Tableau 2. *Longueurs de liaison* (Å) *et angles de valence* (°)

I–C(2)	2,156 (5)	C(3)–C(8)	1,390 (7)
O–C(1)	1,218 (6)	C(4)–C(5)	1,389 (8)
C(1)–C(2)	1,504 (7)	C(5)–C(6)	1,383 (9)
C(1)–C(3)	1,488 (7)	C(6)–C(7)	1,369 (9)
C(3)–C(4)	1,391 (7)	C(7)–C(8)	1,391 (9)
I–C(2)–C(1)	107,2 (6)	C(4)–C(3)–C(8)	119,6 (10)
O–C(1)–C(2)	118,3 (9)	C(3)–C(4)–C(5)	120,2 (10)
O–C(1)–C(3)	121,2 (9)	C(4)–C(5)–C(6)	120,6 (10)
C(2)–C(1)–C(3)	120,5 (9)	C(5)–C(6)–C(7)	118,6 (13)
C(1)–C(3)–C(4)	118,4 (9)	C(6)–C(7)–C(8)	122,4 (13)
C(1)–C(3)–C(8)	121,9 (9)	C(7)–C(8)–C(3)	118,7 (10)

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(3S,7R,11E)-3,4,5,6,7,8,9,10-Octahydro-7,14,16-trihydroxy-3-methyl-1H-2-benzoxacyclotetradecen-1-one Methanol Solvate*

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Abstract. $C_{18}H_{24}O_5 \cdot CH_3OH$, $M_r = 352 \cdot 43$, monoclinic, $P2_1$, $a = 11 \cdot 212$ (2), $b = 8 \cdot 487$ (1), $c = 10 \cdot 319$ (2) Å, $\beta = 101 \cdot 55$ (2)°, $V = 962 \cdot 0$ (3) Å³, $\mu = 7 \cdot 02$ cm⁻¹, $d_c = 1 \cdot 217$ g cm⁻³, $Z = 2$. Full-matrix least-squares refinement (non-H atoms anisotropic, H atoms isotropic) based on 1783 reflexions led to a final R of 0·078. The title compound, α-zearalenol, is a naturally occurring mycotoxin isolated from the fungus *Fusarum roseum* and exhibits potent estrogenic activity. The molecule consists of a 14-membered lactone ring fused *ortho* to a 1,3-dihydroxybenzene moiety. The absolute configuration is inferred from the known C(3) stereochemistry of zearalenone from which α-zearalenol can be prepared. The solid-state conformation is similar to that of 5-hydroxyzearalenone which was determined in an earlier study. A methanol of solvation is in a position to be hydrogen bonded to three α-zearalenol molecules.
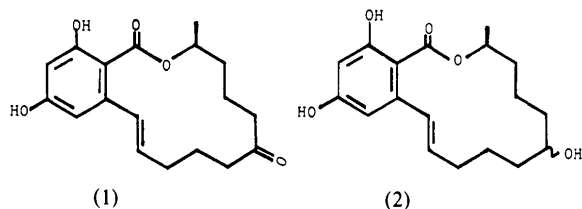
Introduction. Zearalenone (1) (Urry, Wehrmeister, Hodge & Hidy, 1966) is an estrogenic secondary metabolite produced by several species of *Fusarium*. This metabolite causes hyperestrogenism in farm animals such as swine and cattle and in a host of laboratory animals (Mirocha & Christensen, 1974).

(1)   (2)

Among a number of derivatives of zearalenone isolated from *F. roseum* (Stipanovic & Schroeder, 1975), zearalenol (2) was found to be four times more active than zearalenone in rat uterotropic assay (Pathre & Mirocha, 1976). Sodium reduction of zearalenone yields diastereomeric zearalenols with the lower melting point compound (444–444·5 K) being identical to that produced by *F. roseum* in cultures (Hagler, Mirocha, Pathre & Behrens, 1979). This naturally occurring diastereomer is also a principal metabolite identified in the urine of swine administered zearalenone (Mirocha, Pathre & Robison, 1981). The configuration at C(7) for the zearalenols prepared from zearalenone has been assigned (Shipchandler, 1975; Hidy, Baldwin, Greasham, Keith & McMullen, 1977) with the hydroxyl group of the lower melting diastereomer designated as *trans* (α) to the methyl group at C(3). Because of the importance of these compounds and the possible ambiguity of the α,β notation in large ring systems, we have determined the structure and relative configuration of the low melting zearalenol. Assuming the configuration at C(3) to be the same as in zearalenone (Kuo, Taub, Hoffsommer, Wendler, Urry & Mullenbach, 1967; Taub, Girotra, Hoffsommer, Kuo, Slater, Weber & Wendler, 1968), α-zearalenol is the (3*S*,7*R*) isomer. It is anticipated that a detailed structural knowledge of these compounds may be of assistance in mapping the active sites of estrogenic activity.

The naturally occurring diastereomer of zearalenol was dissolved in a minimum volume of hot methanol–water (65:35) and the solvent allowed to evaporate slowly under atmospheric pressure. A transparent crystal of dimensions 0·18 × 0·70 × 0·30 mm was selected for all X-ray measurements. Intensity data were collected on a Syntex $P2_1$ diffractometer system by the θ–2θ scanning technique using a variable scan speed, Cu Kα radiation (λ = 1·54178 Å) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the diffractometer. The unit cell was found to be monoclinic and systematic absences were consistent with space group $P2_1$. A periodically monitored reflexion showed no significant change in intensity. Of the 1819 independent reflexions measured (2θ < 140°) 1783 had intensities greater than 2σ(I). Lorentz and polarization corrections were applied, but no absorption corrections were made.

Table 1. *Atomic positional parameters* (×10⁴, ×10³ *for* H) *and isotropic thermal parameters*

$$U_{eq} = (U_{11}\,U_{22}\,U_{33})^{1/3}.$$

	x	y	z	U_{eq} or U (Å²)
C(1)	4414 (3)	4617 (5)	2471 (3)	43 (1)
O(1)	4121 (2)	4196 (6)	3503 (2)	67 (2)
O(2)	3608 (2)	5200 (3)	1486 (2)	44 (1)
C(3)	2342 (3)	5329 (5)	1678 (3)	47 (2)
C(4)	1565 (3)	5283 (5)	313 (4)	51 (2)
C(5)	1529 (3)	3661 (5)	−323 (4)	53 (2)
C(6)	936 (3)	3636 (5)	−1796 (4)	55 (2)
C(7)	1732 (4)	4303 (4)	−2696 (3)	45 (2)
O(7)	1036 (3)	4457 (4)	−4026 (2)	62 (2)
C(8)	2796 (3)	3250 (4)	−2758 (3)	48 (1)
C(9)	3757 (3)	3944 (5)	−3438 (3)	50 (2)
C(10)	4500 (3)	5246 (5)	−2623 (3)	47 (2)
C(11)	5261 (3)	4669 (4)	−1343 (3)	41 (1)
C(12)	5227 (3)	5257 (4)	−164 (3)	38 (1)
C(12a)	6055 (2)	4721 (3)	1071 (3)	35 (1)
C(13)	7257 (3)	4475 (4)	1002 (3)	41 (1)
C(14)	8114 (3)	3975 (4)	2107 (3)	43 (1)
O(14)	9259 (2)	3732 (4)	1940 (3)	56 (1)
C(15)	7768 (3)	3754 (4)	3301 (3)	42 (1)
C(16)	6568 (3)	4000	3384 (3)	41 (1)
O(16)	6296 (2)	3732 (4)	4581 (2)	52 (1)
C(16a)	5675 (2)	4497 (4)	2279 (3)	37 (1)
C(17)	2224 (4)	6834 (8)	2430 (5)	72 (2)
C(CH₃OH)	−1831 (14)	6514 (11)	−3718 (7)	127 (7)
O(CH₃OH)	−570 (3)	7190 (4)	−4058 (3)	63 (1)
H(3)	223 (4)	435 (7)	219 (4)	47 (11)
H(4a)	55 (6)	573 (8)	16 (6)	76 (15)
H(4b)	191 (3)	625 (5)	−26 (3)	37 (8)
H(5a)	219 (4)	303 (6)	−7 (4)	45 (9)
H(5b)	102 (6)	297 (11)	21 (6)	90 (18)
H(6a)	16 (6)	442 (9)	−203 (5)	74 (14)
H(6b)	77 (5)	247 (7)	−198 (5)	55 (11)
H(7a)	211 (4)	535 (7)	−246 (4)	48 (10)
H(8a)	319 (4)	283 (6)	−177 (4)	56 (11)
H(8b)	229 (4)	242 (6)	−325 (4)	49 (10)
H(9a)	447 (6)	295 (6)	−355 (4)	72 (14)
H(9b)	323 (6)	421 (9)	−427 (6)	73 (14)
H(10a)	516 (5)	596 (7)	680 (5)	57 (12)
H(10b)	388 (3)	615 (5)	−240 (3)	35 (8)
H(11)	571 (9)	383 (16)	−133 (9)	120 (28)
H(12)	488 (4)	621 (7)	−5 (5)	47 (10)
H(13)	747 (3)	469 (5)	15 (4)	40 (9)
H(15)	831 (4)	337 (6)	394 (5)	44 (10)
H(17a)	153 (6)	677 (7)	289 (5)	56 (11)
H(17b)	205 (5)	772 (7)	179 (5)	54 (12)
H(17c)	297 (4)	701 (7)	309 (4)	53 (11)

Table 2. *Interatomic distances* (Å)

C(1)–O(2)	1·315 (3)	C(9)–C(10)	1·531 (5)
C(1)–O(1)	1·228 (4)	C(10)–C(11)	1·503 (4)
C(1)–C(16a)	1·469 (4)	C(11)–C(12)	1·323 (4)
O(2)–C(3)	1·476 (4)	C(12)–C(12a)	1·490 (4)
C(3)–C(4)	1·501 (5)	C(12a)–C(13)	1·380 (4)
C(3)–C(17)	1·514 (7)	C(12a)–C(16a)	1·408 (4)
C(4)–C(5)	1·523 (6)	C(13)–C(14)	1·402 (4)
C(5)–C(6)	1·532 (5)	C(14)–O(14)	1·345 (4)
C(6)–C(7)	1·520 (6)	C(14)–C(15)	1·377 (5)
C(7)–O(7)	1·443 (4)	C(15)–C(16)	1·381 (5)
C(7)–C(8)	1·502 (5)	C(16)–O(16)	1·349 (4)
C(8)–C(9)	1·518 (6)	C(16)–C(16a)	1·423 (4)

The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 350 $|E|$ values greater than 1·23. The phase set with the largest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of 18 atoms. Alternate least-squares refinements and difference Fourier calculations were used to locate the remaining atoms. The three hydroxyl H atoms could not be found. Full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms was terminated at an R of 0·078 where $R = \sum||F_o| - |F_c||/\sum|F_o|$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(I)$ was determined from counting statistics. H-atom thermal parameters were refined isotropically.

Atomic scattering factors and the real and imaginary parts of the anomalous dispersion were calculated by the XRAY 76 program (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic positional parameters and U_{eq} values are presented in Table 1 while interatomic distances, valence angles and torsion angles are given in Tables 2, 3 and 4.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36494 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Valence angles* (°)

O(2)–C(1)–O(1)	121·1 (3)	C(10)–C(11)–C(12)	124·7 (3)
O(2)–C(1)–C(16a)	116·9 (3)	C(11)–C(12)–C(12a)	123·0 (3)
O(1)–C(1)–C(16a)	121·9 (3)	C(12)–C(12a)–C(13)	116·7 (3)
C(1)–O(2)–C(3)	117·1 (2)	C(12)–C(12a)–C(16a)	123·5 (3)
O(2)–C(3)–C(17)	108·5 (3)	C(13)–C(12a)–C(16a)	119·8 (3)
O(2)–C(3)–C(4)	105·4 (3)	C(12a)–C(13)–C(14)	121·4 (3)
C(4)–C(3)–C(17)	114·1 (3)	C(13)–C(14)–O(14)	117·3 (3)
C(3)–C(4)–C(5)	112·9 (3)	C(13)–C(14)–C(15)	119·9 (3)
C(4)–C(5)–C(6)	114·1 (3)	O(14)–C(14)–C(15)	122·8 (3)
C(5)–C(6)–C(7)	114·2 (3)	C(14)–C(15)–C(16)	119·2 (3)
C(6)–C(7)–O(7)	110·0 (3)	C(15)–C(16)–O(16)	115·7 (2)
C(6)–C(7)–C(8)	111·9 (3)	C(15)–C(16)–C(16a)	122·2 (3)
O(7)–C(7)–C(8)	107·2 (3)	O(16)–C(16)–C(16a)	122·1 (3)
C(7)–C(8)–C(9)	115·6 (3)	C(16)–C(16a)–C(1)	117·0 (3)
C(8)–C(9)–C(10)	112·6 (3)	C(16)–C(16a)–C(12a)	117·4 (3)
C(9)–C(10)–C(11)	113·5 (3)	C(1)–C(16a)–C(12a)	125·4 (2)

Table 4. *Torsion angles* (°)

Standard deviations are in the range 0·2–0·5°.

1–O(2)–3–4	−154·6 (−163)*	8–9–10–11	65·2 (118)
O(2)–3–4–5	71·3 (65)	9–10–11–12	−125·5 (−131)
3–4–5–6	−169·7 (−171)	10–11–12–12a	−175·9 (−172)
4–5–6–7	75·5 (73)	11–12–12a–16a	−139·6 (−139)
5–6–7–8	69·8 (80)	12–12a–16a–1	5·7 (−3)
6–7–8–9	−169·9 (−167)	12a–16a–1–O(2)	−10·4 (1)
7–8–9–10	71·1 (64)	16a–1–O(2)–3	−179·7 (−175)
5–6–7–O(7)	−171·1	15–16–16a–1	176·1
9–8–7–O(7)	69·3	14–13–12a–12	179·8
1–O(2)–3–17	82·8	12a–13–14–O(14)	178·6
5–4–3–17	−169·8	14–15–16–O(16)	178·9
O(1)–1–O(2)–3	0·2	16–16a–12a–12	−179·2
O(1)–1–16a–16	−5·4	O(16)–16–16a–12a	−179·1
O(16)–16–16a–1	−3·6		

* Torsion angles for 5-hydroxyzearalenone (Taylor & Watson, 1976) are in parentheses.

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1965) of α-zearalenol. As indicated by the torsion angles in Table 4, the phenyl ring along with C(1)O(1)O(2)C(3)C(12)O(14) and O(16) form a planar system. The coplanarity of the phenyl ring and the conjugated carbonyl is further assisted by an internal hydrogen bond between O(1) and O(16) of 2·502 (3) Å. Although the O(16) hydrogen cannot be located, the present structure is analogous to that of 5-hydroxyzearalenone in which hydrogen bonding has been demonstrated (Taylor & Watson, 1976). The C(11)–C(12) *trans* double bond is twisted out of the plane of the phenyl ring as indicated by the C(16a)C(12a)C(12)C(11) torsion angle of −139·6°; however, the C(12)–C(12a) distance of 1·490 (4) Å indicates some degree of conjugation. The torsion angles around the 14-membered ring are similar to those reported for 5-hydroxyzearalenone (Taylor & Watson, 1976) with the maximum deviation occurring about the C(9)–C(10) bond. Atoms C(6)C(7)C(8)C(9) and C(5)C(6)C(7)O(7) form reasonably planar segments within the molecule as indicated by torsion angles of −169·9 and −171·1° respectively. The absolute configuration at C(3) has been assigned in zearalenone (Kuo *et al.*, 1967; Taub *et al.*, 1968) and naturally occurring α-zearalenol, which can be prepared by the sodium reduction of zearalenone, must have the same stereochemistry at C(3). The stereochemistry at C(7) is then established and the absolute configuration of the low melting stereoisomer must be (3S,7R). A molecule of solvation is most likely methanol from which α-zearalenol was recrystallized. The oxygen position is well defined due to possible hydrogen bonding with three different zearalenol molecules. The angles around the O atom are approximately tetrahedral with distances O(7)···O(MeOH) 2·933 (5), O(14)···O(MeOH) (1 − x, ½ + y, −z) 2·714 (4) and O(7)···O(MeOH) (−x,

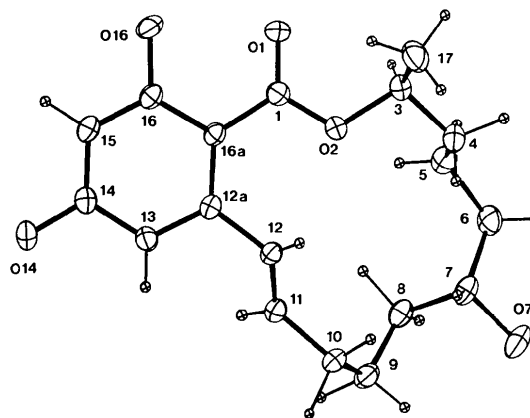Fig. 1. ORTEP drawing of α-zearalenol. Thermal ellipsoids are drawn at the 35% probability level while H atoms are represented by spheres of arbitrary size.

$\frac{1}{2} + y$, $-1 - z$) 2·733 Å. The C—O distance in the solvated molecule is unacceptably long at 1·63 Å; however, the electron density associated with the carbon position is not well defined.

Although the conformation of the phenyl ring and the attached atoms is similar to that of the *A* and *B* rings in estrone and estradiol, the conformation of the remainder of the 14-membered ring differs considerably from the perimeter atom arrangement in the steroids. The functional groups and their geometric relationship must be of importance in active-site binding; however, the 14-membered ring is flexible and the solid-state conformation may differ significantly from that in solution. Nevertheless, it should be noted that the $O(3)\cdots O(17)$ and $O(3)\cdots O(18)$ separations in estradiol and its derivatives (Duax & Norton, 1975) average 11·0 and 8·6 Å while the $O(14)\cdots O(7)$ and $O(14)\cdots C(17)$ distances in α-zearalenol are 10·03 and 8·43 Å respectively. The relationships between C(18), O(17) and C(7), O(7) are not comparable.

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Structure of 1,1,1-Tris[(diphenylphosphino)methyl]ethane (Triphos)

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Abstract. $C_{41}H_{39}P_3$, $M_r = 624\cdot69$, triclinic, $P\bar{1}$, $a = 13\cdot487$ (5), $b = 13\cdot573$ (5), $c = 10\cdot484$ (5) Å, $\alpha = 104\cdot73$ (9), $\beta = 106\cdot37$ (8), $\gamma = 97\cdot73$ (8)°, $V = 1736\cdot4$ Å^3, $Z = 2$, $F(000) = 660$, $D_c = 1\cdot19$, $D_m = 1\cdot19$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1\cdot58$ mm^{-1}; $R = 0\cdot077$, $R_w = 0\cdot093$ for 3073 unique reflections. The structure is composed of isolated molecules. The three-armed molecule has neither crystallographic nor pseudo threefold symmetry as the conformation of one of the three aliphatic chains markedly differs from that of the other two. A comparison between the geometries of uncoordinated and coordinated triphos shows that only a minor rearrangement of the chains, such as a crossing of the torsional barrier from one staggered conformation to an equivalent one, is sufficient to coordinate most metal atoms.

Introduction. 1,1,1-Tris[(diphenylphosphino)methyl]-ethane, triphos, has been shown to be a ligand which can stabilize a great variety of coordination compounds (Sacconi & Mani, 1982). At least 16 X-ray structure determinations of such compounds have been carried out in recent years in this laboratory (Bianchini, Dapporto & Meli, 1979; Bianchini, Dapporto, Meli &