angles around the amide N in (II)–(V) show this atom to be only slightly pyramidal. For this reason we believe it is highly unlikely that there would be slow inversion about the benzoxazine ring N atom. We conclude, therefore, that the second process which is slow on the NMR time scale for (III) at 243 K is ring reversal in the benzoxazine ring, and the structures (*A*)–(*D*) are indeed the four species observed by ^{13}C NMR. Structure (*C*) is the isomer for which the crystal structure has been obtained. It is also the only species in the solid as determined by powder diffraction data.

References

Heine, H. W., Barchiesi, B. J. & Williams, E. A. (1984). *J. Org. Chem.* **49**, 2560–2565.

Pfundt, G. & Farid, S. (1966). *Tetrahedron*, **22**, 2237–2247.

Sheldrick, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

Stewart, W. E. & Sidall, T. H. III (1970). *Chem. Rev.* pp. 517–551.

Williams, E. A., Heine, H. W., Donahue, P. E. & Smith, J. F. (1985). In preparation.

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A New 20,24-Dimethylscalarane Derivative Isolated from the Sponge *Carteriospongia foliascens*, $C_{30}H_{42}O_6$

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Abstract. Methyl 12α-acetoxy-20,24-dimethyl-16,24-dioxoscalara-14,17-dien-25-oate, $M_r = 498{\cdot}66$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}943\ (2)$, $b = 14{\cdot}198\ (5)$, $c = 25{\cdot}232\ (6)$ Å, $V = 2845\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}16$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}85$ cm^{-1}, $F(000) = 1080$, $T = 291$ K, $R = 0{\cdot}053$ for 1676 observed reflections. Particular features of this molecule are the high degree of unsaturation of ring *D* [it contains two double bonds of 1·327 (8) and 1·339 (8) Å] and the presence of an axial ethyl group at the C(4) position.

Introduction. In the course of our work on the chemical defense of sponges, six new 20,24-dimethylscalarane derivatives have been isolated from the ichthyotoxic fraction of the chloroform extract of the marine sponge *Carteriospongia foliascens* (Spongiidae–Dictyoceratida) collected around Laing Island (King Leopold III Biological Station, Laing Island, Papua–New Guinea; contribution No. 78). We describe here the determination of the molecular structure of one of these (1) (Fig. 1), isolated as its methyl ester (2).

Experimental. D_m not measured. Parallelepiped crystal 0·22 × 0·25 × 0·45 mm. Lattice parameters refined using 15 reflections in the range 3° ≤ 2θ ≤ 17°. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 2418 independent *hkl* reflections with $\sin\theta/\lambda \leq 0{\cdot}561$ Å^{-1}, 1676 with $I \geq 2{\cdot}5\sigma(I)$. Standard reflection 201 checked every 50 reflections: no significant variation. No correction for absorption or extinction. Structure solved by *MULTAN*80 (Main, Fiske, Hull,

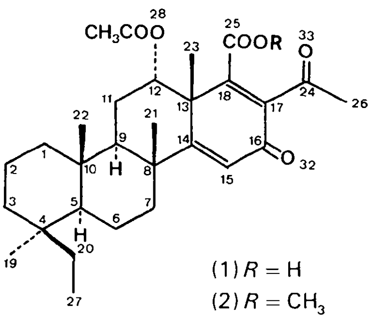

Fig. 1. Scheme of the molecule and atom numbering; also: –O(28)–C(29)[O(31)]–C(30)H_3 and –C(25)[O(34)]–O(35)–C(36)H_3.

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Lessinger, Germain, Declercq & Woolfson, 1980). H atoms in computed positions. Anisotropic least-squares refinement (*SHELX*76, Sheldrick, 1976) using F; H isotropic with common refined temperature factor ($B = 9\cdot4$ Å^2). $w = 1/(\sigma^2 + 0\cdot0011F^2)$. 326 independent parameters refined. $R = 0\cdot053$, $wR = 0\cdot059$, $S = 1\cdot76$ for 1676 observed reflections. Final $(\Delta/\sigma)_{\max} = 0\cdot06$. Max. and min. heights in final difference Fourier synthesis 0·20 and $-0\cdot18$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The absolute configuration is taken to be that found for other scalarane derivatives (Kazlauskas, Murphy, Wells & Daly, 1980). The atomic parameters are given in Table 1.* A local disorder appeared, implying the refinement of two distinct positions for atom O(33). For this reason, this atom was kept isotropic during the refinement. Fig. 2 is a stereoscopic view of the molecule (*PLUTO*, Motherwell & Clegg, 1978).

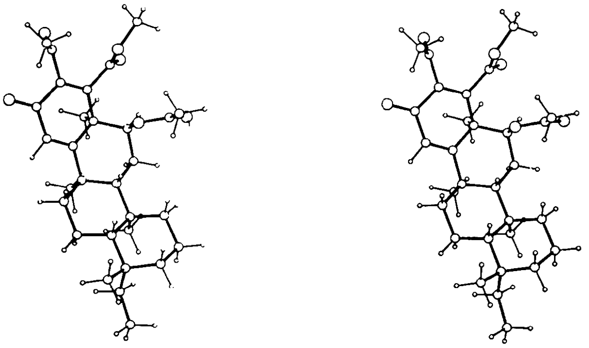

Fig. 2. Stereoscopic view of the molecule.

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic temperature coefficients* (Å^2)

$$B_{eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	324 (10)	4001 (4)	3938 (2)	6·26 (14)
C(2)	23 (13)	5061 (5)	4008 (3)	8·31 (19)
C(3)	1648 (14)	5594 (5)	4046 (3)	8·43 (19)
C(4)	2817 (11)	5469 (4)	3578 (2)	6·28 (15)
C(5)	3036 (9)	4386 (4)	3481 (2)	4·99 (12)
C(6)	4268 (9)	4136 (5)	3041 (3)	5·77 (13)
C(7)	4857 (8)	3111 (5)	3103 (3)	5·79 (14)
C(8)	3389 (7)	2392 (4)	3107 (2)	4·59 (11)
C(9)	2051 (7)	2729 (4)	3507 (2)	4·13 (10)
C(10)	1436 (8)	3779 (4)	3454 (2)	4·58 (11)
C(11)	638 (7)	2002 (4)	3552 (2)	4·31 (11)
C(12)	1275 (7)	1099 (4)	3798 (2)	3·99 (10)
C(13)	2789 (7)	685 (4)	3494 (2)	4·19 (11)
C(14)	4039 (7)	1425 (4)	3299 (2)	4·12 (11)
C(15)	5666 (8)	1216 (5)	3276 (2)	4·82 (12)
C(16)	6377 (8)	317 (5)	3443 (2)	4·66 (12)
C(17)	5273 (8)	−275 (4)	3781 (2)	4·60 (12)
C(18)	3623 (7)	−90 (4)	3813 (2)	4·47 (11)
C(19)	4544 (12)	5874 (5)	3736 (3)	8·80 (19)
C(20)	2165 (11)	5989 (4)	3075 (2)	6·77 (15)
C(21)	2788 (9)	2281 (5)	2523 (2)	6·12 (14)
C(22)	352 (8)	3925 (5)	2952 (3)	6·10 (14)
C(23)	2051 (8)	149 (4)	2990 (2)	5·57 (13)
C(24)	6117 (8)	−1100 (4)	4052 (3)	5·80 (14)
C(25)	2547 (9)	−722 (4)	4142 (3)	5·35 (14)
C(26)	7402 (9)	−920 (6)	4444 (3)	7·27 (17)
C(27)	2066 (12)	7055 (5)	3121 (3)	8·21 (18)
O(28)	1928 (5)	1304 (3)	4328 (1)	4·20 (7)
C(29)	792 (9)	1376 (4)	4720 (2)	5·09 (13)
C(30)	1613 (11)	1650 (6)	5230 (2)	7·71 (17)
O(31)	−677 (6)	1254 (4)	4659 (2)	7·55 (12)
O(32)	7811 (5)	71 (4)	3329 (2)	6·12 (9)
O(33)†	5867 (13)	−1854 (6)	3832 (6)	7·21 (36)
O(33′)‡	5357 (20)	−1908 (9)	4121 (8)	6·45 (55)
O(34)	1292 (6)	−1100 (4)	3986 (2)	7·53 (11)
O(35)	3134 (7)	−828 (3)	4623 (2)	7·48 (11)
C(36)	2296 (13)	−1546 (6)	4946 (3)	9·58 (21)

† Site occupation factor 0·61.
‡ Site occupation factor 0·39.

Table 2. *Bond distances* (Å) *and angles* (°)

C(2)–C(1)	1·533 (8)	C(10)–C(1)	1·538 (8)
C(3)–C(2)	1·500 (12)	C(4)–C(3)	1·512 (11)
C(5)–C(4)	1·567 (8)	C(20)–C(4)	1·557 (9)
C(19)–C(4)	1·539 (10)	C(6)–C(5)	1·521 (9)
C(10)–C(5)	1·537 (8)	C(7)–C(6)	1·537 (9)
C(8)–C(7)	1·550 (8)	C(9)–C(8)	1·541 (8)
C(14)–C(8)	1·545 (8)	C(21)–C(8)	1·557 (7)
C(10)–C(9)	1·574 (7)	C(11)–C(9)	1·530 (7)
C(22)–C(10)	1·546 (8)	C(12)–C(11)	1·511 (7)
C(13)–C(12)	1·543 (8)	O(28)–C(12)	1·463 (6)
C(14)–C(13)	1·527 (8)	C(18)–C(13)	1·515 (8)
C(23)–C(13)	1·594 (8)	C(15)–C(14)	1·327 (8)
C(16)–C(15)	1·457 (8)	C(17)–C(16)	1·485 (8)
O(32)–C(16)	1·226 (7)	C(18)–C(17)	1·339 (8)
C(24)–C(17)	1·512 (9)	C(25)–C(18)	1·492 (9)
C(27)–C(20)	1·520 (9)	C(26)–C(24)	1·444 (9)
O(33′)–C(24)	1·308 (16)	O(33)–C(24)	1·223 (11)
O(34)–C(25)	1·200 (7)	O(35)–C(25)	1·309 (8)
C(29)–O(28)	1·342 (7)	C(30)–C(29)	1·496 (9)
O(31)–C(29)	1·189 (7)	C(36)–O(35)	1·464 (8)

C(10)–C(1)–C(2)	112·4 (5)	C(3)–C(2)–C(1)	111·7 (7)
C(4)–C(3)–C(2)	114·8 (6)	C(5)–C(4)–C(3)	107·8 (5)
C(19)–C(4)–C(3)	107·5 (6)	C(19)–C(4)–C(5)	107·9 (6)
C(20)–C(4)–C(3)	112·1 (7)	C(20)–C(4)–C(5)	112·1 (5)
C(20)–C(4)–C(19)	109·3 (6)	C(6)–C(5)–C(4)	114·4 (5)
C(10)–C(5)–C(4)	117·7 (6)	C(10)–C(5)–C(6)	111·7 (5)
C(7)–C(6)–C(5)	110·0 (5)	C(8)–C(7)–C(6)	113·3 (5)
C(9)–C(8)–C(7)	108·5 (5)	C(14)–C(8)–C(7)	109·6 (5)
C(14)–C(8)–C(9)	107·5 (4)	C(21)–C(8)–C(7)	107·0 (5)
C(21)–C(8)–C(9)	116·1 (5)	C(21)–C(8)–C(14)	108·1 (5)
C(10)–C(9)–C(8)	117·0 (4)	C(11)–C(9)–C(8)	110·2 (4)
C(11)–C(9)–C(10)	114·7 (4)	C(5)–C(10)–C(1)	109·0 (5)
C(9)–C(10)–C(1)	107·8 (4)	C(9)–C(10)–C(5)	105·7 (4)
C(22)–C(10)–C(1)	107·6 (5)	C(22)–C(10)–C(5)	114·9 (5)
C(22)–C(10)–C(9)	111·6 (5)	C(12)–C(11)–C(9)	111·0 (4)
C(13)–C(12)–C(11)	112·3 (5)	O(28)–C(12)–C(11)	109·0 (4)
O(28)–C(12)–C(13)	104·7 (4)	C(14)–C(13)–C(12)	113·9 (5)
C(18)–C(13)–C(12)	110·7 (5)	C(18)–C(13)–C(14)	112·7 (4)
C(23)–C(13)–C(12)	107·0 (4)	C(23)–C(13)–C(14)	108·1 (5)
C(23)–C(13)–C(18)	103·8 (5)	C(13)–C(14)–C(8)	119·7 (5)
C(15)–C(14)–C(8)	120·7 (5)	C(15)–C(14)–C(13)	119·6 (6)
C(16)–C(15)–C(14)	124·1 (6)	C(17)–C(16)–C(15)	115·7 (5)
O(32)–C(16)–C(15)	122·8 (6)	O(32)–C(16)–C(17)	121·4 (6)
C(18)–C(17)–C(16)	120·1 (6)	C(24)–C(17)–C(16)	115·9 (5)
C(24)–C(17)–C(18)	124·0 (6)	C(17)–C(18)–C(13)	122·6 (6)
C(25)–C(18)–C(13)	118·8 (5)	C(25)–C(18)–C(17)	118·4 (6)
C(27)–C(20)–C(4)	115·3 (6)	C(26)–C(24)–C(17)	119·1 (6)
O(33′)–C(24)–C(17)	122·3 (7)	O(33′)–C(24)–C(26)	113·0 (8)
O(33)–C(24)–C(17)	113·6 (7)	O(33)–C(24)–C(26)	125·5 (7)
C(36)–O(35)–C(25)	115·7 (6)	O(34)–C(25)–C(18)	124·2 (7)
O(35)–C(25)–C(18)	112·4 (6)	O(35)–C(25)–O(34)	123·4 (7)
C(29)–O(28)–C(12)	116·7 (4)	C(30)–C(29)–O(28)	111·1 (6)
O(31)–C(29)–O(28)	123·7 (6)	O(31)–C(29)–C(30)	125·2 (6)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42177 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This molecule is remarkable for the high degree of unsaturation of ring *D*: C(14)—C(15) and C(17)—C(18) are typical double bonds with lengths 1·327 (8) and 1·339 (8) Å respectively. Amongst the known scalarane derivatives, only a few possess an ethyl group at C(4). In the present case, this ethyl group was determined in an axial position, in agreement with the X-ray analysis of (20*S*, 24*S*)-20-acetoxy-12β-hydroxy-20,24-dimethyl-25-norscalar-17-ene-18,24-carbolactone isolated from a *Carteriospongia* sp. (Croft, Ghisalberti, Skelton & White, 1983). Kikuchi, Tsukitani, Shimizu, Kobayashi & Kitagawa (1981) isolated foliaspongin from an Okinawan sample of *Carteriospongia foliascens*. On the basis of ^{13}C NMR arguments, they proposed the C(4) ethyl group to be equatorial. Comparison of these ^{13}C NMR data with those of our molecule leads us to correct this attribution and to propose an axial position for the ethyl group in foliaspongin. Bond distances and angles are given in Table 2.

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References

CROFT, K. D., GHISALBERTI, E. L., SKELTON, B. M. & WHITE, A. H. (1983). *J. Chem. Soc. Perkin Trans.* 1, pp. 155–159.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KAZLAUSKAS, R., MURPHY, P. T., WELLS, R. J. & DALY, J. J. (1980). *Aust. J. Chem.* **33**, 1783–1797.

KIKUCHI, H., TSUKITANI, Y., SHIMIZU, I., KOBAYASHI, M. & KITAGAWA, I. (1981). *Chem. Pharm. Bull. Jpn*, **29**, 1492–1494.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for drawing crystal structures. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Crystallographic Studies and Physicochemical Properties of π-Electron Compounds. IV. Structure of 2,5-Dinitrobenzoic Acid (2,5-DNBA), $C_7H_4N_2O_6$

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Abstract. $M_r = 212\cdot12$, monoclinic, $C2/c$, $a = 12\cdot5512\ (9)$, $b = 11\cdot8834\ (9)$, $c = 11\cdot5880\ (9)$ Å, $\beta = 108\cdot882\ (6)°$, $V = 1635\cdot35$ Å^3, $Z = 8$, $D_m = 1\cdot68$, $D_x = 1\cdot681$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1\cdot54178$ Å, $\mu = 13\cdot82$ cm^{-1}, $F(000) = 864$, room temperature. The final R is 0·0359 for 962 counter intensities. The mean e.s.d.'s of bond lengths between the heavy atoms are 0·003 Å. The molecules are paired by hydrogen bonding between the carboxy groups [O—H···O 2·621 (2) Å], the two halves of the dimer being related by a centre of symmetry. The planes of the two carboxy groups in the dimer are separated by 0·023 Å. Non-additivity of substituent effects on the geometry of the benzene ring is observed for angles at C(1), C(5) and C(6) when the Domenicano & Murray-Rust [*Tetrahedron Lett.* (1979), **24**, 2283–2286] angular parameters are applied to DNBA.

Introduction. The crystal and, in particular, molecular structures of dinitrobenzoic acids are of interest because of the strong and naturally similar electronic properties of the substituents. Hence their influence on ring geometry has in recent years often been studied (Colapietro, Domenicano & Marciante, 1982; Więckowski & Krygowski, 1985).

Experimental. Pale-yellow prismatic crystals grown from an aqueous solution of the commercial product (Fluka). Monoclinic symmetry from oscillation and Weissenberg photographs. Crystal, *ca* 0·3 × 0·3 × 0·25 mm, mounted on a Syntex $P2_1$ single-crystal diffractometer. D_m measured at 293 K by flotation in chloroform–bromoform. Systematic absences: hkl $h+k$ odd, $h0l$ l odd, space group $C2/c$ or Cc. Cell constants determined by least-squares treatment of 15 reflexions with 2θ values between 11·7 and 31·2°. Intensities collected at room temperature using Cu $K\alpha$ radiation monochromated by graphite up to $2\theta = 115\cdot0°$, $h = -13$ to 12, $k = 0$ to 12, $l = 0$ to 12. Profile analysis according to Lehmann & Larsen (1974), no significant variation for 2 standard reflexions.

1140 unique intensities collected, of which 962 classified as observed, 54 of them systematically absent, other reflexions being suppressed on the criterion

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