

Table 3. Details of the sugar pucker in terms of torsion angles and atomic displacements

Torsion angles in degrees (average e.s.d. = 1°)		
$\tau_0$	-18	C(4')-O(4')-C(1')-C(2')
$\tau_1$	34	O(4')-C(1')-C(2')-C(3')
$\tau_2$	-39	C(1')-C(2')-C(3')-C(4')
$\tau_3$	29	C(2')-C(3')-C(4')-C(4')
$\tau_4$	-6	C(3')-C(4')-O(4')-C(1')
Displacement from C(4')-O(4')-C(1') plane in Å (average e.s.d. = 0.03 Å)		
C(2')	0.46	
O(3')	-0.17	
C(5')	1.31	

The molecular structure found (Fig. 2) confirms the chemical and spectral assignments of a  $\beta$ -D-ribose sugar. The molecule adopts a propeller shape with the benzoyl substituents attached to the hydroxyl positions of the deoxyribose sugar; phenyl rings *B2* and *B3* are protecting groups and *B1* a substitute for a base. Since the *B2* phenyl ring is symmetric, it is not possible to define a glycosidic angle as in nucleosides and nucleotides. The ribofuranose ring is in the unsymmetric twist  ${}^2T_3$  conformation, which can also be defined in terms of the C(2')-endo-C(3')-exo sugar pucker. The pseudo-rotation angle (Altona & Sundaralingam, 1972) *P* is 172 (2)° and maximum degree of sugar pucker  $\tau_m$  is 39 (2)°. The sugar-ring torsion angles are given in Table 3.

Biophysical studies (Millican *et al.*, 1984) have shown that the insertion of this deoxyribose base analogue into a pentadecanucleotide destabilizes base stacking. This may be related to the lack of stacking shown by the pseudo-base phenyl ring in the present structure.

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*Acta Cryst.* (1985). **C41**, 722-725

Supinine, C<sub>15</sub>H<sub>25</sub>NO<sub>4</sub>, and Heleurine, C<sub>16</sub>H<sub>27</sub>NO<sub>4</sub>, Pyrrolizidine Alkaloids

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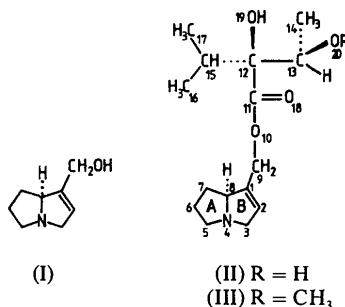
(Received 10 October 1984; accepted 30 November 1984)

**Abstract.** Orthorhombic,  $P2_12_12_1$ ,  $Z = 4$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ ,  $T = 290 (1) \text{ K}$ . Supinine:  $M_r = 283.4$ ,  $a = 10.068 (1)$ ,  $b = 11.644 (1)$ ,  $c = 13.086 (1) \text{ \AA}$ ,  $U = 1534.1 (2) \text{ \AA}^3$ ,  $D_m(\text{floatation}) = 1.23 (1)$ ,  $D_x = 1.230 \text{ Mg m}^{-3}$ ,  $F(000) = 616$ ,  $\mu(\text{Cu } K\alpha) = 0.64 \text{ mm}^{-1}$ . Heleurine:  $M_r = 297.4$ ,  $a = 9.269 (1)$ ,  $b = 11.175 (1)$ ,  $c = 16.345 (2) \text{ \AA}$ ,  $U = 1693.0 (3) \text{ \AA}^3$ ,  $D_m(\text{floatation}) = 1.18 (1)$ ,  $D_x = 1.167 \text{ Mg m}^{-3}$ ,  $F(000) = 648$ ,  $\mu(\text{Cu } K\alpha) = 0.60 \text{ mm}^{-1}$ . Full-matrix least-squares refinement converged at *R* values of 0.041 and 0.048 for 1411 and 1367 reflections of supinine and heleurine respectively. The absolute molecular structures have been assigned by comparison with that of the amino-alcohol, supinidine. Both alkaloid molecules adopt similar extended conformations which differ from that of intermedine, a retronecine alkaloid also containing

the trachelanthic acid moiety, by an approximate twofold rotation about the C(1)-C(9) bond. Consequently, in supinine and heleurine the carbonyl group is antiparallel with the C(8)-H(8) bond whereas in intermedine it is synparallel.

**Introduction.** The two alkaloids, monoesters of the amino-alcohol supinidine (I), have been isolated from *Heliotropium europaeum* L. (Culvenor, 1954), supinine being only a minor product; the latter was however isolated from *H. supinum* L. as one of three major bases (Crowley & Culvenor, 1959). As in the retronecine monoester, intermedine, the acid moiety in supinine (II) is (+)-trachelanthic acid; the acid moiety in heleurine (III) is (-)-heliotric acid as in the heliotridine monoester, heliotrine (Bull, Culvenor &

Dick, 1968). Methylation of the hydroxyl substituent at C(13) in supinine produces heleurine. The analyses reported here are the first reported for a supinidine alkaloid. The results define the effect on conformation of the monoester alkaloids when there is no hydroxyl substituent on the pyrrolizidine nucleus at C(7), and form part of a conformational study of hepatotoxic pyrrolizidine alkaloids.



**Experimental.** Both compounds formed prismatic crystals, supinine from acetone and heleurine from light petroleum (b.p. 303–313 K). Specific rotations  $[\alpha]_D^{17^\circ\text{C}} = -12.1^\circ$  ( $c = 1.98 \text{ g dm}^{-3}$  in ethanol) and  $[\alpha]_D^{16^\circ\text{C}} = -12.0^\circ$  ( $c = 5.15 \text{ g dm}^{-3}$  in ethanol) for supinine and heleurine respectively (Culvenor, 1954). A crystal  $ca 0.36 \times 0.33 \times 0.28 \text{ mm}$  of supinine and a crystal  $ca 0.45 \times 0.30 \times 0.25 \text{ mm}$  of heleurine were aligned on a Rigaku AFC diffractometer; cell parameters determined by least squares from  $2\theta$  values for 25 strong reflections; 3 standard reflections, no significant intensity variation; Cu  $K\alpha$  radiation (graphite-crystal monochromator);  $\omega$ - $2\theta$  scan,  $2\theta$  scan rate  $2^\circ \text{ min}^{-1}$ , scan range  $1.2^\circ + 0.5^\circ \tan\theta$ ,  $2\theta_{\text{max}} = 130^\circ$ ; for supinine 1411 of the 1467 non-equivalent terms ( $h 0-11, k 0-13, l 0-15$ ) for which  $I_o > 2.5\sigma(I_o)$  were used for structure refinement; for heleurine 1367 terms of a total 1580 ( $h 0-10, k 0-13, l 0-19$ ) were used; no correction for absorption; four large terms apparently seriously affected by extinction omitted from final refinement of heleurine structure; scattering factors for O, N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections with values of Cromer & Liberman (1970). Structures solved by direct methods with *SHELX76* (Sheldrick, 1976). The sites of five H atoms in each structure [at C(5) and C(16) in supinine and C(6) and C(21) in heleurine] were not clearly resolved on difference maps; these atoms therefore were included at idealized positions; the remaining H-atom sites were located; refinement, with anisotropic temperature factors given to the C, N and O atoms and isotropic for H atoms, converged at  $R = 0.041$  and  $wR = 0.048$  for supinine and  $R = 0.048$  and  $wR = 0.050$  for heleurine; max.  $\Delta/\sigma 0.02:1$  (non-H atoms) and  $0.14:1$  (H atoms) for supinine; max.  $\Delta/\sigma$  for

heleurine  $0.004:1$ ; largest peaks on final difference map  $+0.22$  and  $-0.22 \text{ e } \text{\AA}^{-3}$  for supinine and  $+0.32$  and  $-0.22 \text{ e } \text{\AA}^{-3}$  for heleurine; function minimized was  $\sum w(|F_o| - |F_c|)^2$ ;  $w = (\sigma^2 |F_o| + 0.00005 |F_o|^2)^{-1}$ .

**Discussion.** Final atomic coordinates are given in Tables 1 and 2;\* Fig. 1 which contains the atom numbering and Fig. 2 which illustrates the crystal packing have been prepared from the output of *ORTEP* (Johnson, 1965). Bond lengths and angles are given in Table 3 and selected torsional angles in Table 4.

The absolute molecular structures illustrated in Fig. 1, (–)-supinine (12*S*,13*R*) and (–)-heleurine (12*S*,13*R*), have been assigned by comparison with that of supinidine, in agreement with the absolute configuration established by Kochetkov, Likhoshesterov & Kulakov (1969) for (+)-trachelanthic (2*S*,3*R*) acid, the moiety in supinine, which has the same absolute configuration as heliotric acid, the acid moiety in heleurine.

The conformations adopted by the two alkaloid molecules are similar (see Table 4) apart from the pyrrolizidine nucleus which is *endo*-buckled in supinine but *exo*-buckled in heleurine, the pucker angles having the respective values  $30.1 (3)$  and  $44.7 (5)^\circ$  [*cf.*  $40.2 (4)^\circ$  in lycopsamine and  $38.5 (5)^\circ$  in intermedine (Mackay, Sadek & Culvenor, 1983)]. To date the *exo* pucker has been observed in all crystals of retronecine alkaloids, whereas in crystals of the heliotridine alkaloids, lasiocarpine (Hay, Mackay & Culvenor, 1982) and heliotrine (Wodak, 1975), the *endo* pucker is observed. The angles between the mean planes defined by ring B atoms and C(5), N(4), C(8), C(7) of ring A are  $121.9 (4)$  and  $117.8 (5)^\circ$  in supinine and heleurine respectively [*cf.* values of  $125.4 (3)^\circ$  in lycopsamine and  $127.2 (4)^\circ$  in intermedine]. As noted in a number of pyrrolizidine alkaloids, one H atom at C(9) lies close to the plane of ring B; in supinine and heleurine this is reflected in the respective torsional angles C(2)–C(1)–C(9)–H(9a) of  $11 (3)$  and  $-25 (4)^\circ$  [*cf.* for example, the comparable value of  $13 (3)^\circ$  in senecionine (Mackay & Culvenor, 1982)].

As observed in the other monoesters, lycopsamine, intermedine and heliotrine, the esterifying acid moieties in supinine and heleurine adopt extended conformations with the atoms C(1), C(9), O(10), C(11), C(12), O(18), O(19) nearly coplanar [see torsional angles C(1)–C(9)–O(10)–C(11), C(9)–O(10)–C(11)–C(12) and O(18)–C(11)–C(12)–O(19)]. In supinine, the O of the hydroxyl substituent at C(12), O(19), lies within the ester plane, atoms C(9), O(10), C(11), O(18), C(12)

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and intermolecular approach distances for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39942 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates of the non-hydrogen atoms ( $\times 10^4$ ) and equivalent isotropic temperature factors for supinine

	E.s.d.'s are given in parentheses.			
	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)^\dagger$
C(1)	709 (3)	-6420 (2)	6054 (2)	2.6 (1)
C(2)	-586 (3)	-6569 (3)	6103 (2)	3.5 (1)
C(3)	-992 (3)	-7102 (3)	7092 (2)	3.9 (1)
N(4)	262 (2)	-7322 (2)	7643 (2)	2.9 (1)
C(5)	565 (5)	-8563 (3)	7785 (3)	5.1 (1)
C(6)	1622 (6)	-8835 (4)	7016 (4)	7.2 (2)
C(7)	2383 (4)	-7787 (4)	6888 (3)	6.1 (1)
C(8)	1364 (3)	-6817 (3)	7024 (2)	3.0 (1)
C(9)	1479 (3)	-5978 (3)	5159 (2)	3.2 (1)
O(10)	2370 (2)	-5093 (2)	5535 (1)	2.8 (1)
C(11)	3304 (3)	-4739 (2)	4867 (2)	2.3 (1)
C(12)	4190 (2)	-3808 (2)	5337 (2)	2.2 (1)
C(13)	3290 (3)	-2797 (2)	5629 (2)	2.6 (1)
C(14)	4059 (4)	-1732 (3)	5967 (3)	4.2 (1)
C(15)	5011 (3)	-4278 (2)	6251 (2)	2.7 (1)
C(16)	4270 (3)	-4388 (3)	7271 (2)	3.9 (1)
C(17)	5687 (4)	-5414 (4)	5973 (3)	4.9 (1)
O(18)	3407 (2)	-5120 (2)	4020 (1)	3.6 (1)
O(19)	5157 (2)	-3479 (2)	4600 (1)	2.6 (1)
O(20)	2518 (2)	-2547 (2)	4731 (1)	3.5 (1)

$\dagger$  Calculated from the refined anisotropic thermal parameters (deposited):  
 $B_{eq} = 8\pi^2 U_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ .

Table 2. Final atomic coordinates of the non-hydrogen atoms ( $\times 10^4$ ) and equivalent isotropic temperature factors for heleurine

	E.s.d.'s are given in parentheses.			
	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)^\dagger$
C(1)	3647 (4)	-862 (3)	6881 (2)	3.1 (1)
C(2)	2750 (5)	-1717 (4)	7122 (3)	4.0 (1)
C(3)	1209 (5)	-1336 (4)	7021 (4)	4.9 (1)
N(4)	1288 (3)	-44 (3)	6820 (2)	3.7 (1)
C(5)	1029 (5)	718 (5)	7548 (3)	5.5 (2)
C(6)	1860 (6)	1819 (5)	7358 (4)	7.7 (2)
C(7)	3199 (6)	1407 (4)	6959 (4)	5.3 (2)
C(8)	2814 (4)	207 (4)	6577 (3)	3.4 (1)
C(9)	5238 (5)	-881 (5)	6969 (3)	4.5 (1)
O(10)	5923 (3)	-469 (2)	6208 (1)	3.4 (1)
C(11)	7224 (4)	49 (3)	6311 (3)	3.2 (1)
C(12)	7932 (4)	370 (3)	5500 (2)	3.4 (1)
C(13)	8060 (5)	-754 (4)	4979 (2)	3.8 (1)
C(14)	8949 (8)	-575 (6)	4205 (3)	6.3 (2)
C(15)	7109 (5)	1404 (4)	5058 (3)	4.3 (1)
C(16)	5720 (6)	1039 (6)	4620 (4)	5.8 (2)
C(17)	6840 (6)	2448 (5)	5644 (4)	5.6 (2)
O(18)	7745 (3)	225 (3)	6970 (2)	5.2 (1)
O(19)	9322 (3)	853 (3)	5662 (3)	4.1 (1)
O(20)	8695 (3)	-1635 (2)	5502 (2)	4.7 (1)
C(21)	8457 (8)	-2831 (4)	5256 (3)	6.9 (2)

$\dagger$  Calculated from the refined anisotropic thermal parameters (deposited):  
 $B_{eq} = 8\pi^2 U_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ .

being coplanar to within 0.00 (1) Å, whereas in heleurine O(19) lies 0.12 (1) Å from the ester plane, the five atoms of which are coplanar within  $\pm 0.04$  (1) Å. The relative orientation of the trachelanthic acid moiety with respect to the pyrrolizidine nucleus in supinine and heleurine is different from that observed in intermedine; in the latter, the hydroxyl substituent at C(7) on the pyrrolizidine nucleus forms an intramolecular hydrogen bond with the hydroxyl substituent C(13). To accommodate this interaction both the hydroxyl substituents in intermedine lie on the same side of the extended chain, and consequently the carbonyl group is synparallel with the C(8)—H(8) bond. In supinine and heleurine which

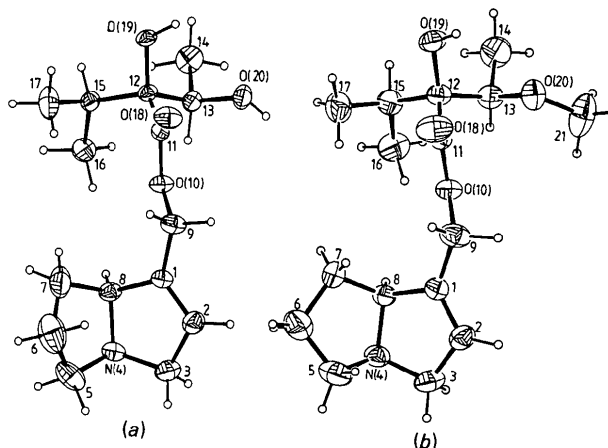


Fig. 1. Perspective views of the molecules with thermal ellipsoids scaled to 40% probability: (a) supinine, (b) heleurine.

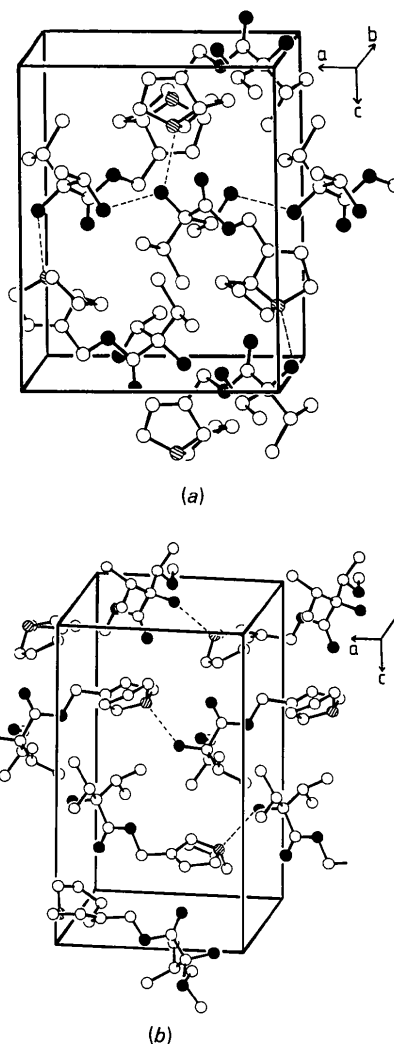


Fig. 2. The molecular packing: (a) supinine, (b) heleurine.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

	Supinine	Heleurine
C(1)–C(2)	1.317 (4)	1.326 (6)
C(1)–C(8)	1.503 (4)	1.507 (6)
C(1)–C(9)	1.496 (4)	1.483 (6)
C(2)–C(3)	1.492 (4)	1.500 (7)
C(3)–N(4)	1.476 (4)	1.483 (6)
N(4)–C(5)	1.489 (4)	1.483 (6)
N(4)–C(8)	1.494 (4)	1.496 (5)
C(5)–C(6)	1.498 (7)	1.484 (8)
C(6)–C(7)	1.451 (7)	1.476 (8)
C(7)–C(8)	1.536 (5)	1.522 (7)
C(9)–O(10)	1.452 (4)	1.469 (5)
O(10)–C(11)	1.348 (3)	1.348 (5)
C(11)–C(12)	1.533 (3)	1.522 (6)
C(11)–O(18)	1.198 (3)	1.197 (6)
C(12)–C(13)	1.534 (3)	1.523 (5)
C(12)–C(15)	1.553 (4)	1.562 (6)
C(12)–O(19)	1.423 (3)	1.422 (5)
C(13)–C(14)	1.527 (4)	1.523 (7)
C(13)–O(20)	1.439 (3)	1.430 (5)
C(15)–C(16)	1.534 (4)	1.529 (8)
C(15)–C(17)	1.532 (5)	1.530 (8)
O(20)–C(21)		1.413 (5)
C(2)–C(1)–C(8)	110.7 (3)	110.4 (4)
C(2)–C(1)–C(9)	126.6 (3)	125.8 (4)
C(8)–C(1)–C(9)	122.7 (2)	123.6 (4)
C(1)–C(2)–C(3)	111.6 (3)	111.1 (4)
C(2)–C(3)–N(4)	105.2 (2)	104.7 (4)
C(3)–N(4)–C(5)	113.9 (3)	111.9 (4)
C(3)–N(4)–C(8)	107.6 (2)	106.8 (3)
C(5)–N(4)–C(8)	107.3 (3)	105.0 (3)
N(4)–C(5)–C(6)	105.5 (3)	103.0 (4)
C(5)–C(6)–C(7)	106.0 (4)	105.7 (5)
C(6)–C(7)–C(8)	104.6 (4)	105.0 (4)
C(1)–C(8)–N(4)	104.7 (2)	104.4 (3)
C(1)–C(8)–C(7)	114.9 (3)	116.3 (4)
N(4)–C(8)–C(7)	105.6 (3)	106.2 (4)
C(1)–C(9)–O(10)	107.4 (2)	110.1 (4)
C(9)–O(10)–C(11)	115.3 (2)	114.6 (3)
O(10)–C(11)–C(12)	111.2 (2)	112.3 (3)
O(10)–C(11)–O(18)	123.2 (3)	122.9 (4)
C(12)–C(11)–O(18)	125.6 (2)	124.8 (4)
C(11)–C(12)–C(13)	107.4 (2)	109.0 (3)
C(11)–C(12)–C(15)	111.7 (2)	111.5 (3)
C(11)–C(12)–O(19)	108.5 (2)	108.5 (3)
C(13)–C(12)–C(15)	113.1 (2)	113.0 (3)
C(13)–C(12)–O(19)	111.5 (2)	110.3 (3)
C(15)–C(12)–O(19)	104.6 (2)	104.4 (3)
C(12)–C(13)–C(14)	113.3 (2)	113.4 (4)
C(12)–C(13)–O(20)	105.7 (2)	105.4 (3)
C(14)–C(13)–O(20)	110.3 (2)	111.4 (4)
C(12)–C(15)–C(16)	116.1 (2)	115.5 (4)
C(12)–C(15)–C(17)	111.0 (2)	110.7 (4)
C(16)–C(15)–C(17)	110.5 (3)	111.1 (4)
C(13)–O(20)–C(21)		114.6 (3)

Table 4. Selected torsional angles (°)

E.s.d.'s are about 0.4°. Atoms are represented by their identification number.

	Supinine	Heleurine
1–9–10–11	–168.9	–151.9
2–1–8–7	–119.8	–127.0
2–1–9–10	–131.8	–135.9
9–10–11–12	180.0	–175.6
9–10–11–18	0.1	4.2
10–11–12–13	59.8	56.9
10–11–12–15	–64.8	–68.5
10–11–12–19	–179.5	177.1
11–12–13–14	171.7	171.6
11–12–13–20	50.8	49.5
11–12–15–16	79.2	77.9
11–12–15–17	–48.0	–49.4
12–13–20–21		–158.8
13–12–11–18	–120.3	–122.9
14–13–12–15	–64.6	–63.8
15–12–11–18	115.1	111.7
18–11–12–19	0.3	–2.7
19–12–13–20	–67.9	–69.6

have no hydroxyl substituent at C(7), the O at C(13) lies on the opposite side of the extended chain compared with intermedine so that the carbonyl is antiparallel with the C(8)–H(8) bond. The two conformations are related by an approximate twofold rotation about the C(1)–C(9) bond. There is no intramolecular hydrogen bonding in the supinine and heleurine molecules.

The molecular packing in the two crystals is illustrated in Fig. 2. As observed in the intermedine crystal, two unique intermolecular hydrogen-bonding interactions in the supinine crystal link the molecules into a three-dimensional network, each molecule being H-bonded to four others. The hydroxyl substituent at C(12) is H-bonded to the N atom of an adjacent molecule related by the screw axis along *c*; the N(4)···O(19), N(4)···H(19) and H(19)–O(19) distances are 2.758 (3), 1.82 (4) and 0.95 (4) Å respectively with the angle N(4)···H(19)–O(19) 169 (3)°. For the other interaction, the hydroxyl at C(13) is H-bonded to O(19) of a molecule related by the screw axis along *a*; the O(19)···O(20), O(19)···H(20) and H(20)–O(20) distances are 2.801 (3), 1.95 (4) and 0.85 (4) Å respectively with the angle O(19)···H(20)–O(20) 180 (3)°. In the heleurine crystal there is only one H-bonding interaction. This links the molecules into chains along *a*. The N atom is H-bonded to the hydroxyl substituent of an adjacent molecule related by a cell translation along *a*; the N(4)···O(19), N(4)···H(19) and H(19)–O(19) distances have the respective values 2.812 (5), 2.02 (4) and 0.85 (4) Å and the angle N(4)···H(19)–O(19) is 155 (4)°.

Financial support from the Australian Research Grants Scheme and assistance from the Network for the Chemistry of Biologically Important Natural Products are gratefully acknowledged.

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