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Two crystal polymorphs of a flavonoid from *Melicope ellyrana*

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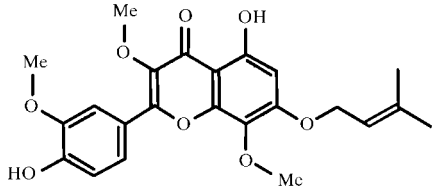
The crystal structure determinations of two crystalline components of the hexane extract of the fruit of the indigenous Australian tree *Melicope ellyrana* have shown them to be polymorphs of the same compound, namely the flavonoid 4′,5-dihydroxy-3,3′,8-trimethoxy-7-(3-methylbut-2-enyloxy)flavone [systematic name: 5-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-3,8-dimethoxy-7-(3-methylbut-2-enyloxy)-4*H*-1-benzopyran-4-one], $C_{23}H_{24}O_8$. The two polymorphs, one monoclinic (polymorph *A*) and the other triclinic (polymorph *B*), show significant conformational differences, particularly in the enyloxy side chain, while only one (polymorph *A*) shows intermolecular hydrogen bonding.

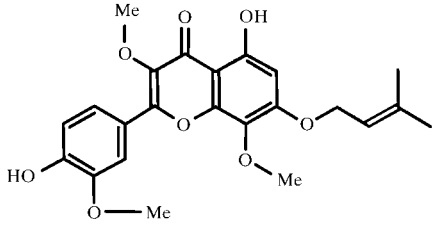
Comment

Investigation of the hexane extract of the fruit of the indigenous Australian tree *Melicope ellyrana* (formerly *Euodia ellyrana* F. Meull) (Hartley, 1981) resulted in the isolation of three flavonoids, namely 4′,5-dihydroxy-3,3′,8-trimethoxy-7-(3-methylbut-2-enyloxy)flavone, (I), pachypodol (4′,5-dihydroxy-3,3′,7-trimethoxyflavone), (II), and ternatin (4′,5-dihydroxy-3,3′,7,8-tetramethoxyflavone), (III). Although compound (I) has previously been isolated from *Boronia coerulescens* (Ashan *et al.*, 1994), and other prenylated flavones similar to (I) have been reported, *e.g.* from *M. triphylla* (Higa *et al.*, 1987) and *M. micrococca* (Nasim, 1999), this represents the first report and crystallographic characterization of (I) from *M. ellyrana*.

Two morphologically different crystalline forms of (I) obtained from *n*-hexane (monoclinic polymorph *A*) and ethyl acetate (triclinic polymorph *B*) extracts allowed, in the first instance (because of the minute quantities of the available sample involved), determination of the identity of both polymorphs as the title compound and, in the second instance, confirmation of the existence of two significantly different molecular conformations (Figs. 1 and 2). Triclinic form *B* has a more compact molecular form than is found for monoclinic form *A* due mainly to the more convoluted enyloxy side chain (comparative molecular volumes of 506 and 526 Å^3, respectively). This is reflected particularly in the C7—O7—C71—C72 and O7—C71—C72—C73 torsion angles of 81.9 (4) and 107.4 (5)°, respectively, in polymorph *B*, and −174.6 (3) and 143.5 (4)° in polymorph *A*. In addition, the benzene ring substituent at C2, although essentially coplanar with the



(I), polymorph *A*



(I), polymorph *B*

parent ring, is rotated about the C2—C12 bond vector such that the *meta*-substituted methoxy groups in the two polymorphs are *ca* 180° apart. Intramolecular C—H···O(methoxy) and C—H···O(ether) interactions are significant in maintaining the coplanarity of the two ring systems [C22—H22···O3 2.888 (5) Å and C62—H62···O1 2.627 (4) Å for polymorph *A*; C22—H22···O1 2.664 (5) Å and C62—H62···O3 2.858 (5) Å for polymorph *B*]. Relatively minor conformational differences are found in the methoxy substituents at C3, C8 and C52, while in each, there are intramolecular hydrogen-bonding interactions involving the hydroxyl group at C5 and the adjacent ketone O atom at C4 [O5—H5···O4: 2.600 (4) Å in form *A* and 2.586 (4) Å in form *B*], and the hydroxyl group at C42 and the adjacent methoxy O atom at C52 [O42—H42···O52: 2.692 (4) Å in form *A* and 2.657 (4) Å in form *B*].

A major difference between polymorphs *A* and *B* lies in the packing; in *A*, a single intermolecular hydrogen-bond inter-

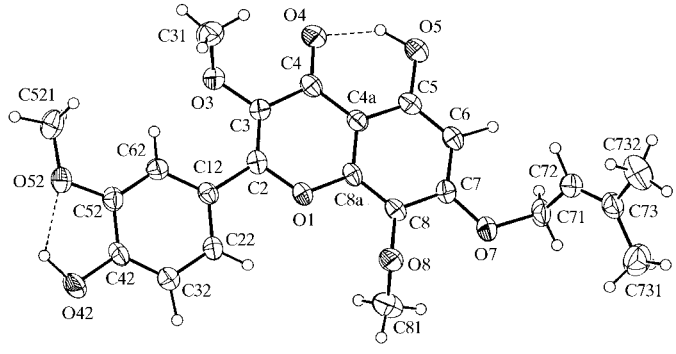


Figure 1
The molecular configuration and atom-numbering scheme for monoclinic polymorph *A*. Atoms are shown as 40% probability ellipsoids.

action is found between the H atom of the hydroxyl group at C42 and a ketone O atom of a glide-related neighbour [O42—H42···O4^{i} 2.784 (4) Å; symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$]. This completes a three-centred hydrogen-bond association about H42, with a relatively long H42···O4^{i} separation of 1.87 Å.

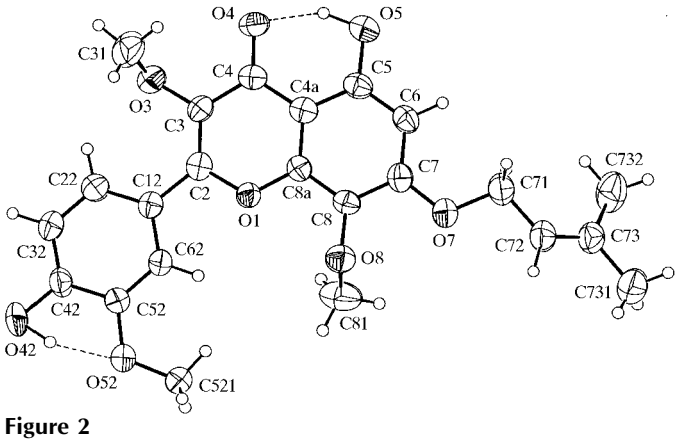


Figure 2
The molecular configuration and atom-numbering scheme for triclinic polymorph *B*. Atoms are shown as 40% probability ellipsoids.

Experimental

Fresh fruit from *Melicope ellyrana* (1.5 kg) was extracted with *n*-hexane (4.5 l) for 72 h at room temperature and the extract concentrated by rotary evaporation. The extract (20 g) was subjected to gel filtration chromotographic (GFC) separation using methanol (monitored at λ = 254 nm), the eluent yielding 23 separate fractions. Two of these fractions gave crystals of the title compound in morphologically different and visually identifiable forms, one monoclinic (polymorph *A*) and the other triclinic (polymorph *B*).

Compound (I), polymorph *A*

Crystal data

$C_{23}H_{24}O_8$	D_x = 1.352 Mg m^{-3}
M_r = 428.42	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
a = 14.238 (4) Å	θ = 20.1–27.2°
b = 11.053 (5) Å	μ = 0.10 mm^{-1}
c = 14.426 (5) Å	T = 293 (2) K
β = 111.979 (18)°	Prism, yellow
V = 2105.3 (13) Å^3	0.40 × 0.30 × 0.30 mm
Z = 4	

Data collection

Rigaku AFC-7*R* diffractometer	$h = 0 \rightarrow 16$
ω–2θ scans	$k = 0 \rightarrow 13$
3865 measured reflections	$l = -17 \rightarrow 15$
3709 independent reflections	3 standard reflections every 150 reflections
1532 reflections with $I > 2\sigma(I)$	intensity decay: 0.3%
R_{int} = 0.026	
θ_{max} = 25.0°	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2 + 0.3178P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.048	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.180	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
S = 0.95	$\Delta\rho_{min}$ = −0.27 e Å^{-3}
3709 reflections	
280 parameters	
H-atom parameters constrained	

Compound (I), polymorph *B*

Crystal data

$C_{23}H_{24}O_8$	Z = 2
M_r = 428.44	D_x = 1.405 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 12.291 (5) Å	Cell parameters from 17 reflections
b = 13.075 (5) Å	θ = 20.1–25.6°
c = 7.099 (3) Å	μ = 0.11 mm^{-1}
α = 93.85 (5)°	T = 293 (2) K
β = 104.33 (4)°	Prism, yellow
γ = 111.52 (3)°	0.45 × 0.10 × 0.10 mm
V = 1012.3 (7) Å^3	

Data collection

Rigaku AFC-7*R* diffractometer	$h = 0 \rightarrow 14$
ω–2θ scans	$k = -15 \rightarrow 14$
3754 measured reflections	$l = -8 \rightarrow 8$
3571 independent reflections	3 standard reflections every 150 reflections
1609 reflections with $I > 2\sigma(I)$	intensity decay: 3.5%
R_{int} = 0.097	
θ_{max} = 25.0°	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.055	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.199	$(\Delta/\sigma)_{max} < 0.001$
S = 1.00	$\Delta\rho_{max}$ = 0.32 e Å^{-3}
3571 reflections	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
280 parameters	

With the exception of those H atoms involved in hydrogen-bonding interactions, H atoms were included at calculated positions and were constrained in the refinement (C—H = 0.94–0.96 Å).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1324). Services for accessing these data are described at the back of the journal.

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