THE X-RAY ANALYSIS OF ONE RACEMIC STEREOISOMER OF DEACETYLASPIDOSPERMINE

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The crystal structure of aspidospermine N(b)-methiodide was established as formula (I) by Mills and Nyberg (1) in terms of X-ray analysis. Based upon this result, Smith and Wrobel (2) suggested that ring D of aspidospermine $(C_{22}H_{30}N_2O_2)$ itself constitutes a chair form, since it indicates a clear absorption in the region of 2750-2800 cm⁻¹ (3). If the alkaloid had the same conformation as formula (I), no band in this region would be observed. Aspidospermine, therefore, has been represented by formula (II).



The racemic stereoisomer $(C_{20}H_{28}N_2^{0})$, colorless prisms, m.p. 89.5-90.5°, of deacetylaspidospermine synthesized by Ban and Iijima (4), was converted to the corresponding N(a)hydriodide $(C_{20}H_{28}N_2^{0})$ HI), m.p. 245-246°, which was reconverted into the initial base without any stereochemical change observed with natural aspidospermine. Thus, the above salt was subjected to X-ray analysis.

^{*} The reprint request and inquiry of this paper should be addressed to Y. Ban.

TABLE I

| Atom | X/a | Ү/Ъ | Z/c | В | Nr | Atom | X/a | Y/b | Z/c | В |
|------|---|---|--|--|--|---|---|---|---|--|
| N | .3538 | .2836 | .2464 | 3.309 | 13 | С | .5100 | .1467 | .2000 | 3.226 |
| С | .4691 | .2581 | .3054 | 3.447 | 14 | C | .5555 | .0606 | .1484 | 3.471 |
| С | .4041 | .1656 | .3574 | 4.966 | 15 | С | .4590 | .0353 | .0944 | 3.619 |
| С | .5164 | .0712 | .3875 | 3.844 | 16 | С | .3221 | .0841 | .0865 | 3.897 |
| С | .6707 | .1076 | .3874 | 3.430 | 17 | С | .2776 | .1694 | .1361 | 3.417 |
| С | .7764 | .0057 | .4104 | 4.793 | 18 | С | .3745 | .2010 | .1923 | 3.260 |
| С | .9408 | .0356 | .3910 | 4.831 | 19 | С | .7002 | .1286 | .3069 | 3.441 |
| С | .9572 | .0778 | .3107 | 4.499 | 20 | С | .7039 | .2217 | .4354 | 3.027 |
| N | .8495 | .1741 | .2980 | 3.619 | 21 | С | .6497 | .2125 | .5125 | 5.103 |
| С | .8439 | .2308 | .2251 | 3.956 | 22 | С | .1512 | .2259 | .1338 | 3.256 |
| С | .7048 | .2991 | .2310 | 3.961 | 23 | С | .0599 | .2060 | .0678 | 4.856 |
| С | .5968 | .2087 | .2620 | 2.904 | 24 | I | .0644 | .3919 | .3674 | 4.009 |
| | Atom N C C C C C C N C C C C C | Atom X/a N .3538 C .4691 C .4041 C .5164 C .5164 C .9408 C .9572 N .8495 C .7048 C .7048 C .5968 | Atom X/a Y/b N .3538 .2836 C .4691 .2581 C .4041 .1656 C .5164 .0712 C .6707 .1076 C .7764 .0057 C .9408 .0356 C .9572 .0778 N .8495 .1741 C .8439 .2308 C .7048 .2991 C .5968 .2087 | Atom X/a Y/b Z/c N .3538 .2836 .2464 C .4691 .2581 .3054 C .4041 .1656 .3574 C .5164 .0712 .3875 C .6707 .1076 .3874 C .7764 .0057 .4104 C .9408 .0356 .3910 C .9572 .0778 .3107 N .8495 .1741 .2980 C .8439 .2308 .2251 C .7048 .2991 .2310 C .5968 .2087 .2620 | Atom X/a Y/b Z/c B N .3538 .2836 .2464 3.309 C .4691 .2581 .3054 3.447 C .4041 .1656 .3574 4.966 C .5164 .0712 .3875 3.844 C .6707 .1076 .3874 3.430 C .7764 .0057 .4104 4.793 C .9408 .0356 .3910 4.831 C .9572 .0778 .3107 4.499 N .8495 .1741 .2980 3.619 C .8439 .2308 .2251 3.956 C .7048 .2991 .2310 3.961 C .5968 .2087 .2620 2.904 | Atom X/a Y/b Z/c B Nr N .3538 .2836 .2464 3.309 13 C .4691 .2581 .3054 3.447 14 C .4041 .1656 .3574 4.966 15 C .5164 .0712 .3875 3.844 16 C .6707 .1076 .3874 3.430 17 C .7764 .0057 .4104 4.793 18 C .9408 .0356 .3910 4.831 19 C .9572 .0778 .3107 4.499 20 N .8495 .1741 .2980 3.619 21 C .8439 .2308 .2251 3.956 22 C .7048 .2991 .2310 3.961 23 C .5968 .2087 .2620 2.904 24 | Atom X/a Y/b Z/c B Nr Atom N .3538 .2836 .2464 3.309 13 C C .4691 .2581 .3054 3.447 14 C C .4041 .1656 .3574 4.966 15 C C .5164 .0712 .3875 3.844 16 C C .5164 .0712 .3874 3.430 17 C C .5774 .0057 .4104 4.793 18 C C .9408 .0356 .3910 4.831 19 C C .9572 .0778 .3107 4.499 20 C N .8495 .1741 .2980 3.619 21 C C .8495 .2511 3.956 22 C C .7048 .2991 .2310 3.961 23 C C .5968 <td< td=""><td>Atom X/a Y/b Z/c B Nr Atom X/a N .3538 .2836 .2464 3.309 13 C .5100 C .4691 .2581 .3054 3.447 14 C .5555 C .4041 .1656 .3574 4.966 15 C .4590 C .5164 .0712 .3875 3.844 16 C .3221 C .6707 .1076 .3874 3.430 17 C .2776 C .7764 .0057 .4104 4.793 18 C .3745 C .9408 .0356 .3910 4.831 19 C .7002 C .9572 .0778 .3107 4.499 20 C .7039 N .8495 .1741 .2980 3.619 21 C .6497 C .8439 .2308 .2251 3.956 <t< td=""><td>Atom X/a Y/b Z/c B Nr Atom X/a Y/b N .3538 .2836 .2464 3.309 13 C .5100 .1467 C .4691 .2581 .3054 3.447 14 C .5555 .0606 C .4041 .1656 .3574 4.966 15 C .4590 .0353 C .5164 .0712 .3875 3.844 16 C .3221 .0841 C .6707 .1076 .3874 3.430 17 C .2776 .1694 C .7764 .0057 .4104 4.793 18 C .3745 .2010 C .9408 .0356 .3910 4.831 19 C .7002 .1286 C .9572 .0778 .3107 4.499 20 C .7039 .2217 N .8495 .1741 .2980 .619</td></t<></td></td<> <td>Atom X/a Y/b Z/c B Nr Atom X/a Y/b Z/c N .3538 .2836 .2464 3.309 13 C .5100 .1467 .2000 C .4691 .2581 .3054 3.447 14 C .5555 .0606 .1484 C .4041 .1656 .3574 4.966 15 C .4590 .0353 .0944 C .5164 .0712 .3875 3.844 16 C .3221 .0841 .0865 C .6707 .1076 .3874 3.430 17 C .2776 .1694 .1361 C .7764 .0057 .4104 4.793 18 C .3745 .2010 .1923 C .9408 .0356 .3910 4.831 19 C .7002 .1286 .3069 C .9572 .0778 .3107 4.499 20 <t< td=""></t<></td> | Atom X/a Y/b Z/c B Nr Atom X/a N .3538 .2836 .2464 3.309 13 C .5100 C .4691 .2581 .3054 3.447 14 C .5555 C .4041 .1656 .3574 4.966 15 C .4590 C .5164 .0712 .3875 3.844 16 C .3221 C .6707 .1076 .3874 3.430 17 C .2776 C .7764 .0057 .4104 4.793 18 C .3745 C .9408 .0356 .3910 4.831 19 C .7002 C .9572 .0778 .3107 4.499 20 C .7039 N .8495 .1741 .2980 3.619 21 C .6497 C .8439 .2308 .2251 3.956 <t< td=""><td>Atom X/a Y/b Z/c B Nr Atom X/a Y/b N .3538 .2836 .2464 3.309 13 C .5100 .1467 C .4691 .2581 .3054 3.447 14 C .5555 .0606 C .4041 .1656 .3574 4.966 15 C .4590 .0353 C .5164 .0712 .3875 3.844 16 C .3221 .0841 C .6707 .1076 .3874 3.430 17 C .2776 .1694 C .7764 .0057 .4104 4.793 18 C .3745 .2010 C .9408 .0356 .3910 4.831 19 C .7002 .1286 C .9572 .0778 .3107 4.499 20 C .7039 .2217 N .8495 .1741 .2980 .619</td></t<> | Atom X/a Y/b Z/c B Nr Atom X/a Y/b N .3538 .2836 .2464 3.309 13 C .5100 .1467 C .4691 .2581 .3054 3.447 14 C .5555 .0606 C .4041 .1656 .3574 4.966 15 C .4590 .0353 C .5164 .0712 .3875 3.844 16 C .3221 .0841 C .6707 .1076 .3874 3.430 17 C .2776 .1694 C .7764 .0057 .4104 4.793 18 C .3745 .2010 C .9408 .0356 .3910 4.831 19 C .7002 .1286 C .9572 .0778 .3107 4.499 20 C .7039 .2217 N .8495 .1741 .2980 .619 | Atom X/a Y/b Z/c B Nr Atom X/a Y/b Z/c N .3538 .2836 .2464 3.309 13 C .5100 .1467 .2000 C .4691 .2581 .3054 3.447 14 C .5555 .0606 .1484 C .4041 .1656 .3574 4.966 15 C .4590 .0353 .0944 C .5164 .0712 .3875 3.844 16 C .3221 .0841 .0865 C .6707 .1076 .3874 3.430 17 C .2776 .1694 .1361 C .7764 .0057 .4104 4.793 18 C .3745 .2010 .1923 C .9408 .0356 .3910 4.831 19 C .7002 .1286 .3069 C .9572 .0778 .3107 4.499 20 <t< td=""></t<> |

Final atomic co-ordinates and temperature factors.

* The (B)-column indicates temperature factors of output, and each temperature factor of input is put as 3.00. R-factor = 14.33%.

FIG. 1





No.30

The colorless crystals recrystallized from methanol are monoclinic with the unit cell of the dimensions, a=9.17, b=11.51, c=18.44 Å and β =93°, the space group being P 2₁/c, and there are four melecules per unit cell. The observed crystal density, Do=1.512 g.cm.⁻³, was almost same as the calculated one, Dc=1.504 g.cm.⁻³.

Intensity data were collected with Cu-Ka radiation from equi-inclination Weissenberg photographs of the layers h01— h71 and hk0— hk8 by applying the multiple film technique. The relative intensities of 3384 reflections were estimated visually by comparison with the standard charts and the relative values of the observed structure factors were converted into absolute scale by Wilson's method (5). In this stage were obtained co-ordinates of twenty four atoms. The whole structure was elucidated by successive application of the Fourier synthesis and the least-squares method. Final atomic co-ordinates and temperature factors are listed in TABLE I, and the crystal structure projected along the b axis are illustrated in FIG. 1 with bond lengths and bond angles. The R-factor calculated with all structure factors is 14.33%. Thus, the complete chemical formula of this compound is represented by formula (III).

As mentioned above, the crystal structure of aspidospermine N(b)-methiodide (I) analyzed by Mills and Nyberg (1) does not reflect the molecular structure of aspidospermine (II) <u>in situ</u>. It is noteworthy that the crystal structure analyzed in this work directly proves the actual stereochemistry of one racemic stereoisomer of deacetylaspidospermine itself.

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