Naturally Occurring Quinones. Part XXVI.[1] A Synthesis of Tetrangulol (1,8-Dihydroxy-3-methylbenz[*a*]anthracene-7,12-quinone)

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Hydroxybenz[*a*]anthracene-7,12-quinones can be prepared from 2-chloro-1,4-naphthoquinones by decarboxylative alkylation at C-3 with β-(3-acetoxyphenyl)propionic acids followed by treatment with sodium carbonate, which results in hydrolysis, cyclisation, and dehydrogenation. In this way tetrangulol and its 3,8-dihydroxy-1-methyl isomer were obtained from 5-acetoxy-3-[β-(3-acetoxy-5-methylphenyl)ethyl]-2-chloro-4-naphthoquinone.

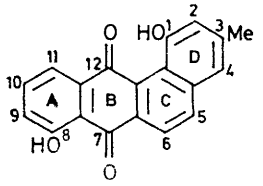
TETRANGULOL (I),[2] produced by cultures of *Streptomyces rimosus*, is the simplest member of a small group of metabolites, elaborated by streptomycetes,[3] having a benz[*a*]anthracene-7,12-quinone skeleton. The structure, originally determined by spectroscopic and chemical methods, we have now confirmed by synthesis. Our approach was to start with a 1,4-naphthoquinone and then construct rings C and D by suitable aralkylation and cyclisation methods.

Torssell[4] has shown that quinones can be alkylated with alkyl radicals generated by oxidative decarboxylation of carboxylic acids with silver ions and persulphate, and the method was used[5] to synthesise some simple naturally occurring quinones. By similar treatment of 2-chloro-1,4-naphthoquinone with β-phenylpropionic acid, the corresponding aralkyl derivative (II; $R^1 = R^2 = H$) was obtained in 94% yield, but attempts to cyclise it to (III; $R^1 = R^2 = H$) did not succeed. Tetrangulol has a phenolic group in ring D, and to take advantage of this we next prepared another model compound (II; $R^1 = OH$, $R^2 = H$) with the intention of converting it into (III; $R^1 = OH$, $R^2 = H$ and/or $R^1 = H$, $R^2 = OH$) by treatment with base. As it is necessary to protect the hydroxy-group during the oxidative alkylation step we made the acetoxy-derivative (II; $R^1 = OAc$, $R^2 = H$) by treating 2-chloro-1,4-naphthoquinone with β-(3-acetoxyphenyl)-propionic acid under Torssell conditions. A very minor product of this reaction was 2-chloro-3-methyl-1,4-naphthoquinone, presumably arising from partial hydrolysis of the acetate and decarboxylation of the resulting acetic acid. To remove the protecting group from the acetoxyquinone (II; $R^1 = OAc$, $R^2 = H$) it was warmed with sodium carbonate. The product, however, was not (II; $R^1 = OH$, $R^2 = H$) but a mixture containing essentially three components. One of these was identified as the dihydroxy-quinone (IV), this being the main product formed when the acetoxy-chloro-quinone was treated with methanolic potassium hydroxide. The other two components were isomers, $C_{18}H_{10}O_3$, whose n.m.r. spectra revealed only aromatic protons and an acidic hydroxy-proton signal at low field. It was apparent that hydrolysis had been followed by cyclisation and dehydrogenation to give two hydroxybenz[*a*]-anthracenequinones. The more soluble isomer, m.p. 234°, isolated in smaller amount, is a purple solid similar to tetrangulol which must be 1-hydroxybenz[*a*]anthracene-7,12-quinone (V; $R^1 = OH$, $R^2 = H$). In benz[*a*]-anthracene-7,12-quinone itself H-1 is deshielded by the neighbouring carbonyl group and resonates at $\delta(CDCl_3)$ 9.72, well separated from the other aromatic proton signals at δ 8.42—7.60. This signal is absent from the spectrum of the compound, m.p. 234°, but is present in the spectrum of the major isomer, m.p. 240° (V; $R^1 = H$, $R^2 = OH$), as a doublet at $\delta[(CD_3)_2SO]$ 9.40 (J 9 Hz).

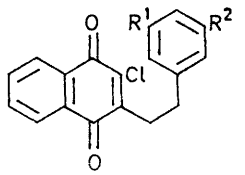
It seemed likely that tetrangulol could be obtained in the same way; accordingly we prepared the protected diacetoxy-chloro-quinone (VI; $R^1 = R^2 = Ac$) by alkylation of 5-acetoxy-2-chloro-1,4-naphthoquinone[6] with

[1] Part XXV, M. A. Ferreira, M. Moir, and R. H. Thomson, *J.C.S. Perkin I*, 1975, 1113.
[2] M. P. Kuntsmann and L. A. Mitscher, *J. Org. Chem.*, 1966, **31**, 2920.
[3] J. H. Bowie and A. W. Johnson, *Tetrahedron Letters*, 1967, **1449**; M. Sezaki, S. Kondo, K. Maeda, and H. Umezawa, *Tetrahedron*, 1970, **26**, 5171.
[4] N. Jacobsen and K. Torssell, *Annalen*, 1972, **763**, 135.
[5] N. Jacobsen and K. Torssell, *Acta Chem. Scand.*, 1973, **27**, 3211.
[6] R. H. Thomson, *J. Org. Chem.*, 1948, **13**, 371; A. S. Wheeler and W. J. Mattox, *J. Amer. Chem. Soc.*, 1933, **55**, 686.

β-(3-acetoxy-5-methylphenyl)propionic acid (2-chloro-5-hydroxy-3-methyl-1,4-naphthoquinone was a minor



(I)



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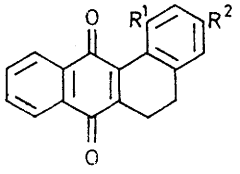

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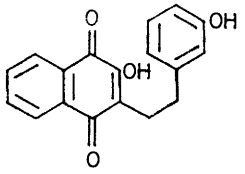

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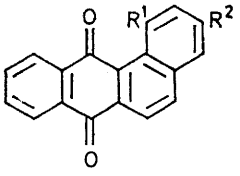

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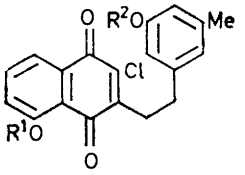

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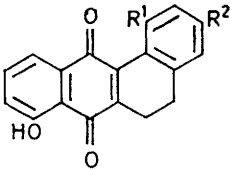

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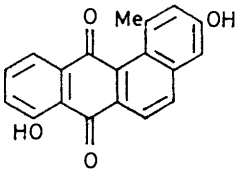
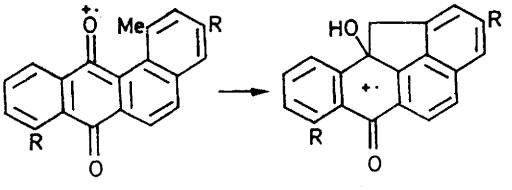


(VIII)

product). On treatment with sodium carbonate it gave a more complex mixture of products comprising (VI; $R^1 = R^2 = H$) and (VI; $R^1 = H$, $R^2 = Ac$), the dihydrobenzanthracenequinones (VII; $R^1 = HO$, $R^2 = Me$) and (VII; $R^1 = Me$, $R^2 = OH$), and (I), which was identical with tetrangulol. As before, cyclisation occurred predominately *para* to the 3'-phenolic group, and tetrangulol was the product obtained in smallest yield. Attempts to promote dehydrogenation and improve the yield by altering the reaction conditions and using different bases were not successful. More prolonged treatment of (VI; $R^1 = R^2 = Ac$) with sodium carbonate, for example, gave (VIII) as the main product with only a trace of tetrangulol. Surprisingly, we could not convert (VII; $R^1 = Me$, $R^2 = OH$) into (VIII) by using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) but dehydrogenation was effected with hot nitrobenzene containing pyridine. The dihydrocompound (VII; $R^1 = OH$, $R^2 = Me$) appeared to undergo dehydrogenation to tetrangulol in the molten state, judging by its behaviour during m.p. determination (melting, solidification, and remelting at 202—203°).

The hydrolysis products (VI; $R^1 = R^2 = H$) and (VI; $R^1 = H$, $R^2 = Ac$) were easily recognised from spectroscopic data. In the monoacetate the 5-hydroxy-group must be unesterified to account for the carbonyl absorption at 1 647 cm^{-1} and the low-field hydroxy-resonance at δ 11.9. The two pairs of isomeric quinones (I) and (VIII), and (VII; $R^1 = OH$, $R^2 = Me$) and (VII; $R^1 = Me$, $R^2 = OH$) could be distinguished by the greater solubility of the 1-hydroxy-isomers (I) and (VII; $R^1 = OH$, $R^2 = Me$), the absence of hydroxy-absorption in the 3 μm region of their i.r. spectra, and the lower chemical shift of the 1-hydroxy-protons relative to the 3-hydroxy-protons. In tetrangulol (I) the 1-hydroxy-proton resonates at $\delta(CDCl_3)$ 11.20 whereas the 3-hydroxy-proton signal in the spectrum of the isomer (VIII) appears at $\delta[(CD_3)_2SO]$ 10.37.

The base peak in the mass spectrum of (VIII) falls at *m/e* 287, *i.e.* $M^+ - OH$ (by accurate mass measurement), and the same is true for the mass spectrum of 1-methylbenz[*a*]anthracene-7,12-quinone (IX; R = H),



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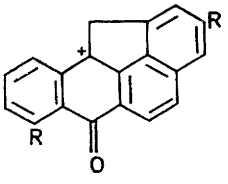

(X)

where the methyl group is also close to the C-12 carbonyl group. We suggest that these ions may be (X; R = OH or H, respectively), formed as indicated.

EXPERIMENTAL

β-(3-*Hydroxyphenyl*)*propionic Acid*.—3-Hydroxycinnamic acid (7.4 g) in a solution of sodium hydroxide (27 g) in water (667 ml) was heated to 90 °C on a steam-bath, and Raney nickel alloy (20 g) was added over 45 min with vigorous stirring.[7a] The mixture was heated and stirred 1 h further, and filtered hot. After addition of an excess of concentrated hydrochloric acid, and cooling, extraction

[7] (*a*) D. B. Bruce, Ph.D. Thesis, University of Aberdeen, 1953; (*b*) E. Schwenk and D. Papa, *J. Org. Chem.*, 1945, **10**, 232.

with ether yielded the required compound, m.p. 112—113.5° (lit.,[8] 110°; lit.,[7b] 99—100°) (6.7 g, 97%). The acetate, prepared by heating with acetic anhydride–sodium acetate, was a liquid which decomposed on distillation, and was used without further purification.

β-(3-*Acetoxy*-5-*methylphenyl*)*propionic Acid*.—3,5-Dimethylphenyl acetate (32.8 g), 1,3-dibromo-5,5-dimethylhydantoin (29 g), and benzoyl peroxide (1 g) in carbon tetrachloride (400 ml) were boiled gently under reflux for 5 h. The mixture was then cooled and filtered, the solvent was evaporated off, and the residue was distilled. The ω-bromide was collected as a fraction of b.p. 132—152° at 0.3 mmHg (20 g) [δ 2.70—3.05 (3 H, m, ArH), 4.33 (2 H, s, CH_2Br), and 2.32 and 2.19 (each 3 H, s, Me and OAc), $\nu_{max.}$ 1 770 cm^{-1}]. Without further purification the bromide (31 g) was converted into 3-*hydroxy*-5-*methylbenzaldehyde* by the method of Hass and Bender.[9] The crude product was chromatographed on silica gel in benzene, and crystallised from chloroform; m.p. 107—108° (7.5 g) (Found: C, 70.5; H, 5.8. $C_8H_8O_2$ requires C, 70.5; H, 5.9%), $\nu_{max.}$(KBr) 3 880 and 1 662 cm^{-1}, δ($CDCl_3$) 9.84 (1 H, s, CHO), 6.78br (1 H, s, OH), 2.35 (3 H, s, Me), and ArH signals. The aldehyde (2.41 g) was condensed with malonic acid (3.7 g) by the general procedure[10] to give 3-*hydroxy*-5-*methylcinnamic acid*, m.p. 208—209° (2.4 g) (Found: C, 67.2; H, 5.7. $C_{10}H_{10}O_3$ requires C, 67.4; H, 5.7%), $\nu_{max.}$(KBr) 3 370, 1 661, and 1 614 cm^{-1}, δ(CD_3OD) 7.59 and 6.47 (each 1 H, d, *J* 13 Hz, CH=CH), 6.8 (3 H, m, ArH), and 2.30 (3 H, s, Me). Reduction of the cinnamic acid with nickel alloy, as above, yielded the dihydro-acid, m.p. 93—94° (60%), which was acetylated (acetic anhydride–sodium acetate, hot) to give β-(3-*acetoxy*-5-*methylphenyl*)*propionic acid*, m.p. 65—67° (Found: C, 64.7; H, 6.2. $C_{12}H_{14}O_4$ requires C, 64.8; H, 6.3%), $\nu_{max.}$ 3 410, 1 760, 1 700, and 1 616 cm^{-1}, δ($CDCl_3$) 9.98br (1 H, s, CO_2H), 2.99—2.54 (4 H, m, $CH_2{\cdot}CH_2$), 2.30 and 2.25 (each 3 H, s, ArMe and OAc), and ArH signals.

2-*Chloro*-3-(β-*phenylethyl*)-1,4-*naphthoquinone* (II; R^1 = R^2 = H).—To a solution of 2-chloro-1,4-naphthoquinone (1.9 g) and β-phenylpropionic acid (1.5 g) in acetonitrile (17 ml) stirred vigorously at 95 °C with silver nitrate (0.5 g), ammonium persulphate (6 g) in water (30 ml) was added during 1 h. Heating was continued for 1 h further with addition of more acetonitrile to maintain a homogeneous system. The organic solution was then evaporated, and the aqueous residue was extracted with ethyl acetate; the extract was washed with saturated aqueous sodium hydrogen carbonate, and water, and dried ($MgSO_4$). Evaporation left a residue which crystallised on addition of methanol. The *quinone* (2.79 g) separated from aqueous acetone in golden-brown needles, m.p. 122—123° (Found: C, 72.9; H, 4.5; Cl, 11.8%; M^+, 296.0604. $C_{18}H_{13}{}^{35}ClO_2$ requires C, 72.8; H, 4.4; Cl, 11.9%; *M*, 296.0603), $\lambda_{max.}$(MeOH) 246, 251.5, 274, and 339 nm (log ε 4.20, 4.22, 4.15, and 3.26), $\nu_{max.}$(KBr) 1 678, 1 665, and 1 606 cm^{-1}, δ($CDCl_3$) 8.15 and 7.75 (each 2 H, m, Ar), 7.25 (5 H, s, C_6H_5), and 3.10 and 2.83 (each 2 H, m, $CH_2{\cdot}CH_2$), *m/e* 298 (1.5%), 296 (5.5), 261 (28), 260 (9), 92 (20), and 91 (100).

3-[β-(3-*Acetoxyphenyl*)*ethyl*]-2-*chloro*-1,4-*naphthoquinone* (II; R^1 = OAc, R^2 = H).—2-Chloro-1,4-naphthoquinone (5.8 g) was alkylated, as above, with β-(3-acetoxyphenyl)-propionic acid (6.3 g), ammonia persulphate (18 g) in water (90 ml), and silver nitrate (1.5 g) in acetonitrile (51 ml) and water (111 ml). Work-up, as above, gave a crude product which was chromatographed on a column of silica gel (elution with benzene and then ethyl acetate) to give the *quinone* (9.46 g), yellow crystals, m.p. 111—112.5° (from aqueous acetone) (Found: C, 67.6; H, 4.2; Cl, 10.2%; M^+, 354.0661. $C_{20}H_{15}{}^{35}ClO_4$ requires C, 67.7; H, 4.3; Cl, 10.0%; *M*, 354.0658), $\lambda_{max.}$(MeOH) 245.5, 251.5, 274, and 341 nm (log ε 4.17, 4.20, 4.13, and 3.45), $\nu_{max.}$(KBr) 1 760, 1 674, and 1 660 cm^{-1}, δ($CDCl_3$) 8.20—6.85 (8 H, m, ArH), 3.10 and 2.83 (each 2 H, m, $CH_2{\cdot}CH_2$), and 2.28 (3 H, s, OAc), *m/e* 356 (5%), 354 (14), 312 (2), 277 (94), 276 (18), 107 (100), and 77 (14). The first fractions from the column contained 2-chloro-3-methyl-1,4-naphthoquinone (110 mg), identified by direct comparison with an authentic sample.

5-*Acetoxy*-3-[β-(3-*acetoxy*-5-*methylphenyl*)*ethyl*]-2-*chloro*-1,4-*naphthoquinone* (VI; R^1 = R^2 = Ac).—5-Acetoxy-2-chloro-1,4-naphthoquinone[6] (2.50 g) was alkylated with β-(3-acetoxy-5-methylphenyl)propionic acid (2.22 g), ammonium persulphate (6 g) in water (30 ml), and silver nitrate (0.5 g) in acetonitrile (17 ml) and water (37 ml). Work-up, as above, gave a yellow oil which crystallised from aqueous acetone to give the *quinone* (3.5 g), m.p. 147—148° (Found: C, 64.5; H, 4.7%; M^+, 426.0867. $C_{23}H_{19}{}^{35}ClO_6$ requires C, 64.7; H, 4.5%; *M*, 426.0869), $\lambda_{max.}$(MeOH) 244.5, 250sh, 274, and 338 nm (log ε 4.02, 4.00, 3.98, and 2.84), $\nu_{max.}$(KBr) 1 767, 1 677, 1 661, 1 620, and 1 607 cm^{-1}, δ($CDCl_3$) 8.14—7.20 (3 H, m, H-6, -7, and -8), 6.96—6.70 (3 H, m, H-2′, -4′, and -6′), 3.00 and 2.70 (each 2 H, m, $CH_2{\cdot}CH_2$), 2.43 and 2.24 (each 3 H, s, OAc), and 2.30 (3 H, s, ArMe), *m/e* 386 (14%), 384 (79), 344 (13), 342 (75), 307 (35), 306 (26), 305 (14), and 121 (100). T.l.c. of the mother liquor on silica gel in benzene–ethyl acetate (10 : 1) afforded 2-*chloro*-5-*hydroxy*-3-*methyl*-1,4-*naphthoquinone*, golden spangles, m.p. 141—142° (from aqueous acetone) (14 mg) (Found: C, 59.4; H, 3.4%; M^+, 222.0087. $C_{11}H_7{}^{35}ClO_3$ requires C, 59.3; H, 3.2%; *M*, 222.0084), $\lambda_{max.}$(MeOH) 280 and 431 nm (log ε 4.07 and 3.59), $\lambda_{max.}$(MeOH–HO^-) 282.5 and 541 nm (log ε 4.13 and 3.71), $\nu_{max.}$ 1 677 and 1 642 cm^{-1}, δ($CDCl_3$) 11.88 (1 H, s, OH), 2.30 (3 H, s, Me), and ArH signals, *m/e* 224 (30%), 222 (100), 187 (89), 159 (32), and 131 (11).

Cyclisation of 3-[β-(3-*Acetoxyphenyl*)*ethyl*]-2-*chloro*-1,4-*naphthoquinone* (II; R^1 = OAc, R^2 = H).—The quinone (0.864 g) in 2N-sodium carbonate (86.4 ml) was stirred on a steam-bath for 1 h, cooled, poured into ice and hydrochloric acid, and extracted with ethyl acetate. The crude product was separated by t.l.c. on silica gel in benzene–ethyl acetate (10 : 4) into three main bands.

Band 1 (lowest R_F) yielded an orange-red oil (264 mg) and was 2-*hydroxy*-3-[β-(3-*hydroxyphenyl*)*ethyl*]-1,4-*naphthoquinone* (IV), m.p. 207—209° (decomp.) (from aqueous acetone) (Found: C, 73.4; H, 5.0%; M^+, 294.0892. $C_{18}H_{14}O_4$ requires C, 73.5; H, 4.8%; *M*, 294.0892), $\lambda_{max.}$(MeOH) 255, 277, and 342sh nm (log ε 4.36, 4.39, and 2.75), $\lambda_{max.}$(MeOH–HO^-) 235, 277, and 496 nm (log ε 4.40, 4.52, and 3.53), $\lambda_{max.}$(KBr) 3 500—3 000, 1 666, and 1 625 cm^{-1}, δ(C_5D_5N) 3.4—3.0 (4 H, m, $CH_2{\cdot}CH_2$), and ArH signals, *m/e* 294 (60%), 187 (6), 159 (8), 108 (7), 107 (100), and 77 (16). This compound was the main product when the acetoxy-chloro-quinone was treated with methanolic potassium hydroxide.

[8] J. Salway, *J. Chem. Soc.*, 1910, **97**, 2413.
[9] H. B. Hass and M. L. Bender, *Org. Synth.*, Coll. Vol. 4, 1963, 932.
[10] J. Kov, M. S. Fish, G. N. Walker, and J. Blake, *Org. Synth.*, Coll. Vol. 4, 1963, 327.

Band 2 (174 mg) yielded 3-*hydroxybenz*[a]*anthracene*-7,12-*quinone* (V; R^1 = H, R^2 = OH) as red-gold crystals, m.p. 240—240.5° (from aqueous acetone) [Found: C, 75.8; H, 4.8%; M^+, 274.0626. $C_{18}H_{10}O_3$,$(CH_3)_2CO$ requires C, 75.9; H, 4.8%; *M*, 274.0629 (without solvent)], $\lambda_{max.}$(MeOH) 225, 245sh, 305.5, and 390 nm (log ε 4.35, 4.16, 4.28, and 3.59), $\lambda_{max.}$(MeOH–HO^-) 240.5, 337, 420, and 538 nm (log ε 4.34, 4.13, 3.38, and 3.59), $\nu_{max.}$(KBr) 3 400, 1 660, 1 625, and 1 612 cm^{-1}, δ[$(CD_3)_2SO$] 10.40 (1 H, s, OH), 9.40 (1 H, d, *J* 9 Hz, H-1), and 8.2—7.2 (8 H, m, ArH), *m/e* 274 (100%), 273 (8), 246 (19), 218 (8), and 189 (18).

Band 3 (30 mg) was further purified by t.l.c. in benzene–ethyl acetate (10 : 4), and then benzene, to give 1-*hydroxybenz*[a]*anthracene*-7,12-*quinone* (V; R^1 = OH, R^2 = H) as purple crystals, m.p. 234—235° (6 mg) (Found: M^+, 274.0626. $C_{18}H_{10}O_3$ requires *M*, 274.0629), $\lambda_{max.}$(MeOH) 251, 311, and 485 nm (log ε 4.35, 4.31, and 3.09), $\lambda_{max.}$(MeOH–OH^-) 594 nm (log ε 2.98), $\nu_{max.}$(KBr) 1 673 and 1 645 cm^{-1}, δ($CDCl_3$) 11.21 (1 H, s, OH) and ArH signals, *m/e* 274 (100%), 257 (5), 246 (5), 218 (5), and 189 (16).

Cyclisation of 5-*Acetoxy*-3-[β-(3-*acetoxy*-5-*methylphenyl*)-*ethyl*]-2-*chloro*-1,4-*naphthoquinone* (VI; R^1 = R^2 = Ac).—The quinone (785 mg) was treated with 2N-sodium carbonate (78.5 ml), and the product worked up as above. The mixture was separated by t.l.c. on silica gel in benzene–ethyl acetate (10 : 1) into four bands.

Band 1 (lowest R_F) (394 mg) was 5,6-*dihydro*-3,8-*dihydroxy*-1-*methylbenz*[a]*anthracene*-7,12-*quinone* (VII; R^1 = Me, R^2 = OH), red crystals, m.p. 246.5—248.5° (from aqueous acetone) (Found: C, 74.8; H, 4.5%; M^+, 305.0891. $C_{19}H_{14}O_4$ requires C, 74.5; H, 4.6%; *M*, 306.0892), $\lambda_{max.}$(MeOH) 273, 313sh, and 478 nm (log ε 4.35, 3.95, and 3.82), $\lambda_{max.}$(MeOH–HO^-) 299 and 552 nm (log ε 4.34 and 3.96), $\nu_{max.}$(KBr) 3 450, 1 670, 1 638, and 1 603 cm^{-1}, δ[$(CD_3)_2SO$] 11.95 (1 H, s, 8-OH) and 9.83br (1 H, s, 3-OH), δ(C_5D_5N) 7.04 and 6.92 (each 1 H, d, *J* 2 Hz, H-2 and -4), 2.63br (4 H, s, CH_2·CH_2), 2.33 (3 H, s, Me), and other ArH signals, *m/e* 306 (100%), 291 (14), and 289 (9).

Band 2 was purified by t.l.c. in benzene–ethyl acetate (10 : 1), and then benzene. The product (63 mg) separated from aqueous acetone to give 2-*chloro*-5-*hydroxy*-3-[β-(3-*hydroxy*-5-*methylphenyl*)*ethyl*]-1,4-*naphthoquinone* (VI; R^1 = R^2 = H) as red crystals, m.p. 200—201.5° (Found: C, 66.2; H, 4.7; Cl, 10.3%; M^+, 342.0660. $C_{19}H_{15}{}^{35}ClO_4$ requires C, 66.5; H, 4.4; Cl, 10.4%; *M*, 342.0658), $\lambda_{max.}$(MeOH) 281 and 433 nm (log ε 4.01 and 3.40), $\lambda_{max.}$(MeOH–HO^-) 286 and 547 nm (log ε 4.04 and 3.53), $\nu_{max.}$(KBr) 3 370, 1 673, 1 645, and 1 605 cm^{-1}, δ[$(CD_3)_2SO$] 11.67 (1 H, s, 5-OH) and 9.09 (1 H, s, 3′-OH), δ($CDCl_3$) 7.80—7.14 (3 H, m, H-6, -7, and -8), 6.72—6.50 (3 H, m, H-2′, -4′, and -6′), 3.12 and 2.73 (each 2 H, m, CH_2CH_2), and 2.28 (3 H, s, Me), *m/e* 342 (1%), 307 (8), 121 (100), and 77 (9). The same quinone was also obtained by heating the starting compound in methanol containing sulphuric acid.

Band 3 was separated by t.l.c. in benzene–ethyl acetate (10 : 1), and then benzene, into two components. The main product was 3-[β-(3-*acetoxy*-5-*methylphenyl*)*ethyl*]-2-*chloro*-5-*hydroxy*-1,4-*naphthoquinone* (VI; R^1 = H, R^2 = Ac), orange crystals, m.p. 165—167° (from aqueous acetone) (115 mg) (Found: C, 65.5; H, 4.8; Cl, 9.2%; M^+, 384.0763. $C_{21}H_{17}{}^{35}ClO_5$ requires C, 65.5; H, 4.5; Cl, 9.2%; *M*, 384.0763), $\lambda_{max.}$(MeOH) 281, 293sh, and 435 nm (log ε 3.95, 3.60, and 3.27), $\lambda_{max.}$(MeOH–HO^-) 285, 300sh, and 545 nm (log ε 4.06, 3.91, and 3.42), $\nu_{max.}$(KBr) 1 770, 1 680, and 1 647 cm^{-1}, δ($CDCl_3$) 11.9 (1 H, s, HO), 7.76—7.18 (3 H, m, H-6, -7, and -8), 6.98—6.70 (3 H, m, H-2′, -4′, and -6′), 3.10 and 2.66 (4 H, m, CH_2·CH_2), and 2.32 and 2.26 (each 3 H, s, Me and Ac), *m/e* 386 (3%), 384 (10), 307 (35), 306 (11), 121 (100), 91 (7), and 77 (7). After further chromatography the second component (14 mg), 5,6-*dihydro*-1,8-*dihydroxy*-3-*methylbenz*[a]*anthracene*-7,12-*quinone* (VII; R^1 = OH, R^2 = Me) was obtained as dark red plates, m.p. 158.5—159.5 and 202—203° (from aqueous acetone) [Found: C, 73.4; H, 5.4%; M^+, 306.0894. $C_{19}H_{14}O_4$,0.5$(CH_3)_2CO$ requires C, 73.4; H, 5.1%; *M*, 306.0892 (without solvent)], $\lambda_{max.}$(MeOH) 269, 390sh, and 458 nm (log ε 4.25, 3.48, and 3.86), $\lambda_{max.}$(MeOH–HO^-) 246sh, 314sh, and 561 nm (log ε 4.37, 4.04, and 3.70), $\nu_{max.}$(KBr) 1 640 and 1 620 cm^{-1}, δ($CDCl_3$) 12.03 (1 H, s, 8-OH), 9.10br (1 H, s, 1-OH), 7.80—7.20 (3 H, m, H-9, -10, and -11), 6.77 (1 H, d, *J* 3 Hz, H-4), 6.65 (1 H, d, *J* 3 Hz, H-2), 2.75br (4 H, s, CH_2·CH_2), and 2.30 (3 H, s, Me).

Band 4 afforded 1,8-*dihydroxy*-3-*methylbenz*[a]*anthracene*-*quinone* (I), purple-brown crystals, m.p. 201—203° (lit.,[1] 198—200°) (from aqueous acetone) (32 mg) (Found: M^+, 304.0735. $C_{19}H_{12}O_4$ requires *M*, 304.0735), $\lambda_{max.}$(MeOH) 227, 249sh, 318, and 435 nm (log ε 4.58, 4.24, 4.26, and 3.72), $\lambda_{max.}$(MeOH–HO^-) 310 and 527 nm (log ε 4.28 and 3.73), $\nu_{max.}$(KBr) 1 640 and 1 615 cm^{-1}, δ($CDCl_3$) 12.14 (1 H, s, 8-OH), 11.20 (1 H, s, 1-OH), 8.26—7.01 (7 H, m, ArH), and 2.44 (3 H, s, Me), identical (direct comparison including t.l.c. and mass spectrometry) with an authentic sample of tetrangulol (some of the above data differ from those published [1]).

Dehydrogenation of 5,6-*Dihydro*-3,8-*dihydroxy*-1-*methylbenz*[a]*anthracene*-7,12-*quinone* (VII; R^1 = H, R^2 = OH).—The quinone (54 mg) was boiled under reflux in nitrobenzene (8 ml) and pyridine (2 ml) for 5 h. The solvents were removed by distillation, and after cooling the residual solid was collected and crystallised from aqueous acetone to give 3,8-*dihydroxy*-1-*methylbenz*[a]*anthracene*-7,12-*quinone* (VIII), dark red crystals, m.p. 255—256° (decomp.) (27 mg) (Found: C, 74.7; H, 4.0%; M^+, 304.0735. $C_{19}H_{12}O_4$ requires C, 74.9; H, 3.9%; *M*, 304.0735), $\lambda_{max.}$(MeOH) 226, 262sh, 312, and 413 nm (log ε 4.40, 4.17, 4.34, and 3.75), $\lambda_{max.}$(MeOH–HO^-) 237, 332, and 504 nm (log ε 4.36, 4.26, and 3.69), $\nu_{max.}$(KBr) 3 400, 1 650, 1 623, and 1 606 cm^{-1}, δ[$(CD_3)_2SO$] 12.01br (1 H, s, 8-OH), 10.37br (1 H, s, 3-OH), 8.10—7.23 (7 H, m, ArH), and 2.37 (3 H, s, Me), *m/e* 304 (50%), 288 (10), and 287 (100). This compound was the main product (355 mg) when (VI; R^1 = R^2 = Ac) (814 mg) was treated with sodium carbonate for 5 h; traces of starting material and tetrangulol were also isolated.

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