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(2*S*,3*S*,3a*S*)-5-Allyl-3a-methoxy-2-(3′,4′,5′-trimethoxyphenyl)-3-methyl-2,3,3a,6-tetrahydro-6-oxobenzofuran (a Neolignan: Mirandin-A)

By Koychi Tomita,* Robert D. Rosenstein and G. A. Jeffrey

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *USA*

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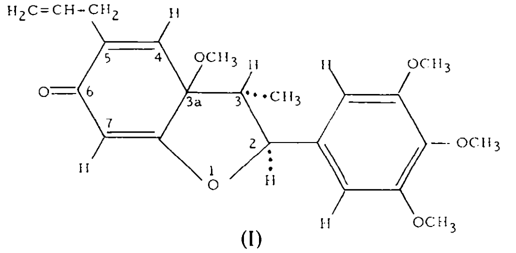
Abstract. $C_{22}H_{26}O_6$, monoclinic, $P2_1$, a = 10·635 (3), b = 10·021 (3), c = 10·708 (3) Å, β = 115·72 (2)°, Z = 2, D_o = 1·27, D_c = 1·25 g cm^{-3}. The structure was solved by the direct method and Fourier difference syntheses and refined by full-matrix least squares to an R value of 0·044 for 1473 structure amplitudes measured with Cu $K\alpha$ radiation.

Introduction. Mirandin-A (I), a neolignan, was isolated from the trunk of the Nectandra miranda tree as part of a series of studies of natural products which can be extracted from the Brazilian *Lauraceae* (Aiba, Fernandes, Gottlieb & Maia, 1975).



(I)

The compound was obtained from Professor Gottlieb of the Instituto de Quimica da Universidade de São Paulo, SP, Brazil, in the form of slightly yellow prisms. Weissenberg and precession photographs showed the systematic absences (0*k*0, *k* odd) of the space group $P2_1$. The intensity data were measured from a crystal with dimensions 0·3 × 0·3 × 0·1 mm, on a Nonius CAD-4 diffractometer, with graphite-monochromated Cu $K\alpha$ radiation; 2222 independent reflections were measured up to θ = 75° with the $\theta/2\theta$ scan method, of which 1473 with $I > 2\sigma(I)$ were accepted as observed.

The application of *MULTAN* (Germain, Main & Woolfson, 1971), together with the negative quartet programs (Ernst, 1974), gave the positions of 23 out of the 28 non-hydrogen atoms in the molecule. Successive difference Fourier syntheses were then used to locate the five remaining non-hydrogen atoms and 16 H atoms. The positions of 10 H atoms were not revealed by the difference syntheses and were generated from the positions of the atoms to which they are bonded, tetrahedral angles and C–H distances of 1·0 Å being assumed. The full-matrix least-squares refinement of $\Sigma\, w(|F_o| - 1/k|F_c|)^2$ gave a final R value of 0·044 for

Table 1. *Positional parameters* (×10⁴, *for* H ×10³) *for mirandin-A*

Estimated standard deviations are given in parentheses. E.s.d.'s for C(13) and C(14) are underestimated, due to the large thermal motion.

	x	*y*	*z*
O(1)	2849 (2)	2395 (3)	−2885 (2)
O(2)	1305 (2)	4551 (3)	−2340 (3)
O(3)	−268 (4)	115 (3)	−1547 (4)
O(4)	5480 (2)	7023 (3)	−1343 (2)
O(5)	6851 (2)	7055 (2)	−2934 (2)
O(6)	6216 (2)	5343 (3)	−5041 (2)
C(2)	2513 (4)	3254)4)	−4083 (4)
C(3)	988 (4)	3732 (4)	−4524 (4)
C(4)	−706 (4)	3148 (5)	−3420 (4)
C(5)	−1037 (4)	2113 (5)	−2862 (4)
C(6)	30 (4)	1091 (5)	−2102 (4)
C(7)	1398 (5)	1175 (5)	−2078 (4)
C(8)	1690 (4)	2234 (4)	−2683 (4)
C(9)	743 (3)	3408 (4)	−3251 (3)
C(10)	−38 (5)	3011 (7)	−5836 (5)
C(11)	1549 (5)	4376 (6)	−905 (5)
C(12)	−2488 (5)	1895 (7)	−2946 (6)
C(13)	−2775 (8)	2405 (7)	−1811 (8)
C(14)	−2096 (9)	3009 (8)	−799 (8)
C(15)	3655 (3)	4292 (3)	−3762 (3)
C(16)	3999 (3)	5181 (4)	−2675 (3)
C(17)	5063 (3)	6096 (4)	−2398 (3)
C(18)	5808 (3)	6109 (3)	−3185 (3)
C(19)	5448 (3)	5248 (3)	−4284 (3)
C(20)	4369 (3)	4314 (3)	−4583 (3)
C(21)	4695 (6)	7091 (8)	−557 (7)
C(22)	8169 (4)	6695 (5)	−1893 (5)
C(23)	5782 (5)	4571 (5)	−6267 (5)
H1(C2)	251 (3)	274 (3)	−476 (3)
H1(C3)	108 (4)	470 (5)	−450 (4)
H1(C4)	−135 (4)	388 (5)	−381 (4)
H1(C7)	221 (5)	53 (6)	−147 (5)
H1(C10)	−102 (5)	352 (5)	−610 (4)
H2(C10)	20 (3)	328 (4)	−663 (4)
H3(C10)	17 (5)	221 (7)	−572 (5)
H1(C11)	260 (7)	400 (9)	−29 (7)
H2(C11)	193 (5)	522 (7)	−39 (5)
H3(C11)	90 (4)	389 (5)	−71 (4)
H1(C12)	−318 (5)	232 (6)	−384 (5)
H2(C12)	−275 (6)	87 (8)	−314 (6)

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* Present address: Faculdade de Filosofia de Araraquara, Caixa Postal 174, 14800 Araraquara, São Paulo, Brazil.

Table 1 (*cont.*)

H1(C13)	−342 (9)	259 (13)	−142 (9)
H1(C14)	−116 (8)	330 (12)	−48 (8)
H2(C14)	−238 (7)	320 (9)	3 (7)
H1(C16)	350 (4)	519 (4)	−213 (3)
H1(C20)	397 (3)	370 (4)	−552 (3)
H1(C21)	520 (5)	799 (5)	9 (5)
H2(C21)	480 (6)	626 (7)	1 (6)
H3(C21)	370 (5)	734 (5)	−119 (4)
H1(C22)	857 (5)	606 (6)	−234 (4)
H2(C22)	877 (5)	741 (5)	−162 (4)
H3(C22)	817 (3)	649 (4)	−99 (4)
H1(C23)	588 (5)	354 (6)	−624 (5)
H2(C23)	486 (5)	484 (5)	−694 (4)
H3(C23)	628 (4)	482 (4)	−678 (3)

1473 observed data,* using $w = 1/\sigma^2$ from counting statistics as weights. The scattering factors used were those of Cromer & Waber (1965). The final positional parameters, with their estimated standard deviations, are listed in Table 1. All calculations were carried out on the University of Pittsburgh PDP-10 computer, using programs of Shiono (1971).

Discussion. The atomic numbering and the bond lengths in the molecule of mirandin-A are given in Fig. 1. The relative configuration of the molecule is as shown in (I). The absolute configuration at the three asymmetric carbon atoms, C(2), C(3), C(3a), is therefore either all *S*,† as suggested by the chemistry of the biosynthesis (Gottlieb, 1976), or all *R*. The conformation of the molecule is illustrated in the stereoview shown in Fig. 2, and described quantitatively by the torsion angles given in Table 2.

The central furan ring (*A*) has the twist conformation, ${}^{C(2)}T_{O(1)}$, with O(1) *exo* with respect to the fused benzo ring. The benzo ring (*B*), which has quinoidal character, as shown by the bond lengths given in Fig. 1, is distorted in the direction of a half-boat conformation. The phenyl ring is almost planar, as shown by the small values of the ring torsion angles. The C(5)–C(12)–C(13)–C(14) atoms, which include the allyl group, are close to planar and inclined at ~90° to the benzo ring. The phenyl ring is inclined ~60° to the furan ring. Of the three methoxy groups, those at C(17) and C(19) are almost in the plane of the phenyl ring, while the central methoxy group at C(18) is nearly normal to the ring.

The bond lengths, shown in Fig. 1, are consistent with the molecular configuration I, within their 3σ values. The only abnormal distances are those of C(12)–C(13) and C(13)–C(14), both of which are short, particularly the former. This is a result of large thermal motion, or possibly disorder, with respect to oscillation about the C(5)–C(12) bond.

The molecular packing has the familiar herring-bone pattern when viewed down the *a* axis, as shown in Fig. 3. The closer O···H intermolecular approaches are O(5)···H1(C20) 2·23 Å and O(3)···H2(C10) 2·70 Å.

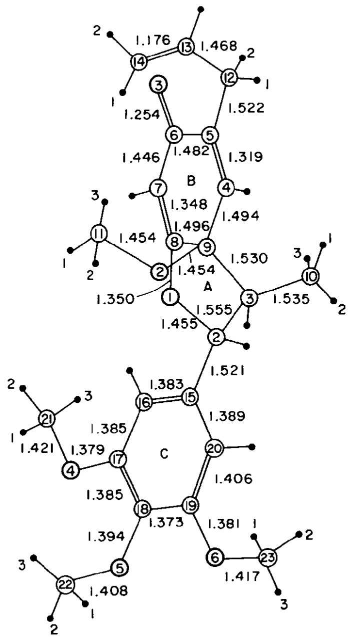

Fig. 1. Atomic numbering and bond distances. [The atomic numbering complies with the chemical notation for benzofuran ring systems, except for carbon 3a, which becomes C(9) in our notation.] The standard deviations range from 0·005 to 0·010 Å for C–C and C–O bonds, except for C(12)–C(13) and C(13)–C(14), where they are ~0·05 Å.

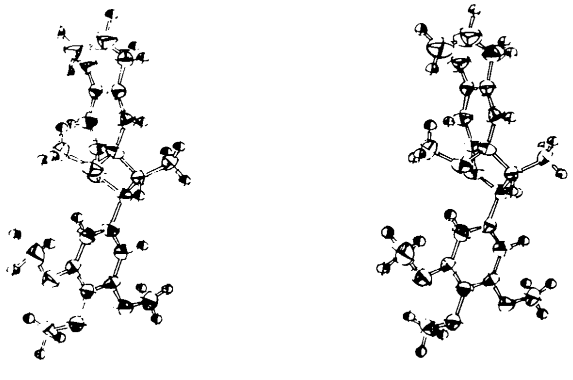

Fig. 2. Stereoview of the neolignan molecule, mirandin-A (Johnson, 1965).

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* Lists of structure factors, thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32645 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† The *R*/*S* configuration at C(3) is particularly difficult to assign using the priority rules of Cahn, Ingold & Prelog (1956).

Table 2. *The molecular conformation: selected torsion angles* (°)

Furan ring (*A*)	
O(1)–C(2)–C(3)–C(9)	+16·0
C(2)–C(3)–C(9)–C(8)	−29·2
C(3)–C(9)–C(8)–O(1)	+35·6
C(9)–C(8)–O(1)–C(2)	−26·4
C(8)–O(1)–C(2)–C(3)	+5·6
Benzo ring (*B*)	
C(4)–C(5)–C(6)–C(7)	−5·3
C(5)–C(6)–C(7)–C(8)	+4·0
C(6)–C(7)–C(8)–C(9)	+6·8
C(7)–C(8)–C(9)–C(4)	−15·0
C(8)–C(9)–C(4)–C(5)	+13·5
C(9)–C(4)–C(5)–C(6)	−4·2
Phenyl ring (*C*)	
C(15)–C(16)–C(17)–C(18)	−1·4
C(16)–C(17)–C(18)–C(19)	+2·9
C(17)–C(18)–C(19)–C(20)	−2·7
C(18)–C(19)–C(20)–C(15)	+1·1
C(19)–C(20)–C(15)–C(16)	+0·4
C(20)–C(15)–C(16)–C(17)	−0·2
Exocyclic torsion angles	
O(1)–C(2)–C(15)–C(16)	−59·0
C(4)–C(5)–C(12)–C(13)	−92·7
C(5)–C(12)–C(13)–C(14)	+2·0
C(4)–C(9)–O(2)–C(11)	+66·7
C(16)–C(17)–O(4)–C(21)	−4·4
C(17)–C(18)–O(5)–C(22)	+85·8
C(18)–C(19)–O(6)–C(23)	−173·5
Asymmetric centers	
C(8)–O(1)–C(2)–C(15)	+135·2
O(1)–C(2)–C(3)–C(10)	−105·1
C(2)–C(3)–C(9)–O(2)	+84·7

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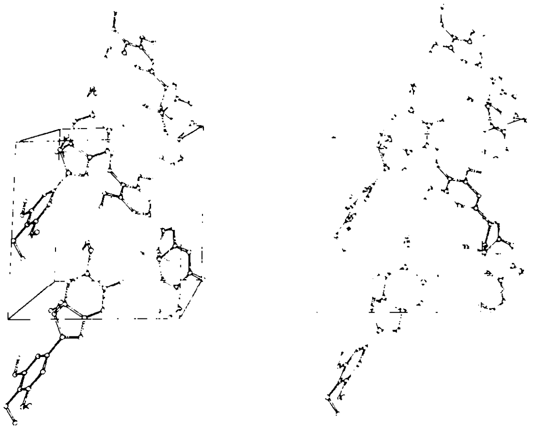

Fig. 3. Unit-cell contents and molecular packing, viewed in the direction of **c** with **b** horizontal.

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Rubidium Neodymium Metaphosphate

By H. Koizumi and J. Nakano

Musashino Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Musashino-shi, Tokyo 180, *Japan*

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Abstract. RbNdP$_4$O$_{12}$, monoclinic, $C2/c$ (C^6_{2h}), a = 7·845 (2), b = 12·691 (3), c = 10·688 (3) Å, β = 112·34 (1)°, Z = 4, U = 984·23 Å^3, D_x = 3·681 g cm^{-3}, μ(Mo $K\alpha$) = 112·2 cm^{-1}. The tetrametaphosphate (P$_4$O$_{12}$)$^{4-}$ rings, located on symmetry centres, are connected by isolated NdO$_8$ dodecahedra