Chemistry of Natural Compounds, Vol. 30, No. 6, 1994

FIRST EXAMPLE OF THE FORMATION OF HIGHLY ORDERED SUPERMOLECULAR STRUCTURES IN A SERIES OF GIBBERELLIN DERIVATIVES

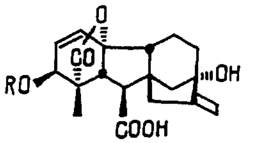
A. G. Druganov, V. V. Lapachev,
O. P. Petrenko, and V. A. Raldugin

UDC 538.975+547.992

The 3-O-palmitate and 3-O-tridecanoate of gibberellin A_3 have been synthesized and monomolecular Langmuir-Blodgett films have been obtained from them.

The creation of ordered molecular assemblies and of the corresponding materials involves many branches of fundamental and applied science [1, 2]. One of the most productive methods of obtaining such assemblies is the Langmuir-Blodgett (LB) technology [3]. Recently, with its aid, a unique series of experiments has been conducted on obtaining ordered supermolecular structures from biochemical materials, including enzymes [4]. The corresponding film coatings offer wide possibilities for the investigation of the effects of molecular recognition, and supersensitive sensors for pesticides and narcotics has been constructed from layers of them [4].

Interesting possibilities for the construction of highly ordered and highly specific "recognizing" surfaces with complex reliefs are presented by suitable chemical derivatives of biologically active isoprenoids. We have synthesized previously unknown esters of the phytohormone gibberellin A_3 (GA_3) (1) with higher fatty acids — the 3-O-palmitate (2) and the 3-O-tridecanoate (3) — using GA_3 and the chlorides of the corresponding acids as the initial compounds.



1. $R=H$
2. $R=CO(CH_2)_{14}CH_3$
3. $R=CO(CH_2)_{11}CH_3$

The molecules of compounds (2) and (3) consist of two fragments in each case — a hydrophilic cyclic part and a hydrophobic alkyl residue. The combination of these fragments should, as may be assumed, lead to the formation of a stable monomeric layer when using the LB technology. When a dilute solution of derivative (2) in chloroform was deposited on the surface of water and the layer was gradually compressed by a barrier [3], an increase in the surface pressure connected with an intermolecular reaction between the molecules of the gibberellin A_3 derivative was observed (at an area of less than 100—150 Å^2 per molecule; Fig. 1). Such a large area is apparently connected with an initial predominant orientation of the molecules under investigation on the water surface that is favorable for the solvation of all the hydrophilic fragments and corresponds approximately to the maximum cross-section of the gibberellin fragment. Further compressive movement of the barrier led to more dense packing of the molecules. Apparently, the molecules are smoothly oriented, without phase transitions, in such a way that only the hydroxy and carboxy groups of the cyclic fragment are oriented towards the surface of the water. For compound (2), as can be seen from π—σ diagrams (see Fig. 1) an exceptionally stable film was formed for which no destruction of the monolayer was observed at a pressure of 50—60 mN/m.

We may note that for traditional amphiphils (long-chain fatty acids) the minimum length of the hydrocarbon chain ensuring stability of a LB film is 16—18 carbon atoms [1]. To evaluate the dependence of the stability of the monomolecular films of acylgibberellins formed on the length of the acyl "tail", we investigated compound (3), with a shorter hydrophobic

---

Novosibirsk Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 793-795, November-December, 1994. Original article submitted August 10, 1994.

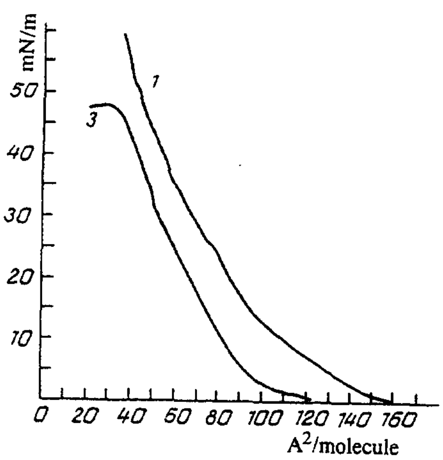


Fig. 1. Dependence of the surface pressure in the area per molecule of GA_3 3-O-palmitate (2) and GA_3 3-O-tridecanoate (3).

fragment. However, in this case, as well, a stable, although somewhat weaker, film was formed; on the compression isotherm collapse (crumpling) was observed at an area of 30 $Å^2$ (see Fig. 1), which corresponds approximately to the section of the molecule perpendicular to the surface of the water.

The monomolecular films of compounds (2) and (3) were readily transferred to a silica support by Langmuir's method [3], and it was possible to obtain a silica surface covered with molecules of the acylgibberellins A_3.

EXPERIMENTAL

Gibberellin A_3 3-O-Palmititate and 3-O-Tridecanoate. With stirring, 1.5 g of tridecanoyl chloride was added dropwise to a solution of 1.5 g of gibberellin A_3 in 5 ml of pyridine. After being kept at room temperature for 15 h, the reaction mixture was treated with 10 ml of ethyl acetate and 10 ml of water. The organic layer was separated off and washed with 5 ml of 10% hydrochloric acid and with water (4 × 10 ml). The extract was dried over $MgSO_4$, filtered, and evaporated to dryness. The crude residue was chromatographed on 50 g of SiO_2 with elution by chloroform. The yield of the ester (3) was 1.91 g (81%). Similarly, 2.10 g (83%) of ester (2) was obtained from 1.5 g of GA_3 and 1.8 g of palmitoyl chloride. The homogeneity of the esters (2) and (3) obtained was confirmed by TLC and reversed-phase HPLC.

The ester (3) — colorless crystals with mp 136-138°C (from hexane—$CHCl_3$). PMR spectrum (Py-d_5 200 MHz): 0.77 (CH_3—CH_2—), 1.13 (broad singlet, methylene protons of the acyl residue), 1.47 (3H, s, Me-4), 3.19 (1H, d, J = 11.0 Hz, H-6), 3.70 (1H, d, J = 11.0 Hz, H-5), 4.96 (1H, s, H-17a), 5.54 (1H, s, H-17b), 5.69 (1H, d, J = 4.0 Hz, H-3), 5.94 (1H, dd, J = 9.5 and 4.0 Hz, H-2), 6.54 (1H, d, J = 9.5 Hz, H-1). IR spectrum (in KBr): 1760, 1735, 1165 cm^{-1}.

The ester (2) — crystalline powder, mp 127-131°C (from hexane—$CHCl_3$). Its PMR and IR spectra were practically identical with those of the ester (3).

Monomolecular films of compounds (2) and (3) were investigated in an apparatus constructed of polytetrafluoroethylene by the classical scheme [3] and manufactured by Évrika NTTs [Scientific and Technical Center, Moscow]. The surface tension was measured with the aid of a Wilhelmy balance, and π—σ isotherms (π being the surface pressure, σ the area occupied by one molecule) were recorded and processed with the aid of a PC. As the subphase we used double-distilled water containing 10^{-4} M $CdCl_2$. On the surface of the water was deposited 40-60 μl of a solution of compound (2) or (3) in $CHCl_3$ (c = 1 mg/ml). To evaluate the cross-section of the molecule we used X-ray structural characteristics [5].

REFERENCES

1. L. M. Blinov, Usp. Khim., **52**, No. 8, 1263 (1983).
2. O. V. Chechel' and E. N. Nikolaev, Pribory Tekhn. Éxperim., No. 9, 19 (1991).

3. V. S. Gevod, O. S. Ksenzhek, and I. L. Reshetnyak, Biol. Membrany, **5**, No. 2, 1237 (1988).
4. G. C. Guilbault and J. H. Luong, J. Biotechnology, **9**, 1 (1988).
5. L. Kutschabsky and G. Adam, J. Chem. Soc. Perkin I, 1653 (1983).