Crystal and Molecular Structure of the Germination Stimulant Strigol by *X*-Ray Analysis [1]

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Single crystal *X*-ray analysis has defined the constitution and relative stereochemistry of strigol (1) a potent seed germination stimulant for witchweed (*Striga lutea* Lour.). Crystals are orthorhombic, space group $P2_12_12_1$ with $Z = 4$ in a unit cell of dimensions $a = 9{\cdot}15$, $b = 12{\cdot}37$, $c = 15{\cdot}37$ Å. The crystal structure was elucidated from photographic data by direct phase-determining methods, and the molecular parameters refined by full-matrix least-squares calculations to R 0·082 over 1650 independent reflections.

STRIGOL, $C_{19}H_{22}O_6$, a highly potent seed germination stimulant was isolated from the root exudates of cotton, *Gossypium hirsutum* L.[2] Extensive spectroscopic and n.m.r. studies established the presence of hydroxy, butenolide, and enol ether moieties, and permitted unambiguous assignment of all the proton resonances, but the complete structure could not be derived. We therefore undertook an *X*-ray study of this novel compound.

EXPERIMENTAL

Strigol crystallizes from benzene–hexane as colourless needles [m.p. 200—202 °C (decomp.)] elongated in the a direction. All data were obtained from a single crystal of dimensions *ca.* 2·0 × 0·2 × 0·2 mm.

Crystal Data.—$C_{19}H_{22}O_6$, $M = 346{\cdot}4$. Orthorhombic, $a = 9{\cdot}15(2)$, $b = 12{\cdot}37(2)$, $c = 15{\cdot}37(2)$ Å, $U = 1740$ Å^3, $D_m = 1{\cdot}32$, $Z = 4$, $D_c = 1{\cdot}322$, $F(000) = 736$, μ(Cu-K_α, $\lambda = 1{\cdot}542$ Å) $= 8{\cdot}2$ cm^{-1}. Space group $P2_12_12_1$ (D_2^4) from systematic absences: $h00$ when $h \neq 2n$, $0k0$ when $k \neq 2n$, and $00l$ when $l \neq 2n$.

Crystallographic Measurements.—Unit-cell dimensions were evaluated from precession photographs taken with Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation.

Intensity data for the 0—$8kl$ reciprocal lattice nets were recorded by equi-inclination multiple-film Weissenberg photography by use of Cu-K_α radiation. Intensity measurements were made on a Joyce–Loeble integrating microdensitometer, and the usual Lorentz and polarization corrections applied to yield 1650 observed structure amplitudes. Absorption was neglected.

Structure Analysis.—The structure was solved by direct phase-determining methods. Initially, three origin-defining reflections were chosen and phases assigned, 3,7,10, $|E|$ 3·03, $\phi = 0$; 1,7,11, $|E|$ 2·77, $\phi = 0$; and 2,7,4, $|E|$ 2·46, $\phi = 0$. A fourth reflection (6,3,0, $|E|$ 2·47) was assigned a phase, $\phi = \pi$, to specify the enantiomorph, and one further reflection (1,11,2, $|E|$ 2·40) was assigned a symbolic phase, $\phi = a$. These five reflections were expanded into a set of twenty-four reflections for which $|E_H{\cdot}E_K{\cdot}E_{H-K}| > 10{\cdot}0$, and the tangent formula [3] was used to generate phases for other reflections with $|E_H| > 1{\cdot}0$. The unknown phase, a, was allowed to assume values $0 < a < \pi$ in increments of $\pi/4$ when input to the tangent refinement program. During the first nine iterations 150 reflections with the largest $|E_H|$ values were refined and 498 were included in the next fifteen cycles. In any cycle a phase assignment was rejected if the consistency index, $t = \sqrt{A^2 + B^2}/\Sigma_K|E_K| \cdot |E_{H-K}|$ was $<0{\cdot}40$, and $\alpha = |E_H| \cdot \sqrt{A^2 + B^2}$ was $<6{\cdot}0$. The set for which $a = 3\pi/4$ assigned the greatest number of phases, 218, and an E map was evaluated by use of the generated phases.

From the E map a thirteen-atom partial structure [C(1), C(3)—(7), C(10)—(12), O(15), O(17), O(18), and C(19)] was identified, and these atoms were included, all weighted as carbon atoms with B 3·5 Å^2, in a structure-factor calculation for which R was 0·55. Five cycles of full-matrix least-squares calculations refined the positional and isotropic thermal parameters, and reduced R to 0·49.

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[1] Preliminary communication, C. E. Cook, L. P. Whichard, M. E. Wall, G. H. Egley, P. Coggon, P. A. Luhan, and A. T. McPhail, *J. Amer. Chem. Soc.*, 1972, **94**, 6198.

[2] C. E. Cook, L. P. Whichard, B. Turner, M. E. Wall, and G. H. Egley, *Science*, 1966, **154**, 1189.

[3] J. Karle and H. Hauptmann, *Acta Cryst.*, 1956, **9**, 635.

A three-dimensional difference-Fourier synthesis with weighted coefficients[4] was then evaluated. Approximate positions for a further twelve atoms were thus obtained, and when these were included in the subsequent structure-factor calculation R decreased to 0·39. Six cycles of least-squares adjustment of the positional and isotropic thermal parameters reduced R to 0·28. During these iterations it became apparent that two atoms were misplaced since their temperature factors became unreasonably large, and so they were omitted from the calculations. As a result of these calculations it was also evident that atoms (15), (16), and (17) were oxygen atoms and they were appropriately weighted in subsequent calculations.

A three-dimensional difference-Fourier synthesis was computed and gave improved positions for the two previously misplaced atoms. Three cycles of least-squares refinement of positional and isotropic thermal parameters of all twenty-five atoms decreased R to 0·15 at which point atoms (18), (20), and (24) were also identified as oxygen atoms. Two cycles of adjustment of positional and anisotropic temperature factor parameters reduced R to 0·108. In a subsequent difference-Fourier map, significant electron density was present at most positions calculated for the hydrogen atoms, assuming C–H 1·07 and O–H 1·05 Å, and geometries appropriate to the state of hybridization at the bonded atom. In addition, for the C(13) and C(14) methyl groups the C–H bonds were assumed to be staggered with respect to the C–C bonds from C(1), and the hydroxy-proton was taken to lie on the line of centres between O(15) and O(24) at 2·8 Å in a neighbouring molecule. The C(25) methyl hydrogen atoms could not be placed with certainty. Inclusion of nineteen hydrogen atoms, with B 4·0 Å^2, in the next structure-factor calculation decreased R to 0·097. Five further rounds of least-squares calculations in which fixed hydrogen atom contributions were included, brought the refinement to convergence at R 0·082. Final atomic positions and thermal parameters are given in Table 1.

For all structure-factor calculations scattering factors for carbon, hydrogen, and oxygen were taken from ref. 5. In the least-squares calculations weights w were assigned according to the scheme $\sqrt{w} = 1$ for $|F_o| \leqslant 12{\cdot}0$ and $\sqrt{w} = 12{\cdot}0/|F_o|$ for $|F_o| > 12{\cdot}0$, and $\Sigma w\Delta^2$ was minimized. At the end of the refinement, analysis of $\langle w\Delta^2\rangle$ in ranges of $|F_o|$ and $\sin\theta$ confirmed that this scheme was adequate.†

RESULTS AND DISCUSSION

This X-ray analysis defines the structure and relative stereochemistry of strigol as (1) which constitution is entirely consistent with all the spectral data reported in ref. 1. The molecular conformation in the crystal is shown in Figure 1, and distances and angles in Table 2.

Displacements of various atoms from least-squares planes through groups of atoms were calculated in order to define the shape of the molecule; the results are in Table 3. Rings A, B, and C form a rigid molecular

TABLE 1

Fractional atomic co-ordinates and anisotropic thermal parameters, with estimated standard deviations in parentheses

(a) Fractional co-ordinates

Atom	x/a	y/b	z/c
C(1)	0·1426(6)	0·2760(4)	−0·2118(3)
C(2)	0·1361(7)	0·1608(3)	−0·2506(4)
C(3)	0·2309(7)	0·0822(5)	−0·1991(4)
C(4)	0·1762(7)	0·0688(4)	−0·1077(4)
C(5)	0·1403(6)	0·1763(4)	−0·0693(3)
C(6)	0·1237(6)	0·2684(4)	−0·1155(3)
C(7)	0·1104(7)	0·1915(4)	0·0270(4)
C(8)	0·0711(6)	0·3118(4)	0·0354(3)
C(9)	0·0743(6)	0·3586(4)	−0·0584(4)
C(10)	0·1797(6)	0·3835(4)	0·0810(4)
C(11)	0·2408(6)	0·4611(4)	0·0200(3)
C(12)	0·2183(6)	0·3850(5)	0·1643(4)
C(13)	0·0220(8)	0·3452(6)	−0·2512(4)
C(14)	0·2906(7)	0·3292(5)	−0·2326(4)
O(15)	0·2817(5)	0·0116(3)	−0·0586(3)
O(16)	0·3316(5)	0·5311(3)	0·0331(3)
O(17)	0·1786(5)	0·4491(3)	−0·0584(2)
O(18)	0·1644(5)	0·3096(3)	0·2211(2)
C(19)	0·1733(6)	0·3413(5)	0·3098(3)
O(20)	0·0596(5)	0·4157(3)	0·3286(3)
C(21)	−0·0225(7)	0·3739(5)	0·3927(4)
C(22)	0·0367(7)	0·2664(5)	0·4195(4)
C(23)	0·1498(7)	0·2469(4)	0·3671(4)
O(24)	−0·1287(6)	0·4201(4)	0·4210(3)
C(25)	−0·0282(10)	0·2010(7)	0·4904(5)
H(2α)	0·026	0·133	−0·249
H(2β)	0·174	0·163	−0·316
H(3α)	0·340	0·113	−0·198
H(3β)	0·229	0·006	−0·231
H(4)	0·080	0·020	−0·108
H(7α)	0·021	0·142	0·048
H(7β)	0·205	0·172	0·065
H(8)	−0·033	0·319	0·064
H(9)	−0·031	0·386	−0·078
H(12)	0·306	0·436	0·197
H(13α)	−0·081	0·308	−0·237
H(13β)	0·036	0·351	−0·320
H(13γ)	0·026	0·425	−0·225
H(14α)	0·375	0·281	−0·205
H(14β)	0·304	0·335	−0·301
H(14γ)	0·295	0·409	−0·206
H(15)	0·227	−0·021	−0·009
H(19)	0·278	0·376	0·323
H(23)	0·193	0·171	0·386

(b) Anisotropic thermal parameters ($\times 10^4$) *

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	48(6)	50(3)	25(2)	5(8)	−6(6)	6(4)
C(2)	98(8)	55(4)	30(2)	6(10)	3(7)	−7(5)
C(3)	92(8)	47(3)	35(2)	−12(9)	17(7)	−23(5)
C(4)	84(7)	34(3)	33(2)	−16(8)	26(7)	3(4)
C(5)	43(6)	45(3)	29(2)	−9(7)	12(6)	−6(4)
C(6)	45(6)	42(3)	27(2)	3(7)	4(6)	−1(4)
C(7)	102(8)	42(3)	27(2)	−11(9)	34(7)	−5(5)
C(8)	66(6)	44(3)	24(2)	8(8)	27(6)	−4(4)
C(9)	53(6)	45(3)	30(2)	5(8)	−2(6)	4(4)
C(10)	60(7)	43(3)	31(2)	−5(8)	10(6)	−5(4)
C(11)	83(7)	43(3)	27(2)	−1(8)	19(7)	−4(4)
C(12)	60(7)	60(4)	26(2)	−1(8)	12(6)	12(5)
C(13)	102(9)	88(5)	33(2)	42(12)	−26(8)	8(7)
C(14)	91(8)	66(4)	35(2)	−26(10)	43(7)	−1(6)
O(15)	105(6)	47(2)	44(2)	37(6)	17(6)	12(4)
O(16)	119(6)	57(2)	41(2)	−52(7)	4(6)	13(4)
O(17)	111(6)	37(2)	28(1)	−22(6)	9(5)	2(3)
O(18)	117(6)	58(2)	22(1)	−39(7)	6(5)	5(3)
C(19)	74(7)	57(3)	25(2)	5(9)	8(6)	−6(5)
O(20)	107(6)	50(2)	34(2)	18(7)	−9(6)	−3(4)
C(21)	64(7)	72(4)	34(2)	14(9)	−23(7)	−37(5)
C(22)	83(7)	57(4)	26(2)	−38(9)	9(7)	−10(5)
C(23)	80(7)	48(3)	31(2)	−6(9)	10(7)	−3(5)
O(24)	110(6)	112(4)	57(2)	67(9)	0(7)	−82(5)
C(25)	188(12)	101(6)	90(3)	−98(14)	62(10)	21(7)

* In the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

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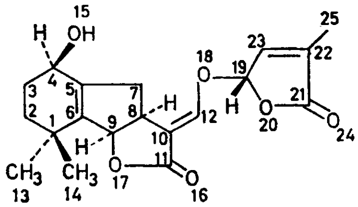
† Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20617 (9 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

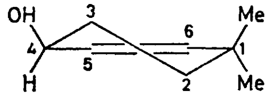
[4] G. A. Sim, in 'Computing Methods and the Phase Problem in X-Ray Crystal Analysis,' ed. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon, Oxford, 1961, p. 227.

[5] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

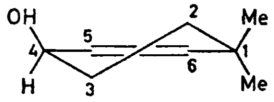


(1)

framework with conformational flexibility occurring only in ring A which would be expected to adopt either of the two half-chair[6] forms (2a) or (2b). In the crystals the cyclohexene ring adopts conformation (2a) with atoms C(2) and C(3) displaced by 0·403 and 0·348 Å to opposite sides of the plane through C(1), C(4)—(6), and C(3) is on the same side as the *quasi*-equatorial hydroxyl substituent O(15). Ring A torsion angles (Figure 2) also demonstrate that the conformation deviates by only a small amount from C_2 symmetry, probably owing to the strong intermolecular hydrogen



(2a)



(2b)

TABLE 2

Interatomic distances (Å) and valency angles (deg.), with standard deviations in parentheses

(*a*) Bonded distances

C(1)–C(2)	1·545(8)	C(9)–O(17)	1·471(7)
C(1)–C(6)	1·494(7)	C(10)–C(11)	1·454(8)
C(1)–C(13)	1·523(9)	C(10)–C(12)	1·328(8)
C(1)–C(14)	1·539(9)	C(11)–O(16)	1·218(7)
C(2)–C(3)	1·525(9)	C(11)–O(17)	1·341(7)
C(3)–C(4)	1·501(8)	C(12)–O(18)	1·369(7)
C(4)–C(5)	1·492(7)	O(18)–C(19)	1·422(6)
C(4)–O(15)	1·415(7)	C(19)–O(20)	1·418(7)
C(5)–C(6)	1·350(7)	C(19)–C(23)	1·478(8)
C(5)–C(7)	1·516(8)	O(20)–C(21)	1·342(7)
C(6)–C(9)	1·489(7)	C(21)–C(22)	1·494(8)
C(7)–C(8)	1·536(7)	C(21)–O(24)	1·208(8)
C(8)–C(9)	1·553(7)	C(22)–C(23)	1·333(8)
C(8)–C(10)	1·505(8)	C(22)–C(25)	1·482(10)

(*b*) Valency angles

C(2)–C(1)–C(6)	108·6(4)	C(6)–C(9)–O(17)	111·9(4)
C(2)–C(1)–C(13)	109·7(5)	C(8)–C(9)–O(17)	107·2(4)
C(2)–C(1)–C(14)	110·4(5)	C(8)–C(10)–C(11)	110·0(4)
C(6)–C(1)–C(13)	110·2(5)	C(8)–C(10)–C(12)	129·3(5)
C(6)–C(1)–C(14)	109·6(4)	C(11)–C(10)–C(12)	120·7(5)
C(13)–C(1)–C(14)	108·4(5)	C(10)–C(11)–O(16)	128·7(5)
C(1)–C(2)–C(3)	111·5(5)	C(10)–C(11)–O(17)	110·1(4)
C(2)–C(3)–C(4)	111·4(5)	O(16)–C(11)–O(17)	121·2(5)
C(3)–C(4)–C(5)	110·2(4)	C(10)–C(12)–O(18)	120·6(5)
C(3)–C(4)–O(15)	109·1(5)	C(9)–O(17)–C(11)	111·0(4)
C(5)–C(4)–O(15)	112·7(4)	C(12)–O(18)–C(19)	113·7(4)
C(4)–C(5)–C(6)	124·7(5)	O(18)–C(19)–O(20)	109·4(4)
C(4)–C(5)–C(7)	122·4(4)	O(18)–C(19)–C(23)	110·2(4)
C(6)–C(5)–C(7)	112·8(4)	O(20)–C(19)–C(23)	106·5(4)
C(1)–C(6)–C(5)	124·1(5)	C(19)–O(20)–C(21)	108·0(4)
C(1)–C(6)–C(9)	124·9(4)	O(20)–C(21)–C(22)	110·0(5)
C(5)–C(6)–C(9)	110·8(4)	O(20)–C(21)–O(24)	122·1(6)
C(5)–C(7)–C(8)	104·1(4)	C(22)–C(21)–O(24)	127·8(6)
C(7)–C(8)–C(9)	106·2(4)	C(21)–C(22)–C(23)	106·0(5)
C(7)–C(8)–C(10)	117·1(5)	C(21)–C(22)–C(25)	123·0(6)
C(9)–C(8)–C(10)	101·5(4)	C(23)–C(22)–C(25)	131·0(6)
C(6)–C(9)–C(8)	105·9(4)	C(19)–C(23)–C(22)	109·2(5)

(*c*) Some intramolecular non-bonded distances (Å)

C(7) ··· O(18)	3·36	C(12) ··· C(23)	3·61
		C(14) ··· O(17)	3·23

(*d*) Intermolecular separations <3·6 Å

O(24) ··· O(15^{II})	2·78	O(24) ··· C(7^{II})	3·46
C(21) ··· O(16^{I})	3·02	O(16) ··· C(25^{II})	3·50
O(24) ··· O(16^{I})	3·28	C(2) ··· O(24^{III})	3·54
C(22) ··· O(16^{I})	3·28	O(15) ··· C(25^{IV})	3·54
O(20) ··· O(16^{I})	3·36	C(11) ··· C(25^{II})	3·55
O(20) ··· O(17^{I})	3·40	C(19) ··· O(17^{I})	3·56
O(24) ··· C(4^{II})	3·44	O(17) ··· C(25^{II})	3·56
O(15) ··· C(8^{III})	3·45	O(20) ··· C(14^{I})	3·57
O(15) ··· C(23^{IV})	3·45	O(16) ··· C(4^{III})	3·58

Roman numeral superscripts refer to the following co-ordinate transformations:

I $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
II $-x, \frac{1}{2} + y, \frac{1}{2} - z$
III $\frac{1}{2} + x, \frac{1}{2} - y, -z$
IV $\frac{1}{2} - x, -y, -\frac{1}{2} + z$

TABLE 3

Equations of mean planes, through groups of atoms, in the form $AX + BY + CZ - D = 0$ where X, Y, and Z are orthogonal co-ordinates in Å; displacements (Å) of some atoms from the planes are given in square brackets

Plane (*A*):

C(1), C(4)—(6) $-0·974X - 0·194Y - 0·120Z + 1·538 = 0$
[C(1) −0·003, C(4) 0·003, C(5) −0·006, C(6) 0·006, C(2) 0·403, C(3) −0·348, C(7) 0·045, C(8) 0·090, C(9) 0·123, C(13) 0·980, C(14) −1·410, O(15) −0·891]

Plane (*B*):

C(5)—(9) $-0·960X - 0·239Y - 0·145Z + 1·605 = 0$
[C(5) 0·006, C(6) −0·018, C(7) 0·009, C(8) −0·019, C(9) 0·023, C(1) 0·007, C(4) 0·093]

Plane (*C*):

C(8)—(11), O(17) $0·730X - 0·639Y - 0·244Z + 2·122 = 0$
[C(8) 0·002, C(9) 0·006, C(10) −0·010, C(11) 0·014, O(17) −0·013, C(12) −0·075, O(16) 0·018, O(18) −0·053]

Plane (*D*):

C(19), O(20), C(21)—(23) $-0·592X - 0·434Y - 0·679Z + 5·988 = 0$
[C(19) −0·016, O(20) 0·006, C(21) 0·007, C(22) −0·017, C(23) 0·021, O(24) 0·039, C(25) −0·054, O(18) 1·129]

Plane (*E*):

C(8), C(10)—(12), O(18) $0·737X - 0·639Y - 0·218Z + 2·097 = 0$
[C(8) −0·007, C(10) 0·006, C(11) 0·009, C(12) −0·025, O(18) 0·016, C(11) 0·009, O(16) 0·024]

Dihedral angles (deg.) between planes are:

(*A*)–(*B*)	3	(*C*)–(*E*)	2
(*B*)–(*C*)	59		

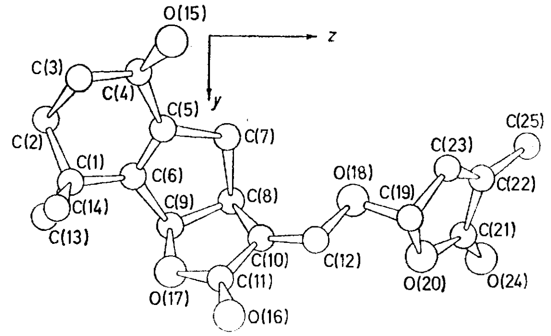


FIGURE 1 Molecular structure of strigol, viewed in projection along the *a* axis

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[6] F. R. Jensen and C. H. Bushweller, *J. Amer. Chem. Soc.*, 1969, **91**, 5774, and references therein.

bond (*vide infra*). Dreiding molecular models show that alternative conformation (2b) for ring A would have an unfavourable non-bonded separation of *ca.* 2·83 Å between the *quasi*-axial C(14) methyl group and O(17) of γ-lactone ring C compared to the observed conformation which has C(14) in a *quasi*-equatorial orientation and a C(14) · · · O(17) distance (3·23 Å) which is only slightly shorter than the sum of the van der Waals radii [7] (3·40 Å).

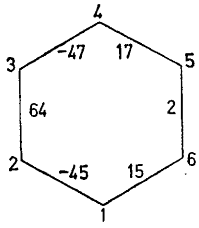


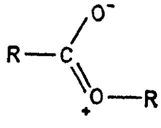
FIGURE 2 Torsion angles (deg.) in ring A of strigol

The mean internal angle in the *cis*-fused five-membered B and C rings is 108°, and consequently these rings are planar with a dihedral angle of 59° between the planes. Atoms C(12), O(16), and O(18) lie close to planar ring C, the dihedral angle between planes (*E*) [C(8), C(10), C(11), C(12), O(18)] and (*C*) being 3°. In the absence of steric overcrowding the preferred conformation at phenyl methoxy-groups is that which has the methyl carbon atom in or near the ring plane [8-12] and thus provides maximum delocalization of the non-bonded oxygen lone pair electrons with the ring π-electron system. A similar conformational preference would be expected to exist in α,β-unsaturated ethers and this has been found in 7-hydroxy-1,9,10-trimethoxy-4-azabicyclo[5,2,2]-undeca-8,10-dien-3-one [13] where the methyl groups are close to the C·C:C(O)·C plane and are *cis*-oriented with respect to the double bond. In strigol, non-bonded interactions prevent adoption of a *cis*-orientation with respect to the C(10)–C(12) double bond. The H(12) · · · H(19) repulsive interaction results in a C(10)–C(12)–O(18)–C(19) torsion angle [14] of 160° which places C(19) 0·472 Å from plane (*E*), and the geometry approximates to *trans*-planar.

Unsaturated γ-lactone ring D has a mean internal angle of 108° and it is therefore planar. This ring is linked to the rigid C(1)–O(18) framework by the O(18)–C(19) single-bond around which there is relatively free rotation. The torsion angle of 78° found in the crystal results from a conformation which minimizes non-bonded repulsive interactions between H(12) and ring D atoms.

The mean C(*sp*^{3})–C(*sp*^{3}) and C(*sp*^{3})–C(*sp*^{2}) bond lengths (1·532 and 1·494 Å), agree satisfactorily with normal values [15] [1·537(5) and 1·505(5) Å] and none of the individual lengths deviates significantly from the mean. The mean C(*sp*^{2})–C(*sp*^{2}) double-bond value (1·337 Å) agrees well with that accepted [15] for such bonds [1·335(5) Å]. The mean value of the C(*sp*^{2})–C(*sp*^{2}) single bonds (1·474 Å) is close to the sum of the covalent radii [16] (1·48 Å).

The C(4)–O(15) bond length, 1·415(7) Å, is similar to the mean of C–O(hydroxy) bonds in *e.g.* methyl-α-D-galactopyranoside monohydrate [17] (1·419 Å) and 1,6-anhydro-β-D-glucopyranose [18] (1·413 Å), and is only slightly shorter than the mean [1·426(5) Å] for saturated alcohols.[15] The C(12)–O(18) single-bond length [1·369(7) Å] is close to C(Ph)–O(methoxy) lengths at phenyl methoxy-groups, *e.g.* 1·360(7) and 1·363(6) in sceletium alkaloid A_4,[8] 1·373(6) and 1·374(6) Å in mesembranol,[9] and to the mean of 1·361 Å at two methoxy-groups in 7-hydroxy-1,9,10-trimethoxy-4-azabicyclo[5,2,2]undeca-8,10-dien-3-one.[13] In the lactone groups the mean C=O length (1·213 Å) is normal but the C–O single-bond lengths require further comment. It is a well established feature of lactone groups that the C·C(O)·O·C moiety is planar [19] unless subjected to severe steric strain,[20] and the observed geometry may be explained on the basis of contributions from resonance form (3). Moreover, the results from a number of accurate *X*-ray analyses led Merlino [21] to suggest that differences observed in C(*sp*^{2})–O and C(*sp*^{3})–O single-bond lengths in esters and lactones could be ascribed to varying contributions from (3). A consequence of this conclusion is that the sum of the C(*sp*^{2})–O and C(*sp*^{3})–O bond lengths in esters and lactones remains constant, the mean sum of the values cited by Merlino being 2·807(8) Å. In ring C of strigol, the sum of the C(9)–O(17) and C(11)–O(17) lengths, 2·812 Å, agrees well with this value. However, in ring D the corresponding lengths, C(21)–O(20) and C(20)–O(19), total 2·760 Å, a distance which is significantly less than 2·807 Å. The bond



(3)

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lengths obtained from recent *X*-ray analyses of carbohydrates[22] reveal that in the C·CH(OR)·O· moieties the C–O lengths are unequal (anomeric effect). In furanosides it has been found that the endocyclic C–O bond is shortened, and we conclude that a similar effect is in operation at C(19) in strigol, and that it results in a significant reduction of the endocyclic C(19)–O(20) distance.

The molecular arrangement in the crystal as seen in projection along the *a* axis is illustrated in Figure 3, and the shorter intermolecular separations are listed in Table 2. The shortest of these, (2·78 Å) is between the hydroxy-oxygen atom O(15) and the carbonyl oxygen atom O(24) of ring D, and it is typical for a hydrogen bond.[23] It is probable that the hydrogen atom H(15) lies near to the line of centres for the angle C(4)–O(15)–O(24) is 105·4°. At the carbonyl group the C(21)–O(24)–O(15) angle is 150·7°. All other distances correspond to normal van der Waals separations.

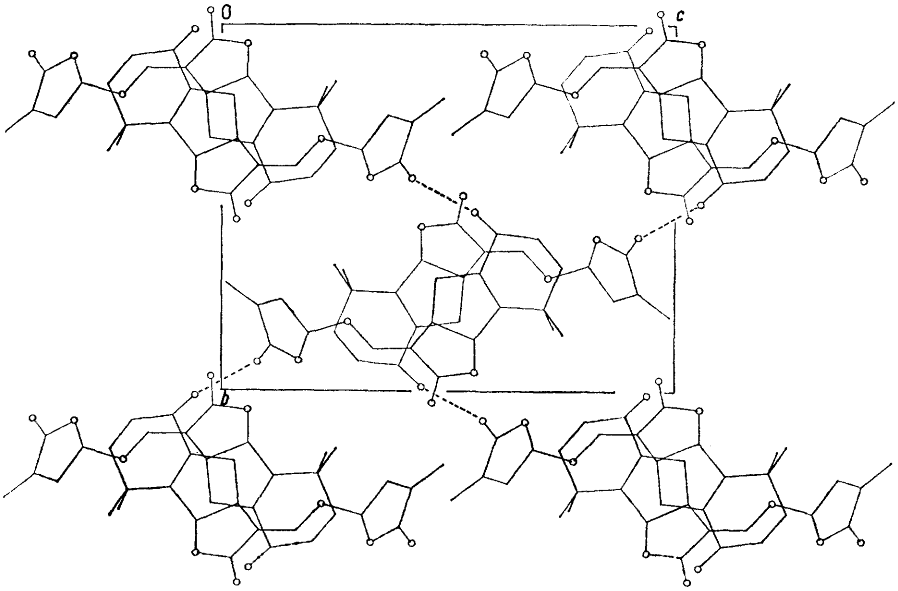

FIGURE 3 The crystal structure viewed in projection along the *a* axis; hydrogen bonds are denoted by broken lines and oxygen atoms by small circles

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