Structural Studies of Some Serrulatane Diterpenes

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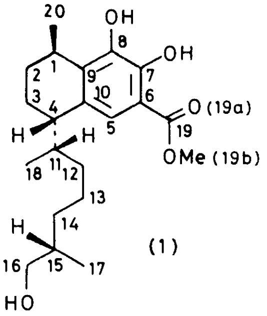
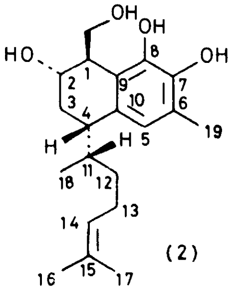
The crystal structures of methyl (15*S*)-7,8,16-trihydroxyserrulatan-19-oate (1) and 2,7,8,20-tetrahydroxyserrulat-14-ene (2) have been established by single crystal *X*-ray diffraction techniques at 295 K, being refined by least squares to residuals of 0.046 and 0.053 for 1 153 and 1 513 ' observed ' reflections respectively. Crystals of (1) are orthorhombic, $P2_12_12_1$, a = 21.78(2), b = 18.42(2), c = 5.101(3) Å, Z = 4 while those of (2) are monoclinic, $C2$, a = 14.96(1), b = 12.315(6), c = 21.75(1) Å, β = 107.21(5)°, Z = 8. As well as establishing total relative stereochemistry in (1), an interesting intramolecular hydrogen-bonding system is observed, together with an alicyclic ring conformation differing from that found in the previously studied dihydroxyserrulatic acid (3). In (2), the two independent molecules of the asymmetric unit have different conformations, corresponding broadly to those of (1) and (3).

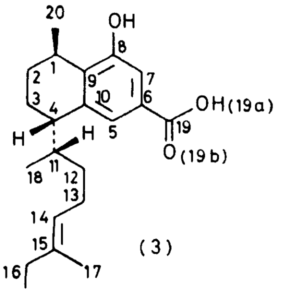
In a previous report[1] we have described the chemistry and structure determination of dihydroxyserrulatic acid (3), an example of the new diterpene skeleton serrulatane (4), whose derivatives have subsequently been found to be widespread among species of the genus *Eremophila*; the absolute stereochemistry of the skeleton was subsequently assigned by chemical methods.[2] A number of the oxygenated derivatives also isolated present additional stereochemical problems by virtue of the provision of additional chiral centres.[1,3] Chemical studies on some of these have shown the basic skeleton to have the same absolute configuration as (3), but the chirality of any additional centres in many cases is not easily derived.[3] In particular, in (1) the chirality of the remote C(15) centre could not be conveniently established, while in (2), although n.m.r. studies suggested the presence of the 1,3-diol system, the stereochemistry of the secondary hydroxy-group could not be unambiguously derived. We report in this paper, the resolution of those two stereochemical problems, by *X*-ray crystallographic methods, in the process elucidating the relative stereochemistry within each compound and bringing to light a number of interesting aspects of hydrogen-bonding and alicyclic ring conformation within the system.



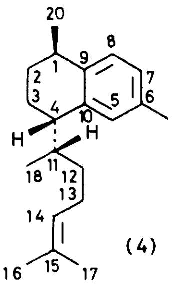
(1)



(2)



(3)



(4)

Crystal Data.—(1) $C_{21}H_{32}O_5$, M = 364.5, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a = 21.78(2), b = 18.42(2), c = 5.101(3) Å, U = 2047(3) Å^3, D_m = 1.18(1), D_c = 1.18 g cm^{-3}, Z = 4, $F(000)$ = 792. Ni-filtered Cu-K_α radiation, λ = 1.5418 Å, μ = 6.8 cm^{-1}. Specimen size: 0.15 × 0.15 × 0.20 mm. T = 295(1) K. A unique data set was measured to $2\theta_{max.}$ 100, yielding 1 267 independent reflections, 1 153 with $I > 2\sigma(I)$ being considered ' observed ' and used without absorption correction in the refinement. Final residuals (R,R') 0.046, 0.055.

(2) $C_{20}H_{30}O_4 \cdot 1/4H_2O$, M = 339.0, monoclinic, space group $C2$(C_2^3, No. 5), a = 14.96(1), b = 12.315(6), c = 21.75(1) Å, β = 107.21(5)°, U = 3829(6) Å^3, D_m = 1.16(1), D_c = 1.18 g cm^{-3}, Z = 8, $F(000)$ = 1 476. Monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ = 0.85 cm^{-1}. Specimen size: 0.22 × 0.16 × 0.36 mm. T = 295(1) K. A unique data set was measured to $2\theta_{max.}$ 40°, yielding 1 905 independent reflections, 1 513 of these with $I > 3\sigma(I)$ being considered ' observed ' and used without absorption correction in the refinement. Final residuals (R,R') 0.053, 0.065.

Data for the two structures was measured on Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers in the conventional 2θ—θ scan mode. Structures were solved by direct methods. Block diagonal 9 × 9 least squares refinement was used throughout; in (1), most hydrogen atoms could be refined in $(x, y, z)_H$, and were included as variables in the parent C,O block. In (2) hydrogen atoms (x, y, z) were included as estimates as invariants. U_H was set at 1.5 $\bar{U}_{ii}$ (parent C) (methyl), 1.25 $\bar{U}_{ii}$ (parent C) (others). Reflection weights were $[\sigma^2(F_0) + 0.0005(F_0)^2]^{-1}$. Neutral atom scattering factors were used, corrected for anomalous dispersion (f',f''),[4] chirality being assumed to conform to that established for dehydroxyserrulatic acid. Computation was carried out using the *X*-Ray 76 program system[5] implemented on CYBER 73 and Perkin-Elmer 8/32 computers. Material deposited comprises structure factor amplitudes,

TABLE 1

Non-hydrogen atom co-ordinates of (1)

Atom	10^4x	10^4y	10^4z
C(1)	2 550(2)	1 735(3)	3 632(14)
C(2)	2 598(2)	0 914(3)	3 362(15)
C(3)	3 253(2)	0 644(3)	3 442(13)
C(4)	3 541(2)	0 815(3)	6 091(11)
C(5)	3 924(2)	1 986(3)	8 199(11)
C(6)	3 915(2)	2 722(2)	8 607(11)
C(7)	3 496(2)	3 136(2)	7 194(11)
O(7)	3 479(2)	3 883(2)	7 374(10)
C(8)	3 083(2)	2 809(3)	5 554(12)
O(8)	2 676(2)	3 232(2)	4 147(9)
C(9)	3 057(2)	2 060(2)	5 282(10)
C(10)	3 514(2)	1 635(2)	6 535(10)
C(11)	4 193(2)	0 500(3)	6 339(11)
C(12)	4 613(2)	0 743(3)	4 111(12)
C(13)	5 297(2)	0 715(3)	4 687(12)
C(14)	5 686(2)	0 908(3)	2 281(12)
C(15)	6 377(2)	1 000(3)	2 794(11)
C(16)	6 652(2)	0 279(3)	3 594(14)
O(16)	7 296(1)	0 330(2)	4 213(8)
C(17)	6 691(3)	1 300(4)	0 375(15)
C(18)	4 194(3)	−0 316(3)	6 614(17)
C(19)	4 350(2)	3 086(2)	10 390(13)
O(19a)	4 367(2)	3 752(2)	10 724(10)
O(19b)	4 729(2)	2 649(2)	11 616(8)
C(19b)	5 161(3)	2 962(4)	13 430(16)
C(20)	1 909(3)	1 924(3)	4 692(23)

TABLE 2

Hydrogen atom co-ordinates of (1)

Atom	10^3x	10^3y	10^3z
H(1)	262(2)	197(3)	171(11)
H(2a)	237(2)	071(3)	479(13)
H(2b)	241(2)	079(3)	172(12)
H(3a)	326(2)	013(2)	326(11)
H(3b)	349(2)	078(3)	199(10)
H(4)	328(2)	057(2)	752(10)
H(5)	426(2)	182(2)	913(10)
H(7)	385(2)	403(3)	921(14)
H(8)	280(2)	382(3)	474(14)
H(11)	440(2)	073(2)	797(10)
H(12a)	448(2)	049(2)	261(10)
H(12b)	453(2)	119(2)	356(10)
H(13a)	540(2)	120(2)	626(10)
H(13b)	542(2)	022(2)	513(11)
H(14a)	559(2)	051(2)	105(11)
H(14b)	552(2)	135(2)	150(11)
H(15)	644(2)	137(2)	425(10)
H(16a)	647(2)	001(3)	489(11)
H(16b)	656(2)	−017(3)	227(11)
H(16)	744(3)	026(3)	248(12)
H(17a)	662(3)	107(3)	−123(14)
H(17b)	647(3)	175(3)	001(14)
H(17c)	712(2)	140(3)	080(14)
H(18a)	394(3)	−051(4)	779(14)
H(18b)	406(3)	−056(4)	507(15)
H(18c)	465(2)	−048(3)	690(14)
H(19a) *	541(—)	330(—)	1 250(—)
H(19b) *	493(—)	323(—)	1 473(—)
H(19c) *	543(—)	265(—)	1 437(—)
H(20a)	161(3)	168(4)	336(16)
H(20b)	187(3)	166(4)	653(17)
H(20c)	191(3)	237(3)	497(19)

* (x,y,z) constrained at tetrahedral positions.

thermal parameters, and hydrogen atom geometries.[*]

Atom numbering follows that previously used for dihydroxyserrulatic acid (3) with hydrogen and peripheral carbon and oxygen atoms labelled according to the parent carbon. (Suffixes a—c are used where distinction is necessary.)

The chirality of dihydroxyserrulatic acid has recently been established by chemical means and is opposite to that shown in ref. 1. The chirality of (1) and (2) as reported here conforms to the correct chirality of dihydroxyserrulatic acid; where parameters (*e.g.* torsion, angles, least squares plane deviations, *etc.*) are displayed for the three compounds on a comparative basis, the signs of those for dihydroxyserrulatic acid have been adjusted to conform to those of (1) and (2). It should be noted, however, that it has not been conclusively demonstrated chemically that (2) has the same chirality as (3) and (1).[3]

(1) The unit cell contents comprise discrete molecules of compound (1). Intermolecular hydrogen bonding is found as follows: H(8) ··· O(16) $(x - \frac{1}{2}, \frac{1}{2} - y, 1 - z)$, 1.99(5) Å [O–H ··· O, 132(4)°]; H(16) ··· O(16) $(1\frac{1}{2} - x, \bar{y}, z - \frac{1}{2})$, 2.07(6) Å [O–H ··· O, 156(5)°]. In (3), H(8), although hydrogen-bonded intermolecularly to a carboxy oxygen atom, lies closely coplanar with the ring system (deviation 0.08 Å) and, *cis* to C(7); in (1), the additional hydroxy-group at C(7) enables a strongly hydrogen-bonded co-planar series of intramolecular interactions to occur: H(5) ··· O(19b), 2.24(5) Å; H(7) ··· O(19a), 1.46(6) Å; H(8) ··· O(7), 2.00(6) Å. Notable among these is the H(7) ··· O(19a) interaction where the hydrogen atom is shared between O(7) [a long bond, 1.26(6) Å] and O(19a) [a close contact at 1.46(6) Å]. Deviations from the plane of Figure 2 are H(7), −0.14 Å; H(8), 0.12 Å. O(7) ··· O(8) is 2.683(6) Å while O(7) ··· O(19a) is 2.592(6) Å. The influence of

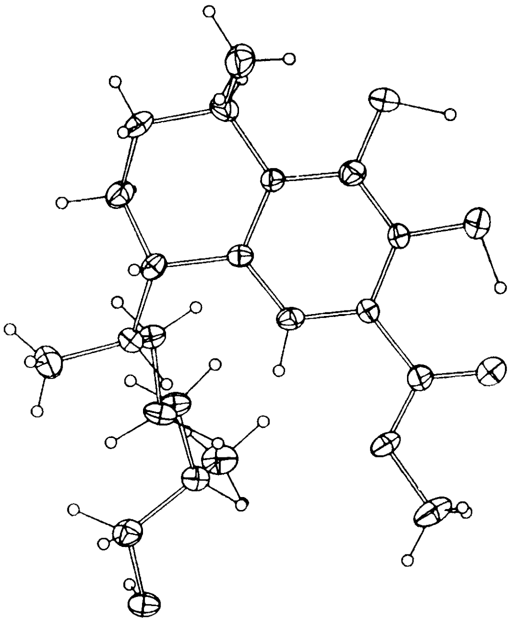


FIGURE 1 Molecular projection of (1). The projection is normal to the aromatic ring plane and shows 20% thermal ellipsoids for the non-hydrogen atoms, while hydrogen atoms are given an arbitrary radius of 0.1 Å

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[*] Supplementary Publication No. SUP 23130 (19 pp.). For details see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 2*, 1980, Index Issue.

TABLE 3

Non-hydrogen atom co-ordinates of (2)

Atom	Molecule 1			Molecule 2		
	$10x$	10^4y	10^4z	10^4x	10^4y	10^4z
C(1)	0 141(5)	0 863(6)	1 288(3)	3 180(6)	3 136(7)	0 521(4)
C(2)	−0 394(5)	1 583(6)	1 631(4)	3 498(6)	1 968(8)	0 410(4)
O(2)	−1 329(4)	1 780(4)	1 229(2)	3 963(6)	1 983(7)	−0 092(3)
C(3)	−0 403(5)	1 151(6)	2 274(3)	4 118(6)	1 464(8)	1 007(4)
C(4)	0 596(5)	0 949(6)	2 700(3)	3 551(5)	1 305(7)	1 498(3)
C(5)	1 601(5)	−0 720(6)	2 746(3)	2 877(5)	2 539(6)	2 185(3)
C(6)	1 922(5)	−1 594(6)	2 460(3)	2 520(5)	3 501(6)	2 324(4)
C(7)	1 611(6)	−1 651(7)	1 795(4)	2 373(6)	4 320(6)	1 869(3)
O(7)	1 856(4)	−2 557(5)	1 478(3)	1 980(5)	5 286(5)	2 019(3)
C(8)	1 027(6)	−0 866(7)	1 436(4)	2 590(6)	4 196(7)	1 306(3)
O(8)	0 763(4)	−1 025(5)	0 771(2)	2 471(4)	5 094(5)	0 898(3)
C(9)	0 726(5)	0 010(6)	1 720(3)	2 967(5)	3 242(6)	1 159(3)
C(10)	1 011(5)	0 054(—) *	2 397(3)	3 115(5)	2 387(6)	1 612(4)
C(11)	0 664(5)	0 802(6)	3 416(3)	4 119(5)	0 722(7)	2 107(4)
C(12)	0 047(5)	−0 123(7)	3 526(4)	5 000(5)	1 361(7)	2 480(4)
C(13)	0 266(6)	−0 453(8)	4 229(4)	5 386(6)	1 044(9)	3 194(4)
C(14)	1 198(7)	−0 984(8)	4 484(4)	4 780(6)	1 427(8)	3 589(4)
C(15)	1 934(6)	−0 612(9)	4 955(5)	4 330(6)	0 864(8)	3 915(4)
C(16)	2 839(8)	−1 230(17)	5 165(7)	3 750(8)	1 395(11)	4 296(4)
C(17)	1 958(8)	0 392(11)	5 326(5)	4 344(9)	−0 343(9)	3 964(6)
C(18)	0 428(6)	1 888(7)	3 690(4)	4 350(8)	−0 463(8)	1 957(5)
C(19)	2 558(6)	−2 425(8)	2 865(4)	2 264(7)	3 660(8)	2 945(4)
C(20)	0 677(6)	1 623(4)	0 980(4)	2 395(7)	3 494(8)	−0 068(4)
O(20)	0 967(5)	1 122(7)	0 524(3)	1 549(4)	2 981(6)	−0 103(3)
Solvent						
O	5 000(—)	−0 581(12)	0 000(−)			

* Defines origin.

TABLE 4

Hydrogen atom co-ordinates of (2)

Atom	Molecule 1			Molecule 2		
	10^3x	10^3y	10^3z	10^3x	10^3y	10^3z
H(1)	−034(—)	050(—)	095(—)	371(—)	360(—)	053(—)
H(2a)	−008(—)	226(—)	169(—)	291(—)	152(—)	027(—)
H(2)	−165(—)	109(—)	113(—)	340(—)	220(—)	−042(—)
H(3a)	−074(—)	166(—)	247(—)	438(—)	078(—)	091(—)
H(3b)	−077(—)	048(—)	222(—)	465(—)	193(—)	119(—)
H(4)	096(—)	163(—)	269(—)	303(—)	078(—)	131(—)
H(5)	177(—)	−069(—)	321(—)	298(—)	193(—)	249(—)
H(7)	260(—)	−258(—)	166(—)	188(—)	586(—)	170(—)
H(8)	058(—)	−047(—)	047(—)	182(—)	530(—)	079(—)
H(11)	130(—)	057(—)	366(—)	378(—)	070(—)	244(—)
H(12a)	−059(—)	012(—)	337(—)	548(—)	124(—)	227(—)
H(12b)	012(—)	−074(—)	327(—)	487(—)	213(—)	246(—)
H(13a)	028(—)	021(—)	449(—)	541(—)	025(—)	324(—)
H(13b)	−019(—)	−092(—)	430(—)	602(—)	129(—)	339(—)
H(14)	129(—)	−162(—)	427(—)	472(—)	222(—)	358(—)
H(16a)	330(—)	−083(—)	506(—)	311(—)	115(—)	413(—)
H(16b)	299(—)	−143(—)	559(—)	397(—)	122(—)	473(—)
H(16c)	280(—)	−194(—)	492(—)	373(—)	218(—)	426(—)
H(17a)	212(—)	030(—)	578(—)	459(—)	−057(—)	442(—)
H(17b)	244(—)	090(—)	525(—)	373(—)	−063(—)	381(—)
H(17c)	140(—)	088(—)	522(—)	473(—)	−071(—)	375(—)
H(18a)	085(—)	246(—)	365(—)	369(—)	−083(—)	170(—)
H(18b)	−020(—)	213(—)	345(—)	461(—)	−044(—)	158(—)
H(18c)	046(—)	179(—)	413(—)	463(—)	−081(—)	227(—)
H(19a)	224(—)	−310(—)	278(—)	259(—)	426(—)	318(—)
H(19b)	311(—)	−245(—)	275(—)	160(—)	382(—)	284(—)
H(19c)	278(—)	−239(—)	334(—)	234(—)	308(—)	327(—)
H(20a)	030(—)	224(—)	080(—)	228(—)	428(—)	−004(—)
H(20b)	121(—)	187(—)	131(—)	256(—)	339(—)	−046(—)
H(20)	149(—)	080(—)	063(—)	164(—)	221(—)	−013(—)
Solvent						
H	445(—)	−104(—)	008(—)			

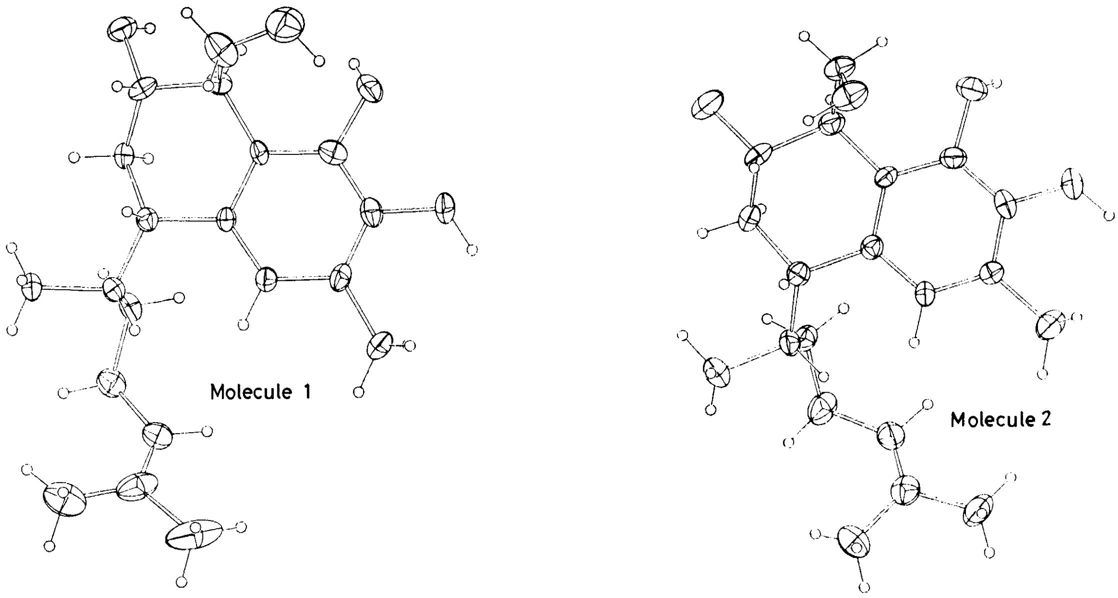

FIGURE 2 Molecular projection of the two molecules of (2), as in Figure 1

these interactions is observed also in the changes found in the exocyclic angles at C(6,8) on passing from (3) to (1) (Table 5). In (1) C(19)—O(19a) may well be longer [1.240(6) Å] relative to (3) [1.211(8) Å]; the angular geometry about C(19), however, is distorted in the manner expected in both compounds and exhibits no significant difference. In (3) the carboxy C=O is '*cis*' to the molecular 'tail' but '*trans*' in (1), presumably a result of the hydrogen-bonding. The chirality of C(15) in the molecular tail of (1) is found to be *S*.

The conformation of the alicyclic ring is the most interesting feature of the structure. In (3) a curious aspect of the structure of this ring was the abnormally high thermal motion on C(2) (in particular) and C(3), relative to the neighbouring C(1) and C(4),* resulting in the unbelievably short value of 1.42(1) Å for C(2)–C(3). It is possible that the energy difference between boat and half-chair conformers is comparable to thermal energy at room temperature, and the observed positions for C(2) and C(3) represent the centres of gravity for a molecule which is pseudo-fluxional or disordered between two possible conformers in the solid state. In (1) no such abnormalities are found. To what extent are the differences evident in Table 7 which arise from (3) meaningful and, if so, what do they mean? Clearly the variation of the deviation of C(11) is significant, but what of C(2,3,20)? Consideration of the data of (3) shows that all hydrogen atoms associated with C(3,20) were located in difference maps and refined meaningfully, suggesting that the dispositions of these carbon atoms, at least, have some credibility; by contrast the hydrogen atoms associated with C(2) could not be located. Construction of a scale model suggests that a facile movement of C(2) relative to the plane is feasible with a large concomitant motion of C(20) and is accompanied by movement of C(11) but *not* C(3) in the manner expected.

(2) The unit cell contents comprise discrete molecules of (2). The asymmetric unit of this structure comprises two molecules, with some interesting conformational differences apparent between them, probably a consequence of hydrogen-bonding, most evident in the OH(20) disposition which, in molecule 1, shows some interaction internally with OH(8) while in molecule 2, the interactions of these two substituents are directed intermolecularly. Substitution of the methyl at C(6) in (2) relative to (1) destroys the hydrogen-bonding pattern observed in the latter (Figure 3), continuous from OH(8) to H(5) and with implications for C(2) and H(4) (see below).

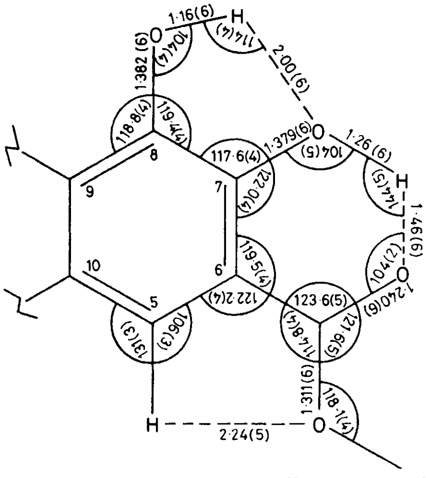

FIGURE 3 The hydrogen bonding scheme of (1)

Consideration of the ring conformations (Tables 6 and 7) shows the two molecules to be different and compar-

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* U_{ij} are given in full in ref. 1 and the interested reader is referred to that paper.

TABLE 5

Molecular non-hydrogen geometry

Atoms Distances (Å)	Parameters Compound/molecule (2)/1, (2)/2	(3)	(1)
C(1)–C(2)	1.530(12), 1.556(13)	1.522(11)	1.521(8)
C(1)–C(9)	1.506(10), 1.520(12)	1.504(8)	1.511(7)
C(1)–C(20)	1.511(13), 1.525(11)	1.507(12)	1.538(10)
C(2)–C(3)	1.499(11), 1.490(11)	1.423(11)	1.512(8)
C(2)–O(2)	1.434(8), 1.459(13)		
C(3)–C(4)	1.527(9), 1.559(13)	1.507(10)	1.523(8)
C(4)–C(10)	1.508(10), 1.536(11)	1.539(8)	1.528(7)
C(4)–C(11)	1.541(10), 1.525(10)	1.542(8)	1.539(7)
C(5)–C(6)	1.397(11), 1.369(12)	1.377(8)	1.372(7)
C(5)–C(10)	1.366(8), 1.406(12)	1.382(8)	1.392(7)
C(6)–C(7)	1.384(11), 1.383(11)	1.402(8)	1.392(7)
C(6)–C(19)	1.494(11), 1.523(13)	1.492(9)	1.474(9)
C(7)–C(8)	1.380(11), 1.365(12)	1.368(8)	1.367(7)
C(7)–O(7)	1.416(11), 1.408(11)		1.379(6)
C(8)–O(8)	1.395(9), 1.397(10)	1.386(6)	1.382(6)
C(8)–C(9)	1.383(12), 1.381(12)	1.396(8)	1.388(7)
C(9)–C(10)	1.408(9), 1.414(11)	1.406(7)	1.419(6)
C(11)–C(12)	1.529(12), 1.544(11)	1.519(9)	1.526(8)
C(11)–C(18)	1.548(12), 1.556(13)	1.549(10)	1.511(8)
C(12)–C(13)	1.521(11), 1.539(11)	1.515(9)	1.519(7)
C(13)–C(14)	1.491(13), 1.498(14)	1.515(9)	1.533(8)
C(14)–C(15)	1.343(12), 1.311(14)	1.330(10)	1.536(7)
C(15)–C(16)	1.502(18), 1.514(16)	1.488(10)	1.514(8)
C(15)–C(17)	1.471(17), 1.489(15)	1.492(10)	1.515(9)
C(16)–O(16)		1.425(9)	1.441(6)
C(19)–O(19a)		1.211(8)	1.240(6)
C(19)–O(19b)		1.308(8)	1.311(6)
O(19b)–C(19b)			1.439(8)
Angles (°)			
C(2)–C(1)–C(9)	113.1(6), 112.1(7)	113.3(5)	113.2(4)
C(2)–C(1)–C(20)	106.3(7), 109.4(6)	110.2(7)	108.6(4)
C(9)–C(1)–C(20)	115.0(6), 115.2(8)	110.3(6)	112.1(6)
C(1)–C(2)–C(3)	113.5(6), 113.0(7)	119.8(6)	112.9(5)
C(1)–C(2)–O(2)	110.9(6), 109.9(8)		
C(3)–C(2)–O(2)	110.7(7), 110.2(8)		
C(2)–C(3)–C(4)	110.3(7), 108.9(8)	117.3(7)	110.1(5)
C(3)–C(4)–C(10)	108.0(6), 110.2(7)	110.7(5)	108.7(4)
C(3)–C(4)–C(11)	113.2(6), 112.1(7)	111.5(5)	112.0(4)
C(10)–C(4)–C(11)	116.3(6), 114.9(6)	113.6(5)	113.3(4)
C(6)–C(5)–C(10)	122.8(6), 121.9(7)	121.6(5)	122.8(5)
C(5)–C(6)–C(19)	120.6(7), 121.6(7)	119.2(5)	122.2(4)
C(5)–C(6)–C(7)	116.7(7), 117.6(8)	119.5(5)	118.2(5)
C(7)–C(6)–C(19)	122.7(8), 120.7(8)	121.3(5)	119.5(4)
C(6)–C(7)–C(8)	121.2(8), 122.0(8)	119.0(5)	120.4(4)
C(6)–C(7)–O(7)	119.5(7), 116.1(8)		122.0(4)
C(8)–C(7)–O(7)	119.2(7), 121.9(7)		117.6(4)
C(7)–C(8)–C(9)	121.9(7), 121.7(7)	122.1(5)	121.8(5)
C(7)–C(8)–O(8)	115.3(8), 117.6(7)	121.1(5)	119.4(4)
C(9)–C(8)–O(8)	122.9(7), 120.7(7)	116.8(5)	118.8(4)
C(1)–C(9)–C(8)	118.1(6), 119.7(7)	119.5(5)	118.7(4)
C(1)–C(9)–C(10)	124.5(6), 122.7(7)	122.2(5)	123.0(4)
C(8)–C(9)–C(10)	117.4(6), 117.5(7)	118.4(5)	118.3(4)
C(4)–C(10)–C(5)	123.3(6), 119.4(7)	123.7(5)	121.7(4)
C(4)–C(10)–C(9)	116.7(5), 121.3(7)	117.0(5)	120.4(4)
C(5)–C(10)–C(9)	119.9(6), 119.3(7)	119.3(5)	117.9(4)
C(4)–C(11)–C(12)	112.5(7), 112.8(7)	113.0(5)	112.5(4)
C(4)–C(11)–C(18)	109.5(6), 111.2(7)	110.5(5)	112.6(4)
C(12)–C(11)–C(18)	111.4(7), 112.3(7)	110.8(5)	111.1(5)
C(11)–C(12)–C(13)	113.3(6), 114.1(7)	112.4(6)	115.7(4)
C(12)–C(13)–C(14)	113.0(8), 112.9(7)	112.8(6)	112.3(5)
C(13)–C(14)–C(15)	126.8(9), 129.7(9)	126.1(6)	115.5(5)
C(14)–C(15)–C(16)	121.4(11), 122.5(10)	118.6(6)	109.7(4)
C(14)–C(15)–C(17)	125.9(10), 124.6(10)	122.4(6)	110.1(5)
C(16)–C(15)–C(17)	112.7(10), 113.0(10)	119.0(6)	111.2(5)
C(15)–C(16)–O(16)		113.0(6)	112.8(4)
C(6)–C(19)–O(19a)		123.0(6)	123.6(5)
C(6)–C(19)–O(19b)		113.9(5)	114.8(4)
O(19a)–C(19)–O(19b)		123.1(6)	121.6(5)
C(19)–O(19b)–C(19b)			118.1(4)
C(1)–C(20)–O(20)	111.8(9), 112.1(7)		

TABLE 6

Torsion angles (°) for the alicyclic ring skeleton. Atoms, being carbon throughout, are denoted by number only

Atoms	(2) (molecules 1,2)	(3)	(1)
20–1–9–8	−75.6, −47.9	−82.2	−60.2
20–1–9–10	102.7, 130.4	98.6	120.9
20–1–2–3	−139.9, −168.0	−108.1	−156.1
9–1–2–3	−12.8, −38.9	16.2	−30.8
1–2–3–4	54.8, 64.9	20.2	63.0
2–3–4–10	−65.3, −54.4	−47.1	−58.2
2–3–4–11	164.5, 176.2	−174.7	175.8
3–4–10–9	33.8, 21.8	38.0	25.7
3–4–10–5	−143.2, −156.9	−144.9	−155.4
11–4–10–5	−14.7, −29.0	−18.3	−30.3
11–4–10–9	162.3, 149.7	164.6 *	150.9

* Not given in ref. 1.

TABLE 7

Least squares planes calculated through the C(1,4—10)-O[(7),8] sections of the molecular skeletons of (1)—(3), and are given in the form $pX + qY + rZ = s$. Atom deviations, δ, are in Å as is σ, the e.s.d. of the defining atoms; signs of δ have been adjusted to a common chirality

Compound/ molecule	(2)/1	(2)/2	(3)	(1)
10^4p	8 460	8 267	9 010	6 352
10^4q	5 324	3 429	−0 733	0 931
10^4r	−0 299	4 461	−4 275	−7 667
s	−0.139	5.504	−0.851	2.553
σ	0.06	0.03	0.03	0.07
δC(1)	0.10	0.04	0.04	0.15
δC(20)	1.46	1.09	1.45	1.42
δC(2)	−0.31	0.18	−0.57	0.12
δC(3)	−1.00	−0.61	−0.78	−0.71
δC(4)	−0.12	−0.03	0.02	−0.10
δC(11)	−0.57	−0.73	−0.04	−0.85
δC(5)	0.03	0.01	0.05	−0.01
δC(6)	0.03	−0.01	−0.02	0.04
δC(19)	0.05	−0.01	0.00	0.07
δC(7)	0.01	0.01	−0.01	−0.01
δO(7)	−0.08	0.02		−0.04
δC(8)	0.00	0.01	0.00	−0.02
δO(8)	−0.03	−0.06	0.00	−0.08
δC(9)	0.02	0.01	0.01	0.04
δC(10)	0.00	0.01	−0.03	−0.03

able in most respects with (3) and (1) (corresponding to molecules 1 and 2 respectively). Between molecules 1 and 2 we note further differences in respect of variations in the angles C(2)–C(1)–C(20), C(3)–C(4)–C(11), and C(4)–C(10)–C(5,9). The distances C(5) ··· C(11) are relatively constant [2.97(1), 2.95(1) Å] and comparable to those found in (3) and (1) [2.963(8), 2.955(7) Å]; the corresponding four values for H(5) ··· H(11) are 2.0_6, 1.9_5, 2.11(6), and 2.05(7) Å and are very short. The transannular distance H(2) ··· H(4) is 2.4 Å in all four molecules. O(8) (molecule 2) and H(2) (molecule 1) are involved in a short hydrogen bond (1.7 Å); this appears to have no perceptible effect on the C(8)–O(8) distance but may influence the exocyclic geometry at C(8) which nevertheless retains its asymmetry. Possibly, this is the determinant of the ring conformation in (2) as it has been noted above that C(2) appears to be peculiarly susceptible to disturbances. Nevertheless, we note that H(2) [and through it H(4)] is also influenced by the disposition of the

TABLE 8

Interspecies hydrogen contents (2) (O $\cdots$ H, <2.5 Å)
Atoms of molecule 2 are italicized

Parent atoms	Hydrogen contact	$r_{\text{O}\cdots\text{X}}$/Å	$r_{\text{O}\cdots\text{H}}$/Å	X $\cdots$ H –O (°)
O(7) $\cdots$ O(7) ^{i}	*H(7)* $\cdots$ O(7) ^{i}	2.889(9)	2.0_0	151
O(8) $\cdots$ O(2) ^{ii}	*O(8)* $\cdots$ H(2) ^{ii}	2.699(8)	1.7_6	163
O(2) $\cdots$ O(7) ^{iii}	O(2) $\cdots$ H(7) ^{iii}	3.034(9)	2.2_2	132
O(2) $\cdots$ *O(2)* ^{iv}		3.008(12)		
O(20) $\cdots$ O(20) ^{v}		3.111(10)		
O(2) $\cdots$ *O(20)* ^{v}	O(2) $\cdots$ *H(20)* ^{v}	2.796(8)	2.3_7	106
O(7) $\cdots$ *O(2)* ^{vi}	O(7) $\cdots$ *H(2)* ^{vi}	2.955(8)	2.2_4	130
O(8) $\cdots$ *O(2)* ^{vi}	O(8) $\cdots$ H(2) ^{vi}	2.955(11)	2.7_4	93
O(8) $\cdots$ O(7)	*O(8)* $\cdots$ *H(7)*	2.758(10)	2.3_8	102
O(20) $\cdots$ *O(20)*	O(20) $\cdots$ *H(20)*	2.926(11)	2.3_7	116
O(20) $\cdots$ O(8)	O(20) $\cdots$ H(8)	2.733(11)	2.0_4	130
	(0(8) $\cdots$ H(20))		2.5_5	93
O(20) $\cdots$ *O(8)*		3.412(8)		

Transformations of the asymmetric unit: i, $(x, 1 + y, z)$; ii, $(\frac{1}{2} + x, \frac{1}{2} + y, z)$; iii, $(x - \frac{1}{2}, \frac{1}{2} + y, z)$; iv, $(1 - x, y, \bar{z})$: v $(\bar{x}, y, \bar{z})$; vi $(\frac{1}{2} - x, y - \frac{1}{2}, \bar{z})$

CH_2OH substituent. In molecule 1, OH(20) interacts intramolecularly with OH(8), so that H(2) is confronted by H(20 a,b) at 2.2 and 2.4 Å, whereas in molecule 2, H(2) confronts O(20) at 2.6_6 Å. It is also possible, however, that C(20) $\cdots$ O(8) substituent interactions are a contributing element in the stereochemistry, as this distance is quite short in molecule 2 and in (1) [2.86(1), 2.945(8) Å] and much longer in molecule 1 and in (3) [3.412(8), 3.23(1) Å].

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