NATURE OF THE TRANSFORMATIONS OF OLEANOLIC ACID IN AN ACID MEDIUM

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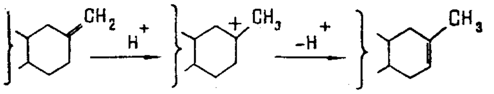
3-Trifluoroacetoxyoleanolic acid and 3-trifluoroacetoxyolean-13(18)-en-28-oic acid have been isolated from the mixture of the products of the transformation of oleanolic acid in a trifluoroacetic acid medium, and their structures have been established with the aid of IR, PMR and mass spectra. The formation of these products indicates an unambiguous route of the stabilization of the intermediate carbocation with the charge on the C-13 atom. The hydroxy group at C-3 is esterified by the trifluoroacetic acid.

The interaction of pentacyclic triterpenoids with acids has been the object of numerous investigations [1-3]. The question has not only a theoretical value but also a practical aspect. Thus, in the evaluation of the quantitative amount of oleanolic acid glycosides in a plant raw material using titration with alkali of the carboxy group of the aglycon, possible processes involving the transformation of the aglycon in an acid phase must be taken into account. According to results obtained by Brieskorn et al. [1, 2], in pentacyclic triterpenoids with a Δ^{12} double bond and an OH group at C-3 the action of sulfuric acid leads to dehydration in ring A and to the migration of the double bond with the formation of a $\Delta^{11,13(18)}$ dienic system. Oganesyan [3] has shown that, in sulfuric acid, triterpenoids with a Δ^4 double bond are protonated at the double bond with the formation of a carbocation in accordance with Markovnikov's rule, and when a carboxy group is present at C-28 subsequent lactonization takes place.

Earlier, in the course of a study of the nature of the protonation of unsaturated sesquiterpenoid coumarins of the iresane series in trifluoroacetic acid (TFA) [4], we came to the conclusion that the migration of an α,α-disubstituted exocyclic double bond into the ring also takes place through its carbocation. Studying the nature of the transformations of oleanolic acid (I) in TFA, we concluded that the lactonization described by Oganesyan [3] is not the only route for the stabilization of the carbocation formed in an acid medium.



When the PMR spectra of a solution of oleanolic acid in TFA was recorded every 20-30 min for 5 h from the moment of dissolution, a gradual downfield shift of the H-3 signal from 3.64 to 4.88 ppm was observed: The intensity of the first signal decreased as far as complete disappearance and the intensity of the second increased. This fact permits the assumption of the esterification of the hydroxyl at C-3 by the trifluoroacetic acid. In addition to the change in the chemical shift, a change in the multiplicity of the signal took place. With the weakfield shift, the relatively sharp triplet at 3.64 ppm became a broadened multicomponent multiplet which was due to the superposition of the H-3 signals of more than one compound. The intensity of the signal of the olefinic proton in the final stage of recording the spectrum was several times less than the intensity of the H-3 signal.

From the reaction mixture of oleanolic acid and TFA, two main reaction products were isolated by chromatography on a column of silica gel: compound (II) — $C_{32}H_{47}F_3O_4$, mp 235-238°C, M^+ 552; and (III) — $C_{32}H_{47}F_3O_4$, mp 300-303°C, M^+ 552. In the PMR spectra of both compounds ($CDCl_3$) there are no signals of olefinic protons, and the signals of the H-3 protons appear in the form of triplets at 4.71 and 4.73 ppm, respectively.

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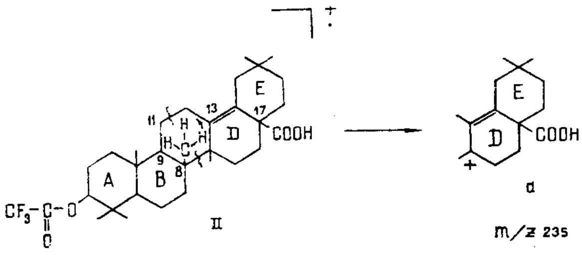
There are no absorption bands of OH groups and C=C bonds in the IR spectrum of (III), which, in combination with the presence of an absorption band at 1763 cm^{-1} (ν_{CO} of a trifluoroacetoxy group and of a γ-lactone) and the features of the PMR spectrum correspond to the structure of a lactone of trifluoroacetoxyoleanolic acid.

The molecule of (II) retains the carboxy group, since the IR spectrum exhibits a broad diffuse band in the 3500-2800 cm^{-1} region (ν_{OH}) and an intense band at 1690 cm^{-1} ($\nu_{C=O}$). Since the molecular weight of (II) is the same as that of the trifluoroacetoxyoleanolic acid lactone and there is a free COOH group, the molecule must contain a double bond. The absence from the PMR spectrum of the signal of an olefinic proton shows the tetrasubstituted nature of this bond, the only possible variant of which is $\Delta^{13(18)}$. The nature of the fragmentation of (II) under the action of electron impact also indicates that the double bond is located between C-13 and C-18.

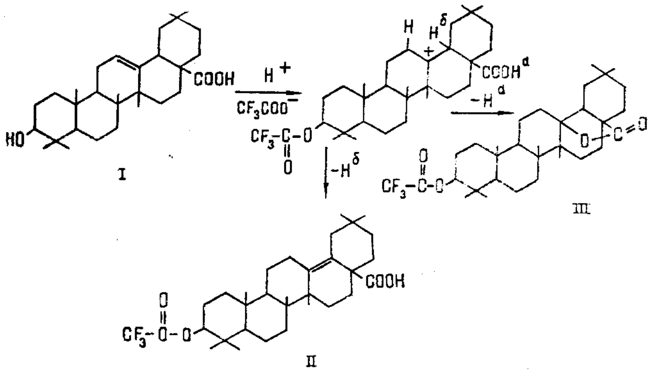
The peak of the ion with m/z 235 (a) is characteristic for the fragmentation of a pentacyclic triterpene with $\Delta^{13(18)}$ and COOH at C-17 [5].



The peaks of ions with m/z 248 (rings D and E) and 303 (rings A and B) correspond to another fragmentation pathway with the cleavage of the C_{11}—C_{12} and C_8—C_{14} bonds of ring C, which is also typical for the compounds mentioned [5]. Other ion peaks in the mass spectrum confirm the presence of COOH and CF_3COO groups in the molecule of (II): m/z 552 (M^+), 506 (M − 46, M − HCOOH), 439 (M − 113, M − CF_3COO—), 438 (M − 114, M − CF_3COOH), 189 (m/z 235 − 46, 235 − HCOOH and 303 − 114, m/z 303 − CF_3COOH).

On the basis of the facts given above, the compound described is represented by structure (II).

Thus, the formation of the $\Delta^{13(18)}$-oleanene derivative (II) together with lactone (III) from oleanolic acid in an acid medium can be explained by the assumption that the carbocation formed on the protonation of the olefinic bond is stabilized by deprotonation not only at the carboxyl (lactonization) but also at C-18.



TFA is a weaker acid than sulfuric and does not cause degradation in ring A but esterifies the hydroxyl at C-3; however, the model of the protonation of the olefinic bond and the stabilization of the carbocation must be the same in both cases.

In addition to the two substances described, two other weakly polar products were formed in the course of the reaction and were isolated in trace amounts in the form of a noncrystalline mixture with M^+ 508 and 506. Apparently, in addition to the two directions of deprotonation of the carbocation that have been mentioned a decarboxylation process with the formation of compounds with one and two olefinic bonds is also possible.

EXPERIMENTAL

The IR spectra of the substances were measured on a UR-20 instrument, PMR spectra on a Varian HA-100D instrument in $CDCl_3$ and CF_3COOH, and mass spectra on a Varian instrument.

Reaction of Oleanolic Acid with Trifluoroacetic Acid (TFA). A solution of 0.5 g of oleanolic acid (I) in 10 ml of TFA was left at room temperature for two days. Then the reaction mixture was poured into 100 ml of water and the resulting precipitate was filtered off, washed with water to neutrality, and dried at 60°C for 6 h.

The mixture of reaction products (0.525 g) was chromatographed on a column (diameter 2 cm) of 40/100 μm silica gel (10.0 g). Elution was performed with chloroform, 3-ml fractions being collected. Fractions 4 and 5 contained traces of an oily product consisting of two substances with M^+ 508 and 506. Fractions 7 and 8 yielded compound (III) — $C_{32}H_{47}F_3O_4$, mp 300-303°C (from ethanol), M^+ 552.

From fractions 17, 18, and 19 was isolated compound (II) — $C_{32}H_{47}F_3O_4$, mp 235-248°C (from aqueous ethanol), M^+ 552.

SUMMARY

Under the action of trifluoroacetic acid, oleanolic acid forms a γ-lactone at the COOH group and C-13 and also 3-trifluoroacetoxyolean-13(18)-en-28-oic acid, which indicates an unambiguous route of the stabilization of the intermediate carbocation with the charge at C-13. The hydroxy group at C-3 is esterified by the trifluoroacetic acid.

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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*

X. SILENEOSIDE E — 2-DEOXY-α-ECDYSONE 3-O-β-D-GLUCOPYRANOSIDE — FROM *Silene brahuica*

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A new ecdysteroid has been isolated from the epigeal organs of *Silene brahuica* Boiss. — 2-deoxy-α-ecdysone 3-O-β-D-glucopyranoside (I), $C_{33}H_{54}O_{10}$, mp 195-196°C, $[\alpha]_D^{20}$ + 44.4° (methanol). The enzymatic hydrolysis of (I) led to 2-deoxy-α-ecdysone. Details of the IR, UV, mass, and ^1H and ^{13}C NMR spectra of all the compounds are given.

We are continuing a study of the ecdysteroids of plants of the genus *Silene* (family Caryophyllaceae) [1, 2]. From the epigeal organs of the plant *S. brahuica* Boiss. collected in the valley of the R. Chomkemin (Kungei-Alatau range, northern Tien-Shan), in addition to the known 2-deoxy-α-ecdysone (I), 2-deoxyecdysterone (II), and ecdysterone (III), we have isolated a new ecdysteroid — sileneoside E (IV).

Compound (IV) proved to be a glycoside and, according to GLC [3] contained one D-glucose residue. In the products of the enzymatic hydrolysis of sileneoside E performed with the gastric juice of the snail *Helix plectotropis* 2-deoxy-α-ecdysone (I) was detected as the aglycon.

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