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Note

Crystal and molecular structure of (3aR,8bS,5′R)3-[(2,5-dihydro-3-methyl-2-oxo-5-furanyl)oxymethylene]-3,3a,4,8b-tetrahydroindeno[1,2-b]furan-2-one

F.G. Moers,[1] J.M.M. Smits,[1] Paul T. Beurskens,[1]* J.W. Thuring,[2] and B. Zwanenburg[2]

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The stereogeometry and absolute configuration of the title compound has been proved by an X-ray diffraction analysis. Crystal data: monoclinic, C2, a = 20.2528(4), b = 6.7254(2), c = 10.6748(2) Å, β = 94.699(3), Z = 4. The crystal structure has been solved by vector search methods and refined to R_1 = 0.053 for 2043 observed reflections.

KEY WORDS: Crystal and molecular structure; stereoisomer of GR24; (+)-strigel.

Introduction

Germination of the seeds of root parasitic plants of the genera *Striga, Alectra,* and *Orobanche* is induced by compounds exuded from their host plants.[1]

(+)-Strigol (Fig. 1) is a prominent example of such a compound, whose presence in the root exudate of maize, a host plant for *Striga* species,[2] recently has been demonstrated. The absolute configuration of (+)-strigol has unambiguously been established by X-ray crystallographic analysis after derivatization with a homochiral isocyanate of known absolute configuration.[3] As part of our interest in the synthesis and biological evaluation of enantiopure synthetic strigol analogues, we synthesized all four stereoisomers of GR24 (Fig. 1) in an enantiopure form.[4] In order to establish unambiguously its absolute configuration, we selected one enantiomer ($[\alpha]_D^{20}$ = + 447 ° (c = 0.25, $CHCl_3$)), denoted MANG4 for further references, and subjected it to an X-ray crystallographic analysis. The absolute configuration of MANG4 was determined and the stereochemistry is assigned as: 3aR, 8bS, 5′R. It was shown that MANG4 possesses the same absolute stereochemistry at the corresponding stereogenic centres as naturally occurring (+)-strigol. It should be noted that it is extremely difficult to establish the absolute configuration of this types of compounds by other means. The structure of the racemic compound, denoted MANG3, was determined earlier.[5]

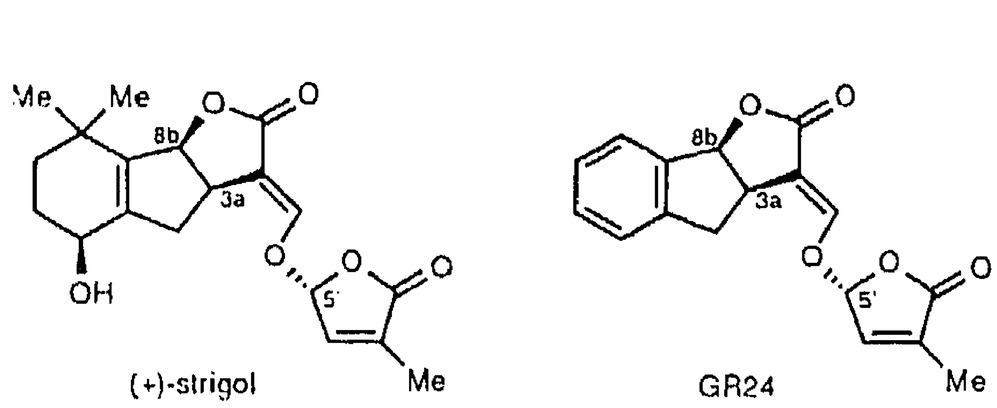

Fig. 1. Chemical formulae of (+)-Strigol and GR24 with numbering of the asymmetric centers.

Experimental

The crystal data and a summary of the data collection and the structure solution and refinement are given in Table 1. Treatment of hydrogen atoms: the hydrogen atoms of the methyl group were obtained by rotation of an idealized methyl group to match maximum electron

[1] Crystallography Laboratory, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands.
[2] Department of Organic Chemistry, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands.
* To whom correspondence should be addressed.

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Table 1. Crystal data and summary of intensity data collection and structure solution and refinement.

	Crystal data
Compound	$C_{17}H_{14}O_5$
Color/shape	Colorless/needle
Crystallization	H_2O/acetone
Melting point, °C	154
Formula weight	298.3
Crystal system	Monoclinic
Space group	C2
Temperature, K	293
Cell constants[a]	
a, Å	20.2528(4)
b, Å	6.7254(2)
c, Å	10.6748(2)
β, °	94.699(3)
Cell volume, Å^3	1449.12(5)
Formula units/unit cell	4
D_{calc}, g cm^{-3}	1.367
μ_{calc}, cm^{-1}	8.02
F(000), electrons	624
	Intensity data collection
Diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ
Radiation, graphite monochromator	Cu*K*α (λ = 1.54184 Å)
Crystal dimensions, mm	0.09 × 0.21 × 0.50
Scan width, °	1.5
Standard reflections	3
Decay of standards	2%
Reflections measured	4218
2θ-range, °	120
Range of *h*, *k*, *l*	$-22 \leq h \leq 22$ $-7 \leq k \leq 7$ $-11 \leq l \leq 11$
Corrections:	
Lorentz-polarization	
EMPABS[9] correction	0.93–1.10
Computer programs[b]	local programs
	Structure solution and refinement
Structure solution	Vector search methods[10] on a 13-atoms fragment from MANG3
Computer programs[b]	DIRDIF[11]
DIFABS[12]-correction	0.89–1.36
R_{merge}	0.040
Unique reflections (obs.: $F_o > 4\sigma(F_o)$)	2116 (2043)
Structure refinement	anisotropic: C(2′), C(3′), C(3C), C(5), O(1), O(2A), O(1′), O(2′), O(5′) isotropic: remaining atoms
Computer programs[b]	SHELXL-93[13]
Treatment of hydrogen atoms: see experimental	
Weights	$1/[\sigma^2(F_o^2) + (0.0791\ P)^2 + 1.67\ P]$ where $P = [\mathrm{Max}(0,F_o^2) + 2F_c^2]/3$
Shift/esd	less than 0.061
No. of parameters	147
No. of restraints	1
GOOF	1.07
R_1	0.053
wR_2	0.143
Residual el.dens., e.Å^{-3}	0.29

[a] Least-squares refinement for 25 reflections $24° < \theta < 33°$.
[b] Neutral scattering factors and anomalous dispersion corrections.[14]

Table 2. Atomic coordinates (×10000) and equivalent isotropic displacement parameters (×1000 Å^2)

Atom	*x*	*y*	*z*	U_{eq}[a]
O(1)	7643(1)	7755(3)	7640(2)	59(1)
C(2)	7946(2)	7424(5)	8803(3)	50(1)
O(2A)	7896(1)	8611(4)	9634(2)	67(1)
C(3)	8302(2)	5541(5)	8805(3)	45(1)
C(3A)	8244(2)	4632(5)	7524(3)	49(1)
C(3B)	8567(2)	4818(5)	9888(3)	50(1)
C(4)	7885(2)	2612(5)	7451(3)	55(1)
C(4A)	7216(2)	3060(5)	6783(3)	49(1)
C(5)	6686(2)	1748(6)	6536(4)	62(1)
C(6)	6109(2)	2455(7)	5879(4)	69(1)
C(7)	6069(2)	4399(7)	5495(4)	69(1)
C(8)	6590(2)	5715(7)	5727(3)	60(1)
C(8A)	7165(2)	4990(5)	6389(3)	48(1)
C(8B)	7784(2)	6126(6)	6771(3)	54(1)
O(1′)	9389(1)	3290(4)	11993(2)	60(1)
C(2′)	9903(2)	2093(6)	12432(3)	54(1)
O(2′)	10316(2)	2695(6)	13210(3)	87(1)
C(3′)	9822(2)	136(6)	11828(3)	54(1)
C(3C)	10316(3)	−1483(8)	12115(4)	92(2)
C(4′)	9273(2)	195(6)	11092(4)	60(1)
C(5′)	8958(2)	2160(6)	11154(3)	52(1)
O(5′)	8899(1)	3054(4)	9946(2)	57(1)

[a] U_{eq} for anisotropic atoms (= 1/3 of the trace of the orthogonalized U_{ij} matrix).

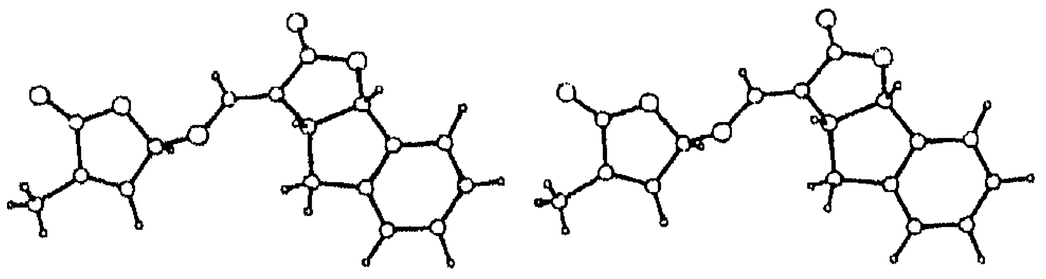

Fig. 2. Stereoview of the molecule. Oxygen atoms are shown as larger circles.

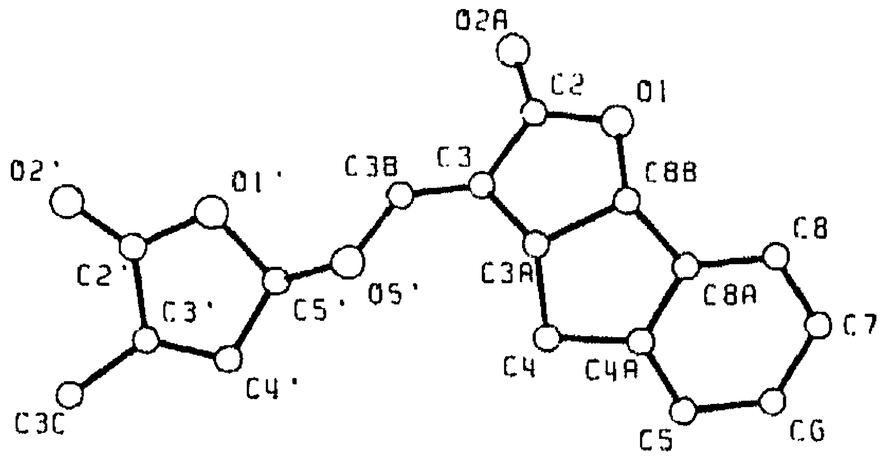

Fig. 3. Crystallographic numbering scheme. Oxygen atoms are shown as larger circles.

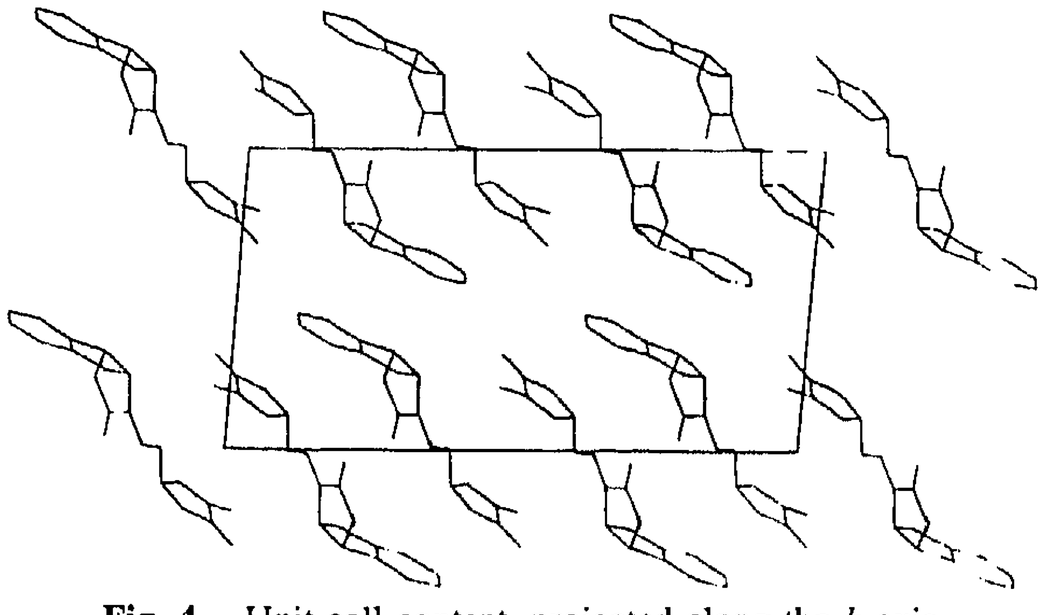

Fig. 4. Unit cell content, projected along the *b*-axis.

Table 3. Selected bond lengths (Å) and angles (°)

O(1)–C(2)	1.357(4)
O(1)–C(8B)	1.479(4)
C(2)–O(2A)	1.204(4)
C(2)–C(3)	1.458(5)
C(3)–C(3B)	1.326(5)
C(3)–C(3A)	1.493(5)
C(3B)–O(5′)	1.363(4)
O(1′)–C(2′)	1.368(4)
O(1′)–C(5′)	1.419(4)
C(2′)–O(2′)	1.200(4)
C(2′)–C(3′)	1.468(6)
C(3′)–C(4′)	1.308(5)
C(3′)–C(3C)	1.493(6)
C(4′)–C(5′)	1.471(5)
C(5′)–O(5′)	1.418(4)
C(2)–O(1)–C(8B)	110.9(3)
O(2A)–C(2)–O(1)	120.4(3)
O(2A)–C(2)–C(3)	130.3(3)
O(1)–C(2)–C(3)	109.3(3)
C(3B)–C(3)–C(2)	119.0(3)
C(3B)–C(3)–C(3A)	130.1(3)
C(2)–C(3)–C(3A)	110.6(3)
C(3)–C(3A)–C(8B)	102.1(3)
C(4)–C(3A)–C(8B)	106.5(3)
C(3)–C(3B)–O(5′)	121.4(3)
O(1)–C(8B)–C(3A)	107.1(3)
C(2′)–O(1′)–C(5′)	108.2(3)
O(2′)–C(2′)–O(1′)	120.4(4)
O(2′)–C(2′)–C(3′)	130.7(4)
O(1′)–C(2′)–C(3′)	108.9(3)
C(4′)–C(3′)–C(2′)	107.2(3)
C(4′)–C(3′)–C(3C)	131.8(4)
C(2′)–C(3′)–C(3C)	121.0(3)
C(3′)–C(4′)–C(5′)	110.5(4)
O(1′)–C(5′)–O(5′)	110.4(3)
O(1′)–C(5′)–C(4′)	105.3(3)
O(5′)–C(5′)–C(4′)	110.2(3)
C(3B)–O(5′)–C(5′)	114.5(3)

Table 4. Selected torsion angles (°) of MANG4 and MANG3

	MANG4	MANG3
C(3A)–C(3)–C(3B)–O(5′)	6.2	0.2
C(3)–C(3B)–O(5′)–C(5′)	−160.0	−169.9
C(3B)–O(5′)–C(5′)–O(1′)	−68.9	−70.6

density in the difference Fourier synthesis, and they were included in the refinement in riding mode and constrained isotropic temperature factors (one U for three hydrogens of the methyl group). The remaining hydrogen atoms were calculated and refined riding on the parent atoms with free isotropic temperature factors. Absolute structure: to determine the absolute configuration of the molecule the weighted Bijvoet coefficient was calculated and found to be negative ($B = -0.17(3)$ on 100 Bijvoet pairs, using the program BIJVOET);[6] consequently the structure was inverted. Refinement then continued. The atomic positional and vibrational parameters are given in Table 2.

Discussion

Selected bond lengths and angles are given in Table 3. The structure is presented in Figs. 2–4.[7] Comparing its absolute configuration with the configuration of naturally occuring (+)-strigol, it is seen that the two molecules possess the same absolute stereochemistry at the corresponding stereogenic centres. Consequently, MANG4 is the stereoisomer of GR24 presented in Fig. 1.

The structure of the present compound shows no unusual geometry.[8] Its molecular geometry agrees with the results obtained for MANG3; various torsion angles of the molecule as found in the two structures are compared in Table 4. The shortest intermolecular oxygen–carbon distances are O(2A) ··· C(4′) 3.258 Å and O(1) ··· C(4) 3.311 Å.

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