The Structure of Daturametelin D[1)]

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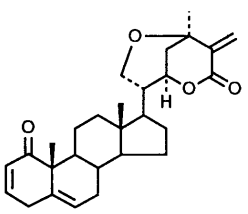
The structure of a new withanolide, (17*R*,20*R*,22*R*,25*R*)-21,24*R*-epoxy-27-methoxy-1-oxowitha-2,5-dienolide, isolated from the methanolic extract of the fresh aerial parts of *Datura metel* L. (Solanaceae), was established by X-ray analysis.

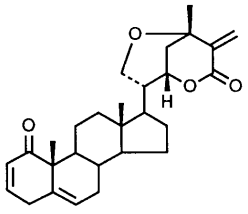
Keywords *Datura metel*; Solanaceae; withanolide; daturametelin D; withametelin; X-ray analysis

Hikino *et al.* reported a hexacyclic withanolide, withametelin (**1**)[2)] with a unique structure, obtained from *Datura metel* L. We also described independently the structures of seven withanolides, daturametelins A (**2**), B (**3**), C (**4**),[3)] D (**5**), E (**6**), F (**7**) and G-Ac (**8**), isolated from the fresh aerial parts of the same plant used in the preceding paper.[4)] Their structures, including **1**, were estimated mainly on the basis of spectroscopy, and their configurations at C-17, C-20, C-22, C-24 and C-25 were not perfectly established. Furthermore, at almost the same time, papers written by Hikino *et al.* and us, Ahmad *et al.* reported withanolides named daturilin (**9**),[5)] daturilinol (**10**)[6)] and datumetelin (**11**)[7)] from the same plant. Compounds **9** and **11**, in which a desmethyl compound was also reported similar to **10** in the same group, have the same plane structures as **1** and **5**, respectively. However, configurations at both C-22 and C-24 were different between **1** and **5** (22*R*, 24*R*), and **9** and **11** (22*S*, 24*S*). Thus, in order to clarify stereochemistries at C-22 and C-24 together with C-17, C-20 and C-25 in relation to the other withanolides such as **2**, **3**, **4**, **6**, **7** and **8** obtained from *D. metel*, an X-ray analysis of the single crystal of daturametelin D (**5**) crystallized from $CHCl_3$–MeOH was performed.

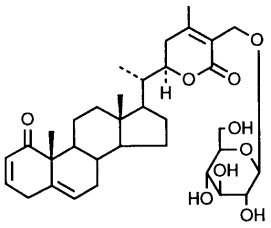
The crystallographic data was as follows: formula, $C_{29}H_{40}O_5$; space group, $P2_12_12_1$ (orthorhombic); $Z=4$; cell constants, $a=12.010$ (2), $b=18.838$ (5), $c=11.267$ (2) Å; density, $D_x=1.221$ g/cm^3. All data was collected on an Enraf-Nonius CAD4F-11 diffractometer using CuK_α radiation and a graphite monochrometer. The structure was first solved by direct methods and then refined by



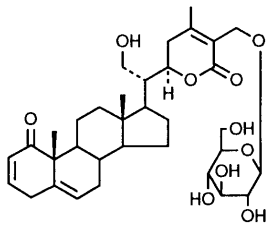
withametelin (**1**)



daturilin (**9**)



daturametelin A (**2**)



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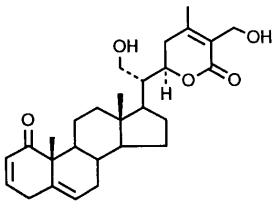
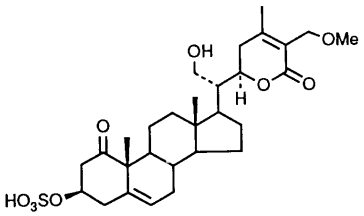
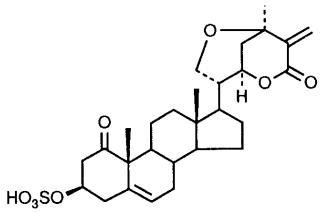


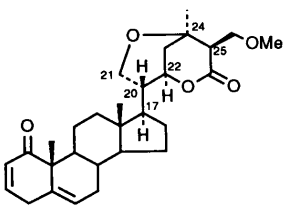
daturametelin C (**4**)



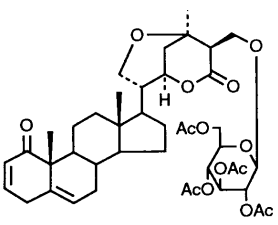
daturametelin E (**6**)



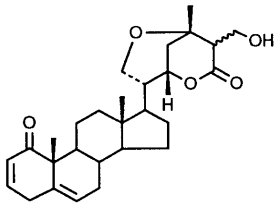
daturametelin F (**7**)



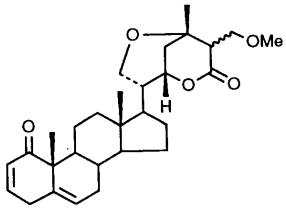
daturametelin D (**5**)



daturametelin G-Ac (**8**)



daturilinol (**10**)



datumetelin (**11**)

TABLE I. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Parameters of Daturametelin D (**5**)

Atom	*X*	*Y*	*Z*	*B*
O1	−154 (2)	5634 (1)	10 (3)	6.20 (9)
O21	3194 (2)	2175 (1)	−98 (2)	3.47 (6)
O22	5870 (2)	2064 (1)	−1107 (2)	4.20 (7)
O26	5606 (2)	1168 (1)	−2281 (3)	6.25 (9)
O27	3057 (2)	1130 (1)	−2122 (3)	5.51 (8)
C1	344 (3)	6189 (2)	100 (4)	4.53 (11)
C2	−263 (3)	6826 (2)	509 (4)	5.81 (14)
C3	234 (4)	7447 (2)	691 (4)	6.22 (14)
C4	1441 (4)	7560 (2)	554 (4)	5.10 (12)
C5	2091 (3)	6861 (2)	546 (3)	3.76 (10)
C6	3000 (3)	6795 (2)	1164 (3)	3.91 (10)
C7	3712 (3)	6144 (2)	1212 (3)	3.60 (10)
C8	3454 (3)	5629 (2)	199 (3)	2.99 (8)
C9	2190 (3)	5539 (2)	24 (3)	3.03 (8)
C10	1582 (3)	6269 (2)	−215 (3)	3.52 (9)
C11	1971 (3)	4987 (2)	−964 (3)	3.74 (10)
C12	2503 (3)	4256 (2)	−667 (3)	3.50 (9)
C13	3753 (3)	4326 (2)	−499 (3)	2.68 (8)
C14	3928 (3)	4894 (2)	489 (3)	2.75 (8)
C15	5174 (3)	4829 (2)	816 (4)	4.39 (11)
C16	5421 (3)	4022 (2)	654 (4)	4.26 (11)
C17	4353 (3)	3682 (2)	107 (3)	2.75 (8)
C18	4319 (4)	4517 (2)	−1668 (3)	4.34 (11)
C19	1623 (4)	6487 (2)	−1551 (3)	4.50 (11)
C20	4622 (3)	3042 (2)	−711 (3)	3.12 (9)
C21	3596 (3)	2609 (2)	−1048 (4)	3.37 (9)
C22	5472 (3)	2534 (2)	−151 (4)	3.77 (10)
C23	4983 (3)	2108 (2)	854 (3)	3.76 (10)
C24	3999 (3)	1688 (2)	374 (3)	3.53 (10)
C25	4451 (3)	1159 (2)	−559 (4)	3.88 (10)
C26	5333 (3)	1465 (2)	−1392 (4)	4.35 (11)
C27	3613 (3)	712 (2)	−1251 (4)	4.70 (12)
C28	3389 (4)	1299 (2)	1374 (4)	5.78 (14)
C29	2542 (4)	706 (2)	−2987 (4)	5.85 (13)

leastsquares method to an *R* factor of 0.044 for 1864 reflections. The ORTEP drawing and its atomic parameters are shown in Fig. 1 and Table I, respectively. The asymmetric centers at C-17, C-20, C-22, C-24 and C-25 in the crystal structure were revealed to possess all *R* configurations since **5** was supposed to possess a normal steroid configuration. Thus, the whole chemical structure was established.

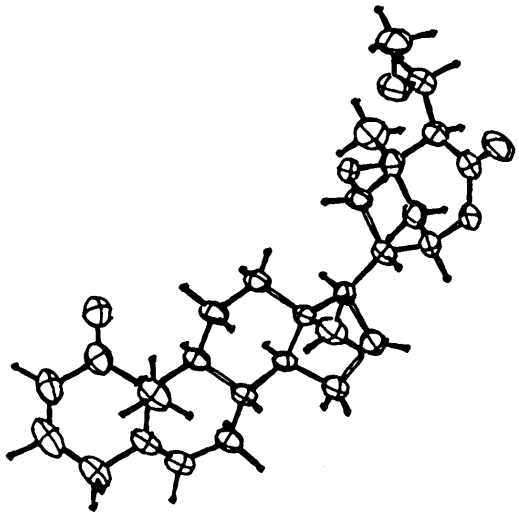


Fig. 1. ORTEP Drawing of Daturametelin D (**5**)

References and Notes

1) This work is part XIX in a series of studies on the constituents of solanaceous plants, Part XVIII: K. Shingu, N. Marubayashi, I. Ueda, S. Yahara and T. Nohara, *Chem. Pharm. Bull.*, **38**, 1107 (1990).
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3) Ray *et al.* concurrently reported secowithametelin having the same structure as daturametelin C from *Daurta metel*: S. Kundu, S. C. Sinha, A. Bagchi and A. B. Ray, *Phytochemistry*, **28**, 1769 (1989).
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