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Références

Baggio, R., Woolfson, M. M., Declercq, J. P. & Germain, G. (1978). *Acta Cryst.* A**34**, 883–892.

Barton, D. H. R. & Kirby, G. W. (1960). *Proc. Chem. Soc.* pp. 392–393.

Barton, D. H. R. & Kirby, G. W. (1962). *J. Chem. Soc.* pp. 806–817.

Boit, H. G. & Döpke, W. (1960). *Naturwissenschaften*, **47**, 109.

Boit, H. G., Döpke, W. & Beitner, A. (1957). *Chem. Ber.* **90**, 2197–2202.

Boit, H. G. & Ehmke, H. (1956). *Chem. Ber.* **89**, 163–167.

Cruickshank, D. W. J. (1965). *Computing Methods in Crystallography*, édité par J. S. Rollett, pp. 113–114. Oxford: Pergamon Press.

Fales, H. M., Giuffrida, L. D. & Wildman, W. C. (1956). *J. Am. Chem. Soc.* **78**, 4145–4150.

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

Klyne, W. & Prelog, V. (1960). *Experientia*, **16**, 521–523.

Laiho, S. M. & Fales, H. M. (1964). *J. Am. Chem. Soc.* **86**, 4434–4438.

Roques, R. & Lapasset, J. (1976). *Acta Cryst.* B**32**, 579–582.

Roques, R., Lapasset, J., Rogers, D. & Williams, D. J. (1976). *Acta Cryst.* B**32**, 3358.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Williams, D. J. & Rogers, D. (1964). *Proc. Chem. Soc.* p. 357.

Acta Cryst. (1980). B**36**, 1593–1598

The Structure of Acetylated Napoleogenin

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Abstract

Acetylated napoleogenin, $C_{58}H_{84}O_{18}$, crystallizes in space group $P2_1$ with two molecules in a unit cell of dimensions $a = 19{\cdot}127\,(1)$, $b = 10{\cdot}812\,(1)$, $c = 14{\cdot}879\,(1)$ Å, $\beta = 102{\cdot}540\,(2)°$. The crystal structure was solved by direct methods. Full-matrix least-squares refinement with all atoms treated isotropically and using 3139 reflections gave an R value of 0·108. The compound possesses a triterpene skeleton with *cis*-fused *D* and *E* rings in the chair form. A 3,4-di-*O*-angelyl-6-deoxy-β-glucopyranosyl group sits at C(21) on the *E* ring. The molecular structure of acetylated napoleogenin is formulated by the present analysis as 21β-(2-*O*-acetyl-3,4-di-*O*-angelyl-6-deoxy-β-glucopyranosyloxy)-3β,16α,22α,24,28-pentaacetoxy-olean-12-ene. The large distortion of the whole molecular skeleton may result from 1,3 diaxial interaction. The packing is mainly dictated by close van der Waals contacts between the molecules.

Introduction

Within the framework of chemical taxonomy studies, the acetylated form of napoleogenin, a new pentacyclic

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triterpene, was isolated from the seeds of *Napoleonaea imperialis*, a plant native to Zaïre. An X-ray crystal-structure investigation of the compound was undertaken in order to establish unequivocally its chemical structure and stereochemistry.

Table 1. *Atomic positional and isotropic thermal parameters with standard deviations in acetylated napoleogenin*

	x	*y*	*z*	*B* (Å^2)
(i) Triterpene nucleus				
C(1)	0·5868 (7)	0·047 (1)	−0·0589 (9)	6·3 (3)
C(2)	0·5595 (8)	0·063 (2)	−0·164 (1)	7·2 (3)
C(3)	0·6094 (7)	−0·002 (2)	−0·214 (1)	6·1 (3)
C(4)	0·6195 (7)	−0·142 (2)	−0·1966 (9)	5·9 (3)
C(5)	0·6442 (6)	−0·159 (1)	−0·1917 (8)	5·1 (2)
C(6)	0·6609 (6)	−0·290 (1)	−0·0571 (8)	4·8 (2)
C(7)	0·7072 (7)	−0·287 (1)	0·0403 (9)	5·5 (3)
C(8)	0·6706 (6)	−0·222 (1)	0·1111 (7)	4·4 (2)
C(9)	0·6418 (6)	−0·094 (1)	0·0712 (7)	4·4 (2)
C(10)	0·5957 (6)	−0·096 (1)	−0·0314 (8)	4·8 (2)
C(11)	0·6039 (7)	−0·027 (2)	0·136 (1)	6·8 (3)
C(12)	0·6383 (7)	−0·045 (2)	0·2365 (9)	5·7 (3)
C(13)	0·6943 (6)	−0·124 (1)	0·2691 (8)	4·8 (2)
C(14)	0·7283 (6)	−0·196 (1)	0·2040 (7)	4·3 (2)
C(15)	0·7571 (6)	−0·319 (1)	0·2482 (8)	5·1 (2)
C(16)	0·7920 (6)	−0·319 (1)	0·3532 (8)	4·7 (2)
C(17)	0·7468 (6)	−0·253 (1)	0·4107 (7)	4·4 (2)
C(18)	0·7208 (6)	−0·124 (1)	0·3740 (8)	4·4 (2)
C(19)	0·7756 (5)	−0·022 (1)	0·4064 (7)	4·4 (2)
C(20)	0·8003 (6)	−0·010 (1)	0·5115 (8)	4·6 (2)
C(21)	0·8372 (5)	−0·137 (1)	0·5414 (7)	3·8 (2)
C(22)	0·7860 (6)	−0·242 (1)	0·5156 (7)	4·5 (2)
(ii) Extranuclear				
C(23)	0·6816 (9)	−0·188 (2)	−0·241 (1)	8·0 (4)
C(24)	0·5513 (7)	−0·207 (1)	−0·244 (1)	6·2 (3)
C(25)	0·5199 (8)	−0·150 (2)	−0·042 (1)	6·8 (3)
C(26)	0·6107 (7)	−0·301 (2)	0·1299 (9)	5·8 (3)
C(27)	0·7924 (6)	−0·117 (1)	0·1880 (8)	5·2 (2)
C(28)	0·6778 (6)	−0·329 (1)	0·4023 (8)	5·1 (2)
C(29)	0·8561 (7)	0·095 (2)	0·531 (1)	6·0 (3)
C(30)	0·7390 (7)	0·020 (2)	0·5577 (9)	5·7 (3)
C(31)	0·5960 (9)	0·132 (2)	−0·348 (1)	7·7 (4)
C(32)	0·553 (1)	0·139 (2)	−0·445 (2)	10·5 (6)
C(33)	0·523 (1)	−0·422 (2)	−0·291 (1)	8·5 (4)
C(34)	0·549 (1)	−0·545 (2)	−0·281 (2)	10·6 (5)
C(35)	0·9223 (7)	−0·314 (2)	0·3678 (9)	5·9 (3)
C(36)	0·983 (1)	−0·231 (2)	0·379 (1)	9·0 (4)
C(37)	0·6493 (9)	−0·545 (2)	0·401 (1)	8·4 (4)
C(38)	0·673 (1)	−0·665 (2)	0·439 (2)	10·7 (5)
C(39)	0·8109 (8)	−0·430 (2)	0·606 (1)	6·9 (3)
C(40)	0·866 (1)	−0·536 (2)	0·617 (1)	9·5 (5)
O(1)	0·5805 (6)	0·018 (1)	−0·3126 (7)	7·7 (2)
O(2)	0·6359 (7)	0·200 (2)	−0·3110 (9)	10·2 (3)
O(3)	0·5631 (6)	−0·340 (1)	−0·2356 (7)	7·5 (2)
O(4)	0·4668 (8)	−0·378 (2)	−0·343 (1)	11·5 (4)
O(5)	0·8612 (4)	−0·252 (1)	0·3665 (5)	4·3 (1)
O(6)	0·9218 (5)	−0·426 (1)	0·3673 (7)	7·7 (2)
O(7)	0·6974 (5)	−0·458 (1)	0·4258 (6)	5·8 (2)
O(8)	0·597 (1)	−0·517 (2)	0·332 (1)	15·3 (5)
O(9)	0·8288 (4)	−0·353 (1)	0·5383 (5)	5·0 (2)
O(10)	0·7681 (7)	−0·412 (1)	0·6413 (8)	9·0 (3)
O(11)	0·8596 (4)	−0·138 (1)	0·6416 (5)	4·5 (1)
(iii) Glucopyranosyl moiety				
C(1′)	0·9320 (6)	−0·128 (1)	0·6775 (7)	4·3 (2)
C(2′)	0·9452 (6)	−0·079 (1)	0·7747 (8)	4·5 (2)
C(3′)	1·0269 (5)	−0·072 (1)	0·8153 (8)	4·7 (2)
C(4′)	1·0603 (6)	−0·192 (1)	0·8042 (8)	4·7 (2)
C(5′)	1.0391 (7)	−0·240 (1)	0·7026 (9)	5·6 (2)
O(1′)	0·9637 (4)	−0·247 (1)	0·6774 (5)	4·7 (1)
C(6′)	1·0692 (8)	−0·370 (2)	0·691 (1)	6·4 (3)
C(7′)	1·1814 (8)	−0·212 (2)	0·897 (1)	6·4 (3)
C(8′)	1·260 (1)	−0·187 (2)	0·893 (1)	8·2 (4)
C(9′)	1.301 (1)	−0·156 (3)	0·977 (2)	11·2 (6)
C(10′)	1·2873 (7)	−0·142 (2)	1·0605 (9)	9·1 (3)
C(11′)	1.279 (1)	−0·192 (3)	0·798 (2)	11·2 (7)
C(7″)	1·0759 (8)	0·047 (2)	0·948 (1)	6·5 (3)
C(8″)	1.078 (1)	0·061 (2)	1·053 (1)	8·8 (5)
C(9″)	1·0416 (7)	0·015 (2)	1·0960 (9)	8.0 (3)
C(10″)	0·9722 (7)	−0·058 (2)	1·0686 (9)	9·1 (3)
C(11″)	1·142 (1)	0·149 (2)	1·093 (1)	8·8 (5)
C(12′)	0·8652 (7)	0·064 (2)	0·817 (1)	6·5 (3)
C(13′)	0·840 (1)	0·196 (2)	0·807 (1)	8·8 (4)
O(2′)	1·1383 (4)	−0·172 (1)	0·8199 (5)	5·6 (2)
O(3′)	1·1558 (8)	−0·258 (2)	0·956 (1)	11·0 (4)
O(2″)	1·0318 (4)	−0·051 (1)	0·9124 (6)	5·6 (2)
O(3″)	1·1033 (8)	0·116 (2)	0·907 (1)	10·0 (3)
O(4′)	0·9187 (4)	0·044 (1)	0·7743 (5)	5·4 (2)
O(5′)	0·8376 (6)	−0·014 (1)	0·8567 (9)	8·9 (3)

Experimental

Colorless needle-shaped crystals, elongated along the *b* axis, were grown from methanol.

The space group was unequivocally established by Weissenberg and precession photographs.

Cell parameters and intensities were measured with a four-circle Hilger diffractometer using Cu $K\alpha$ radiation (λ = 1·5418 Å, ω–2θ scan). Integrated intensities were recorded for 3353 independent reflections. They were corrected for Lorentz and polarization effects but not for absorption (μ for Cu $K\alpha$ = 0·72 mm^{-1}).

The structure was solved by direct methods using *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). A large number of cycles of structure factor and Fourier calculations were necessary to find all the atoms. The oxygen atoms were identified with the help of chemical and structural considerations. Refinement of atomic coordinates and individual isotropic thermal parameters for C and O atoms was carried out by a full-matrix least-squares method (program *SFLS*, Prewitt, 1967) on 3139 reflections for which $I > 2\sigma(I)$. In the last cycles of refinement, H atoms were included in calculated positions assuming C–H bond lengths of 1·087 Å. All were given the same isotropic temperature factor B = 4·0 Å^2. A Cruickshank (1961) type of weighting scheme was used. The final value of the conventional discrepancy factor R is 0·108. We could not carry out further refinement with anisotropic thermal parameters: the large number of variables would have involved too much computing time and expense. Our final positional and thermal parameters are listed in Table 1.*

Discussion

Our structural results indicate that acetylated napoleogenin is a pentacyclic oleanene-type triterpene of the β-amyrin series with a 3,4-di-*o*-angelyl-6-deoxy-β-glucopyranosyl group located on the *E* ring at C(21). Moreover, in the triterpene nucleus, a geminal dimethyl group is situated at C(20) and four other methyl groups at C(4), C(8), C(10) and C(14). Acetyl groups are located at C(3), C(16) and C(22) while two acetoxymethyl groups are found at C(4) and C(17). We deduced that acetylated napoleogenin should be formulated as 21β-(2-*O*-acetyl-3,4-di-*O*-angelyl-6-deoxy-β-glucopyranosyloxy)-3β,16α,22α,24,28-pentaacetoxyolean-12-ene. The numbering of the atoms is illustrated in Fig. 1. The molecular conformation is shown in Fig. 2, a stereodrawing produced by the program *PLUTO* (Crystallographic Data Files, 1979). Bond lengths and angles are listed in Tables 2 and 3.

Table 2. *Bond lengths* (Å) *with standard deviations in parentheses*

(i) Triterpene nucleus		(ii) Extranuclear	
C(1)–C(2)	1·54 (2)	C(3)–O(1)	1·47 (2)
C(1)–C(10)	1·60 (2)	C(4)–C(23)	1·56 (2)
C(2)–C(3)	1·51 (2)	C(4)–C(24)	1·51 (2)
C(3)–C(4)	1·54 (2)	C(8)–C(26)	1·51 (2)
C(4)–C(5)	1·54 (2)	C(10)–C(25)	1·54 (2)
C(5)–C(6)	1·52 (2)	C(14)–C(27)	1·56 (2)
C(5)–C(10)	1·58 (2)	C(16)–O(5)	1·48 (1)
C(6)–C(7)	1·53 (2)	C(17)–C(28)	1·54 (2)
C(7)–C(8)	1·56 (2)	C(20)–C(29)	1·54 (2)
C(8)–C(9)	1·56 (2)	C(20)–C(30)	1·52 (2)
C(8)–C(14)	1·59 (2)	C(21)–O(11)	1·46 (1)
C(9)–C(10)	1·59 (2)	C(22)–O(9)	1·45 (2)
C(9)–C(11)	1·51 (2)	C(31)–O(1)	1·40 (2)
C(11)–C(12)	1·51 (2)	C(31)=O(2)	1·11 (2)
C(12)=C(13)	1·37 (2)	C(31)–C(32)	1·50 (3)
C(13)–C(14)	1·50 (2)	C(33)–O(3)	1·34 (2)
C(13)–C(18)	1·53 (2)	C(33)=O(4)	1·27 (2)
C(14)–C(15)	1·52 (2)	C(33)–C(34)	1·42 (3)
C(15)–C(16)	1·56 (2)	C(35)–O(5)	1·34 (2)
C(16)–C(17)	1·52 (2)	C(35)=O(6)	1·21 (2)
C(17)–C(18)	1·54 (2)	C(35)–C(36)	1·45 (3)
C(17)–C(22)	1·58 (2)	C(37)–O(7)	1·31 (2)
C(18)–C(19)	1·53 (2)	C(37)=O(8)	1·30 (3)
C(19)–C(20)	1·54 (2)	C(37)–C(38)	1·46 (3)
C(20)–C(21)	1·56 (2)	C(39)–O(9)	1·40 (2)
C(21)–C(22)	1·50 (2)	C(39)=O(10)	1·08 (2)
		C(39)–C(40)	1·55 (3)
(iii) Glucopyranosyl moiety			
C(1')–O(11)	1·38 (1)	C(7')–C(8')	1·54 (2)
C(1')–O(1')	1·42 (2)	C(7")–O(2")	1·38 (2)
C(1')–C(2')	1·51 (2)	C(7")=O(3")	1·16 (2)
C(2')–O(4')	1·42 (1)	C(7")–C(8")	1·56 (3)
C(2')–C(3')	1·55 (2)	C(8')–C(11')	1·53 (3)
C(3')–O(2")	1·45 (1)	C(8')=C(9')	1·38 (3)
C(3')–C(4')	1·48 (2)	C(8")–C(11")	1·56 (3)
C(4')–O(2')	1·48 (1)	C(8")=C(9")	1·15 (3)
C(4')–C(5')	1·57 (2)	C(9')–C(10')	1·53 (2)
C(5')–O(1')	1·41 (1)	C(9")–C(10")	1·53 (2)
C(5')–C(6')	1·54 (2)	C(12')–O(4')	1·34 (2)
C(7')–O(2')	1·34 (2)	C(12')=O(5')	1·21 (2)
C(7')=O(3')	1·20 (2)	C(12')–C(13')	1·52 (3)

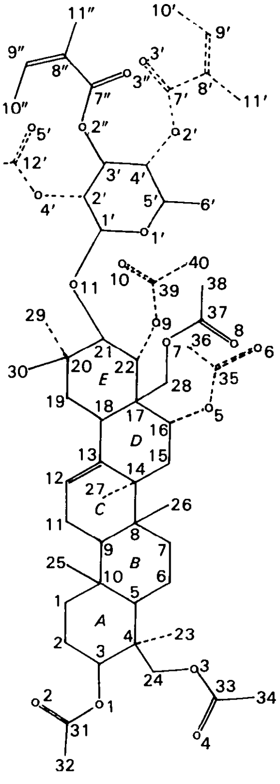

Fig. 1. Numbering of atoms in acetylated napoleogenin.

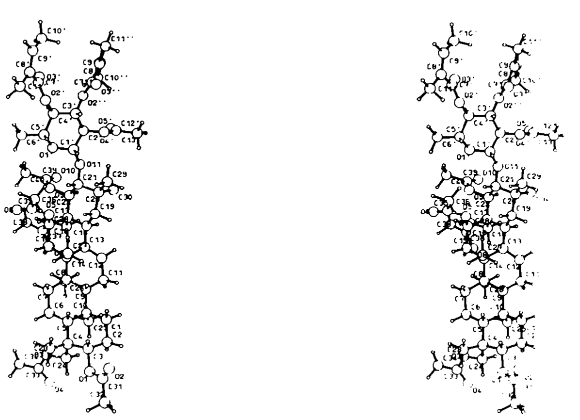

Fig. 2. Stereoscopic drawing of the molecule.

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* Lists of structure factors and hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35161 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles (°) with standard deviations in parentheses*

(i) Triterpene nucleus			
C(2)–C(1)–C(10)	111 (1)	C(12)=C(13)–C(18)	115 (1)
C(1)–C(2)–C(3)	109 (1)	C(14)–C(13)–C(18)	124 (1)
C(2)–C(3)–C(4)	117 (1)	C(8)–C(14)–C(13)	110 (1)
C(2)–C(3)–O(1)	107 (1)	C(8)–C(14)–C(15)	110 (1)
C(4)–C(3)–O(1)	108 (1)	C(8)–C(14)–C(27)	112 (1)
C(3)–C(4)–C(5)	106 (1)	C(13)–C(14)–C(15)	110 (1)
C(3)–C(4)–C(23)	109 (1)	C(13)–C(14)–C(27)	106 (1)
C(3)–C(4)–C(24)	108 (1)	C(15)–C(14)–C(27)	109 (1)
C(5)–C(4)–C(23)	107 (1)	C(14)–C(15)–C(16)	118 (1)
C(5)–C(4)–C(24)	117 (1)	C(15)–C(16)–C(17)	113 (1)
C(23)–C(4)–C(24)	108 (1)	C(15)–C(16)–O(5)	108·0 (9)
C(4)–C(5)–C(6)	117 (1)	C(17)–C(16)–O(5)	107 (1)
C(4)–C(5)–C(10)	116 (1)	C(16)–C(17)–C(18)	114 (1)
C(6)–C(5)–C(10)	108 (1)	C(16)–C(17)–C(22)	113 (1)
C(5)–C(6)–C(7)	110 (1)	C(16)–C(17)–C(28)	107 (1)
C(6)–C(7)–C(8)	114 (1)	C(18)–C(17)–C(22)	110 (1)
C(7)–C(8)–C(9)	109 (1)	C(18)–C(17)–C(28)	105 (1)
C(7)–C(8)–C(14)	110 (1)	C(22)–C(17)–C(28)	109 (1)
C(7)–C(8)–C(26)	110 (1)	C(13)–C(18)–C(17)	112 (1)
C(9)–C(8)–C(14)	107·3 (9)	C(13)–C(18)–C(19)	112 (1)
C(9)–C(8)–C(26)	111 (1)	C(17)–C(18)–C(19)	113 (1)
C(14)–C(8)–C(26)	110 (1)	C(18)–C(19)–C(20)	115 (1)
C(8)–C(9)–C(10)	115 (1)	C(19)–C(20)–C(21)	104 (1)
C(8)–C(9)–C(11)	111 (1)	C(19)–C(20)–C(29)	108 (1)
C(10)–C(9)–C(11)	112 (1)	C(19)–C(20)–C(30)	112 (1)
C(1)–C(10)–C(5)	108 (1)	C(21)–C(20)–C(29)	110 (1)
C(1)–C(10)–C(9)	104 (1)	C(21)–C(20)–C(30)	114 (1)
C(1)–C(10)–C(25)	107 (1)	C(29)–C(20)–C(30)	109 (1)
C(5)–C(10)–C(9)	106 (1)	C(20)–C(21)–C(22)	112 (1)
C(5)–C(10)–C(25)	116 (1)	C(20)–C(21)–O(11)	108·5 (9)
C(9)–C(10)–C(25)	115 (1)	C(22)–C(21)–O(11)	106·4 (9)
C(9)–C(11)–C(12)	114 (1)	C(17)–C(22)–C(21)	117 (1)
C(11)–C(12)–C(13)	125 (1)	C(17)–C(22)–O(9)	107·2 (9)
C(12)=C(13)–C(14)	121 (1)	C(21)–C(22)–O(9)	105·4 (9)
(ii) Extranuclear			
C(24)–O(3)–C(24)	123 (1)	O(4)–C(33)–C(34)	131 (2)
C(16)–O(5)–C(35)	121 (1)	O(5)–C(35)–O(6)	120 (1)
C(28)–O(7)–C(28)	119 (1)	O(5)–C(35)–C(36)	111 (1)
C(21)–O(11)–C(1′)	116·3 (9)	O(6)=C(35)–C(36)	129 (2)
C(4)–C(24)–O(3)	109 (1)	O(7)–C(37)=O(8)	116 (2)
C(17)–C(28)–O(7)	109 (1)	O(7)–C(37)–C(38)	113 (2)
O(1)–C(31)=O(2)	125 (2)	O(8)=C(37)–C(38)	129 (2)
O(1)–C(31)–C(32)	106 (2)	O(9)–C(39)–O(10)	125 (2)
O(2)=C(31)–C(32)	128 (2)	O(9)–C(39)–C(40)	104 (1)
O(3)–C(33)=O(4)	115 (2)	O(10)=C(39)–C(40)	130 (2)
O(3)–C(33)–C(34)	114 (2)		
(iii) Glucopyranosyl moiety			
O(11)–C(1′)–C(2′)	110 (1)	C(2′)–O(4′)–C(12′)	117 (1)
O(11)–C(1′)–O(1′)	108·8 (9)	O(2′)–C(7′)–O(3′)	119 (2)
C(2′)–C(1′)–O(1′)	109 (1)	O(2′)–C(7′)–C(8′)	109 (1)
C(1′)–C(2′)–C(3′)	110 (1)	O(3′)–C(7′)–C(8′)	132 (2)
C(1′)–C(2′)–C(4′)	110 (1)	O(2″)–C(7″)–O(3″)	126 (2)
C(3′)–C(2′)–O(4′)	106·3 (9)	O(2″)–C(7″)–C(8″)	110 (1)
C(2′)–C(3′)–C(4′)	110 (1)	O(3″)–C(7″)–C(8″)	124 (2)
C(2′)–C(3′)–O(2″)	104 (1)	C(7′)–C(8′)=C(9′)	112 (2)
C(4′)–C(3′)–O(2′)	108 (1)	C(7′)–C(8′)–C(11′)	118 (2)
C(3′)–C(4′)–C(5′)	112 (1)	C(9′)=C(8′)–C(11′)	130 (2)
C(3′)–C(4′)–O(2′)	108 (1)	C(7″)–C(8″)–C(9″)	129 (2)
O(2′)–C(4′)–C(5′)	104 (1)	C(7″)–C(8″)–C(11″)	106 (2)
C(4′)–C(5′)–C(6′)	113 (1)	C(9″)=C(8″)–C(11″)	125 (2)
C(4′)–C(5′)–O(1′)	108 (1)	C(8′)=C(9′)–C(10′)	134 (2)
C(8′)–C(5′)–O(1′)	108 (1)	C(8″)=C(9″)–C(10″)	132 (2)
C(1′)–O(1′)–C(1′)	111·6 (9)	O(4′)–C(12′)=O(5′)	125 (1)
C(4′)–O(2′)–C(7′)	120 (1)	O(4′)–C(12′)–C(13′)	112 (1)
C(3′)–O(2″)–C(7″)	114 (1)	O(5′)=C(12′)–C(13′)	123 (2)

In the triterpene skeleton, several C–C bonds [C(1)–C(10); C(5)–C(10); C(8)–C(14); C(9)–C(10); C(17)–C(22)] deviate from the mean value of 1·54 Å. it seems significant that all these long C–C bonds are attached to at least one of the fully substituted carbon atoms [C(8), C(10), C(14) and C(17)]. Several C–C–C angles also deviate from the accepted value of 109·3°. The degrees of substitution of the carbon atoms and long-range steric strain in the structure (see below) seem to be responsible for these deviations.

The C(12)–C(13) bond [1·37 (2) Å] is shorter than the remainder of the ring-system bonds and corresponds to the expected location of the double bond in oleanene triterpenes.

In Table 4, the conformation of the ring system is analyzed in terms of the least-squares planes and interplanar angles. The equations of the least-squares planes were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959). The torsional angles in the ring system are given in Table 5(i). From Tables 4 and 5, it is clear that the rings *A*, *B*, *D* and *E* take a

Table 4. *Least-squares planes*

(*a*) Equations of the planes

Plane *A* C(1), C(2), C(3), C(4), C(5), C(10)

$$-0{\cdot}8682x - 0{\cdot}4203y - 0{\cdot}2637z + 9{\cdot}6570 = 0$$

Plane *B* C(5), C(6), C(7), C(8), C(9), C(10)

$$-0{\cdot}8343x - 0{\cdot}5346y + 0{\cdot}1344z + 9{\cdot}2884 = 0$$

Plane *C* C(8), C(9), C(11), C(12), C(13), C(14)

$$-0{\cdot}7409x - 0{\cdot}6612y + 0{\cdot}1178z + 7{\cdot}8474 = 0$$

Plane *D* C(13), C(14), C(15), C(16), C(17), C(18)

$$-0{\cdot}8455x - 0{\cdot}5273y - 0{\cdot}0838z + 10{\cdot}3836 = 0$$

Plane *E* C(17), C(18), C(19), C(20), C(21), C(22)

$$-0{\cdot}8856x + 0{\cdot}1556y + 0{\cdot}4376z + 9{\cdot}1570 = 0$$

Plane *F* C(21), O(11), C(1′)

$$0{\cdot}0951x - 0{\cdot}9953y - 0{\cdot}0203z - 2{\cdot}6655 = 0$$

Plane *G* C(1′), C(2′), C(3′), C(4′), C(5′), O(1′)

$$-0{\cdot}4992x - 0{\cdot}6567y + 0{\cdot}5653z + 1{\cdot}0736 = 0$$

(*b*) Deviations (Å) from the least-squares planes

Plane *A*		Plane *B*		Plane *C*	
C(1)	−0·24 (1)	C(5)	−0·50 (1)	C(8)	0·38 (1)
C(2)	0·25 (2)	C(6)	0·15 (1)	C(9)	−0·29 (1)
C(3)	−0·24 (2)	C(7)	−0·15 (1)	C(11)	0·04 (2)
C(4)	0·22 (1)	C(8)	0·39 (1)	C(12)	0·09 (1)
C(5)	−0·23 (1)	C(9)	−0·08 (1)	C(13)	−0.004 (1)
C(10)	0·23 (1)	C(10)	0·19 (1)	C(14)	−0·23 (1)
O(1)	0·26 (1)	C(25)	1·66 (2)	C(26)	1·88 (1)
C(23)	−0·56 (2)	C(26)	1·89 (1)	C(27)	−1·77 (1)
C(24)	1·69 (1)				
C(25)	1·75 (2)				

Plane *D*		Plane *E*		Plane *G*	
C(13)	0·11 (1)	C(17)	−0·13 (1)	C(1′)	−0·26 (1)
C(14)	−0·12 (1)	C(18)	0·18 (1)	C(2′)	0·22 (1)
C(15)	0·17 (1)	C(19)	−0·27 (1)	C(3′)	−0·21 (1)
C(16)	−0·23 (1)	C(20)	0·30 (1)	C(4′)	0·21 (1)
C(17)	0·21 (1)	C(21)	−0·26 (1)	C(5′)	−0·24 (1)
C(18)	−0·16 (1)	C(22)	0·19 (1)	O(1′)	0·28 (1)
C(27)	−1·63 (1)	C(28)	0·83 (1)	O(11)	0·15 (1)
O(5)	−1·71 (1)	C(29)	−0·29 (1)	O(4′)	−0·40 (1)
C(28)	1·75 (1)	C(30)	1·81 (1)	O(2″)	0·54 (1)
		O(11)	0·28 (1)	O(2′)	−0·52 (1)
		O(9)	−0·52 (1)	C(6′)	0·28 (2)

(*c*) Interplanar angles (°)

A/*B*	156·0 (4)	*D*/*E*	129·1 (3)
B/*C*	170·9 (4)	*E*/*F*	75·6 (2)
C/*D*	164·9 (4)	*F*/*G*	126·5 (3)

Table 5. *Torsional angles* (°)

(i) Triterpene nucleus		C(8)–C(9)–C(11)–C(12)	37·0 (1)	(ii) Glucopyranosyl ring	
C(10)–C(1)–C(2)–C(3)	55·6 (2)	C(9)–C(11)–C(12)–C(13)	6·5 (1)	O(1′)–C(1′)–C(2′)–C(3′)	58·6 (2)
C(1)–C(2)–C(3)–C(4)	58·1 (2)	C(11)–C(12)–C(13)–C(14)	2·0 (1)	C(2′)–C(1′)–O(1′)–C(5′)	−67·1 (3)
C(2)–C(3)–C(4)–C(5)	54·8 (2)	C(12)–C(13)–C(14)–C(15)	−150·0 (3)	C(1′)–C(2′)–C(3′)–C(4′)	−54·2 (2)
C(3)–C(4)–C(5)–C(10)	−53·6 (2)	C(18)–C(13)–C(14)–C(15)	32·3 (2)	C(2′)–C(3′)–C(4′)–C(5′)	−53·0 (2)
C(10)–C(5)–C(6)–C(7)	64·9 (2)	C(14)–C(13)–C(18)–C(17)	−35·8 (2)	C(3′)–C(4′)–C(5′)–O(1′)	−56·9 (2)
C(4)–C(5)–C(10)–C(9)	−165·5 (4)	C(13)–C(14)–C(15)–C(16)	37·4 (2)	C(4′)–C(5′)–O(1′)–C(1′)	63·8 (3)
C(6)–C(5)–C(10)–C(1)	171·9 (3)	C(14)–C(15)–C(16)–C(17)	48·5 (3)		
C(6)–C(5)–C(10)–C(9)	61·1 (2)	C(15)–C(16)–C(17)–C(18)	50·4 (3)	(iii) Angelyl groups	
C(5)–C(6)–C(7)–C(8)	60·3 (2)	C(16)–C(17)–C(18)–C(13)	42·9 (3)	C(4′)–C(3′)–O(2″)–C(7″)	113·4 (3)
C(6)–C(7)–C(8)–C(9)	50·4 (2)	C(16)–C(17)–C(18)–C(19)	83·5 (3)	O(2″)–C(7″)–C(8″)–C(9″)	−11·60 (2)
C(7)–C(8)–C(9)–C(10)	50·5 (2)	C(22)–C(17)–C(18)–C(13)	−169·1 (3)	O(3″)–C(7″)–C(8″)–C(11″)	−19·54 (2)
C(7)–C(8)–C(9)–C(11)	179·7 (4)	C(22)–C(17)–C(18)–C(19)	42·6 (3)	C(11″)–C(8″)–C(9″)–C(10″)	171·14 (3)
C(14)–C(8)–C(9)–C(10)	169·1 (3)	C(18)–C(17)–C(22)–C(21)	43·1 (2)	C(3′)–C(4′)–O(2′)–C(7′)	106·8 (4)
C(14)–C(8)–C(9)–C(11)	−61·7 (2)	C(17)–C(18)–C(19)–C(20)	56·7 (3)	O(2′)–C(7′)–C(8′)–C(9′)	144·3 (4)
C(9)–C(8)–C(14)–C(13)	56·3 (1)	C(18)–C(19)–C(20)–C(21)	−62·2 (3)	O(3′)–C(7′)–C(8′)–C(11′)	149·1 (3)
C(11)–C(9)–C(10)–C(1)	61·5 (2)	C(19)–C(20)–C(21)–C(22)	59·6 (3)	C(11′)–C(8′)–C(9′)–C(10′)	174·6 (4)

chair conformation while the *C* ring adopts a half-chair conformation as a result of the double bond between C(12) and C(13). The junctions of the *A*/*B* and *B*/*C* rings are in the *trans* form while that between the *D* and *E* rings is *cis*. The rings *B*, *D* and *E* are significantly distorted as is the whole molecular skeleton. These distortions seem to be caused mainly by the interactions between the bulky axial groups [at C(4), C(8), C(10) on one hand and at C(14) and C(16) on the other] which push each other away in order to release the repulsive forces. Actually, the non-bonded distances between 1,3 diaxial groups are larger than the expected values in non-distorted rings. We have reported these distances in Table 6. In a regular chair-form six-membered ring, the non-bonded distances between 1,3 diaxial groups would be 2·52 Å. These distances are here increased to, for example, 3·27 (2) Å [C(24)···C(25)].

The distortion of ring *C* from a regular half-chair conformation may be due to the degree of substitution at C(8) and C(14). Also resulting from 1,3 diaxial interaction is the distortion of the whole molecule. As shown by the angles between the mean planes of the rings *A*, *B*, *C* and *D*, the triterpene skeleton is convex towards the axial groups C(24), C(25), C(26) and C(28). On the other hand there is twisting between rings *E* and *D* about the long direction of the molecule. The reason for this distortion appears to be the *cis D*/*E* ring junction and the steric effect of the three bulky axial acetate groups situated at C(16), C(17) and C(22). A similar conformation of the triterpenic nucleus has been previously observed in gymnemagenin by Hoge & Nordman (1974).

The glucopyranosyl ring has an almost regular chair conformation with all the substituent groups in equatorial positions. The bond distances agree with the values reported for *β*-D-glucose (Chu & Jeffrey, 1968) with one exception: the C(3′)–C(4′) bond is significantly shorter in comparison with the accepted value of 1·54 Å. Moreover, the two angles C(2′)–C(3′)–O(2″) and C(5′)–C(4′)–O(2′) differ from the tetrahedral angle of 109·5°. Steric strain resulting from the two long angelyl side chains situated at C(3′) and C(4′) could be responsible for these unusual values. Indeed, these angelyl groups, in order to overcome any overlapping, are rotated with respect to each other by

Table 6. *Some non-bonded distances* (Å) *between 1,3 diaxial groups*

C(24)···C(25)	3·27 (2)
C(25)···C(26)	3·20 (2)
C(27)···O(5)	3·06 (2)
O(5)···O(9)	2·97 (1)

Table 7. *Shortest intermolecular distances* (Å) *with standard deviations in parentheses*

Key to symmetry operations relating designated atoms to reference atoms at (x,y,z):

(i) $\bar{x}+1, \frac{1}{2}+y, \bar{z}$
(ii) $\bar{x}+2, \frac{1}{2}+y, \bar{z}+1$
(iii) $x, y, z+1$
(iv) $\bar{x}+1, \frac{1}{2}+y, \bar{z}+1$
(v) $x, y-1, z$
(vi) $\bar{x}+2, \frac{1}{2}+y, \bar{z}+2$.

C(2)···O(8^{i})	3·56 (3)	C(30)···O(2^{iii})	3·63 (2)
C(7)···O($3^{\prime\prime\,\mathrm{ii}}$)	3·69 (2)	C(32)···O(4^{iv})	3·10 (3)
C(12)···C(33^{i})	3·60 (2)	C(34)···O(2^{v})	3·30 (3)
C(12)···O(4^{i})	3·35 (2)	C(36)···C(40^{ii})	3·57 (3)
C(23)···O(10^{iii})	3·60 (2)	C(38)···O(4^{i})	3·58 (3)
C(23)···O($5^{\prime\,\mathrm{iii}}$)	3·56 (2)	O(1)···O(8^{i})	3·36 (2)
C(24)···O(8^{i})	3·52 (3)	O(6)···C($3^{\prime\,\mathrm{ii}}$)	3·46 (2)
C(29)···C(36^{ii})	3·61 (3)	O(6)···C($5^{\prime\,\mathrm{ii}}$)	3·68 (2)
C(30)···C(31^{iii})	3·55 (2)	C(13′)···O($3^{\prime\,\mathrm{vi}}$)	3·54 (3)

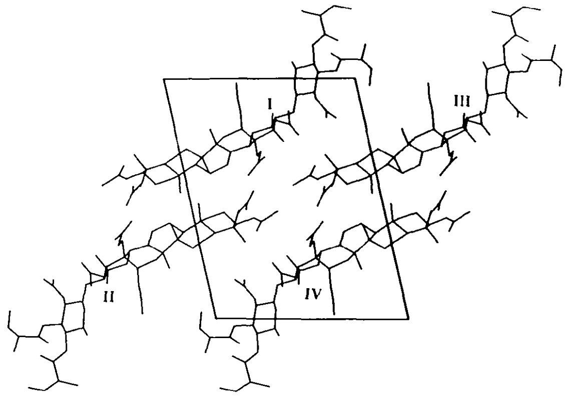

Fig. 3. Projection of the acetylated napoleogenin structure along the *b* axis. The positions of the molecules are; (I) at x, y, z; (II) at $\bar{x}+1, \frac{1}{2}+y, z$; (III) at $x, y, z+1$; (IV) at $x+1, \frac{1}{2}+y, \bar{z}+1$ with x, y and z coordinates given in Table 1.

about 180° about the C(7')–C(8') bond [the corresponding torsional angles are reported in Table 5(iii)].

One should also notice that in both angelyl and acetyl groups, the accuracy of bond lengths and valency angles is highly restricted by a large thermal motion of the end-chain atoms.

A packing diagram of the crystal structure viewed along the *b* axis is shown in Fig. 3. The intermolecular distances less than 3·7 Å are reported in Table 7. There is no abnormal feature in the packing, which appears to be dictated mainly by close van der Waals contacts between the molecules.

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References

CHU, S. S. C. & JEFFREY, G. A. (1968). *Acta Cryst.* **B24**, 830–838.

CRUICKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. Oxford: Pergamon Press.

Crystallographic Data Files (1979). *PLUTO*. Crystallographic Data Centre, Univ. Chemical Laboratory, Cambridge, England.

HOGE, R. & NORDMAN, C. E. (1974). *Acta Cryst.* **B30**, 1435–1440.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England.

PREWITT, C. T. (1967). *SFLS*. State Univ. of New York, Stony Brook, Long Island, New York 11794, USA.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.

Acta Cryst. (1980). **B36**, 1598–1601

The Structure of 2-Amino-5-nitrophenol: a Comparison with 2-Aminophenol

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Abstract

The crystal structure of 2-amino-5-nitrophenol has been determined from visually estimated Cu $K\alpha$ data, and refined to an R value of 0·072 for 1138 non-zero reflexions. The crystals are monoclinic, $P2_1/c$, with $a = 8{\cdot}49\,(1)$, $b = 10{\cdot}34\,(1)$, $c = 8{\cdot}05\,(1)$ Å, $\beta = 113{\cdot}1\,(1)^\circ$ and $Z = 4$. The molecules, related by a glide plane, are held together by $\text{O—H}\cdots\text{NH}_2$ hydrogen bonds [$\text{O}\cdots\text{N}$ 2·801 (3), $\text{H}\cdots\text{N}$ 1·89 (4) Å, $\text{O—H}\cdots\text{N}$ 174 (3)°] to form a ribbon along **c**. The ribbons are held together by dipole–dipole interactions between the molecules related by $\bar{1}$, as found commonly in mononitrophenols. The morphotropism in mononitrophenols and aminophenols is discussed.

Introduction

As part of a programme of studies on the crystal and molecular structures of phenols (Kagawa, Kawai, Kashino & Haisa, 1976) and the systemization of organic crystals (Haisa, 1978), the structure of 2-amino-5-nitrophenol has been determined in order to

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