alcohol 62 (obtained from 54 by treatment with 1N NaOH) in 120 mL of acetic acid was treated with a solution of 1.20 g (1.2 mmol) of CrO_3 in 5 mL of H_2O. After 4 h 200 mL of H_2O were added and the precipitate was collected on a Büchner funnel (0.99 g). An additional amount of 0.49 g of acid 67 was obtained by extraction of the mother liquor with CH_2Cl_2; total yield 84 %; mp 207-209°. 20 mg of the acid 67 was treated with 3 mL of diazomethane in ether. The solution was evaporated after 5 min to afford the ester 68 quantitatively; mp 171°. - IR: 1722, 1705, 1673, 1633, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 211 (4.35), 229 (4.34), 249 (4.49), 256 (4.50), 329 (3.52), 408 nm (3.87). - ^1H NMR (90 MHz): δ = 2.20 (s; 3H, $COCH_3$), 2.71-3.37 (m; 4H, 2 CH_2), 3.97 (s; 3H, CO_2CH_3), 7.82 (m; 2H, 6-H, 7-H), 8.09 (s; 1H, 4-H), 8.27 (m; 2H, 5-H, 8-H), 13.01 (s; 1H, OH). - Calcd. for $C_{20}H_{16}O_6$: C,68.18 H, 4.58; Found: C,67.50 H,4.03.

Methyl [4-hydroxy-3-(3-oxopentyl)-anthraquinone-2-yl]carboxylate (70). 1.25 g (3.7 mmol) of benzyl alcohol 64 were oxidized with 0.80 g of CrO_3 to afford 1.09 g (84%) of acid 69; mp 211-213°. 20 mg of the acid 69 were converted to the methyl ester 70; mp 171°. IR and UV see 68. - ^1H NMR (90 MHz): δ = 1.07 (t, J = 7.5 Hz; 3H, CH_2CH_3), 2.47 (q; 2H, CH_2CH_3), 2.63-3.38 (m; 4H, 2 CH_2), 3.98 (s; 3H, CO_2CH_3), 7.80 (m; 2H, 6-H, 7-H), 8.16 (s; 1H, 4-H), 8.31 (m; 2H, 5-H, 8-H), 13.06 (s; 1H, OH). - Calcd. for $C_{21}H_{18}O_6$: C,68.84 H,4.95; Found: C,68.17 H,5.04.

Methyl [4-hydroxy-5,8-dimethoxy-3-(3-oxopentyl)-anthraquinone-2-yl]carboxylate (72). 1.25 g (3.1 mmol) of benzyl alcohol 66 were oxidized with 0.75 g of CrO_3 as described for 67 to afford 0.79 g (61 %) of acid 71; mp 210-213°. 50 mg of the acid 71 were transformed with CH_2N_2 to the methyl ester 72; mp 171-173°. - IR: 1723, 1712, 1669, 1620 cm^{-1}. - UV: λ_{max} (lg ε) = 233 (4.47), 253 (4.30), 440 nm (3.81. - ^1H NMR (300 MHz): δ = 1.08 (t; 3H, CH_3), 2.45 (q, J = 7.5 Hz; 2H, CH_2CH_3), 2.81 and 3.24 (2 t; 4H, 2 CH_2), 3.89, 3.92 and 3.98 (3 s; 9H, 3 OCH_3), 7.38 (q; 2H, 6-, 7-H), 8.49 (s; 1H, 4-H), 13.11 (s; 1H, OH).

Methyl [4-hydroxy-3-(3-oxobutyl)-anthraquinone-2-yl]acetate (73). The Arndt-Eistert homologization was performed as described in the lit.[9,11] starting from 430 mg (1.27 mmol) of acid 67 to afford 163 mg (35 %) of the ester 73; mp 180°. - IR: 1723, 1703, 1672, 1628, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 207 (4.27), 227 (4.30), 237 sh, 246 (4.46), 257 (4.48), 280 sh, 329 (3.53), 390 sh, 409 (3.83), 430 nm (3.72). - ^1H NMR (400 MHz): δ = 2.17 (s; 3H, $COCH_3$), 2.85 and 3.03 (2 t, J = 7.5 Hz; 4H, 2 CH_2), 3.73 (s; 3H, CO_2CH_3), 3.89 (s; 2H, $CH_2CO_2CH_3$), 7.71 (s; 1H, 4-H), 7.82 and 8.32 (m; 4H), 13.08 (s; 1H, OH). - High-resolution mass spectrum: Calcd. for $C_{21}H_{18}O_6$: 366.1103; Found: 366.1103.

Methyl [4-hydroxy-3-(3-oxopentyl)-anthraquinone-2-yl]acetate (74). 3.90 mg (1.1mmol) of acid 69 were transformed to the ester 74 as described in the lit.[9,11] to afford 165 mg (39 %) of 74; mp 170-172°. - IR and UV see 74. - ^1H NMR (400 MHz): δ = 1.08 (t, J = 7.4 Hz; 3H, CH_2CH_3), 2.45 (q; 2H, CH_2CH_3), 2.81 (t, J = 7.5 Hz; 2H, CH_2), 3.04 (t, J = 7.5 Hz; 2H, CH_2), 3.73 (s; 3H, CO_2CH_3), 3.92 (s; 2H, $CH_2CO_2CH_3$), 7.71 (s; 1H, 4-H), 7.82 (m; 2H, 6-H, 7-H), 8.31 (m; 2H, 5-H, 8-H), 13.08 (s; 1H, OH).- Calcd. for $C_{22}H_{20}O_6$: C,69.46 H,5.30; Found: C,69.14 H,5.26.

Methyl [4-hydroxy-5,8-dimethoxy-3-(3-oxopentyl)-anthraquinone-2-yl]acetate (75). 360 mg (0.87 mmol) of acid 71 were transformed to 43 mg (11 %) of ester 75 as described in the lit.[9,11]; mp 207° (lit.[12] 213°).

4,7-Dideoxyauramycinone (76). A solution of 150 mg (0.41 mmol) of keto ester 73 in 10 mL of pyridine and 60 mL of CH_3OH was treated at -15° under N_2 with 2 mL of triton B (40 % in CH_3OH). After 3 h the solution was acidified with HCl and extracted with 150 mL of CH_2Cl_2. The organic phase was washed with water, dried over Na_2SO_4, and evaporated. The residue was crystallized twice from $CHCl_3/Et_2O$ to afford 48 mg of 76. TLC separation (1 mm silica gel, CH_2Cl_2/2 % CH_3OH) of the mother liquor yielded another 41 mg of 76 (total yield 59 %); mp 165°. - IR: 3545, 1730, 1669, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 208 (4.16), 230 sh, 245 (4.44), 257 sh, 263 (4.49), 280 sh, 3.26 (3.46), 390 sh, 408 nm (3.82). - ^1H NMR (400 MHz): δ = 1.45 (s; 3H, CH_3), 1.95 (dddd, J_{gem} = 14.0, $J_{3e,4a}$ = 6.9 Hz, $J_{3e,4e}$ = 3.0, $J_{1e,3e}$ = 1.6 Hz, 1H, 3e-H), 2.35 (ddd, J_{gem} = 14.0, $J_{3a,4a}$ = 10.2, $J_{3a,4e}$ = 6.9 Hz; 1H, 3a-H), 2.90 (ddd, J_{gem} = 19.1, $J_{3a,4a}$ = 10.2, $J_{3e,4a}$ = 6.9 Hz; 1H, 4a-H), 3.09 (ddd, J_{gem} = 19.1, $J_{3a,4e}$ = 6.9, $J_{3e,4e}$ = 3.1 Hz; 1H, 4e-H), 3.78 (s; 3H, CO_2CH_3), 3.94 (s; 1H, 1-H), 7.65 (s; 1H, 12-H), 7.83 (m; 2H, 8-H, 9-H), 8.34 (m; 2H, 7-H, 10-H), 13.08 (s; 1H, OH). - MS (120 °C): m/e = 367 (5 %, M^+ + 1), 366 (25, M^+), 348 (54, $M^+ - H_2O$), 334 (27, $M^+ - CH_3OH$), 324 (17), 316 (25), 307 (11, $M^+ - CO_2CH_3$), 289 (100, $M^+ - H_2O - CO_2CH_3$), 275 (40), 263 (58). - Calcd. for $C_{21}H_{18}O_6$: C,68.85 H,4.95; Found: C,68.63 H,5.01.

1-epi-4,7-Dideoxyauramycinone (80). From the polar fraction of the TLC chromatographie (see 76) 43 mg of 80 (29 %) were isolated; mp 161°. - UV see 76. - IR: 3490, 1730, 1672, 1635, 1591 cm^{-1}. - ^1H NMR (400 MHz): δ = 1.38 (s; 3H, CH_3), 1.83 (quint, J_{gem} = 13.7, J = 6.8 Hz; 1H, 3e-H), 2.36 (quint, J_{gem} = 13.7, J = 6.8 Hz; 1H, 3a-H), 2.85 (dt, J_{gem} = 19.5, J = 6.8 Hz; 1H, 4a-H), 3.13 (dt, J_{gem} = 19.3, J = 6.8 Hz; 1H, 4e-H), 3.15 (s; 1H, 2-OH), 3.88 (s; 3H, CO_2CH_3), 3.90 (s; 1H, 1-H),

7.61 (s; 1H, 12-H), 7.84 (m; 2H, 8-H, 9-H), 8.33 (m; 2H, 7-H, 10-H), 13.05 (s; 1H, 5-OH). - MS (150 °C): m/e = 367 (1 %, M^+ + 1), 366 (4, M^+), 348 (28, $M^+ - H_2O$), 334 (5, $M^+ - CH_3OH$), 324 (4), 316 (3), 307 (4, $M^+ - CO_2CH_3$), 289 (100, $M^+ - H_2O - CO_2CH_3$), 275 (15), 263 (51). - Calcd. for $C_{21}H_{18}O_6$: C,68.85 H,4.95; Found: C,68.74 H,4.97.

4,7-Dideoxyaklavinone (77). 145 mg (0.38 mmol) of ketoester 74 were cyclized as described for 76 to afford 103 mg (71 %) of 77 from the polar fraction of the TLC separation; mp 165°. - IR: 3480, 1737, 1662, 1634, 1598 cm^{-1}. - UV: λ_{max} (lg ε) = 207 (4.22), 233 sh, 246 (4.48), 260 (4.52), 409 nm (3.85). - ^1H NMR (400 MHz): δ = 1.10 (t; 3H, CH_2CH_3), 1.61 (sext, J_{gem} = 14.4, J = 7.5 Hz; 1H, CH_2CH_3), 1.73 (sext; 1H, CH_2CH_3), 1.94 (ddt, J_{gem} = 14.1, $J_{1,3e}$ = 2.0, $J_{3e,4e}$ = 2.5, $J_{3e,4a}$ = 7.0 Hz; 1H, 3e-H), 2.33 (ddd, J_{gem} = 14.1, $J_{3a,4a}$ = 10.5, $J_{3a,4e}$ = 7.0 Hz; 1H, 3a-H), 2.85 (ddd, J_{gem} = 18.8, $J_{3e,4e}$ = 2.5, $J_{3a,4e}$ = 7.0 Hz; 1H, 4e-H), 3.71 (s; 3H, CO_2CH_3), 3.97 (s; 1H, 1-H), 7.66 (s; 1H, 12-H), 7.80 (m; 2H, 8-H, 9-H), 8.31 (m; 2H, 7-H, 10-H), 13.09 (s; 1H, 5-OH). - MS (160 °C): m/e = 381 (6 %, M^+ + 1), 380 (27, M^+), 362 (55, $M^+ - H_2O$), 348 (37, $M^+ - CH_3OH$), 333 (34), 324 (37), 303 (100, $M^+ - H_2O - CO_2CH_3$), 291 (83), 277 (42), 263 (78), 249 (41), 235 (18). - Calcd. for $C_{22}H_{20}O_6$: C,69.46 H,5.30; Found: C,68.10 H,5.29.

1-epi-4,7-Dideoxyaklavinone (81). From the less polar fraction of the TLC separation 29 mg (20 %) of 81 were isolated; mp 161°. - IR: 1723, 1670, 1632, 1588 cm^{-1}. - ^1H NMR (400 MHz): δ = 1.02 (t; 3H, CH_2CH_3), 1.56 (m; 2H, CH_2CH_3), 1.86 (quint, J_{gem} = 13.4, J = 6.5 Hz; 1H, 3e-H), 2.31 (quint, J_{gem} = 13.4, J = 7.0 Hz; 1H, 3a-H), 2.79 (dt, J_{gem} = 19.3, J = 7.0 Hz; 1H, 4a-H), 2.98 (s; 1H, 2-OH), 3.11 (dt, J_{gem} = 19.3, J = 6.5 Hz; 1H, 4e-H), 3.84 (s; 3H, CO_2CH_3), 3.93 (s; 1H, 1-H), 7.61 (s; 1H, 12-H), 7.81 (m; 2H, 8-H, 9-H), 8.31 (m; 2H, 7-H, 10-H), 13.03 (s; 1H, 5-OH). - MS (110 °C): m/e = 380 (3 %, M^+), 362 (35, $M^+ - H_2O$), 348 (7, $M^+ - CH_3OH$), 333 (18), 324 (12), 319 (13), 303 (100, $M^+ - H_2O - CO_2CH_3$), 291 (66, $M^+ - CH_3OH - CO_2CH_3$), 275 (49), 263 (70), 249 (31), 235 (14). - Calcd. for $C_{22}H_{20}O_6$: C,69.46 H, 5.30; Found: C,69.53 H,5.33.

7,10-Di-O-methyl-ξ-pyrromycinone (78). 23 mg of ketoester 75 in a solution of pyridine/methanol were treated with Triton B as described for 76. From the polar fraction of the TLC separation (silica gel, CH_2Cl_2/2 % CH_3OH) 16 mg (69 %) of 78 were isolated; mp 126°. - IR: 3440, 1732, 1662, 1630 cm^{-1}. - UV: λ_{max} (lg ε) = 231 (4.65), 259 (4.35), 259 (4.35), 279 sh, 449 nm (4.08). - ^1H NMR (400 MHz): δ = 1.08 (t, J = 7.5 Hz; 3H, CH_2CH_3), 1.60 (m; 1H, CH_2CH_3), 1.72 (m; 1H, CH_2CH_3), 1.92 (ddt, J_{gem} = 14.2 Hz, $J_{3e,4a}$ = 7.3, $J_{3e,4e}$ = 2.5, $J_{1,3e}$ = 1.5 Hz; 1H, 3e-H), 2.33 (ddd, J_{gem} = 14.2, $J_{3a,4a}$ = 11, $J_{3a,4e}$ = 7.3 Hz; 1H, 3a-H), 2.84 (ddd, J_{gem} = 19.0, $J_{3a,4a}$ = 11.0, $J_{3e,4a}$ = 7.3 Hz; 1H, 4a-H), 3.07 (ddd, J_{gem} = 19.0, $J_{3a,4e}$ = 7.3, $J_{3e,4e}$ = 2.5 Hz; 1H, 4e-H), 3.72 (s; 3H, CO_2CH_3), 3.95 (s; 1H, 1e-H), 4.00 and 4.04 (2 s; 6-H, 2 OCH_3), 7.37 (q; 2H, 6-H, 7-H), 7.55 (s; 1H, 12-H), 13.16 (s; 1H, 5-OH).- MS (160 °C): m/e = 441 (10 %, M^+ + 1), 440 (39, M^+), 422 (25, $M^+ - H_2O$), 411 (5, $M^+ - C_2H_5$), 408 (8, $M^+ - CH_3OH$), 393 (7), 390 (2), 384 (37), 363 (100, $M^+ - H_2O - CO_2CH_3$), 351 (41), 323 (77), 309 (27), 265 (17).

ξ-Pyrromycinone (79) 5 mg of 78 were treated with $AlCl_3$ as described in the lit.[12] to afford 4 mg of 79 mp 213-215° (lit.[12] mp 215°). The spectroscopic data of 79 were identical with those given for the natural product 3).

1-epi-7,10-Di-O-methyl-ξ-pyrromycinone (82). From the less polar fraction of the TLC separation (see 78) 5 mg (22 %) of 82 were isolated; mp 196-197°. - ^1H NMR (400 MHz): δ = 1.02 (t; 3H, CH_3), 1.60 (m; 2H, CH_2), 1.81 (quint, J_{gem} = 13.5, J = 6.8 Hz; 1H, 3e-H), 2.29 (quint, J_{gem} = 13.5, J = 7.1 Hz; 1H, 3a-H), 2.77 (dt, J_{gem} = 18.9, J = 7.1 Hz; 1H, 4a-H), 3.01 (s; 1H, 2-OH), 3.08 (dt, J_{gem} = 18.9, J = 6.8 Hz; 1H, 4e-H), 3.81 (s; 3H, CO_2CH_3), 3.91 (s; 1H, 1-H), 3.99 and 4.01 (2 s; 6H, 2 OCH_3), 7.37 (q; 2H, 8-, 9-H), 7.47 (s; 1H, 12-H), 13.12 (s; 1H, OH).

7-Deoxyauramycinone (4). A solution of 50 mg (0.14 mmol) of 76 in 50 mL of CCl_4 was treated with 40 mg of Br_2 and irridiated with a day light lamp (300 Watt) for 8 min. The solvent was evaporated at reduced pressure and the residue stirred for 30 min in a mixture of 20 mL of THF and 20 mL of H_2O. The solvent was again evaporated at reduced pressure and the residue separated by TLC. From the zone of medium polarity 34 mg (65 %) of 4 were isolated; mp 174°. - IR: 3450, 1732, 1655, 1625,1583 cm^{-1}. - UV: λ_{max} (lg ε) = 208 (4.22), 227 (4.28), 247 (4.42), 255 (4.43), 260 sh, 278 sh, 327 (3.44), 395 sh, 405 (3.78), 425 nm sh. - ^1H NMR (400 MHz): δ = 1.44 (s; 3H, CH_3), 226 (dt, J_{gem} = 15.1, $J_{1,3e}$ = 1.5, $J_{3e,4}$ = 1.5 Hz; 1H, 3e-H), 263 (ddd, J_{gem} = 15.1, $J_{3a,4}$ = 5.3, $J_{4-OH,3a}$ = 1.6 Hz; 1H, 3a-H), 3.37 (m; 1H, 4-OH), 3.74 (s; 3H, CO_2CH_3), 4.06 (s; 1H, 2-OH), 4.07 (d; 1H, 1-H), 5.42 (m; 1H, 4-H), 7.72 (s; 1H, 12-H), 7.86 (m; 2H, 8-H, 9-H), 8.33 (m; 2H, 7-H, 10-H), 13.34 (s; 1H, 5-OH).- MS (100 °C): m/e = 383 (5 %, M^+ + 1), 382 (26, $M^+ - H_2O$), 346 (57, $M^+ - 2\ H_2O$), 331 (33), 322 (9), 315 (40), 305 (100, $M^+ - H_2O - CO_2CH_3$), 289 (39). - Calcd. for $C_{21}H_{18}O_7$: C,65.97 H,4.75; Found: C,65.84 H,4.76.

4-epi-7-Deoxyauramycinone (83). From the polar zone of the TLC separation (see 4) 4.5 mg (9 %) of the 2,4-trans-diol 83 were isolated; mp 193°. - UV see 4. - IR: 1733, 1673, 1625, 1588 cm^{-1}. - ^1H NMR (400 MHz): δ = 1.46 (s; 3H, CH_3), 2.41 (q; 2H, 3-H), 3.76 (s; 3H, CO_2CH_3), 3.88 (d, $J_{1,3e}$ = 1.7 Hz; 1H, 1-H), 4.07 (d, $J_{4,OH}$ = 2.5 Hz; 1H, 4-OH), 5.34 (dt, $J_{3a,4}$ = 8.1, $J_{4,4-OH}$ = 2.5 Hz; 1H, 4-H), 7.67 (s; 1H, 12-H), 7.81 (m; 2H, 8-H, 9-H), 8.30 (m; 2H, 7-H, 10-H), 13.52 (s; 1H, 5-OH). - MS (180 °C): m/e = 383 (0.1 %, M^+ + 1), 382 (9, M^+), 364 (25, $M^+ - H_2O$), 346 (100, M^+-

2 H_2O), 331 (57), 315 (68), 305 (60, M^+ - H_2O - CO_2CH_3), 287 (49). - Calcd. for $C_{21}H_{18}O_7$: C,65.97 H,4.75; Found: C,65.39 H,4.66.

7-Deoxyaklavinone (5). 50 mg 77 were treated as described for 4 to afford from the polar fraction of the TLC separation 36 mg (69 %) of 5; mp 179-181°. - IR: 1728, 1654, 1629, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 208 (4.21), 227 (4.30), 247 (4.46), 255 (4.46), 279 sh, 330 (3.47), 405 nm (3.82). - ^1H NMR (400 MHz): δ = 1.12 (t, J = 7.4 Hz; CH_2CH_3), 1.59 (sext; 1H, CH_2CH_3), 1.74 (sext, dt, J_{gem} = 14.4, J = 7.3 Hz; 1H, CH_2CH_3), 2.28 (dt, J_{gem} = 14.9, $J_{1,3e}$ = 1.3, $J_{3e,4}$ = 1.3 Hz; 1H, 3e-H), 2.56 (ddd, J_{gem} = 14.9, $J_{3a,4}$ = 5.3, $J_{4-OH,3a}$ = 1.6 Hz; 1H, 3a-H), 3.40 (dd, $J_{4-OH,4}$ = 3.2, $J_{4-OH,3a}$ = 1.6 Hz; 1H, 4-OH), 3.72 (s; 3H, CO_2CH_3), 3.89 (s; 1H, 2-OH), 4.11 (d, $J_{1,3e}$ = 1.3 Hz; 1H, 1-H), 5.42 (dt, $J_{3a,4}$ = 5.3, $J_{3e,4}$ = 1.3 Hz; 1H, 4-H), 7.74 (s; 1H, 12-H), 7.85 (m; 2H, 8-H, 9-H), 8.33 (m; 2H, 7-H, 10-H), 13.33 (s; 1H, OH).- MS (180 °C): m/e = 397 (10 %, M^+ + 1), 396 (34, M^+), 378 (54, M^+ - H_2O), 360 (76, M^+ - 2 H_2O), 349 (49), 345 (60), 328 (38), 319 (100, M^+ - H_2O - CO_2CH_3), 307 (24), 291 (41). - Calcd. for $C_{22}H_{20}O_7$: C,66.66 H,5.09; Found: C,66.40 H,5.14.

4-epi-7-Deoxyaklavinone (84). From the less polar zone of the TLC separation 3.0 mg (6 %) of 84 were isolated; mp 153-155°. - UV see 5. - IR: 1723, 1672, 1662, 1632, 1586 cm^{-1}. - ^1H NMR (400 MHz): δ = 1.12 (t, J = 7.3 Hz; 3H, CH_2CH_3), 1.76 (m; 2H, CH_2CH_3), 2.82 (dd, J_{gem} = 18.2, $J_{1,3e}$ = 1.8 Hz; 1H, 3e-H), 3.38 (d, J_{gem} = 18.2 Hz; 1H, 3a-H), 3.77 (s; 3H, CO_2CH_3), 3.93 (s; 1H, 2-OH), 4.22 (d, $J_{1,3e}$ = 1.8 Hz; 1H, 1-H), 7.82 (s; 1H, 12-H), 7.86 (dt, $J_{8,9}$ = $J_{9,10}$ = 7.5 Hz, $J_{7,9}$ = $J_{8,10}$ = 1.8 Hz; 2H, 8-H, 9-H), 8.29 and 8.33 (each dd; 2H, 7-H, 10-H), 13.97 (s; 1H, OH). - MS (185 °C): m/e = 376 (100 %, M^+ - H_2O), 361 (61, M^+ - CH_3), 345 (81, M^+ - OCH_3), 317 (14, M^+ - CO - OCH_3). - High-resolution mass spectrum: Calcd. for 376.0947; Found: 376.0947.

1-epi-7-Deoxyauramycinone (85). 22 mg (0.06 mmol) of 80 were treated as described for 4 to yield from the less polar fraction 2.1 mg (9.5 %) of 2,4-cis-diol 85; mp 162°. - IR: 3450, 1735, 1670, 1633, 1590 cm^{-1}. - UV: λ_{max} (lg ε) = 208 (4.26), 226 (4.31), 249 sh, 256 (4.53), 260 (4.52), 279 sh, 325 (3.49), 385 sh, 405 (3.81), 425 nm sh. - ^1H NMR (400 MHz): δ = 1.44 (s; 3H, CH_3), 1.99 (dd, J_{gem} = 14.8, $J_{3,4}$ = 5.1 Hz; 1H, 3-H), 2.53 (dd, J_{gem} = 14.8, $J_{3,4}$ = 2.8 Hz; 1H, 3-H), 3.82 (s; 1H, 1-H), 3.98 (s; 3H, CO_2CH_3), 4.31 (d, J = 1.6 Hz; 1H, 2-OH), 4.38 (d, $J_{4-OH,4}$ = 7.5 Hz; 1H, 4-OH), 5.19 (m; 1H, 4-H), 7.56 (s; 1H, 12-H), 7.85 (m; 2H, 8-H, 9-H), 8.31 (m; 2H, 7-H, 10-H), 13.27 (s; 1H, 5-OH). - MS (140 °C): m/e = 383 (7 %, M^+ + 1), 382 (30, M^+), 364 (79, M^+ - H_2O), 346 (42, M^+ - 2 H_2O), 331 (17), 322 (59, M^+ - CH_3COOH), 305 (100, M^+ - H_2O - CO_2CH_3), 289 (73), 273 (41), 262 (87), 238 (24).

1,4-Diepi-7-deoxyauramycinone (86). From the polar zone of the TLC separation (see 85) 12.6 mg (57 %) of the trans diol 86 were isolated; mp 176°. - IR: 3555 and 3430, 1715, 1671, 1633, 1588 cm^{-1}. - UV: λ_{max} (lg ε) = 208 (4.25), 227 (4.31), 247 (4.46), 256 (4.48), 260 sh, 280 sh, 327 (3.49), 395 sh, 404 (3.83), 420 nm sh. - ^1H NMR (400 MHz): δ = 1.44 (s; 3H, CH_3), 1.91 (ddd, J_{gem} = 13.9, $J_{3,4}$ = 7.2, $J_{2-OH,3}$ = 1.5 Hz; 1H, 3-H), 2.67 (dd, J_{gem} = 13.9, $J_{3,4}$ = 7.2 Hz; 3-H), 3.26 (d, $J_{2-OH,3}$ = 1.5 Hz; 1H, 2-OH), 3.84 (d, $J_{4,4-OH}$ = 2.5 Hz; 1H, 4-OH), 3.92 (s; 3H, CO_2CH_3), 3.97 (s; 1H, 1-H), 5.44 (dt, $J_{3,4}$ = 7.5, $J_{4,4-OH}$ = 2.5 Hz; 1H, 4-H), 7.58 (s; 1H, 12-H), 7.84 (m; 2H, 8-H, 9-H), 8.30 (m; 2H, 7-H, 10-H), 13.44 (s; 1H, 5-OH).- MS (160 °C): m/e = 382 (0.1 %, M^+), 364 (23, M^+ - H_2O), 346 (7, M^+ - 2 H_2O), 322 (2), 305 (100, M^+ - H_2O - CO_2CH_3), 289 (23), 277 (8). - Calcd. for $C_{21}H_{18}O_7$: C,65.97 H,4.75; Found: C,65.90 H,4.73.

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