Acta Cryst. (1977). B33, 261–263

Papyriogenin-A

BY SAKAE AMAGAYA, MAKOTO TAKAI AND YUKIO OGIHARA

Faculty of Pharmaceutical Sciences, Nagoya City University, Mizuhoku, Nagoya, Japan

AND YOICHI IITAKA

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan

(*Received* 21 *July* 1976; *accepted* 17 *August* 1976)

Abstract. $C_{30}H_{42}O_4$, m.p. 262–264 °C, orthorhombic, space group $P2_12_12_1$, with $a = 18{\cdot}308(9)$, $b = 21{\cdot}44(1)$, $c = 6{\cdot}562(3)$ Å, $Z = 4$, $d_x = 1{\cdot}234$ g cm^{-3}. The structure was solved by direct methods and refined to an R value of 0·053 for 1688 observed reflexions. The chemical structure of papyriogenin-A has been established as 3,21-dioxooleana-11,13(18)-dien-28-oic acid.

Introduction. Papyriogenin-A is the main sapogenin obtained by acid hydrolysis of papyrioside L-II, which was isolated from *Tetrapanax papyriferum* (Araliaceae). On the basis of the chemical and spectroscopic data, papyriogenin-A was shown to be a new pentacyclic triterpene having a heteroannular diene, a carboxyl and two carbonyl groups.

The crystals were grown from an aqueous methanol

Table 1. *Atomic parameters of the heavy atoms*

All parameters are multiplied by 10^4. Temperature factors are of the form: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2027 (3)	4155 (2)	10303 (10)	17 (2)	16 (1)	344 (20)	−1 (1)	30 (5)	3 (5)
C(2)	1293 (3)	3819 (3)	10731 (13)	15 (2)	22 (2)	568 (29)	−3 (1)	18 (6)	−15 (6)
C(3)	1203 (3)	3279 (3)	9398 (14)	15 (2)	34 (2)	508 (28)	−8 (2)	4 (7)	−38 (7)
C(4)	1830 (3)	2814 (2)	9101 (10)	23 (2)	19 (1)	272 (18)	−6 (1)	−6 (5)	−1 (5)
C(5)	2561 (3)	3184 (2)	8862 (9)	18 (1)	14 (1)	208 (15)	−2 (1)	0 (4)	1 (4)
C(6)	3244 (3)	2779 (2)	8665 (10)	25 (2)	12 (1)	266 (17)	−1 (1)	−2 (5)	2 (4)
C(7)	3892 (3)	3151 (2)	7869 (9)	21 (2)	15 (1)	227 (16)	1 (1)	2 (5)	−20 (4)
C(8)	4084 (2)	3721 (2)	9197 (8)	17 (1)	13 (1)	196 (15)	0 (1)	−6 (4)	−5 (4)
C(9)	3368 (3)	4092 (2)	9617 (8)	16 (1)	15 (1)	171 (13)	−1 (1)	−1 (4)	−6 (4)
C(10)	2688 (3)	3723 (2)	10439 (8)	17 (2)	14 (1)	196 (14)	0 (1)	4 (4)	2 (4)
C(11)	3543 (3)	4680 (2)	10741 (10)	20 (2)	14 (1)	266 (17)	1 (1)	21 (5)	−19 (4)
C(12)	4198 (3)	4953 (2)	10697 (9)	20 (2)	14 (1)	224 (16)	1 (1)	8 (5)	−14 (4)
C(13)	4817 (3)	4715 (2)	9520 (8)	17 (1)	12 (1)	169 (13)	1 (1)	3 (4)	−2 (4)
C(14)	4627 (2)	4180 (2)	8064 (8)	15 (1)	13 (1)	144 (13)	2 (1)	−5 (4)	−3 (3)
C(15)	5318 (3)	3835 (2)	7419 (8)	20 (2)	18 (1)	169 (14)	1 (1)	3 (4)	−24 (4)
C(16)	5910 (3)	4274 (3)	6684 (9)	19 (2)	23 (1)	217 (16)	−5 (1)	12 (5)	−31 (4)
C(17)	6120 (3)	4756 (2)	8307 (9)	17 (1)	18 (1)	223 (16)	−3 (1)	11 (4)	−10 (4)
C(18)	5494 (3)	4967 (2)	9671 (8)	20 (2)	13 (1)	161 (13)	−1 (1)	−7 (4)	3 (4)
C(19)	5703 (3)	5482 (2)	11100 (8)	19 (1)	17 (1)	190 (14)	−1 (1)	−3 (4)	−6 (4)
C(20)	6008 (3)	6072 (2)	10007 (9)	19 (2)	17 (1)	271 (18)	−3 (1)	3 (5)	−5 (4)
C(21)	6600 (3)	5880 (3)	8605 (10)	32 (2)	21 (1)	278 (19)	−8 (1)	20 (6)	−4 (5)
C(22)	6406 (4)	5329 (3)	7190 (11)	45 (3)	25 (2)	301 (21)	−13 (2)	73 (7)	−23 (5)
C(23)	1685 (4)	2451 (3)	7109 (11)	31 (2)	29 (2)	347 (22)	−5 (2)	−19 (6)	−27 (6)
C(24)	1819 (4)	2353 (3)	10830 (12)	54 (3)	33 (2)	349 (23)	−21 (2)	6 (8)	20 (6)
C(25)	2787 (3)	3519 (3)	12649 (9)	27 (2)	28 (2)	165 (15)	−5 (2)	11 (5)	3 (5)
C(26)	4455 (3)	3484 (3)	11183 (9)	23 (2)	20 (1)	207 (16)	5 (1)	−3 (5)	3 (4)
C(27)	4273 (3)	4480 (3)	6179 (9)	21 (2)	21 (1)	178 (14)	−2 (1)	−7 (5)	15 (4)
C(28)	6748 (3)	4471 (3)	9541 (12)	22 (2)	29 (2)	442 (25)	6 (2)	−28 (6)	−62 (6)
C(29)	5407 (4)	6389 (3)	8804 (13)	40 (2)	25 (2)	409 (26)	0 (2)	−25 (8)	18 (6)
C(30)	6300 (3)	6529 (3)	11656 (12)	28 (2)	22 (2)	358 (23)	−3 (1)	4 (6)	−27 (5)
O(1)	631 (3)	3205 (4)	8527 (16)	33 (2)	90 (3)	1174 (45)	8 (2)	−72 (9)	−184 (11)
O(2)	7188 (2)	6140 (2)	8474 (9)	39 (2)	27 (1)	585 (21)	−16 (1)	73 (5)	−38 (5)
O(3)	6584 (2)	4232 (2)	11262 (8)	39 (2)	29 (1)	367 (16)	0 (1)	−17 (5)	29 (4)
O(4)	7358 (2)	4460 (4)	8838 (10)	25 (2)	107 (3)	443 (20)	23 (2)	−18 (5)	−75 (8)

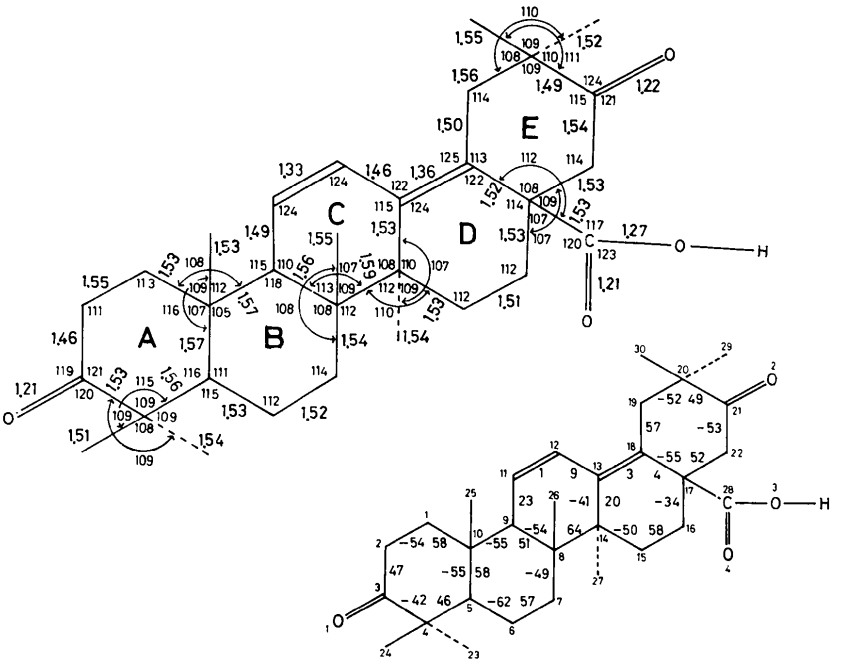

Fig. 1. Bond lengths (Å), bond angles (°) and endocyclic torsion angles (°).

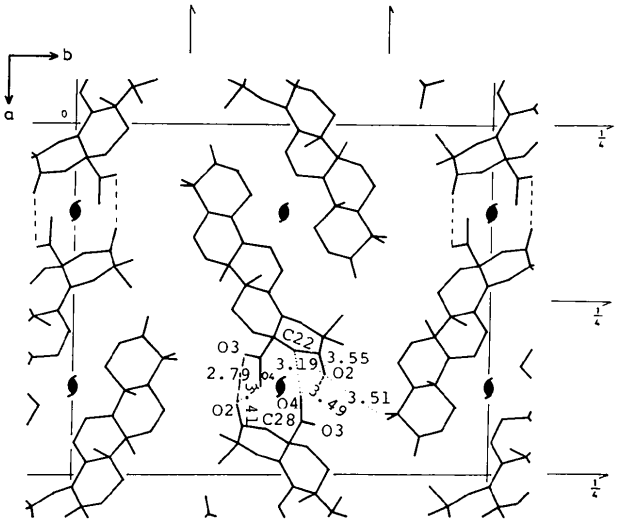

Fig. 2. Projection of the crystal structure along c. Hydrogen bonds are shown by broken lines and intermolecular contacts shorter than 3·6 Å by dotted lines.

solution as colourless prisms. A total of 1688 independent structure factors within $2\theta = 135°$ were collected on a Philips four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Intensities were measured by the θ–2θ scan method with a 2θ scan speed of 4° min^{-1}. The scans were repeated twice when the total counts during a single scan were less than 10^4. The background was measured at each end of the scan for half the total scan time. The intensities were corrected for Lorentz and polarization factors but not for absorption.

The structure was solved by the multisolution technique with *MULTAN* (Main, Woolfson & Germain, 1971). One of the solutions, based on 191 phases with E values greater than 1·4, gave an E map which showed the locations of 25 non-hydrogen atoms in the molecule. The whole structure was revealed by the subsequent difference Fourier synthesis. Refinement of the structure was carried out by the block-diagonal least-squares method (Okaya & Ashida, 1967). 41 H atoms out of 42 could be located on the difference electron density map calculated at the stage when $R = 0{\cdot}082$. Subsequent least-squares refinement including all the atoms except the H atom of the carboxylic acid gave an R value of 0·053. The weighting scheme was $\sqrt{w} = 30/F_o$, when $F_o > 30$; $w = 1$, when $3 < F_o \leq 30$; $\sqrt{w} = 0{\cdot}25$, when $F_o \leq 3$. The final atomic coordinates are listed in Table 1.*

Discussion. The present X-ray analysis established the structure of papyriogenin-A as 3,21-dioxooleana-11,13(18)-dien-28-oic acid in accordance with the results of chemical and spectroscopic studies. The structure belongs to a partially modified oleanane-type

* The atomic parameters of the hydrogen atoms and the list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32061 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

triterpene having *trans* fusion of the *A*/*B* and *B*/*C* rings. As is clear from the endocyclic torsion angles (Fig. 1) each of the *A*, *B* and *E* rings takes a chair form. The atoms C(9), C(11), C(12), C(13), C(14), C(18), C(19), C(17) and C(16) lie roughly on a plane and the heteroannular diene group is on this plane extending from the *C* to the *D* ring. The bond lengths and angles and the endocyclic torsion angles along the bonds involved in the *A*, *B*, *C*, *D* and *E* rings are shown in Fig. 1. The mean estimated standard deviations in the interatomic distances are 0·008 Å for C–C and 0·008 Å for C–O and those in the bond angles are 0·4° for tetrahedral C–C–C bonds. The mean values of C–C bonds and C–H bond lengths are 1·514 and 0·96 Å respectively.

The projection of the crystal structure viewed along **c** is shown in Fig. 2. The short intermolecular distances less than 3·6 Å are also shown in this figure. The existence of the intermolecular hydrogen bond between O(3)–H and O(2) [the distance between O(3) and O(2) is 2·791 Å] inhibits the association of the carboxyl groups, which explains a high-frequency C=O stretching absorption at 1730 cm^{-1} comparable to that of oleanolic acid (1690 cm^{-1}).

References

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN, a Computer Program for the Automatic Solution of Crystal Structures*, Univs. of York (England) and Leuven (Belgium).

OKAYA, Y. & ASHIDA, T. (1967). *HBLS* IV, *The Universal Crystallographic Computing System* (I), p. 65. Tokyo: The Crystallographic Society of Japan.

Acta Cryst. (1977). B**33**, 263–265

Variscite

BY RÜDIGER KNIEP, DIETRICH MOOTZ AND ANGEL VEGAS*

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstrasse 1, 4000 *Düsseldorf, Germany (BRD)*

(*Received* 5 *August* 1976; *accepted* 21 *August* 1976)

Abstract. $AlPO_4.2H_2O$, orthorhombic, *Pbca*, $a = 9·822\,(3)$, $b = 8·561\,(3)$, $c = 9·630\,(3)$ Å, $Z = 8$, $D_x = 2·59$ g cm^{-3}. Material from Montgomery County, Arkansas, USA. PO_4 tetrahedra share vertices with four $AlO_4(OH_2)_2$ octahedra and *vice versa*, resulting in a three-dimensional network which shows relations to the metavariscite ($AlPO_4.2H_2O$, monoclinic) structure [Kniep & Mootz, *Acta Cryst.* (1973), B**29**, 2292–2294]. With Al···O distances of 1·963 (4)

* On leave from: Instituto de Química Inorgánica 'Elhuyar', CSIC, Madrid, Spain.

Table 1. *The atomic parameters and their standard deviations*

The B_{ij} (×10²) in Å² are from the expression: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \cdots + 2B_{23}klb^*c^* + \cdots)]$. Hydrogen atoms were refined isotropically. The positional parameters are ×10⁵, except for H (×10³).

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al	13389 (7)	15500 (8)	16841 (6)	44 (2)	50 (2)	43 (2)	−1 (2)	−1 (2)	−5 (2)
P	14779 (6)	46844 (6)	35284 (6)	41 (2)	44 (2)	38 (2)	−2 (2)	1 (2)	1 (2)
O(1)	11180 (16)	29870 (19)	31525 (17)	86 (6)	50 (6)	61 (6)	−15 (5)	11 (5)	−19 (5)
O(2)	4030 (17)	58186 (21)	29453 (17)	54 (6)	95 (7)	73 (6)	19 (5)	7 (5)	26 (5)
O(3)	28545 (16)	51247 (20)	29006 (16)	55 (6)	74 (6)	71 (6)	−3 (5)	17 (5)	22 (5)
O(4)	14997 (16)	47916 (19)	51224 (16)	82 (6)	59 (6)	46 (5)	−2 (5)	0 (5)	8 (5)
O(*W*1)	6041 (19)	32564 (23)	5469 (19)	114 (7)	116 (7)	64 (6)	30 (6)	−10 (6)	−7 (5)
O(*W*2)	30726 (18)	23597 (21)	11499 (19)	71 (5)	78 (6)	95 (7)	−12 (6)	−8 (5)	16 (5)

	x	*y*	*z*	*B* (Å²)		*x*	*y*	*z*	*B* (Å²)
H(11)	63 (5)	310 (5)	−28 (4)	3·8 (10)	H(21)	362 (4)	201 (4)	168 (4)	2·0 (8)
H(12)	−12 (5)	371 (5)	68 (4)	4·0 (10)	H(22)	314 (5)	334 (6)	85 (5)	4·7 (11)