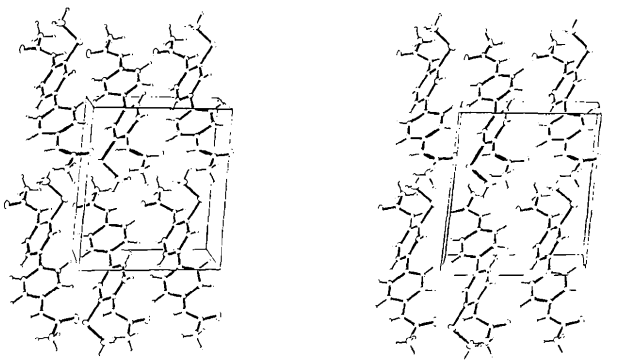

Fig. 3. *ORTEP* packing drawing and intermolecular hydrogen bonding (Johnson, 1965).

& Merritt, 1962). The hydrogen bonding may be responsible for the differences in the dimensions of the two *N*-acetyl groups in the molecule.

This work was supported by Grant CA 17562, awarded by the National Cancer Institute. The authors express their gratitude to Dr F. A. Beland who supplied us with the material and to the University of Oklahoma for providing computing facilities.

References

BROCK, C. P., KUO, M.-S. & LEVY, H. A. (1978). *Acta Cryst.* B**34**, 981–985.

BROCK, C. P., NAAE, D. G., GOODHAND, N. & HAMOR, T. A. (1978). *Acta Cryst.* B**34**, 3691–3696.

CASALONE, G., MARIONI, C., MUGNOLI, A. & SIMONETTA, M. (1969). *Acta Cryst.* B**25**, 1741–1750.

CHARBONNEAU, G.-P. & DELUGEARD, Y. (1976). *Acta Cryst.* B**32**, 1420–1423.

EALICK, S. E., VAN DER HELM, D. & WEINHEIMER, A. J. (1975). *Acta Cryst.* B**31**, 1618–1626.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HAMOR, M. J. & HAMOR, T. A. (1978). *Acta Cryst.* B**34**. 863–866.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MARSH, R. E. & DONOHUE, J. (1967). *Adv. Protein Chem.* **22**, 235–256.

MICHEL, A. G. & DURANT, F. (1976). *Acta Cryst.* B**32**, 1574–1576.

MORTON, K. C., BELAND, F. A., EVANS, F. E., HULSE, N. F. & KADLUBAR, F. F. (1980). *Cancer Res.* **40**, 751–758.

RUŽIĆ-TOROŠ, Ž. & LAZARINI, F. (1978). *Acta Cryst.* B**34**, 854–858.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VAN DER HELM, D., LESSOR, A. E. JR & MERRITT, L. L. JR (1962). *Acta Cryst.* **15**, 1227–1232.

WINKLER, F. K. & DUNITZ, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.

Acta Cryst. (1980). B**36**, 2447–2450

Structure of the 4-Nitroguaiacyl Ester of *N*-Benzyloxycarbonyl-L-isoleucine

BY Z. URBANCZYK-LIPKOWSKA, J. W. KRAJEWSKI AND P. GLUZIŃSKI

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 *Warszawa, Poland*

AND A. W. LIPKOWSKI AND S. DRABAREK

Peptide Laboratory, Chemistry Department, Warsaw University, 02-932 *Warszawa, Poland*

(*Received* 12 *February* 1980; *accepted* 30 *April* 1980)

Abstract. $C_{21}H_{24}N_2O_7$, $M_r = 416{\cdot}42$, monoclinic, $P2_1$, $a = 19{\cdot}433\ (3)$, $b = 5{\cdot}143\ (2)$, $c = 10{\cdot}926\ (3)$ Å, $\beta = 104{\cdot}30\ (2)°$, $V = 1058{\cdot}2$ Å^3, $Z = 2$, $D_m = 1{\cdot}30$ Mg m^{-3}, $F(000) = 440$, μ(Cu $K\alpha$) $= 0{\cdot}74$ mm^{-1}. The structure was solved by direct methods and refined by the full-matrix least-squares procedure to $R = 0{\cdot}060$ and $R_w = 0{\cdot}044$ for 1443 F_o values obtained by a combination of two independent measurements. The molecule exists in a bow-like form with aromatic rings at the ends lying nearly perpendicular one to another. The torsion angles φ and ψ are $86{\cdot}7\ (5)$ and $-146{\cdot}3\ (3)°$, respectively.

Introduction. 4-Nitroguaiacyl esters of amino acids have been proposed (Bankowski & Drabarek, 1971) as acylating agents in peptide synthesis. It was found that 4-nitroguaiacyl esters of N-protected amino acids react faster than *p*-nitrophenyl esters and the danger of racemization at the chiral center is then lowered. As an attempt to elucidate the racemization stability of 4-nitroguaiacyl esters, the formation of an intramolecular hydrogen bond between the methoxy group in the *ortho* position and the H atom at C(6) was postulated (Bankowski & Drabarek, 1972; Bankowski, Lipkowski & Drabarek, 1974). Since it was impossible

0567-7408/80/102447-04$01.00

to confirm this hypothesis by inspection of IR spectra in solution, the crystal structure analysis of the title compound (ZING) was undertaken. The structure of the *p*-nitrophenyl ester of *N*-benzyloxycarbonyl-L-leucine (ZLNP) (Coiro, Mazza & Mignucci, 1974) gives an opportunity to compare the structures of the esters in the solid state.

Unit-cell dimensions determined from preliminary film data were refined by a least-squares procedure implemented on a CAD-4 automatic diffractometer (SLAF&BS, Jagiellonian University, Kraków). 1331 reflections obtained by this experiment with $I > 2\sigma_I$ were considered as observed ($\omega/2\theta$ scan technique) and, after Lp correction, used for structure determination. The structure was solved by direct methods using *SHELX*76 (Sheldrick, 1976). The best set of phases gave all but two atoms of the molecule. The coordinates of these two were found from difference Fourier maps. Positional parameters for all non-hydrogen atoms were refined by the full-matrix least-squares routine (Stewart, Kundell & Baldwin, 1970) with isotropic and then anisotropic thermal parameters. After six cycles of anisotropic refinement the difference Fourier synthesis was computed in the environment of the peptide *N* atom. No peaks of reasonable geometry were found (all maximum heights below 0·2 e Å^{-3}). The coordinates for the H atoms were then computed (Roberts & Sheldrick, 1975). Three further cycles of anisotropic refinement with H atomic parameters held invariant gave $R = 0{\cdot}071$ and $R_w = 0{\cdot}055$ ($w = 1/\sigma_I^2$). The unsatisfactory geometry and relatively high standard deviations caused us to collect a second set of data on a Syntex $P2_1$ diffractometer (A. Mickiewicz University, Poznań) with the same measurement technique and radiation length as before. All corrections were made as previously. However, the number of data collected was only slightly greater than in the first experiment. The refining process, with 1414 structure factors considered as observed ($I > 2\sigma_I$), gave a very similar (within three standard deviations) geometry and R and R_w factors of 0·064 and 0·066, respectively (unit weights). A difference Fourier synthesis also failed to reveal the position of the peptide H atom. So, it was decided to take the average set of both experiments, with the already refined scale factors and equivalence of reflections. The averaged data set finally contained 1443 structure factors (most reflections measured at least twice). The coordinates of the non-hydrogen atoms were then refined (three cycles) in the anisotropic mode with newly computed (invariant) positions for the H atoms. The position for the peptide H atom was calculated assuming the N atom to be of trigonal geometry. The final R and R_w factors ($w = 1/\sigma_I^2$) were 0·060 and 0·044, respectively. The final coordinates for the non-hydrogen atoms are listed in Table 1.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with their e.s.d.'s in parentheses*

	x	y	z	B_{iso} (Å^2)
C(1)	10118 (2)	1236 (14)	1463 (5)	6·4 (3)
O(2)	9530 (1)	3044 (7)	1136 (3)	5·0 (2)
C(3)	8868 (2)	2055 (12)	793 (4)	4·2 (3)
O(4)	8740 (2)	−250 (7)	758 (3)	5·5 (2)
N(5)	8403 (2)	4004 (0)	506 (3)	3·5 (2)
C(6)	7651 (2)	3437 (9)	162 (3)	3·5 (2)
C(7)	7389 (2)	3277 (9)	1372 (4)	3·2 (2)
O(8)	7623 (1)	4540 (8)	2283 (2)	5·8 (2)
O(9)	6861 (1)	1495 (6)	1281 (2)	4·0 (1)
C(10)	7231 (2)	5594 (9)	−699 (4)	3·7 (2)
C(11)	7559 (2)	6210 (11)	−1822 (4)	4·9 (2)
C(12)	6446 (2)	4907 (12)	−1149 (3)	4·8 (2)
C(13)	7557 (3)	3950 (11)	−2712 (4)	7·0 (3)
N(14)	5791 (2)	901 (10)	5587 (3)	4·5 (2)
O(15)	5369 (2)	2580 (8)	5714 (3)	5·7 (2)
O(16)	6006 (2)	−835 (9)	6326 (3)	6·3 (2)
O(17)	5787 (1)	4631 (7)	1466 (2)	4·6 (2)
C(18)	5180 (2)	6208 (11)	1483 (4)	5·1 (3)
C(21)	10504 (2)	1703 (13)	2829 (5)	5·1 (3)
C(22)	10392 (3)	20 (13)	3741 (7)	7·5 (4)
C(23)	10739 (4)	443 (17)	4993 (7)	9·3 (5)
C(24)	11200 (4)	2444 (19)	5335 (6)	7·9 (5)
C(25)	11328 (3)	4127 (14)	4412 (7)	7·2 (4)
C(26)	10973 (3)	3732 (13)	3154 (5)	5·9 (3)
C(31)	6588 (2)	1335 (10)	2362 (4)	3·9 (2)
C(32)	6030 (2)	3001 (10)	2442 (4)	3·7 (2)
C(33)	5761 (2)	2830 (10)	3520 (4)	3·8 (2)
C(34)	6065 (2)	1015 (10)	4426 (4)	3·8 (2)
C(35)	6596 (2)	−685 (11)	4350 (4)	4·4 (2)
C(36)	6864 (2)	−491 (10)	3297 (4)	4·2 (2)

Discussion. The bond lengths and valence angles for the non-hydrogen atoms are given in Tables 2 and 3. The *ORTEP* (Johnson, 1965) diagram of the L form of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35322 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

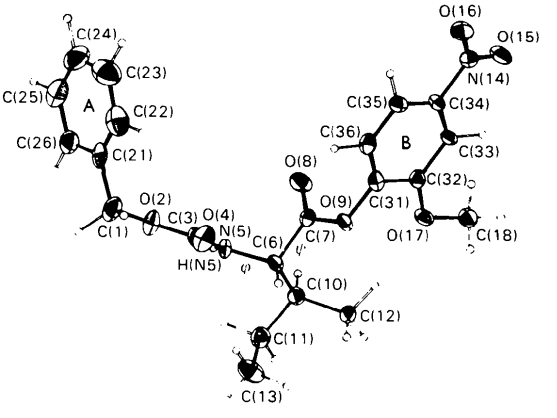

Fig. 1. Projection on the *ac* plane (*ORTEP*; Johnson, 1965) of the molecule (L form) with the atom numbering. Thermal motion ellipsoids are set at the 40% probability level.

ZING (in contrast to the coordinates of the D form given in Table 1) is presented in Fig. 1.

The geometry of the ZING molecule does not reveal any unexpected features. The bond lengths and valence angles for the benzyloxycarbonyl group are in agreement with those cited for CBz-Gly-Pro-LeuOH (Yamane, Ashida, Shimonishi, Kakudo & Sasada, 1976), CBz-Gly-ProOH (Tanaka, Kozima, Ashida, Tanaka & Kakudo, 1977) and CBz-Leu-*p*-ONp (ZLNP) (Coiro, Mazza & Mignucci, 1974). The characteristic feature of the benzyloxycarbonyl groups in all the compounds cited above is that the average C=C bond length in the phenyl rings is shorter than the expected 1·39 Å: very short aromatic C=C bonds in the range 1·32–1·36 Å (1·35 Å in ZING) are observed. Additionally, in all cases the anisotropic thermal parameters for the phenyl C atoms are higher than those for other C atoms in the molecules. Because of the absence of an experimentally derived position for the peptide H atom, the conformation of the peptide group may be established from the torsion angles O(4)–C(3)–N(5)–C(6) and O(2)–C(3)–N(5)–C(6) (Table 4). These values [for ZING 3·0 (7) and −177·2 (3)°, for ZLNP −13·0 and 169·6°, respectively] show that the peptide group in ZING is more planar than that in ZLNP.

The φ and ψ angles found for the isolated amino acid residue of ZING to be 86·7 (5) and −146·3 (3)°, respectively, deviate significantly from the values of −93·5 and 48·8° reported for the *p*-nitrophenyl ester of leucine (ZLNP). The analogous values reported for some tetra- and penta-peptides with leucyl residues (Rudko & Low, 1975) are found to be within the ranges −104 to 118° for φ and 8–21° for ψ.

The conformation of the isoleucine side chain may be described by the torsion angles C(7)–C(6)–C(10)–C(11) = 169·6 (3), C(6)–C(10)–C(11)–C(13) = 62·2 (4), C(7)–C(6)–C(10)–C(12) = −65·0 (4) and C(12)–C(10)–C(11)–C(13) = −63·2 (5)° (Table 4).

The postulated intermolecular hydrogen bond (Bankowski & Drabarek, 1972), which would form a seven-membered ring *via* the α carbon [C(6)] and the O atom of the methoxy group, was not observed. The higher stability of 4-nitroguaiacyl esters towards racemization may be explained by the fact that in polar solvents the 4-nitroguaiacyl esters with their solvation envelope are more voluminous than *p*-nitrophenyl

Table 2. *Interatomic distances* (Å) *with their e.s.d.'s in parentheses*

		Ring *A*	
C(1)–O(2)	1·448 (6)	C(21)–C(22)	1·376 (10)
C(1)–C(21)	1·516 (7)	C(21)–C(26)	1·373 (8)
O(2)–C(3)	1·347 (5)	C(22)–C(23)	1·385 (10)
C(3)–O(4)	1·210 (7)	C(23)–C(24)	1·355 (12)
C(3)–N(5)	1·334 (6)	C(24)–C(25)	1·396 (11)
N(5)–C(6)	1·446 (5)	C(25)–C(26)	1·392 (9)
C(6)–C(7)	1·532 (6)		
C(7)–O(8)	1·181 (5)	Ring *B*	
C(7)–O(9)	1·362 (5)	C(31)–C(32)	1·402 (6)
O(9)–C(31)	1·411 (5)	C(31)–C(36)	1·393 (6)
C(6)–C(10)	1·550 (6)	C(32)–C(33)	1·404 (6)
C(10)–C(11)	1·550 (6)	C(33)–C(34)	1·383 (6)
C(10)–C(12)	1·524 (5)	C(34)–C(35)	1·370 (7)
C(11)–C(13)	1·515 (7)	C(35)–C(36)	1·378 (6)
		C(34)–N(14)	1·493 (6)
		N(14)–O(15)	1·223 (6)
		N(14)–O(16)	1·206 (6)
		C(32)–O(17)	1·347 (5)
		O(17)–C(18)	1·436 (6)

Table 3. *Valence angles* (°) *with their e.s.d.'s in parentheses*

O(2)–C(1)–C(21)	108·0 (5)	Ring *B*	
C(1)–O(2)–C(3)	117·9 (4)	O(9)–C(31)–C(32)	118·2 (4)
O(2)–C(3)–O(4)	123·6 (4)	O(9)–C(31)–C(36)	119·8 (4)
O(2)–C(3)–N(5)	109·1 (5)	C(32)–C(31)–C(36)	121·9 (4)
O(4)–C(3)–N(5)	127·3 (4)	C(31)–C(32)–C(33)	117·9 (4)
C(3)–N(5)–C(6)	119·5 (3)	C(31)–C(32)–O(17)	117·2 (4)
N(5)–C(6)–C(7)	108·4 (3)	C(33)–C(32)–O(17)	124·9 (4)
N(5)–C(6)–C(10)	111·2 (3)	C(32)–C(33)–C(34)	117·4 (4)
C(7)–C(6)–C(10)	108·9 (3)	C(33)–C(34)–C(35)	125·6 (4)
C(6)–C(7)–O(8)	123·9 (4)	C(33)–C(34)–N(14)	117·2 (4)
C(6)–C(7)–O(9)	112·2 (3)	C(35)–C(34)–N(14)	117·2 (4)
O(8)–C(7)–O(9)	123·9 (4)	C(34)–C(35)–C(36)	116·7 (4)
C(7)–O(9)–C(31)	114·2 (3)	C(35)–C(36)–C(31)	120·3 (4)
C(6)–C(10)–C(11)	111·6 (3)	C(32)–O(17)–C(18)	118·0 (3)
C(6)–C(10)–C(12)	111·4 (4)	O(15)–N(14)–O(16)	125·3 (4)
C(11)–C(10)–C(12)	111·5 (3)	C(34)–N(14)–O(15)	117·3 (4)
C(10)–C(11)–C(13)	114·5 (4)	C(34)–N(14)–O(16)	117·4 (4)
Ring *A*			
C(1)–C(21)–C(22)	119·0 (5)		
C(1)–C(21)–C(26)	120·7 (6)		
C(22)–C(21)–C(26)	120·3 (5)		
C(21)–C(22)–C(23)	119·4 (6)		
C(22)–C(23)–C(24)	121·2 (8)		
C(23)–C(24)–C(25)	119·7 (6)		
C(24)–C(25)–C(26)	119·3 (6)		
C(25)–C(26)–C(21)	120·1 (6)		

Table 4. *Torsion angles* (°) *in the main chain of the molecule* (*e.s.d.'s in parentheses*)

C(26)–C(21)–C(1)–O(2)	−79·5 (6)	C(3)–N(5)–C(6)–C(10)	−153·6 (4)	C(18)–O(17)–C(32)–C(33)	−4·0 (6)
C(21)–C(1)–O(2)–C(3)	−118·1 (5)	N(5)–C(6)–C(7)–O(8)	33·1 (5)	C(11)–C(10)–C(6)–N(5)	50·2 (4)
C(1)–O(2)–C(3)–O(4)	1·0 (7)	N(5)–C(6)–C(7)–O(9)	−146·3 (3)	C(11)–C(10)–C(6)–C(7)	169·6 (3)
C(1)–O(2)–C(3)–N(5)	−178·8 (4)	C(10)–C(6)–C(7)–O(8)	−88·0 (5)	C(6)–C(10)–C(11)–C(13)	62·2 (4)
O(2)–C(3)–N(5)–C(6)	−177·2 (3)	C(10)–C(6)–C(7)–O(9)	92·6 (4)	C(7)–C(6)–C(10)–C(12)	−65·0 (4)
O(4)–C(3)–N(5)–C(6)	3·0 (7)	C(6)–C(7)–O(9)–C(31)	−178·2 (3)	O(15)–N(14)–C(34)–C(33)	−7·1 (6)
C(3)–N(5)–C(6)–C(7)	86·7 (5)	C(7)–O(9)–C(31)–C(32)	88·0 (4)	O(16)–N(14)–C(34)–C(33)	173·2 (4)

esters which have all substituents hydrophobic. These steric effects protect the H atom against proton-acceptor elements in the reaction mixture. Computation of a least-squares plane through three atoms surrounding the α carbon [N(5), C(10) and C(7)] reveals that above this plane are located the phenyl ring and the guaiacyl ring with the methoxy group above them. The isoleucyl chain is situated entirely on the other side of this plane. The dihedral angle between least-squares planes of the aromatic rings is 89·4 (9)°, in contrast to the 1·6° reported for the *p*-nitrophenyl ester (ZLNP), thus suggesting different spatial locations of the bulky substituents in the two esters.

The insertion of a calculated amide H atom with an N–H distance of 0·94 Å leads to the possibility (if the H atom position is approximately correct) of a weak intermolecular hydrogen bridge N(5)–H···O(4)′ [atom O(4)′ is generated by a *b*-axis translation]. The N(5)–O(4)′ distance is 3·024 (5) Å and the H···O(4)′ distance would be 2·10 Å, forming a *D*–H···*A* angle of 166°. Similar parameters for the intermolecular hydrogen bridge were found for CBz-Gly-ProOH (Tanaka *et al.*, 1977), with a *D*–*A* distance of 2·906 Å, H···*A* = 2·16 Å and a *D*–H···*A* angle of 167°.

There are few intermolecular distances less than 3·5 Å in the crystal lattice, of which the shortest are the molecular interactions between the O(15) atom of the nitro group (asymmetric unit) and the 4-nitroguaiacyl group of the molecule generated by the symmetry operation $1 - x, \frac{1}{2} + y, 1 - z$. The distances are: O(15)–N(14)′ 2·905 (5), O(15)–O(15)′ 3·163 (5), and O(15)–C(34)′ 3·271 (6) Å. This may be caused by a polar resonance effect of the nitro group.

The courtesy of the Head Manager Mr A. Plenkiewicz MSc, Dr J. Szymczyk DSc and Dr A. Koczyk, of the Research and Development Center of Industrial Projecting 'BISTYP', Warszawa, enabled the authors to prepare the *ORTEP* diagram.

References

BANKOWSKI, K. & DRABAREK, S. (1971). *Rocz. Chem.* **45**, 1205–1212.

BANKOWSKI, K. & DRABAREK, S. (1972). *Rocz. Chem.* **46**, 607–614.

BANKOWSKI, K., LIPKOWSKI, A. W. & DRABAREK, S. (1974). *Rocz. Chem.* **48**, 715–719.

COIRO, V. M., MAZZA, F. & MIGNUCCI, G. (1974). *Acta Cryst.* B**30**, 2607–2613.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

ROBERTS, P. & SHELDRICK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

RUDKO, A. D. & LOW, B. W. (1975). *Acta Cryst.* B**31**, 713–725.

SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TANAKA, I., KOZIMA, T., ASHIDA, T., TANAKA, N. & KAKUDO, M. (1977). *Acta Cryst.* B**33**, 116–119.

YAMANE, T., ASHIDA, T., SHIMONISHI, K., KAKUDO, M. & SASADA, Y. (1976). *Acta Cryst.* B**32**, 2071–2076.

Acta Cryst. (1980). B**36**, 2450–2453

D:*C*-*friedo*-*B*′:*A*′-*neo*-Gammacer-9(11)-ene*

BY HELMUT W. SCHMALLE AND OTTO H. JARCHOW

Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelalle 48, *D*-2000 *Hamburg* 13, *Federal Republic of Germany*

AND BJÖRN M. HAUSEN

Universitäts-Hautklinik Hamburg-Eppendorf, Martinistrasse 52, *D*-2000 *Hamburg* 20, *Federal Republic of Germany*

(*Received* 12 *March* 1980; *accepted* 14 *May* 1980)

Abstract. $C_{30}H_{50}$, orthorhombic, $P2_12_12_1$, a = 7·669 (6), b = 10·571 (7), c = 32·01 (5) Å (λ = 1·5418 Å, T = 293 K), V = 2639·5 Å^3, Z = 4, M_r = 410·4, D_x = 1·03 Mg m^{-3}, $F(000)$ = 920, μ(Cu $K\alpha$) = 0·354 mm^{-1}; R = 7·95%. The molecule is shown to be the pentacyclic triterpene 9(11)-fernene, consisting of four fused all-*trans* six-membered rings *A*, *B*, *C*, *D* with a five-membered *E* ring *trans*-fused to ring *D*. Ring *B* is intermediate between twist and boat conformations.

Introduction. In the course of the investigation of the unknown allergenic compound of the leatherleaf fern *Arachnoides adiantiformis* (Forst) Tindale (fam. Aspidiaceae) (Hausen & Schulz, 1978) the title

* IUPAC name: *ent*-13,17-dimethyl-26,28-dinor-5β,10α-hop-9(11)-ene.

0567-7408/80/102450-04$01.00