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Crystal and Molecular Structure of Synthetic Cholesterol Compounds – Vitamin D3-Analogues

(I) 24(S)-Hydroxy Coprastan-3-one & (II) 24(R)-Hydroxy Coprastan-3-one

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The title compound **I** (24-(S)-Hydroxy Coprastan-3-one) crystallises in orthorhombic space group $P2_12_12_1$ with Z = 4. The unit cell dimensions are a = 6.701(2)Å, b = 11.506(8)Å, c = 32.183(4)Å, V = 2481(2)Å^3, D_{cal} = 1.077 Mg/m^3. The title compound **II** (24-(R)-Hydroxy Coprastan-3-one) crystallises in orthorhombic space group $P2_12_12_1$ with two molecules per assymetric unit and with Z = 8. The Unit cell dimensions are a = 10.954(2)Å, b = 21.757(6)Å, c = 21.130(7)Å, V = 5035.0(2)Å^3, D_{cal} = 1.062 Mg/m^3. In compound **I** and in both the molecules of compound **II**, the rings A, B & C are in chair conformation and the five membered ring D is in envelope conformation. The priority sequence attached to the chiral carbon C24 has "S" designation in compound **I** and "R" designation in compound **II**. The structures are stabilized by C-H...O and O-H---O hydrogen bonds.

Keywords: Vitamin D3 analogues; Crystal structure; Cholestrol; Compounds; Steroids; Chair conformation

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INTRODUCTION

Among the vitamin D3 analogues, those having a hydroxyl at C24 with "R" configuration appears to be critical for biological activity. For instance: 1α,24(R)-dihydroxy vitamin D3 (Tacalcitol) (I) [1] and Calcipotriol (II) [2] exhibit antipsoriatic activity. The absolute configuration at C24 in these molecules was assigned by physical methods involving optical rotation [3] and NMR spectra [4]. The two intermediates (V) & (VI) epimeric at C24 are synthesized from lithocholic acid. The synthesis involves esterification, oxidation, ketalisation, side chain introduction, deketalisation and chromatographic separation of the two isomers, the details of which will be published elsewhere. X-ray crystallographic studies were carried out for the confirmation of the synthesis and to determine the configuration at C24.

TABLE IA Atomic coordinates and equivalent isotropic displacement parameters of non- hydrogen atoms with e.s. d's in parenthesis for compound I

Atom	*x*	*y*	*z*	*U(eq)(Å²)*
O(1)	6901(7)	3491(4)	−222(1)	113(2)
O(2)	10995(5)	7262(3)	4169(1)	62(1)
C(1)	6794(8)	6132(5)	293(1)	68(2)
C(2)	8058(8)	5091(6)	182(2)	91(2)
C(3)	6754(9)	4053(6)	95(2)	77(2)
C(4)	5247(8)	3795(4)	426(2)	70(2)
C(5)	4033(7)	4873(4)	552(1)	50(1)
C(6)	2640(7)	4550(4)	911(1)	57(1)
C(7)	3750(8)	4398(4)	1322(1)	57(1)
C(8)	4964(7)	5474(3)	1429(1)	39(1)
C(9)	6434(6)	5764(3)	1075(1)	38(1)
C(10)	5336(7)	5939(4)	655(1)	46(1)
C(11)	7842(7)	6760(4)	1197(1)	47(1)
C(12)	8845(6)	6619(4)	1621(1)	42(1)
C(13)	7316(6)	6404(3)	1966(1)	35(1)
C(14)	6106(6)	5334(3)	1833(1)	37(1)
C(15)	4915(7)	4993(4)	2220(1)	51(1)
C(16)	6320(7)	5330(4)	2582(1)	51(1)
C(17)	8121(6)	5987(3)	2393(1)	38(1)
C(18)	6004(7)	7482(3)	2028(1)	47(1)
C(19)	3971(8)	7023(4)	673(2)	68(2)

Atom	*x*	*y*	*z*	*U(eq)*($Å^2$)
C(20)	9010(6)	6855(3)	2704(1)	39(1)
C(21)	10635(7)	7615(4)	2521(1)	62(1)
C(22)	9767(7)	6214(3)	3090(1)	49(1)
C(23)	10444(8)	6997(4)	3444(1)	52(1)
C(24)	10536(7)	6401(4)	3866(1)	52(1)
C(25)	12017(9)	5398(4)	3890(1)	63(2)
C(26)	11855(12)	4805(5)	4313(1)	102(2)
C(27)	14146(9)	5762(6)	3804(2)	110(3)

where Ueq = $(1/3)\Sigma_i\Sigma_j U_{ij}\, a_i^*\, a_j^*\, a_i\, a_j$

TABLE IB Aand equivalent isotropic displacement parameters of non- hydrogen atoms with e.s. d's in parenthesis for compound II

Atom	*x*	*y*	*z*	*U(eq)*($Å^2$)
O(1)	11225(6)	159(2)	2157(2)	115(2)
O(2)	1806(5)	454(2)	6514(3)	103(2)
C(1)	11292(7)	793(4)	3631(4)	98(2)
C(2)	10955(7)	228(3)	3260(3)	91(2)
C(3)	10721(8)	396(3)	2591(3)	86(2)
C(4)	9798(8)	888(3)	2521(3)	89(2)
C(5)	10106(7)	1456(3)	2893(3)	89(2)
C(6)	9167(8)	1961(3)	2800(4)	112(3)
C(7)	7998(8)	1798(4)	3151(3)	106(3)
C(8)	8176(7)	1654(3)	3849(3)	79(2)
C(9)	9122(6)	1145(3)	3925(3)	71(2)
C(10)	10348(7)	1319(3)	3597(4)	86(2)
C(11)	9256(6)	939(4)	4613(3)	91(2)
C(12)	8013(6)	772(3)	4913(3)	87(2)
C(13)	7105(6)	1290(3)	4869(3)	75(2)
C(14)	7005(6)	1462(3)	4169(3)	74(2)
C(15)	5932(8)	1911(4)	4141(4)	108(3)
C(16)	5046(7)	1638(4)	4643(4)	103(3)
C(17)	5747(6)	1138(3)	5012(3)	76(2)
C(18)	7518(7)	1842(3)	5285(3)	103(3)
C(19)	10974(8)	1873(4)	3940(4)	140(4)
C(20)	5323(7)	1086(3)	5703(3)	89(2)
C(21)	5998(8)	590(4)	6078(4)	122(3)
C(22)	3947(7)	974(4)	5739(3)	97(2)

Atom	*x*	*y*	*z*	*U(eq)(Å²)*
C(23)	3351(6)	1224(3)	6342(3)	81(2)
C(24)	2000(6)	1099(3)	6405(3)	77(2)
C(25)	1392(6)	1472(4)	6917(4)	101(3)
C(26)	1849(10)	1350(5)	7565(3)	151(4)
C(27)	−7(7)	1426(4)	6868(5)	144(4)
O(1′)	6005(8)	246(3)	3076(4)	176(3)
O(2′)	−3013(6)	463(3)	−1488(5)	164(3)
C(1′)	4756(10)	1514(4)	2367(4)	123(3)
C(2′)	4443(10)	931(7)	2708(5)	149(4)
C(3′)	5458(11)	495(5)	2619(6)	127(4)
C(4′)	5809(8)	371(4)	1971(5)	117(3)
C(5′)	6005(8)	966(4)	1587(5)	109(3)
C(6′)	6288(8)	824(5)	902(6)	148(4)
C(7′)	5130(7)	608(4)	556(4)	129(3)
C(8′)	4092(8)	1079(4)	597(4)	95(2)
C(9′)	3847(7)	1223(3)	1301(3)	82(2)
C(10′)	4984(7)	1443(3)	1663(4)	96(2)
C(11′)	2749(8)	1647(4)	1375(4)	107(3)
C(12′)	1606(7)	1442(4)	1014(4)	100(2)
C(13′)	1871(8)	1335(3)	318(3)	84(2)
C(14′)	2908(7)	868(4)	303(4)	89(2)
C(15′)	2953(9)	663(6)	−379(5)	165(5)
C(16′)	1606(10)	678(5)	−599(4)	140(4)
C(17′)	898(8)	992(4)	−45(4)	95(2)
C(18′)	2176(9)	1951(4)	−2(4)	138(3)
C(19′)	5437(10)	2073(4)	1434(5)	152(4)
C(20′)	−260(8)	1337(4)	−284(4)	109(3)
C(21′)	−986(8)	1615(4)	262(5)	135(3)
C(22′)	1057(9)	939(4)	−684(6)	161(4)
C(23′)	−2112(10)	1294(5)	−982(6)	170(5)
C(24′)	−2536(8)	1059(5)	−1604(5)	131(4)
C(25′)	−3493(9)	1479(6)	−1884(5)	165(5)
C(26′)	−4623(9)	1592(6)	−1519(5)	183(5)
[a]C(271)	−3186(17)	1848(8)	−2450(7)	139(10)
[a]C(272)	3710(30)	1320(13)	−2567(7)	145(14)

where Ueq = $(1/3)\Sigma_i\Sigma_j U_{ij}\, a_i^*\, a_j^*\, a_i.\, a_j$

a. disordered atoms. C(272) is the alternate position of C(271). The occupancies for C(271) and C(272) are 0.6 and 0.4.

TABLE IIA Selected torsion angles for compound I

Atoms	*Angle*
C(13)-C(17)-C(20)-C(22)	−177.6(4)
C(17)-C(20)-C(22)-C(23)	−172.6(4)
C(20)-C(22)-C(23)-C(24)	160.8(4)
C(22)-C(23)-C(24)-C(25)	62.2(6)
C(23)-C(24)-C(25)-C(27)	60.4(6)
C(23)-C(24)-C(25)-C(26)	−175.2(5)
C(19)-C(10)-C(5)-H(5)	48.2(5)
H(8)-C(8)-C(9)-H(9)	−176.5(3)
C(18)-C(13)-C(14)-H(14)	176.7(3)

TABLE IIB Selected torsion angles for compound II

Atoms	*Angle*	*Atoms*	*Angle*
C(13)-C(17)-C(20)-C(22)	176.5(6)	C(13′)-C(17′)-C(20′)-C(22′)	174.5(8)
C(17)-C(20)-C(22)-C(23)	−151.2(7)	C(17′)-C(20′)-C(22′)-C(23′)	−173.3(9)
C(20)-C(22)-C(23)-C(24)	−177.6(7)	C(20′)-C(22′)-C(23′)-C(24′)	149.7(10)
C(22)-C(23)-C(24)-C(25)	−166.4(7)	C(22′)-C(23′)-C(24′)-C(25′)	−174.5(10)
C(23)-C(24)-C(25)-C(26)	−62.6(10)	C(23′)-C(24′)-C(25′)-C(271)	110.4(14)
C(23)-C(24)-C(25)-C(27)	168.4(6)	C(23′)-C(24′)-C(25′)-C(26′)	−58.8(15)
C(19)-C(10)-C(5)-H(5)	49.7(9)	C(23′)-C(24′)-C(25′)-C(272)	167.3(17)
H(8)-C(8)-C(9)-H(9)	−177.6(6)	C(19′)-C(10′)-C(5′)-H(5′)	46.8(10)
C(18)-C(13)-C(14)-H(14)	−179.3(6)	H(8′)-C(8′)-C(9′)-H(9′)	−178.5(7)
		C(18′)-C(13′)-C(14′)-H(14′)	175.3(7)

TABLE IIIA Details of hydrogen bonds in compound I

Donor(D)	*Acceptor(A)*	*D...A(Å)*	*H...A(Å)*	*D-H...A(°)*	*Symmetry*
O(2)-H(2)	H(2)...O(1)	2.9(1)	2.11(1)	158(2)	(1)
C(4) H(4A)	H(4A)...O(2)	3.3(1)	2.56(1)	138(3)	(2)
C(4)-H(4B)	H(4B)...O(1)	3.5(1)	2.56(1)	168(3)	(3)
C(6)-H(6B)	H(6B)...O(2)	3.6(1)	2.68(1)	158(3)	(4)

Equivalent positions: (1) -x+1/2+1,-y+1,z+1/2; (2) -x+2, y-1/2,-z+1/2; (3) x-1/2,-y+1/2,-z; (4)-x+1,y-1/2,-z+1/2.

TABLE IIIB Details of hydrogen bonds in compound II

Donor(D)	*Acceptor(A)*	*D...A(Å)*	*H...A(Å)*	*D-H...A(°)*	*Symmetry*
O(2)-H(2)	H(2)...O(1)	2.9(1)	2.17(1)	145(4)	(1)
O(2')-H(2')	H(2')...O(1')	2.8(1)	2.05(1)	163(6)	(3)
C(4')-H(4'1)	H(4'1)...O(2)	3.5(1)	2.57(1)	164(5)	(3)

Equivalent positions: (1) -x+1/2+1,-y,z+1/2; (3) -x+1/2,-y,z-1/2.

TABLE IV.A Bond lengths (Å) and Bond angles (°) between non-hydrogen atoms for compound I with e.s. d's in parenthesis

Atoms	*Length*	*Atoms*	*Length*
O(1)-C(3)	1.210(5)	C(11)-C(12)	1.530(5)
O(2)-C(24)	1.423(4)	C(12)-C(13)	1.532(5)
C(1)-C(2)	1.511(7)	C(13)-C(18)	1.533(5)
C(1)-C(10)	1.536(6)	C(13)-C(14)	1.535(5)
C(2)-C(3)	1.506(8)	C(13)-C(17)	1.554(5)
C(3)-C(4)	1.498(7)	C(14)-C(15)	1.519(5)
C(4)-C(5)	1.538(6)	C(15)-C(16)	1.536(5)
C(5)-C(10)	1.542(6)	C(16)-C(17)	1.548(5)
C(5)-C(6)	1.531(6)	C(17)-C(20)	1.535(5)
C(6)-C(7)	1.527(5)	C(20)-C(21)	1.516(6)
C(7)-C(8)	1.521(5)	C(20)-C(22)	1.530(5)
C(8)-C(14)	1.518(5)	C(22)-C(23)	1.522(5)
C(8)-C(9)	1.543(5)	C(23)-C(24)	1.524(5)
C(9)-C(10)	1.552(5)	C(24)-C(25)	1.524(6)
C(9)-C(11)	1.535(5)	C(25)-C(27)	1.512(9)
C(10)-C(19)	1.548(6)	C(25)-C(26)	1.526(6)
Atoms	*Angle*	*Atoms*	*Angle*
C(2)-C(1)-C(10)	114.9(4)	C(12)-C(13)-C(18)	110.3(3)
C(1)-C(2)-C(3)	110.4(4)	C(12)-C(13)-C(14)	106.4(3)
O(1)-C(3)-C(4)	123.2(6)	C(18)-C(13)-C(14)	112.5(3)
O(1)-C(3)-C(2)	122.2(6)	C(12)-C(13)-C(17)	117.4(3)
C(4)-C(3)-C(2)	114.5(4)	C(18)-C(13)-C(17)	109.5(3)
C(3)-C(4)-C(5)	112.7(4)	C(14)-C(13)-C(17)	100.4(3)
C(10)-C(5)-C(4)	113.5(4)	C(8)-C(14)-C(15)	118.1(4)
C(10)-C(5)-C(6)	112.1(3)	C(8)-C(14)-C(13)	114.8(3)
C(4)-C(5)-C(6)	109.1(4)	C(15)-C(14)-C(13)	104.5(3)

C(7)-C(6)-C(5)	112.6(4)	C(14)-C(15)-C(16)	104.4(3)
C(8)-C(7)-C(6)	111.4(3)	C(15)-C(16)-C(17)	107.0(3)
C(14)-C(8)-C(7)	112.2(3)	C(20)-C(17)-C(13)	120.7(3)
C(14)-C(8)-C(9)	109.5(3)	C(20)-C(17)-C(16)	111.4(3)
C(7)-C(8)-C(9)	110.5(3)	C(13)-C(17)-C(16)	103.2(3)
C(8)-C(9)-C(10)	111.6(3)	C(21)-C(20)-C(22)	110.8(4)
C(8)-C(9)-C(11)	111.5(3)	C(21)-C(20)-C(17)	113.7(3)
C(10)-C(9)-C(11)	114.6(3)	C(22)-C(20)-C(17)	110.1(3)
C(5)-C(10)-C(1)	108.2(3)	C(23)-C(22)-C(20)	114.9(3)
C(5)-C(10)-C(9)	110.6(3)	C(22)-C(23)-C(24)	114.4(3)
C(1)-C(10)-C(9)	112.2(3)	O(2)-C(24)-C(25)	110.6(4)
C(5)-C(10)-C(19)	108.3(4)	O(2)-C(24)-C(23)	107.8(3)
C(1)-C(10)-C(19)	106.7(4)	C(25)-C(24)-C(23)	114.4(4)
C(9)-C(10)-C(19)	110.6(3)	C(27)-C(25)-C(24)	113.3(5)
C(12)-C(11)-C(9)	114.7(3)	C(27)-C(25)-C(26)	110.8(5)
C(13)-C(12)-C(11)	111.7(3)	C(24)-C(25)-C(26)	109.8(4)

TABLE IV.B Bond lengths (Å) and Bond angles (°) between non-hydrogen atoms for compound II with e.s. d's in parenthesis

Atoms	*Length*	*Atoms*	*Length*
O(1)-C(3)	1.188(8)	O(1')-C(3')	1.258(10)
O(2)-C(24)	1.436(8)	O(2')-C(24')	1.420(10)
C(1)-C(2)	1.504(9)	C(1')-C(2')	1.499(14)
C(1)-C(10)	1.544(10)	C(1')-C(10')	1.517(11)
C(2)-C(3)	1.482(10)	C(2')-C(3')	1.474(14)
C(3)-C(4)	1.479(11)	C(3')-C(4')	1.449(13)
C(4)-C(5)	1.503(10)	C(4')-C(5')	1.543(11)
C(5)-C(10)	1.540(10)	C(5')-C(6')	1.511(12)
C(5)-C(6)	1.518(10)	C(5')-C(10')	1.535(11)
C(6)-C(7)	1.521(10)	C(6')-C(7')	1.537(12)
C(7)-C(8)	1.520(10)	C(7')-C(8')	1.533(10)
C(8)-C(14)	1.509(10)	C(8')-C(14')	1.509(10)
C(8)-C(9)	1.525(9)	C(8')-C(9')	1.543(9)
C(9)-C(10)	1.558(10)	C(9')-C(11')	1.525(9)
C(9)-C(11)	1.527(9)	C(9')-C(10')	1.538(10)
C(10)-C(19)	1.565(10)	C(10')-C(19')	1.536(11)
C(11)-C(12)	1.545(10)	C(11')-C(12')	1.534(11)

C(12)-C(13)	1.506(9)	C(12')-C(13')	1.517(9)
C(13)-C(14)	1.530(9)	C(13')-C(17')	1.509(10)
C(13)-C(17)	1.554(10)	C(13')-C(14')	1.525(9)
C(13)-C(18)	1.556(9)	C(13')-C(18')	1.538(9)
C(14)-C(15)	1.530(10)	C(14')-C(15')	1.509(11)
C(15)-C(16)	1.557(10)	C(15')-C(16')	1.547(13)
C(16)-C(17)	1.542(9)	C(16')-C(17')	1.562(11)
C(17)-C(20)	1.537(9)	C(17')-C(20')	1.559(10)
C(20)-C(22)	1.528(10)	C(20')-C(22')	1.493(8)
C(20)-C(21)	1.527(10)	C(20')-C(21')	1.526(11)
C(22)-C(23)	1.532(9)	C(22')-C(23')	1.527(8)
C(23)-C(24)	1.511(10)	C(23')-C(24')	1.484(8)
C(24)-C(25)	1.508(10)	C(24')-C(25')	1.512(8)
C(25)-C(26)	1.482(11)	C(25')-C(27')	1.479(9)
C(25)-C(27)	1.539(11)	C(25')-C(26')	1.479(8)
		C(25')-C(272)	1.503(10)
		C(271)-C(272)	1.31(3)

Compound II

Atoms	*Angle*	*Atoms*	*Angle*
C(2)-C(1)-C(10)	114.6(7)	C(17)-C(16)-C(15)	107.6(6)
C(1)-C(2)-C(3)	109.8(6)	C(20)-C(17)-C(16)	112.5(6)
O(1)-C(3)-C(4)	123.7(8)	C(20)-C(17)-C(13)	119.4(6)
O(1)-C(3)-C(2)	123.2(8)	C(16)-C(17)-C(13)	103.2(6)
C(4)-C(3)-C(2)	113.1(6)	C(17)-C(20)-C(22)	110.9(7)
C(3)-C(4)-C(5)	112.9(7)	C(17)-C(20)-C(21)	113.5(7)
C(4)-C(5)-C(10)	112.7(6)	C(22)-C(20)-C(21)	109.9(7)
C(4)-C(5)-C(6)	112.1(7)	C(20)-C(22)-C(23)	113.8(7)
C(10)-C(5)-C(6)	112.3(6)	C(24)-C(23)-C(22)	115.3(6)
C(7)-C(6)-C(5)	109.9(6)	O(2)-C(24)-C(23)	109.6(6)
C(6)-C(7)-C(8)	114.4(8)	O(2)-C(24)-C(25)	110.2(6)
C(7)-C(8)-C(14)	112.5(7)	C(23)-C(24)-C(25)	113.5(7)
C(7)-C(8)-C(9)	109.9(6)	C(26)-C(25)-C(24)	114.6(7)
C(14)-C(8)-C(9)	109.3(5)	C(26)-C(25)-C(27)	112.7(9)
C(8)-C(9)-C(10)	111.2(6)	C(24)-C(25)-C(27)	110.9(8)
C(8)-C(9)-C(11)	112.2(6)	C(2')-C(1')-C(10')	115.0(8)
C(10)-C(9)-C(11)	114.3(6)	C(3')-C(2')-C(1')	108.1(9)

C(5)-C(10)-C(9)	109.2(7)	O(1')-C(3')-C(4')	121.3(13)
C(5)-C(10)-C(1)	107.6(6)	O(1')-C(3')-C(2')	122.5(13)
C(9)-C(10)-C(1)	112.1(6)	C(4')-C(3')-C(2')	116.2(9)
C(5)-C(10)-C(19)	112.0(7)	C(3')-C(4')-C(5')	112.2(8)
C(9)-C(10)-C(19)	111.0(6)	C(6')-C(5')-C(4')	111.2(9)
C(1)-C(10)-C(19)	104.8(7)	C(6')-C(5')-C(10')	112.8(8)
C(12)-C(11)-C(9)	112.0(6)	C(4')-C(5')-C(10')	114.2(7)
C(13)-C(12)-C(11)	112.4(6)	C(5')-C(6')-C(7')	110.4(7)
C(12)-C(13)-C(14)	106.9(6)	C(8')-C(7')-C(6')	112.4(7)
C(12)-C(13)-C(17)	117.5(6)	C(14')-C(8')-C(7')	114.3(7)
C(14)-C(13)-C(17)	99.9(6)	C(14')-C(8')-C(9')	108.0(6)
C(12)-C(13)-C(18)	110.5(6)	C(7')-C(8')-C(9')	108.6(7)
C(14)-C(13)-C(18)	112.2(6)	C(11')-C(9')-C(10')	113.5(6)
C(17)-C(13)-C(18)	109.4(6)	C(11')-C(9')-C(8')	111.0(6)
C(15)-C(14)-C(13)	104.4(6)	C(10')-C(9')-C(8')	113.7(7)
C(15)-C(14)-C(8)	117.4(6)	C(1')-C(10')-C(19')	105.7(8)
C(13)-C(14)-C(8)	116.1(6)	C(1')-C(10')-C(9')	112.7(8)
C(14)-C(15)-C(16)	102.1(6)	C(19')-C(10')-C(9')	112.5(7)
C(1')-C(10')-C(5')	107.0(7)	C(20')-C(17')-C(16')	111.8(7)
C(19')-C(10')-C(5')	109.6(7)	C(22')-C(20')-C(21')	110.7(9)
C(9')-C(10')-C(5')	109.1(6)	C(22')-C(20')-C(17')	112.3(7)
C(9')-C(11')-C(12')	114.6(6)	C(21')-C(20')-C(17')	111.7(7)
C(13')-C(12')-C(11')	111.7(7)	C(20')-C(22')-C(23')	112.5(8)
C(17')-C(13')-C(12')	115.6(7)	C(24')-C(23')-C(22')	115.3(9)
C(17')-C(13')-C(14')	100.7(6)	O(2')-C(24')-C(23')	106.1(9)
C(12')-C(13')-C(14')	105.4(6)	O(2')-C(24')-C(25')	111.4(9)
C(17')-C(13')-C(18')	111.2(7)	C(23')-C(24')-C(25')	110.8(9)
C(12')-C(13')-C(18')	109.5(7)	C(271)-C(25')-C(26')	121.5(11)
C(14')-C(13')-C(18')	114.2(7)	C(271)-C(25')-C(272)	52.0(12)
C(8')-C(14')-C(15')	117.1(7)	C(26')-C(25')-C(272)	113.9(15)
C(8')-C(14')-C(13')	115.4(7)	C(271)-C(25')-C(24')	119.1(10)
C(15')-C(14')-C(13')	103.9(7)	C(26')-C(25')-C(24')	118.5(9)
C(14')-C(15')-C(16')	104.5(7)	C(272)-C(25')-C(24')	110.3(15)
C(15')-C(16')-C(17')	104.9(7)	C(272)-C(271)-C(25')	64.9(8)
C(13')-C(17')-C(20')	120.1(7)	C(271)-C(272)-C(25')	63.1(8)
C(13')-C(17')-C(16')	104.3(7)		

TABLE V.A Torsion angles (°) involving non- hydrogen atoms for compound I with e.s. d's in parenthesis

Atoms	*Angle*	*Atoms*	*Angle*
C(10)-C(1)-C(2)-C(3)	54.9(6)	C(11)-C(12)-C(13)-C(17)	167.3(3)
C(1)-C(2)-C(3)-O(1)	127.5(5)	C(7)-C(8)-C(14)-C(15)	−54.3(5)
C(1)-C(2)-C(3)-C(4)	51.2(6)	C(9)-C(8)-C(14)-C(15)	−177.4(3)
O(1)-C(3)-C(4)-C(5)	−129.0(6)	C(7)-C(8)-C(14)-C(13)	−178.3(4)
C(2)-C(3)-C(4)-C(5)	49.7(6)	C(9)-C(8)-C(14)-C(13)	58.6(4)
C(3)-C(4)-C(5)-C(10)	−50.2(5)	C(12)-C(13)-C(14)-C(8)	−61.2(4)
C(3)-C(4)-C(5)-C(6)	−176.1(4)	C(18)-C(13)-C(14)-C(8)	59.7(4)
C(10)-C(5)-C(6)-C(7)	−53.0(5)	C(17)-C(13)-C(14)-C(8)	176.0(3)
C(4)-C(5)-C(6)-C(7)	73.7(5)	C(12)-C(13)-C(14)-C(15)	167.8(3)
C(5)-C(6)-C(7)-C(8)	55.1(5)	C(18)-C(13)-C(14)-C(15)	−71.3(4)
C(6)-C(7)-C(8)-C(14)	−179.1(4)	C(17)-C(13)-C(14)-C(15)	45.0(4)
C(6)-C(7)-C(8)-C(9)	−56.6(5)	C(8)-C(14)-C(15)-C(16)	−161.3(3)
C(14)-C(8)-C(9)-C(10)	−178.9(3)	C(13)-C(14)-C(15)-C(16)	−32.3(4)
C(7)-C(8)-C(9)-C(10)	56.9(4)	C(14)-C(15)-C(16)-C(17)	6.5(5)
C(14)-C(8)-C(9)-C(11)	−49.3(4)	C(12)-C(13)-C(17)-C(20)	80.4(5)
C(7)-C(8)-C(9)-C(11)	−173.4(4)	C(18)-C(13)-C(17)-C(20)	−46.3(5)
C(4)-C(5)-C(10)-C(1)	51.2(5)	C(14)-C(13)-C(17)-C(20)	−164.9(4)
C(6)-C(5)-C(10)-C(1)	175.4(4)	C(12)-C(13)-C(17)-C(16)	−154.5(3)
C(4)-C(5)-C(10)-C(9)	−72.0(4)	C(18)-C(13)-C(17)-C(16)	78.7(4)
C(6)-C(5)-C(10)-C(9)	52.2(5)	C(14)-C(13)-C(17)-C(16)	−39.8(4)
C(4)-C(5)-C(10)-C(19)	166.5(4)	C(15)-C(16)-C(17)-C(20)	151.9(3)
C(6)-C(5)-C(10)-C(19)	−69.3(5)	C(15)-C(16)-C(17)-C(13)	21.0(4)
C(2)-C(1)-C(10)-C(5)	−54.8(5)	C(13)-C(17)-C(20)-C(21)	−52.6(5)
C(2)-C(1)-C(10)-C(9)	67.5(5)	C(16)-C(17)-C(20)-C(21)	−173.8(3)
C(2)-C(1)-C(10)-C(19)	−171.2(4)	C(13)-C(17)-C(20)-C(22)	−177.6(4)
C(8)-C(9)-C(10)-C(5)	−54.5(4)	C(16)-C(17)-C(20)-C(22)	61.2(5)
C(11)-C(9)-C(10)-C(5)	177.6(3)	C(21)-C(20)-C(22)-C(23)	60.7(5)
C(8)-C(9)-C(10)-C(1)	−175.4(4)	C(17)-C(20)-C(22)-C(23)	−172.6(4)
C(11)-C(9)-C(10)-C(1)	56.6(5)	C(20)-C(22)-C(23)-C(24)	160.8(4)
C(8)-C(9)-C(10)-C(19)	65.6(4)	C(22)-C(23)-C(24)-O(2)	−174.4(4)
C(11)-C(9)-C(10)-C(19)	−62.4(5)	C(22)-C(23)-C(24)-C(25)	62.2(6)
C(8)-C(9)-C(11)-C(12)	49.0(5)	O(2)-C(24)-C(25)-C(27)	−61.5(5)
C(10)-C(9)-C(11)-C(12)	177.0(4)	C(23)-C(24)-C(25)-C(27)	60.4(6)
C(9)-C(11)-C(12)-C(13)	53.5(5)	O(2)-C(24)-C(25)-C(26)	62.8(6)
C(11)-C(12)-C(13)-C(18)	−66.3(4)	C(23)-C(24)-C(25)-C(26)	−175.2(5)
C(11)-C(12)-C(13)-C(14)	55.9(4)		

TABLE V.B Torsion angles (°) involving non- hydrogen atoms for compound I with e.s. d's in parenthesis

Atoms	*Angle*	*Atoms*	*Angle*
C(10)-C(1)-C(2)-C(3)	55.5(9)	C(11)-C(12)-C(13)-C(17)	166.6(6)
C(1)-C(2)-C(3)-O(1)	125.6(8)	C(11)-C(12)-C(13)-C(18)	−66.9(8)
C(1)-C(2)-C(3)-C(4)	−54.4(9)	C(12)-C(13)-C(14)-C(15)	171.1(6)
O(1)-C(3)-C(4)-C(5)	−125.1(8)	C(17)-C(13)-C(14)-C(15)	48.2(7)
C(2)-C(3)-C(4)-C(5)	54.9(9)	C(18)-C(13)-C(14)-C(15)	−67.6(8)
C(3)-C(4)-C(5)-C(10)	−53.7(9)	C(12)-C(13)-C(14)-C(8)	−58.1(8)
C(3)-C(4)-C(5)-C(6)	178.5(6)	C(17)-C(13)-C(14)-C(8)	179.1(6)
C(4)-C(5)-C(6)-C(7)	73.1(9)	C(18)-C(13)-C(14)-C(8)	63.2(8)
C(10)-C(5)-C(6)-C(7)	−54.9(10)	C(7)-C(8)-C(14)-C(15)	−57.3(9)
C(5)-C(6)-C(7)-C(8)	54.1(10)	C(9)-C(8)-C(14)-C(15)	−179.6(6)
C(6)-C(7)-C(8)-C(14)	−176.9(6)	C(7)-C(8)-C(14)-C(13)	178.4(6)
C(6)-C(7)-C(8)-C(9)	−54.9(9)	C(9)-C(8)-C(14)-C(13)	56.1(8)
C(7)-C(8)-C(9)-C(10)	55.7(8)	C(13)-C(14)-C(15)-C(16)	−36.6(8)
C(14)-C(8)-C(9)-C(10)	179.5(6)	C(8)-C(14)-C(15)-C(16)	−166.7(6)
C(7)-C(8)-C(9)-C(11)	−174.8(7)	C(14)-C(15)-C(16)-C(17)	10.7(9)
C(14)-C(8)-C(9)-C(11)	−51.0(8)	C(15)-C(16)-C(17)-C(20)	148.3(7)
C(4)-C(5)-C(10)-C(9)	−70.7(8)	C(15)-C(16)-C(17)-C(13)	18 3(8)
C(6)-C(5)-C(10)-C(9)	57.0(8)	C(12)-C(13)-C(17)-C(20)	79.4(9)
C(4)-C(5)-C(10)-C(1)	51.2(9)	C(14)-C(13)-C(17)-C(20)	−165.5(6)
C(6)-C(5)-C(10)-C(1)	178.9(6)	C(18)-C(13)-C(17)-C(20)	−47.6(9)
C(4)-C(5)-C(10)-C(19)	165.9(7)	C(12)-C(13)-C(17)-C(16)	−154.9(6)
C(6)-C(5)-C(10)-C(19)	−66.4(9)	C(14)-C(13)-C(17)-C(16)	−39.9(7)
C(8)-C(9)-C(10)-C(5)	−57.1(8)	C(18)-C(13)-C(17)-C(16)	78.1(7)
C(11)-C(9)-C(10)-C(5)	174.5(6)	C(16)-C(17)-C(20)-C(22)	55.4(9)
C(8)-C(9)-C(10)-C(1)	−176.3(6)	C(13)-C(17)-C(20)-C(22)	176.5(6)
C(11)-C(9)-C(10)-C(1)	55.3(9)	C(16)-C(17)-C(20)-C(21)	179.6(7)
C(8)-C(9)-C(10)-C(19)	66.8(9)	C(13)-C(17)-C(20)-C(21)	−59.3(10)
C(11)-C(9)-C(10)-C(19)	−61.6(9)	C(17)-C(20)-C(22)-C(23)	−151.2(7)
C(2)-C(1)-C(10)-C(5)	−53.5(8)	C(21)-C(20)-C(22)-C(23)	82.6(8)
C(2)-C(1)-C(10)-C(9)	66.6(8)	C(20)-C(22)-C(23)-C(24)	−177.6(7)
C(2)-C(1)-C(10)-C(19)	−172.9(7)	C(22)-C(23)-C(24)-O(2)	69.9(8)
C(8)-C(9)-C(11)-C(12)	52.1(8)	C(22)-C(23)-C(24)-C(25)	−166.4(7)
C(10)-C(9)-C(11)-C(12)	−180.0(6)	O(2)-C(24)-C(25)-C(26)	60.7(9)
C(9)-C(11)-C(12)-C(13)	−55.6(9)	C(23)-C(24)-C(25)-C(26)	−62.6(10)

Atoms	*Angle*	*Atoms*	*Angle*
C(11)-C(12)-C(13)-C(14)	55.4(8)	O(2)-C(24)-C(25)-C(27)	-68.3(9)
C(23)-C(24)-C(25)-C(27)	168.3(8)	C(9')-C(8')-C(14')-C(15')	-176.3(8)
C(10')-C(1')-C(2')-C(3')	58.7(12)	C(7')-C(8')-C(14')-C(13')	-178.1(6)
C(1')-C(2')-C(3')-O(1')	124.7(10)	C(9')-C(8')-C(14')-C(13')	61.0(8)
C(1')-C(2')-C(3')-C(4')	-54.5(12)	C(17')-C(13')-C(14')-C(8')	176.4(6)
O(1')-C(3')-C(4')-C(5')	-129.3(10)	C(12')-C(13')-C(14')-C(8')	-63.0(8)
C(2')-C(3')-C(4')-C(5')	50.0(13)	C(18')-C(13')-C(14')-C(8')	57.1(9)
C(3')-C(4')-C(5')-C(6')	-176.2(9)	C(17')-C(13')-C(14')-C(15')	46.9(8)
C(3')-C(4')-C(5')-C(10')	-47.1(12)	C(12')-C(13')-C(14')-C(15')	167.5(8)
C(4')-C(5')-C(6')-C(7')	73.5(10)	C(18')-C(13')-C(14')-C(15')	-72.4(10)
C(10')-C(5')-C(6')-C(7')	-56.3(11)	C(8')-C(14')-C(15')-C(16')	-162.7(9)
C(5')-C(6')-C(7')-C(8')	56.8(11)	C(13')-C(14')-C(15')-C(16')	-34.2(11)
C(6')-C(7')-C(8')-C(14')	-176.0(7)	C(14')-C(15')-C(16')-C(17')	8.6(12)
C(6')-C(7')-C(8')-C(9')	-55.3(10)	C(12')-C(13')-C(17')-C(20')	80.2(9)
C(14')-C(8')-C(9')-C(11')	-50.7(8)	C(14')-C(13')-C(17')-C(20')	-166.8(7)
C(7')-C(8')-C(9')-C(11')	-175.2(6)	C(18')-C(13')-C(17')-C(20')	-45.4(10)
C(14')-C(8')-C(9')-C(10')	179.8(6)	C(12')-C(13')-C(17')-C(16')	-153.6(7)
C(7')-C(8')-C(9')-C(10')	55.4(8)	C(14')-C(13')-C(17')-C(16')	-40.6(8)
C(2')-C(1')-C(10')-C(19')	-173.2(9)	C(18')-C(13')-C(17')-C(16')	80.8(8)
C(2')-C(1')-C(10')-C(9')	63.5(11)	C(15')-C(16')-C(17')-C(13')	20.2(10)
C(2')-C(1')-C(10')-C(5')	56.4(11)	C(15')-C(16')-C(17')-C(20')	151.4(9)
C(11')-C(9')-C(10')-C(1')	58.1(9)	C(13')-C(17')-C(20')-C(22')	174.5(8)
C(8')-C(9')-C(10')-C(1')	-173.7(7)	C(16')-C(17')-C(20')-C(22')	51.9(11)
C(11')-C(9')-C(10')-C(19')	-61.3(10)	C(13')-C(17')-C(20')-C(21')	-60.4(10)
C(8')-C(9')-C(10')-C(19')	66.8(9)	C(16')-C(17')-C(20')-C(21')	177.0(8)
C(11')-C(9')-C(10')-C(5')	176.9(7)	C(21')-C(20')-C(22')-C(23')	61.1(12)
C(8')-C(9')-C(10')-C(5')	-55.0(9)	C(17')-C(20')-C(22')-C(23')	-173.3(9)
C(6')-C(5')-C(10')-C(1')	177.2(8)	C(20')-C(22')-C(23')-C(24')	149.7(10)
C(4')-C(5')-C(10')-C(1')	48.9(10)	C(22')-C(23')-C(24')-O(2')	64.5(12)
C(6')-C(5')-C(10')-C(19')	-68.7(10)	C(22')-C(23')-C(24')-C(25')	174.5(10)
C(4')-C(5')-C(10')-C(19')	163.1(9)	O(2')-C(24')-C(25')-C(27')	131.7(13)
C(6')-C(5')-C(10')-C(9')	54.9(10)	C(23')-C(24')-C(25')-C(27')	110.4(14)
C(4')-C(5')-C(10')-C(9')	-73.4(10)	O(2')-C(24')-C(25')-C(26')	59.1(15)
C(10')-C(9')-C(11')-C(12')	179.5(7)	C(23')-C(24')-C(25')-C(26')	-58.8(15)
C(8')-C(9')-C(11')-C(12')	50.0(9)	O(2')-C(24')-C(25')-C(27')	74.8(18)
C(9')-C(11')-C(12')-C(13')	53.9(10)	C(23')-C(24')-C(25')-C(27')	167.3(17)

Atoms	*Angle*	*Atoms*	*Angle*
C(11′)-C(12′)-C(13′)-C(17′)	166.1(7)	C(26′)-C(25′)-C(271)-C(272)	−97(2)
C(11′)-C(12′)-C(13′)-C(14′)	55.9(9)	C(24′)-C(25′)-C(271)-C(272)	94(2)
C(11′)-C(12′)-C(13′)-C(18′)	−67.4(9)	C(26′)-C(25′)-C(272)-C(271)	112.2(17)
C(7′)-C(8′)-C(14′)-C(15′)	−55.3(11)	C(24′)-C(25′)-C(272)-C(271)	−111.7(16)

TABLE VI.A Anisotropic displacement parameters ($Å^2 \times 10^3$) for the non-hydrogen atoms with e.s. d's in paranthesis for compound I. The anisotropic displacement parameter factor exponent takes the form $2\pi^2 (h^2a^{*2}u_{11}+....+2hka^*b^*u_{12})$

Atom	*U11*	*U22*	*U33*	*U23*	*U13*	*U12*
O(1)	117(3)	152(4)	70(2)	−52(3)	−24(3)	61(3)
O(2)	81(3)	61(2)	44(2)	−15(2)	−15(2)	15(2)
C(1)	68(3)	100(4)	36(2)	6(3)	−4(2)	−23(4)
C(2)	59(3)	169(7)	47(3)	−13(4)	9(3)	−1(5)
C(3)	68(3)	110(5)	52(3)	−25(3)	−18(3)	36(4)
C(4)	85(4)	63(3)	60(3)	−17(2)	−22(3)	2(3)
C(5)	49(3)	59(3)	40(2)	−1(2)	−12(2)	−5(3)
C(6)	52(3)	69(3)	50(3)	1(2)	−10(2)	−24(3)
C(7)	65(3)	57(3)	48(2)	2(2)	−4(2)	−25(3)
C(8)	42(2)	37(2)	39(2)	2(2)	−4(2)	−11(2)
C(9)	40(2)	42(2)	32(2)	−2(2)	0(2)	−2(2)
C(10)	48(3)	53(2)	37(2)	4(2)	−6(2)	−6(2)
C(11)	52(3)	54(3)	36(2)	2(2)	0(2)	−12(2)
C(12)	39(2)	49(2)	37(2)	−3(2)	3(2)	−15(2)
C(13)	42(2)	31(2)	33(2)	−1(2)	1(2)	−2(2)
C(14)	42(2)	35(2)	34(2)	3(2)	1(2)	−2(2)
C(15)	58(3)	57(3)	39(2)	7(2)	0(2)	−18(3)
C(16)	64(3)	54(2)	35(2)	5(2)	0(2)	−14(3)
C(17)	42(2)	36(2)	35(2)	−1(2)	2(2)	2(2)
C(18)	49(3)	45(2)	47(2)	−3(2)	−3(2)	8(3)
C(19)	79(4)	59(3)	66(3)	11(2)	−25(3)	6(3)
C(20)	43(2)	39(2)	35(2)	−2(2)	−3(2)	1(2)
C(21)	65(3)	63(3)	58(3)	1(2)	−10(3)	−22(3)
C(22)	63(3)	45(2)	41(2)	−6(2)	−4(2)	4(3)
C(23)	67(3)	45(2)	43(2)	−3(2)	−11(2)	6(3)
C(24)	66(3)	51(3)	38(2)	−8(2)	−4(2)	4(3)

Atom	*U11*	*U22*	*U33*	*U23*	*U13*	*U12*
C(25)	89(4)	57(3)	42(2)	−9(2)	−11(3)	25(3)
C(26)	170(7)	79(4)	56(3)	6(3)	-10(4)	47(5)
C(27)	74(4)	149(7)	107(5)	−20(5)	-3(4)	54(5)

TABLE VI.B Anisotropic displacement parameters ($Å^2 \times 10^3$) for the non-hydrogen atoms with e.s.d's in paranthesis for compound II. The anisotropic displacement parameter factor exponent takes the form $2\pi^2 (h^2a^{*2}u_{11}+....+2hka^*b^*u_{12})$

Atom	*U11*	*U22*	*U33*	*U23*	*U13*	*U12*
O(1)	146(5)	105(4)	96(4)	32(3)	29(4)	20(4)
O(2)	88(4)	76(3)	145(5)	1(3)	17(4)	10(3)
C(1)	75(5)	117(6)	102(6)	-17(5)	7(5)	10(5)
C(2)	79(5)	90(5)	102(6)	−5(5)	24(5)	15(5)
C(3)	121(7)	71(5)	67(5)	−23(4)	21(5)	1(5)
C(4)	109(6)	83(5)	76(5)	-3(4)	15(5)	5(5)
C(5)	94(6)	71(5)	104(6)	10(4)	40(5)	1(5)
C(6)	130(7)	84(5)	121(6)	20(5)	43(6)	4(6)
C(7)	116(7)	92(5)	108(6)	30(5)	42(6)	34(5)
C(8)	93(6)	54(4)	91(5)	-4(4)	24(5)	-7(4)
C(9)	67(4)	62(4)	83(5)	-4(3)	9(4)	-2(4)
C(10)	83(5)	68(5)	109(6)	-24(4)	25(5)	-11(5)
C(11)	77(5)	113(6)	82(5)	−5(4)	13(4)	15(5)
C(12)	84(5)	97(5)	80(5)	6(4)	0(4)	14(5)
C(13)	74(5)	73(4)	78(5)	−5(4)	5(4)	11(4)
C(14)	70(5)	64(4)	79(5)	3(4)	11(4)	6(4)
C(15)	107(6)	113(6)	103(6)	24(5)	32(5)	31(6)
C(16)	90(6)	103(6)	112(6)	0(5)	2(5)	25(5)
C(17)	73(5)	83(5)	69(4)	−5(4)	6(4)	1(4)
C(18)	97(6)	112(6)	101(5)	-39(5)	32(5)	-6(5)
C(19)	117(7)	132(7)	172(9)	−66(7)	35(7)	55(7)
C(20)	70(5)	92(5)	96(6)	−6(5)	10(5)	-1(5)
C(21)	115(7)	139(7)	112(6)	37(6)	30(6)	34(7)
C(22)	75(5)	120(6)	97(6)	-10(5)	13(5)	12(5)
C(23)	78(5)	77(4)	88(5)	4(4)	3(4)	1(4)
C(24)	59(5)	75(5)	99(5)	11(4)	6(4)	10(4)
C(25)	69(5)	80(5)	157(8)	0(6)	42(5)	12(4)

Atom	*U11*	*U22*	*U33*	*U23*	*U13*	*U12*
C(26)	171(10)	210(10)	73(6)	−19(6)	14(7)	33(9)
C(27)	96(7)	127(8)	208(10)	2(8)	45(7)	20(6)
O(1′)	195(8)	140(6)	192(7)	50(5)	−63(7)	−8(6)
O(2′)	114(5)	134(5)	244(8)	13(6)	−20(6)	−13(5)
C(1′)	124(8)	117(7)	127(8)	−2(6)	−13(7)	26(7)
C(2′)	120(9)	218(13)	110(7)	−6(8)	2(7)	17(10)
C(3′)	127(10)	115(8)	139(10)	17(7)	−48(9)	−27(8)
C(5′)	57(5)	106(6)	164(8)	−4(6)	10(6)	0(5)
C(6′)	67(7)	184(10)	193(11)	−3(8)	36(7)	23(7)
C(7′)	75(6)	168(9)	143(8)	−15(7)	21(6)	47(7)
C(8′)	91(6)	105(6)	90(6)	2(5)	8(5)	−5(6)
C(9′)	72(5)	65(4)	110(6)	11(4)	6(5)	4(4)
C(10′)	78(6)	66(5)	145(8)	15(5)	−12(6)	−1(5)
C(11′)	108(7)	96(6)	115(6)	−3(5)	8(6)	38(6)
C(12′)	77(6)	111(6)	111(6)	−7(5)	6(5)	25(5)
C(13′)	94(6)	72(5)	85(5)	14(4)	24(5)	11(5)
C(14′)	85(6)	96(5)	88(6)	−8(4)	13(5)	13(5)
C(15′)	113(8)	263(14)	119(8)	−43(8)	16(7)	65(9)
C(16′)	156(9)	161(8)	103(6)	−47(6)	−11(7)	57(8)
C(17′)	95(6)	89(5)	100(6)	10(5)	−1(5)	20(6)
C(18′)	151(8)	105(6)	157(8)	60(6)	−2(7)	−25(7)
C(19′)	157(9)	83(6)	217(11)	23(7)	−47(8)	−29(6)
C(20′)	119(7)	98(6)	112(6)	19(5)	6(6)	17(6)
C(21′)	103(7)	136(7)	167(9)	−15(7)	2(7)	34(7)
C(22′)	157(9)	103(7)	222(12)	−28(8)	−75(9)	43(8)
C(23′)	148(10)	136(9)	227(12)	3(9)	−67(10)	51(8)
C(24′)	80(6)	128(8)	185(10)	74(8)	−5(7)	14(6)
C(25′)	107(8)	230(12)	156(9)	27(10)	3(8)	65(9)
C(26′)	121(9)	220(12)	208(12)	25(10)	−22(9)	55(9)

EXPERIMENTAL

A suspension of the 1:1 epimeric mixture of the hydroxy ketal (10.5 g, 23.5 mmols) in 80% aqueous acetic acid (100 ml) was heated on a steam bath for 1 hr. It was then cooled to room temperature, poured into ice water (200 ml) and

extracted with ether (3 × 80 ml). Evaporation of the solvent furnished a 1:1 mixture of the epimeric keto alcohols (8.9 g, 94%). The mixture was separated on a silica gel (400 g) MPLC column using ethyl acetate-pet ether (1:20) as eluent to give the 24(S)-hydroxy coprastan (less polar, 3.7 g) and the 24(R)-hydroxy coprastan (more polar, 3.65 g) as white solids, which were recrystallised from a 1:10 mixture of ethyl acetate-pet ether.

TABLE VII.A Coordinates of hydrogen atoms ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for compound

Atom	*x*	*y*	*z*	*U(eq)*
H(2)	10405	7114	4385	93
H(1A)	6035	6361	50	82
H(1B)	7672	6772	364	82
H(2A)	8956	4914	410	110
H(2B)	8857	5267	-61	110
H(4A)	5928	3491	668	84
H(4B)	4341	3200	326	84
H(5)	3191	5083	315	59
H(6A)	1641	5153	943	68
H(6B)	1955	3832	844	68
H(7A)	2795	4249	1542	68
H(7B)	4632	3733	1302	68
H(8)	4041	6129	1460	47
H(9)	7278	5076	1040	46
H(11A)	8872	6827	986	57
H(11B)	7090	7480	1197	57
H(12A)	9771	5972	1610	50
H(12B)	9602	7315	1684	50
H(14)	7077	4712	1786	44
H(15A)	4671	4165	2222	61
H(15B)	3691	5412	2235	61
H(16A)	6770	4641	2728	61
H(16B)	5615	5825	2777	61
H(17)	9155	5406	2336	45
H(18A)	6827	8131	2104	70
H(18B)	5052	7335	2244	70
H(18C)	5313	7655	1774	70

Atom	*x*	*y*	*z*	*U(eq)*
H(19A)	3251	7093	416	102
H(19B)	4772	7705	715	102
H(19C)	3044	6943	898	102
H(20)	7927	7369	2794	47
H(21A)	11149	8122	2733	93
H(21B)	10092	8071	2299	93
H(21C)	11692	7135	2417	93
H(22A)	8711	5712	3191	59
H(22B)	10876	5721	3009	59
H(23A)	9538	7652	3462	62
H(23B)	11757	7300	3378	62
H(24)	9205	6093	3928	62
H(25)	11638	4828	3679	75
H(26A)	12781	4170	4326	153
H(26B)	10523	4518	4351	153
H(26C)	12159	5355	4528	153
H(27A)	14183	6240	3560	165
H(27B)	14954	5084	3762	165
H(27C)	14651	6194	4037	165

TABLE VII.B Coordinates of hydrogen atoms ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for compound II

Atom	*x*	*y*	*z*	*U(eq)*
H(2)	2190	346	6828	155
H(1A)	12069	945	3477	118
H(1B)	11402	678	4071	118
H(2A)	10231	41	3441	109
H(2B)	11615	−69	3281	109
H(4A)	9012	733	2660	107
H(4B)	9728	995	2077	107
H(5)	10875	1612	2718	107
H(6A)	9488	2346	2959	134
H(6B)	8995	2010	2353	134
H(7A)	7627	1445	2948	127
H(7B)	7433	2139	3114	127
H(8)	8483	2024	4060	95

Atom	*x*	*y*	*z*	*U(eq)*
H(9)	8803	789	3691	85
H(11A)	9791	584	4631	109
H(11B)	9632	1266	4856	109
H(12A)	7684	413	4701	105
H(12B)	8137	667	5354	105
H(14)	6733	1089	3949	89
H(15A)	5562	1917	3724	129
H(15B)	6183	2324	4253	129
H(16A)	4770	1957	4930	124
H(16B)	4337	1460	4437	124
H(17)	5567	745	4808	91
H(18A)	7569	1715	5719	155
H(18B)	6936	2170	5246	155
H(18C)	8304	1983	5145	155
H(19A)	11783	1929	3775	210
H(19B)	11018	1791	4386	210
H(19C)	10504	2240	3870	210
H(20)	5488	1481	5909	107
H(21A)	6076	227	5823	183
H(21B)	5547	495	6455	183
H(21C)	6795	738	6190	183
H(22A)	3796	535	5714	117
H(22B)	3562	1164	5375	117
H(23A)	3765	1047	6704	97
H(23B)	3479	1665	6357	97
H(24)	1612	1205	6002	92
H(25)	1594	1902	6827	121
H(26A)	1589	949	7698	227
H(26B)	1530	1653	7850	227
H(26C)	2725	1368	7567	227
H(27A)	−239	1003	6821	216
H(27B)	−284	1656	6508	216
H(27C)	371	1590	7246	216
H(25')	−3885	1080	−2120	173
H(2')	−2483	205	1556	246
H(1'1)	5480	1689	2560	148
H(1'2)	4093	1804	2427	148
H(2'1)	4325	1013	3156	179

Atom	*x*	*y*	*z*	*U(eq)*
H(2'2)	3693	759	2540	179
H(4'1)	5178	127	1769	141
H(4'2)	6557	132	1969	141
H(5')	6743	1157	1760	131
H(6'1)	6907	506	880	178
H(6'2)	6607	1189	697	178
H(7'1)	5324	534	114	154
H(7'2)	4859	223	739	154
H(8')	4353	1457	386	114
H(9')	3611	832	1496	99
H(11C)	2977	2055	1230	128
H(11D)	2550	1678	1821	128
H(12C)	1296	1065	1200	120
H(12D)	978	1754	1055	120
H(14')	2633	512	550	107
H(15C)	3287	252	−414	198
H(15D)	3447	942	−630	198
H(16C)	1304	265	−672	168
H(16D)	1522	913	−986	168
H(17')	611	661	233	114
H(18D)	2312	1886	−445	206
H(18E)	2899	2121	186	206
H(18F)	1508	2231	55	206
H(19D)	4922	7390	1603	229
H(19E)	5413	2087	980	229
H(19F)	6261	2136	1576	229
H(20')	20	1678	−550	131
H(21D)	−1730	1789	103	203
H(21E)	−510	1931	462	203
H(21F)	−1173	1301	566	203
H(22C)	−1384	609	−426	193
H(22D)	−568	755	−1017	193
H(23C)	−2795	1289	−691	204
H(23D)	−1862	1719	−1035	204
H(24')	−1841	1029	−1894	157
H(26D)	−4711	2025	−1444	275
H(26E)	−4579	1379	−1122	275
H(26F)	−5313	1445	−1755	275

Single crystals were obtained by slow evaporation method for the compounds dissolved in ethonol and water.

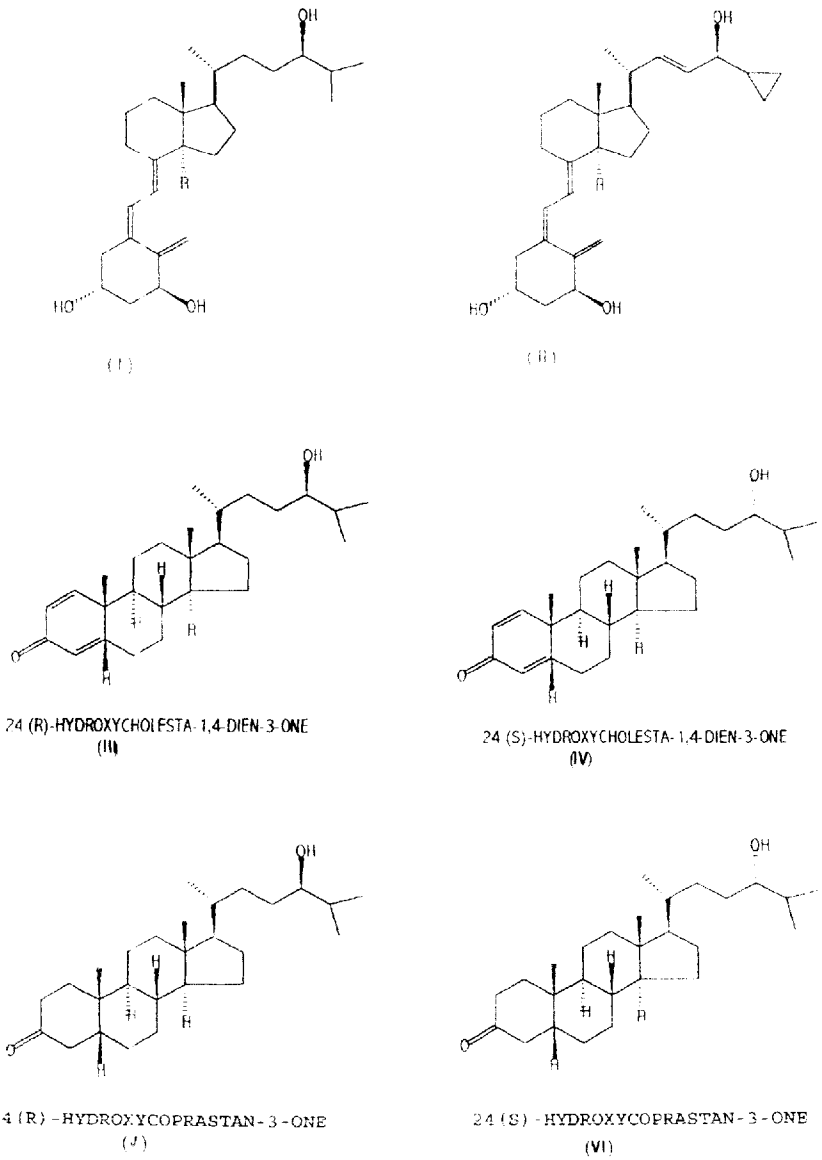

FIGURE 1 Chemical structure of the title compound

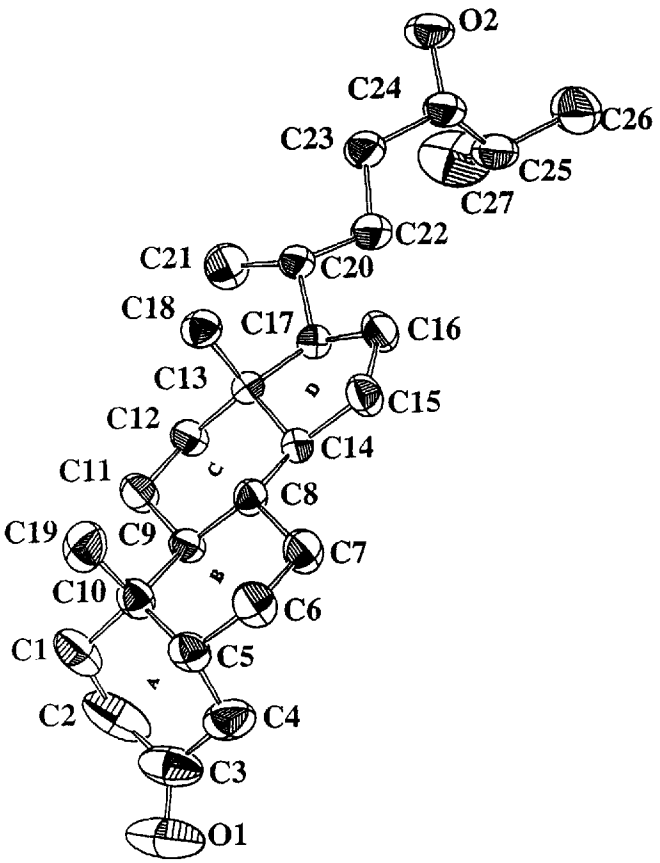

FIGURE 2 Zortep diagram of the molecule with 30% probability displacement ellipsoids for compound I

Crystal structure of I

A colourless rectangular crystal of dimension 0.25 × 0.15 × 0.1 mm was selected for X-ray data collection. All X-ray measurments were made at room temperature on an ENRAF-NONIUS (CAD-4 diffractometer [5] using CuK_α radiation ($\lambda = 1.5418$Å). The cell refinement and data reduction were done using CAD4-software [6]. The data were collected at 293K using ($\omega/2\theta$) scanning mode. Least-squres refinement of 25 well-centered reflections in the range $13° \leq \theta \leq 24°$ yielded a primitive orthorhombic cell in the space group $P2_12_12_1$. During data collection three standard reflections periodically monitored showed

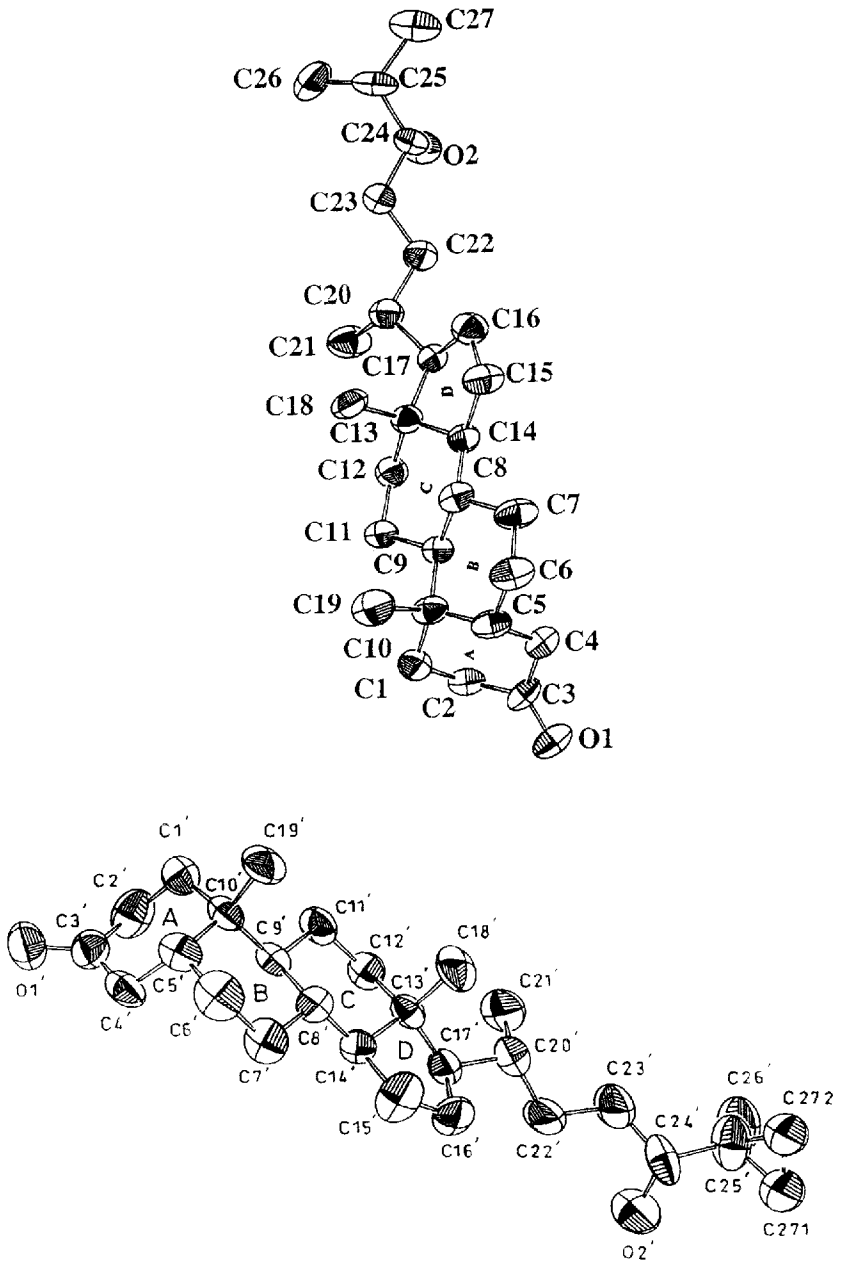

FIGURE 3 Zortep diagram of the molecule with 30% probability displacement ellipsoids for molecules 1 & 2 of compound II

no significant intensity variation. Corrections for Lorentz and polarisation factors were applied to intensity values but no absorption correction was made. A total of 3098 intensities were collected in the range $2.75° \leq \theta \leq 71.91°$ of which 2822 were unique ($R_{int} = 0.064$).

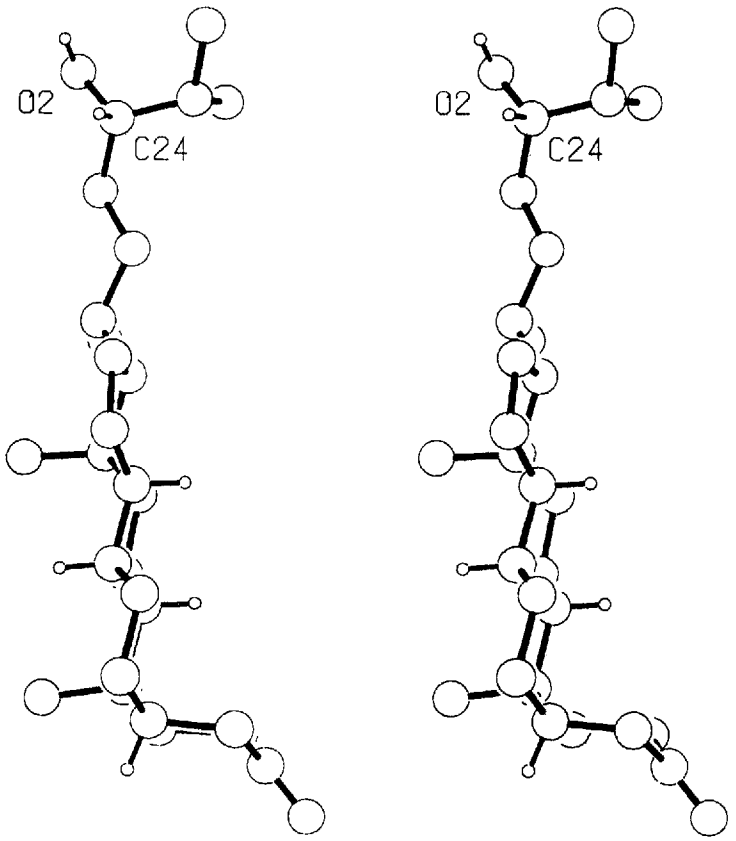

FIGURE 4 Stereo view of the molecule in compound I

The structure was solved by direct methods SHELXS97 [7] and refined by full matrix least squares method on $|F^2|$ using SHELXL97[8]. Final refinement was carried out with anisotropic thermal parameters for all non H atoms. As only two oxygens are present in the molecule the absolute configuration could not be established unequivocally. However the assignment is based on the fact that C18 and C19 in the steroid molecule will have to be in the β-conformation. All the hydrogens were geometrically fixed and allowed to ride on the corresponding carbon atoms. The final cycle of full matrix refinement based on 2822 observed

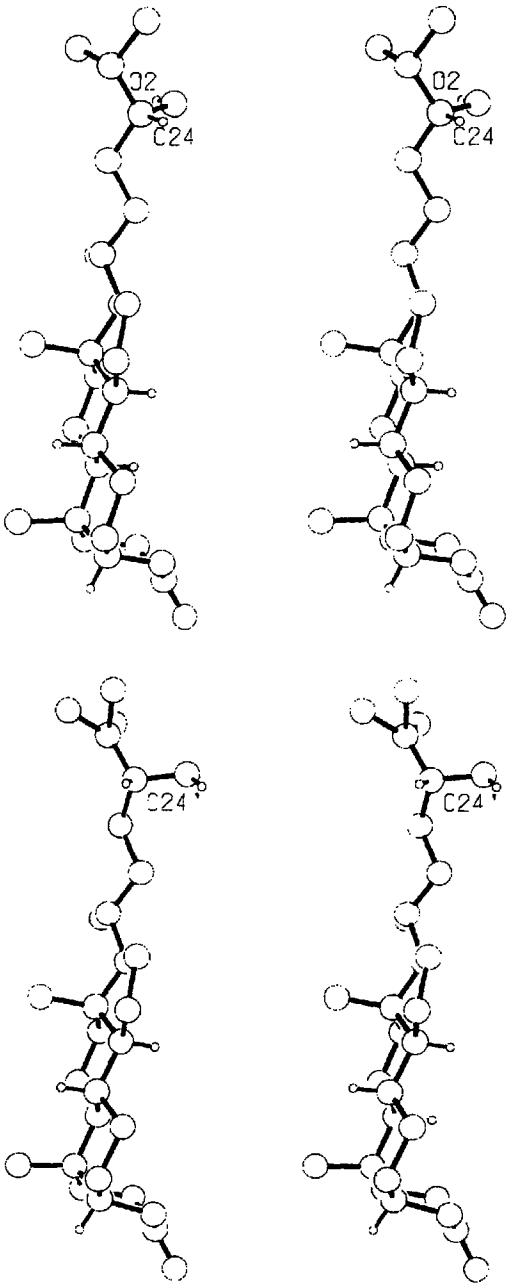

FIGURE 5 Stereo view of the molecule in compound II

reflections [I>2σ(I)] and 269 parameters converged to R = 0.052 with goodness of fit = 0.956. The largest peak and the deepest hole in the final difference map were 0.197 and −0.189 e.Å^{-3}

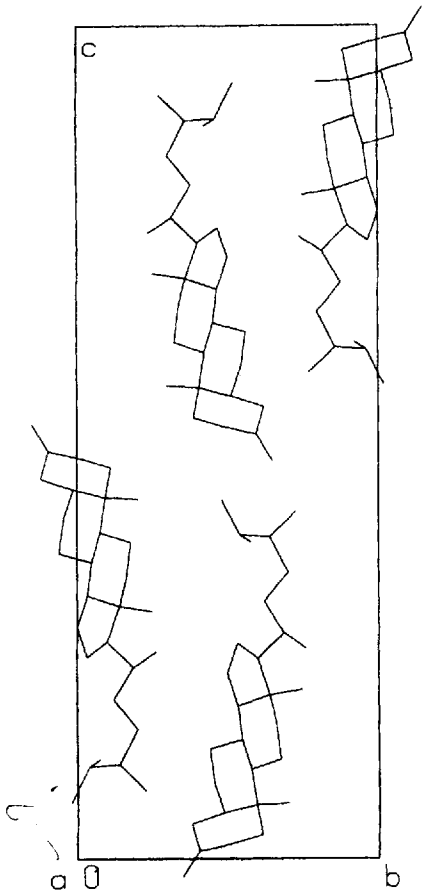

FIGURE 6 Packing diagram down a-axis in compound I

Crystal structure of II

A yellow coloured rectangular crystal of dimension 0.4 × 0.2 x 0.1 mm was selected for X-ray data collection. All X-ray measurments were made at room temperature on an ENRAF-NONIUS (CAD-4 diffractometer) [5] using CuK_α radiation (λ = 1.5418Å). The cell refinement and data reduction were done using

CAD4-software [6]. The data were collected at 293K using ($\omega/2\theta$) scanning mode. Least-squres refinement of 25 well-centered reflection in the ranges $8° \leq \theta \leq 22°$ yielded a primitive orthorhombic cell in the space group $P2_12_12_1$. During data collection three standard reflections periodically monitored showed no significant intensity variation. Corrections for Lorentz and polarisation factors were applied to the intensities but no absorption correction was made. A total of 5130 intensities were collected in the range $2.72° \leq \theta \leq 69.99°$ of which 5118 were unique ($R_{int} = 0.022$).

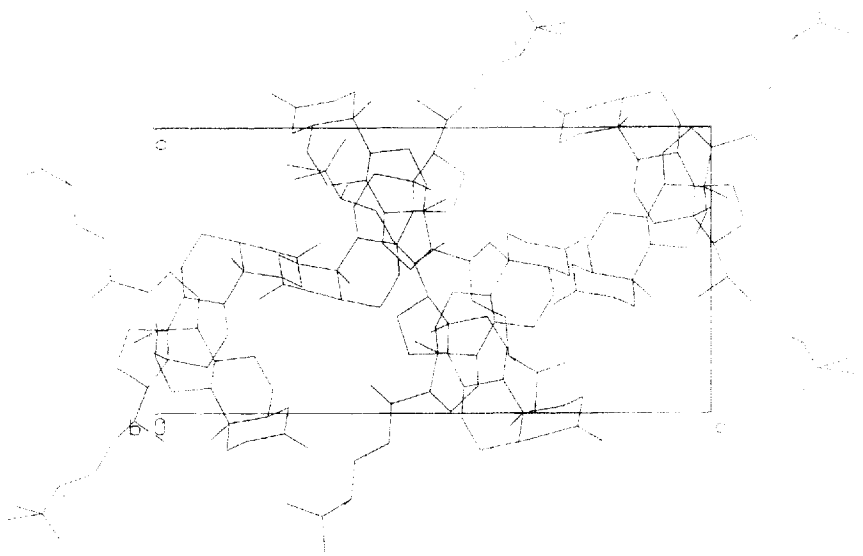

FIGURE 7 Packing diagram down b-axis in compound II

The structure was solved by direct methods SHELXS 97 [7] and refined by full matrix least-squares method on $|F^2|$ using SHELXL 97[8]. Final refinement was carried out with anisotropic thermal parameters for all non H atoms. As only two oxygens are present in the molecule the absolute configuration could not be established unequivocally. However the assignment is based on the fact that C18 & C19 in the steroid molecule will have to be in the β-conformation. All the hydrogens were geometrically fixed and allowed to ride on the corresponding carbon atoms. The final cycle of full matrix refinement based on 5118 observed reflections [$I>2\sigma(I)$] and 535 parameters converged to R = 0.0697 with goodness of fit = 0.953. The largest peak and the deepest hole in the final difference map were 0.207 and $-0.190 e.Å^{-3}$ respectively.

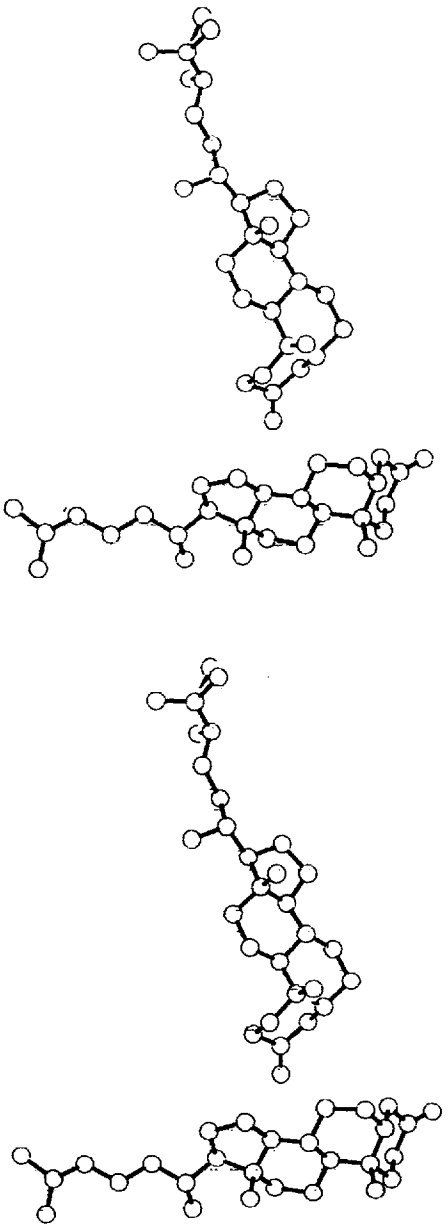

FIGURE 8 Stereo view showing the relative orientation of two molecules in the asymmetric unit in compound II

RESULTS AND DISCUSSIONS

The fractional and atomic coordinates with equivalent isotropic displacement parameters for non-hydrogen atoms, selected torsion angles and hydrogen bonds for **I** and **II** are listed in Tables. Ia,Ib, IIa,IIb, and IIIa,IIIb respectively. The conformations of rings were analysed using PARST [9]. Fig. 1 shows the structural formulae, Fig. 2 and Fig. 3 were plotted (displacement ellipsoids are drawn at 30% probabilty level) using ZORTEP Programme [10] for compound **I** & **II** respectively. The priority sequence attached to the chiral carbon C24 has "S" designation in compound **I** (Fig. 4) & "R" designation in both the molecules of the compound **II** (Fig. 5). In compound **I** (Fig. 6) and in compound **II** (Fig. 7) the packing of the molecule is established by intermolecular O-H...O and C-H...O hydrogen bonds (Figs 6 -8). The molecules are packed head to tail in compound **I** whereas in compound **II** the packing is different since the two molecules in the asymetric unit are almost perpendicular (Fig. 8) to each other. The average e.s. ds in bond lengths are 0.006Å and 0.010Å and in bond angles are 0.4° and 0.8° in isomers **I** and **II** respectively. The methyl atom C27′ of the second molecule in compound **II** is disordered with occupancies 0.6 and 0.4. The chair conformation of the rings A, B and C are confirmed by the asymmetry parameters φ2 = 157(7)°, −169(8)°, −97(3)°; θ2 = 176(5)°, 3(4)°, 8(4)° and q3 = -0.525(5), 0.562(4), 0.558(3) respectively in compound **I** and φ2 = -175(31)°, −77(12)°, −125(11)°; θ2 = 179(8)°, 3(8)°,4(7)° and q3 = -0.541(8), 0.571(7), 0.556(7) in molecule 1 and φ2 = -172(8)°, 118(61)°, 40(4)°; θ2 = 172(11)°, 1(1)°, 9(7)° and q3 = 0.523(10), 0.571(9), 0.684(9) [11] in molecule 2 of compound **II** respectively. The five membered ring D adopts envelope conformation with asymmetry parameter φ2 = -172(6)° and q2 = 0.445(4) in compound **I** and with φ2 = -167(1),°-170(1)° and q2 = 0.468(7),0.451(8) respectively in both the molecules of compound **II**. A/B rings are cis fused and substituents at (C8 & C9) and (C13 & C14) are at diaxial position in cyclohexane rings leading to trans conformation in both the compounds. The side chain attached to "D" ring at C17 is in extended conformation in compound II, whereas in compound I except at the position C23-C24 [the torsion angle C22-C23-C24-C25 = 62.2(6)°] the side chain is in extended conformation. The "S" conformer has been reported to be less potent [12] and it is not clear whether the difference in activity can be attributed to the change in conformation at C23-C24. In compound **I** the best plane passing through ring A makes a dihedral angle of 63(1)° with the best plane passing through the cyclohexane ring B. The dihedral angles between ring B & C and ring C & D are 3.0(1)° & 6.8(2)° respectively. In both the molecules of compound **II** the angle between the planes A & B are 64(2)° & 65(3)° while that between the planes B & C are 4.1(2)° & 7.5(3)° and between C & D are 2.3(2)° & 10.4(3)°.

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