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MOLECULAR STRUCTURE OF METHYL 1-ISOPROPENYL-5a,5b,8,8,11a-PENTAMETHYL-9-OXO-10-[(*E*)-1-PHENYLMETHYLIDENE] PERHYDROCYCLOPENT [*a*]CHRYSENE-3a-CARBOXYLATE

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The molecular structure of methyl 1-isopropenyl-5a,5b,8,8,11a-pentamethyl-9-oxo-10-[(*E*)-1-phenylmethylidene]perhydrocyclopent[*a*]chrysene-3a-carboxylate **II** is determined. Compound **II** $C_{38}H_{52}O_3$ crystallizes in the non-centrosymmetric $P2_1$ space group with the cell parameters: $a = 11.4450(8)$ Å, $b = 11.1995(8)$ Å, $c = 12.5179(9)$ Å, $\beta = 93.984(2)°$.

Keywords: methyl 1-isopropenyl-5a,5b,8,8,11a-pentamethyl-9-oxo-10-[(*E*)-1-phenylmethylidene] perhydrocyclopent[*a*]chrysene-3a-carboxylate, single crystal X-ray diffraction.

2-Benzylidenetriterpenoids exhibit valuable pharmacologic properties; these compounds are used in the synthesis of heterocycles annulated with the ring A [1, 2]. Ozone treatment of 2-benzylidenesteroids of the androstane series is a short way to 2,3-diketones [3]. The literature contains no information on the structural determination of 2-benzylidenetriterpenoids and steroids by single crystal X-ray diffraction. This paper presents the synthesis and molecular structure of methyl 1-isopropenyl-5a,5b,8,8,11a-pentamethyl-9-oxo-10-[(*E*)-1-phenylmethylidene]perhydrocyclopent[*a*]chrysene-3a-carboxylate **II**.

Experimental. Synthesis of methyl 1-isopropenyl-5a,5b,8,8,11a-pentamethyl-9-oxo-10-[(*E*)-1-phenylmethylidene]perhydrocyclopent[*a*]chrysene-3a-carboxylate II (Fig. 1). 2.6 mmol of benzaldehyde and 5 ml of 40% KOH solution in ethanol were added under stirring and cooling (≤10°C) to the solution of 2 mmol (0.88 g) betulonic acid methyl ether **I** in 10 ml ethanol. The mixture was kept for 30 min at this temperature, 24 h at room temperature and then poured into 50 ml of 5% HCl solution; the residue was filtered, washed with water, air dried, and purified by column chromatography on aluminium oxide; the eluent was benzene; the yield was 0.97 g (87%). The crystals for X-ray diffraction were obtained by slow crystallization of the substance from benzene at room temperature followed by drying in vacuum. Found, %: C 81.96, H 9.30, $C_{38}H_{52}O_3$. Calculated, %: C 81.97, H 9.41. R_f 0,80. T_m 202-204°C. The ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.80, 0.93, 1.00, 1.12, 1.17 5 s (15H, 5CH_3), 1.20—1.90 m (17H, CH_2, CH), 1.71 s (3H, H-30), 2.17-2.32 m (1H, H-1), 3.65 s (3H, OCH_3), 4.64 s (1H, H-28), 4.76 s (1H, H-28), 7.27-7.62 m (10H, H-arom.), 7.50 s(1H, H-32). The ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5, 15.2, 15.6, 19.4, 20.2, 21.5, 22.2, 25.5, 29.3, 29.5, 30.5, 31.9, 32.9, 36.3, 36.7, 38.1, 40.4, 42.3, 44.3, 45.0, 46.7, 48.4, 49.2, 51.4, 52.7, 56.4, 109.4, 128.2, 128.2, 128.2, 130.1, 130.1, 134.1, 135.8, 137.1, 150.5, 176.4, 207.9.

The NMR spectra of^{13}C and ^{1}H were recorded on a Bruker AM-300 spectrometer (75.5 MHz and 300 MHz respectively) with tetramethylsilane (TMS) as the internal standard. Single crystal X-ray diffraction was measured on a

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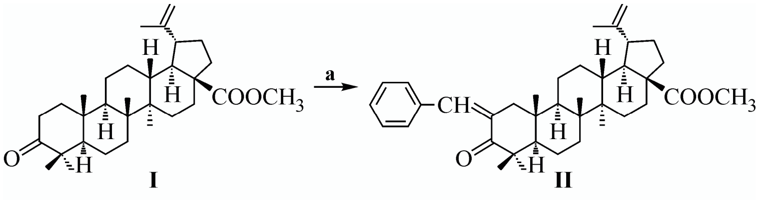

Reaction conditions: (a) benzaldehyde, 40% KOH/EtOH

Fig. 1. Synthesis scheme of methyl 1-isopropenyl-5a,5b,8,8,11a-pentamethyl-9-oxo-10-[(*E*)-1-phenylmethylidene]perhydrocyclopent[*a*]chrysene-3a-carboxylate **II**.

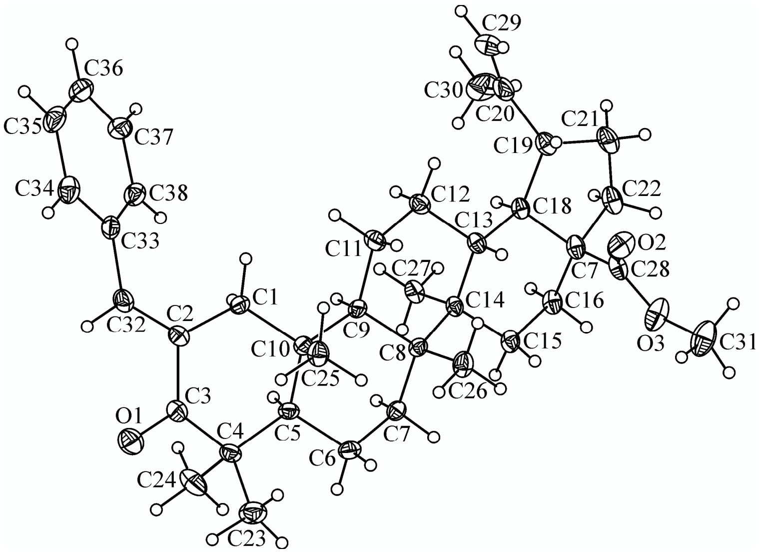

Fig. 2. Structure of methyl 1-isopropenyl-5a,5b,8,8,11a-pentamethyl-9-oxo-10-[(*E*)-1-phenylmethylidene]perhydrocyclopent[*a*]chrysene-3a-carboxylate **II**.

Bruker SMART APEX II diffractometer. The melting temperature was determined on a Boetius heating stage. TLC was performed on Silufol plates (Chemapol, Czech Republic) using the 25:1 chloroform–methanol solvent system. The substances were detected with a 10% solution of phosphotungstic acid in ethanol followed by heating at 100-120°C for 2-3 min.

Single Crystal X-Ray Diffraction of Compound II. The colorless prismatic crystals of $C_{38}H_{52}O_3$ (M = 556.800) are monoclinic; at 100 K, $a = 11.4450(8)$ Å, $b = 11.1995(8)$ Å, $c = 12.5179(9)$ Å, $\beta = 93.984(2)°$, $V = 1600.6(2)$ Å^3, $P2_1$ space group, $Z = 2$, $d_x = 1.155$ g/cm^3. The experimental set of 21,155 reflexes was collected on a Bruker SMART APEX II diffractometer at 100 K (λMoK_α radiation, $\theta_{max} = 30.14°$) from a single crystal with dimensions of 0.20×0.15×0.10 mm. The initial array of the measured intensities was processed using the SAINT [4] and SADABS programs [5]. The structure was solved by the direct method and refined by the full matrix LSM in an anisotropic approximation for non-hydrogen atoms against F^2_{hkl}. Hydrogen atoms were placed into geometrically calculated positions and refined using the riding model ($U_{iso}(H) = nU_{eq}(C)$, where $n = 1.5$ for carbon atoms of methyl groups and $n = 1.2$ for other C atoms). We used 4942 independent reflections in the refinement ($R_{int} = 0.0437$). The refinement convergence over all independent reflections was $wR_2 = 0.1113$ ($R_1 = 0.0424$ in 4278 reflections with $I > 2\sigma(I)$). All the computations were made on an IBM PC using the SHELXTL software package [6]. Atomic coordinates and temperature factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC) No. 731389; http://www.ccdc.cam.ac.uk/products/csd/request/.

Results and Discussion. Compound **II** was synthesized by the interaction of betulonic acid methyl ether **I** with benzaldehyde in alcoholic alkali. The product of the reaction was purified by column chromatography on aluminium oxide with an 87% yield. Single crystal XRD was used to determine the molecular (Fig. 2) and crystal structure of methyl 1-isopropenyl-5a,5b,8,8,11a-pentamethyl-9-oxo-10-[(*E*)-1-phenylmethylidene]perhydrocyclopent[*a*]chrysene-3a-carboxylate **II**. Compound **II** crystallizes in the non-centrosymmetric $P2_1$ space group. The five-membered ring is characterized by *envelope* conformation (with the C17 atom being out of the plane of the other four atoms at 0.647(3) Å), and the cycles *B*, *C* and *D* have *chair* conformation, which is typical of the compounds of this class. The ring *A* is in distorted *boat* conformation. The C10 and C3 atoms are out of the plane of the other four atoms C1, C2, C4, and C5 in the same direction at 0.769(3) Å and 0.155(3) Å respectively. Note that the cycles similar to the ring *A*, i.e. with substituents forming double bonds with the neighboring carbon atoms of the ring, are characterized by various conformations from slightly distorted *chair* to distorted *boat* [7], and the opposite carbon atoms may be out of the planar tetragonal fragment (C1, C2, C4, and C5, in the case of the molecule of **II**) both in the same and opposite directions. The bond lengths and bond angles in the structure of **II** are typical of the compounds of this class [8], and the crystal structure is stabilized by common van der Waals interactions.

Conclusions. Single crystal XRD has been used for the first time to characterize the structure of methyl 1-isopropenyl-5a,5b,8,8,11a-pentamethyl-9-oxo-10-[(*E*)-1-phenylmethylidene]perhydrocyclopent[*a*]chrysene-3a-carboxylate **II**.

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