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3-Oxoolean-12-en-20-yl *α*-methylcarboxylate

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The title compound, $C_{31}H_{48}O_3$, was obtained by methylation of 3-oxoolean-12-en-20-α-oic acid, isolated from the root bark of *Austroplenckia populnea* (*Celastraceae*). Rings *A*, *B*, *D* and *E* are in chair conformations and ring *C* is in an envelope conformation.

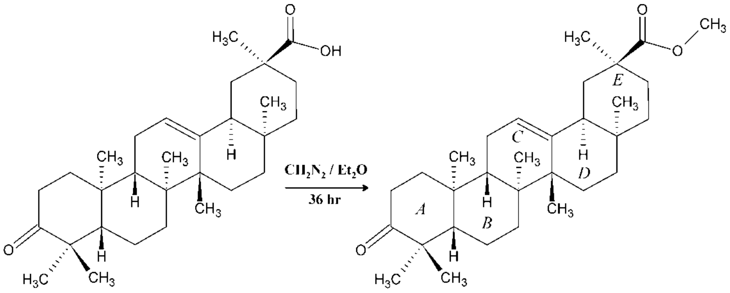
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.007 Å
R factor = 0.055
wR factor = 0.159
Data-to-parameter ratio = 7.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Considerable attention has arisen from the investigation of chemical constituents of plants of the *Celastraceae* family, on account of the antitumor and antileukemic activities found in maytansinoids and quinonemethide triterpenes isolated from plants of that family (Marine-Bettolo, 1974). In previous papers, we described the chemical constitution of the root bark (Sousa *et al.*, 1988), bark wood (Sousa, Silva, Pedersoli & Alves, 1990) and root wood (Sousa, Silva & Pedersoli, 1990) of *Austroplenckia populnea (Reiss) Lundell*, a specimen of the *Celastraceae* family. The plant is popularly known in the state of Minas Gerais (Brazil) as 'mangabeira-brava', and the decoction of its branches is used as a traditional antidysenteric medicine (Corrêa, 1978).



(1) **(2)**

The title compound, (2), was isolated according to the procedure described in the *Experimental* section. Fig. 1 shows an *ORTEP*-3 (Farrugia, 1997) view of (2), with the atom-numbering scheme. All rings adopt chair conformations, except for the partially unsaturated ring C, which is in an envelope conformation, with C18 in the flap position. The ring junctions *A*/*B*, *B*/*C*, and *D*/*E* are *trans*, *trans*, and *cis*, respectively. Selected bond lengths and angles are given in Table 1. The mean length of C—C single bonds is 1.52 (2) Å and the C7═C8 bond length is 1.331 (6) Å, which agree well with the range expected for formal single and double bonds, respectively. The two carbonyls have very similar bond lengths: C1═O1 = 1.213 (7) Å and C27═O2 = 1.197 (5) Å. On the other hand, the two C—O bonds differ from each other by 0.1 Å; C27—O3 = 1.356 (5) Å and C28—O3 = 1.456 (5) Å. This difference, which is comparable to that in other similar

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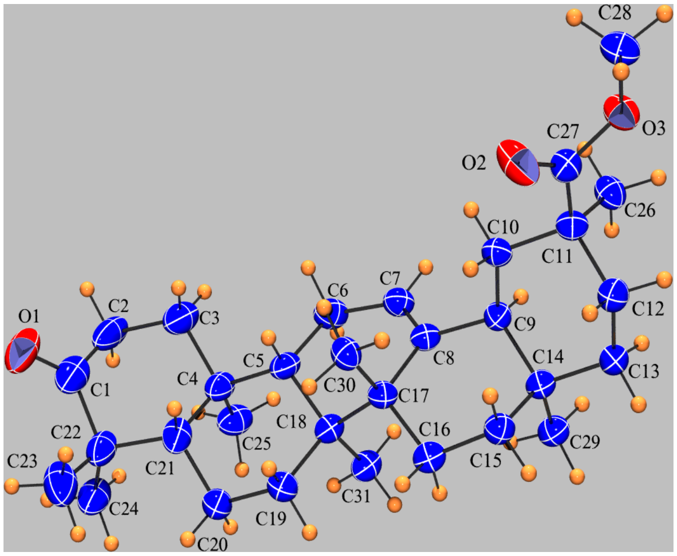

Figure 1
View of (2) (50% probability displacement ellipsoids).

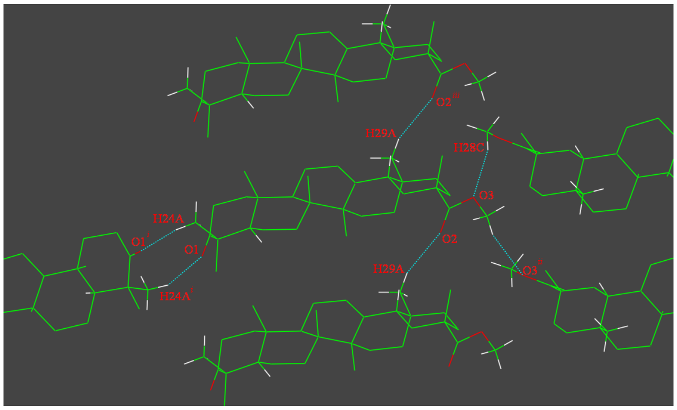

Figure 2
Packing of (2); weak hydrogen-bond contacts are shown as dotted lines.

triterpenes (Cota *et al.*, 1990*a*,*b*), is probably due to resonance involving the carboxyl group O2═C27—O3.

In the crystal structure, molecules are connected by weak C—H···O hydrogen bonds. The crystal packing and the intermolecular interactions of (2) are shown in Fig. 2.

Experimental

The bark wood of *Austroplenckia populnea* (a voucher specimen, number 10473, deposited at the Herbarium of the Natural History Museum of The Universidade Federal de Minas Gerais) was reduced to a powder and extracted with methanol at room temperature. Further extraction was carried out using hexane, benzene and ethyl acetate. The extract from hexane was purified by column chromatography (silica gel), using increasing proportions of CH_2Cl_2 in hexane and ethyl acetate in $CHCl_3$ as solvent. The benzene extract was purified by column chromatography (silica gel). 3-Oxoolean-12-ene-20-α-carboxylic acid [katonic acid, (1)], was isolated, in both extracts, by elution with $CHCl_3$ and crystallized from methanol/$CHCl_3$. 3-Oxoolean-12-ene-20-α-methylcarboxylate [methyl katononate, (2)] was obtained from (1) by treatment with CH_2N_2 in $(C_2H_5)_2O$ over a period of 36 h (Coxon & Wells, 1980). The pure methyl katononate was obtained as lustrous plates, crystallized from $CH_3OH/CHCl_3$. MS, ^{13}C, ^{1}H NMR and X-ray data gave the formula $C_{31}H_{48}O_3$. The MS showed the molecular ion at *m*/*z* 468 and a fragment at *m*/*z* 262, associated with a retro-Diels–Alder fragmentation, indicating (2) was a member of an olean-12-ene system (Doddrell *et al.*, 1974). The ^{1}H NMR spectrum revealed the presence of seven methyl groups, one methoxy group, and one methine proton attached to the double bond. Unequivocal proof of the structure and the complete stereochemistry of (2) was obtained by the single-crystal X-ray analysis.

Crystal data

$C_{31}H_{48}O_3$
$M_r = 468.69$
Monoclinic, $C2$
$a = 12.0144\ (4)$ Å
$b = 7.2750\ (4)$ Å
$c = 30.364\ (2)$ Å
$\beta = 99.565\ (2)°$
$V = 2617.1\ (2)$ Å^3
$Z = 4$

$D_x = 1.19$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2486 reflections
$\theta = 2.0$–$25.1°$
$\mu = 0.07$ mm^{-1}
$T = 100\ (2)$ K
Prism, colorless
$0.10 \times 0.05 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans winth κ offsets
Absorption correction: none
4283 measured reflections
2486 independent reflections
1679 reflections with $I > 2\sigma(I)$

$R_{int} = 0.049$
$\theta_{max} = 25.1°$
$h = -13 \rightarrow 14$
$k = -8 \rightarrow 8$
$l = -35 \rightarrow 35$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma\ (F^2)] = 0.055$
$wR(F^2) = 0.159$
$S = 1.09$
2486 reflections
315 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 0.1561P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.213 (7)	O3—C27	1.356 (5)
O2—C27	1.197 (5)	O3—C28	1.456 (5)
C27—O3—C28	116.2 (3)	O2—C27—O3	121.0 (4)
O1—C1—C2	122.2 (6)	O2—C27—C11	125.8 (4)
O1—C1—C22	122.1 (7)	O3—C27—C11	113.2 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C24—H24*A*···O1^{i}	0.98	2.49	3.364 (6)	148
C28—H28*C*···O3^{ii}	0.98	2.55	3.493 (6)	162
C29—H29*A*···O2^{iii}	0.98	2.65	3.587 (6)	160

Symmetry codes: (i) $1 - x, y, -z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, 1 - z$; (iii) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

Since the X-ray data do not allow the determination of the absolute configuration, intensities of the Friedel pair reflections were averaged before refinement. All H atoms were included in calculated positions with C—H distances ranging from 0.98 to 1.00 Å and then included in the refinement in the riding motion approximation, with $U_{iso} = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl groups) of the carrier atom.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Corrêa, M. P. (1978). *Dicionário das Plantas Uteis do Brasil e das Plantas Exóticas Cultivadas*. Rio de Janeiro: Imprensa Nacional.

Cota, A. B., Mascarenhas, Y. P., Silva, G. D. F. & Souza, J. R. (1990*a*). *Acta Cryst.* C**46**, 326–327.

Cota, A. B., Mascarenhas, Y. P., Silva, G. D. F. & Souza, J. R. (1990*b*). *Acta Cryst.* C**46**, 328–329.

Coxon, D. T. & Wells, J. W. (1980). *Phytochemistry*, **19**, 1247–1248.

Doddrell, D. T., Khong, P. W. & Lewis, K. G. (1974). *Tetrahedron Lett.* **27**, 2381–2384.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Marine-Bettolo, G. B. (1974). *Il Farmaco Ed. Sci.* **29**, 551–568.

Nonius (1997–2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Sousa, J. R., Jannotti, N. K., Silva, G. D. F. & Pinheiro, J. A. (1988). *Gazz. Chim. Ital.* **118**, 821–822.

Sousa, J. R., Silva, G. D. F. & Pedersoli, J. L. (1990). *Quím. Nova*, **13**, 252–253.

Sousa, J. R., Silva, G. D. F., Pedersoli, J. L. & Alves, R. J. (1990). *Phytochemistry*, **29**, 3259–3261.