CYCLIZATION AND REARRANGEMENT OF DITERPENOIDS.
V. STRUCTURALLY SELECTIVE STEREOSPECIFIC CYCLIZATION OF all-trans-GERANYLGERANIOL AND ITS ACETATE BY FLUOROSULFONIC ACID

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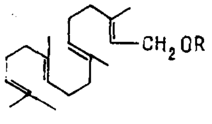
Two studies devoted to the cyclization of the p-nitrobenzoate [1] and acetate [2] of all-trans-geranylgeraniol by the complex of mercury trifluoromethanesulfonate and N,N-dimethylaniline are known. In both cases, the reaction took place with low structural selectivity and the yield of tricyclic isoagathane diterpenoids was low. A similar pattern has also been observed in the cyclization of the acetate of the terminal epoxide of all-trans-geranylgeraniol by tin tetrachloride [3] and of epoxygeranylgeraniol (methyl carbonate) by boron trifluoride etherate [4].

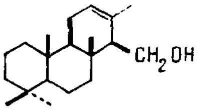
We have investigated the cyclization of geranylgeraniol (I) and its acetate (II) in a superacid medium. On the interaction of all-trans-geranylgeraniol (I) with fluorosulfonic acid in 1-nitropropane, the main reaction product proved to be (±)-14αH-isoagath-12-en-15-ol (III). In addition to this, a small amount of hydrocarbons was formed. The following reaction conditions were the optimum: ratio of substrate to cyclizing agent 1:20; temperature −70 to −82°C; time 4 min. The reaction was stopped by the addition of triethylamine. After the usual working up of the reaction mixture, the product was separated by chromatography on a silica gel column. The yield of (±)-agath-12-en-15-ol (III) was 87%, and that of the hydrocarbon fraction 8%.

The main cyclization product of all-trans-geranylgeraniol acetate (II) with fluorosulfonic acid was (±)-14αH-isoagathane-13α,15α-diol 15-monoacetate (IV). Its maximum yield (58% or, taking the unchanged initial compound into account, 72%) was achieved when the reaction was performed at −70 to −75°C for 20 min at a ratio of substrate to cyclizing agent of 1:10. Under these conditions, 10% of the initial substance was recovered unchanged. The yield of hydrocarbon fraction was 5.4%. About 17% of the reaction product consisted of a polymeric substance.

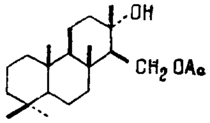
Compounds (III) and (IV) were identified chromatographically and by spectral comparison samples of their optically active forms that we had obtained previously [5, 6].



I. R = H
II. R = Ac



III



IV

Thus, fluorosulfonic acid has proved to be a highly effective cyclizing agent, performing the conversion of geranylgeraniol and its acetate into tricyclic isoagathane diterpenoids. In contrast to the media tried previously [1-4], it ensures a high structural selectivity of the cyclization reaction, and also its chemo- and stereospecificity.

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ESSENTIAL OIL OF Eucalyptus macarthuri

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The chemical composition of the essential oil of Eucalyptus macarthuri Deane et Maid., cultivated on the territory of the USSR has not previously been studied. There is information [1] that this oil possesses a high biological activity.

We have investigated the essential oil obtained by the steam-distillation method from the leaves of plants gathered in the flowering stage at the Sukhumi experimental station of the All-Union Scientific-Research Institute of Plant Growing. Yield 1.6%; light yellow liquid with a pleasant smell; n_D^{20} 1.4730, d_{20}^{20} 0.9045.

The composition of the essential oil was determined by capillary gas chromatography and by chromato-mass spectrometry. This was carried out in a HP-5840 capillary gas chromatograph and a Hewlett-Packards HP-5995B quadrupole chromato-mass spectrometer. The mass spectrometer was linked to the gas chromatograph through a system of direct introduction with open discharge. In both cases, the components were separated in capillary columns with a chemically grafted-on phase (5% of phenylmethylsilicone). The thickness of the layer of this phase was 0.5 μ, the internal diameter of the column 0.32 mm and its length 25 m, with a rate of flow of carrier gas (helium) of 2.5 ml/min.

The analysis was performed with programming of the temperature from 100 to 250°C at the rate of 10°C per minute. The initial temperature was maintained for 2 min and the final temperature for 3 min. Mass spectra were recorded at the rate of 690 amu per second in the range of mass numbers of from 340 to 4000. Ionization was brought about by electron impact at the standard voltage of 70 eV.

The identification and structural assignment of the components to definite classes from their mass spectra was performed on the basis of the general laws of the fragmentation of the molecular ions of compounds of the terpene series known from the literature [2-4] and from the mass spectra of standard substances.

The amounts of the components present were determined by the internal-normalization and internal-standard methods [5].

The essential oil of Eucalyptus macarthuri contains (%) on the whole oil): α-pinene, 2.44; camphene, 0.26; β-pinene, 0.07; Δ^3-carene, 0.11; p-cymene, 0.18; 1,8-cineole, 30.21; α-terpineol, 3.22; terpenyl acetate, 8.91; a terpene alcohol, 15.93; a sesquiterpene hydrocarbon, 3.91; palustrol, 1.66; a sesquiterpene alcohol, 2.53; globulol, 8.62; ledol, 3.68; a sequiterpene alcohol, 17.56; and unidentified components not assigned to a definite class, 0.53.

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