The structures and stereochemistries of the compounds synthesized were shown on the basis of spectral features and by a comparison of their physicochemical and spectral characteristics with those given in the literature [1].

Thus, fluorosulfonic acid in 2-nitropropane is an effective reagent for the structurally selective stereospecific cyclization of 13E,17E- and 13E,17Z-bicyclogeranylfarnesols and their acetates into tetracyclic compounds of the scalarane series.

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STRUCTURALLY SELECTIVE STEREOSPECIFIC CYCLIZATION OF E,E,E,E-GERANYLFARNESOL AND ITS ACETATE BY FLUOROSULFONIC ACID

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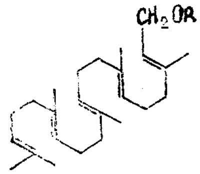
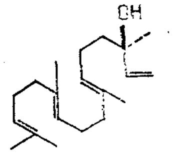
UDC 547.596/599

We have shown previously for the case of sesqui- and diterpenes that fluorosulfonic acid is an effective cyclizing agent, ensuring the structurally selective stereospecific occurrence of the reaction [1, 2]. It appeared of interest to investigate the interaction of fluorosulfonic acid with E,E,E,E-geranylfarnesol (I) and its acetate (II), since, in the first place, the cyclization of acyclic sesterterpenoids has not yet been studied at all and, in the second place, the result of the reaction should be the formation of tetracyclic hydrocarbon systems which it has not yet been possible to obtain in satisfactory yields by the cyclization of aliphatic compounds without the introduction into the molecules of the latter of additional structural fragments arranged in a definite way which stabilize the carbocations arising during the reaction [3].

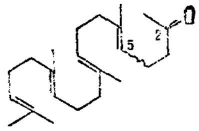
Compounds (I) and (II) were synthesized from E,E-geranyllinalool (III). The latter on interaction with acetoacetic ester by the Carrol reaction gave a mixture (∿3:1) of the ketones (IV) and (V) (85%), which was separated by column chromatography on silica gel. The E,E,E-geranylgeranylacetyl (IV) was converted by the Wittig–Horner reaction with triethyl phosphonoacetate into a mixture (9:1) of the esters (VI) and (VII) (∿70%). Reduction of the first of them with lithium ethoxytrihydroaluminate led to the alcohol (I) (93%), which was acetylated with acetic anhydride in pyridine to the acetate (II) (∿92%).



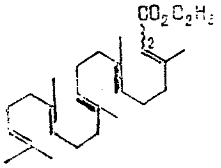
I. R = H
II. R = Ac



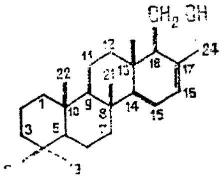
III



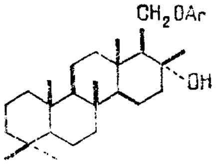
IV. 5E
V. 5Z



VI. 2E
VII. 2Z



VIII



IX

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0009-3130/88/2405-0651$12.50

On the interaction of E,E,E,E-geranylfarnesol (I) in fluorosulfonic acid in 2-nitropropane (ratio of substrate to cyclizing agent = 1:25; concentration of substrate 0.15 M and of reagent 2.05 M; −(80-85)°C, 2 h), the main reaction product was (±)-18αH-scalar-16-en-25-ol (VIII) (~56%). In addition to this, a small amount (∿8.7%) of hydrocarbons was formed but these have not yet been investigated.

Under the same conditions, E,E,E,E-geranylfarnesyl acetate (II) gave the 25-monoacetate of (±)-18αH-scalar-17α-25-diol (IX) (∿59%) and a small amount (∿9%) of a hydrocarbon fraction. The remainder of the cyclization products consisted of polymeric material.

Compounds (VIII) and (IX) were identified by a chromatographic and spectral comparison with samples of their optically active forms obtained in the cyclization of trans-trans-bicyclogeranylfarnesol and its acetate [4].

Thus, it has been shown for the first time that the cyclization of E,E,E,E-geranylfarnesol and its acetate to form tetracyclic scalarane sesterterpenoids by fluorosulfonic acid in 2-nitropropane takes place, in relatively good yield, structurally selectively and stereospecifically.

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