

## NEW TERPENOID ALDEHYDES FROM *KIGELIA PINNATA*: CRYSTAL STRUCTURE OF PINNATAL

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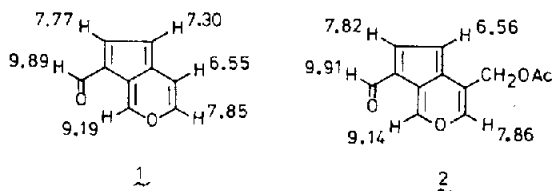
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**Abstract**—From the root bark of *Kigelia pinnata* (Bignoniaceae) two aldehydes, norviburtinal(6-formylcyclopenta[c]pyran) and pinnatal, 11-formyl-2, 3, 3a, 5, 10, 10a, 11, 11a-octahydro-8-hydroxy-3, 11-dimethyl-3, 10a-epoxy-1H-cyclopent[blanthracene-5, 10-dione, have been isolated. The structures were determined by spectroscopic methods, and X-ray crystallographic analysis of pinnatal.

In pursuing our interest<sup>1</sup> in the quinone constituents of the Bignoniaceae we have examined *Kigelia pinnata* DC (syn. *K. africana* Benth.) an African tree introduced to India. Previous work<sup>2</sup> on this plant led to the isolation of lapachol<sup>3a</sup> from the roots, and other quinones from the wood,<sup>3b</sup> and we now describe two non-quinonoid aldehydes, norviburtinal and pinnatal obtained from the root bark.

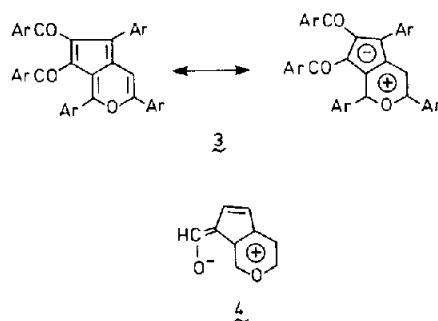
**Norviburtinal.** This yellow compound, C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>, sublimes at ambient temperature and co-distils with organic solvents. It is a conjugated aldehyde ( $\delta$  9.89, s) showing  $\nu_{\text{CO}}$  at relatively low frequency (1635 cm<sup>-1</sup>), and as no OH group is present the second O atom must exist in an ether linkage. The <sup>1</sup>H NMR spectrum shows, in addition to the aldehyde signal, coupled one-proton doublets at  $\delta$  7.85 and 6.55, and at 7.77 and 7.30, and a one-proton singlet at 9.19. This suggests the cyclopenta[c]pyran structure 1 which is also consistent with the mass spectrum, *m/e* 146, 145, 117, 89, and 63 corresponding to consecutive losses of H, CO, CO, and C<sub>2</sub>H<sub>2</sub>. The <sup>1</sup>H NMR spectrum is in good agreement with that reported for baldrinal 2<sup>4</sup> although we did not observe long range coupling (0.7 Hz), between H-1 and H-5. Similarly, baldrinal shows  $\nu_{\text{CO}}$  1637 cm<sup>-1</sup>, and UV absorption at 227, 244, 287, and 425 nm compared to 228, 242, 293, and 424 nm for 1.



This new compound is the fourth member of the group of cyclopenta[c]pyran aldehydes. Baldrinal and viburtinal (2, Me in place of CH<sub>2</sub>OAc)<sup>5</sup> were obtained by degradation of iridoid esters found in *Valeriana*, and in *Viburnum* and *Sambucus* spp., respectively, while cerbinal (2, CO<sub>2</sub>Me in place of CH<sub>2</sub>OAc)<sup>6</sup> is the main yellow pigment in the bark

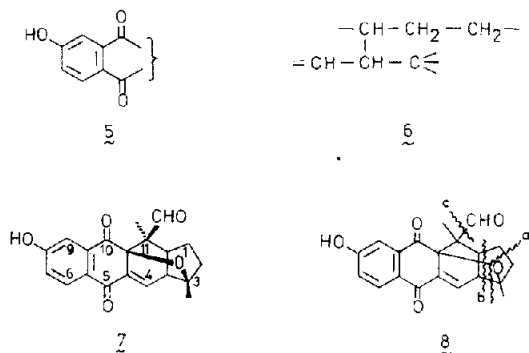
of *Cerbera manghas*. The aldehyde 1, norviburtinal, becomes the simplest member of the aucubin (C<sub>9</sub>) group of iridoids, all the other iridoids isolated from Bignoniaceae being also of the aucubin type.<sup>7</sup>

Norviburtinal and the related aldehydes are of some theoretical interest. The first compounds of this type 3<sup>8</sup> were said to possess a new heteroaromatic system but beyond writing the structures in the zwitterionic form no evidence was provided for aromaticity. Subsequent theoretical studies<sup>9</sup> have confirmed that the cyclopentapyran system is aromatic, and PPP-modified Hückel calculations<sup>10</sup> predicted the UV spectrum of the parent compound 1 (H in place of CHO) to show  $\lambda_{\text{max}}$  248, 300 and 426 nm in good agreement with the observed values for 1 of  $\lambda_{\text{max}}$  242, 293, and 424 nm. The low frequency for the CO absorption (1635 cm<sup>-1</sup>) suggests that structure 4 makes an appreciable contribution to the mesomeric structure.



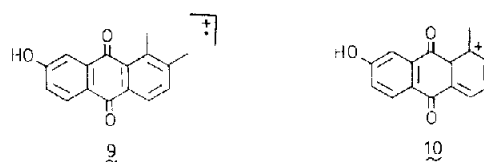
**Pinnatal.** This compound, C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>, is phenolic and shows  $\nu_{\text{max}}$  3280 cm<sup>-1</sup> and  $\lambda_{\text{max}}$  317 nm which shifts to 401 nm in alkaline solution. Signals from three aromatic protons are seen in the <sup>1</sup>H NMR spectrum, and decoupling revealed the substitution pattern shown in 5. CO absorptions at 1705, 1691, and 1649 cm<sup>-1</sup> and <sup>13</sup>C signals at 204, 193, and 177 show that three CO groups are present, two keto and one aldehyde ( $\delta_{\text{CHO}}$  10.28), and the chemical shifts of the aromatic protons in 5 are consistent<sup>11</sup> with the partial diketone structure shown. Further decoupling of the

400 MHz  $^1\text{H}$  NMR spectrum established the existence of grouping 6 which together with two tertiary Me groups (singlets at  $\delta$  0.56 and 0.95) and three aliphatic quaternary carbons ( $^{13}\text{C}$ ) account for all the atoms in pinnatal except for the fifth oxygen. This must be in an ether linkage attached to the quaternary carbons which resonate at  $\delta$  77.8 and 84.5. As several possible structures can be deduced from these data pinnatal was submitted to X-ray analysis (Experimental and Tables) which established the structure and relative stereochemistry as shown in 7.



In the mass spectrum of pinnatal the most significant peaks fall at  $m/e$  252 ( $\text{C}_{16}\text{H}_{12}\text{O}_3$ ) and 239 ( $\text{C}_{15}\text{H}_{11}\text{O}_3$ ), and both appear to arise from cleavage of the ether bridge and 5-membered ring, and loss of CHO. Fragmentations *a* and *c* (8) probably lead to the formation of ion 9 ( $m/e$  252), while  $m/e$  239 may be the ion 10 resulting from fragmentations *b* and *c* and hydrogen transfer. It is interesting that a strong peak in the mass spectrum appears at

$m/e$  43. This fragment ion ( $\text{CH}_3\text{CO}$ ) must also derive from the 5-membered ring.

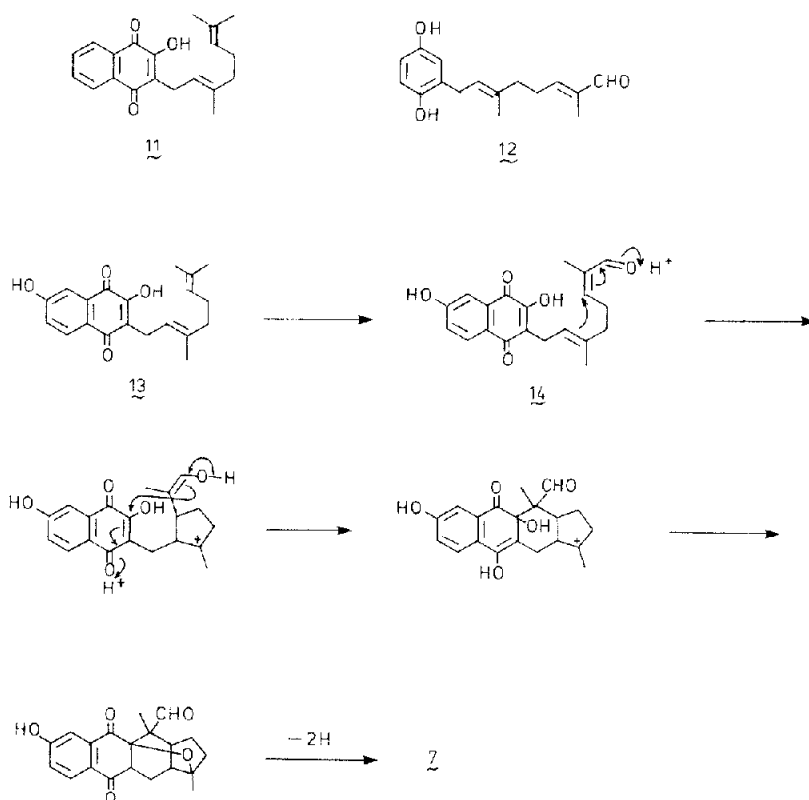


Biogenetically pinnatal is probably formed by cyclisation of the geranylquinone 13 (Scheme 1) although that was not found in the bark, and as yet is an unknown compound. However, as already noted, lapachol occurs in the wood<sup>3b</sup> of *K. pinnata*, and its prenylogue geranyl-lawsone 11 is found in *Conospermum teretifolium*.<sup>12</sup> It seems likely that cyclisation of 13 is preceded by oxidation of a terminal allylic Me group to form the aldehyde 14 for which there is precedent, e.g. alliodorin 12.<sup>13</sup> In the absence of the aldehyde function the side chain would probably cyclise in other ways.<sup>13, 14</sup>

#### EXPERIMENTAL

Plant material was collected from the campus of the University of Rajasthan and voucher specimens are deposited in the Herbarium of the Rajasthan University Botanical Laboratories (Herbarium sheet No. RUBL-12973).

**Extraction and purification.** The air-dried root bark (4 kg) was extracted with benzene. The dark brown extract was fractionated on a column of silica gel, eluting with solvents of increasing polarity, i.e. petroleum ether, benzene, EtOAc, and MeOH. Individual fractions were examined by TLC, and those showing yellow spots which turned green when sprayed with 2M  $\text{H}_2\text{SO}_4$



SCHEME 1

ceric ammonium sulphate soln and heated, were combined and eluted down a second column of silica gel with petroleum ether-benzene (1:1) to give norviburtinal which crystallised from petroleum ether (b.p. 60–80) as yellow needles, m.p. 58° (20 mg). Further elution with benzene-EtOAc (3:1) yielded pinnatal which crystallised from MeOH as prisms, m.p. 182° (60 mg).

**Norviburtinal.** Found: C, 74.0; H, 4.2%; M<sup>+</sup>, 146.0365. C<sub>9</sub>H<sub>6</sub>O<sub>2</sub> requires: C, 74.0; H, 4.1%; M<sup>+</sup>, 146.0367; UV  $\lambda_{\text{max}}^{\text{MeOH}}$ , 228, 242, 293, 424 nm; IR  $\nu_{\text{max}}^{\text{KBr}}$ , 1635, 1618, 1452, 1391, 1118, 1020, 970, 862, 740 cm<sup>-1</sup>; <sup>1</sup>H NMR (220 MHz, CDCl<sub>3</sub>)  $\delta$  9.89 (1H, s, CHO), 9.19 (1H, s, H-1), 7.85 (1H, d, J = 3.5 Hz, H-3), 7.77 (1H, d, J = 6 Hz, H-6), 7.30 (1H, d, J = 6 Hz, H-5), 6.55 (1H, d, J = 3.5 Hz, H-4); MS *m/e* 146(M<sup>+</sup>, 79%), 145(100), 117(14), 89(10), 63(10), 59(5).

**Pinnatal.** Found: C, 71.3; H, 5.65%; M<sup>+</sup>, 338.1157. C<sub>20</sub>H<sub>18</sub>O<sub>5</sub> requires: C, 71.0; H, 5.4%; M, 338.1154;  $[\alpha]_D^{25}$  -85.4° (c 0.44, CHCl<sub>3</sub>); UV  $\lambda_{\text{max}}^{\text{MeOH}}$ , 261, 317, 347 nm (log  $\epsilon$  4.39, 4.07, 3.92); UV  $\lambda_{\text{max}}^{\text{MeOH/H}_2\text{O}}$ , 261, 402 nm (log  $\epsilon$  4.30, 4.13); IR  $\nu_{\text{max}}^{\text{KBr}}$ , 3280, 2840, 1705, 1691, 1649, 1610, 1591, 1580, 1300, 1240, 992, 732, 709 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> + C<sub>6</sub>D<sub>6</sub>, 50°); 10.28 (1H, s, CHO), 8.06 (1H, d, J = 8.5 Hz, ArH), 7.56 (1H, d, J = 7 Hz, =CH-), 7.1 (1H, d, J = 3 Hz, ArH), 6.77 (1H, dd, J = 8.5 and 3 Hz, ArH), 5.22 (1H, bs, OH), 2.37 (1H, dd, J = 7 and 3.5 Hz, =CH-CH<sub>2</sub>-), 2.0 (1H, m, -MeC(CHO)-CH<sub>2</sub>-CH<sub>2</sub>-), 1.65 (2H, m, -MeC(CHO)-CH<sub>2</sub>-CH<sub>2</sub>-), 1.44 (2H, m, >CH-CH<sub>2</sub>-CH<sub>2</sub>-), 0.95 (3H, s, Me), 0.56 (3H, s, Me); <sup>13</sup>C NMR (90.56 MHz, Me<sub>2</sub>CO-d<sub>6</sub>), 18.49 (q, Me), 23.93 (q, Me), 25.76 (t, C-1), 37.73 (t, C-2), 47.10 (d, C-11a), 50.27 (d, C-3a), 56.40 (s, C-3), 78.67 (s, C-11), 84.87 (s, C-10a), 112.64 (d, C-9), 123.33 (s, C-7), 128.10 (s, C-5a), 130.67 (d, C-6), 137.66 (s, C-9a), 140.26 (s, C-4a), 142.03 (d, C-4), 163.25 (s, C-8), 177.40 (s, C-5), 193.45 (s, C-10), 203.56 (d, CHO); MS *m/e* 340(3.5%), 338(M<sup>+</sup>, 6.3), 310(36.5), 295(33.6), 277(16.9), 263(26.7), 252.0783

(C<sub>16</sub>H<sub>12</sub>O<sub>3</sub> requires 252.0786, 71.4), 251(74.2), 239.0707 (C<sub>15</sub>H<sub>11</sub>O<sub>3</sub> requires 239.0708, 100), 223(10.5), 209(14.7), 195(5.6), 181(17.6), 165(18.3), 152(19.0), 139(9.1), 121(13.3), 91(13.3), 81(17.6), 65(9.5), 43.0183(C<sub>2</sub>H<sub>3</sub>O requires 43.0183, 48.0).

**Crystal data.** C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>, *M* = 338.1. Trigonal, *a* = *b* = 7.836(4), *c* = 23.45(2) Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ , *U* = 1247 Å<sup>3</sup>, *D<sub>c</sub>* = 1.35 g cm<sup>-3</sup>, *Z* = 3, *F*(000) = 534. Space group *P*3<sub>1</sub>. Mo-K $\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 0.58$  cm<sup>-1</sup>.

**Crystallographic measurements.** X-ray intensities were measured on a Nicolet P3 automated diffractometer using monochromatized MoK $\alpha$  radiation. Integrated relative intensities for 1747 independent reflections with  $2\theta < 50$  were obtained from  $\theta$ - $2\theta$  scans; 1471 reflections had *I* > 2.5 $\sigma$ (*I*).

**Structure analysis.** The crystal structure was elucidated by direct methods using the program MULTAN. All the C and O atoms were identified in the *E*-map and the H atoms were located on electron density maps calculated at intermediate stages of structure refinement. In the final cycles of full matrix least-squares refinement the positional parameters for all atoms, anisotropic thermal parameters for the C and O atoms and isotropic thermal parameters for the H atoms were varied. The weighting scheme adopted in the final calculations was

$$w = 0.55(\sigma^2(F_o))$$

and convergence was reached at *R* = 3.5%.

The molecular structure is shown in Fig. 1 and the atomic co-ordinates are listed in Table 1. The bond lengths, valency angles and torsion angles are in Tables 2–4; the H–bonds range from 0.95(3)–1.02(3) Å. The molecules in the crystal are linked together by H–bonding and details are given in Table 5. The

Table 1. Fractional atomic co-ordinates with estimated standard deviation in parentheses

O(1)	3519(4)	3884(3)	3499
O(2)	0215(4)	2182(4)	1807(2)
O(3)	6943(4)	10812(4)	1163(2)
O(4)	5895(5)	7556(3)	3104(1)
O(5)	9247(5)	5736(6)	3034(2)
C(1)	4123(5)	4110(4)	2917(2)
C(2)	5804(5)	3557(5)	2865(2)
C(3)	4913(6)	1466(5)	3152(2)
C(4)	5544(7)	1451(6)	3771(2)
C(5)	4156(7)	1823(6)	4132(2)
C(6)	2655(6)	1862(6)	3717(2)
C(7)	2656(6)	0570(5)	3219(2)
C(8)	1681(6)	0847(5)	2715(2)
C(9)	2422(5)	2710(5)	2555(2)
C(10)	1746(5)	3327(5)	2048(2)
C(11)	3040(5)	5342(5)	1837(2)
C(12)	2782(5)	5893(5)	1293(2)
C(13)	4061(5)	7721(5)	1075(2)
C(14)	5669(5)	9053(5)	1403(2)
C(15)	5912(5)	8573(5)	1954(2)
C(16)	4626(5)	6722(5)	2167(2)
C(17)	4938(5)	6265(5)	2761(2)
C(18)	7583(6)	5048(6)	3200(2)
C(19)	6400(7)	3500(7)	2253(2)
C(20)	0654(8)	1282(7)	3958(3)
HU(3)	8120(50)	11460(64)	1391(18)
H(3)	5170(55)	0593(49)	2901(14)
H(4A)	6953(43)	2348(60)	3877(19)
H(4B)	5282(70)	0115(47)	3876(21)
H(5A)	3507(57)	0714(49)	4400(15)
H(5B)	4764(72)	3038(54)	4353(20)
H(7)	2078(54)	-0774(41)	3389(16)
H(8)	0527(46)	-0189(47)	2515(15)
H(12)	1659(43)	4983(48)	1038(14)
H(13)	3893(53)	8060(50)	0698(11)
H(15)	7011(44)	9533(46)	2188(15)
H(18)	7211(53)	5365(54)	3587(12)
H(19A)	5214(39)	2475(43)	2048(19)
H(19B)	7502(40)	3211(47)	2207(17)
H(19C)	6827(50)	4817(35)	2060(17)
H(20A)	0009(55)	-0103(36)	4100(15)
H(20B)	-0180(75)	1381(62)	3650(17)
H(20C)	0745(84)	2164(54)	4285(15)

Table 2. Bond lengths (Å) with estimated standard deviations in parentheses

C(1) - C(1)	1.428(4)	C(4) - C(5)	1.517(8)
C(1) - C(6)	1.469(5)	C(5) - C(6)	1.539(8)
C(2) - C(10)	1.220(4)	C(6) - C(7)	1.546(7)
C(3) - C(13)	1.355(4)	C(6) - C(20)	1.507(8)
C(4) - C(17)	1.214(4)	C(7) - C(8)	1.481(7)
C(5) - C(18)	1.200(6)	C(8) - C(9)	1.327(5)
C(1) - C(2)	1.584(6)	C(9) - C(10)	1.478(6)
C(1) - C(9)	1.496(5)	C(10) - C(11)	1.471(5)
C(1) - C(17)	1.521(5)	C(11) - C(12)	1.394(6)
C(2) - C(3)	1.575(5)	C(11) - C(16)	1.403(4)
C(2) - C(18)	1.516(5)	C(12) - C(13)	1.372(5)
C(2) - C(19)	1.517(6)	C(13) - C(14)	1.398(5)
C(3) - C(4)	1.535(7)	C(14) - C(15)	1.385(6)
C(3) - C(7)	1.550(6)	C(15) - C(16)	1.381(4)
C(16) - C(17)	1.489(6)		

Table 3. Valency angles (°) with estimated standard deviations in parentheses

C(6) - C(1) - C(1)	114.4(3)	C(2) - C(1) - O(1)	108.0(3)
C(9) - C(1) - O(1)	109.5(3)	C(17) - C(1) - O(1)	107.3(3)
C(5) - C(6) - O(1)	107.3(3)	C(7) - C(6) - O(1)	107.0(3)
C(20) - C(6) - O(1)	107.7(4)	C(9) - C(10) - O(2)	120.9(3)
C(11) - C(10) - O(2)	122.0(4)	C(13) - C(14) - O(3)	117.5(4)
C(15) - C(14) - O(3)	122.1(3)	C(1) - C(17) - O(4)	120.5(4)
C(16) - C(17) - O(4)	121.8(3)	C(2) - C(18) - O(5)	123.5(4)
C(9) - C(1) - C(2)	108.3(3)	C(17) - C(1) - C(2)	109.9(3)
C(3) - C(2) - C(1)	104.8(3)	C(18) - C(2) - C(1)	108.6(3)
C(19) - C(2) - C(1)	113.0(4)	C(17) - C(1) - C(9)	113.8(3)
C(8) - C(9) - C(1)	112.7(4)	C(10) - C(9) - C(1)	123.4(3)
C(16) - C(17) - C(1)	117.6(3)	C(18) - C(2) - C(3)	109.8(3)
C(19) - C(2) - C(3)	110.9(3)	C(4) - C(3) - C(2)	115.8(3)
C(7) - C(3) - C(2)	109.0(4)	C(19) - C(2) - C(18)	109.6(4)
C(7) - C(3) - C(4)	101.5(4)	C(5) - C(4) - C(3)	105.2(5)
C(6) - C(7) - C(3)	98.9(3)	C(8) - C(7) - C(3)	114.1(4)
C(6) - C(5) - C(4)	106.2(4)	C(7) - C(6) - C(5)	102.4(4)
C(20) - C(6) - C(5)	116.6(4)	C(20) - C(6) - C(7)	115.3(4)
C(18) - C(7) - C(6)	109.7(4)	C(9) - C(8) - C(7)	114.4(4)
C(10) - C(9) - C(8)	123.8(4)	C(11) - C(10) - C(9)	117.0(3)
C(12) - C(11) - C(10)	120.8(4)	C(16) - C(11) - C(10)	120.7(4)
C(16) - C(11) - C(12)	118.4(3)	C(13) - C(12) - C(11)	121.4(4)
C(15) - C(16) - C(11)	120.7(4)	C(17) - C(16) - C(11)	121.3(3)
C(14) - C(13) - C(12)	119.3(4)	C(15) - C(14) - C(13)	120.4(3)
C(16) - C(15) - C(14)	119.7(3)	C(17) - C(16) - C(15)	118.0(3)

Table 4. Torsion angles (°) with estimated standard deviations in parentheses

C(6) - O(1) - C(1) - C(2)	-62.6(4)	C(6) - O(1) - C(1) - C(9)	55.1(4)
C(6) - O(1) - C(1) - C(17)	178.9(3)	C(1) - O(1) - C(6) - C(5)	108.5(4)
C(1) - O(1) - C(6) - C(7)	-0.8(4)	C(1) - O(1) - C(6) - C(20)	-125.3(4)
O(1) - C(1) - C(2) - C(3)	52.2(4)	O(1) - C(1) - C(2) - C(18)	-65.1(4)
O(1) - C(1) - C(2) - C(19)	173.0(3)	C(9) - C(1) - C(2) - C(3)	-66.3(4)
C(9) - C(1) - C(2) - C(18)	176.4(3)	C(9) - C(1) - C(2) - C(19)	54.6(4)
C(17) - C(1) - C(2) - C(3)	168.9(3)	C(17) - C(1) - C(2) - C(18)	51.6(4)
C(17) - C(1) - C(2) - C(19)	-70.2(4)	O(1) - C(1) - C(9) - C(8)	-57.2(5)
O(1) - C(1) - C(9) - C(10)	127.2(4)	C(2) - C(1) - C(9) - C(8)	60.3(5)
C(2) - C(1) - C(9) - C(10)	-115.2(4)	C(17) - C(1) - C(9) - C(8)	-177.2(4)
C(17) - C(1) - C(9) - C(10)	7.2(5)	O(1) - C(1) - C(17) - O(4)	37.5(5)
O(1) - C(1) - C(17) - C(16)	-146.2(3)	C(2) - C(1) - C(17) - O(4)	-79.7(4)
C(2) - C(1) - C(17) - C(16)	96.6(4)	C(9) - C(1) - C(17) - O(4)	158.7(4)
C(9) - C(1) - C(17) - C(16)	-25.0(5)	C(1) - C(2) - C(3) - C(4)	-98.8(4)
C(1) - C(2) - C(3) - C(7)	14.8(4)	C(18) - C(2) - C(3) - C(4)	17.7(5)
C(18) - C(2) - C(3) - C(7)	131.3(4)	C(19) - C(2) - C(3) - C(4)	138.9(4)
C(19) - C(2) - C(3) - C(7)	-107.4(4)	C(1) - C(2) - C(18) - O(5)	-138.5(5)
C(3) - C(2) - C(18) - O(5)	107.5(5)	C(19) - C(2) - C(18) - O(5)	-14.5(6)
C(2) - C(3) - C(4) - C(5)	84.2(5)	C(7) - C(3) - C(4) - C(5)	-33.7(5)
C(2) - C(3) - C(7) - C(6)	-73.6(4)	C(2) - C(3) - C(7) - C(8)	42.8(5)
C(4) - C(3) - C(7) - C(6)	49.1(4)	C(4) - C(3) - C(7) - C(8)	165.4(4)
C(3) - C(4) - C(5) - C(6)	4.8(5)	C(4) - C(5) - C(6) - O(1)	-86.4(4)
C(4) - C(5) - C(6) - C(7)	26.1(5)	C(4) - C(5) - C(6) - C(20)	152.8(4)
O(1) - C(6) - C(7) - C(3)	66.6(4)	O(1) - C(6) - C(7) - C(8)	-53.0(4)
C(5) - C(6) - C(7) - C(3)	-46.0(4)	C(5) - C(6) - C(7) - C(8)	-165.7(4)

Table 4 (Contd)

C(20) - C(6) - C(7) - C(3)	-173.6(4)	C(20) - C(6) - C(7) - C(8)	66.8(5)
C(3) - C(7) - C(8) - C(9)	-55.8(5)	C(6) - C(7) - C(8) - C(9)	54.1(5)
C(7) - C(8) - C(9) - C(1)	1.4(5)	C(7) - C(8) - C(9) - C(10)	177.0(4)
C(1) - C(9) - C(10) - O(2)	-171.1(4)	C(1) - C(9) - C(10) - C(11)	11.4(6)
C(8) - C(9) - C(10) - O(2)	13.8(7)	C(8) - C(9) - C(10) - C(11)	-163.7(4)
O(2) - C(10) - C(11) - C(12)	-13.2(6)	O(2) - C(10) - C(11) - C(16)	170.1(4)
C(9) - C(10) - C(11) - C(12)	164.2(4)	C(9) - C(10) - C(11) - C(16)	-12.4(6)
C(10) - C(11) - C(12) - C(13)	-175.3(4)	C(16) - C(11) - C(12) - C(13)	1.4(6)
C(10) - C(11) - C(16) - C(15)	175.9(4)	C(10) - C(11) - C(16) - C(17)	-6.1(6)
C(12) - C(11) - C(16) - C(15)	-0.8(6)	C(12) - C(11) - C(16) - C(17)	177.2(4)
C(11) - C(12) - C(13) - C(14)	0.7(6)	C(12) - C(13) - C(14) - O(3)	177.3(4)
C(12) - C(13) - C(14) - C(15)	-3.4(6)	O(3) - C(14) - C(15) - C(16)	-176.7(4)
C(13) - C(14) - C(15) - C(16)	4.0(6)	C(14) - C(15) - C(16) - C(11)	-1.9(6)
C(14) - C(15) - C(16) - C(17)	-180.0(4)	C(11) - C(16) - C(17) - O(4)	-158.1(4)
C(11) - C(16) - C(17) - C(1)	25.7(5)	C(15) - C(16) - C(17) - O(4)	20.0(6)
C(15) - C(16) - C(17) - C(1)	-156.2(3)		

Table 5. Hydrogen bonding details

D-H ... A	D ... A (Å)	D-H (Å)	H ... A (Å)	D-H ... A (°)
O(3)-HO(3) ... O(2) <sup>I</sup>	2.693(4)	0.96(4)	1.74(4)	169(4)

<sup>I</sup> Co-ordinates transposed by: 1 + x, 1 + y, z

Table 6. Ring conformations

Ring	Parameters	Description
Aromatic	$\Delta C_S(11) = 0.85^\circ$	Planar
Quinone	$\Delta C_S(10) = 0.99^\circ$	Boat
Cyclohexene	$\Delta C_S(1) = 12.5^\circ$	Twist boat
Cyclopentane	$\Delta = -25.1^\circ, \phi_m = 50.3^\circ$	Distorted C(7) envelope
Dihydropyran	$\Delta C_S(1) = 1.41^\circ$	Boat
Oxepane	$\Delta C_S(1) = 8.31^\circ$	Chair, mirror plane between C(1) and midpoint of C(4)-C(5) bond

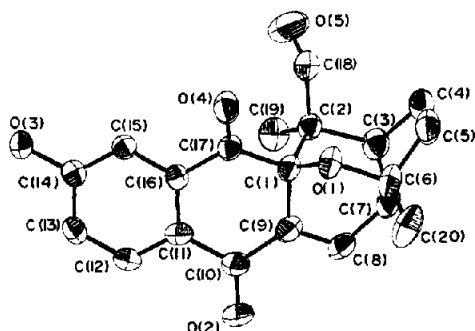


Fig. 1.

band distances C(1)-C(2) 1.584(6) and C(2)-C(3) 1.575(5) Å are long and may be due to repulsion between O(4), C(18) and C(4) (numbering as in Fig. 1). The ring conformations of the hexacyclic system are described in Table 6.

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#### REFERENCES

- K. C. Joshi, P. Singh and S. Taneja, *J. Indian Chem. Soc.* **58**, 825 (1981); A. R. Burnett and R. H. Thomson, *J. Chem. Soc. (C)* 850 (1968).
- T. R. Govindachari, S. J. Jadhav, B. S. Joshi, V. N. Kamat, P. A.

- Mohamed, P. C. Parthasarathy, S. J. Patankar, D. Prakash, D. F. Rane and N. Viswanathan, *Indian J. Chem.* **7**, 308 (1969); H. K. Dasai, D. H. Gawad, T. R. Govindachari, B. S. Joshi, V. N. Kamat, J. D. Modi, P. C. Parthasarathy, S. J. Patankar, A. R. Sidhaye and N. Viswanathan, *Indian J. Chem.* **9**, 611 (1971).
- <sup>3a</sup>T. R. Govindachari, S. J. Patankar and N. Viswanathan, *Phytochemistry* **10**, 1603 (1971); <sup>6</sup>K. Inoue, H. Inoue and C.-C. Chen. *Ibid.* **20**, 2271 (1981).
- <sup>4</sup>P. W. Thies, *Tetrahedron* **24**, 313 (1968).
- <sup>5</sup>R. -P. Godeau, J. -C. Rossi and I. Fourasté, *Phytochemistry* **16**, 604 (1977); R. -P. Godeau, Y. Pélissier and I. Fourasté, *Trav. Soc. Pharm. Montpellier* **38**, 343 (1978).
- <sup>6</sup>F. Abe, H. Okabe and T. Yamauchi, *Chem. Pharm. Bull.* **25**, 3422 (1977).
- <sup>7</sup>L. J. El-Naggar and J. L. Beal, *J. Nat. Prod.* **43**, 649 (1980).
- <sup>8</sup>J. Harley-Mason and C. R. Harrison, *J. Chem. Soc.* 4872 (1963).
- <sup>9</sup>R. Borsdorf, *Z. Chem.* **4**, 422 (1964); J. Fabian, A. Mehlhorn, and R. Zahradnik, *Theor. Chim. Acta* **12**, 247 (1968).
- <sup>10</sup>J. Fabian, *Z. Phys. Chem. Leipzig* **260**, 81 (1979).
- <sup>11</sup>J. A. Ballantine and C. T. Pillinger, *Tetrahedron* **23**, 1691 (1967).
- <sup>12</sup>J. R. Cannon, K. R. Joshi, I. A. McDonald, R. W. Retallack, A. F. Sierakowski and L. C. H. Wong, *Tetrahedron Letters* 2795 (1975).
- <sup>13</sup>K. L. Stevens and L. Jurd, *Tetrahedron* **32**, 665 (1976).
- <sup>14</sup>G. D. Manners and L. Jurd, *J. Chem. Soc. Perkin I* 405 (1977).

### Thermal parameters

O(1)	59(2)	31(1)	35(1)	20(1)	9(1)	4(1)
O(2)	43(2)	48(2)	65(2)	3(1)	-20(1)	2(1)
O(3)	52(2)	41(1)	38(1)	14(1)	-4(1)	12(1)
O(4)	85(2)	32(1)	40(1)	19(1)	-18(1)	-2(1)
O(5)	48(2)	81(2)	95(3)	7(2)	-2(2)	4(2)
C(1)	40(2)	27(2)	32(2)	14(1)	2(1)	2(1)
C(2)	43(2)	29(2)	37(2)	16(1)	-1(1)	1(1)
C(3)	61(2)	33(2)	50(2)	25(2)	-3(2)	-1(2)
C(4)	67(3)	41(2)	60(2)	24(2)	-9(2)	10(2)
C(5)	85(3)	40(2)	42(2)	23(2)	-8(2)	6(2)
C(6)	64(2)	38(2)	42(2)	20(2)	13(2)	14(2)
C(7)	60(2)	22(2)	49(2)	13(2)	-6(2)	1(2)
C(8)	42(2)	33(2)	51(2)	6(2)	-5(2)	0(2)
C(9)	39(2)	34(2)	40(2)	13(2)	2(1)	0(2)
C(10)	38(2)	41(2)	38(2)	15(2)	-8(2)	-4(2)
C(11)	32(2)	37(2)	41(2)	16(2)	-5(1)	-6(1)
C(12)	34(2)	44(2)	40(2)	17(2)	-10(1)	-4(1)
C(13)	46(2)	48(2)	30(2)	26(2)	-4(2)	5(2)
C(14)	40(2)	37(2)	34(2)	22(2)	-1(1)	1(1)
C(15)	37(2)	32(2)	33(2)	17(2)	-3(1)	-2(1)
C(16)	36(2)	34(2)	30(2)	21(1)	1(1)	1(1)
C(17)	40(2)	28(2)	32(2)	14(1)	-1(1)	-2(1)
C(18)	52(2)	40(2)	59(3)	20(2)	-4(2)	12(2)
C(19)	60(2)	54(2)	44(2)	32(2)	9(2)	0(2)
C(20)	79(3)	59(3)	78(4)	24(3)	40(3)	25(3)
H(3)	59(12)					
H(3)	43(9)					
H(4A)	65(13)					
H(4B)	72(13)					
H(5A)	54(11)					
H(5B)	78(15)					
H(7)	47(10)					
H(8)	43(10)					
H(12)	41(9)					
H(13)	32(8)					
H(15)	39(9)					
H(18)	40(10)					
H(19A)	66(13)					
H(19B)	49(10)					
H(19C)	59(12)					
H(20A)	50(11)					
H(20B)	101(21)					
H(20C)	99(19)					

The anisotropic temperature factors are expressed as

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$

with final parameters  $U_{ij} \times 10^3$