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# Sesquiterpene Lactones of the *Umbelliferae*. Structural Characterization of Badkhysin* and its C(5)-Epimer, Isobadkhysin†

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**Abstract.** Badkhysin (III), $C_{20}H_{24}O_5$, $M_r = 344·407$, monoclinic, $P2_1$, $a = 12·331$ (2), $b = 6·024$ (1), $c = 24·915$ (5) Å, $\beta = 98·03$ (1)°, $V = 1832·6$ (6) Å$^3$, $Z = 4$, $D_x = 1·25$, $D_m = 1·25$ Mg m$^{-3}$, $\lambda$(Cu K$\alpha$) = $1·54178$ Å, $\mu = 0·69$ mm$^{-1}$, $F(000) = 736$, $T = 293$ K, $R = 0·063$ for 3402 observed $[I > 1·96\sigma(I)]$ reflections and 480 refined parameters. Isobadkhysin (IV), $C_{20}H_{24}O_5$, $M_r = 344·407$, monoclinic, $P2_1$, $a = 13·082$ (4), $b = 5·184$ (3), $c = 14·212$ (4) Å, $\beta = 109·92$ (2)°, $V = 906·2$ (7) Å$^3$, $Z = 2$, $D_x = 1·26$, $D_m = 1·24$ Mg m$^{-3}$, $\lambda$(Cu K$\alpha$) = $1·54178$ Å, $\mu = 0·70$ mm$^{-1}$, $F(000) = 368$, $T = 293$ K, $R = 0·046$ for 1323 unique observed reflections $[I > 1·96\sigma(I)]$ and 240 refined parameters. Initial assignment of the stereostructure of (III) is now revised on grounds of the X-ray analysis. (III) belongs to the 2-oxo-$5\beta H,6\alpha H,7\alpha H$-guaia-1(10),3-dien-6,12-olides which are characteristic for plants of the *Umbelliferae* family. Isomerization of (III), induced by alkali

treatment, takes place at C(5) as shown by the X-ray analysis of (IV).

**Introduction.** While naturally occurring sesquiterpene lactones are characteristic components in the species of the *Compositae* (daisy family) they are also present in other plant families of which the *Umbelliferae* (parsley family) takes the second place in a number of isolated and described sesquiterpene lactones. In the group of 2-oxoguaia-1(10),3-dien-6,12-olides two basic stereostructural types (I) and (II) can be distinguished which differ mainly in the configurations at C(5) and C(6). Our recent investigations indicate that the different stereostructural types are indicative of their differing plant sources (Holub & Buděšínský, 1986; Rychlewska, 1986). Guaianolides of type (I) with the 'usual' arrangement of substituents are synthesized in plants of the *Compositae*, while quaianolides of type (II) seem characteristic for the species of the *Umbelliferae*. Badkhysin (III), isolated from roots of *Ferula oopoda* (Boiss. et Buhse) Boiss. was initially assigned as belonging to the class of lactones with the basic stereostructure (I) (Serkerov, 1980) and was sub-

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sequently reclassified as stereostructure (II) on the basis of a new interpretation of NMR data (Rychlewska, Hodgson, Holub, Budešinsky & Smítalová, 1985). Here we describe the crystal structure of badkyhsin (III) and its C(5)-epimer, isobadkhysin (IV), which was obtained from the alkaline treatment of the native lactone.



(I)

(III)

(II)

(IV)
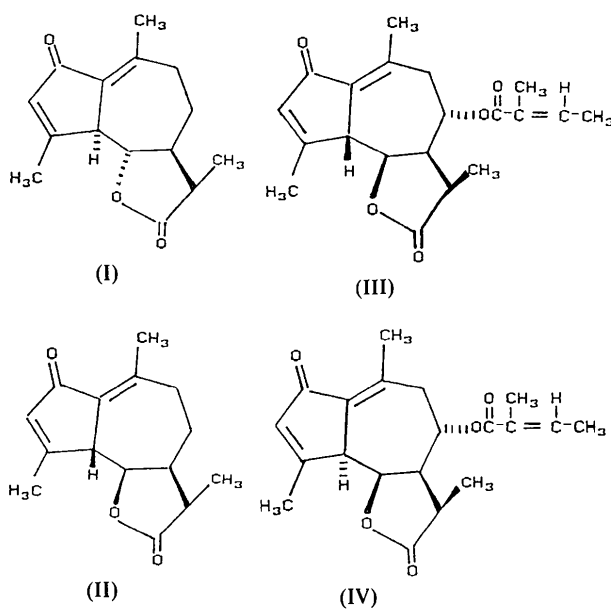
**Experimental.** Crystals of (III) and (IV) were grown from ethanol solutions; densities were measured by flotation in aqueous solutions of KI; the space groups and initial cell dimensions were obtained from Weissenberg photographs. Intensity data were collected on a Syntex $P2_1$ diffractometer using graphite-monochromated Cu $K\alpha$ radiation. Cell parameters were from the least-squares refinement of setting angles of 15 reflections in the range $16 \rightarrow 21°$. Intensity data were measured using $\theta/2\theta$ scans in the range $0 < 2\theta < 115°$, variable scan rate. Two standard reflections were measured every 100 reflections. Structures solved using *SHELXS*86 (Sheldrick, 1986) and refined using $F$ magnitudes by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). Non-H atoms were refined anisotropically. H atoms were included in calculated positions with fixed isotropic temperature factors and allowed to ride on their parent atoms; methyl groups were refined as rigid groups. Atomic scattering factors were from *SHELX*76. *ORTEP* (Johnson, 1965) was used for diagrams and *PARST* (Nardelli, 1983) for geometry calculations, as implemented in the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1986).

(III). The crystal had approximate dimensions 0·2 × 0·2 × 0·4 mm. Range of indices: $h\ 0/13$, $k\ -6/6$,

$l\ -27/27$. The intensities of standard reflections varied by less than $3.5\sigma$ from their means throughout the data collection. The background and integrated intensity for each reflection were evaluated from a profile analysis according to the Lehmann & Larsen (1974) method using the *PRARA* program (Jaskólski, 1982). Lorentz and polarization factors were applied. No corrections were made for absorption. 5743 reflections were measured giving 3406 observed $[I > 1.96\sigma(I)]$ reflections (the $hkl$ and $h\bar{k}l$ Bijvoet pairs were not merged). The $E$ map revealed the positions of 45 out of 50 non-H atoms in the two crystallographically independent molecules. At the stage when anisotropic temperature factors were used, the refinement proceeded separately for the two parts of the asymmetric unit. During the refinement a disorder of the angelate group in molecule $B$ was noticed. Large displacement parameters for atoms C(17') and C(18') in connection with relatively lower values for the methyl C(19') and C(20') atoms suggested a two-positional disorder in which the C(19') methyl group of one form lies in the proximity of the C(20') methyl of the other form so that the two forms share two common C atoms but the inner C(16')—C(17') and C(17')—C(18') bonds are different. No additional atoms were introduced to take account of this due to the unsatisfactory data/parameter ratio (1857 unique observed reflections). An attempt to establish the absolute configuration on the basis of the anomalous scattering of Cu radiation by O atoms failed. Therefore, the usual assumption was made that the C(7) equatorial substituent is $\beta$ (Fisher, Olivier & Fisher, 1979) and, accordingly, the signs of all atomic coordinates were reversed. An empirical isotropic extinction parameter $x$ was introduced to correct the calculated structure factors by multiplying them by a factor $1 - xF_c^2/\sin\theta$ and it refined to a value $8.8 (1.0) \times 10^{-7}$. Four reflections (200, 400, 541, 304) with large $\Delta F/\sigma$ were excluded from the final refinement. $R = 0.063$ and $wR = 0.071$ for 3402 reflections and 481 parameters $[w^{-1} = \sigma^2(F) + 0.0001F^2]$. The maximum $\Delta/\sigma = 0.76$ for the non-H atoms; residual electron density in the difference map showed a maximum of $0.60\ e\ Å^{-3}$ lying in the vicinity of atoms C(17') and C(18') whose displacement parameters refined to rather large values, all other peaks were less than $0.35\ e\ Å^{-3}$.

(IV). Crystal $ca\ 0.15 \times 0.15 \times 0.80$ mm selected for data collection. Standard reflections showed no change in intensity greater than $3.8\sigma(I)$. 1492 reflections were measured, 1323 observed $[I > 1.96\sigma(I)]$, index range: $h\ 0/13$, $k\ 0/5$, $l\ -15/15$. The data were corrected for backgrounds and for Lorentz-polarization effects, but not for absorption. No attempt was made to establish the absolute configuration of the molecule on the basis of the present

crystallographic experiment, but the positions in Table 1 and elsewhere were assigned on the assumption of the established configuration at C(7) (Fisher, Olivier & Fisher, 1979). $R = 0.046$ and $wR = 0.062$ for 1323 reflections and 240 parameters [$w^{-1} = \sigma^2(F)$ + $0.0002F^2$]. The maximum $\Delta/\sigma = 0.62$ for the non-H atoms; residual electron density in the difference map was within $-0.19$ and $+0.16$ e Å$^{-3}$.

**Discussion.** Final atomic coordinates for compounds (III) and (IV) are given in Table 1.* Bond lengths, angles and torsion angles are listed in Table 2. Fig. 1 shows the shapes of the two independent molecules of (III) (hereafter molecules $A$ and $B$) in the crystal with the atom labelling. The stereochemistry at the ring junctions in these tricyclic molecules is $5\beta H,6\alpha H,7\alpha H$. The two molecules are conformationally similar but not the same. The main structural difference is seen in the ester side chain where the angeloyloxy groups differ in conformation around the C(16)—C(17) bond [*e.g.* the O(8)—C(16)—C(17)—C(18) torsion angle is $-150.5$ (6)° in molecule $A$ but $-51.5$ (13)° for molecule $B$]. Moreover, the angeloyloxy substituent in molecule $B$ shows pronounced signs of disorder. Throughout the literature examples of angelyl groups with elevated displacement parameters may be found (Hay, Mackay & Culvenor, 1982, and references therein). Since no account was taken of the disorder, the accuracy of bond lengths, and valency and torsion angles is highly restricted. Within the three-ring skeleton the molecules show similar conformations. The cyclopentenone rings in both molecules are slightly puckered with average endocyclic torsion angles of $8.6$ (3.6) and $6.6$ (2.8)°, for molecules $A$ and $B$, respectively, and they adopt the twist conformation with C(1) and C(5) sticking out of the best plane through the ring, a conformation most common for puckered cyclopenten-2-ones (Schweizer, 1989). The seven-membered cycloheptene ring adopts a conformation in which atoms C(5), C(1), C(10), C(9) and C(8) are approximately coplanar [maximum deviation $0.217$ (6) and $0.179$ (6) Å, for molecules $A$ and $B$, respectively] while atoms C(6) and C(7) are both below this plane [$1.281$ (5) and $0.922$ (5) Å, respectively in molecule $A$; $1.262$ (6) and $0.914$ (6) Å, respectively in molecule $B$]. This type of conformation was also observed in related species, *i.e.* 2-oxo-8$\alpha$-angeloyloxy-11$\alpha$-acetoxy-$5\beta H,6\alpha H,7\alpha H$-guaia-1(10),3-dien-6,12-olide (Rychlewska, Hodgson, Holub, Budĕšínský &

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53947 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$) *with e.s.d.'s in parentheses for non-*H *atoms*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| **(III) Molecule $A$** | | | | |
| C(1) | $-1961$ (4) | $-7564$ (9) | $-362$ (2) | 488 (17) |
| C(2) | $-2078$ (4) | $-8473$ (11) | 183 (2) | 597 (22) |
| C(3) | $-2893$ (4) | $-7092$ (10) | 399 (2) | 608 (20) |
| C(4) | $-3331$ (4) | $-5575$ (10) | 50 (2) | 548 (21) |
| C(5) | $-2902$ (4) | $-5874$ (9) | $-506$ (2) | 485 (18) |
| C(6) | $-2526$ (4) | $-3700$ (9) | $-747$ (2) | 498 (20) |
| C(7) | $-2351$ (4) | $-3865$ (9) | $-1349$ (2) | 501 (19) |
| C(8) | $-2004$ (4) | $-6146$ (9) | $-1521$ (2) | 533 (19) |
| C(9) | $-970$ (4) | $-6983$ (10) | $-1173$ (2) | 566 (20) |
| C(10) | $-1124$ (4) | $-7980$ (9) | $-637$ (2) | 506 (01) |
| C(11) | $-3421$ (4) | $-2968$ (9) | $-1651$ (2) | 571 (19) |
| C(12) | $-3837$ (5) | $-1494$ (11) | $-1248$ (2) | 628 (23) |
| C(13) | $-4313$ (5) | $-4648$ (12) | $-1866$ (2) | 816 (27) |
| C(14) | $-193$ (4) | $-9480$ (9) | $-420$ (2) | 566 (21) |
| C(15) | $-4184$ (4) | $-3975$ (12) | 135 (2) | 780 (27) |
| C(16) | $-1813$ (5) | $-7642$ (13) | $-2384$ (2) | 687 (25) |
| C(17) | $-1530$ (5) | $-7218$ (12) | $-2932$ (2) | 729 (26) |
| C(18) | $-1936$ (6) | $-8384$ (15) | $-3355$ (2) | 941 (33) |
| C(19) | $-2730$ (7) | $-10272$ (17) | $-3394$ (3) | 1366 (46) |
| C(20) | $-741$ (6) | $-5301$ (14) | $-2972$ (3) | 1018 (33) |
| O(2) | $-1601$ (3) | $-10077$ (8) | 414 (1) | 827 (17) |
| O(6) | $-3338$ (3) | $-1977$ | $-738$ (1) | 603 (14) |
| O(8) | $-1767$ (3) | $-5829$ (6) | $-2076$ (1) | 699 (14) |
| O(12) | $-4517$ (3) | $-43$ (8) | $-1311$ (2) | 891 (18) |
| O(16) | $-2054$ (4) | $-9453$ (8) | $-2223$ (2) | 1021 (22) |
| **(III) Molecule $B$** | | | | |
| C(1') | $-8113$ (4) | $-310$ (9) | $-4553$ (2) | 566 (22) |
| C(2') | $-8095$ (5) | $-1169$ (12) | $-5116$ (2) | 719 (25) |
| C(3') | $-7256$ (5) | 111 (11) | $-5348$ (2) | 680 (21) |
| C(4') | $-6736$ (4) | 1533 (10) | $-4987$ (2) | 597 (22) |
| C(5') | $-7147$ (4) | 1258 (9) | $-4435$ (2) | 530 (19) |
| C(6') | $-7458$ (4) | 3444 (10) | $-4181$ (2) | 599 (20) |
| C(7') | $-7545$ (4) | 3268 (10) | $-3570$ (2) | 632 (23) |
| C(8') | $-7879$ (4) | 1021 (10) | $-3387$ (2) | 583 (20) |
| C(9') | $-8955$ (4) | 150 (11) | $-3693$ (2) | 639 (22) |
| C(10') | $-8899$ (4) | $-774$ (9) | $-4253$ (2) | 574 (19) |
| C(11') | $-6423$ (4) | 4151 (11) | $-3298$ (2) | 692 (24) |
| C(12') | $-6077$ (6) | 5599 (13) | $-3728$ (3) | 815 (30) |
| C(13') | $-5535$ (5) | 2392 (12) | $-3127$ (2) | 835 (25) |
| C(14') | $-9862$ (4) | $-2243$ (10) | $-4436$ (2) | 679 (23) |
| C(15') | $-5834$ (4) | 3057 (11) | $-5085$ (2) | 758 (26) |
| C(16') | $-7990$ (6) | $-476$ (14) | $-2504$ (2) | 862 (29) |
| C(17') | $-8370$ (10) | $-230$ (19) | $-1912$ (4) | 1370 (51) |
| C(18') | $-7933$ (9) | 1241 (24) | $-1684$ (5) | 1561 (63) |
| C(19') | $-7091$ (6) | 2944 (14) | $-1725$ (3) | 940 (32) |
| C(20') | $-9190$ (6) | $-1998$ (15) | $-1769$ (3) | 1028 (33) |
| O(2') | $-8643$ (4) | $-2649$ (9) | $-5347$ (2) | 1037 (20) |
| O(6') | $-6664$ (3) | 5159 (7) | $-4218$ (2) | 741 (17) |
| O(8') | $-8048$ (3) | 1359 (7) | $-2822$ (1) | 741 (17) |
| O(12') | $-5385$ (4) | 7011 (9) | $-3697$ (2) | 1109 (24) |
| O(16') | $-7812$ (5) | $-2290$ (9) | $-2658$ (2) | 1202 (27) |
| **(IV)** | | | | |
| C(1) | $-5922$ (3) | $-1224$ (11) | $-2959$ (3) | 407 (13) |
| C(2) | $-5410$ (4) | 54 (12) | $-3614$ (3) | 499 (17) |
| C(3) | $-5846$ (3) | $-1201$ (13) | $-4592$ (3) | 544 (17) |
| C(4) | $-6597$ (3) | $-2930$ (13) | $-4606$ (3) | 523 (17) |
| C(5) | $-6729$ (3) | $-3146$ (11) | $-3587$ (3) | 434 (15) |
| C(6) | $-7925$ (3) | $-2750$ (10) | $-3662$ (3) | 380 (14) |
| C(7) | $-8268$ (3) | $-2870$ (11) | $-2737$ (3) | 388 (14) |
| C(8) | $-7507$ (3) | $-1588$ (10) | $-1781$ (3) | 386 (13) |
| C(9) | $-6326$ (3) | $-2510$ (12) | $-1461$ (3) | 461 (15) |
| C(10) | $-5690$ (3) | $-944$ (11) | $-1977$ (3) | 421 (15) |
| C(11) | $-9380$ (3) | $-1540$ (11) | $-3184$ (3) | 447 (14) |
| C(12) | $-9171$ (3) | 423 (11) | $-3867$ (3) | 431 (15) |
| C(13) | $-9933$ (4) | $-384$ (16) | $-2487$ (3) | 716 (24) |
| C(14) | $-4862$ (3) | 876 (13) | $-1326$ (3) | 573 (19) |
| C(15) | $-7232$ (4) | $-4578$ (17) | $-5454$ (4) | 779 (26) |
| C(16) | $-7673$ (3) | $-816$ (11) | $-183$ (3) | 451 (16) |
| C(17) | $-8147$ (4) | $-1813$ (12) | 563 (3) | 514 (18) |
| C(18) | $-7869$ (4) | $-876$ (13) | 1479 (3) | 619 (20) |
| C(19) | $-7085$ (5) | 1191 (15) | 1984 (4) | 794 (24) |
| C(20) | $-8941$ (4) | $-4020$ (13) | 238 (4) | 631 (20) |
| O(2) | $-4744$ (3) | 1841 (10) | $-3393$ (2) | 760 (16) |
| O(6) | $-8275$ (2) | $-201$ | $-4083$ (2) | 422 (10) |
| O(8) | $-7946$ (2) | $-2343$ (8) | $-1011$ (2) | 428 (10) |
| O(12) | $-9671$ (2) | 2364 (9) | $-4188$ (2) | 581 (11) |
| O(16) | $-7119$ (3) | 1070 (9) | $-106$ (2) | 665 (14) |

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

| | (III) Molecule A | Molecule B | (IV) |
|---|---|---|---|
| C(1)—C(2) | 1·490 (7) | 1·498 (7) | 1·476 (8) |
| C(1)—C(5) | 1·548 (7) | 1·517 (7) | 1·504 (6) |
| C(1)—C(10) | 1·340 (8) | 1·334 (8) | 1·331 (6) |
| C(2)—C(3) | 1·464 (8) | 1·472 (9) | 1·463 (6) |
| C(2)—O(2) | 1·231 (7) | 1·214 (8) | 1·237 (7) |
| C(3)—C(4) | 1·324 (8) | 1·339 (8) | 1·325 (8) |
| C(4)—C(5) | 1·561 (7) | 1·540 (7) | 1·520 (7) |
| C(4)—C(15) | 1·464 (8) | 1·488 (8) | 1·480 (8) |
| C(5)—C(6) | 1·539 (8) | 1·533 (8) | 1·545 (6) |
| C(6)—C(7) | 1·548 (7) | 1·545 (7) | 1·528 (7) |
| C(6)—O(6) | 1·445 (6) | 1·435 (7) | 1·458 (5) |
| C(7)—C(8) | 1·519 (8) | 1·504 (8) | 1·535 (6) |
| C(7)—C(11) | 1·524 (7) | 1·547 (7) | 1·538 (6) |
| C(8)—C(9) | 1·524 (7) | 1·528 (8) | 1·531 (6) |
| C(8)—O(8) | 1·465 (6) | 1·466 (6) | 1·452 (6) |
| C(9)—C(10) | 1·500 (7) | 1·513 (7) | 1·518 (7) |
| C(10)—C(14) | 1·501 (7) | 1·500 (7) | 1·496 (7) |
| C(11)—C(12) | 1·485 (8) | 1·489 (10) | 1·494 (7) |
| C(11)—C(13) | 1·535 (8) | 1·540 (9) | 1·534 (8) |
| C(12)—O(6) | 1·364 (6) | 1·356 (8) | 1·348 (5) |
| C(12)—O(12) | 1·206 (7) | 1·200 (9) | 1·202 (7) |
| C(16)—C(17) | 1·478 (8) | 1·616 (12) | 1·491 (7) |
| C(16)—O(8) | 1·331 (7) | 1·356 (8) | 1·361 (6) |
| C(16)—O(16) | 1·214 (8) | 1·189 (10) | 1·200 (7) |
| C(17)—C(18) | 1·307 (9) | 1·146 (17) | 1·319 (6) |
| C(17)—C(20) | 1·522 (9) | 1·544 (15) | 1·508 (8) |
| C(18)—C(19) | 1·495 (15) | 1·473 (15) | 1·488 (9) |
| | | | |
| C(5)—C(1)—C(10) | 127·6 (5) | 129·4 (5) | 123·9 (4) |
| C(2)—C(1)—C(10) | 125·2 (5) | 124·0 (5) | 128·5 (4) |
| C(2)—C(1)—C(5) | 106·8 (4) | 106·4 (4) | 107·5 (4) |
| C(1)—C(2)—O(2) | 127·9 (5) | 128·1 (5) | 127·4 (4) |
| C(1)—C(2)—C(3) | 106·6 (5) | 106·9 (5) | 106·6 (4) |
| C(3)—C(2)—O(2) | 125·6 (5) | 125·0 (5) | 126·0 (4) |
| C(2)—C(3)—C(4) | 112·9 (5) | 111·6 (5) | 111·2 (4) |
| C(3)—C(4)—C(15) | 126·5 (5) | 125·7 (5) | 121·3 (4) |
| C(3)—C(4)—C(5) | 110·2 (5) | 110·2 (5) | 111·1 (4) |
| C(5)—C(4)—C(15) | 123·0 (4) | 124·0 (4) | 121·3 (4) |
| C(1)—C(5)—C(4) | 101·9 (4) | 104·0 (4) | 103·4 (4) |
| C(4)—C(5)—C(6) | 114·0 (4) | 114·1 (5) | 111·4 (3) |
| C(1)—C(5)—C(6) | 113·2 (4) | 112·3 (4) | 116·2 (4) |
| C(5)—C(6)—O(6) | 111·0 (4) | 112·3 (4) | 108·5 (3) |
| C(5)—C(6)—C(7) | 114·4 (4) | 113·8 (5) | 121·5 (4) |
| C(7)—C(6)—O(6) | 104·6 (4) | 104·8 (4) | 104·3 (3) |
| C(6)—C(7)—C(11) | 103·1 (4) | 103·1 (4) | 98·1 (3) |
| C(6)—C(7)—C(8) | 114·5 (4) | 114·9 (4) | 116·9 (4) |
| C(8)—C(7)—C(11) | 116·1 (4) | 116·3 (5) | 114·1 (4) |
| C(7)—C(8)—O(8) | 104·5 (4) | 104·4 (4) | 104·3 (3) |
| C(7)—C(8)—C(9) | 112·7 (4) | 114·4 (5) | 114·4 (4) |
| C(9)—C(8)—O(8) | 108·6 (4) | 107·3 (4) | 108·1 (3) |
| C(8)—C(9)—C(10) | 116·0 (4) | 116·0 (4) | 110·7 (4) |
| C(1)—C(10)—C(9) | 125·6 (5) | 124·8 (5) | 118·8 (4) |
| C(9)—C(10)—C(14) | 112·1 (4) | 111·2 (4) | 116·1 (4) |
| C(1)—C(10)—C(14) | 122·2 (5) | 124·0 (5) | 125·2 (4) |
| C(7)—C(11)—C(13) | 117·9 (5) | 116·2 (5) | 119·8 (4) |
| C(7)—C(11)—C(12) | 103·6 (4) | 102·4 (5) | 102·5 (4) |
| C(12)—C(11)—C(13) | 109·4 (5) | 109·7 (5) | 112·6 (4) |
| C(11)—C(12)—O(12) | 130·2 (5) | 129·9 (7) | 128·3 (4) |
| C(11)—C(12)—O(6) | 110·4 (5) | 111·3 (6) | 110·5 (4) |
| O(6)—C(12)—O(12) | 119·4 (5) | 118·8 (7) | 121·2 (4) |
| O(8)—C(16)—O(16) | 122·7 (5) | 123·9 (5) | 121·7 (4) |
| C(17)—C(16)—O(16) | 124·1 (5) | 118·0 (6) | 127·0 (4) |
| C(17)—C(16)—O(8) | 113·2 (5) | 117·4 (6) | 111·3 (4) |
| C(16)—C(17)—C(20) | 115·3 (5) | 115·5 (8) | 117·1 (4) |
| C(16)—C(17)—C(18) | 122·6 (6) | 110·3 (10) | 122·2 (5) |
| C(18)—C(17)—C(20) | 122·1 (5) | 134·2 (11) | 120·7 (5) |
| C(17)—C(18)—C(19) | 129·4 (6) | 142·3 (12) | 130·9 (5) |
| C(6)—O(6)—C(12) | 111·3 (3) | 111·5 (5) | 107·4 (3) |
| C(8)—O(8)—C(16) | 116·0 (4) | 116·4 (4) | 116·1 (4) |

Five-membered ring

| | | | |
|---|---|---|---|
| C(5)—C(1)—C(2)—C(3) | −10·7 (6) | −8·3 (6) | −3·8 (5) |
| C(2)—C(1)—C(5)—C(4) | 12·7 (5) | 9·8 (5) | 2·3 (5) |
| C(1)—C(2)—C(3)—C(4) | 3·9 (7) | 3·2 (7) | 4·0 (6) |
| C(2)—C(3)—C(4)—C(5) | 4·7 (7) | 3·3 (7) | −2·6 (6) |
| C(3)—C(4)—C(5)—C(1) | −10·9 (6) | −8·3 (6) | 0·2 (6) |

Seven-membered ring

| | | | |
|---|---|---|---|
| C(10)—C(1)—C(5)—C(6) | −37·7 (7) | −41·4 (8) | 64·1 (6) |
| C(5)—C(1)—C(10)—C(9) | −4·7 (9) | −3·0 (9) | −4·5 (7) |
| C(1)—C(5)—C(6)—C(7) | 77·5 (5) | 78·7 (6) | −61·7 (6) |
| C(5)—C(6)—C(7)—C(8) | −29·8 (6) | −29·5 (6) | 40·8 (6) |
| C(6)—C(7)—C(8)—C(9) | −55·9 (6) | −55·6 (6) | −53·8 (6) |
| C(7)—C(8)—C(9)—C(10) | 80·7 (6) | 77·4 (6) | 87·0 (5) |
| C(8)—C(9)—C(10)—C(1) | −23·5 (8) | −20·7 (8) | −69·0 (6) |

Table 2 (*cont.*)

| | (III) Molecule A | Molecule B | (IV) |
|---|---|---|---|
| γ-Lactone ring | | | |
| O(6)—C(6)—C(7)—C(11) | −24·3 (5) | −25·0 (5) | 40·0 (4) |
| C(7)—C(6)—O(6)—C(12) | 14·2 (5) | 15·9 (6) | −31·0 (4) |
| C(6)—C(7)—C(11)—C(12) | 25·3 (5) | 24·7 (6) | −35·3 (4) |
| C(7)—C(11)—C(12)—O(6) | −18·3 (6) | −16·7 (7) | 19·4 (5) |
| C(11)—C(12)—O(6)—C(6) | 2·5 (6) | 0·7 (7) | 7·0 (5) |
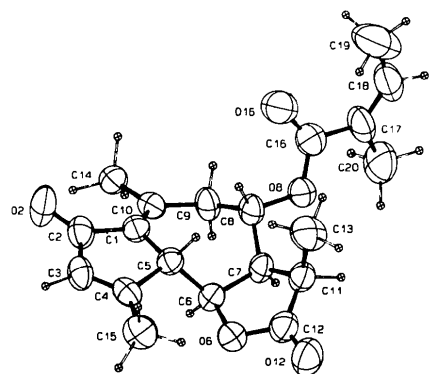


(a)
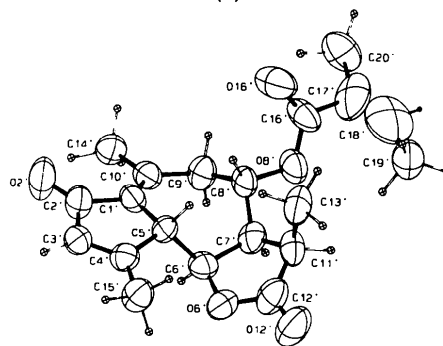


(b)

Fig. 1. Perspective views of the two molecules of badkhysin (III) present in the asymmetric part of the unit cell with their atom-numbering schemes. (a) Molecule A and (b) molecule B. Thermal ellipsoids are drawn at the 40% probability level. H atoms are represented by spheres of arbitrary size.

Smítalová, 1985) and in ferulid (Tashkhodzhaev, Makhmudov, Nurmukhamedova & Talipov, 1988), and seems to be characteristic for 2-oxoguaia-1(10),3-dien-6,12-olides with a 5βH,6αH,7αH configuration. Lactones of this stereostructural type (type II, see above) are typical for species of the Umbelliferae family. The degree of puckering of the γ-lactone ring is the same in both molecules, the average torsion angle moduli being 16·6 (8·8) and 16·9 (8·3)° for molecules A and B, respectively. Both rings approximate to the C(7) envelope conformation, which is common among saturated γ-lactones, although the deviations from the ideal form are more pronounced in molecule A. The molecules are held

together mainly by van der Waals forces. No unusual intermolecular contacts are observed, the shortest being between O(6) and translationally equivalent (+y direction) C(1) atoms [3·222 (6) and 3·305 (7) Å, respectively for molecules A and B] and between O(16) and translationally equivalent (−y direction) C(11) atoms [3·167 (7) and 3·292 (8) Å, respectively for molecules A and B].

Upon alkaline treatment, (III) undergoes isomerization to its C(5)-epimer as shown by the present X-ray analysis of (IV). To the authors' knowledge this type of isomerization reaction has not been reported so far in a group of sesquiterpene lactones. Fig. 2 shows a perspective view of molecule (IV). The stereochemistry at the ring junctions in this tricyclic molecule is $5\alpha H,6\alpha H,7\alpha H$. The change of configuration at C(5) considerably alters the shape of the molecule. The seven-membered cycloheptene ring adopts a chair conformation, the approximate mirror plane passing through C(7) and the midpoint of the C(1)—C(10) bond. Surprisingly, this type of conformation is almost invariably present in 2-oxoguaia-1(10),3-dien-6,12-olides of the stereostructural type (I), *i.e.* possessing a $5\alpha H,6\beta H,7\alpha H$ configuration (Ruban, Zabel, Gensch & Smalla, 1978; Korp, Bernal, Fisher, Leonard, Lee & Le Van, 1982; Watson, Tavanaiepour, Gao & Mabry, 1987; Campos, Silva, Watson & Nagl, 1989; Seaman, Malcolm, Fronczek, Lee & Fisher, 1984). Thus the change of configuration at C(6) and, connected with it, the change of the γ-lactone orientation has little effect on the type of conformation of the seven-membered ring. However, in order to accommodate a *cis*-fused γ-lactone, the ring is flattened and this is accomplished by the closing of the junction torsion angle [40·8 (6)°] and by the valence-angle deformation [C(5)—C(6)—C(7) 121·5 (4)°]. The required flattening of the seven-membered ring is minimized by the simultaneous puckering of the γ-lactone

which is decidedly non-planar as shown by the average torsion angle moduli 26·6 (12·0)°. This is not common in *cis*-fused lactones where the lactone ring is fairly flat; in (IV) the maximum torsion angle in the lactone ring is 40·4 (4)° and may be compared with the values of 25·3 (5) and 25·0 (5)° observed in (III) and with the values of 17·7 (5), 22·3 (6), 27·5 (6) and 22·5 (6)° found in the other slovanolide analogues* (Rychlewska, Hodgson, Holub, Buděšínský & Smítalová, 1985; Rychlewska & Holub, 1990; Rychlewska, Holub, Buděšínský & Smítalová, 1984; Krstanović, Karanović, Stefanović & Dermanović, 1981). The γ-lactone ring in (IV) adopts a conformation in which the C(7)—H(7) and C(6)—O(6) bonds are antiperiplanar giving rise to a positive torsion angle at the junction O(6)—C(6)—C(7)—C(11), while in slovanolides studied previously, including (III), the mutual orientation of the C(7)—H(7) and C(6)—O(6) bonds was synclinal causing the torsion angle at the junction to be negative. Thus, if we extend the notation of Samek (1978) (originally used for α-methylene-γ-lactones) to the saturated γ-lactones, (IV) has conformational type A while all other slovanolides are type S or P(S). The mode of puckering of the γ-lactone in (IV) is intermediate between an ideal C(7) envelope and the C(6), C(7) half-chair forms. The cyclopentenone ring in (IV) is approximately planar, with no atom deviating by more than 0·025 (6) Å; the average magnitude of the endocyclic torsion angles in the cyclopentenone moiety is 2·6 (1·4)°.

The molecular packing is due to van der Waals forces; no short intermolecular contacts were noted.

* The name slovanolides was proposed (Smítalová, Buděšínský, Šaman, Vašíčková & Holub, 1984) for a group of sesquiterpene lactones which are based on the $1\beta H,5\beta H,6\alpha H,7\alpha H$-guaian-6,12-olide structure.
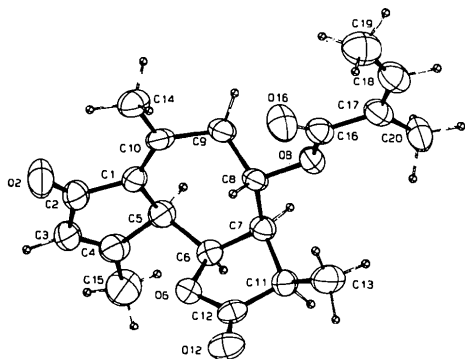


Fig. 2. A perspective view of the molecule of isobadkhysin (IV) with its atom-numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. H atoms are represented by spheres of arbitrary size.

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# Synthesis and Structure of a New DDQ Derivative: 3-{[3,5-Bis(2-pyridyl)-1,2,4-triazol-4-yl]amino}-5,6-dichloro-2-cyanobenzoquinone

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**Abstract.** $C_{19}H_9Cl_2N_7O_2$, $M_r = 438$, monoclinic, $P2_1/n$, $a = 8\cdot500$ (4), $b = 14\cdot224$ (3), $c = 17\cdot451$ (10) Å, $\beta = 91\cdot72$ (2)°, $V = 2108\cdot9$ Å$^3$, $Z = 4$, $D_x = 1\cdot477$ g cm$^{-3}$, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 2\cdot96$ cm$^{-1}$, $F(000) = 940$, room temperature, $R = 0\cdot0433$, $wR = 0\cdot0513$, 2916 unique reflections. A new quinoid compound is formed by the substitution of one of the CN groups in 2,3-dichloro-5,6-dicyanobenzoquinone with a 3,5-disubstituted-4-aminotriazole in anhydrous media.

**Introduction.** 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) is well known to act as a powerful acceptor in synthetic oxidative processes (Fatiadi, 1983) and in the formation of highly conductive charge transfer complexes (Mayerle & Torrance, 1981), especially with amino compounds (Ottenberg, Brandon & Browne, 1964). During the course of our investigations upon the complexing properties of 3,5-bis-(2-pyridyl)-4-aminotriazole, we have investigated the possibilities of it acting as a donor in charge transfer complexes especially with DDQ. In rigorously anhydrous conditions, a new quinoid compound is formed by the substitution of one of the CN groups in DDQ. Indeed the literature reports the substitution of the CN group by an alkoxy or hydroxy group (Middleton, Little, Coffmann & Engelhardt, 1958; Reynolds & Van Allan, 1964; Becker, 1969; Bruni, Tosi & Valle, 1988). To our knowledge, this is the first report of the substitution of a cyano group by an $R$NH$_2$ group [$R = $ 3,5-bis(2-pyridyl)-4-triazolyl]. The compound under study is in fact a new DDQ derivative which can act as a new organic acceptor. These properties are under investigation.

**Experimental.** *Synthesis.* The compound was obtained by mixing equimolecular amounts of dipyridylaminotriazole (dpat) with DDQ in rigorously anhydrous methanol. After standing for 48 h at room temperature, red crystals were recovered. They were air stable and suitable for X-ray analysis. The solvent must be dry to avoid the possibility of substitution of one of the CN ligands by an OH group. Details of the crystal data collection are given in Table 1. The structure was phased and refined by the *SHELX76* program (Sheldrick,