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A second determination of the structure of hydroxyurea*.

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The structure of hydroxyurea has been determined independently of the analysis by Larsen & Jerslev (1966). With data collected on a Picker automatic four-angle diffractometer, the final R index is 0·050. The space group is $P2_1/c$ with four molecules in a unit cell of dimensions $a=8{\cdot}393$, $b=4{\cdot}907$, $c=8{\cdot}798$ Å, $\beta=121{\cdot}2°$.

Unaware of the work of Larsen & Jerslev (1966), we simultaneously determined the structure of hydroxyurea. Since they used film data and we used an automatic diffractometer, resulting in substantially lower standard deviations, we are briefly reporting our results.

The crystals had the same morphology as previously reported and the crystal data are compared in Table 1. A single crystal of size $0{\cdot}15 \times 0{\cdot}3 \times 0{\cdot}2$ mm^3 ($\mu = 13{\cdot}5$ cm^{-1} for Cu $K\alpha$) mounted along the b axis was selected for data collection on the Picker four-angle diffractometer with 2θ scan. No absorption corrections were applied in the data reduction. There were 394 observed reflections out of a possible 650, as compared with 435 collected by Larsen & Jerslev.

Table 1. *Crystal data*

Hydroxyurea, $NH_2CONHOH$, M.W. 76·06
Space group $P2_1/c$, $Z=4$

$a=8{\cdot}393\pm0{\cdot}008$	(8·46) Å*
$b=4{\cdot}907\pm0{\cdot}005$	(4·89)
$c=8{\cdot}798\pm0{\cdot}008$	(8·86)
$\beta=121{\cdot}2°$	(121·9°)
$D_x=1{\cdot}630$ g.cm^{-3}	(1·625 g.cm^{-3})

* Parameters in parentheses are by Larsen & Jerslev.

The structure was solved by application of superposition methods (Corfield, 1965) after an attempt at a direct sign determination was unsuccessful. The refinement was carried out with the full-matrix least-squares program of Busing, Martin & Levy (1962) as modified by Shiono (1966), using Cruickshank's (1961) weighting scheme. The hydrogen atoms were located unambiguously on a difference Fourier synthesis with no spurious peaks of comparable height. The hydrogen parameters were not refined. With the unobserved reflections and three strong low order reflections omitted from the refinement, our final R value was 0·050. Our final positional and thermal parameters are given in Tables 2 and 3.

When Δ/σ ratios were calculated for the differences between the positional parameters of the two determinations, none were found greater than two and most were less than one. Since the standard deviations of this determination are lower by a factor of two, there are a few structure features which can now be discussed with more certainty. Table 4

Table 2. *Fractional atomic coordinates* of hydroxyurea*

	x	y	z
C	0·2738 (4)	0·0255 (5)	0·0269 (4)
O(1)	0·1252 (3)	−0·0381 (4)	−0·2827 (3)
O(2)	0·3022 (3)	−0·0491 (4)	0·1752 (3)
N(1)	0·1598 (3)	−0·1219 (5)	−0·1166 (3)
N(2)	0·3561 (3)	0·2436 (5)	0·0061 (3)
H(O1)	0·210	−0·175	−0·310
H(N1)	0·075	−0·225	−0·100
H(N2)	0·300	0·305	−0·120
H(N2′)	0·475	0·335	0·125

* Numbers in parentheses are estimated standard deviations of the respective coordinates.

The origin of Larsen & Jerslev's cell is shifted by ½ along the a axis of our unit cell.

Table 3. *Anisotropic thermal parameters in hydroxyurea*
U_{ij} (Å$^2 \times 10^2$)

$U_{ij}=\beta_{ij}/2\pi^2a_i{}^*a_j{}^*$ for $i,j=1,2,3$ where $a_1{}^*=a^*$, $a_2{}^*=b^*$, $a_3{}^*=c^*$. and the temperature factor expression used was $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C	2·75	2·09	2·53	0·43	1·37	0·22
O(1)	4·35	3.36	1·99	0·56	1·37	0·34
O(2)	4·07	3·47	2·21	−0·20	1·49	0·29
N(1)	4·52	3·36	2·38	−1·10	1·81	−0·3
N(2)	3·78	3·19	2·67	−0·72	1·35	0·1

Table 4. *Bond distances and angles* in hydroxyurea*

i	j	D_{ij} This work	D_{ij} Larsen & Jerslev
O(1)	N(1)	1·396 (4) Å	1·408 Å
N(1)	C	1·334 (4)	1·336
C	O(2)	1·253 (4)	1·265
C	N(2)	1·336 (4)	1·325

i	j	k	Angle ijk This work	Angle ijk Larsen & Jerslev
O(1)	N(1)	C	119·3 (3)°	118·5°
N(1)	C	O(2)	118·9 (3)	117·7
O(2)	C	N(2)	122·9 (3)	123·9
N(1)	C	N(2)	118·2 (3)	118·4

* Numbers in parentheses are estimated standard deviations.

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shows comparable values of bond distances and angles. The N–C bond lengths are indeed equivalent and this confirms Larsen & Jerslev's statement that their observed differences are not significant. Also confirmed is the fact that the N(1)–C–O(2) and N(2)–C–O(2) angles are different by 10σ. The molecular planarity is also in agreement with the previous results.

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Crystallographic data for derivatives of retusamine.

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The unit-cell dimensions and space groups of the hydrobromide, ethobromide, chromate, fluorotitanate, and monohydrate of retusamine ($C_{19}H_{25}O_7N$) are reported.

During the search for a crystalline derivative of the alkaloid retusamine [Fig. 1(*a*)] suitable for a complete X-ray analysis, a number were prepared and briefly investigated. The most suitable was the monohydrated α′-bromocamphor-*trans*-π-sulphonate, the crystal and molecular structure of which has been described (Wunderlich, 1962, 1966).

The cell dimensions were obtained from oscillation and Weissenberg photographs (Cu *Kα* radiation). Densities were not measured owing to the small amount of material available.

Since the alkaloid is optically active and can be regenerated unchanged from its hydro-salts, it has been assumed that the space groups of the three monoclinic species described below possess neither a mirror plane nor a center of symmetry.

Retusamine hydrobromide

($C_{19}H_{26}O_7N$)$^+$Br$^-$ F.W. 460·33

Monoclinic, very fine needles, $a=22{\cdot}33\pm0{\cdot}06$, $b=6{\cdot}71\pm0{\cdot}07$, $c=15{\cdot}51\pm0{\cdot}06$ Å and $\beta=103{\cdot}8\pm0{\cdot}3°$, $U=2256$ Å^3,

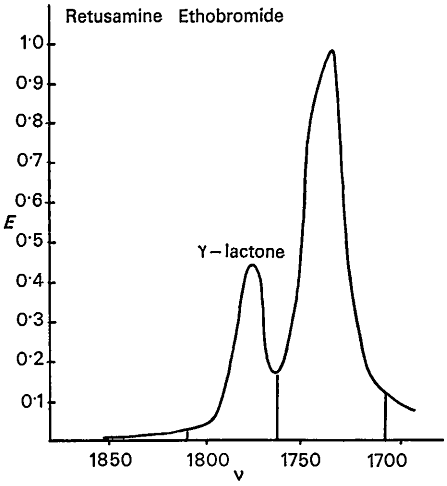
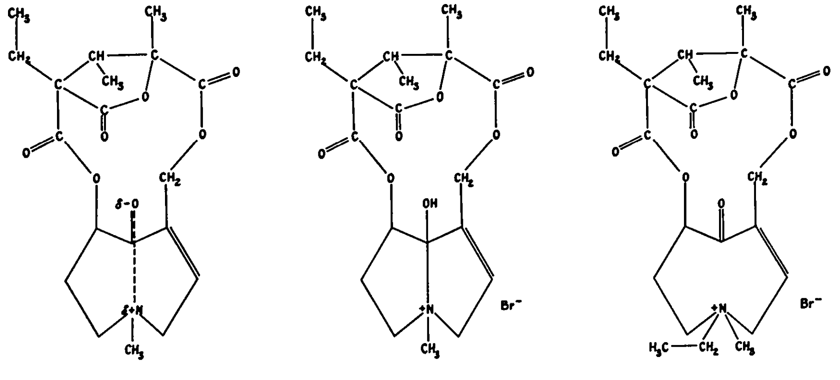


Fig. 2. Infrared absorbance (*E*) of retusamine ethobromide *versus* frequency (*ν*).



(*a*) (*b*) (*c*)

Fig. 1. (*a*) Retusamine. (*b*) Retusamine hydrobromide. (*c*) Retusamine ethobromide.