

## STRUCTURE OF DIBENZOYLBROWNIINE

Sh. M. Adizov, B. T. Salimov,  
and B. Tashkhodzhaev\*

UDC 547.944/945+548.737

The C<sub>19</sub>-norditerpenoid alkaloid 14-benzoylbrowniine that was isolated from *Delphinium biternatum* is known to exhibit valuable pharmacological properties [1]. It can be obtained from browniine (an alkaloid of the plants *D. biternatum*, *D. corymbosum*, *D. iliense*, *D. rotundifolium*, etc.) by benzylation with benzoylchloride. In addition to it as the main product, the dibenzoyl derivative of browniine can also be produced. The structure 8,14-*O,O'*-dibenzoylbrowniine was proposed based on PMR and mass spectra [2].

According to the chemical structure of browniine, the benzylation reaction could occur at three positions of the carbon framework, which has a secondary and two tertiary hydroxyls. The question of which positions (C7, C8, or C14) were benzylated was answered by us (in favor of C7 and C14) by performing an x-ray crystal structure analysis (XSA) of the reaction product. The C8 hydroxyl remained unaffected as a result of the reaction. The chemical formula and molecular structure of the alkaloid from the XSA are shown below (Fig. 1).

All stereochemical issues of the synthesized molecule were resolved by the XSA. Figure 1 shows the established absolute configuration of the carbon skeleton. The hydroxymethyl group in the C1 position and the benzoyl group in the C14 position had the  $\alpha$ -orientation. The other hydroxyls in the C6, C7, C8, and C16 positions and the methoxymethyl in the C4 position had the  $\beta$ -orientation.

The hydroxyl O atom on C8 in dibenzoylbrowniine was simultaneously close to three O atoms, i.e., the carbonyl O of the C7 benzoyl group (distance O6...O5 3.018 Å), the C6 methoxyl O (distance O6...O3 2.703 Å), and the ester O of the second benzoyl group on C14 (distance O6...O7 2.898 Å). The position of the H atom that was found experimentally indicated that a bidentate intramolecular H-bond of this proton and the C6 methoxyl O atoms (distance H...O3 2.30 Å, angle O6–H...O3 128°) and the C7 benzoyl carbonyl O atom (distance H...O5 2.51 Å, angle O6–H...O5 129°) could form. Apparently, this was responsible for the formation of dibenzoylbrowniine with benzoyl groups on C14 and C7.

The molecules in the crystal were situated within van-der-Waals distances. Short intermolecular contacts were not observed.

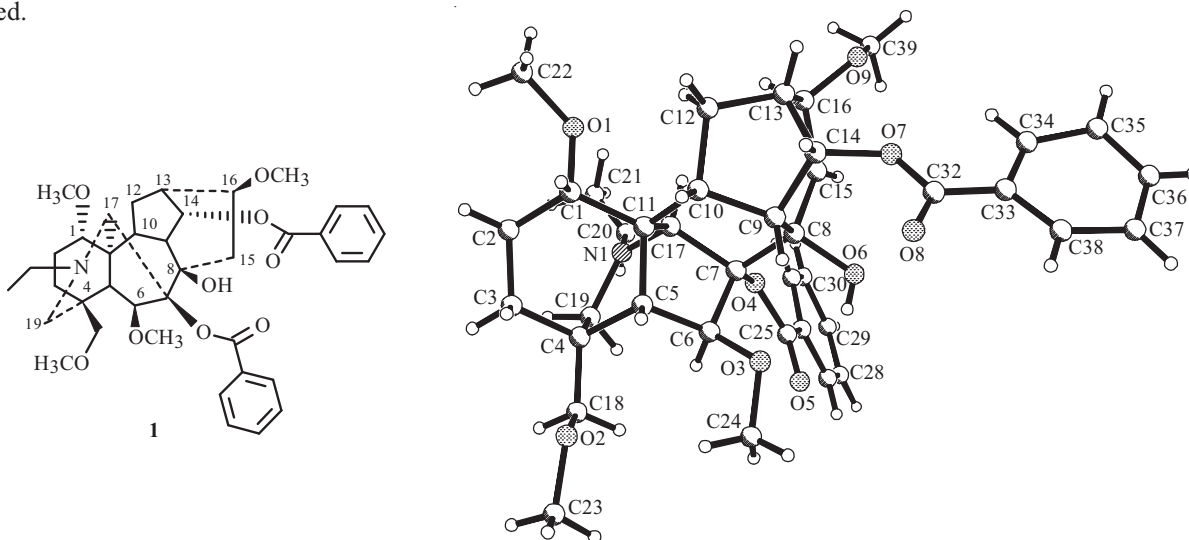


Fig. 1. Chemical and molecular structure of dibenzoylbrowniine.

S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax: (99871) 120 64 75, e-mail: tashkhodjaev@rambler.ru. Translated from *Khimiya Prirodnikh Soedinenii*, No. 1, January–February, 2013, pp. 165–166. Original article submitted October 8, 2012.

The purity of the compounds were checked on KSK silica gel plates using C<sub>6</sub>H<sub>6</sub>:EtOH (9:1) and chromatographic grade Al<sub>2</sub>O<sub>3</sub> using hexane:Et<sub>2</sub>O (3:1) and C<sub>6</sub>H<sub>6</sub>:EtOH (20:1).

**7,14-O,O'-Dibenzoylbrowniine.** A mixture of browniine (1.2 g), Py (10 mL), and benzoylchloride (5 mL) was left at room temperature for 4 d. Traces of Py were removed *in vacuo* upon adding EtOH to the reaction mixture to afford crystalline 7,14-O,O'-dibenzoylbrowniine (1.4 g, C<sub>39</sub>H<sub>48</sub>NO<sub>9</sub>), mp 192–193°C (MeOH).

**X-ray Crystal Structure Analysis.** Single crystals of the compound for the XSA were obtained by slow evaporation at room temperature of an EtOH solution. Monoclinic crystals had parameters  $a = 8.918(2)$ ,  $b = 19.556(4)$ ,  $c = 10.189(2)$ ,  $\beta = 93.92(2)$  ( $P2_1$ ,  $Z = 2$ ,  $\rho = 1.264$  g/cm<sup>3</sup>) that were determined and refined on a CCD Xcalibur diffractometer (Oxford Diffraction) (300 K, graphite monochromator). A three-dimensional data set of reflections ( $4.90 \leq \theta \leq 77.20^\circ$ ) was obtained from the crystals using  $\omega/2\theta$ -scanning and Cu K $\alpha$ -radiation. Absorption corrections were made by the Multi-scan method [3]. The total number of reflections was 5103 [ $I > 2\sigma(I)$  1669].

The structure was solved by direct methods using the SHELXS-97 programs. The structure was refined using the SHELXL-97 program. All non-hydrogen atoms were refined by anisotropic full-matrix least-squares methods (over  $F^2$ ). The final agreement factor [ $I > 2\sigma(I)$  and total]  $R_1 = 0.0525$  (0.1291) and  $wR_2 = 0.1317$  (0.1621). Positions of H atoms were found geometrically and refined with fixed isotropic thermal parameters  $U_{iso} = nU_{eq}$ , where  $n = 1.2$  for all types of H atoms and  $U_{eq}$  is the equivalent isotropic thermal parameter of the corresponding C atoms. The hydroxyl H atom was found in a difference electron-density synthesis and refined isotropically.

The x-ray structure data were deposited as a CIF-file in the Cambridge Crystallographic Data Centre (CCDC No. 911448).

## REFERENCES

1. R. Shakirov, M. V. Telezhenetskaya, I. A. Bessonova, S. F. Aripova, I. A. Israilov, M. N. Sultankhodzhaev, V. I. Vinogradova, V. I. Akhmedzhanova, T. S. Tulyaganov, B. T. Salimov, and V. Tel'nov, *Khim. Prir. Soedin.*, 244 (1996).
2. B. T. Salimov, F. N. Dzhakhangirov, and M. S. Yunusov, in: *Nitrogenous Heterocycles and Alkaloids*, Vol. 1, V. G. Kartsev and G. A. Tolstikov, eds., Iridium-press, Moscow, 2001, 603 pp.
3. G. M. Sheldrick, *Program for Empirical Absorption Correction of Area Detector Data*, University of Goettingen, Goettingen, 1996.