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ISOFURANONAPHTHOQUINONES FROM *VENTILAGO MADERASPATANA*

CRYSTAL STRUCTURE OF VENTILONE-C

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Abstract—From the root bark of *Ventilago maderaspatana* (Rhamnaceae) five isofuranonaphthoquinones have been isolated. Ventilone-A is 4,9-dihydro-5,8-dihydroxy-6,7-methylenedioxy-1-methylnaphtho[2,3-c]furan-4,9-dione and B is the 5-methyl ether. Ventilone-C has the structure 1,3,4,9-tetrahydro-8-hydroxy-5-methoxy-6,7-methylenedioxy-1-methylnaphtho[2,3-c]furan-4,9-dione, D is the isomeric 8-methyl ether, and E is the 5,8-dimethyl ether. Structures were determined by spectroscopic methods, and X-ray crystallographic analysis of ventilone-C.

In Perkin and Hummel's original investigation[1] on *Ventilago maderaspatana* they encountered a complex mixture of pigments, apparently anthraquinones and anthrones. In fact, as we have already reported,[2] this plant contains numerous anthraquinones and, as we will show, there are even more naphthoquinones. Herein we describe a new group of five isofuranonaphthoquinones, ventilones A–E, isolated from the acetone extract of the root bark.

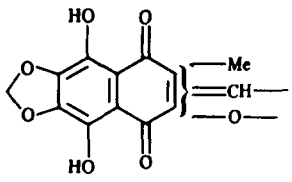
Ventilone-A, $C_{14}H_8O_7$, forms a dimethyl ether and a diacetate, and its ^{1}H-NMR spectrum comprises singlets from a methyl and a methylenedioxy group, an aromatic proton (δ 8.03) and two *peri*-hydroxyls. The latter, and the IR-carbonyl band at 1612 cm^{-1} suggest a naphthazarin structure although the VIS maximum at 433 nm (MeOH), shifting to 488 nm (MeOH—HO$^-$), is inconsistent. However, the dihydro compound, obtained by reduction with zinc and acetic acid, has a VIS spectrum with λ_{max} 527 nm shifting to 590 nm in alkaline solution which is more naphthazarin-like. The ^{1}H-NMR spectrum of the dihydro derivative reveals the presence of a secondary methyl group, and also a methylene group which replaces the aromatic proton in the parent compound.

The PMR evidence indicates partial structure **1** for ventilone-A in which the remaining oxygen must be in an ether function. Two structures, **2** and **4**, are possible, and the latter is most likely as the aromatic signal from **2** would not be as far downfield as δ 8.03 (*cf* **3**[3] and **6**[4]); structure **4** is also preferred on biogenetic grounds, and was confirmed by correlation with ventilone-C (below). It follows that dihydroventilone-A has the tautomeric structure **7**.

Ventilone-B, $C_{15}H_{10}O_7$, has a ^{1}H-NMR spectrum very similar to that of A but one *peri*-hydroxy signal is replaced by a methoxy. Hence B is a monomethyl ether of A, and on methylation it forms a dimethoxy compound identical with ventilone-A dimethyl ether. As reduction of B with zinc and acetic acid gives racemic ventilone-C of established structure **13** (see below) ventilone-B must be the monomethyl ether **8**. Unlike juglones, ventilone-B shows no peak in the visible region and the long-wave maximum at 392 nm is close to that of 1-hydroxyanthraquinone (402 nm).

After we had identified ventilone-B Barbier *et al.*[5] reported nectriafurone **9**, the first natural isofuranonaphthoquinone, which they isolated from cultures of the fungus *Nectria haematococca*. In principle ventilone-A and nectriafurone have tautomeric structures but we have little evidence. Ventilone-A **4** forms only one diacetate and one dimethyl ether in which H-3 resonates at δ 7.88 and 7.87, respectively. As these values are close to that of H-3 in ventilone-B (δ 7.92) presumably the diacetate and dimethyl ether of A are derivatives of **4** which has a benzenoid ring, rather than **5**. In ventilone-A **4** and nectriafurone **9** H-3 resonates further downfield at 8.03 and 8.10, respectively, suggesting the existence of a naphthazarin-type equilibrium in solution.

The ^{1}H-NMR spectrum of ventilone-C, $C_{15}H_{12}O_7$, comprises singlets for methoxy, methylenedioxy and *peri*-hydroxy groups, and coupled signals for $CH_3CH<$ and $—CH_2—$ in which the methine (δ 5.40) and the methylene (δ 5.04) protons form an ABX system. The spectrum is very similar to that of dihydroventilone-A **7** but one *peri*-hydroxyl signal is replaced by methoxy. The data, including the ^{13}C-NMR spectrum, are consistent with structures **10** and **11**. Alternative dihydrofuran structures can be excluded by comparison with the ^{1}H-NMR spectrum of haemoventosin **12**.[6] Structure **10** is preferred to **11** on the basis of the long-range coupling constants observed in the dihydroisofuran ring. In the ABX system J_{AB} = 16, J_{AX} = 5, and J_{BX} = 4 Hz the smallest coupling being *cis*.[7] The long-range couplings are larger than those observed in phthalans[8] implying that the dihydrofuran ring is fused to a quinone and not to a benzene ring.



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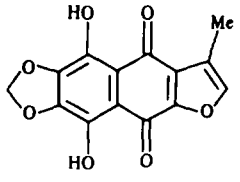

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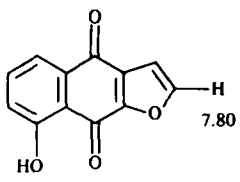

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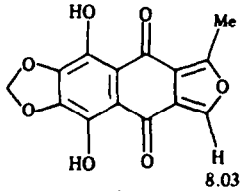

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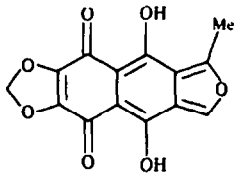

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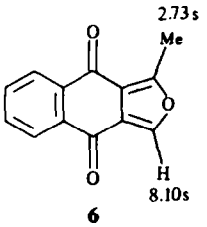

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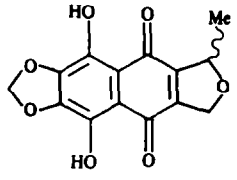

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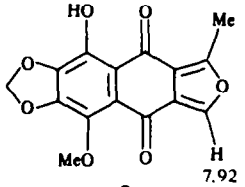

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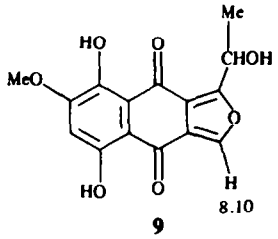

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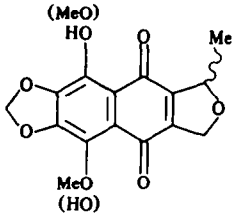
Further, ventilone-C forms a methyl ether which was reduced to a quinol 15 (R = H); in the ^{1}H-NMR spectra of **15** (R = H) and **15** (R = Ac) the methylene proton signals comprise an AB quartet (J = 12.5 Hz) and long-range coupling to the methine proton was too small to be observed showing that the dihydrofuran ring is now fused to a benzene ring. Thus ventilone-C is one of the structures **10** and the stereochemistry and the position of the methoxy group were finally ascertained by X-ray analysis which established structure **13** for ventilone-C.

Ventilone-D is isomeric with C and has structure **14**



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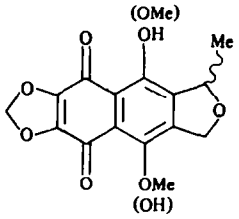

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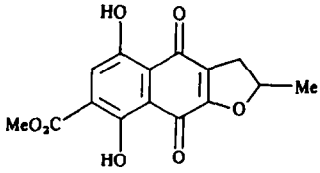

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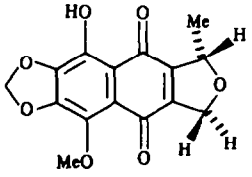

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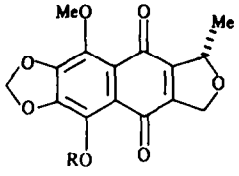

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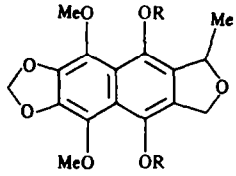

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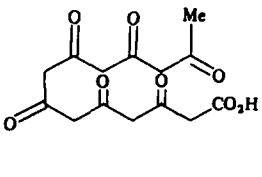

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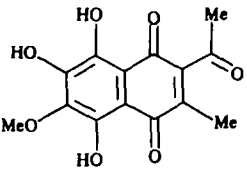

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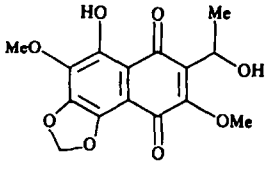

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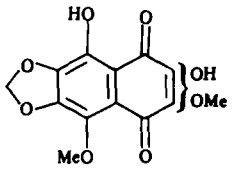

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(R = H). Both C and D give the same dimethoxy compound on methylation which proved to be identical with ventilone-E; E has therefore structure **15** (R = Me).

Biogenetically these quinones are probably derived from a heptaketide **16** from which the terminal carboxyl group is lost, and it is significant that cordeauxione **17**[9] has also been isolated from *V. maderaspatana*.[10] Formation of a dihydrofuran ring from the side chains of **17**, or an equivalent, is clearly possible in several ways.

It is of interest that all the ventilones possess a methylenedioxy group ($\nu \sim 930$ cm^{-1}, ^{1}H-$\delta \sim 6.2$, ^{13}C-$\delta \sim 104$) which is a rare substituent in natural quinones. Only two methylenedioxynaphthoquinones have been reported previously, lomastilone **18**[11] and nepenthone-A **19**.[12]

EXPERIMENTAL

Plant material was obtained from Srisailam Forest, Andhra Pradesh, India.

Extraction and purification. The air-dried root bark (2.5 kg) was powdered and extracted with acetone. The dark brown extract was fractionated on a column of silica gel, eluting with solvents of increasing polarity, i.e. petroleum ether, C_6H_6 and EtOAc. Individual fractions were examined by TLC and those showing the same spot pattern were combined and subjected to column chromatography again. Ventilone-A was purified on a silica gel column using C_6H_6 as eluting solvent. It crystallised from a large volume of C_6H_6 as orange-red micro crystals, m.p. 275° (dec) (65 mg). Column chromatography of the fractions containing ventilone-B, -C, -D and -E with C_6H_6: EtOAc (9:1) gave ventilone-B which crystallised from C_6H_6 as bright yellow needles, m.p. 236° (dec) (18 mg), and ventilone-C and -D as a mixture. These two compounds were separated by PLC in C_6H_6: EtOAc (4:1) and crystallised from C_6H_6-pet. ether (b.p. 60–80°); ventilone-C red needles, m.p. 196° (32 mg), ventilone-D, dark red needles, m.p. 177–178° (20 mg). Further elution of the column with C_6H_6–EtOAc (4:1) gave ventilone-E which on crystallisation from MeOH separated as yellow micro crystals, m.p. 180–181° (48 mg).

Ventilone-A **4**. Found: C, 58.26; H, 2.74%; M$^+$, 288.0270. $C_{14}H_8O_7$ requires C, 58.34; H, 2.80%; M$^+$, 288.0270; UV λ_{max}^{MeOH} 283, 413, 433 nm (log ε 4.09, 3.78, 3.82); $\lambda_{max}^{MeOH/HO^-}$ 488 nm; ν_{max}^{KBr} 930, 1612 cm^{-1}; ^{1}H-NMR (220 MHz, $CDCl_3$) δ 2.78 (3H, s, Me), 6.27 (2H, s, —OCH_2O—), 8.03 (1H, s, H-3), 12.98, 13.16 (each 1H, s, exchangeable with D_2O, 2 *peri*-OH); MS *m/z* 288 (100%), 242 (21), 232 (7), 231 (8), 214 (13). The *dimethyl ether* ($Me_2SO_4/K_2CO_3/Me_2CO$) was obtained as pale yellow crystalline globulets, m.p. 189° (C_6H_6-pet. ether); Found: C, 60.72; H, 3.90. $C_{16}H_{12}O_7$ requires: C, 60.76; H, 3.82%; IR ν_{max}^{Nujol} 924, 1658 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 2.66 (3H, s, Me), 3.98 (3H, s, OMe), 4.00 (3H, s, OMe), 6.15 (2H, s, —OCH_2O—), 7.87 (1H, s, H-3); MS *m/z* 316 (45%), 315 (100), 301 (17), 299 (10), 282 (15), 273 (29), 271 (13), 270 (13), 269 (36), 260 (17), 259 (13), 258 (35). The *diacetate* (Ac_2O/pyridine) formed light yellow needles, m.p. 230° (C_6H_6-pet. ether); Found: C, 58.24; H, 3.34. $C_{18}H_{12}O_9$ requires: C, 58.09; H, 3.25%; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 2.41, 2.43 (each 3H, s, OAc), 2.65 (3H, s, Me), 6.20 (2H, s, —OCH_2O—), 7.88 (1H, s, H-3). Ventilone-A (25 mg), Zn powder (500 mg) in AcOH (8 ml) was heated on a steam bath for 60 min and worked up in the usual way. The product **7** was obtained as dark red needles, m.p. 174° (C_6H_6-pet. ether); Found: C, 57.86; H, 3.52. $C_{14}H_{10}O_7$ requires: C, 57.94; H, 3.47%; UV λ_{max}^{MeOH} 235, 308, 465, 495, 527 nm; $\lambda_{max}^{MeOH/HO^-}$ 235, 312, 560, 590 nm; IR $\nu_{max}^{CHCl_3}$ 925, 1615 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 1.58 (3H, d, J = 7 Hz, Me), 5.10 (2H, m, CH_2-3), 5.50 (1H, m, H-1), 6.20 (2H, s, —OCH_2O—), 11.82, 12.50 (each 1H, exchanged with D_2O, *peri*-OH).

Ventilone-B **8**. Found: C, 59.70; H, 3.36%; M$^+$, 302.0427. $C_{15}H_{10}O_7$ requires C, 59.61; H, 3.33%; M$^-$, 302.0426; UV λ_{max}^{EtOH} 290, 392 nm (log ε 4.18, 3.82); $\lambda_{max}^{EtOH/HO^-}$ 467 nm; IR ν_{max}^{KBr} 928, 1610, 1650 cm^{-1}; ^{1}H-NMR (220 MHz, $CDCl_3$) δ 2.70 (3H, s, Me), 3.97 (3H, s, OMe), 6.20 (2H, s, —OCH_2O—), 7.92 (1H, s, H-3), 13.35 (1H, s, exchangeable with D_2O, *peri*-OH); MS *m/z* 302 (100%), 285 (6), 284 (14), 273 (19), 256 (40), 255 (6), 231 (13), 229 (26), 228 (16), 215 (9). The methyl ether of ventilone-B ($Me_2SO_4/K_2CO_3/Me_2CO$) was identical (TLC, m.m.p. and IR) with the dimethyl ether of ventilone-A. Ventilone-B was reduced with zinc and acetic acid, and the product showed the same R_f value (co-TLC) as ventilone-C.

Ventilone-C **13**. Found: C, 59.28; H, 4.00%; M$^+$, 304.0580. $C_{15}H_{12}O_7$ requires C, 59.21; H, 3.98%; M$^+$, 304.0582; $[\alpha]_D^{22}$ +144° ($CHCl_3$ c 0.16); UV λ_{max}^{EtOH} 230, 270, 323, 454 nm (log ε 4.28, 4.21, 3.14, 3.46); $\lambda_{max}^{EtOH/HO^-}$ 550 nm; IR ν_{max}^{KBr} 930, 1625, 1655 cm^{-1}; ^{1}H-NMR (220 MHz, $CDCl_3$), δ 1.54 (3H, d, J = 7 Hz, Me), 4.0 (3H, s, OMe), 5.04 (2H, ddd, J = 16, 5, 4 Hz, 2 × H-3), 5.40 (1H, m, H-1), 6.22 (2H, s, —OCH_2O—), 12.52 (1H, s, exchangeable with D_2O, *peri*-OH); ^{13}C-NMR (90.56 MHz, $CDCl_3$), 20.43 (q, C-1a), 60.76 (q, OMe), 71.97 (t, C-3), 81.14 (d, C-1), 103.75 (t, —O<u>C</u>H_2O—), 113.39[b] (s, C-8a), 119.09[b] (s, C-

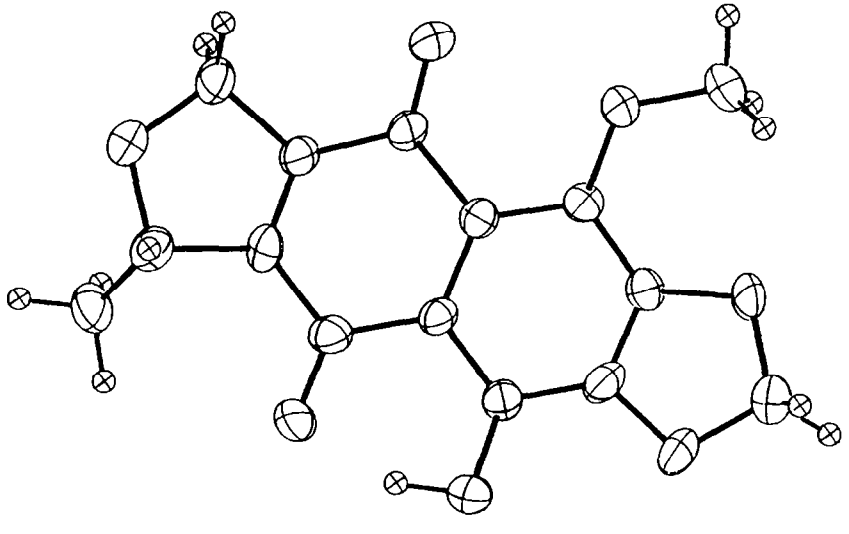

Fig. 1.

Table 1. Fractional atomic co-ordinates (× 10^4) with esds

C(1)	2787(15)	−0611(4)	10612(8)
O(2)	2772(19)	−1349(3)	10602(6)
C(3)	2858(17)	−1629(4)	9212(9)
C(3A)	2671(15)	−0982(3)	8336(7)
C(4)	2605(18)	−0950(3)	6832(7)
C(4A)	2465(18)	−0267(3)	6208(6)
C(5)	2443(20)	−0236(3)	4737(7)
C(6)	2465(20)	0409(3)	4155(7)
C(7)	2534(22)	1008(3)	4905(8)
C(8)	2488(18)	1005(3)	6370(7)
C(8A)	2471(16)	0354(3)	7013(7)
C(9)	2476(16)	0292(3)	8552(7)
C(9A)	2568(16)	−0422(3)	9113(7)
O(10)	2444(19)	1564(2)	4024(5)
C(11)	2413(27)	1281(4)	2659(9)
O(12)	2404(18)	0551(3)	2781(6)
C(13)	2739(21)	2245(4)	6554(8)
C(14)	1252(17)	−2162(5)	9027(10)
O(15)	2509(16)	1581(2)	7165(6)
O(16)	2538(14)	−0795(2)	3912(5)
O(17)	2396(12)	0775(2)	9364(5)
O(18)	2551(15)	−1487(2)	6120(5)
H(1A)	1517(76)	−0502(43)	11109(85)
H(1B)	3814(96)	−0365(38)	11182(80)
H(3)	4350(37)	−1681(41)	9209(89)
H(11A)	3820(62)	1383(43)	2349(90)
H(11B)	1760(117)	1484(38)	1820(55)
H(13A)	3104(113)	2534(39)	7347(55)
H(13B)	1375(66)	2361(50)	6201(80)
H(13C)	3713(96)	2279(52)	5781(58)
H(14A)	1167(136)	−2381(40)	8078(40)
H(14B)	−0110(69)	−1984(40)	9269(85)
H(14C)	1591(129)	−2545(33)	9702(64)
HO(16)	2297(228)	−1163(38)	4611(82)

Table 2. Bond lengths (Å) with esds

C(1)—O(2)	1.429(9)	C(5)—O(16)	1.346(8)
C(1)—C(9A)	1.501(10)	C(6)—C(7)	1.368(10)
O(2)—C(3)	1.449(10)	C(6)—O(12)	1.356(9)
C(3)—C(3A)	1.517(10)	C(7)—C(8)	1.415(10)
C(3)—C(14)	1.503(14)	C(7)—O(10)	1.374(8)
C(3A)—C(4)	1.455(10)	C(8)—C(8A)	1.405(9)
C(3A)—C(9A)	1.321(9)	C(8)—O(15)	1.354(8)
C(4)—C(4A)	1.456(9)	C(8A)—C(9)	1.491(9)
C(4)—O(18)	1.247(8)	C(9)—C(9A)	1.486(9)
C(4A)—C(5)	1.422(9)	C(9)—O(17)	1.222(8)
C(4A)—C(8A)	1.432(8)	O(10)—C(11)	1.428(10)
C(5)—C(6)	1.370(9)	C(11)—O(12)	1.419(10)
C(13)—O(15)	1.423(9)		

4a), 140.87[c] (s, C-6), 141.02[c] (s, C-7), 144.53[a] (s, C-3a), 146.06[a] (s, C-9a), 146.42 (s, C-5), 148.86 (s, C-8), 179.51 (s, C-4), 186.37 (s, C-9) (values with the same superscript may be interchanged); MS *m/z* 304 (89%), 289 (100), 275 (7), 271 (6), 261 (20); CD λ_{max}^{MeOH} 280, 320, 368, 408 nm ($\Delta\varepsilon$ −0.17, +0.09, −0.28, −0.15). The methyl ether of ventilone-C ($Me_2SO_4/K_2CO_3/Me_2CO$) was identical (TLC, m.m.p.) with ventilone-E.

Ventilone-D **14** (R = H). Found: C, 59.28; H, 4.02%; M^+, 304.0585. $C_{15}H_{12}O_7$ requires C, 59.21; H, 3.98%; M^+, 304.0583; $[\alpha]_D$ +240° ($CHCl_3$, c 0.10); UV λ_{max}^{MeOH} 226, 270, 320, 440 nm (log ε 4.37, 4.19, 3.53, 3.64); IR ν_{max}^{KBr} 930, 1630, 1660 cm^{-1}; ^{1}H-NMR (220 MHz, $CDCl_3$) δ 1.56 (3H, d, J = 7 Hz, Me), 4.03 (3H, s, OMe), 5.04 (2H, ddd, J = 15.5, 5.5, 4 Hz, 2 × H-3), 5.39 (1H, m, H-1), 6.20 (2H, s, —OCH_2O—), 12.45 (1H, s, exchangeable with D_2O, *peri*-OH); MS *m/z* 304 (100%), 289.0341 ($C_{14}H_9O_7$ requires 289.0345, 61), 275 (11), 274 (9), 262 (51), 261.0383 ($C_{13}H_9O_6$ requires 261.0389, 47), 247 (18), 246 (9), 233 (15), 219 (19). The *acetate* (Ac_2O/pyridine) formed bright yellow needles, m.p. 198–199° (pet. ether) Found: C, 59.88; H, 4.06. $C_{17}H_{14}O_8$ requires: C, 58.96; H, 4.07%; ^{1}H-NMR (100 MHz, $CDCl_3$) δ 1.56 (3H, d, J = 7 Hz, Me), 2.44 (3H, s, OAc), 4.06 (3H, s, OMe), 5.00 (2H, m, CH_2-3), 5.36 (1H, m, H-1), 6.20 (2H, s, —OCH_2O—). The methyl ether of ventilone-D ($Me_2SO_4/K_2CO_3/Me_2CO$) was found to be identical (TLC, IR, m.m.p.) with ventilone-E.

Ventilone-E **14** (R = Me). Found: C, 60.52; H, 4.46%; M^+, 318.0748. $C_{16}H_{14}O_7$ requires: C, 60.38; H, 4.43%; M^+, 318.0739. $[\alpha]_D^{22}$ +174° ($CHCl_3$, c 0.13); UV λ_{max}^{EtOH} 272, 308, 400 nm (log ε 4.23, 3.55, 3.49); IR ν_{max}^{KBr} 925, 1660 cm^{-1}; ^{1}H-NMR (220 MHz, $CDCl_3$) δ 1.56 (3H, d, J = 7 Hz, Me), 4.02 and 4.03 (6H, s, 2 × OMe), 5.00 (2H, ddd, J = 15, 5, 4 Hz, 2 × H-3), 5.36 (1H, m, H-1), 6.16 (2H, s, —OCH_2O—); MS *m/z* 318 (60%), 303.0505 ($C_{15}H_{11}O_7$ requires 303.0504, 100), 290 (6), 289 (8), 288 (9), 285 (10), 275 (17), 273 (20), 261 (6), 260 (8). Ventilone-E (32 mg) in ether (40 ml) was reduced by shaking with a saturated solution of sodium dithionite (4 × 25 ml). The ether layer was evaporated and the residue was immediately sublimed at 177°/0.001 mm Hg to give the quinol (16 mg). Found: M^+, 320.0895. $C_{16}H_{16}O_7$ requires: 320.0896. ^{1}H-NMR (220 MHz, $CDCl_3$), δ 1.60 (3H, d, J = 7 Hz, Me), 4.13 (6H, s, 2 × OMe), 5.09, 5.23 (2H, ABq, J = 12.5 Hz, CH_2-3), 5.50 (1H, q, J = 7 Hz, H-1), 6.03 (2H, s, —OCH_2O—), 8.85, 8.90 (each 1H, s, exchanged with D_2O, —OH). With Ac_2O, Zn dust, and NaOAc, ventilone-E formed a leuco-diacetate as needles (from MeOH) (Found: C, 59.70; H, 4.94%. $C_{20}H_{20}O_9$

Table 3. Bond angles (°) with esds

C(9A)—C(1)—O(2)	103.7(6)	C(3)—O(2)—C(1)	112.3(6)
C(3A)—C(9A)—C(1)	110.0(6)	C(9)—C(9A)—C(1)	125.6(6)
C(3A)—C(3)—O(2)	101.8(6)	C(14)—C(3)—O(2)	109.8(8)
C(14)—C(3)—C(3A)	116.2(8)	C(4)—C(3A)—C(3)	126.5(6)
C(9A)—C(3A)—C(3)	111.4(6)	C(9A)—C(3A)—C(4)	122.1(6)
C(4A)—C(4)—C(3A)	117.0(6)	O(18)—C(4)—C(3A)	121.1(6)
C(9)—C(9A)—C(3A)	124.0(6)	O(18)—C(4)—C(4A)	121.8(6)
C(5)—C(4A)—C(4)	116.9(5)	C(8A)—C(4A)—C(4)	122.5(6)
C(8A)—C(4A)—C(5)	120.5(5)	C(6)—C(5)—C(4A)	116.6(6)
O(16)—C(5)—C(4A)	123.9(5)	C(8)—C(8A)—C(4A)	120.9(6)
C(9)—C(8A)—C(4A)	118.3(5)	O(16)—C(5)—C(6)	119.3(6)
C(7)—C(6)—C(5)	123.8(6)	O(12)—C(6)—C(5)	125.9(6)
O(12)—C(6)—C(7)	110.3(6)	C(8)—C(7)—C(6)	121.7(6)
O(10)—C(7)—C(6)	109.6(6)	C(11)—O(12)—C(6)	106.5(6)
O(10)—C(7)—C(8)	128.4(6)	C(8A)—C(8)—C(7)	116.5(6)
O(15)—C(8)—C(7)	124.3(6)	C(11)—O(10)—C(7)	105.8(5)
O(15)—C(8)—C(8A)	119.2(6)	C(9)—C(8A)—C(8)	120.8(5)
C(13)—O(15)—C(8)	120.7(6)	C(9A)—C(9)—C(8A)	116.0(5)
O(17)—C(9)—C(8A)	125.3(6)	O(17)—C(9)—C(9A)	118.7(6)
O(12)—C(11)—O(10)	107.8(6)		

Table 4. Torsion angles (°) with esds

C(9A)—C(1)—O(2)—C(3)	8.5(9)	O(2)—C(1)—C(9A)—C(3A)	−7.1(9)
O(2)—C(1)—C(9A)—C(9)	179.3(8)	C(1)—O(2)—C(3)—C(3A)	−6.7(9)
C(1)—O(2)—C(3)—C(14)	−130.4(8)	O(2)—C(3)—C(3A)—C(4)	−178.0(8)
O(2)—C(3)—C(3A)—C(9A)	2.0(10)	C(14)—C(3)—C(3A)—C(4)	−58.8(12)
C(14)—C(3)—C(3A)—C(9A)	121.2(9)	C(3)—C(3A)—C(4)—C(4A)	−178.6(8)
C(3)—C(3A)—C(4)—O(18)	5.5(14)	C(9A)—C(3A)—C(4)—C(4A)	1.4(12)
C(9A)—C(3A)—C(4)—O(18)	−174.5(8)	C(3)—C(3A)—C(9A)—C(1)	3.2(10)
C(3)—C(3A)—C(9A)—C(9)	176.9(8)	C(4)—C(3A)—C(9A)—C(1)	−176.8(7)
C(4)—C(3A)—C(9A)—C(9)	−3.1(13)	C(3A)—C(4)—C(4A)—C(5)	178.7(8)
C(3A)—C(4)—C(4A)—C(8A)	2.5(12)	O(18)—C(4)—C(4A)—C(5)	−5.5(13)
O(18)—C(4)—C(4A)—C(8A)	178.3(8)	C(4)—C(4A)—C(5)—C(6)	−175.2(8)
C(4)—C(4A)—C(5)—O(16)	0.2(13)	C(8A)—C(4A)—C(5)—C(6)	1.2(13)
C(8A)—C(4A)—C(5)—O(16)	176.5(8)	C(4)—C(4A)—C(8A)—C(8)	175.1(8)
C(4)—C(4A)—C(8A)—C(9)	−4.4(12)	C(5)—C(4A)—C(8A)—C(8)	−1.0(12)
C(5)—C(4A)—C(8A)—C(9)	179.5(8)	C(4A)—C(5)—C(6)—C(7)	0.9(14)
C(4A)—C(5)—C(6)—O(12)	−178.4(9)	O(16)—C(5)—C(6)—C(7)	−174.6(9)
O(16)—C(5)—C(6)—O(12)	6.1(15)	C(5)—C(6)—C(7)—C(8)	−3.2(16)
C(5)—C(6)—C(7)—O(10)	−177.2(9)	O(12)—C(6)—C(7)—C(8)	176.2(9)
O(12)—C(6)—C(7)—O(10)	2.2(12)	C(5)—C(6)—O(12)—C(11)	178.7(10)
C(7)—C(6)—O(12)—C(11)	−0.7(11)	C(6)—C(7)—C(8)—C(8A)	3.2(14)
C(6)—C(7)—C(8)—O(15)	−178.5(9)	O(10)—C(7)—C(8)—C(8A)	175.9(9)
O(10)—C(7)—C(8)—O(15)	−5.8(16)	C(6)—C(7)—O(10)—C(11)	−2.8(11)
C(8)—C(7)—O(10)—C(11)	−176.2(10)	C(7)—C(8)—C(8A)—C(4A)	−1.1(12)
C(7)—C(8)—C(8A)—C(9)	178.4(8)	O(15)—C(8)—C(8A)—C(4A)	−179.5(8)
O(15)—C(8)—C(8A)—C(9)	0.0(12)	C(7)—C(8)—O(15)—C(13)	−5.0(13)
C(8A)—C(8)—O(15)—C(13)	173.3(8)	C(4A)—C(8A)—C(9)—C(9A)	2.7(11)
C(4A)—C(8A)—C(9)—O(17)	−176.7(8)	C(8)—C(8A)—C(9)—C(9A)	−176.8(7)
C(8)—C(8A)—C(9)—O(17)	3.8(13)	C(8A)—C(9)—C(9A)—C(1)	173.8(7)
C(8A)—C(9)—C(9A)—C(3A)	1.0(12)	O(17)—C(9)—C(9A)—C(1)	−6.8(12)
O(17)—C(9)—C(9A)—C(3A)	−179.6(8)	C(7)—O(10)—C(11)—O(12)	2.4(11)
O(10)—C(11)—O(12)—C(6)	−1.1(11)		

requires: C, 59.41; H, 4.99%); IR ν_{max}^{KBr} 925, 1745 cm^{-1}; ^{1}H-NMR (220 MHz, $CDCl_3$) 1.55 (3H, d, J = 7 Hz, Me), 2.37, 2.36 (6H, s, 2 × OAc), 3.94 (6H, s, 2 × OMe), 5.04, 5.17 (2H, ABq, J = 12.5 Hz, CH_2-3), 5.46 (1H, q, J = 7 Hz, H-1), 6.06 (2H, s, —OCH_2O—).

Crystal data. $C_{15}H_{12}O_7$, M = 304.258. Orthorhombic, a = 6.715 (5), b = 19.365 (11), c = 9.658 (8) Å, U = 1255 (2) $Å^3$, Z = 4, D_c = 1.58 cm^{-3}. Space group $P2_12_12$. Mo-Kα radiation, μ = 0.82 cm^{-1}, 820 independent reflections.

The reflection were measured on a Nicolet P3 automated diffractometer ($2\theta \leq 50°$). The structure was solved by direct methods[13] and refined[14] by full matrix least squares. The carbons and oxygens were given anisotropic temperature factors and the hydrogen isotropic temp factors. The final weighting scheme used was $\omega = 1.00/[\sigma^2(F) + 0.00987F^2]$. Convergence was achieved at R = 5.33%.

The molecular structure is shown in Fig. 1. Atomic coordinates and other data are listed in Tables 1–5.

Table 5. Observed and calculated structure factors

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	3376	3734	3	7	0	136	27	2	0	1	520	541	3	6	1	160	153	6	13	1	45	48
4	0	0	1396	1410	0	8	0	130	123	3	0	1	81	87	4	6	1	56	56	0	14	1	142	138
6	0	0	558	580	1	8	0	77	78	4	0	1	297	298	5	6	1	61	65	1	14	1	151	145
8	0	0	239	249	2	8	0	79	82	5	0	1	90	100	1	7	1	149	165	2	14	1	87	87
3	1	0	90	89	4	8	0	59	61	6	0	1	119	117	2	7	1	126	117	3	14	1	126	115
4	1	0	137	125	1	9	0	73	93	7	0	1	57	49	3	7	1	114	126	4	14	1	58	47
5	1	0	75	68	2	9	0	53	57	0	1	1	525	523	4	7	1	92	93	5	14	1	81	77
6	1	0	100	100	3	9	0	53	63	1	1	1	164	174	5	7	1	42	44	6	14	1	41	47
7	1	0	45	52	0	10	0	667	661	2	1	1	421	406	7	7	1	49	36	0	15	1	460	453
0	2	0	1177	1194	2	10	0	481	474	3	1	1	98	104	0	8	1	242	239	1	15	1	101	101
2	2	0	1076	1098	4	10	0	169	164	4	1	1	279	293	1	8	1	93	100	2	15	1	384	382
3	2	0	81	85	2	11	0	96	104	5	1	1	64	72	2	8	1	147	150	3	15	1	94	101
4	2	0	576	598	4	11	0	63	62	6	1	1	173	185	3	8	1	64	78	4	15	1	242	247
6	2	0	276	278	1	12	0	84	80	0	2	1	236	235	4	8	1	94	101	5	15	1	58	51
2	3	0	382	403	2	12	0	64	61	1	2	1	678	677	6	8	1	56	60	6	15	1	141	144
3	3	0	135	115	3	12	0	49	57	3	2	1	197	181	7	8	1	43	47	0	16	1	254	271
4	3	0	200	221	5	12	0	41	30	5	2	1	48	66	0	9	1	283	264	1	16	1	331	335
5	3	0	111	91	2	14	0	56	51	6	2	1	46	47	1	9	1	140	149	2	16	1	236	252
6	3	0	89	111	4	14	0	145	140	0	3	1	246	237	2	9	1	146	140	3	16	1	269	269
7	3	0	42	45	6	14	0	123	123	1	3	1	271	291	3	9	1	107	101	4	16	1	170	169
0	4	0	828	823	0	16	0	555	564	2	3	1	213	222	0	10	1	64	56	5	16	1	172	172
2	4	0	666	683	1	16	0	243	234	3	3	1	178	172	1	10	1	163	155	0	17	1	240	239
3	4	0	74	77	2	16	0	458	455	4	3	1	83	94	2	10	1	117	122	2	17	1	219	206
4	4	0	274	290	3	16	0	163	157	5	3	1	70	62	4	10	1	61	71	4	17	1	157	144

Table 5—*continued.*

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	5	0	101	128	4	16	0	302	294	0	4	1	97	102	6	10	1	39	30	1	18	1	192	189
2	5	0	190	186	5	16	0	84	95	1	4	1	365	350	0	11	1	163	151	3	18	1	134	127
3	5	0	58	71	1	18	0	68	73	2	4	1	73	70	2	11	1	139	133	4	18	1	39	22
4	5	0	59	66	2	18	0	73	74	3	4	1	98	99	4	11	1	73	71	0	19	1	69	67
0	6	0	219	206	3	18	0	71	74	0	5	1	353	348	0	12	1	155	159	1	19	1	52	70
1	6	0	144	150	4	18	0	91	86	1	5	1	273	291	1	12	1	190	186	3	19	1	67	62
2	6	0	153	153	5	18	0	41	29	2	5	1	153	134	2	12	1	97	94	0	20	1	69	77
3	6	0	191	195	1	20	0	51	56	3	5	1	121	128	3	12	1	78	74	1	20	1	58	72
4	6	0	68	67	2	20	0	43	35	5	5	1	63	61	4	12	1	51	58	2	20	1	66	58
6	6	0	53	51	2	21	0	39	29	0	6	1	149	143	6	12	1	47	38	1	21	1	81	79
1	7	0	155	95	1	22	0	41	22	1	6	1	83	77	0	13	1	73	74	3	21	1	60	57
2	7	0	82	83	0	0	1	413	411	2	6	1	160	169	1	13	1	107	101	0	22	1	46	48
1	22	1	74	68	4	7	2	88	95	4	13	2	41	55	0	2	3	100	103	0	9	3	161	153
0	0	2	250	250	5	7	2	105	101	6	13	2	48	48	1	2	3	93	99	1	9	3	497	466
1	0	2	200	192	6	7	2	43	50	0	14	2	89	93	2	2	3	69	75	2	9	3	69	66
2	0	2	100	89	7	7	2	61	61	1	14	2	137	136	4	2	3	53	36	3	9	3	389	372
3	0	2	149	130	1	8	2	773	728	2	14	2	66	73	5	2	3	44	43	5	9	3	197	190
0	1	2	411	405	2	8	2	63	43	3	14	2	108	104	1	3	3	637	623	7	9	3	91	86
2	1	2	292	276	3	8	2	472	448	5	14	2	44	43	2	3	3	159	152	0	10	3	343	316
3	1	2	145	154	5	8	2	234	225	6	14	2	52	57	3	3	3	229	234	1	10	3	78	75
4	1	2	132	136	7	8	2	106	108	3	15	2	82	81	4	3	3	77	92	2	10	3	276	277
5	1	2	45	55	0	9	2	301	293	5	15	2	69	60	5	3	3	64	59	4	10	3	128	130
0	2	2	152	155	1	9	2	451	434	4	16	2	46	29	0	4	3	307	314	0	11	3	83	83
1	2	2	616	620	2	9	2	277	266	0	17	2	44	38	1	4	3	67	88	1	11	3	76	85
2	2	2	173	182	3	9	2	246	238	1	17	2	157	155	2	4	3	233	220	2	11	3	60	54
3	2	2	211	216	4	9	2	164	162	3	17	2	90	88	4	4	3	95	97	3	11	3	84	83
4	2	2	100	101	5	9	2	116	117	5	17	2	56	55	5	4	3	45	32	5	11	3	44	37
5	2	2	47	53	6	9	2	57	53	0	18	2	82	83	6	4	3	59	58	0	12	3	98	96
0	3	2	257	261	7	9	2	59	63	1	18	2	46	54	0	5	3	165	150	1	12	3	77	89
1	3	2	513	522	0	10	2	89	79	2	18	2	79	73	1	5	3	523	521	2	12	3	64	77
2	3	2	329	332	1	10	2	312	291	3	18	2	59	55	3	5	3	289	282	3	12	3	58	46
3	3	2	98	98	2	10	2	92	83	4	18	2	43	53	5	5	3	89	87	0	13	3	69	66
4	3	2	185	174	3	10	2	175	174	1	19	2	78	76	0	6	3	73	72	1	13	3	177	182
6	3	2	61	62	5	10	2	89	101	4	19	2	55	59	1	6	3	240	238	2	13	3	69	70
1	4	2	101	124	7	10	2	57	61	0	20	2	47	49	2	6	3	69	65	3	13	3	116	122
2	4	2	72	59	0	11	2	190	192	2	20	2	47	50	3	6	3	123	122	4	13	3	57	54
1	5	2	251	233	1	11	2	136	135	3	20	2	38	28	4	6	3	48	47	5	13	3	42	31
2	5	2	121	113	2	11	2	144	149	0	21	2	85	92	5	6	3	61	60	0	14	3	224	219
3	5	2	74	74	3	11	2	64	64	2	21	2	68	55	0	7	3	231	240	1	14	3	56	61
4	5	2	58	63	4	11	2	83	75	3	21	2	36	36	1	7	3	695	649	2	14	3	189	179
1	6	2	292	273	0	12	2	72	70	1	22	2	51	55	2	7	3	74	80	3	14	3	59	54
3	6	2	202	187	1	12	2	290	282	0	0	3	844	838	3	7	3	423	397	4	14	3	100	101
5	6	2	111	121	2	12	2	77	78	1	0	3	119	116	4	7	3	45	30	1	15	3	101	99
7	6	2	72	75	3	12	2	161	157	2	0	3	634	621	5	7	3	201	207	0	16	3	45	36
0	7	2	467	440	5	12	2	51	53	3	0	3	81	84	7	7	3	90	94	1	16	3	108	112
1	7	2	429	407	0	13	2	44	37	4	0	3	278	278	0	8	3	134	130	2	16	3	60	70
2	7	2	271	257	1	13	2	154	151	6	0	3	83	83	2	8	3	145	145	3	16	3	74	84
3	7	2	231	213	3	13	2	125	123	1	1	3	125	114	4	8	3	82	77	4	16	3	44	49
5	16	3	66	79	4	4	4	47	40	1	12	4	137	137	5	0	5	57	56	5	6	5	55	68
1	17	3	347	357	5	4	4	70	60	2	12	4	90	85	6	0	5	68	64	6	6	5	36	38
2	17	3	44	34	6	4	4	37	39	3	12	4	87	78	0	1	5	618	579	0	7	5	87	88
3	17	3	212	212	0	5	4	211	199	4	12	4	43	46	2	1	5	471	461	1	7	5	95	89
1	19	3	119	118	1	5	4	195	198	0	13	4	149	150	3	1	5	51	53	3	7	5	57	59
3	19	3	117	117	2	5	4	108	103	1	13	4	71	74	4	1	5	256	253	4	7	5	45	34
1	20	3	59	52	3	5	4	67	64	2	13	4	134	133	5	1	5	51	36	6	7	5	36	26
1	21	3	91	88	4	5	4	51	50	3	13	4	66	65	6	1	5	140	135	0	8	5	107	111
0	0	4	667	672	1	6	4	73	70	0	14	4	58	56	0	2	5	154	147	1	8	5	60	62
1	0	4	75	81	3	6	4	102	115	1	14	4	53	52	1	2	5	199	203	2	8	5	49	50
2	0	4	422	426	5	6	4	65	70	2	14	4	42	32	2	2	5	166	162	3	8	5	66	63
3	0	4	69	66	0	7	4	163	167	3	14	4	44	41	3	2	5	188	191	0	9	5	214	224
4	0	4	196	200	2	7	4	98	95	0	15	4	302	326	4	2	5	107	117	1	9	5	54	61
6	0	4	122	116	4	7	4	45	47	1	15	4	84	86	5	2	5	93	90	2	9	5	180	192
7	0	4	42	14	6	7	4	44	37	2	15	4	269	277	6	2	5	71	65	3	9	5	58	64
0	1	4	466	460	0	8	4	67	73	3	15	4	72	74	7	2	5	39	30	4	9	5	116	123
1	1	4	380	386	1	8	4	54	54	4	15	4	160	159	1	3	5	181	176	6	9	5	61	66
2	1	4	349	337	2	8	4	57	54	0	16	4	253	271	2	3	5	84	76	1	10	5	99	101
3	1	4	253	265	3	8	4	48	57	2	16	4	198	204	3	3	5	103	104	4	10	5	39	34
4	1	4	214	207	5	8	4	46	32	4	16	4	106	107	4	3	5	68	67	0	11	5	227	229
5	1	4	102	95	0	9	4	144	136	5	16	4	58	41	5	3	5	55	51	1	11	5	116	115
6	1	4	122	118	1	9	4	125	122	0	17	4	160	167	0	4	5	126	111	2	11	5	160	171

Table 5—*continued.*

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10F
7	1	4	39	34	2	9	4	137	124	2	17	4	131	127	1	4	5	228	218	3	11	5	64	70
1	2	4	575	561	4	9	4	89	83	4	17	4	67	86	2	4	5	75	71	4	11	5	60	66
2	2	4	105	88	1	10	4	130	125	0	18	4	54	65	3	4	5	75	82	5	11	5	51	44
3	2	4	283	281	2	10	4	88	82	2	18	4	72	73	4	4	5	45	54	0	12	5	149	162
4	2	4	103	99	3	10	4	102	111	3	18	4	45	34	6	4	5	41	43	1	12	5	46	41
5	2	4	119	135	4	10	4	54	51	4	18	4	66	71	0	5	5	114	102	2	12	5	100	95
6	2	4	58	65	5	10	4	45	54	0	19	4	57	56	1	5	5	166	160	3	12	5	42	50
7	2	4	51	59	0	11	4	164	160	2	19	4	56	40	2	5	5	50	53	5	12	5	43	34
0	3	4	103	115	1	11	4	178	175	0	21	4	79	73	3	5	5	80	71	0	13	5	162	170
1	3	4	279	260	2	11	4	126	126	0	0	5	379	382	0	6	5	77	77	2	13	5	155	152
2	3	4	55	64	3	11	4	92	89	1	0	5	58	57	1	6	5	75	72	4	13	5	111	102
3	3	4	92	97	4	11	4	51	53	2	0	5	223	218	2	6	5	74	76	0	14	5	87	87
1	4	4	201	197	5	11	4	47	45	3	0	5	82	77	3	6	5	44	53	1	14	5	66	59
3	4	4	137	135	0	12	4	83	81	4	0	5	102	97	4	6	5	54	60	2	14	5	111	111
3	14	5	71	74	0	6	6	200	204	0	13	6	61	62	4	4	7	73	70	0	11	7	108	108
4	14	5	98	99	1	6	6	72	78	1	13	6	182	178	5	4	7	46	41	2	11	7	98	97
5	14	5	66	60	2	6	6	152	158	2	13	6	49	37	6	4	7	54	49	3	11	7	51	42
0	15	5	80	88	4	6	6	88	95	3	13	6	103	106	0	5	7	218	218	4	11	7	58	61
1	15	5	121	138	5	6	6	40	41	5	13	6	44	48	2	5	7	175	165	5	11	7	56	46
2	15	5	97	105	0	7	6	60	59	0	14	6	196	190	4	5	7	102	96	1	12	7	141	144
3	15	5	105	101	1	7	6	405	429	2	14	6	147	138	5	5	7	54	55	2	12	7	63	64
4	15	5	94	98	2	7	6	45	49	4	14	6	75	82	6	5	7	60	67	3	12	7	85	84
1	16	5	104	99	3	7	6	316	317	1	15	6	99	104	0	6	7	165	170	4	12	7	62	67
3	16	5	69	81	4	7	6	54	46	3	15	6	85	88	1	6	7	231	229	1	13	7	142	141
1	17	5	144	137	5	7	6	196	198	0	16	6	62	74	2	6	7	150	156	2	13	7	47	39
3	17	5	99	92	6	7	6	49	43	2	16	6	86	94	3	6	7	177	182	3	13	7	67	72
4	17	5	47	45	0	8	6	209	214	0	17	6	42	46	4	6	7	95	95	0	14	7	94	94
0	18	5	97	95	2	8	6	159	167	1	17	6	84	81	5	6	7	146	152	1	14	7	79	81
1	18	5	49	35	3	8	6	42	50	2	17	6	41	31	6	6	7	64	53	2	14	7	57	66
2	18	5	70	59	4	8	6	100	114	3	17	6	43	69	0	7	7	179	178	3	14	7	60	59
0	0	6	535	531	6	8	6	65	67	1	19	6	67	61	1	7	7	359	352	0	15	7	39	27
2	0	6	307	297	0	9	6	105	104	0	0	7	122	133	2	7	7	176	177	1	16	7	36	32
3	0	6	48	49	1	9	6	445	442	2	0	7	60	68	3	7	7	272	269	2	16	7	47	38
4	0	6	82	77	2	9	6	105	111	5	0	7	40	27	4	7	7	124	131	0	1	8	104	101
1	1	6	63	68	3	9	6	328	328	0	1	7	77	84	5	7	7	181	174	1	1	8	42	45
4	1	6	50	53	4	9	6	90	93	1	1	7	197	198	0	8	7	57	56	2	1	8	72	64
6	1	6	54	40	5	9	6	221	208	2	1	7	71	69	1	8	7	584	605	3	1	8	78	79
2	2	6	69	76	6	9	6	60	52	3	1	7	87	95	2	8	7	61	61	4	1	8	45	36
4	2	6	45	59	0	10	6	432	442	4	1	7	60	58	3	8	7	452	463	5	1	8	43	46
0	3	6	140	142	1	10	6	111	119	6	1	7	53	31	5	8	7	275	267	1	2	8	118	127
1	3	6	266	256	2	10	6	383	386	0	2	7	65	68	1	9	7	400	399	3	2	8	84	82
2	3	6	83	89	3	10	6	64	57	1	2	7	260	273	3	9	7	316	308	5	2	8	56	53
3	3	6	175	172	4	10	6	242	238	3	2	7	150	143	4	9	7	60	45	0	3	8	70	66
5	3	6	71	75	5	10	6	38	29	5	2	7	46	51	5	9	7	189	183	1	3	8	56	49
0	4	6	178	173	1	11	6	71	81	2	3	7	59	57	0	10	7	158	156	2	3	8	44	42
1	4	6	81	82	2	11	6	45	62	3	3	7	43	39	1	10	7	139	137	4	3	8	46	38
2	4	6	131	145	3	11	6	84	86	4	3	7	78	67	2	10	7	134	123	0	4	8	42	52
1	5	6	235	237	4	11	6	45	45	0	4	7	110	110	3	10	7	127	129	2	4	8	48	45
3	5	6	132	125	5	11	6	79	73	2	4	7	96	96	4	10	7	78	78	2	5	8	58	63
5	5	6	53	46	0	12	6	47	45	3	4	7	63	62	5	10	7	103	103	4	5	8	49	67
0	6	8	58	62	0	10	8	52	60	2	0	9	427	452	1	9	9	47	48	0	6	10	81	75
1	6	8	199	202	1	10	8	52	52	4	0	9	274	287	3	9	9	53	50	1	6	10	44	54
2	6	8	68	76	2	10	8	66	68	0	1	9	52	41	0	10	9	160	162	2	6	10	78	67
3	6	8	148	143	4	10	8	38	41	1	1	9	72	88	2	10	9	130	128	0	7	10	54	57
4	6	8	58	52	0	11	8	92	101	2	1	9	69	66	3	10	9	43	37	1	7	10	50	45
5	6	8	90	83	2	11	8	71	71	4	1	9	62	54	0	12	9	63	63	2	7	10	65	58
0	7	8	194	197	3	11	8	60	59	0	2	9	173	186	2	12	9	49	47	0	8	10	62	59
2	7	8	141	141	1	12	8	52	53	2	2	9	145	154	1	13	9	78	71	1	8	10	107	101
3	7	8	51	47	3	12	8	44	48	4	2	9	97	93	2	13	9	42	37	2	8	10	47	46
4	7	8	78	75	0	13	8	53	52	1	3	9	38	33	0	14	9	44	63	0	9	10	69	73
0	8	8	97	109	1	13	8	46	47	3	3	9	48	58	0	0	10	94	102	1	9	10	83	74
1	8	8	102	92	2	13	8	48	37	0	4	9	244	250	2	0	10	66	71	2	9	10	63	67
2	8	8	119	116	3	13	8	42	45	2	4	9	189	191	0	3	10	68	67	0	10	10	68	76
3	8	8	108	97	0	14	8	56	39	4	4	9	94	88	1	3	10	45	48	0	11	10	37	37
4	8	8	91	86	1	14	8	68	65	3	5	9	52	45	2	3	10	44	48	1	1	11	58	46
5	8	8	90	94	0	15	8	54	57	1	6	9	47	45	3	3	10	41	37	2	1	11	42	21
0	9	8	53	67	2	15	8	45	49	3	6	9	37	19	1	4	10	40	42	2	2	11	37	17
1	9	8	62	60	0	16	8	61	60	1	7	9	93	93	3	4	10	41	52	1	4	11	34	16
2	9	8	78	73	1	16	8	109	98	3	7	9	68	62	0	5	10	60	58	0	5	11	55	56
4	9	8	53	58	0	0	9	499	531	0	8	9	48	39	2	5	10	52	38	1	6	11	122	116

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