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6-Methyl-3-phenylthiochroman-4-one and 6-Methoxy-3-phenylthiochroman-4-one: Configurational Preference of the Phenylthio Group at the Third Position due to Remote Substitution

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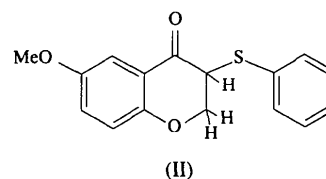
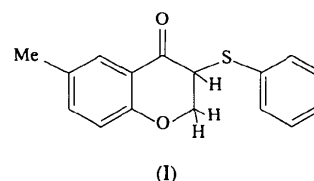
Abstract

The pyran ring adopts a distorted sofa conformation in the title compounds, 6-methyl-3-phenylthiochroman-

4-one (C₁₆H₁₄O₂S), (I), and 6-methoxy-3-phenylthiochroman-4-one (C₁₆H₁₄O₃S), (II). The S atom substituted at the third position is attached equatorially in (II) and axially in (I). High-resolution proton NMR studies could not provide a conclusive explanation for this feature.

Comment

Isoflavanoids, the compounds based on a 3-phenylchroman skeleton, belong to the family Papilionoidae of the Leguminosae of the plant kingdom. They exhibit a large number of structural variations (Dewick, 1988). The title compounds, (I) and (II), belong to the series of 3-phenylchromanones, synthesized by our group, with S as the bridge between the phenyl ring and the C atom at the third position of the heterocycle of the chroman ring system. The bond lengths in the pyran ring (involving atoms O1, C2, C3, C4, C9 and C9') are normal with negligible variations in their values in both compounds. The bond angles around C4 differ significantly from the ideal *sp*² values. Similarly, the bond angles around C9 deviate from the ideal 120°. The bond angle C3—S—C10 in (I) is 3.4° lower than in (II).



The dihedral angles between the planes of the phenyl rings C5–C9 and C10–C15 are 31.9 (4) and 67.1 (9)° in (I) and (II), respectively. In both compounds, the pyran ring adopts a distorted sofa conformation, with C2 deviating from the mean plane formed by the other atoms of this ring [0.651 for (I) and 0.663 Å for (II)], the normal conformation of the pyran ring being half chair (Alex *et al.*, 1993). As seen from the torsion angle O2—C4—C3—S, the S atom is axially connected to the C3 atom in (I) whereas it is connected equatorially in (II). The crystal structures are stabilized by intermolecular van der Waals interactions, although compound (II), which has a relatively higher density, is marked by tighter packing. However, the only difference between the two compounds is the substitution of a methyl group at a remote site (C5) in (I) instead of a methoxy group in (II).

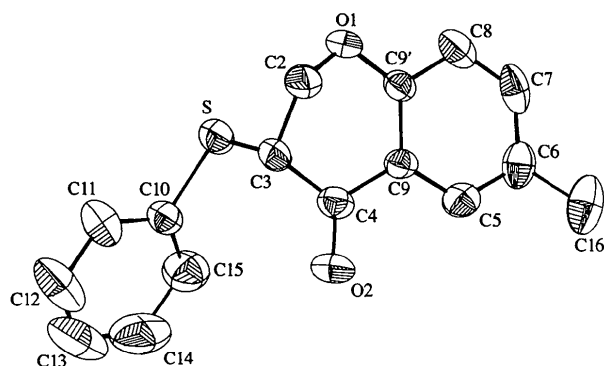


Fig. 1. ORTEP (Johnson, 1976) plot of the molecular structure and atom-numbering scheme of (I). The displacement ellipsoids are drawn at the 50% probability level.

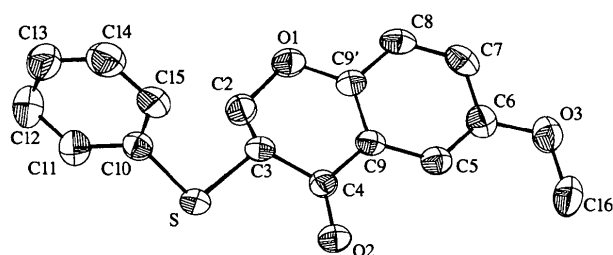


Fig. 2. ORTEP (Johnson, 1976) plot of the molecular structure and atom-numbering scheme of (II). The displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compounds were prepared from their respective bromo derivatives, 6*R*-3-bromochroman-4-one [*R* = methyl in (I) and methoxy in (II)], which were prepared by the reaction of the respective chroman-4-ones with Br in chloroform or diethyl ether at room temperature. Thiophenol (1.2 mmol) was added to a solution of triethylamine (1.5 mmol) in methanol (15 ml) and this mixture was stirred for 5 min. The respective 3-bromochroman-4-one was added in portions over a period of 10 min. The mixture was stirred at room temperature for 45 min, poured into ice-cold water and extracted with diethyl ether. The organic layer was washed with 2*N* hydrochloric acid and then with water to obtain a 90–95% yield of the 3-phenylthiochroman-4-ones (Santhosh, 1994). The details of the proton NMR data of the two compounds are as follows; compound (I): ¹H NMR [400 MHz, CDCl₃, δ (p.p.m.)]: 2.26 (s, 3H, Ar-CH₃), 3.96 (dd, 1H, *J*_{c,b} = 2.32, *J*_{c,a} = 4.62 Hz, H_c), 4.68 (dd, 1H, *J*_{c,a} = 4.62, *J*_{a,b} = 13.87 Hz, H_a), 5.23 (dd, 1H, *J*_{b,c} = 2.32, *J*_{b,a} = 13.87 Hz, H_b), 6.8–7.9 (*m*, 8H, Ar-H); compound (II): ¹H NMR [400 MHz, CDCl₃, δ (p.p.m.)]: 3.77 (s, 3H, ArOCH₃), 4.10 (dd, 1H, *J*_{c,b} = 2.70, *J*_{c,a} = 5.40 Hz, H_c), 4.49 (dd, 1H, *J*_{c,a} = 5.42, *J*_{a,b} = 11.35 Hz, H_a), 4.58 (dd, 1H, *J*_{b,c} = 2.72, *J*_{b,a} = 11.35 Hz, H_b), 6.9–7.5 (*m*, 8H, Ar-H). With respect to the differences in the orientation of the H atom substituting at C3, no conclusions could be drawn from the small differences obtained in the δ values of the proton peaks [3.96 for (I) and 4.1 for (II)].

Compound (I)

Crystal data

C₁₆H₁₄O₂S
M_r = 270.33
 Monoclinic
*P*2₁/*c*
a = 9.278 (5) Å
b = 9.826 (4) Å
c = 15.237 (10) Å
 β = 93.24 (10)°
V = 1386.9 (13) Å³
Z = 4
D_x = 1.295 Mg m^{−3}
D_m not measured

Data collection

Enraf–Nonius CAD-4
 diffractometer
 ω–2θ scans
 Absorption correction: none
 2061 measured reflections
 1909 independent reflections
 1631 reflections with
I > 2σ(*I*)

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.049
wR (*F*²) = 0.131
S = 1.080
 1909 reflections
 228 parameters
 H-atom coordinate
 parameters refined only

Mo *K*α radiation

λ = 0.71073 Å
 Cell parameters from 25
 reflections
 θ = 8–12°
 μ = 0.228 mm^{−1}
T = 293 (2) K
 Prismatic
 0.44 × 0.33 × 0.31 mm
 Yellow

*R*_{int} = 0.041
 θ_{max} = 24.98°
h = 0 → 11
k = −5 → 11
l = −18 → 18
 2 standard reflections
 frequency: 60 min
 intensity decay: 3.5%

w = 1/[σ²(*F*_o²) + (0.0822*P*)²
 + 0.3283*P*]
 (Δ/σ)_{max} = −0.001
 Δρ_{max} = 0.249 e Å^{−3}
 Δρ_{min} = −0.223 e Å^{−3}
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (I)

S—C10	1.766 (10)	C3—C4	1.497 (6)
S—C3	1.833 (7)	C3—C2	1.509 (8)
O1—C9'	1.363 (5)	C9—C4	1.477 (6)
O1—C2	1.434 (7)		
C10—S—C3	102.7 (3)	O1—C9'—C8	117.5 (4)
C9'—O1—C2	114.0 (4)	O1—C9'—C9	122.6 (2)
C4—C3—C2	110.4 (3)	C9'—C9—C4	119.9 (4)
C4—C3—S	107.6 (4)	O2—C4—C9	122.9 (4)
C2—C3—S	108.2 (3)	O2—C4—C3	122.0 (3)
O1—C2—C3	110.9 (5)	C9—C4—C3	115.1 (4)
C9'—O1—C2—C3	−54.5 (4)	C2—C3—C4—O2	152.4 (3)
C4—C3—C2—O1	57.8 (4)	S—C3—C4—O2	−89.6 (3)
S—C3—C2—O1	−59.8 (4)	C2—C3—C4—C9	−30.3 (4)
C2—O1—C9'—C9	22.9 (4)	S—C3—C4—C9	87.6 (3)
O1—C9'—C9—C4	5.2 (4)	C3—S—C10—C11	86.6 (5)
C9'—C9—C4—C3	−0.1 (4)	C3—S—C10—C15	−98.7 (5)

Compound (II)

Crystal data

C₁₆H₁₄O₃S
M_r = 286.33

Mo *K*α radiation
 λ = 0.71073 Å

Monoclinic

 $P2_1/c$ $a = 13.113$ (4) Å $b = 15.260$ (6) Å $c = 6.762$ (5) Å $\beta = 92.36$ (4)° $V = 1352.0$ (12) Å³ $Z = 4$ $D_x = 1.407$ Mg m⁻³ D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer ω -2 θ scans

Absorption correction: none

2274 measured reflections

2088 independent reflections

1749 reflections with

 $I > 2\sigma(I)$ Cell parameters from 25
reflections $\theta = 8$ –12° $\mu = 0.243$ mm⁻¹ $T = 293$ (2) K

Prismatic

 $0.38 \times 0.35 \times 0.18$ mm

Yellow

 $R_{\text{int}} = 0.018$ $\theta_{\text{max}} = 25.00^\circ$ $h = -15 \rightarrow 15$ $k = -18 \rightarrow 0$ $l = 0 \rightarrow 8$

2 standard reflections

frequency: 60 min

intensity decay: 2%

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.047$ $wR(F^2) = 0.131$ $S = 1.058$

2088 reflections

237 parameters

H-atom coordinate

parameters refined only

 $w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 0.3635P]$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.329$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.280$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for
Crystallography (Vol. C)

Table 2. Selected geometric parameters (Å, °) for (II)

S—C10	1.783 (3)	C3—C2	1.513 (4)
S—C3	1.811 (3)	C3—C4	1.516 (4)
O1—C9'	1.367 (3)	C9—C4	1.478 (3)
O1—C2	1.429 (3)		
C10—S—C3	99.3 (1)	O1—C9'—C8	116.8 (2)
C9'—O1—C2	114.3 (2)	O1—C9'—C9	123.1 (2)
C2—C3—C4	108.0 (2)	C9'—C9—C4	120.4 (2)
C2—C3—S	111.8 (2)	O2—C4—C9	124.2 (2)
C4—C3—S	112.7 (2)	O2—C4—C3	123.5 (2)
O1—C2—C3	110.6 (2)	C9—C4—C3	112.2 (2)
C9'—O1—C2—C3	50.7 (3)	C2—C3—C4—O2	-141.2 (3)
C4—C3—C2—O1	-64.8 (3)	S—C3—C4—O2	-17.2 (4)
S—C3—C2—O1	170.8 (2)	C2—C3—C4—C9	42.2 (3)
C2—O1—C9'—C9	-14.4 (4)	S—C3—C4—C9	166.1 (2)
O1—C9'—C9—C4	-7.3 (4)	C3—S—C10—C15	-54.1 (3)
C9'—C9—C4—C3	-8.7 (3)	C3—S—C10—C11	128.1 (3)

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1051). Services for accessing these data are described at the back of the journal.

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 β -1-*N*-Acetamido-D-glucopyranose

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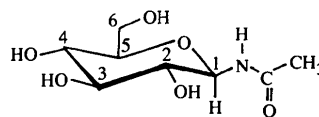
(Received 13 November 1996; accepted 4 March 1997)

Abstract

In the title molecule, C₈H₁₅NO₆, the pyranose ring adopts the usual ⁴C₁(*D*) conformation and the *N*-acetyl group exists in the *Z*-*anti* conformation. The orientation of the primary alcohol group is *gauche*.

Comment

The glycan (oligosaccharide) components of glycoproteins are known to play vital roles in protein folding, protein targeting and cellular recognition (Cumming, 1992; Imperiali & Rickert, 1994). Elucidation of the structural basis of their biological roles represents a fundamental and challenging problem in glycobiological research (Dwek, 1996). A systematic study initiated recently by the present authors is focused on the structural aspects of *N*-glycoproteins. The title compound, (I), was chosen for the current X-ray crystallographic investigation as it represents the simplest model of the linkage region (2-deoxy-2-acetamido- β -D-glucopyranosylasparagine, GlcNAc β Asn).



(I)