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STRUCTURE-SELECTIVE STEREOSPECIFIC CYLCIZATION OF E,E-FARNESOL AND ITS ACETATE BY FLUOROSULFONIC ACID

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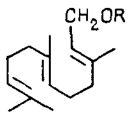
UDC 547.597+542.91

Information on the acid cyclization of farnesol (I) and its acetate (II) is sparse. Under the action of formic acid, depending on the conditions, farnesol is converted into a mixture of bisabolenes or α-cadinene [1], and on interaction with the complex of mercury trifluoromethanesulfonate and N,N-dimethylaniline followed by the reduction of the reaction product with sodium tetrahydroboride it is converted into drimenol (III) (yield 51%) [2]. The cyclization of E,E-farnesyl acid (II) with the mercury trifluoromethanesulfonate—2,6-di-tert-butylpyridine complex takes place structure-specifically and stereospecifically and leads after the reduction of the product with sodium tetrahydroborate to a mixture of a monoacetate of driman-8α,11-diol (IV) (44%) and the acetates of drimenol (V) and of 9-epidrimenol (VI) (23%) [2].

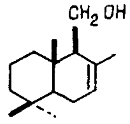
We have investigated the cyclization of E,E-farnesol (I) and its acetate (II) with fluorosulfonic acid in 1-nitropropane. The main product of the reaction of E,E-farnesol (I) proved to be (±)-drimenol (III) (71%). In addition to this, a small amount of hydrocarbons (12%) and of a polymeric substance was formed. The optimum reaction conditions were the following: ratio of substrate to cyclizing agent 1:1; —80 to —85°C; 1 h. Triethylamine was added to the reaction mixture which was then worked up in the usual way, and the product was chromatographed on a column of silica gel impregnated with silver nitrate.

On cyclization with fluorosulfonic acid, E,E-farnesyl acetate (I) gave (±)-drimane-8α,11-diol 11-monoacetate (IV) and a small amount of hydrocarbons. The greatest yield of the hydroxy acetate (IV) (77%) was achieved under the following conditions: ratio of substrate to fluorosulfonic acid 1:10; —80 to —85°C; 5 min. The yield of the hydrocarbon fraction under these conditions was 13%.

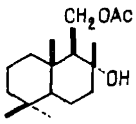
Compounds (III) and (IV) were identified by a spectral comparison with optically active forms of them.



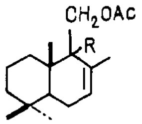
I. R=H
II. R=Ac



III



IV



V. R=αH
VI. R=βH

Thus, fluorosulfonic acid is a highly effective cyclizing agent converting E,E-farnesol (I) and its acetate (II) structure-selectively and stereospecifically into drimane sesquiterpenoids.

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β-AMYRIN AND β-AMYRIN ACETATE FROM *Euphorbia ferganensis*

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We have continued a study of the low-molecular-weight metabolites of the plant *Euphorbia ferganensis* B. Fedtsch. (*Euphorbiaceae*) [1].

A chloroform extract obtained from an ethanolic extract of the roots of *Euphorbia ferganensis* was chromatographed on a column of silica gel with elution by hexane—benzene (7:1). Crystalline substances (I) and (II) were isolated.

Substance (I) had mp 195-197°C, $[\alpha]_D^{24}$ +89 ± 2° (s 1.0; chloroform), M^+ 426, composition $C_{30}H_{50}O$. Its IR spectrum had the absorption band of a hydroxy group (3460-3400 cm^{-1}). In the strong-field region of its PMR spectrum ($CDCl_3$), the signals of eight methyl groups were observed in the form of singlets and a one-proton quartet at 3.18 ppm ($^3J_1$ = 11 and $^3J_1$ = 5 Hz), assigned to a hemihydroxylic proton, and also the signal of an olefinic proton at 5.14 ppm (triplet with ^3J = 3 Hz) of one proton unit.

The facts given permit the assumption that substance (I) belongs to the tetracyclic triterpenoids of the olean-12-ene series. This was also shown by the mass-spectrometric fragmentation of compound (I), which was characteristic for pentacyclic triterpenoids [2]. The peaks of ions with m/z 218 and 207 arising as a consequence of retrodiene decomposition appeared in the mass spectrum. The spectral characteristics and physicochemical constants of substance (I) showed its identity as β-amyrin [3].

Substance (II) had mp 233-235°C, $[\alpha]_D^{24}$ +75 ± 2° (s 1.3 benzene), M^+ 468, composition $C_{32}H_{52}O_2$. The IR spectrum of the compound showed absorption bands of an ester group (1735, 1260 cm^{-1}). The PMR spectrum of substance (II) ($CDCl_3$), having a three-proton singlet at 2.01 ppm, showed that it contained one acetyl group.

The alkaline hydrolysis of substance (II) with 0.5% methanolic potassium hydroxide at room temperature led to a product identified as β-amyrin from physicochemical constants and also from its R_f values on TLC in various solvent systems.

Thus, β-amyrin and β-amyrin acetate have been isolated from the roots of *Euphorbia ferganensis*.

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