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The absolute configuration of a steroidal substance, the *O-p*-bromobenzoate derivative of batrachotoxinin *A*.

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Observation of a number of Bijvoet differences in the X-ray diffraction of the *O-p*-bromobenzoate derivative of batrachotoxinin *A* gave a consistent indication of the correct enantiomorph for this previously reported structure. This derivative of batrachotoxinin has the same absolute configuration as cholesterol at points of similarity.

The crystal and molecular structure of the *O-p*-bromobenzoate derivative of batrachotoxinin *A*, obtained from the native venom of the Colombian arrow poison frog, were recently determined (Karle & Karle, 1969; Tokuyama, Daly, Witkop, Karle & Karle, 1968). Since the physiological activity probably depends upon its absolute configuration, the crystal was again studied to determine if the deviations from Friedel's law due to the anomalously scattering Br atom were large enough to be reliably measured from the small amount of crystalline material available.

The crystal used in the structural work and in this investigation was extremely small (0·05 × 0·03 × 1·0 mm). The crystal was mounted on a 4-circle automatic diffractometer and irradiated with Zr-filtered Mo $K\alpha$ radiation. The anomalous scattering of Br is appreciable at this wavelength. Using the atomic coordinates of Karle & Karle, structure factors were calculated for each enantiomorph of the batrachotoxinin *A* derivative. Those reflections whose structure factors were significantly enantiomorph-dependent were singled out. It was also necessary to restrict the observations to reflections with large structure factor magnitudes since only a few hundred reflections diffracted above background level with Mo radiation.

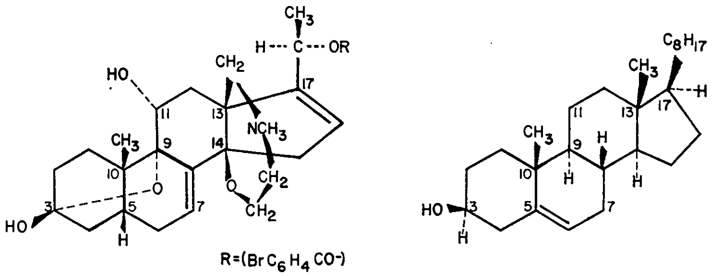
The measurements on this relatively short list of pertinent reflections were confined to the reflection and its Friedel equivalent. The orientation of the crystal relative to the counter (the χ, φ, and ω angles) was not changed between measurements; the counter was moved from the $+2\theta$ position over to the -2θ position between intensity measurements. In scanning the peaks, the counter was moved at a rate of 0·5 deg. min^{-1} and the background at either end of the scan was counted for 100 seconds. The slow scanning tecnique was used in an attempt to make the best of an inherently low signal to background ratio. The background was assumed to be linear. It is possible that this assumption caused significant error in a few of the weaker measurements reported. In Table 1, the square root of the counted intensity, G, is reported for Friedel pairs. The G values have not been placed on an absolute scale or corrected for Lp factors. These corrections will not affect the calculation of the percentage deviation from Friedel's law, as expressed by the parameter, Δ:

$$\Delta = \frac{100[|F_{\bar{h}\bar{k}\bar{l}}| - |F_{hkl}|]}{\left[\dfrac{|F_{\bar{h}\bar{k}\bar{l}}| + |F_{hkl}|}{2}\right]} .$$

The values of Δ_{obs} are listed in Table 1, along with values of Δ_{calc} for the proper enantiomorph. The correlation of magnitudes shows some errors of measurement, but the direction of the deviation is predicted correctly each time by Δ_{calc}.

Table 1. *Observed and calculated Bijvoet differences (percentages) for the bromobenzoate derivative of batrachotoxinin A*

h	k	l	$\lvert G(hkl)\rvert$	$\lvert G(\bar{h}\bar{k}\bar{l})\rvert$	Δ(obs)	Δ(calc)
1	1	10	157	169	7	8
3	1	2	82	85	4	9
2	2	7	107	100	−7	−8
1	3	2	95	99	4	6
7	1	3	81	87	7	12
7	1	1	35	27	−25	−23
2	2	13	50	35	−36	−19



BATRACHOTOXININ *A* CHOLESTEROL

Fig. 1. The structure of batrachotoxinin *A* (from Karle & Karle, 1969) and cholesterol.

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Table 1 (*cont.*)

3	1	10	59	70	17	17
3	1	12	83	73	−13	−14
3	3	4	54	49	−10	−13
6	4	1	36	27	−31	−15
6	4	5	26	35	32	22
7	1	4	51	43	−17	−15
8	2	4	35	40	12	20
9	1	12	46	42	−10	−6
10	2	2	45	45	0	5
3	3	2	3	20	74	25

The correct enantiomorph was found to be the mirror image of that represented by Karle & Karle in the list of coordinates in their Table 3. However, one of their figures, reproduced in Fig. 1, was drawn to emphasize the steroidal nucleus and shows the correct enantiomorph. According to convention, heavy lines for ring substituents indicate that the substituent is directed toward the reader, above the plane of nearest ring neighbors; dotted lines indicate a substituent pointing away from the reader and into the paper. Because of the ether linkage between ring atoms C(3) and C(9), the ring system in three dimensions bears little resemblance to the formal representation shown here. However, the steroidal illustration simplifies comparison with steroids of known configuration. The configuration of cholesterol has been inferred chemically by several investigators (Fieser & Fieser, 1959). It can be seen that batrachotoxinin *A* has the same configuration as cholesterol at points of similarity [*e.g.* C(3), C(9), C(10) and C(13)].

References

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The crystal and molecular structure of the triethylammonium salt of cyclic uridine-3′,5′-phosphate. Corrigendum.

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In a recent article on the title compound (Coulter, 1969) the ribose conformation was incorrectly described as C(3′)-*endo*. The data given in Table 1 indicate that the best description is C(4′)-*endo* for both anions in the asymmetric unit. The presence of this unusual conformation is a further reflection of the distortions needed to form the cyclic phosphate ester.

Table 1. *Least-squares planes for the sugars*

Coordinates of the atoms were obtained from Table 1 of Coulter (1969).

Distance out of plane (Å)

	Plane I; C(4′)-*endo*		Plane II; C(3′)-*endo*	
	Molecule *A*	Molecule *B*	Molecule *A*	Molecule *B*
C(1′)	0·063*	−0·033*	−0·105*	0·127*
C(2′)	−0·059*	0·031*	0·062*	−0·075*
O(2′)	−1·303	1·258	−1·206	1·182
C(3′)	0·039*	−0·021*	0·683	−0·600
O(3′)	−0·560	0·568	0·431	−0·378
C(4′)	−0·662	0·659	−0·068*	0·080*
C(5′)	−0·496	0·437	0·507	−0·535
O(5′)	−1·126	0·995	0·280	−0·376
O(1′)	−0·043*	0·023*	0·110*	−0·132*
N(1)	1·278	−1·200	0·770	−0·694

* These atoms were used to define the planes.

Equations of planes (x,y,z in fractional cell coordinates):

I*A* $-10\cdot000x+8\cdot919y+8\cdot953z=-2\cdot189$ Å
I*B* $-9\cdot644x+9\cdot001y-0\cdot456z=-2\cdot2005$
II*A* $-5\cdot867x+10\cdot650y+2\cdot319z=-2\cdot061$
II*B* $-5\cdot141x+10\cdot676y-1\cdot971z=-0\cdot759$

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