

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  $\alpha$  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  $89.4(9)^\circ$ , in contrast to the  $1.6^\circ$  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  $0.94 \text{ \AA}$  leads to the possibility (if the H atom position is approximately correct) of a weak intermolecular hydrogen bridge N(5)—H $\cdots$ O(4') [atom O(4') is generated by a *b*-axis translation]. The N(5)—O(4') distance is  $3.024(5) \text{ \AA}$  and the H $\cdots$ O(4') distance would be  $2.10 \text{ \AA}$ , forming a *D*—H $\cdots$ *A* angle of  $166^\circ$ . Similar parameters for the intermolecular hydrogen bridge were found for CBz-Gly-ProOH (Tanaka *et al.*, 1977), with a *D*—*A* distance of  $2.906 \text{ \AA}$ , H $\cdots$ *A* =  $2.16 \text{ \AA}$  and a *D*—H $\cdots$ *A* angle of  $167^\circ$ .

There are few intermolecular distances less than  $3.5 \text{ \AA}$  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')  $3.271(6) \text{ \AA}$ . This may be caused by a polar resonance effect of the nitro group.

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#### 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.* **B30**, 2607–2613.  
 JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 ROBERTS, P. & SHELDRIK, G. M. (1975). XANADU. Program for crystallographic calculations. Univ. of Cambridge, England.  
 RUDKO, A. D. & LOW, B. W. (1975). *Acta Cryst.* **B31**, 713–725.  
 SHELDRIK, 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.* **B33**, 116–119.  
 YAMANE, T., ASHIDA, T., SHIMONISHI, K., KAKUDO, M. & SASADA, Y. (1976). *Acta Cryst.* **B32**, 2071–2076.

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### *D*:*C*-*friedo*-*B'*:*A'*-*neo*-*Gammacer*-**9(11)**-*ene*\*

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**Abstract.** C<sub>30</sub>H<sub>50</sub>, orthorhombic,  $P2_12_12_1$ ,  $a = 7.669(6)$ ,  $b = 10.571(7)$ ,  $c = 32.01(5) \text{ \AA}$  ( $\lambda = 1.5418 \text{ \AA}$ ,  $T = 293 \text{ K}$ ),  $V = 2639.5 \text{ \AA}^3$ ,  $Z = 4$ ,  $M_r = 410.4$ ,  $D_x = 1.03 \text{ Mg m}^{-3}$ ,  $F(000) = 920$ ,  $\mu(\text{Cu } K\alpha) = 0.354 \text{ mm}^{-1}$ ;  $R = 7.95\%$ . 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-5 $\beta$ ,10 $\alpha$ -hop-9(11)-ene.

compound has been found among the allergenic fraction as the only acceptable crystal for X-ray structure analysis. The identification by X-ray analysis as 9(11)-fernene has not previously been reported. As a triterpenoid hydrocarbon of a new type (Ageta, Iwata & Natori, 1963) this fernene has been identified by chemical methods in several fern species (Horveth, de Szöcs, Alvarado & Grant, 1975; Khosa, Wahi & Mukherjee, 1978; Wij, 1978; Das Gupta & Khastgir, 1978; Khastgir & Shoolery, 1978), in a moss (Catalano, Marsili, Morelli & Pacchiani, 1976) and even in a yew tree (Silva, Hoeneisen & Sammes, 1972). A small colourless crystal  $0.15 \times 0.15 \times 0.08$  mm was mounted along a for the measurements. The space group and symmetry were determined by photography, and cell parameters obtained by least-squares refinement from the angular settings of 12 reflections on a Syntex  $P2_1$  four-circle computer-controlled diffractometer with graphite-monochromated Cu  $K\alpha$  radiation. The intensities for 2107 independent reflections with  $2\theta \leq 115^\circ$  were measured on the diffractometer by the  $\theta$ - $2\theta$  scan technique at a variable scan rate of 1 to  $29^\circ \text{ min}^{-1}$ . 1383 of these reflections were observed above background with  $I > 2\sigma$ . Data reduction (with Lp corrections) was carried out with *LSAW* (Eck, 1975).

The calculation of normalized structure factors and the solution of the structure were performed with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The density of the initially unknown specimen was estimated to be  $1.25 \text{ Mg m}^{-3}$  with  $M_r = 496$  for  $Z = 4\text{C}_{24}\text{H}_{36}\text{O}_{11}$ . The  $E$  map based on  $392 E's \geq 1.24$  with phases in the most consistent set (combined figure of merit = 2.97) showed 32 independent maxima. After refinement of the positional and isotropic temperature parameters and calculation of difference syntheses with *SHELX* (Sheldrick, 1975), five peaks had to be rejected and three other non-hydrogen atomic positions were located. Four six-membered rings connected with a five-membered ring could be established ( $R = 18.4\%$ ). Bond lengths and angles, and temperature factors as well as site-occupation factors led to the conclusion that the structure must be a hopane-derivative triterpenoid. Furthermore, the 9(11) double bond of  $\sim 1.34 \text{ \AA}$  and the conformation of the methyl groups unequivocally established this compound to be 9(11)-fernene. All the 50 expected H atoms except H(162), H(283) and H(301) were found after refinement of the positional and anisotropic temperature parameters of the C atoms ( $R = 14.4\%$ ) and calculation of three more difference maps. In the final full-matrix least-squares refinement, when the separation of variables into smaller groups was necessary, positional parameters for all atoms and anisotropic temperature parameters for the C atoms were varied. The isotropic temperature factors for all H atoms were fixed at  $U =$

Table 1. Final positional parameters ( $\times 10^4$ ) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	7195 (11)	1658 (12)	3353 (3)
C(2)	6889 (16)	2042 (17)	2891 (4)
C(3)	5104 (15)	2737 (12)	2858 (3)
C(4)	3611 (11)	1848 (7)	2995 (2)
C(5)	4024 (9)	1314 (7)	3436 (2)
C(6)	2528 (10)	516 (9)	3615 (3)
C(7)	3032 (11)	-222 (9)	4007 (3)
C(8)	4548 (8)	307 (6)	4248 (2)
C(9)	6135 (9)	473 (7)	3980 (2)
C(10)	5824 (9)	705 (7)	3510 (2)
C(11)	7750 (8)	330 (8)	4134 (2)
C(12)	8144 (8)	97 (7)	4592 (2)
C(13)	6576 (8)	333 (6)	4871 (2)
C(14)	4935 (8)	-331 (6)	4672 (2)
C(15)	3406 (8)	-284 (6)	4975 (2)
C(16)	3776 (9)	-809 (6)	5420 (2)
C(17)	5346 (8)	-199 (6)	5627 (2)
C(18)	6880 (8)	-195 (6)	5317 (2)
C(19)	8443 (9)	202 (8)	5568 (2)
C(20)	8110 (9)	-400 (8)	6005 (2)
C(21)	6233 (11)	-921 (6)	5994 (2)
C(22)	5367 (12)	-941 (8)	6430 (3)
C(23)	3273 (16)	919 (10)	2655 (3)
C(24)	1970 (13)	2644 (9)	3019 (3)
C(25)	6105 (16)	-505 (11)	3275 (3)
C(26)	6275 (9)	1791 (6)	4886 (2)
C(27)	5299 (9)	-1744 (6)	4582 (2)
C(28)	4820 (9)	1141 (7)	5791 (2)
C(29)	3502 (15)	-1470 (11)	6420 (3)
C(30)	6418 (15)	-1691 (10)	6736 (3)

$0.07 \text{ \AA}^2$ . The final value of  $R$  was 7.95%, based on unit weights ( $R = \sum |F_o| - |F_c| / \sum |F_o|$ ). The positional parameters of the C atoms are given in Table 1.\* A final difference synthesis resulted in peak heights  $< 0.58 \text{ e \AA}^{-3}$  without any chemical significance.

**Discussion.** The structure is shown in Fig. 1. The bond distances, valency angles and endocyclic torsion angles involving the C atoms only are given in Figs. 2-4. The largest e.s.d. for the bond lengths is  $0.019 \text{ \AA}$ , for the valency angles  $1.2^\circ$  and for the torsion angles  $2.2^\circ$ . The steric arrangement of the methyl groups and H atoms (Fig. 5) is also found in retigerate A (Takahashi & Iitaka, 1972), davallic acid (Nakanishi, Lin, Kakisawa, Hsü & Hsiu, 1963) and partly in arundoin (Nishimoto, Ito, Natori & Ohmoto, 1965). The chair-shaped rings *A* and *D* are distorted; Fig. 4 shows the deviation of the torsion angles from the standard value of  $55.9^\circ$  (Geise, Buys & Mijlhoff, 1971). Nakanishi *et al.* (1963) compared fernene with davallic

\* Lists of structure factors, anisotropic thermal parameters of the C atoms and positional parameters of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35248 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

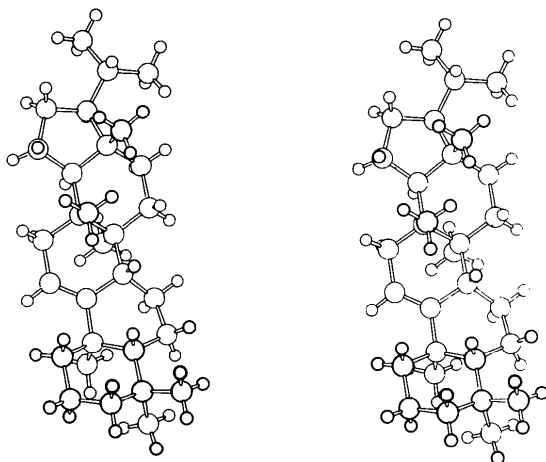


Fig. 1. ORTEP (Johnson, 1971) stereodrawing of the title compound.

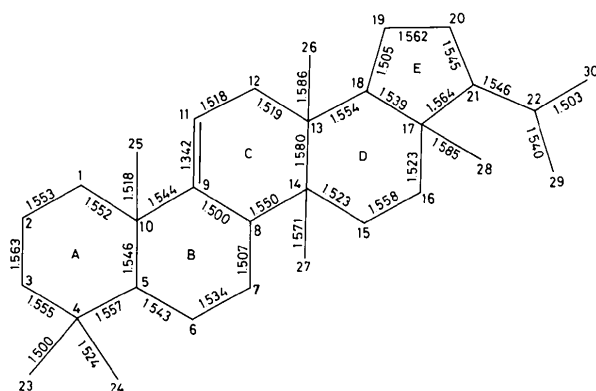


Fig. 2. Bond distances (Å);  $\sigma$  range = 0.009–0.019 Å.

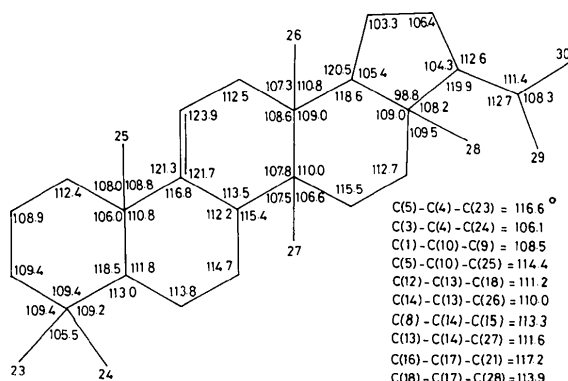


Fig. 3. Bond angles ( $^\circ$ );  $\sigma$  range = 0.5–1.2 $^\circ$ .

acid and postulated with the aid of Dreiding models that ring *B* was fixed in a boat form. From this structure determination ring *B* is intermediate between boat and twist conformations, while the cyclohexene ring *C* has a slightly distorted half-chair form. Ring *E* shows a slightly distorted envelope conformation with

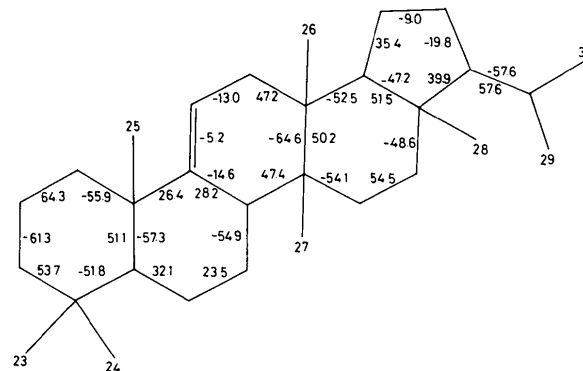


Fig. 4. Endocyclic torsion angles ( $^\circ$ ). A torsion angle  $a-b-c-d$  is positive (viewed down the  $b-c$  bond) if the  $a-b$  bond will eclipse the  $c-d$  bond by a rotation of less than  $180^\circ$  in a clockwise direction.

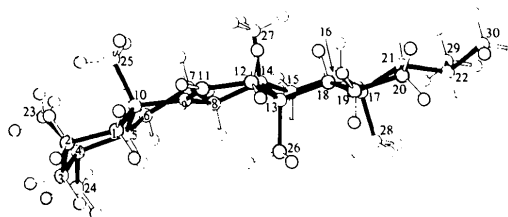


Fig. 5. Perspective view approximately along the mean molecular plane.

torsion angles similar to those in hortensyl *p*-iodobenzoate (McCandlish & Stout, 1976). The mean deviation of C(18) to C(21) from the best plane is 0.045 Å; C(17) deviates 0.694 Å from this plane, calculated with XANADU (Roberts & Sheldrick, 1975).

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## References

- AGETA, H., IWATA, K. & NATORI, S. (1963). *Tetrahedron Lett.* pp. 1447–1450.
- CATALANO, S., MARSILI, A., MORELLI, F. & PACCHIANI, M. (1976). *Phytochemistry*, **15**, 1178–1179.
- DAS GUPTA, A. & KHASTGIR, H. N. (1978). *J. Indian Chem. Soc.* **55**, 198.
- ECK, J. (1975). *LSAW*. Programs for crystallographic data reduction and correction. Univ. of Hamburg.
- GEISE, H. J., BUYS, H. R. & MILHOFF, F. C. (1971). *J. Mol. Struct.* **9**, 447–454.
- HAUSEN, B. M. & SCHULZ, K. H. (1978). *Br. J. Dermatol.* **98**, 325–329.
- HORVETH, A., DE SZÖCS, J., ALVARADO, F. & GRANT, D. J. W. (1975). *Phytochemistry*, **14**, 1641–1642.
- JOHNSON, C. K. (1971). ORTEP. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

- KHASTGIR, H. N. & SHOOLERY, J. N. (1978). *J. Indian Chem. Soc.* **55**, 415–418.
- KHOSA, R. L., WAHI, A. K. & MUKHERJEE, A. K. (1978). *Curr. Sci.* **47**, 624.
- MCCANDLISH, L. E. & STOUT, G. H. (1976). *Acta Cryst.* **B32**, 1788–1792.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- NAKANISHI, K., LIN, Y.-Y., KAKISAWA, H., HSÜ, H.-Y. & HSIU, H. C. (1963). *Tetrahedron Lett.* pp. 1451–1457.
- NISHIMOTO, K., ITO, M., NATORI, S. & OHMOTO, T. (1965). *Tetrahedron Lett.* pp. 2245–2251.
- ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1975). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- SILVA, M., HOENEISEN, M. & SAMMES, P. G. (1972). *Phytochemistry*, **11**, 433–434.
- TAKAHASHI, R. & IITAKA, Y. (1972). *Acta Cryst.* **B28**, 764–770.
- WIJ, M. (1978). *Indian J. Chem. Sect. B*, **16**, 644–645.

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## Structure of (2*RS*,5*RS*,8*RS*,11*SR*)-1,4,7,10-Tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane

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**Abstract.**  $C_{44}H_{60}N_4$ , triclinic,  $P\bar{1}$ ,  $a = 11.56$  (1),  $b = 18.60$  (2),  $c = 9.754$  (5) Å,  $\alpha = 105.10$  (6),  $\beta = 106.68$  (4),  $\gamma = 85.00$  (5)°,  $U = 1939.0$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.10$ ,  $D_c = 1.104$  (1) Mg m<sup>-3</sup>. The crystal structure was solved by the Monte Carlo direct method. The 12-membered ring has a distorted square conformation with the methylene groups at the corners.

**Introduction.** This paper is part of a series of investigations on the cyclic tetramers of chiral aziridines. These tetramers can be divided into four geometrical isomers, *viz*  $C_4$ ,  $C_1$ ,  $S_4$  and  $C_i$  (Tsuboyama, Tsuboyama, Uzawa & Higashi, 1974). Among these, the crystal structures of  $C_4$  (*RRRR*-type) (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978*a,b*), and  $C_i$  (*RRSS*-type) (Hiramatsu, Sakurai, Tsuboyama & Tsuboyama, 1979) have been reported. In this paper the structure of the title compound with  $C_1$  symmetry (*RRRS*-type) is described. Triclinic single crystals of the racemic compound (*RRRS* and *SSSR*) were obtained from ethyl acetate solution. A clear colourless plate crystal with dimensions 0.4 × 0.4 × 0.2 mm was used for the study. X-ray diffraction data were measured on a Rigaku AFC four-circle diffractometer, with graphite-monochromatized  $MoK\alpha$  radiation. Within the range  $2\theta \leq 50^\circ$ , 4583 independent reflections with  $|F| > 3\sigma(F)$  were obtained. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied.

The first attempt to solve the structure by *MULTAN* (Main, Woolfson & Germain, 1971) was not successful. The Monte Carlo method (Furusaki, 1979) was then applied using 24 initial sets, and a reasonable solution was obtained through the *FASTAN* part of *MULTAN*.

The structure was refined by the block-diagonal least-squares method. Unit weight was given to all reflections, and anisotropic temperature factors were used for all non-hydrogen atoms. All H atoms were located by a difference Fourier synthesis, and included in the final refinement with isotropic temperature factors. The final *R* index was 5.4%. Atomic parameters are given in Table 1.\*

\* Lists of structure factors and anisotropic temperature factors and a stereodiagram (with the 12-membered ring viewed from the side) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35281 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

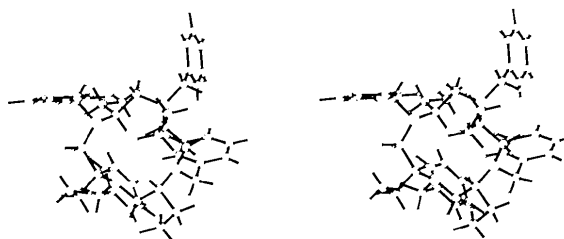


Fig. 1. Stereoscopic drawing of the molecule projected along the normal to the 12-membered ring.