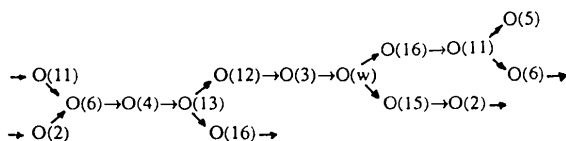


around the central H atom, which amount to 360 (3) and 359 (3)° respectively. The water molecule donates two hydrogen bonds and accepts one, thus serving as an important cohesive element in the hydrogen-bond system. This system consists of a finite chain which stops at ring O(5) and an infinite one which branches at the bifurcated donors and also at the water molecule. This system can be schematically represented (see below).



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Functionalized Hydrocarbons with Condensed Ring Skeletons. X. A Methyltricyclo[7.4.0.0^{2,6}]tetradec-7-ene

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Abstract. (1) 1,9-*trans*-1,2-*cisoid*-2,6-*cis*-4,11,11-Tris(methoxycarbonyl)-6-methyltricyclo[7.4.0.0^{2,6}]tridec-7-ene-4,2-carbolactone, C₂₁H₂₆O₈, M_r = 406.43, monoclinic, *P* $\bar{1}$, *a* = 6.0774 (2), *b* = 12.3784 (5), *c* = 14.2565 (4) Å, α = 72.906 (3), β =

86.361 (3), γ = 78.181 (3)°, *V* = 1003.38 (6) Å³, *D_x* = 1.345 Mg m⁻³, *Z* = 2, λ (Cu *K*α) = 1.54056 Å, μ = 0.82 mm⁻¹, *F*(000) = 432, room temperature, final *R* = 0.043 for 2841 observed reflections. The tricyclic compound (1) has the same carbon framework as in the *BCD* rings in a steroid nucleus. Ring *B* adopts a chair while ring *C* has a half-chair conformation. A *trans* relative stereochemistry is observed at the *BC* ring junction while a *cis* hydrincline is observed for the *CD* junction, the lactone bridge being *cis* to the

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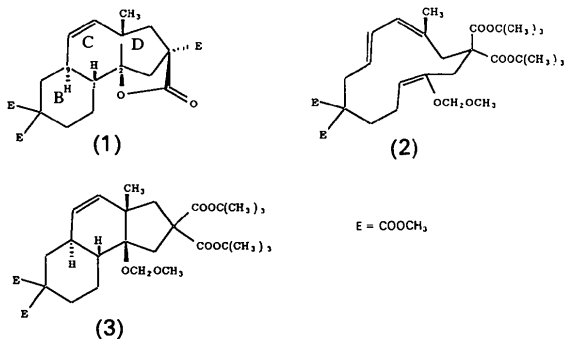
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Table 1. Final coordinates and B_{eq} values for non-hydrogen atoms with *e.s.d.*'s in parentheses
$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
C(1)	0.4152 (4)	0.76563 (18)	0.55372 (16)	2.62 (10)
C(2)	0.2331 (4)	0.85522 (20)	0.48748 (17)	2.85 (11)
C(3)	0.2034 (4)	0.82634 (19)	0.39231 (16)	2.65 (10)
C(4)	0.0235 (4)	0.91263 (21)	0.32724 (19)	3.25 (12)
C(5)	0.0328 (4)	0.94409 (21)	0.23057 (19)	3.48 (12)
C(6)	0.2293 (4)	0.90368 (19)	0.17136 (16)	3.03 (11)
C(7)	0.1657 (5)	0.85199 (22)	0.09173 (19)	3.48 (13)
C(8)	0.2997 (4)	0.72597 (20)	0.12388 (16)	2.96 (11)
C(9)	0.2784 (4)	0.69698 (21)	0.23565 (17)	2.80 (11)
C(10)	0.3829 (4)	0.79803 (19)	0.23997 (16)	2.68 (10)
C(11)	0.4265 (4)	0.81402 (20)	0.33690 (16)	2.64 (10)
C(12)	0.6056 (4)	0.72173 (22)	0.40002 (18)	3.03 (12)
C(13)	0.6362 (4)	0.74963 (23)	0.49514 (19)	3.10 (13)
C(14)	0.4661 (4)	0.80782 (21)	0.63845 (18)	3.13 (12)
C(15)	0.6136 (7)	0.7480 (3)	0.7997 (3)	5.23 (20)
C(16)	0.3472 (4)	0.64794 (20)	0.59698 (16)	3.01 (12)
C(17)	0.0713 (6)	0.5493 (3)	0.6872 (3)	5.11 (17)
C(18)	0.2445 (4)	0.64318 (22)	0.07356 (18)	3.49 (12)
C(19)	0.1694 (8)	0.6186 (4)	-0.0780 (3)	5.99 (24)
C(20)	0.5488 (4)	0.73501 (20)	0.11263 (17)	3.42 (12)
C(21)	0.3532 (6)	1.0043 (3)	0.12613 (23)	4.42 (16)
O(1)	0.4515 (3)	0.90642 (14)	0.63592 (13)	4.90 (11)
O(2)	0.5415 (3)	0.71990 (14)	0.71607 (12)	4.35 (10)
O(3)	0.4639 (3)	0.55739 (13)	0.59697 (12)	4.38 (9)
O(4)	0.1418 (3)	0.65889 (13)	0.63789 (12)	3.87 (8)
O(5)	0.2342 (4)	0.54550 (15)	0.11462 (13)	5.61 (12)
O(6)	0.2159 (3)	0.69200 (15)	-0.02197 (12)	4.49 (10)
O(7)	0.6850 (3)	0.71206 (16)	0.05367 (13)	4.89 (10)
O(8)	0.5957 (3)	0.77664 (13)	0.18605 (11)	3.30 (8)

angular methyl group at C(6) and to the hydrogen at C(1).

Introduction. In the preliminary study directed towards the general synthesis of 14 β -hydroxy steroids by the use of a transannular Diels–Alder reaction (Lamothe, Ndiwami & Deslongchamps, 1988), compound (1) was synthesized starting from macrocyclic triene (2). Diels–Alder reaction of (2) furnished compound (3) plus two minor side products. The relative stereochemistries at C(3), C(6), C(10), and C(11) can be predicted (Soucy & Deslongchamps, 1990). Acidic treatment of the major compound (3) removed the acid labile moiety, and furnished after treatment with diazomethane the lactone triester (1). The present crystallographic study affords details of the relative stereochemistry of this compound.

Table 2. Bond lengths (Å) and valence angles (°) with *e.s.d.*'s in parentheses

C(1)—C(2)	1.537 (3)	C(9)—C(10)	1.532 (3)
C(1)—C(3)	1.545 (3)	C(10)—C(11)	1.499 (3)
C(1)—C(14)	1.521 (3)	C(10)—O(8)	1.479 (3)
C(1)—C(16)	1.536 (3)	C(11)—C(12)	1.520 (4)
C(2)—C(3)	1.531 (3)	C(12)—C(13)	1.525 (3)
C(3)—C(4)	1.505 (3)	C(14)—O(1)	1.195 (3)
C(3)—C(11)	1.528 (3)	C(14)—O(2)	1.331 (3)
C(4)—C(5)	1.318 (4)	C(15)—O(2)	1.451 (3)
C(5)—C(6)	1.505 (4)	C(16)—O(3)	1.197 (3)
C(6)—C(7)	1.559 (3)	C(16)—O(4)	1.342 (3)
C(6)—C(10)	1.550 (3)	C(17)—O(4)	1.469 (3)
C(6)—C(21)	1.544 (4)	C(18)—O(5)	1.191 (3)
C(7)—C(8)	1.553 (4)	C(18)—O(6)	1.324 (3)
C(8)—C(9)	1.530 (3)	C(19)—O(6)	1.451 (4)
C(8)—C(18)	1.510 (3)	C(20)—O(7)	1.195 (3)
C(8)—C(20)	1.536 (3)	C(20)—O(8)	1.363 (3)
C(2)—C(1)—C(13)	109.87 (19)	C(6)—C(10)—C(11)	113.61 (18)
C(2)—C(1)—C(14)	110.20 (18)	C(6)—C(10)—O(8)	106.71 (17)
C(2)—C(1)—C(16)	112.87 (19)	C(9)—C(10)—C(11)	120.41 (18)
C(13)—C(1)—C(14)	106.76 (19)	C(9)—C(10)—O(8)	100.85 (17)
C(13)—C(1)—C(16)	108.92 (19)	C(11)—C(10)—O(8)	110.78 (18)
C(14)—C(1)—C(16)	107.01 (18)	C(3)—C(11)—C(10)	108.29 (19)
C(1)—C(2)—C(3)	112.17 (19)	C(3)—C(11)—C(12)	111.09 (19)
C(2)—C(3)—C(4)	112.75 (19)	C(10)—C(11)—C(12)	115.65 (19)
C(2)—C(3)—C(11)	110.62 (19)	C(11)—C(12)—C(13)	110.23 (20)
C(4)—C(3)—C(11)	110.70 (19)	C(1)—C(13)—C(12)	113.04 (20)
C(3)—C(4)—C(5)	124.07 (23)	C(1)—C(14)—O(1)	125.46 (22)
C(4)—C(5)—C(6)	124.51 (23)	C(1)—C(14)—O(2)	111.16 (19)
C(5)—C(6)—C(7)	114.15 (21)	O(1)—C(14)—O(2)	123.30 (21)
C(5)—C(6)—C(10)	108.31 (18)	C(1)—C(16)—O(3)	124.72 (22)
C(5)—C(6)—C(21)	108.69 (21)	C(1)—C(16)—O(4)	111.33 (19)
C(7)—C(6)—C(10)	101.75 (18)	O(3)—C(16)—O(4)	123.92 (21)
C(7)—C(6)—C(21)	111.58 (21)	C(8)—C(18)—O(5)	123.98 (22)
C(10)—C(6)—C(21)	112.24 (22)	C(8)—C(18)—O(6)	111.43 (20)
C(6)—C(7)—C(8)	102.99 (19)	O(5)—C(18)—O(6)	124.56 (22)
C(7)—C(8)—C(9)	101.30 (19)	C(8)—C(20)—O(7)	130.18 (22)
C(7)—C(8)—C(18)	117.34 (20)	C(8)—C(20)—O(8)	106.54 (20)
C(7)—C(8)—C(20)	105.65 (19)	O(7)—C(20)—O(8)	123.28 (22)
C(9)—C(8)—C(18)	118.78 (19)	C(14)—O(2)—C(15)	116.89 (21)
C(9)—C(8)—C(20)	99.35 (18)	C(16)—O(4)—C(17)	114.59 (21)
C(18)—C(8)—C(20)	112.12 (20)	C(18)—O(6)—C(19)	115.95 (25)
C(8)—C(9)—C(10)	93.19 (17)	C(10)—O(8)—C(20)	106.63 (17)
C(6)—C(10)—C(9)	103.00 (18)		

Experimental. Crystal: 0.20 × 0.20 × 0.12 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromator, Cu $K\alpha$ radiation; cell parameters were obtained by least-squares procedure on 25 reflections with 2θ range 60–80°. The $\omega/2\theta$ scan mode was used for data collection at a constant speed of 4° min⁻¹. Two standard reflections were monitored every 60 min without significant deviation; 3839 unique measured reflections, $R_{int} = 0.016$; 2841 observed with $I_o > 2.5\sigma(I_o)$; $2\theta_{max} = 143.3^\circ$, corresponding to hkl range of $-6-6, 0-14, -16-17$, respectively. No correction was made for absorption. The *NRCVAX* system (Gabe, Lee & LePage, 1985) was used for all calculations. The structure was solved by the application of direct methods and refinement by full-matrix least squares on *F*. All non-H atoms were located in the first Fourier *E* map and were refined anisotropically. All H atoms were calculated and refined isotropically. The last least-squares cycles were calculated with 55 atoms; 367

parameters using weights based on counting statistics. The residuals obtained at convergence were $R = 0.043$, $wR = 0.028$ and $S = 2.589$. Weights based on counting statistics were used. The max. $\Delta/\sigma = 0.138$. In the last D map the deepest hole was $-0.17 \text{ e } \text{\AA}^{-3}$ and the highest peak $0.21 \text{ e } \text{\AA}^{-3}$. The secondary-extinction coefficient was $0.35(2)$ (Larson, 1967; Zachariasen, 1963). Atomic scattering factors from *NRCVAX*.

Discussion. Table 1* gives the final atomic parameters with their B_{eq} values. Bond lengths and angles are given in Tables 2(a) and 2(b). Fig. 1 shows the atom numbering and an *ORTEP* perspective view of the tetracyclic compound. The relative stereochemistry found is *trans-syn-cis* as predicted. The structure is relatively rigid; only ring *B* can exist in two conformations, chair and boat, the former being energetically favorable. The observed *trans* and *cis* junctions at C(3)—C(11) and C(10)—C(11) hold ring

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53098 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

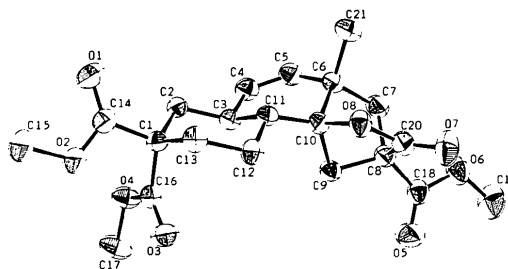


Fig. 1. *ORTEP* (Johnson, 1965) perspective view and crystallographic numbering.

C in a half-chair conformation. No abnormally short intermolecular contacts were observed.

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Molecular Structure of Opiate Alkaloids. IV.* Structure of Two Thioniamorphinans

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Abstract. (I) *S*(equatorial)-Allyl-3-hydroxy-17-thioniamorphinan perchlorate, $\text{C}_{19}\text{H}_{25}\text{OS}^+\cdot\text{ClO}_4^-$, $M_r = 400.91$, monoclinic, $P2_1/n$, $a = 9.4171(8)$, $b = 10.7425(10)$, $c = 19.096(2) \text{ \AA}$, $\beta = 95.666(7)^\circ$, $V = 1922.4(3) \text{ \AA}^3$, $Z = 4$, $D_x = 1.385 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.70930 \text{ \AA}$, $\mu = 0.33 \text{ mm}^{-1}$, $F(000) = 847.92$, room temperature, final $R = 0.052$ for 1742 observed

reflections. (II) *S*(axial)-Allyl-3-hydroxy-17-thioniamorphinan perchlorate, $\text{C}_{19}\text{H}_{25}\text{OS}^+\cdot\text{ClO}_4^-$, $M_r = 400.91$, monoclinic, $P2_1$, $a = 8.4554(10)$, $b = 11.658(3)$, $c = 9.5831(21) \text{ \AA}$, $\beta = 95.620(10)^\circ$, $V = 940.1(3) \text{ \AA}^3$, $Z = 2$, $D_x = 1.416 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.70930 \text{ \AA}$, $\mu = 0.33 \text{ mm}^{-1}$, $F(000) = 423.96$, room temperature, final $R = 0.054$ for 1015 observed reflections. The molecular structures of (I) and (II) are differentiated only by the orientation of the *S*-allyl substituent: the *S*-allyl group is equatorial in (I) and axial in (II). It has been shown that the activities as potent and selective blockers of κ opioid

* Part I: Michel, Proulx, Evrard, Norberg & Milchert (1988). Part II: Michel, Evrard, Norberg & Milchert (1988). Part III: Michel & Michel-Dewez (1990).

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