$C_{18}H_{14}N_2O_6$

l'état solide. La cohésion cristalline est confortée par des contacts de van der Waals (Å):

$C(12)\cdots C(35)(x, \frac{1}{2}-y, \frac{1}{2}+z)$	=	3,413 (5)
$O(11)\cdots C(52)(x, \frac{1}{2}-y, \frac{1}{2}+z)$	=	3,503 (4)
$C(12)\cdots N(51)(x, \frac{1}{2}-y, \frac{1}{2}+z)$	=	3,524 (5)
$O(11)\cdots C(155)(x, \frac{1}{2}-y, \frac{1}{2}+z)$	=	3,504 (4)
$C(35)\cdots O(22)(1+x, y, z)$	=	3,303 (4)
$C(13)\cdots O(154)(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$	=	3,311 (4)
$N(51)\cdots O(11)(x, \frac{1}{2}-y, -\frac{1}{2}+z)$	=	3,199 (3).

Cette structure cristalline est la première détermination de la stéréochimie de l'addition du noyau thymine sur le cycle pyrone du psoralène et vient compléter les résultats structuraux apportés par la détermination de la structure cristalline du photoproduit obtenu par addition du noyau thymine sur le cycle furane (Peckler, Graves, Kanne, Rapoport, Hearst & Kim, 1982; Land, Rushton, Beddoes, Bruce, Cernik, Dawson & Mills, 1982).

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Structure and Stereochemistry of (24R)-27-Nor-5α-cholestane-3β,4β,5,6α,7β,8,14,15α,24-nonaol: a Highly Hydroxylated Marine Steroid from the Starfish *Archaster typicus*

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Abstract. $C_{26}H_{46}O_9$, $M_r = 502.65$, orthorhombic, $P2_12_12_1$, $a = 5.834$ (2), $b = 20.035$ (2), $c = 21.503$ (4) Å, $V = 2513$ (1) Å^3, $Z = 4$, $D_x = 1.328$ Mg m^{-3}, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu(Cu K\alpha) = 0.77$ mm^{-1}, $F(000) = 1096$, room temperature, final $R = 0.048$ for 1813 independent observed reflections and 317 variables. The results confirm for the title compound the structure previously assigned on the basis of chemical and spectroscopic evidence including the chirality at C(20) and C(24). This steroid presents a marked amphiphilic character with the nine hydroxyl groups all grouped on one side of the molecule and shows an internal hydrogen bond between the hydroxyl substituents at C(7) and C(15). In the crystal double layers of molecules, internally linked by an extensive network of hydrogen bonds, interact through their hydrophobic surfaces.

Introduction. Recently Riccio, Squillace-Greco, Minale, Laurent & Duhet (1986) have reported the structure of

a new group of highly hydroxylated steroids, all with a $3\beta,6\alpha,8,14,15\alpha$-pentaol nucleus, isolated from the Pacific starfish *Archaster typicus*. Two of them, having four more hydroxyl groups [three located in the nucleus at $C(4)\beta$, $C(5)$ and $C(7)\beta$ and one in the side chain], are nonaols and constitute, as far as we know, the most highly hydroxylated steroids isolated from a natural source. Their structures were deduced from spectral data, including two-dimensional proton-carbon chemical shift correlation NMR spectroscopy, whilst some stereochemical aspects required an independent confirmation. The common 20*R* configuration proposed was mainly based on the large coupling constant $H(17)/H(20)$ $(J = 8.5\ Hz)$ observed in the ^1H NMR spectrum (deuterated pyridine) of the title compound. However the proton shifts for the $C(21)$ methyl group, which are sensitive to the stereochemistry at $C(20)$ (Nes, Varkey & Krevitz, 1977), were found in the spectra (CD_3OD) of the polar steroids from *A. typicus* at δ values ranging from δH 0.88 (title compound) to 0.91 $(\Delta^{24}$-compounds). These values are upfield shifted relative to the ^1H NMR spectra of several hydroxylated marine steroids (Minale, Riccio, Pizza & Zollo, 1986 and references therein), and led us to suspect an 'unnatural' 20*S* stereochemistry.* In view also of the discovery in a sea pen *Ptilosarcus gurneyi* of 20β-H cholanic acid derivatives with the unexpected 20*S* stereochemistry (Vanderah & Djerassi, 1978), stronger evidence for the stereochemistry at $C(20)$ of the highly hydroxylated steroids of *A. typicus* appeared desirable.

In order to clarify this problem and to confirm the entire structure, a single-crystal X-ray study was carried out on the $(24R)$-27-nor-5α-cholestane-3β,4β,-5,6α,7β,8,14,15α,24-nonaol (I).
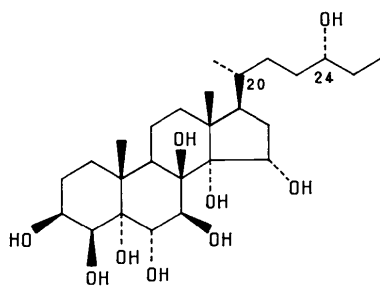
(I)

Experimental. Title compound isolated from starfish *Archaster typicus* (Minale *et al*, 1986), crystals from methanol, $0.4 \times 0.14 \times 0.09$ mm, Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$ radiation; cell dimensions from 25 reflections $(20 \le \theta \le 25°)$; ω–θ scan, as suggested by peak-shape analysis; three

* In hydroxylated marine steroids with saturated side chains the δCH_3-21 values were found to range from 0.93 to 0.97.

Table 1. *Positional parameters* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(Å^2)$ *with e.s.d.'s in parentheses for non-H atoms*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	6148 (9)	8465 (2)	974 (2)	3.4 (2)
C(2)	6530 (10)	9219 (2)	1072 (2)	3.9 (2)
C(3)	6371 (10)	9405 (3)	1759 (2)	4.1 (2)
C(4)	8040 (9)	8997 (2)	2154 (2)	3.5 (2)
C(5)	7673 (8)	8244 (2)	2051 (2)	2.8 (2)
C(6)	9268 (8)	7826 (2)	2451 (2)	3.0 (2)
C(7)	8652 (9)	7086 (2)	2417 (2)	3.0 (2)
C(8)	8578 (8)	6811 (2)	1749 (2)	2.8 (2)
C(9)	7107 (8)	7273 (2)	1329 (2)	2.8 (2)
C(10)	7818 (8)	8021 (2)	1355 (2)	2.8 (2)
C(11)	6872 (10)	6997 (2)	670 (2)	3.4 (2)
C(12)	5863 (9)	6289 (2)	660 (2)	3.4 (2)
C(13)	7322 (9)	5801 (2)	1044 (2)	3.0 (2)
C(14)	7492 (8)	6101 (2)	1721 (2)	2.9 (2)
C(15)	8628 (9)	5518 (2)	2081 (2)	3.2 (2)
C(16)	7562 (10)	4891 (2)	1798 (2)	3.8 (2)
C(17)	6273 (9)	5107 (2)	1195 (2)	3.4 (2)
C(18)	9655 (10)	5689 (3)	731 (2)	3.8 (2)
C(19)	10235 (8)	8118 (2)	1077 (2)	3.2 (2)
C(20)	6388 (9)	4543 (2)	702 (2)	3.6 (2)
C(21)	5190 (12)	4718 (3)	82 (2)	4.7 (2)
C(22)	5332 (10)	3900 (2)	972 (2)	4.0 (2)
C(23)	6225 (11)	3258 (3)	661 (2)	4.1 (2)
C(24)	5428 (10)	2626 (2)	973 (2)	3.7 (2)
C(25)	6200 (13)	2003 (3)	644 (2)	4.9 (2)
C(26)	5141 (18)	1367 (3)	894 (3)	6.6 (3)
O(3)	6845 (8)	10089 (2)	1864 (2)	5.2 (2)
O(4)	10353 (6)	9162 (2)	2006 (2)	4.0 (1)
O(5)	5377 (6)	8110 (2)	2293 (1)	3.5 (1)
O(6)	9085 (7)	8037 (2)	3087 (1)	4.1 (1)
O(7)	10310 (7)	6701 (2)	2763 (1)	4.2 (1)
O(8)	10850 (5)	6787 (2)	1514 (1)	3.1 (1)
O(14)	5164 (6)	6165 (1)	1953 (1)	3.1 (1)
O(15)	8064 (6)	5530 (2)	2737 (1)	3.8 (1)
O(24)	6396 (7)	2597 (2)	1596 (1)	4.0 (1)

standard reflections monitored every 5 h (4% variation); 2641 independent reflections with $\theta \le 68°$, $0 \le h \le 7$, $0 \le k \le 24$, $0 \le l \le 25$, 1813 with $I \ge 3\sigma(I)$; Lp correction, absorption ignored. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); anisotropic full-matrix least-squares refinement (on F), H atoms of hydroxyl and methyl groups from ΔF map, the other hydrogens generated at the expected positions; all H-atom parameters not refined with thermal parameters set equal to B_{eq} of parent atom. Final $R = 0.048$, $wR = 0.067$, $w^{-1} = \sigma^2(F_o)$, correction for secondary extinction [g coefficient $= 3.7\ (2) \times 10^{-7}$], $S = 1.29$; final $(\Delta/\sigma)_{max} = 0.02$; max. and min. heights in final $\Delta\rho$ map 0.19 and $-0.26\ e\ Å^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974), Enraf–Nonius (1979) *SDP* software and PDP 11/34 computer of the 'Centro di Metodologie Chimico-fisiche dell'Università di Napoli'. Final atomic parameters of the non-H atoms are listed in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and ring puckering parameters (Cremer & Pople, 1975) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51240 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. A view of the molecule together with the atomic numbering scheme is shown in Fig. 1. In the absence of atoms with strong anomalous scattering, the absolute configuration could not be determined and the chosen configuration corresponds to that of a normal steroid nucleus, as derived from spectral data (Minale *et al.*, 1986). On this basis the present analysis confirms the structure previously assigned including the *R* configuration of the chiral centres C(20) and C(24).

Intramolecular dimensions involving the non-hydrogen atoms are given in Table 2. All C(sp³)–C(sp³) bond lengths range from 1·502 (7) to 1·578 (6) Å with a mean value of 1·539 (7) Å, whereas the average value of the C(sp³)–O distances is 1·440 (6) Å. In the steroid nucleus the endocyclic bond angles fall in the range 106·7 (4)–114·3 (3)° [average value 111·1 (4)°] for the cyclohexane rings and 100·1 (3)–107·4 (4)° [average value 103·4 (4)°] for the pentaatomic ring. The values of the angles C(8)–C(14)–C(15) 119·7 (4), C(12)–C(13)–C(17) 117·6 (4), C(14)–C(13)–C(17) 100·1 (3)° and of the bond distance C(13)–C(14) 1·578 (6) Å agree with the corresponding values found in steroids and are a consequence of the severe strain caused by the fusion of the five- and six-membered rings.

With respect to steroids, systematic variations in the geometrical parameters can be observed along the spine of the molecule [defined by the atoms C(4),C(5), C(10),C(9),C(8),C(14),C(13),C(17)] and can be related to the presence of the four axial substituents O(4), C(19), O(8), C(18) which protrude from the same side of the fused-ring system. The steric repulsion energy between these substituents causes a lengthening of the bond distances along the spine of the molecule and an increase of the valency angles C(4)–C(5)–C(10), C(8)–C(9)–C(10) and C(8)–C(14)–C(13) which average to 114·2 (2)°. Similar skeletal distortions have been noted in some sesterterpenes which present a sequence of four axial substituents (Croft, Ghisalberti, Skelton & White, 1983; Cimino, De Rosa, De Stefano, Puliti, Strazzullo, Mattia & Mazzarella, 1987). In these cases the greater steric hindrance of four methyl groups causes larger angular distortions.

All rings are *trans*-fused and each of the three cyclohexane rings adopts a chair conformation as shown by the puckering parameters (Cremer & Pople, 1975). For the rings *A, B* and *C* the values of the total puckering amplitude *Q* are 0·561 (6), 0·579 (4) and

Fig. 1. Drawing of the molecule oriented at optimal viewing. Labels for H atoms and a few C atoms have been omitted for clarity.

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

C(1)–C(2)	1·540 (6)	C(10)–C(19)	1·543 (7)
C(1)–C(10)	1·553 (6)	C(11)–C(12)	1·537 (6)
C(2)–C(3)	1·526 (6)	C(12)–C(13)	1·537 (6)
C(3)–C(4)	1·530 (7)	C(13)–C(14)	1·578 (6)
C(3)–O(3)	1·416 (6)	C(13)–C(17)	1·553 (6)
C(4)–C(5)	1·539 (6)	C(13)–C(18)	1·535 (6)
C(4)–O(4)	1·426 (6)	C(14)–C(15)	1·551 (6)
C(5)–C(6)	1·518 (6)	C(14)–O(14)	1·453 (5)
C(5)–C(10)	1·565 (6)	C(15)–C(16)	1·528 (7)
C(5)–O(5)	1·461 (5)	C(15)–O(15)	1·450 (5)
C(6)–C(7)	1·528 (6)	C(16)–C(17)	1·561 (6)
C(6)–O(6)	1·436 (5)	C(17)–C(20)	1·551 (6)
C(7)–C(8)	1·539 (5)	C(20)–C(21)	1·545 (7)
C(7)–O(7)	1·444 (5)	C(20)–C(22)	1·541 (7)
C(8)–C(9)	1·550 (6)	C(22)–C(23)	1·541 (6)
C(8)–C(14)	1·558 (6)	C(23)–C(24)	1·507 (7)
C(8)–O(8)	1·419 (5)	C(24)–C(25)	1·502 (7)
C(9)–C(10)	1·557 (6)	C(24)–O(24)	1·455 (5)
C(9)–C(11)	1·528 (6)	C(25)–C(26)	1·514 (9)
C(2)–C(1)–C(10)	113·5 (4)	C(5)–C(10)–C(19)	112·6 (4)
C(1)–C(2)–C(3)	111·3 (4)	C(9)–C(10)–C(19)	110·6 (4)
C(2)–C(3)–C(4)	111·6 (4)	C(9)–C(11)–C(12)	112·3 (3)
C(2)–C(3)–O(3)	112·4 (4)	C(11)–C(12)–C(13)	111·6 (4)
C(4)–C(3)–O(3)	107·7 (4)	C(12)–C(13)–C(14)	106·7 (4)
C(3)–C(4)–C(5)	110·8 (4)	C(12)–C(13)–C(17)	117·6 (4)
C(3)–C(4)–O(4)	110·7 (4)	C(12)–C(13)–C(18)	110·4 (4)
C(5)–C(4)–O(4)	109·0 (4)	C(14)–C(13)–C(17)	100·1 (3)
C(4)–C(5)–C(6)	111·9 (4)	C(14)–C(13)–C(18)	113·9 (4)
C(4)–C(5)–C(10)	114·3 (3)	C(17)–C(13)–C(18)	108·1 (4)
C(4)–C(5)–O(5)	104·8 (4)	C(8)–C(14)–C(13)	114·2 (3)
C(6)–C(5)–C(10)	110·5 (4)	C(8)–C(14)–C(15)	119·7 (4)
C(6)–C(5)–O(5)	105·0 (3)	C(8)–C(14)–O(14)	106·6 (4)
C(10)–C(5)–O(5)	109·7 (4)	C(13)–C(14)–C(15)	101·5 (3)
C(5)–C(6)–C(7)	111·4 (4)	C(13)–C(14)–O(14)	107·0 (3)
C(5)–C(6)–O(6)	109·4 (4)	C(15)–C(14)–O(14)	107·1 (3)
C(7)–C(6)–O(6)	108·2 (3)	C(14)–C(15)–C(16)	104·4 (4)
C(6)–C(7)–C(8)	113·4 (3)	C(14)–C(15)–O(15)	112·1 (4)
C(6)–C(7)–O(7)	109·7 (4)	C(16)–C(15)–O(15)	108·0 (4)
C(8)–C(7)–O(7)	108·0 (4)	C(15)–C(16)–C(17)	107·4 (4)
C(7)–C(8)–C(9)	110·2 (4)	C(13)–C(17)–C(16)	103·4 (4)
C(7)–C(8)–C(14)	111·9 (3)	C(13)–C(17)–C(20)	119·5 (4)
C(7)–C(8)–O(8)	108·6 (4)	C(16)–C(17)–C(20)	110·2 (4)
C(9)–C(8)–C(14)	107·3 (3)	C(17)–C(20)–C(21)	113·8 (4)
C(9)–C(8)–O(8)	109·3 (3)	C(17)–C(20)–C(22)	109·5 (4)
C(14)–C(8)–O(8)	109·5 (4)	C(21)–C(20)–C(22)	109·5 (4)
C(8)–C(9)–C(10)	114·0 (4)	C(20)–C(22)–C(23)	113·5 (4)
C(8)–C(9)–C(11)	112·0 (4)	C(22)–C(23)–C(24)	113·8 (4)
C(10)–C(9)–C(11)	113·8 (3)	C(23)–C(24)–C(25)	113·3 (4)
C(1)–C(10)–C(5)	107·8 (4)	C(23)–C(24)–O(24)	108·9 (4)
C(1)–C(10)–C(9)	111·5 (4)	C(25)–C(24)–O(24)	106·5 (4)
C(1)–C(10)–C(19)	107·3 (4)	C(24)–C(25)–C(26)	114·2 (5)
C(5)–C(10)–C(9)	107·1 (3)		

0·593 (5) Å respectively. All rings are slightly flattened, with torsion angles less than 60°. The pentaatomic ring has the common half-chair conformation with C(13) 0·468 (5) Å on one side and C(14) 0·318 (4) Å on the other with respect to the plane through C(15), C(16) and C(17): for this ring the *Q* parameter is 0·484 (4) Å. In the present molecule this conformation is further stabilized by the presence of the two hydroxyl groups at C(14) and C(15) and furthermore it places O(15) in the most favourable position to act as a donor towards O(7) in the intramolecular hydrogen bond [O(15)–H···O(7) = 2·688 (4) Å]. The C(17) side chain has an extended conformation with C(21) *trans* to C(16) and *gauche* to C(13) and O(24) approximately *gauche* to C(22) and C(26).

The most remarkable feature of this compound is the presence of nine hydroxyl groups which protrude from the same side of the molecule, which shows a hydrophilic and a hydrophobic region. The crystal
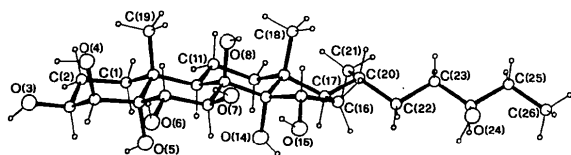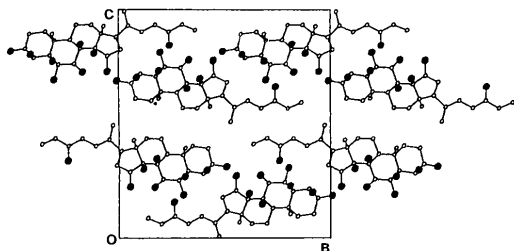
Fig. 2. Crystal packing along the **a** direction; O atoms are represented as filled circles.

Table 3. *Geometry of shortest distances involving hydroxyl groups*

D—H···A	D···A (Å)	H···A (Å)	D—H···A (°)
O(3)—H···O(15^i)	3·117 (6)	2·32	135
O(4)—H···O(15^{ii})	2·945 (4)	2·01	155
O(5)—H···O(4^{iii})	3·662 (5)	2·72	159
O(6)—H···O(24^{ii})	2·862 (5)	2·02	140
O(7)—H···O(24^{ii})	2·967 (5)	1·98	171
O(8)—H···O(14^{iv})	2·963 (4)	2·10	144
O(14)—H···O(3^v)	3·533 (5)	2·58	160
O(15)—H···O(7)	2·688 (4)	1·88	135
O(15)—H···O(3^{vi})	3·215 (6)	2·77	108
O(24)—H···O(5^v)	2·800 (4)	1·91	146
O(24)—H···O(6^v)	3·386 (5)	2·58	138

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

packing shown in Fig. 2 is a consequence of these amphiphilic properties. The four axial hydroxyl groups connect molecules translated along the *a* axis by means of an H bond between O(8) and O(14) and a much weaker interaction between O(4) and O(5) (see Table

3): the remaining hydroxyl groups hold together molecules related by the screw axis parallel to **b**. Altogether the hydroxyl groups form an intricate extensive network of hydrogen bonds which link molecules in double layers parallel to the *ab* plane. The double layers are related by the screw axis parallel to **a** and interact through their hydrophobic surfaces.

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Structure of a 1:2:2 Complex Between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6), 2-Isopropyl-3-methylphenol and Water

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Abstract. $C_{12}H_{24}O_6.2C_{10}H_{14}O.2H_2O$, $M_r = 600\cdot8$, monoclinic, $P2_1/c$, $a = 14\cdot977$ (2), $b = 8\cdot351$ (1), $c = 13\cdot946$ (2) Å, $\beta = 91\cdot55$ (1)°, $V = 1743\cdot6$ (6) Å^3, $Z = 2$, $D_x = 1\cdot145$ g cm^{-3}, $\lambda(Cu K\alpha) = 1\cdot5418$ Å, $\mu(Cu K\alpha) = 6\cdot06$ cm^{-1}, $F(000) = 656$, $T = 293$ K, $R = 0\cdot067$ for 3053 unique observed reflections. A crown ether molecule on an inversion centre accepts a hydrogen bond from each of two inversion-related water molecules that accept a hydrogen bond from two inversion-related phenolic molecules. Binding between host and guest is thus effected by bridging water molecules.

Introduction. This paper is part of our investigation on the ability of the phenols to complex with 18-crown-6. X-ray analyses of complexes with 2,3-