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).

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Variscite

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Abstract. AlPO$_4$.2H$_2$O, 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$_2$O, monoclinic) structure [Kniep & Mootz, *Acta Cryst.* (1973), B29, 2292–2294]. With Al ⋯ O distances of 1·963 (4)

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

The B_{ij} ($\times 10^2$) in Å^2 are from the expression: exp$[-\frac{1}{4}(B_{11} h^2 a^{*2} + \cdots + 2B_{23} klb^* c^* + \cdots)]$. Hydrogen atoms were refined isotropically. The positional parameters are $\times 10^5$, except for H ($\times 10^3$).

	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(W1)	6041 (19)	32564 (23)	5469 (19)	114 (7)	116 (7)	64 (6)	30 (6)	−10 (6)	−7 (5)
O(W2)	30726 (18)	23597 (21)	11499 (19)	71 (5)	78 (6)	95 (7)	−12 (6)	−8 (5)	16 (5)

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
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)

and 1·909 (4) Å the two water molecules coordinate the Al in *cis*-position. Three of the H atoms form single hydrogen bonds to phosphate O atoms. The fourth does not participate in a hydrogen bond.

Introduction. Cell constants were determined from diffractometric measurements. The systematic absences are $0kl$ for k odd, $h0l$ for l odd and $hk0$ for h odd. The intensities of 1175 independent reflexions with $\theta \leq 30°$ were measured with monochromated Mo $K\alpha$ radiation on a computer-controlled Syntex $P2_1$ diffractometer with a $\theta/2\theta$ scan and a crystal $0\cdot2 \times 0\cdot2 \times 0\cdot3$ mm. 960 reflexions had significant intensities $I \geq 1\cdot96\sigma_I$. No correction for absorption $(\mu = 8\cdot4$ cm$^{-1})$ was applied.

A least-squares refinement on F was made from the non-hydrogen atom parameters reported by Mooney-Slater (1961) for the isotypic InPO$_4$.2H$_2$O. The H atoms were located in a difference map. Scattering factors were from *International Tables for X-ray Crystallography* (1974). The weights were $w = 1/\sigma_F^2$, with σ_F estimated from the measurements. The final $R = 0\cdot046$, $R_w = 0\cdot032$ for all reflexions and $R = 0\cdot031$, $R_w = 0\cdot032$ for significant reflexions only. The coordinates and thermal parameters are given in Table 1.*

Discussion. The present determination is part of a systematic study of crystal structures and genetic principles of aluminium phosphate hydrates (Kniep, 1971; Kniep, Schumann & Mootz, 1972; Kniep & Mootz, 1973). In variscite there was a special interest in the nature of the two water molecules. Interpretation of the heavy-atom distances of the isotypic InPO$_4$.2H$_2$O (Mooney-Slater, 1961) as well as an IR spectroscopy investigation of variscite (Tarte &

Table 2. *Lengths (Å) and angles (°) of covalent and ionic bonds*

The e.s.d.'s are about 0·002 Å and 0·1° except for O–H distances and H–O–H angles (0·04 Å and 4° respectively).

P–O(1)	1·539	O(1)–Al–O(2)	88·3
O(2)	1·540	O(3)	90·3
O(3)	1·528	O(4)	175·9
O(4)	1·538	O(W1)	83·7
Al–O(1)	1·887	O(W2)	93·9
O(2^i)	1·856	O(2)–Al–O(3)	92·9
O(3^{ii})	1·868	O(4)	91·4
O(4^{iii})	1·899	O(W1)	91·1
O(W1)	1·963	O(W2)	175·0
O(W2)	1·909	O(3)–Al–O(4)	93·8
O(W1)–H(11)	0·81	O(W1)	172·7
H(12)	0·82	O(W2)	91·6
O(W2)–H(21)	0·80	O(4)–Al–O(W1)	92·2
H(22)	0·89	O(W2)	86·1
O(1)–P–O(2)	110·6	O(W1)–Al–O(W2)	84·7
O(3)	110·1	H(11)–O(W1)–H(12)	105
O(4)	107·1	H(21)–O(W2)–H(22)	121
O(2)–P–O(3)	107·9		
O(4)	109·6		
O(3)–P–O(4)	111·6		

Symmetry code

(i)	$-x,$	$-\frac{1}{2} + y,$	$\frac{1}{2} - z$
(ii)	$\frac{1}{2} - x,$	$-\frac{1}{2} + y,$	z
(iii)	$x,$	$\frac{1}{2} - y,$	$-\frac{1}{2} + z$

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32067 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
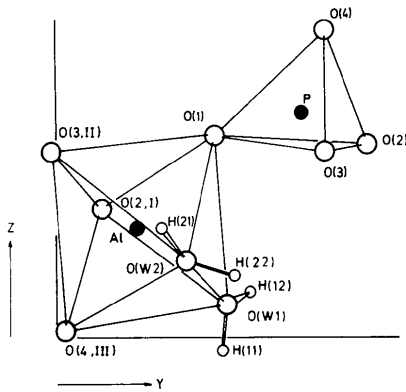
Table 3. *The geometry of hydrogen bonds and other short* O(W) $\cdots$ O *contacts*

Listed are all d[O(W) $\cdots$ O] smaller than 3·0 Å. The e.s.d.'s are 0·002 Å for d[O(W) $\cdots$ O], 0·04 Å for d[H(a/b) $\cdots$ O] and 4° for the angle at H(a/b). The characteristic values for hydrogen bonds are marked with an asterisk.

O(W)–H(a/b) $\cdots$ O	d[O(W) $\cdots$ O]	d[H(a/b) $\cdots$ O]		Angle at H(a/b)	
		a	b	a	b
O(W1)–H(11/12) $\cdots$ O(1)	2·570 Å	3·34 Å	2·74 Å	15°	69°
O(1^i)	2·589	1·84*	3·08	154*	47
O(2^{ii})	2·728	3·15	2·82	52	75
O(4^i)	2·784	2·65	3·44	91	33
O(W2)	2·609	2·84	3·37	66	19
O(W2)–H(21/22) $\cdots$ O(1)	2·774	2·96	2·99	69	67
O(2^{iii})	2·640	1·86*	3·28	167*	38
O(3)	2·914	3·01	2·51	76	108
O(3^{iii})	2·708	2·47	3·53	99	20
O(4^i)	2·600	2·99	3·21	54	41
O(4^{iv})	2·665	3·12	1·78*	49	171*
O(W1)	2·609	3·33	2·51	22	86

Symmetry code

(i)	$x,$	$\frac{1}{2} - y,$	$-\frac{1}{2} + z;$	(iii)	$\frac{1}{2} - x,$	$-\frac{1}{2} + y,$	z
(ii)	$-x,$	$-\frac{1}{2} + y,$	$\frac{1}{2} - z;$	(iv)	$\frac{1}{2} - x,$	$1 - y,$	$-\frac{1}{2} + z$

Fig. 1. The $AlO_4(OH_2)_2$ octahedron and PO_4 tetrahedron of the variscite crystal structure.

Fig. 2. Comparison of the crystal structure of (a) variscite, [001], and (b) metavariscite, [010]. The small circles represent the water molecules.

Paques-Ledent, 1968) suggested the presence of OH^- and H_3O^+ in the orthorhombic $AlPO_4 . 2H_2O$ structure. This is in opposition to recent work on variscite (Salvador & Fayos, 1972), where IR spectroscopy measurements show the presence of two neutral H_2O species with a significant difference in hydrogen bonding.

Bond lengths and angles are listed in Table 2. Table 3 gives the geometry of hydrogen bonds and other short $O(W) \cdots O$ contacts. Fig. 1 shows the asymmetric unit plus some more symmetry-equivalent atoms, necessary to generate a complete $AlO_4(OH_2)_2$ octahedron and a PO_4 tetrahedron.

Despite the significant difference between the two $Al \cdots O(W)$ distances (1·963 and 1·909 Å) both water molecules of the variscite structure are true H_2O species. The two H atoms of $W2$ form two single hydrogen bonds, whereas only one hydrogen bond is formed by $W1$. This observation, which is in agreement with the IR result of Salvador & Fayos (1972), may explain the DTA and TG observation that the loss of water in variscite takes place in two steps (Kotlova & Shchepochkina, 1972).

Fig. 2 shows a comparison of the three-dimensional frameworks of variscite and metavariscite (Kniep & Mootz, 1973). The connexion between anion and cation polyhedra is similar but not equal in both modifications. The different orientation of the hatched tetrahedra implies that a phase transformation between metavariscite and variscite must be of a reconstructive mechanism.

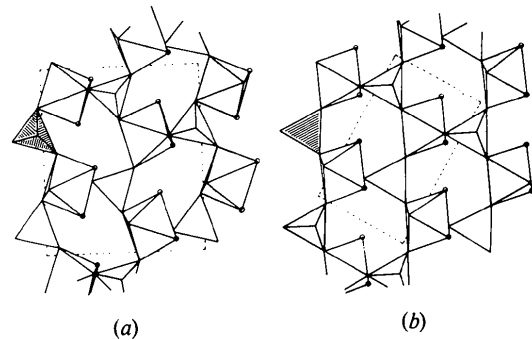The Land Nordrhein–Westfalen (BRD) has supported this research.

Note added in proof.—In a recent X-ray study (Hawthorne, 1976) H atom positions were also determined for scorodite, $FeAsO_4 . 2H_2O$, which is an isotype of variscite. The author lists one hydrogen bond for each proton in two H_2O species, including a configuration $O(W1)-H(1) \cdots O(1)$ at an $O \cdots O$ distance of 3·255 (9) Å and an OHO angle of 175 (9)°. With the numbering scheme and equipoint selection being different in the present study, this corresponds to $O(W1)-H(12) \cdots O(3)$ in variscite with $O(3)$ in $-\frac{1}{2} + x$, y, $\frac{1}{2} - z$, $d(O \cdots O) = 3·477$ (3) Å and $\angle OHO = 158$ (4)°. In both structures the $O \cdots O$ distance appears too large for a directional and individual hydrogen bond.

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