

Mittelwert der beiden Al—C-Abstände fällt genau mit dem Wert aus der Elektronenbeugungsuntersuchung zusammen. Etwas verschieden sind die nach den beiden Methoden erhaltenen Werte für den N—C-Abstand, sie befinden sich jedoch noch im Bereich bekannter Werte für die N—C-Einfachbindung. Die Valenzwinkel liegen innerhalb des Rings dicht bei 90°, ausserhalb des Rings nahe am Tetraederwinkel.

Die kürzesten intermolekularen Abstände sind bei C...Cl(2) mit 3,56 und bei C...Cl(1) mit 3,94 Å zu beobachten, wobei das Chlor-Atom im ersten Fall in die Lücke zwischen drei Wasserstoff-Atomen eingreift, im zweiten Fall einem Wasserstoff-Atom fast direkt gegenübersteht.

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(2S,3S,5R)-5-Allyl-5-methoxy-2-(3',4',5'-trimethoxyphenyl)-3-methyl-2,3,5,6-tetrahydro-6-oxobenzofuran

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Abstract. C₂₂H₂₆O₆, orthorhombic, *P*2₁2₁2₁, *a* = 8.532 (4), *b* = 9.588 (4), *c* = 25.260 (19) Å, *V* = 2066.4 Å³, *Z* = 4, *D_x* = 1.240 g cm⁻³. The structure was solved by direct methods and refined by full-matrix least squares to an *R* value of 0.040 for 2041 observed structure amplitudes measured with Cu Kα radiation on an automatic diffractometer.

Introduction. The title compound, (I), is a neolignan which was isolated from the trunk of the *Nectandra miranda* tree. It closely resembles (2*S*,3*S*,3*aS*)-5-allyl-3*a*-methoxy-2-(3',4',5'-trimethoxyphenyl)-3-methyl-2,3,3*a*,6-tetrahydro-6-oxobenzofuran, mirandin-A (II), the structure of which was reported by Tomita, Rosenstein & Jeffrey (1977).

The compound was obtained from Professor Gottlieb of the Instituto de Química de Universidade de São Paulo, SP, Brazil. It is one of a series of natural products which have been extracted from the Brazilian

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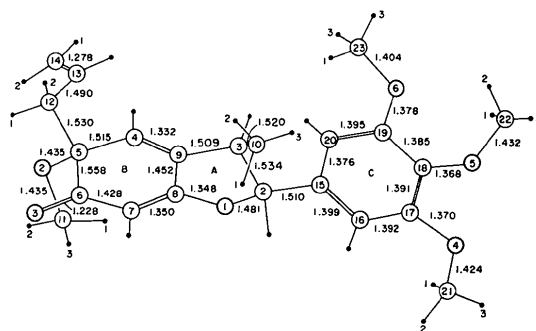
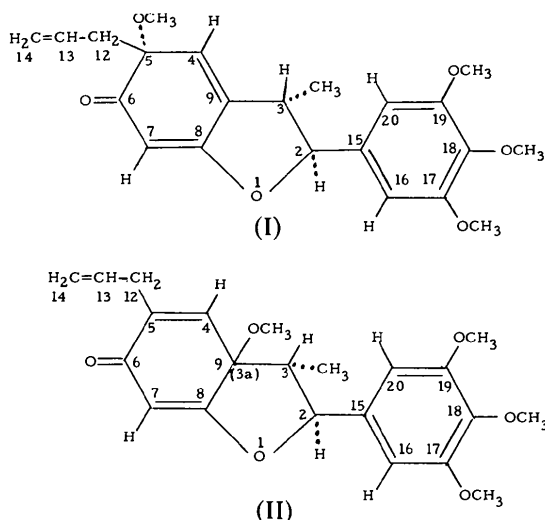


Fig. 1. Atomic numbering and bond distances (Å). (The atomic numbering complies with the chemical notation for benzofuran ring systems.) The standard deviations are 0.004 Å for the C–C and C–O bonds, except for C(12)–C(13) and C(13)–C(14), where they are 0.007 Å.

Lauraceae (Aiba, Fernandes, Gottlieb & Maia, 1975). The slightly yellow crystals of (I) were shown to be orthorhombic, $P2_12_12_1$, from precession photographs. The precise unit-cell dimensions and three-dimensional intensity data were measured by $\theta/2\theta$ scans on a CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation, using a crystal of dimensions $0.6 \times 0.3 \times 0.2$ mm. Of the 2432 independent reflections

measured, 2041 had intensities greater than $2\sigma_c$. The unobserved reflections were given values of $0.5\sigma_c$, where σ_c is the standard deviation calculated from counting statistics. No corrections were made for absorption.

The application of *MULTAN* (Germain, Main & Woolfson, 1971), together with the negative quartet programs (Ernst, 1974), gave an *E* map which showed 25 of the 28 C and O atoms. The three remaining atoms were located on a difference synthesis map. Isotropic

Table 1. Positional parameters ($\times 10^4$, for H $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
O(1)	−2044 (2)	595 (2)	1798 (1)	H1(C2)	−100 (3)	−114 (3)	213 (1)	6
O(2)	−4979 (2)	−2105 (2)	267 (1)	H1(C3)	29 (3)	2 (2)	111 (1)	3
O(3)	−6587 (2)	103 (3)	759 (1)	H1(C4)	−193 (3)	−177 (3)	30 (1)	6
O(4)	3326 (2)	3477 (2)	1992 (1)	H1(C7)	−495 (3)	112 (2)	152 (1)	4
O(5)	4128 (2)	2524 (2)	2958 (1)	H1(C10)	−25 (5)	−283 (4)	142 (1)	9
O(6)	2882 (2)	254 (2)	3365 (1)	H2(C10)	69 (4)	−236 (4)	91 (1)	8
C(2)	−627 (2)	−295 (2)	1822 (1)	H3(C10)	161 (5)	−198 (4)	134 (1)	11
C(3)	−306 (2)	−714 (3)	1246 (1)	H1(C11)	−403 (6)	−309 (5)	95 (2)	14
C(4)	−2535 (3)	−1130 (3)	565 (1)	H2(C11)	−529 (5)	−399 (5)	44 (2)	11
C(5)	−4212 (3)	−825 (3)	406 (1)	H3(C11)	−543 (7)	−272 (6)	98 (2)	15
C(6)	−5173 (3)	−27 (3)	834 (1)	H1(C12)	−535 (4)	7 (3)	−18 (1)	6
C(7)	−4402 (3)	524 (3)	1290 (1)	H2(C12)	−364 (4)	−69 (4)	−37 (1)	8
C(8)	−2878 (2)	210 (2)	1369 (1)	H1(C13)	−226 (7)	125 (5)	−4 (2)	15
C(9)	−1925 (2)	−613 (2)	1009 (1)	H1(C14)	−354 (5)	350 (5)	−16 (2)	11
C(10)	463 (4)	−2138 (4)	1198 (2)	H2(C14)	−531 (8)	255 (7)	−18 (2)	19
C(11)	−5078 (5)	−3112 (4)	686 (1)	H1(C16)	116 (3)	188 (2)	150 (1)	4
C(12)	−4269 (4)	30 (3)	−105 (1)	H1(C20)	63 (3)	−85 (2)	271 (1)	4
C(13)	−3505 (5)	1424 (4)	−71 (1)	H1(C21)	209 (4)	426 (3)	141 (1)	8
C(14)	−4105 (7)	2600 (5)	−196 (2)	H2(C21)	380 (4)	471 (3)	133 (1)	9
C(15)	653 (2)	466 (2)	2117 (1)	H3(C21)	299 (4)	314 (3)	118 (1)	8
C(16)	1368 (2)	1638 (2)	1892 (1)	H1(C22)	589 (7)	150 (5)	260 (2)	16
C(17)	2554 (3)	2315 (2)	2170 (1)	H2(C22)	622 (5)	283 (5)	293 (2)	11
C(18)	3038 (2)	1827 (2)	2662 (1)	H3(C22)	580 (4)	295 (3)	242 (1)	9
C(19)	2324 (2)	660 (2)	2877 (1)	H1(C23)	226 (6)	−191 (5)	347 (2)	15
C(20)	1126 (2)	−21 (2)	2604 (1)	H2(C23)	93 (5)	−68 (4)	378 (1)	11
C(21)	3019 (5)	3945 (4)	1467 (1)	H3(C23)	273 (4)	−107 (3)	394 (1)	8
C(22)	5697 (4)	2473 (6)	2758 (2)					
C(23)	2188 (4)	−908 (4)	3609 (1)					

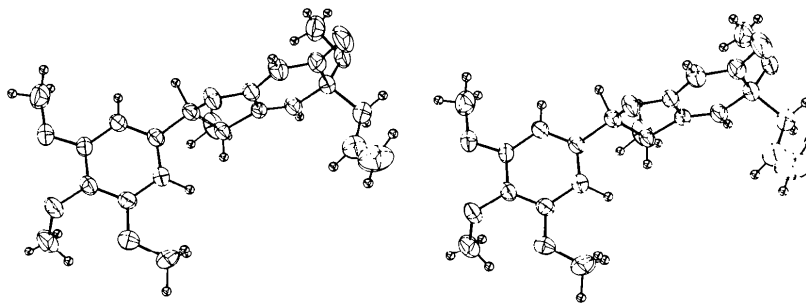


Fig. 2. Stereoview of the molecule. Thermal ellipsoids are at 50% probability (Johnson, 1976).

followed by anisotropic refinement resulted in a conventional R factor of 0.081. At this stage, a difference map showed the positions of 20 H atoms; the remaining six were given positions consistent with C–H bonds of 1.0 Å and tetrahedral C geometry. Final refinement including isotropic H thermal parameters gave a final R value of 0.040. The atomic positional parameters are given in Table 1.*

Discussion. The atomic numbering and the bond lengths of (I) are given in Fig. 1, and a stereoview of the molecule is shown in Fig. 2. Important torsion angles are listed in Table 2. The C–H bond lengths range from 0.71 to 1.18 Å with standard deviations of about 0.1 Å.

The configuration of the molecule is as shown in (I). The absolute configuration at the asymmetric C centers is $2S,3S,5R$ or $2R,3R,5S$; the former is favored by analogy with that of (II), which was extracted from the same source. The difference in the configuration of the two molecules is that a methoxy substituent at C(9) ($\equiv 3a$) in (II) appears at C(5) in this compound. There are, however, significant differences in the valence-bond structure and in the conformation of the molecules, as shown by comparing the bond lengths and torsion angles given in Fig. 1 and Table 2 with the corresponding data for (II). The principal difference in the bond lengths in the two molecules is in the region of C(8) and C(9) ($\equiv 3a$). In (I) the benzopyran ring structure is as represented in (III), with a double bond at C(4)–C(9) and partial double bonds at C(7)–C(8) and C(8)–O(1). In compound II, the presence of the methoxy substituent at C(9) causes a ring structure closer to that of (IV). The double-bond character is located at C(4)–

Table 2. *The molecular conformation: selected torsion angles ($^{\circ}$)*

Furan ring (A)	
O(1)–C(2)–C(3)–C(9)	–26.0
C(2)–C(3)–C(9)–C(8)	+17.1
C(3)–C(9)–C(8)–O(1)	–1.2
C(9)–C(8)–O(1)–C(2)	–16.4
C(8)–O(1)–C(2)–C(3)	+27.1
Benzo ring (B)	
C(4)–C(5)–C(6)–C(7)	+9.0
C(5)–C(6)–C(7)–C(8)	–7.1
C(6)–C(7)–C(8)–C(9)	+2.7
C(7)–C(8)–C(9)–C(4)	–0.5
C(8)–C(9)–C(4)–C(5)	+3.0
C(9)–C(4)–C(5)–C(6)	–6.9
Phenyl ring (C)	
C(15)–C(16)–C(17)–C(18)	+0.8
C(16)–C(17)–C(18)–C(19)	–0.3
C(17)–C(18)–C(19)–C(20)	–0.2
C(18)–C(19)–C(20)–C(15)	+0.2
C(19)–C(20)–C(15)–C(16)	+0.2
C(20)–C(15)–C(16)–C(17)	–0.7
Exocyclic torsion angles	
O(1)–C(2)–C(15)–C(16)	–69.1
C(4)–C(5)–C(12)–C(13)	–61.5
C(5)–C(12)–C(13)–C(14)	–127.6
C(4)–C(5)–O(2)–C(11)	+61.4
C(16)–C(17)–O(4)–C(21)	–6.8
C(17)–C(18)–O(5)–C(22)	–71.0
C(18)–C(19)–O(6)–C(23)	+178.9
Asymmetric centers	
C(8)–O(1)–C(2)–C(15)	+154.3
O(1)–C(2)–C(3)–C(10)	–149.4
C(9)–C(4)–C(5)–C(12)	+115.0

* Lists of structure factors, anisotropic thermal parameters, and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32904 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

C(5), 1.319 Å, and C(7)–C(8), 1.348 Å, giving the benzo ring a quinoid character. In consequence, there are significant ring conformational differences, as discussed above.

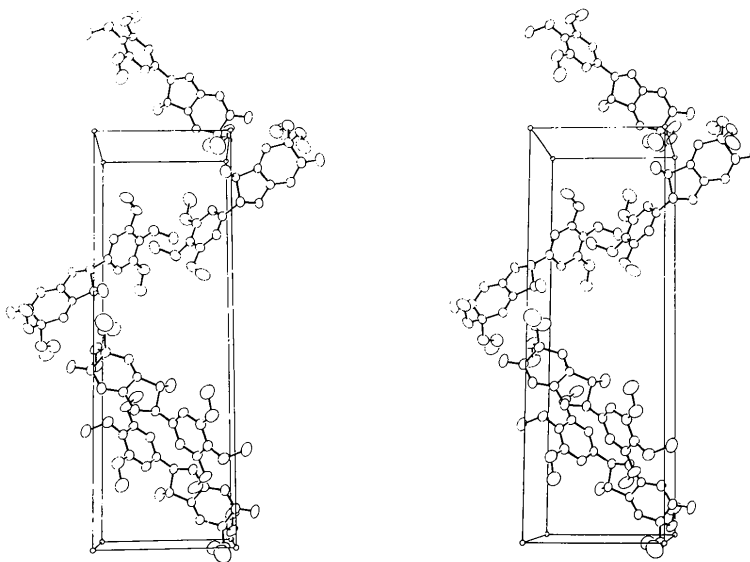
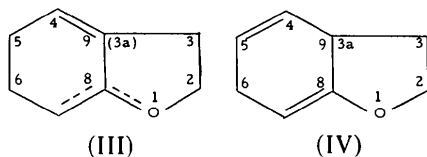


Fig. 3. Unit-cell contents and molecular packing. The a axis is horizontal, and the c axis is vertical.



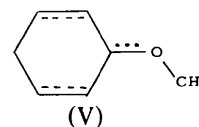
The central furan ring (A) is much closer to the envelope conformation in (I), with C(2) out of the plane, as shown by the small value of the C(3)–C(9)–C(8)–O(1) torsion angle. In (II) this ring has the twist conformation, with a C(8)–O(1)–C(2)–C(3) torsion angle of $+5.6^\circ$. The benzo ring (B) is less distorted in (I) and closer to being planar. The C(7)–C(8)–C(9)–C(4) half of the ring is almost planar, and the principal twist is about C(5)–C(6).

The conformation of the allyl group with respect to the benzo ring is quite different in the two compounds. In compound (II) the allyl group is almost planar and perpendicular to the benzo ring with C(4)–C(5)–C(12)–C(13) and C(5)–C(12)–C(13)–C(14) torsion angles of -93° and $+2.0^\circ$ respectively. In (I) these angles are -62° and -128° , giving a quite different conformation. This difference is probably controlled by the molecular packing.

The phenyl ring (C) has a similar inclination to the furan ring (A) in both molecules: -69° and -59° for (I) and (II) respectively. It is closer to being ideal planar in (I), with the ring torsion angles deviating less than 1° from zero. As in (II), the outermost methoxy groups are almost coplanar with the phenyl

ring, while the central one, O(5)–C(22)H₃, is inclined. In both molecules the inclination is closer to synclinal than perpendicular.

An interesting distinction is observed in both structures between the bond character of the methoxy groups attached to the phenyl ring and that of the methoxy group on the benzopyran ring. On the phenyl ring, the C–O bond of the methoxy group which is adjacent to the ring is significantly shorter than that attached to the methyl group, whereas on the benzopyran ring these two bonds are equal. This corresponds to the resonance contribution (V) for the phenyl substituents, which cannot occur on the benzofuran ring, since the points of substitution, C(5) in (I) and C(9) in (II), are tetrahedral C atoms. The resonance contribution (V), as measured by the C–O bond lengths, is the same whether the plane of the methoxy group is close to the plane of the phenyl ring or inclined to it at an angle between 70 and 90° . This is somewhat surprising because it implies that the interaction of the lone-pair p orbitals of the O atom with the phenyl π orbital is the same for both conformations.



The molecular packing, shown in Fig. 3, is of the herring-bone pattern when viewed down the a axis, and

is very similar to that of compound II (Tomita, Rosenstein & Jeffrey, 1977).

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trans-Nitrato[2-(di-*tert*-butylphosphino)phenyl]di-*tert*-butylphenylphosphineplatinum(II)

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Abstract. $C_{28}H_{45}NO_3P_2Pt$, orthorhombic, $P2_12_12_1$, $a = 8.544$ (2), $b = 10.589$ (3), $c = 32.618$ (8) Å, $Z = 4$, $D_x = 1.577$ g cm⁻³, $V = 2951$ (1) Å³, $\mu(Mo K\alpha) = 49.37$ cm⁻¹. The complex has two di-*tert*-butylphenylphosphine ligands, one of which has undergone internal metallation at the *ortho* position of the phenyl group. The resulting highly strained four-membered PtPC₂ ring has bond angles of C–Pt–P = 69.7 (5), C–P–Pt

= 82.4 (6), C–C–Pt = 106 (1) and C–C–P = 102 (1)°.

Introduction. Measurements were made on a Syntex $P2_1$ diffractometer using monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The cell dimensions and their e.s.d.'s were obtained by least-squares treatment of the setting angles of 15 reflexions with $35^\circ < 2\theta < 40^\circ$. The structure analysis used the 2263 independent reflexions having $5^\circ < 2\theta < 50^\circ$ and $I > 3\sigma(I)$, where $\sigma(I)$ is the standard deviation derived from counting

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Table 1. Atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Pt(1)	-1588 (1)	-1233 (1)	-1329 (1)	C(16)	-2954 (28)	-1758 (18)	-2516 (5)
P(1)	-340 (5)	88 (4)	-866 (1)	C(17)	-5126 (20)	-1628 (16)	-1994 (6)
P(2)	-2482 (5)	-2924 (4)	-1731 (1)	C(18)	-4678 (23)	-3646 (19)	-2357 (6)
C(1)	-253 (19)	-1344 (19)	-564 (4)	C(19)	-3758 (18)	-3963 (16)	-1428 (5)
C(2)	-1054 (19)	-2189 (16)	-809 (6)	C(20)	-4707 (19)	-3367 (16)	-1150 (5)
C(3)	-1228 (21)	-3426 (14)	-667 (5)	C(21)	-5883 (21)	-4033 (19)	-910 (5)
C(4)	-615 (25)	-3773 (22)	-266 (7)	C(22)	-5999 (25)	-5371 (20)	-995 (7)
C(5)	178 (29)	-2900 (19)	-36 (7)	C(23)	-5047 (23)	-5893 (15)	-1306 (5)
C(6)	417 (30)	-1637 (17)	-169 (6)	C(24)	-3947 (20)	-5262 (15)	-1509 (6)
C(7)	1671 (23)	601 (18)	-1010 (7)	C(25)	-684 (19)	-3821 (20)	-1924 (5)
C(8)	2572 (26)	-664 (23)	-1110 (9)	C(26)	58 (24)	-4568 (20)	-1564 (7)
C(9)	1545 (27)	1409 (29)	-1398 (6)	C(27)	455 (22)	-2819 (20)	-2079 (7)
C(10)	2609 (23)	1278 (23)	-699 (6)	C(28)	-1066 (24)	-4773 (20)	-2282 (6)
C(11)	-1445 (21)	1286 (19)	-567 (5)	N(1)	-2587 (21)	1130 (16)	-1763 (5)
C(12)	-732 (31)	1518 (24)	-114 (8)	O(1)	-1694 (17)	102 (11)	-1833 (4)
C(13)	-1471 (32)	2585 (18)	-806 (6)	O(2)	-2166 (26)	2043 (14)	-1973 (6)
C(14)	-3122 (25)	778 (26)	-518 (7)	O(3)	-3701 (16)	1089 (14)	-1541 (5)
C(15)	-3843 (21)	-2504 (17)	-2187 (6)				