diketone (4) must be represented by structure (5). Such a structure is expected to favour the base-catalyzed rearrangement of the system in structure (3) by a concerted mechanism.

Unit-cell packing of the molecules down the *a* axis is shown in Fig. 2. The molecules in the unit cell are stabilized by O2—HO2···O1 intermolecular hydrogen bonds, distance O2···O1 2·799 (2), O2—HO2 1·01 (3) and HO2···O1 1·79 (3) Å and angle O2—HO2···O1 179 (2)°.

We thank Professor Swaminathan for supplying the compound and for discussions. Thanks are also due to Professor R. Srinivasan for discussions. One of the authors (VG) thanks the CSIR for financial assistance.

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Application of the Haller–Bauer Reaction in the Synthesis of Taxol-Related Diterpenes: Structure of the Intramolecular Lactam of 2-Amino-5-hydroxy-4,8,11-trimethylbicyclo[5.3.1]undeca-3,8-diene-11-carboxylic Acid

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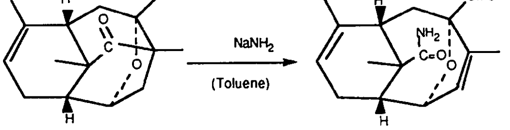
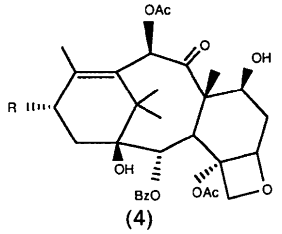
Abstract. 4-Hydroxy-3,7,13-trimethyl-11-azatricyclo[4.4.3.$0^{10,13}$]trideca-2,7-dien-12-one (3), $C_{15}H_{21}NO_2$, $M_r = 247{\cdot}34$, triclinic, $P\bar{1}$, $a = 13{\cdot}454\,(4)$, $b = 12{\cdot}701\,(3)$, $c = 13{\cdot}376\,(3)$ Å, $\alpha = 106{\cdot}18\,(5)$, $\beta = 112{\cdot}13\,(4)$, $\gamma = 95{\cdot}80\,(5)°$, $V = 1978{\cdot}2$ Å^3, $Z = 6$, $D_x = 1{\cdot}241$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 4{\cdot}59$ cm^{-1}, $F(000) = 798$, $T = 293$ K, $R = 0{\cdot}062$ for 5781 observed reflections. The result of the Haller–Bauer reaction was found unexpectedly to be a lactam instead of a dihydrofuran acyclic amide. The molecules of the asymmetric unit are associated in compact trimeric clusters stabilized by six hydrogen bonds with only weak interactions between the clusters.

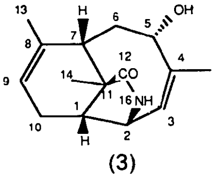
Introduction. In the course of taxol-derivative synthesis (Andriamialisoa, Fétizon, Hanna, Pascard & Prangé, 1984; Cervantes, Do Khac, Fétizon, Guir, Beloeil, Lallemand & Prangé, 1986), general access to the taxane backbone has been investigated. The ring expansion of the compound (1) (Guir, 1990) was thought to be one of the possible routes to synthesize the *A*/*B* structural moiety of the taxol molecule (4), a strong antimitotic natural diterpene (Wani, Taylor, Wall, Coggon & MacPhail, 1971).



(1) (2)



(4)
Taxol
$R = \text{PhCH(NHBz)CH(OH)CO}_2$



(3)
Numbering of the molecule
′ is added for molecule 2
″ is added for molecule 3

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Table 1. *Positional parameters* (× 10^4) *and recalculated isotropic thermal factors* (× 10^3) *for non*-H *atoms*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	U_{eq}(Å^2)
Molecule 1				
C(1)	8412 (3)	2203 (3)	8463 (3)	36 (3)
C(2)	7965 (3)	3223 (3)	8905 (3)	37 (4)
C(3)	6756 (3)	3101 (3)	8194 (3)	42 (4)
C(4)	6258 (3)	3350 (3)	7247 (3)	40 (4)
C(5)	6865 (3)	3911 (3)	6725 (3)	40 (4)
O(5)	6142 (2)	4447 (2)	6021 (2)	55 (3)
C(6)	7300 (3)	3116 (3)	5986 (3)	43 (4)
C(7)	7840 (3)	2180 (3)	6361 (3)	35 (3)
C(8)	7022 (3)	1100 (3)	6038 (3)	39 (4)
C(9)	6941 (3)	621 (3)	6763 (3)	43 (4)
C(10)	7650 (3)	1053 (3)	8034 (3)	48 (4)
C(11)	8779 (3)	2510 (3)	7604 (3)	32 (3)
C(12)	9181 (3)	3788 (3)	8179 (3)	34 (3)
O(12)	9789 (2)	4400 (2)	7972 (2)	45 (3)
C(13)	6299 (4)	533 (4)	4763 (4)	64 (5)
C(14)	9741 (3)	1989 (3)	7517 (3)	44 (4)
C(15)	5020 (3)	3002 (4)	6608 (4)	63 (5)
N(16)	8726 (2)	4126 (2)	8918 (2)	37 (3)
Molecule 2				
C(1′)	8304 (3)	7810 (3)	4873 (3)	46 (4)
C(2′)	7960 (3)	8080 (3)	5875 (3)	52 (4)
C(3′)	8920 (3)	8602 (3)	7045 (3)	49 (4)
C(4′)	9536 (3)	8116 (3)	7745 (3)	42 (4)
C(5′)	9343 (3)	6861 (3)	7478 (3)	34 (3)
O(5′)	9884 (2)	6646 (2)	8536 (2)	42 (2)
C(6′)	9756 (3)	6227 (3)	6609 (3)	38 (4)
C(7′)	9654 (3)	6564 (3)	5546 (3)	35 (3)
C(8′)	10536 (3)	7561 (3)	5826 (3)	40 (4)
C(9′)	10349 (3)	8466 (3)	5552 (3)	48 (4)
C(10′)	9234 (3)	8667 (3)	4971 (4)	54 (5)
C(11′)	8479 (3)	6613 (3)	4727 (3)	36 (3)
C(12′)	7591 (3)	6121 (3)	5025 (3)	41 (4)
O(12′)	7190 (2)	5112 (2)	4758 (2)	53 (3)
C(13′)	11714 (3)	7449 (4)	6392 (4)	63 (5)
C(14′)	8252 (3)	5942 (3)	3480 (3)	49 (4)
C(15′)	10515 (4)	8833 (3)	8845 (4)	64 (5)
N(16′)	7328 (2)	6980 (3)	5649 (3)	49 (3)
Molecule 3				
C(1″)	5452 (3)	2795 (3)	1650 (3)	50 (4)
C(2″)	5137 (3)	3922 (3)	2036 (3)	46 (4)
C(3″)	4383 (3)	4221 (3)	1053 (3)	46 (4)
C(4″)	3286 (3)	3941 (3)	498 (3)	40 (4)
C(5″)	2556 (3)	3311 (3)	865 (3)	35 (3)
O(5″)	1458 (2)	3502 (2)	363 (2)	43 (2)
C(6″)	2462 (3)	2031 (3)	500 (3)	41 (4)
C(7″)	3464 (3)	1522 (3)	476 (3)	41 (4)
C(8″)	3676 (3)	1503 (3)	− 560 (3)	51 (4)
C(9″)	4634 (4)	1923 (4)	− 514 (4)	62 (5)
C(10″)	5656 (4)	2535 (4)	567 (4)	67 (6)
C(11″)	4556 (3)	1926 (3)	1615 (3)	44 (4)
C(12″)	4342 (3)	2619 (3)	2620 (3)	44 (4)
O(12″)	3917 (2)	2229 (2)	3151 (2)	63 (3)
C(13″)	2715 (4)	842 (4)	− 1724 (4)	76 (6)
C(14″)	4972 (4)	891 (4)	1816 (4)	69 (5)
C(15″)	2728 (4)	4195 (4)	− 593 (3)	61 (5)
N(16″)	4686 (2)	3704 (3)	2816 (3)	44 (3)

Table 2. *Distances* (Å) *and angles* (°) *for non*-H *atoms with e.s.d.'s in parentheses*

	Molecule 1	Molecule 2	Molecule 3
C(1)—C(2)	1·546 (5)	1·540 (6)	1·540 (6)
C(1)—C(10)	1·517 (6)	1·512 (6)	1·529 (6)
C(1)—C(11)	1·534 (5)	1·532 (6)	1·527 (6)
C(2)—N(16)	1·450 (5)	1·448 (6)	1·462 (5)
C(2)—C(3)	1·509 (6)	1·511 (6)	1·501 (6)
N(16)—C(12)	1·344 (5)	1·343 (5)	1·328 (5)
C(3)—C(4)	1·335 (5)	1·336 (6)	1·333 (6)
C(4)—C(5)	1·500 (6)	1·505 (5)	1·507 (5)
C(4)—C(15)	1·506 (6)	1·510 (6)	1·510 (6)
C(5)—O(5)	1·448 (5)	1·444 (4)	1·453 (5)
C(5)—C(6)	1·530 (6)	1·538 (5)	1·538 (5)
C(6)—C(7)	1·558 (6)	1·558 (5)	1·560 (6)
C(7)—C(8)	1·512 (5)	1·499 (5)	1·511 (6)
C(7)—C(11)	1·568 (5)	1·568 (5)	1·572 (5)
C(8)—C(9)	1·311 (5)	1·320 (6)	1·316 (7)
C(8)—C(13)	1·516 (5)	1·519 (6)	1·529 (6)
C(9)—C(10)	1·501 (6)	1·493 (7)	1·498 (7)
C(11)—C(12)	1·527 (5)	1·524 (6)	1·533 (5)
C(11)—C(14)	1·540 (6)	1·541 (5)	1·531 (6)
C(12)—O(12)	1·230 (5)	1·233 (5)	1·233 (5)
C(2)—C(1)—C(10)	115·9 (3)	116·8 (4)	116·5 (4)
C(2)—C(1)—C(11)	102·9 (3)	103·1 (3)	103·9 (3)
C(10)—C(1)—C(11)	116·7 (3)	116·3 (3)	115·7 (4)
C(1)—C(2)—N(16)	100·2 (3)	100·4 (3)	100·1 (3)
C(1)—C(2)—C(3)	113·6 (3)	113·7 (4)	113·3 (3)
N(16)—C(2)—C(3)	116·4 (3)	115·6 (4)	116·6 (3)
C(2)—N(16)—C(12)	113·8 (3)	113·9 (3)	114·2 (3)
C(2)—C(3)—C(4)	130·2 (4)	130·2 (4)	130·2 (4)
C(3)—C(4)—C(5)	123·7 (4)	123·4 (4)	123·0 (4)
C(3)—C(4)—C(15)	119·5 (4)	119·9 (4)	119·8 (4)
C(5)—C(4)—C(15)	116·7 (3)	116·6 (3)	117·1 (3)
C(4)—C(5)—O(5)	109·2 (3)	108·5 (3)	107·9 (3)
C(4)—C(5)—C(6)	114·4 (3)	115·3 (3)	114·8 (3)
O(5)—C(5)—C(6)	108·3 (3)	108·2 (3)	108·1 (3)
C(5)—C(6)—C(7)	121·6 (3)	121·6 (3)	121·5 (3)
C(6)—C(7)—C(8)	114·0 (3)	113·3 (3)	113·1 (3)
C(6)—C(7)—C(11)	118·7 (3)	117·3 (3)	118·0 (3)
C(8)—C(7)—C(11)	111·8 (3)	113·1 (3)	112·4 (3)
C(7)—C(8)—C(9)	124·9 (4)	124·6 (4)	124·6 (4)
C(7)—C(8)—C(13)	115·2 (3)	115·6 (3)	115·3 (4)
C(9)—C(8)—C(13)	119·8 (4)	119·7 (4)	119·8 (4)
C(8)—C(9)—C(10)	125·3 (4)	125·0 (4)	125·3 (4)
C(1)—C(10)—C(9)	113·7 (3)	113·6 (4)	113·2 (4)
C(1)—C(11)—C(7)	114·7 (3)	114·0 (3)	114·3 (3)
C(1)—C(11)—C(12)	100·9 (3)	100·8 (3)	100·3 (3)
C(1)—C(11)—C(14)	111·8 (3)	112·3 (3)	111·7 (3)
C(7)—C(11)—C(12)	111·2 (3)	111·4 (3)	109·8 (3)
C(7)—C(11)—C(14)	108·3 (3)	108·6 (3)	108·8 (3)
C(12)—C(11)—C(14)	109·8 (3)	109·7 (3)	111·8 (3)
N(16)—C(12)—C(11)	108·2 (3)	108·1 (3)	108·4 (3)
N(16)—C(12)—O(12)	126·2 (3)	125·6 (4)	126·0 (4)
C(11)—C(12)—O(12)	125·6 (3)	126·3 (3)	125·5 (4)

The non-enolizable tricyclic ketone (1) was treated according to the Haller–Bauer reaction conditions (Gilday & Paquette, 1990) by sodium amide in toluene, the expected product being the bicyclo amide derivative (2). In order to determine whether this structure was the unique isolated product of the reaction and to verify the validity of the proposed ring expansion, the reaction product was subjected to X-ray analysis.

Experimental. A single crystal of the title compound suitable for X-ray diffraction was obtained by slow evaporation of a 1:1 $CHCl_3$/MeOH solution at room temperature. A colourless crystal approximately 0·2 × 0·2 × 0·6 mm was harvested and mounted on a glass fiber. Intensity data collected on a Philips PW1100 automatic four-circle diffractometer operating with Cu $K\alpha$ radiation selected by a graphite monochromator. Orientation matrix and cell dimensions deduced from the angular settings of 25 randomly distributed reflections in the range $20 < 2\theta < 40°$. *UB* matrix refined as usual by a least-squares procedure. Each reflection scanned over a 1·2° angular width at a speed of 0·03° s^{-1} in the $\theta/2\theta$ scanning mode. Background deduced from two stationary measurements on both sides of the reflection, three standard reflections monitored every 2 h. 6734 reflections scanned up to $2\theta = 126°$. $-14 \le h \le 14$, $-14 \le k \le 14$, $0 \le l \le 14$. Standard Lorentz and polarization corrections. F_o observed above the 2σ

background level. Unique data set of 6387 independent reflections (with $R_{\rm sym} = 4{\cdot}5\%$ for the 340 multiple reflections).

No significant decomposition found during data collection and no correction applied; no absorption correction. Structure solved by direct methods using *SHELXS*86 (Sheldrick, 1986)

All atoms located in the initial Fourier map. Atom types assigned from peak heights in the electronic density. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Structural parameters refined (on F) with isotropic then anisotropic thermal factors for the non-H atoms by full-matrix least-squares procedures. All H atoms were located on successive difference Fourier maps, and introduced with a fixed isotropic thermal factor equal to that of the bonded carbon. The hydrogens were not refined. Final unweighted R factor is 0·062 for 5781 observed reflections [$I \geq 2\sigma(I)$] and $wR =$ 0·064 with weights $w = [\sigma^2(F) + 0{\cdot}0005sF^2]^{-1}$. Max. shift/e.s.d. = 0·09 in the last least-squares cycle; $\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ +0·18, −0·23 e Å^{-3} in final difference Fourier map.

The final positional parameters are given in Table 1* for non-H atoms. The bond lengths and angles with e.s.d.'s are given in Table 2.

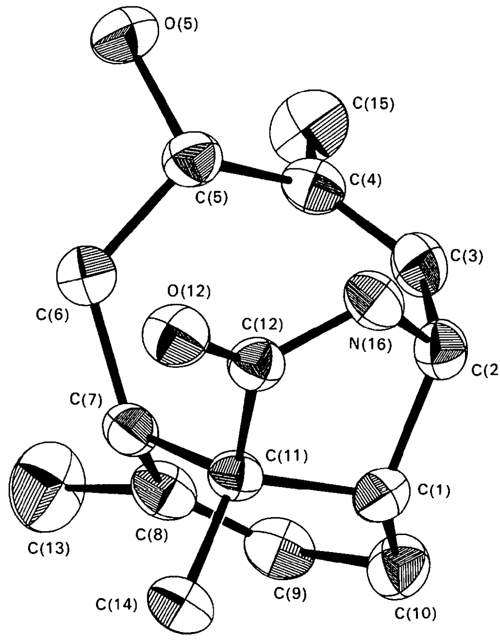

Fig. 1. *ORTEP* representation of a single molecule of the asymmetric unit.

Discussion. The X-ray analysis revealed that (2) was not the final product of the Haller–Bauer reaction but just a possible intermediate: in the highly basic medium of the reaction, the dihydrofuran ring of (2) undergoes a ring opening leading to a β-hydroxyl group at the C(5) position with the formation of a lactam ring at C(2) to give (3) (Guir, 1990).

The *ORTEP* drawing (Johnson, 1976) of one of the three independent molecules is shown in Fig. 1 with thermal ellipsoids drawn at the 50% probability level.

The three independent molecules of the asymmetric unit display similar conformations: a least-squares fit of the three molecules was calculated and is given in Fig. 2 as a stereoscopic view. There are only minor conformational changes in the eight-membered ring, all the r.m.s. deviations on the positional parameters are in the range 0·1–0·2 Å. The molecular structure is in a 'bowl'-shaped conformation tightened by the lactam ring, behaviour which is also observed in the X-ray structure of taxagifine, a natural bridged taxol derivative (Chauvière, Guénard, Pascard, Picot, Potier & Prangé, 1982). The major feature of the present structure is the rather unusual association of the three independent

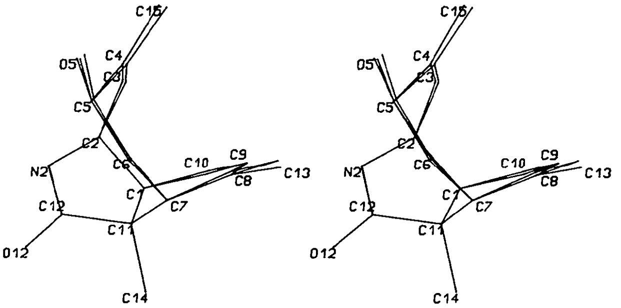

Fig. 2. Least-squares fit of the three independent molecules using the five-membered lactam ring as the fitting group (the most rigid part of the structure).

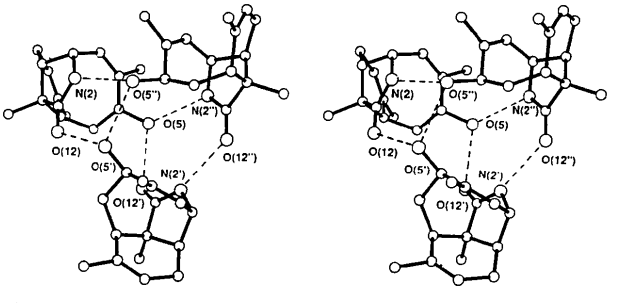

Fig. 3. Stereoscopic pair of the trimeric unit with the following intermolecular contacts: O(5)—H···O(12′) = 1·808 (8) Å; H···O(12′)—C(12′) = 118 (1)°; N(16″)—H···O(5) = 2·028 (8) Å; H···O(5)—C(5) = 121 (1)°; N(16)—H···O(5″) = 1·973 (8) Å; H···O(5″)—C(5″) = 119 (1)°; O(5′)—H···O(12) = 1·731 (8) Å; H···O(12)—C(12) = 118 (1)°; N(16′)—H···O(12″) = 2·018 (7) Å; H···O(12″)—C(12″) = 120 (1)°; O(5″)—H···O(5′) = 1·796 (8) Å; H···O(5′)—C(5′) = 106 (1)°.

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* Lists of structure factors, anisotropic thermal parameters, coordinates of the H atoms, and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54003 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecules in compact clusters stabilized in the packing by six hydrogen bonds.

Fig. 3 displays the trimeric asymmetric unit (*PLUTO*; Motherwell & Clegg, 1978) viewed along the *c* axis with the connecting hydrogen bonds. The molecules are associated using all the possible polar atoms, including both donor and acceptor hydrogen bonds for the O(5) hydroxyl function in the three molecules. As a consequence, there are no polar contacts closer than 3·5 Å between the different trimers of the packing.

In conclusion, this X-ray analysis revealed that the expected ring expansion in (1) was correct but that the reaction proceeded one step ahead of the predicted result, *i.e.* compound (3) and not (2). Further chemical syntheses are in progress to take advantage of this extra step towards a new route to the taxol backbone.

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Structure of Methyl 3-Hydroxy-1-(1-isoquinolyl)-3-phenyl-3,3a,8,8a-tetrahydroindeno[1,2-*c*]pyrrol-8a-ylcarboxylate

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Abstract. $C_{28}H_{22}N_2O_3$, $M_r = 434{\cdot}5$, triclinic, $P\bar{1}$, $a = 11{\cdot}081\,(1)$, $b = 10{\cdot}247\,(1)$, $c = 15{\cdot}074\,(2)$ Å, $\alpha = 93{\cdot}584\,(2)$, $\beta = 130{\cdot}11\,(2)$, $\gamma = 113{\cdot}09\,(2)°$, $V = 1076{\cdot}7\,(9)$ Å^3, $Z = 2$, $D_x = 1{\cdot}340$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}067$ mm^{-1}, $F(000) = 456$, $T = 294$ K, final $R = 0{\cdot}041$ for 2742 unique reflections. The regiochemistry of the condensation product of 2-methoxycarbonylindene with 2-benzoyl-1,2-dihydroisoquinaldonitrile fluoroborate was established in order to show that it was a derivative of indeno[1,2-*c*]pyrrole. The two pentagonal rings have an envelope shape. Molecules are linked by a hydrogen bond, O(31)—H(31)···N(2^{i}) [2·936 (2) Å, 174 (2)°] [(i) $1-x$, $-y$, $1-z$].

Introduction. The reaction of 2-benzoyl-1,2-dihydroisoquinaldonitrile fluoroborate (1) with indene (2) led to a condensation product (see scheme below), the formula of which could not be found completely from ^{1}H NMR data. So the condensation of (1) with

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