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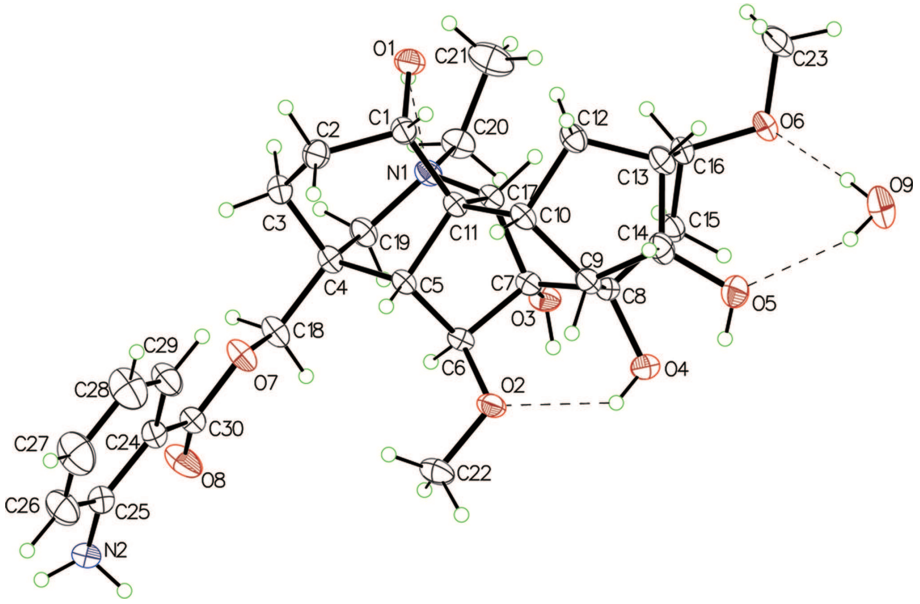
Crystal structure of ajacisine D monohydrate, $C_{30}H_{44}N_2O_9$



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Abstract

$C_{30}H_{44}N_2O_9$, monoclinic, $P2_1$ (no. 4), $a = 7.9827(3)$ Å, $b = 12.6787(6)$ Å, $c = 14.0183(9)$ Å, $\beta = 90.903(5)°$, $V = 1418.62(13)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0607$, $wR_{ref}(F^2) = 0.1298$, $T = 298(2)$ K.

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The title crystal structure (systematic name: *N*-ethyl-18*β*-(o-aminobenzoyl)-6*β*,16*β*-dimethoxy-aconitane-1*α*,7*β*,8*β*,14*α*-tetraol) is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.26 × 0.25 × 0.25 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Gemini S ultra, ω
θ_{max}, completeness:	32.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	19473, 9362, 0.043
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6262
$N(param)_{refined}$:	386
Programs:	CrysAlis^{PRO} [1], SHELX [2]

Source of material

Air-dry roots of the plant *Delphinium grandiflorum* were purchased from Guangzhou qingping medicine market, Guangdong, China. Powder of roots (10 kg) was extracted with 95% ethanol at room temperature. The total alkaloids (63 g) was then obtained by acid extraction and alkali precipitation method. The total alkaloids was loaded on a silica gel

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.0122(3)	−0.09255(18)	0.38972(17)	0.0390(5)
H1	0.0830	−0.0810	0.4099	0.059*
O2	0.2924(3)	0.19199(16)	0.11396(15)	0.0342(5)
O3	0.5416(2)	0.02230(17)	0.23040(16)	0.0341(5)
H3	0.5957	0.0642	0.1987	0.051*
O4	0.4506(3)	0.02337(19)	0.03575(16)	0.0414(5)
H4	0.4251	0.0855	0.0281	0.062*
O5	0.2108(4)	−0.1108(2)	−0.07619(18)	0.0541(7)
H5	0.2583	−0.0555	−0.0895	0.081*
O6	0.3160(3)	−0.31633(17)	0.06658(17)	0.0422(5)
O7	0.0615(3)	0.34374(16)	0.34533(18)	0.0406(5)
O8	0.2084(3)	0.49181(19)	0.3672(2)	0.0544(7)
N1	0.3003(3)	−0.0077(2)	0.38030(17)	0.0300(5)
N2	0.0477(4)	0.6764(2)	0.3377(2)	0.0441(7)
H2A	0.1040	0.6811	0.2859	0.053*
H2B	0.0163	0.7387	0.3546	0.053*
C1	−0.0596(3)	−0.0120(3)	0.3224(2)	0.0316(6)
H1A	−0.1507	−0.0409	0.2827	0.038*
C2	−0.1282(4)	0.0845(3)	0.3724(2)	0.0367(7)
H2C	−0.1780	0.1318	0.3255	0.044*
H2D	−0.2151	0.0632	0.4160	0.044*
C3	0.0086(4)	0.1414(3)	0.4270(2)	0.0370(7)
H3A	0.0435	0.0983	0.4809	0.044*
H3B	−0.0364	0.2067	0.4519	0.044*
C4	0.1649(3)	0.1673(2)	0.3664(2)	0.0310(6)
C5	0.1353(3)	0.1372(2)	0.2593(2)	0.0264(6)
H5A	0.0497	0.1821	0.2292	0.032*
C6	0.3040(3)	0.1445(2)	0.2065(2)	0.0275(6)
H6	0.3818	0.1864	0.2457	0.033*
C7	0.3700(3)	0.0289(2)	0.2037(2)	0.0264(6)
C8	0.3406(3)	−0.0239(2)	0.1050(2)	0.0290(6)
C9	0.1574(3)	−0.0063(2)	0.0715(2)	0.0305(6)
H9	0.1458	0.0628	0.0409	0.037*
C10	0.0295(3)	−0.0174(2)	0.1525(2)	0.0281(6)
H10	−0.0687	0.0249	0.1345	0.034*
C11	0.0857(3)	0.0184(2)	0.2536(2)	0.0255(5)
C12	−0.0246(4)	−0.1363(2)	0.1471(2)	0.0343(7)
H12A	−0.0056	−0.1708	0.2081	0.041*
H12B	−0.1424	−0.1422	0.1300	0.041*
C13	0.0842(4)	−0.1868(3)	0.0700(2)	0.0351(7)
H13	0.0255	−0.2455	0.0386	0.042*
C14	0.1024(4)	−0.0936(3)	0.0025(2)	0.0378(7)
H14	−0.0090	−0.0756	−0.0229	0.045*
C15	0.3925(4)	−0.1413(2)	0.1055(2)	0.0334(7)
H15A	0.4528	−0.1552	0.0473	0.040*
H15B	0.4704	−0.1521	0.1584	0.040*
C16	0.2534(4)	−0.2229(2)	0.1133(2)	0.0330(7)
H16	0.2376	−0.2391	0.1809	0.040*
C17	0.2606(3)	−0.0280(2)	0.2792(2)	0.0262(6)
H17	0.2607	−0.1042	0.2673	0.031*
C18	0.2059(4)	0.2838(2)	0.3775(3)	0.0367(7)
H18A	0.2316	0.2998	0.4438	0.044*
H18B	0.3026	0.3017	0.3397	0.044*
C19	0.3165(4)	0.1043(2)	0.4045(2)	0.0331(7)
H19A	0.4183	0.1322	0.3772	0.040*
H19B	0.3249	0.1121	0.4732	0.040*
C20	0.4420(4)	−0.0706(3)	0.4205(3)	0.0385(7)
H20A	0.4812	−0.0380	0.4793	0.046*
H20B	0.5336	−0.0698	0.3759	0.046*
C21	0.3944(5)	−0.1821(3)	0.4403(4)	0.0633(12)
H21A	0.3559	−0.2150	0.3823	0.095*
H21B	0.3066	−0.1835	0.4863	0.095*
H21C	0.4901	−0.2196	0.4650	0.095*
C22	0.2951(5)	0.3037(3)	0.1174(3)	0.0488(9)
H22A	0.2912	0.3314	0.0537	0.073*
H22B	0.3962	0.3268	0.1491	0.073*
H22C	0.1999	0.3286	0.1519	0.073*
C23	0.2399(5)	−0.4112(3)	0.0995(3)	0.0555(10)
H23A	0.2809	−0.4699	0.0634	0.083*
H23B	0.1206	−0.4062	0.0913	0.083*
H23C	0.2672	−0.4212	0.1658	0.083*
C24	−0.0825(4)	0.5027(2)	0.3244(2)	0.0344(7)
C25	−0.0907(4)	0.6144(3)	0.3226(2)	0.0365(7)
C26	−0.2465(5)	0.6616(3)	0.3051(3)	0.0545(10)
H26	−0.2546	0.7348	0.3040	0.065*
C27	−0.3867(5)	0.6021(4)	0.2895(4)	0.0674(13)
H27	−0.4885	0.6356	0.2775	0.081*
C28	−0.3806(5)	0.4931(4)	0.2911(3)	0.0635(11)
H28	−0.4773	0.4534	0.2809	0.076*
C29	−0.2290(4)	0.4443(3)	0.3082(3)	0.0477(9)
H29	−0.2237	0.3711	0.3089	0.057*
C30	0.0761(4)	0.4492(2)	0.3478(2)	0.0349(7)
O9	0.2853(4)	−0.3169(3)	−0.1356(3)	0.0584(7)
H9A	0.301(7)	−0.321(5)	−0.071(5)	0.11(2)*
H9B	0.250(6)	−0.257(4)	−0.141(4)	0.069(15)*

column chromatography and eluted with $CHCl_3$—CH_3OH solvent system (100:0–0:100) to afford six fractions (Fr. 1–6). The title compound was obtained from Fr. 5 and crystallized in a mixture of methanol and water.

Experimental details

The C-bound H atoms were positioned geometrically and were included in the refinement in the riding-model approximation. The crystal structure was solved by direct method and refined by full-matrix least-squares refinement with SHELX program [2]. The Flack parameter is not conclusive.

Comment

According to our previous work, many alkaloids have been isolated from *Delphinium grandiflorum* [3, 4]. The

title compound, ajacisine D monohydrate, is one of the diterpenoid alkaloids which have been proved to be the main chemical components of genus *Delphinium* [5, 6]. These diterpenoid alkaloids have complex structure skeletons and posess multiple biological activities such as anastalsis, antibacterial activity [7–10]. The single crystals were obtained by slow evaporation from a mixture of methanol and water.

There is one ajacisine D molecule ($C_{30}H_{42}N_2O_8$) and one water molecule (H_2O) in the asymmetric unit (*cf*. the figure). In the crystal structure, the typical bond lengths of C1—O1, N1—C20, O8—C30 and N2—C25 are 1.437(4) Å, 1.488(4) Å, 1.213(4) Å, 1.370(5) Å respectively. The torsion angle of O7—C30—C24—C29 is 3.7(4)°, which demonstrates that the aryl moiety (mean deviation 0.002 Å) and the ester group are not exactly coplanar. The angle of C4—C19—N1 is 110.9(2)°, which is smaller than 114.2(2)° of C17—N1—C19. Intermolecular hydrogen-bonding interactions involving the water molecule, methoxy group, the hydroxy and the phenyl amine give a three-dimensional stucture. Two short intramolecular interactions between the C1 hydroxy and N1, C8 hydroxy and methoxy O at C6 are also present [*cf*. the figure; O1—H1···N1 = 2.722(3) Å, 144°; O4—H4···O2 = 2.722(3) Å, 132°].

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