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Crystal structure of 9-*trans*-*p*-coumaroyloxy-α-terpineol, $C_{19}H_{24}O_4$

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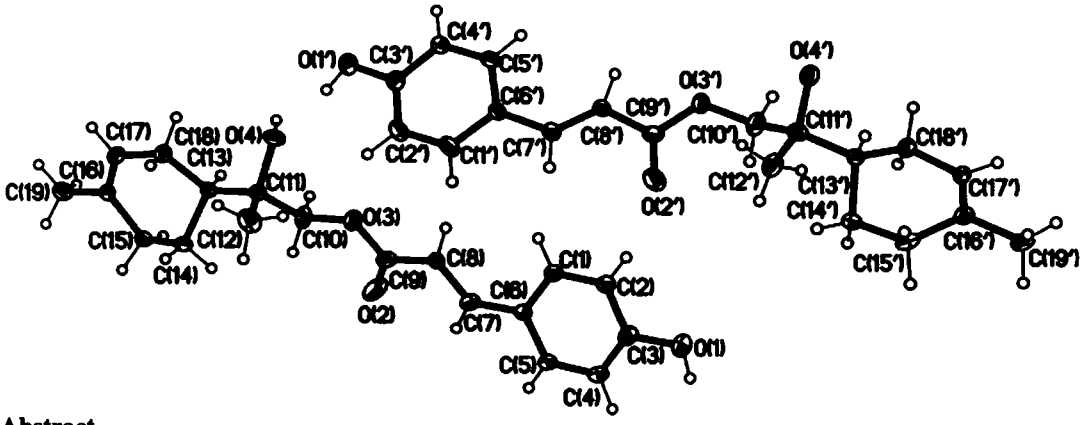

Abstract

$C_{19}H_{24}O_4$, monoclinic, $P2_1$ (no. 4), a = 9.231(2) Å, b = 16.318(3) Å, c = 11.647(2) Å, β = 91.31(3)°, V = 1753.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.124, T = 293 K.

Source of material

The ester 9-*trans*-*p*-coumaroyloxy-α-terpineol was isolated from a dichloromethane extract from the aerial parts of Haplopappus taeda Reiche (Asteraceae) [1] collected at the foothills in the Region del Maule (Chile). The compound was isolated and purified by usual chromatographic methods and its molecular structure was established by spectroscopic analysis [2]. Than it was dissolved in hexane at room temperature and colourless prismatic crystals suitable for X-ray diffraction studies grew over a period of one week when the solution was exposed to the air.

Experimental details

H atoms attached C7, C8, C7' and C8' were located in a difference Fourier map and refined. The rest of the hydrogen atoms were positioned geometrically, with C—H distances constrained to 0.93 Å (aromatic CH), 0.96 Å (methyl CH_3), 0.97 Å (methylene CH_2) and 0.98 Å (methine CH) and refined in riding mode with $U_{iso}(H) = xU_{eq}(C)$, where x = 1.5 for methyl H atoms and x = 1.2 for all other H atoms. The hydroxyl hydrogen atoms were refined with a distance restraint of 0.82 Å, starting from the difference Fourier map coordinates and with $U_{iso}(H) = 1.5\ U_{eq}(O)$.
All problems of the crystal structure refinement of this compound are derived from the small size and bad quality of the crystals. In spite of collecting data of five crystals in four-circle diffractometer, we do not get sufficiently good quality. Nevertheless, we think that the structural model is good enough from the chemical point of view.

Discussion

The spectroscopic data of this natural ester were compared with those of other previously isolated derivatives. The stereochemistry of C7'=C8' double bond was assigned by comparision with reported couplings (J = 16.0 Hz) of the olefinic protons in the NMR spectrum of 9-*trans*-cinnamoyloxy-α-terpineol [3,4] isolated from Haplopappus remyanus. The resinous leaves of Asteraceae are used in traditional medicine as digestive, as antiseptic, and also in relief of liver ailments or intestinal and urinary disorders. The scavenging activity [5] of the new ester was measured with DPPH and found to be IC_{50} 75.5 μg/ml (quercetin as positive control: IC_{50} 15.3 μg/ml).
The title compound was obtained as two symmetrically independent molecules in the crystal lattice with some difference in bond lengths, angles and torsion angles. For example, the hydroxyl group at atom C3 is coplanar with the benzene ring being the O1–C3–C4–C5 and O1'–C3'–C4'–C5' torsion angles of 179.6(5)° and −178.5(5)°, respectively. In the case of methyl group at C16 is also coplanar with the cyclohexene ring, being the values of the torsion angles C19–C16–C17–C18 and C19'–C16'–C17'–C18' of 178.8(5)° and −177.8(5)°, respectively. The greatest dissimilarity is that C9–O3–C10–C11 torsion angle is of 151.5 (5)° while the corresponding C9'–O3'–C10'–C11' torsion angle is of 121.7(5)° in the other molecule.
Due to their structural equivalence the discussion focuses only on the first molecule. All the bond lengths and angles are within the normal ranges. The C16=C17 bond length of 1.319(7) Å correspond to the value for a double bond. The O1—C3 and O4—C11 bond lengths are 1.378(6) Å and 1.461(5) Å, respectively. As ex-

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pected, the C6–C7–C8–C9 torsion angle of 177.9(2)° expresses a *trans* configuration of the molecule around the C7=C8 double bond. The planar conformation of the ester group is established from the torsion angles O2–C9–O3–C10 (1.2(6)°) and C8–C9–O3–C10 (179.4(1)°).

In the crystal structure, molecules are interconnected by intermolecular O–H···O hydrogen bonds to form infinite chains running along [100], which seems to be effective in the stabilization of the structure. Three types of hydrogen bonds can be observed between the hydroxyl and carbonyl groups. The details of the O1'–H1O'···O4 bond are: d(O1'—H1O') = 0.82 Å, d(H1O'···O4) = 1.98 Å, d(O1'···O4) = 2.753(1) Å, ∠O1'–H1O'···O4 = 157°. The details of the O1–H1O···O4' bond are: d(O1—H1O) = 0.82 Å, d(H1O···O4') = 1.95 Å, d(O1···O4') = 2.770(2) Å, ∠O1–H1O···O4' = 173°. The details of the O4–H4O···O2' bond are: d(O4—H4O) = 0.82 Å, d(H4O···O2') = 1.93 Å, d(O4···O2') = 2.705(1) Å, ∠O4–H4O···O2' = 158°.

Table 1. Data collection and handling.

Crystal:	colorless prismatic, size 0.25 × 0.30 × 0.40 mm
Wavelength:	Cu K_α radiation (1.54180 Å)
μ:	6.70 cm^{-1}
Diffractometer, scan mode:	SEIFERT XRD 3003, 2θ-ω
$2\theta_{max}$:	120°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5668, 5190
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2527
$N(param)_{refined}$:	439
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1O)	2a	0.6722	0.3703	−0.8246	0.131
H(4O)	2a	0.2761	0.6225	0.0970	0.107
H(1)	2a	0.4129	0.4732	−0.4805	0.064
H(2)	2a	0.4011	0.444	−0.6752	0.080
H(4)	2a	0.8129	0.3669	−0.6590	0.073
H(5)	2a	0.8232	0.3907	−0.4655	0.066
H(10A)	2a	0.6220	0.5498	0.0564	0.087
H(10B)	2a	0.4649	0.5178	0.0805	0.087
H(12A)	2a	0.5082	0.7066	−0.0729	0.132
H(12B)	2a	0.6474	0.7048	0.0068	0.132
H(12C)	2a	0.5192	0.7639	0.0351	0.132
H(13)	2a	0.4651	0.6007	0.2414	0.052
H(14A)	2a	0.7187	0.6085	0.2005	0.068
H(14B)	2a	0.7100	0.7039	0.2173	0.068
H(15A)	2a	0.6781	0.5833	0.3884	0.061
H(15B)	2a	0.7879	0.6566	0.3915	0.061
H(17)	2a	0.4132	0.7572	0.4352	0.068
H(18A)	2a	0.4657	0.7738	0.2260	0.073
H(18B)	2a	0.3298	0.7198	0.2529	0.073
H(19A)	2a	0.7182	0.7075	0.5779	0.101
H(19B)	2a	0.5975	0.6420	0.5992	0.101
H(19C)	2a	0.5586	0.7356	0.5990	0.101
H(1O')	2a	0.1620	0.6555	−0.0555	0.107
H(4O')	2a	−0.1664	0.3160	−0.9113	0.101
H(1')	2a	0.3113	0.6480	−0.4099	0.086
H(2')	2a	0.2969	0.6747	−0.2163	0.078
H(4')	2a	−0.1088	0.5913	−0.2211	0.073
H(5')	2a	−0.0952	0.5639	−0.4130	0.073
H(10C)	2a	0.0824	0.5005	−0.9473	0.084
H(10D)	2a	−0.0855	0.5078	−0.9690	0.084
H(12D)	2a	0.0469	0.3396	−0.8007	0.115
H(12E)	2a	0.1771	0.3564	−0.8815	0.115
H(12F)	2a	0.0751	0.2811	−0.9045	0.115
H(13')	2a	−0.0443	0.4229	−1.1231	0.049
H(14C)	2a	0.2061	0.4415	−1.0798	0.062
H(14D)	2a	0.2271	0.3462	−1.0863	0.062
H(15C)	2a	0.1617	0.4531	−1.2683	0.074
H(15D)	2a	0.2841	0.3867	−1.2632	0.074
H(17')	2a	−0.0589	0.2570	−1.3056	0.064
H(18C)	2a	0.0019	0.2539	−1.0953	0.072
H(18D)	2a	−0.1471	0.2954	−1.1272	0.072
H(19D)	2a	0.0543	0.2951	−1.4723	0.099
H(19E)	2a	0.2163	0.3201	−1.4490	0.099
H(19F)	2a	0.0988	0.3878	−1.4724	0.099
H(7)	2a	0.718(6)	0.428(4)	−0.287(5)	0.12(3)
H(8)	2a	0.446(5)	0.523(3)	−0.296(4)	0.08(2)
H(7')	2a	0.216(5)	0.615(3)	−0.597(4)	0.08(2)
H(8')	2a	−0.055(5)	0.505(3)	−0.604(4)	0.05(1)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2a	0.5936(4)	0.3848(3)	−0.8001(3)	0.092(3)	0.112(4)	0.059(3)	−0.006(3)	0.010(2)	−0.016(3)
O(2)	2a	0.6720(5)	0.4614(4)	−0.0896(4)	0.104(4)	0.220(6)	0.058(3)	0.092(4)	−0.015(3)	−0.025(3)
O(3)	2a	0.4913(4)	0.5505(3)	−0.0843(3)	0.071(3)	0.094(4)	0.058(3)	0.020(3)	−0.010(2)	−0.024(3)
O(4)	2a	0.3205(3)	0.6536(3)	0.0550(3)	0.038(2)	0.115(4)	0.061(3)	0.003(2)	−0.005(2)	0.002(3)
C(1)	2a	0.4930(6)	0.4506(3)	−0.5158(5)	0.047(3)	0.053(4)	0.061(4)	−0.005(3)	0.008(3)	−0.007(3)
C(2)	2a	0.4851(6)	0.4332(4)	−0.6323(5)	0.048(4)	0.096(5)	0.055(4)	−0.003(3)	0.004(3)	−0.005(4)
C(3)	2a	0.6066(6)	0.3990(4)	−0.6838(5)	0.069(4)	0.073(5)	0.046(4)	0.000(4)	0.014(3)	0.005(3)
C(4)	2a	0.7314(6)	0.3864(4)	−0.6223(5)	0.047(3)	0.068(4)	0.068(4)	−0.001(3)	0.016(3)	0.004(4)
C(5)	2a	0.7382(5)	0.4021(4)	−0.5069(5)	0.045(3)	0.068(4)	0.053(4)	−0.003(3)	0.010(3)	−0.004(3)
C(6)	2a	0.6194(5)	0.4349(3)	−0.4500(4)	0.046(3)	0.038(3)	0.047(3)	−0.010(3)	0.006(3)	0.004(3)
C(7)	2a	0.6318(6)	0.4513(4)	−0.3291(5)	0.048(3)	0.064(4)	0.051(4)	0.010(3)	0.009(3)	0.010(3)
C(8)	2a	0.5428(6)	0.4917(3)	−0.2614(5)	0.044(3)	0.047(4)	0.046(3)	−0.008(3)	0.001(3)	−0.002(3)
C(9)	2a	0.5769(6)	0.4979(4)	−0.1394(5)	0.047(3)	0.069(5)	0.058(4)	0.012(3)	0.005(3)	0.003(4)
C(10)	2a	0.5199(7)	0.5586(4)	0.0393(5)	0.094(5)	0.076(5)	0.048(4)	0.009(4)	−0.009(3)	−0.019(4)
C(11)	2a	0.4760(5)	0.6444(3)	0.0775(4)	0.043(3)	0.041(3)	0.053(3)	−0.002(3)	0.002(2)	−0.001(3)
C(12)	2a	0.5440(7)	0.7111(4)	0.0049(5)	0.090(5)	0.103(6)	0.071(4)	−0.032(4)	0.002(4)	0.016(4)
C(13)	2a	0.5061(4)	0.6500(3)	0.2067(4)	0.036(3)	0.048(3)	0.047(3)	0.001(3)	−0.004(2)	−0.003(3)
C(14)	2a	0.6687(5)	0.6519(4)	0.2404(4)	0.035(3)	0.080(4)	0.054(4)	−0.002(3)	0.002(2)	−0.007(3)
C(15)	2a	0.6898(5)	0.6408(4)	0.3697(4)	0.042(3)	0.043(3)	0.067(4)	−0.001(3)	0.001(3)	−0.001(3)
C(16)	2a	0.5855(6)	0.6903(3)	0.4385(4)	0.047(3)	0.043(3)	0.053(4)	−0.002(3)	0.000(3)	−0.005(3)
C(17)	2a	0.4734(6)	0.7268(3)	0.3884(5)	0.059(4)	0.053(4)	0.058(4)	0.008(3)	0.006(3)	−0.009(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(18)	2*a*	0.4342(6)	0.7238(4)	0.2629(5)	0.055(3)	0.063(4)	0.065(4)	0.011(3)	–0.005(3)	–0.014(3)
C(19)	2*a*	0.6178(6)	0.6942(4)	0.5650(4)	0.058(4)	0.087(5)	0.057(4)	–0.006(3)	0.002(3)	0.010(4)
O(1')	2*a*	0.0824(4)	0.6439(3)	–0.0837(3)	0.075(3)	0.087(3)	0.052(2)	0.006(3)	–0.011(2)	–0.006(2)
O(2')	2*a*	0.1828(4)	0.5537(4)	–0.7887(3)	0.069(3)	0.213(6)	0.055(3)	–0.061(4)	0.016(2)	–0.016(3)
O(3')	2*a*	–0.0305(4)	0.4926(2)	–0.8043(3)	0.060(2)	0.074(3)	0.047(2)	–0.014(2)	0.006(2)	–0.011(2)
O(4')	2*a*	–0.1664(4)	0.3636(2)	–0.9335(3)	0.068(2)	0.073(3)	0.061(3)	–0.021(2)	0.018(2)	–0.013(2)
C(1')	2*a*	0.2263(6)	0.6356(4)	–0.3722(5)	0.054(3)	0.105(6)	0.056(4)	–0.031(4)	–0.002(3)	–0.006(4)
C(2')	2*a*	0.2190(6)	0.6511(4)	–0.2560(5)	0.060(4)	0.074(4)	0.060(4)	–0.016(4)	–0.012(3)	–0.002(4)
C(3')	2*a*	0.0952(6)	0.6310(4)	–0.2000(5)	0.061(4)	0.068(5)	0.042(4)	0.011(3)	–0.010(3)	0.000(3)
C(4')	2*a*	–0.0230(6)	0.6012(3)	–0.2592(5)	0.046(3)	0.078(5)	0.057(4)	0.003(3)	–0.005(3)	–0.009(3)
C(5')	2*a*	–0.0151(5)	0.5858(4)	–0.3741(5)	0.038(3)	0.092(5)	0.053(4)	0.000(3)	–0.004(3)	–0.005(4)
C(6')	2*a*	0.1109(5)	0.6024(3)	–0.4346(4)	0.042(3)	0.055(4)	0.042(3)	–0.004(3)	–0.005(3)	0.001(3)
C(7')	2*a*	0.1281(6)	0.5848(4)	–0.5564(5)	0.047(3)	0.070(4)	0.043(3)	–0.001(3)	–0.001(3)	0.001(3)
C(8')	2*a*	0.0394(6)	0.5439(4)	–0.6244(4)	0.040(3)	0.067(4)	0.043(3)	–0.007(3)	0.002(3)	0.001(3)
C(9')	2*a*	0.0730(6)	0.5311(4)	–0.7444(5)	0.039(3)	0.095(5)	0.052(4)	0.005(3)	0.003(3)	0.001(4)
C(10')	2*a*	–0.0108(7)	0.4788(4)	–0.9255(5)	0.086(4)	0.078(5)	0.045(4)	–0.001(4)	0.007(3)	–0.012(3)
C(11')	2*a*	–0.0177(5)	0.3895(4)	–0.9546(4)	0.045(3)	0.061(4)	0.054(4)	0.004(3)	–0.002(3)	0.010(3)
C(12')	2*a*	0.0792(7)	0.3368(4)	–0.8784(5)	0.099(5)	0.077(5)	0.054(4)	0.029(4)	–0.002(3)	0.002(3)
C(13')	2*a*	0.0104(5)	0.3793(3)	–1.0840(4)	0.040(3)	0.037(3)	0.046(3)	–0.001(2)	0.000(2)	0.000(3)
C(14')	2*a*	0.1695(5)	0.3917(4)	–1.1154(4)	0.037(3)	0.057(4)	0.062(4)	–0.001(3)	0.003(3)	0.001(3)
C(15')	2*a*	0.1841(5)	0.3975(4)	–1.2444(4)	0.051(3)	0.065(4)	0.069(4)	0.013(3)	0.024(3)	0.007(4)
C(16')	2*a*	0.0895(6)	0.3403(3)	–1.3113(4)	0.048(3)	0.046(4)	0.053(4)	0.018(3)	0.002(3)	0.002(3)
C(17')	2*a*	–0.0080(6)	0.2948(4)	–1.2606(4)	0.047(3)	0.066(4)	0.048(3)	–0.006(3)	0.007(3)	–0.014(3)
C(18')	2*a*	–0.0431(6)	0.2995(4)	–1.1359(4)	0.056(3)	0.073(4)	0.052(4)	–0.020(3)	0.013(3)	–0.011(3)
C(19')	2*a*	0.1172(6)	0.3354(4)	–1.4376(4)	0.063(4)	0.073(5)	0.064(4)	0.026(3)	0.017(3)	0.011(3)

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