High peaks on the ΔF map were close to the Br atom. Calculations were carried out on a PS-2 computer using the *SHELXTL/PC* (Sheldrick, 1990) system. H atoms were allowed to ride at idealized distances from their associated C atoms.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71527 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1041]

References

Allen, D. W., Nowell, I. W., March, L. A. & Taylor, B. F. (1984). *J. Chem. Soc. Perkin Trans.* 1, pp. 2523–2528.

Cambridge Structural Database (1992). Version 5. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

Connor, J. A., Kennedy, R. J., Dawes, H. M., Hursthouse, M. B. & Walker, N. P. C. (1990). *J. Chem. Soc. Perkin Trans.* 2, pp. 203–207.

Kaneda, T., Shizaki, Y. I., Misumi, S., Kai, Y., Hirao, G. & Kasai, N. (1988). *J. Am. Chem. Soc.* **110**, 2970–2972.

Larson, A. C. (1967). *Acta Cyst.* **23**, 664–665.

Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1994). C**50**, 460–462

Structure of Trijugin A

K. SEKAR† AND S. PARTHASARATHY*

Department of Crystallography and Biophysics,‡
University of Madras, Guindy Campus,
Madras 600 025, India

V. MATHURAM

Captain Srinivasa Murti Drug Research Institute for
Ayurveda, Arumbakkam, Madras 600 106, India

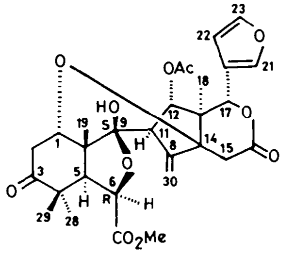
(*Received* 2 *September* 1992; *accepted* 9 *August* 1993)

Abstract

In the title compound, methyl 11-acetoxy-10-(3-furyl)-12a-hydroxy-3,3,10a,12b-tetramethyl-13-methylene-4,8-dioxo-2,2a,3,4,5,5a,7,8,10,10a,11,12,-12a,12b-tetradecahydro-6a*H*-6a,12-methanofuro-[2,3,4-*fg*]pyrano[4,3-*b*][1]benzoxocine-2-carboxylate, $C_{29}H_{34}O_{11}$, several C—C bonds and C—C—C angles deviate by more than 3σ from their expected values. The six-membered benzo and pyrano rings *A* and *D* are in distorted chair conformations. The five-membered furo and cyclopenta (formed by the methano bridge) rings *B* and *C* are in distorted half-chair conformations whereas the furyl ring *E* is planar within the 5σ level. The title structure is stabilized by van der Waals forces.

Comment

Trijugin A was isolated from the leaves of *H. trijuga* by Purushothaman, Mathuram, Sarada, Connolly & Rycroft (1987). This compound (I) represents a new skeletal type of tetranortriterpenoid which were found to be derivatives of methyl angolensate but with a novel carbon skeleton having a contracted ring *C*.



(I)

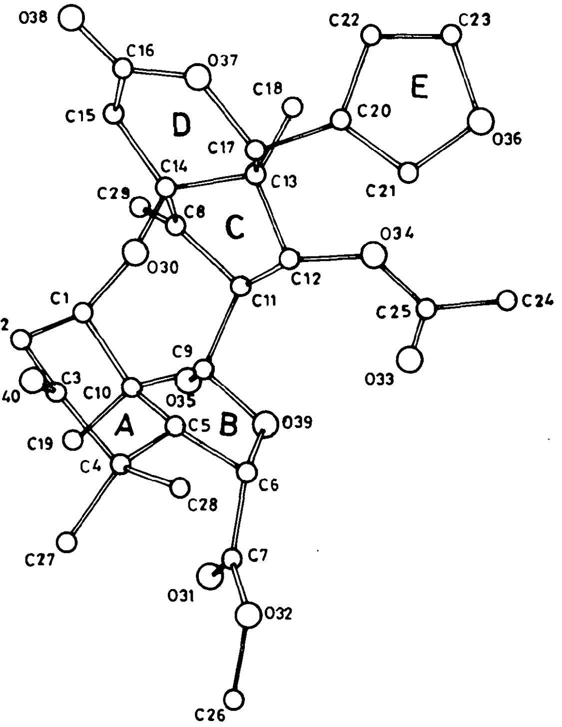


Fig. 1. View of the title molecule with the atom-numbering scheme.

---

† Present address: Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560 012, India.

‡ Contribution No. 826.

Some C—C bonds and C—C—C angles deviate by more than 3σ from their expected values. Similar features are also observed in fused-ring systems having axial substitutions with bulky groups (Hall & Maslen, 1965; Gzella, Zaprutko, Wrezciono & Jaskólski, 1987; Sekar, Parthasarathy, Kundu & Barik, 1992). The six-membered rings *A* and *D* are in distorted chair conformations. In ring *A*, the puckering is enhanced in the region of C10 and decreased in the region of C3. In ring *D*, the puckering is enhanced in the region of C13 and decreased in the region of C16. The five-membered rings *B* and *C* are in distorted half-chair conformations. The structure is stabilized by van der Waals forces.

Experimental

Crystal data

$C_{29}H_{34}O_{11}$
M_r = 558.58
Monoclinic
$P2_1$
a = 11.592 (1) Å
b = 8.031 (2) Å
c = 15.597 (1) Å
β = 109.32 (2)°
V = 1370.2 (4) Å^3
Z = 2
D_x = 1.354 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 20–30°
μ = 0.830 mm^{-1}
T = 293 K
Needle
0.30 × 0.25 × 0.20 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: ψ-scan method
$T_{\min}$ = 0.961, $T_{\max}$ = 0.987
2984 measured reflections
2761 independent reflections

2632 observed reflections [$I > 3.0\sigma(I)$]
$R_{\rm int}$ = 0.0284
$\theta_{\max}$ = 70°
h = 0 → 13
k = 0 → 9
l = −17 → 17
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
R = 0.042
wR = 0.050
S = 1.089
2632 reflections
496 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.003565F^2]$
$(\Delta/\sigma)_{\max}$ = 0.040
$\Delta\rho_{\max}$ = 0.131 e Å^{-3}
$\Delta\rho_{\min}$ = −0.108 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.5115 (2)	0.5503 (4)	0.8915 (1)	0.032 (1)
C2	0.4401 (2)	0.4249 (4)	0.9290 (1)	0.039 (1)
C3	0.3577 (2)	0.3071 (4)	0.8603 (2)	0.040 (1)
C4	0.2777 (2)	0.3754 (4)	0.7676 (2)	0.035 (1)
C5	0.3590 (2)	0.5016 (4)	0.7390 (1)	0.031 (1)
C6	0.3177 (2)	0.5910 (4)	0.6462 (2)	0.039 (1)
C7	0.1927 (2)	0.6746 (5)	0.6151 (2)	0.045 (1)
C8	0.6969 (2)	0.7089 (4)	0.8567 (2)	0.037 (1)
C9	0.4827 (2)	0.7451 (4)	0.7480 (2)	0.038 (1)
C10	0.4229 (2)	0.6388 (3)	0.8075 (1)	0.031 (1)
C11	0.6181 (2)	0.7100 (4)	0.7570 (2)	0.038 (1)
C12	0.6449 (2)	0.5411 (4)	0.7196 (1)	0.036 (1)
C13	0.7510 (2)	0.4621 (4)	0.7969 (2)	0.036 (1)
C14	0.7183 (2)	0.5280 (4)	0.8790 (2)	0.035 (1)
C15	0.8089 (2)	0.4763 (5)	0.9685 (2)	0.045 (1)
C16	0.8399 (3)	0.2926 (5)	0.9705 (2)	0.051 (1)
C17	0.7477 (2)	0.2715 (4)	0.8018 (2)	0.041 (1)
C18	0.8759 (2)	0.5256 (4)	0.7974 (2)	0.047 (1)
C19	0.3384 (2)	0.7529 (4)	0.8392 (2)	0.040 (1)
C20	0.7912 (3)	0.1751 (5)	0.7360 (2)	0.054 (1)
C21	0.7247 (4)	0.1364 (7)	0.6478 (3)	0.082 (2)
C22	0.9049 (4)	0.1036 (8)	0.7504 (4)	0.087 (2)
C23	0.9035 (4)	0.0223 (8)	0.6764 (4)	0.102 (2)
C24	0.6434 (3)	0.5729 (7)	0.4822 (2)	0.068 (2)
C25	0.6000 (3)	0.5195 (5)	0.5584 (2)	0.051 (1)
C26	−0.0179 (3)	0.6248 (7)	0.5401 (4)	0.083 (2)
C27	0.1584 (2)	0.4400 (5)	0.7792 (2)	0.052 (1)
C28	0.2454 (2)	0.2330 (4)	0.6984 (2)	0.048 (1)
C29	0.7393 (3)	0.8359 (5)	0.9113 (2)	0.058 (1)
O30	0.6010 (1)	0.4502	0.8697 (1)	0.032 (1)
O31	0.1713 (2)	0.8173 (4)	0.6254 (2)	0.066 (1)
O32	0.1076 (2)	0.5635 (4)	0.5705 (2)	0.058 (1)
O33	0.5085 (2)	0.4412 (5)	0.5503 (1)	0.071 (1)
O34	0.6788 (2)	0.5700 (4)	0.6397 (1)	0.045 (1)
O35	0.4824 (2)	0.9167 (3)	0.7628 (2)	0.057 (1)
O36	0.7949 (5)	0.0468 (7)	0.6090 (3)	0.123 (2)
O37	0.8268 (2)	0.2132 (4)	0.8911 (1)	0.055 (1)
O38	0.8833 (3)	0.2157 (5)	1.0395 (2)	0.091 (1)
O39	0.4095 (2)	0.7120 (4)	0.6551 (1)	0.051 (1)
O40	0.3518 (3)	0.1619 (4)	0.8802 (2)	0.077 (1)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.537 (4)	C11—C12	1.548 (4)
C1—C10	1.545 (3)	C12—C13	1.545 (3)
C1—O30	1.439 (3)	C12—O34	1.444 (3)
C2—C3	1.509 (4)	C13—C14	1.544 (5)
C3—C4	1.538 (4)	C13—C17	1.534 (5)
C3—O40	1.214 (5)	C13—C18	1.533 (4)
C4—C5	1.547 (4)	C14—C15	1.501 (4)
C4—C27	1.543 (4)	C14—O30	1.459 (3)
C4—C28	1.532 (4)	C15—C16	1.516 (6)
C5—C6	1.543 (4)	C16—O37	1.356 (4)
C5—C10	1.543 (3)	C16—O38	1.198 (5)
C6—C7	1.523 (4)	C17—C20	1.500 (5)
C6—O39	1.414 (4)	C17—O37	1.468 (3)
C7—O31	1.195 (5)	C20—C21	1.372 (5)
C7—O32	1.341 (4)	C20—C22	1.386 (6)
C8—C11	1.521 (4)	C21—O36	1.368 (8)
C8—C14	1.495 (5)	C22—C23	1.322 (9)
C8—C29	1.315 (5)	C23—O36	1.361 (6)
C9—C10	1.580 (4)	C24—C25	1.498 (5)
C9—C11	1.555 (4)	C25—O33	1.203 (5)
C9—O35	1.398 (4)	C25—O34	1.357 (3)
C9—O39	1.441 (3)	C26—O32	1.459 (4)
C10—C19	1.538 (4)		
C11—C9—O39	107.4 (2)	C4—C5—C6	123.1 (2)
C11—C9—O35	102.8 (2)	C6—C5—C10	104.3 (2)
C10—C9—O39	105.3 (2)	C5—C6—O39	103.8 (2)
C10—C9—O35	114.2 (2)	C5—C6—C7	118.1 (2)
C10—C9—C11	118.4 (2)	C7—C6—O39	109.5 (3)
C5—C10—C9	100.5 (2)	C6—C7—O32	109.3 (3)
C1—C10—C9	116.7 (2)	C6—C7—O31	126.7 (3)
C1—C10—C5	106.9 (2)	O31—C7—O32	123.9 (3)
C9—C10—C19	108.5 (2)	C14—C8—C29	127.2 (3)
C5—C10—C19	115.9 (2)	C11—C8—C29	128.8 (3)
C1—C10—C19	108.5 (2)	C11—C8—C14	103.9 (2)
C8—C11—C9	109.9 (2)	O35—C9—O39	108.4 (3)
C9—C11—C12	116.6 (2)	C8—C11—C12	104.6 (2)

C20—C21—O36	110.1 (4)	C11—C12—O34	109.3 (3)
C20—C22—C23	109.1 (5)	C11—C12—C13	105.8 (2)
C22—C23—O36	110.1 (5)	C13—C12—O34	111.5 (2)
C24—C25—O34	110.9 (3)	C12—C13—C18	112.0 (2)
C24—C25—O33	125.6 (3)	C12—C13—C17	115.0 (2)
O33—C25—O34	123.5 (3)	C12—C13—C14	99.0 (2)
C1—O30—C14	117.3 (2)	C17—C13—C18	111.8 (2)
C7—O32—C26	115.3 (3)	C14—C13—C18	111.9 (2)
C12—O34—C25	117.9 (2)	C14—C13—C17	106.5 (2)
C21—O36—C23	105.5 (5)	C8—C14—C13	102.0 (2)
C16—O37—C17	124.2 (3)	C13—C14—O30	104.3 (2)
C6—O39—C9	113.5 (2)	C13—C14—C15	112.8 (2)
C10—C1—O30	112.7 (1)	C8—C14—O30	108.4 (2)
C2—C1—O30	104.2 (2)	C8—C14—C15	119.8 (3)
C2—C1—C10	109.5 (2)	C15—C14—O30	108.4 (2)
C1—C2—C3	115.8 (2)	C14—C15—C16	112.1 (3)
C2—C3—O40	119.8 (3)	C15—C16—O38	123.1 (3)
C2—C3—C4	119.2 (3)	C15—C16—O37	119.0 (3)
C4—C3—O40	121.0 (3)	O37—C16—O38	117.7 (4)
C3—C4—C28	109.1 (3)	C13—C17—O37	110.3 (2)
C3—C4—C27	107.2 (2)	C13—C17—C20	117.5 (3)
C3—C4—C5	105.6 (2)	C20—C17—O37	103.8 (2)
C27—C4—C28	108.3 (2)	C17—C20—C22	128.3 (3)
C5—C4—C28	108.4 (2)	C17—C20—C21	126.8 (4)
C5—C4—C27	118.0 (3)	C21—C20—C22	104.9 (4)
C4—C5—C10	117.8 (2)		

Ring *A*

C1—C2—C3—C4	−43.6 (3)	C4—C5—C10—C1	63.0 (3)
C2—C3—C4—C5	40.4 (3)	C5—C10—C1—C2	−56.6 (2)
C3—C4—C5—C10	−52.0 (3)	C10—C1—C2—C3	50.0 (3)

Ring *B*

C5—C6—O39—C9	−17.6 (3)	C9—C10—C5—C6	−34.3 (2)
C6—O39—C9—C10	−4.5 (3)	C10—C5—C6—O39	32.9 (3)
O39—C9—C10—C5	24.3 (3)		

Ring *C*

C8—C11—C12—C13	−7.5 (3)	C13—C14—C8—C11	45.4 (3)
C11—C12—C13—C14	33.7 (3)	C14—C8—C11—C12	−23.2 (3)
C12—C13—C14—C8	−48.5 (3)		

Ring *D*

C13—C14—C15—C16	−46.9 (4)	C16—O37—C17—C13	37.3 (4)
C14—C15—C16—O37	25.1 (4)	O37—C17—C13—C14	−54.0 (3)
C15—C16—O37—C17	−21.7 (5)	C17—C13—C14—C15	62.3 (3)

Ring *E*

C20—C21—O36—C23	3.6 (6)	C23—C22—C20—C21	−2.4 (6)
C21—O36—C23—C22	−5.1 (7)	C22—C20—C21—O36	−0.8 (6)
O36—C23—C22—C20	4.8 (7)		

The space group was determined using *STATCW* (Sekar, 1991). The structure was solved with *SHELXS*90 (Sheldrick, 1990) and refined with *SHELX*76 (Sheldrick, 1976). *PARST* (Nardelli, 1983) was used to calculate the molecular parameters. The figure was drawn using *PLUTO* (Motherwell & Clegg, 1978). Refinement was by full-matrix least squares and all calculations were performed on a MicroVAX II.

Thanks are due to the Council of Scientific and Industrial Research, India, for the award of Senior Research Fellowship to KS.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and geometry, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71569 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1044]

References

Gzella, A., Zaprutko, L., Wrezciono, U. & Jaskólski, M. (1987). *Acta Cryst.* C**43**, 759–762.

Hall, S. R. & Maslen, E. N. (1965). *Acta Cryst.* **18**, 265–279.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Purushothaman, K. K., Mathuram, V., Sarada, A., Connolly, J. D. & Rycroft, D. S. (1987). *Can. J. Chem.* **65**, 35–37.

Sekar, K. (1991). PhD thesis, Univ. of Madras, India.

Sekar, K., Parthasarathy, S., Kundu, A. B. & Barik, B. R. (1992). *Acta Cryst.* C**49**, 616–618.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Acta Cryst. (1994). C**50**, 462–466

trans-2-Phenyltetrahydropyran-3-ylmethyl *p*-Toluenesulfonate

GERHARD RAABE,* MARTIN SAWICKI AND
HERBERT FRAUENRATH

*Institut für Organische Chemie,
Rheinisch-Westfälische Technische Hochschule Aachen,
Professor-Pirlet-Straße 1, D-52056 Aachen, Germany*

(*Received* 15 *April* 1993; *accepted* 6 *August* 1993)

Abstract

trans-2-Phenyltetrahydropyran-3-ylmethyl *p*-toluenesulfonate, $C_{19}H_{22}O_4S$, (6), crystallizes with two molecules (*A*, *B*) in the asymmetric unit. The shortest intermolecular distance between the independent species involving non-H atoms only (C···O) is 3.138 (4) Å. The bulky substituents in (6) are oriented *trans* to each other and, as expected, occupy equatorial positions (*ee*). However, semi-empirical calculations on one precursor of (6), 2-phenyltetrahydropyran-3-carbaldehyde (4), indicate that at least in the case of isolated molecules the energy difference between an *ee* species and its isomer with both substituents in axial positions (*aa*) might be quite low (< 13 kJ mol^{-1}).

Comment

Compounds of general structure (1) undergo Lewis acid-catalyzed rearrangement resulting in five-membered ring structures (2) which are formed in a *cis*:*trans* ratio of 9–10:1 (Frauenrath, Runsink & Scharf, 1982). 2-Phenyl-5,6-dihydro-4*H*-1,3-dioxocine, (3), undergoes a similar rearrangement when