

STIZOLICIN—A NEW SESQUITERPENE LACTONE FROM STIZOLOPHUS
CORONOPIFOLIUS

M. N. Mukhametzhano, V. I. Sheichenko, K. S. Rybalko, and D. A. Pakaln

Khimiya Prirodnikh Soedinenii, Vol. 5, No. 2, p. 125, 1969

Stizolophus coronopifolius (Lam.) Cass is an annual herbaceous plant of the family Compositae growing in eastern and southern Transcaucasia. From the epigeal part of the plant collected in the budding phase in Azerbaidzhan on the Dzheiranchel mountain plateau on July 5, 1968 we have isolated a colorless crystalline substance with the composition $C_{20}H_{26}O_7$, mp 152–153.5° C (from ethanol), $[\alpha]_D^{25} -32.4^\circ$ (c 2.19; ethanol). The IR spectrum exhibits absorption bands at, cm^{-1} , 3455 and 3480 (OH), 1762 and 1670 (α -methylene of a γ -lactone), 1720 and 1240 (C=O), and 1650 (C=C).

The NMR spectrum has signals of two methyl groups: one of them is present on a double bond—singlet at 1.7 ppm—and the second is probably attached to an epoxide grouping—1.20 ppm. Two doublets, each of one proton unit, at 5.95 and 6.39 ppm ($J = 3$ Hz) show the presence of an exocyclic α -methylene group conjugated with a γ -lactone carbonyl. A complex two-proton signal in the 4.4–4.9 ppm region apparently represents the superposition of the signals of lactone and ester protons.

When the substance was hydrogenated over an Adams Pt catalyst in ethanol, 3 moles of hydrogen were absorbed.

Dehydrogenation of the initial substance over Se at 335–350° C for 10 min led to chamazulene, which was identified by thin-layer chromatography with a reference sample.

The information obtained permits the conclusion that the substance isolated is a sesquiterpene lactone containing an ester group of five carbon atoms. Its constants and IR and NMR spectra show that this lactone is a new one which has not been described previously in the literature. We have called it stizolicin. The study of the structure of stizolicin is continuing.

17 September 1968

All-Union Scientific-Research Institute for Medicinal Plants

UDC 547.925

MICROBIOLOGICAL OXIDATION OF PREGNENOLONE

M. B. Gorovits, A. D. Kovesnikov, and N. K. Abubakirov

Khimiya Prirodnikh Soedinenii, Vol. 5, No. 2, pp. 125–126, 1969

We have studied the microbiological hydroxylation of pregnenolone by means of a strain of Circinella muscae. Two grams of pregnenolone (I) was added to a growing culture of the fungus, and after fermentation 1.8 g of product (II) was obtained.

Compound II, $C_{21}H_{32}O_4$, had mp 234–235° C, $[\alpha]_D^{25} -38.4^\circ$ (c 1.25; methanol). The IR spectrum of the substance exhibited absorption bands corresponding to hydroxyl groups (3250–3500 cm^{-1}), a double bond (3040 cm^{-1}), and a keto group (1695 cm^{-1}). A count of the protons in the NMR spectrum showed the presence of two secondary and one tertiary hydroxyl groups. A qualitative test for the oxidation of compound II with $NaIO_4$ [1] and $Pb(OAc)_4$ [2] was negative.

The acetylation of substance II (acetic anhydride—pyridine, 36° C, 3 days) yielded a diacetate $C_{25}H_{36}O_6$ (III) with mp 175–177° C, $[\alpha]_D^{23} -133.3^\circ$ (c 1.20; chloroform). The catalytic hydrogenation of the diacetate III over platinum was accompanied by the simultaneous hydrogenolysis of one of the acetate groups. Subsequent oxidation of the reduced product with chromic anhydride yielded 3 β ,9 α -dihydroxy-5 α -pregnan-20-one 3-acetate (IV) [3] with mp 183–185° C, $[\alpha]_D^{25} +64.9^\circ$ (c 1.54; chloroform). The treatment of the pregnanediol IV with thionyl chloride in pyridine gave 3 β -hydroxy-5 α -pregn-9(11)-en-20-one 3-acetate (V) [4], with mp 125–129° C, $[\alpha]_D^{24} +77.8^\circ$ (c 0.77; chloroform).

It follows from this that the newly introduced tertiary hydroxyl group is present at C₉ and a secondary hydroxyl group at C₇. The increment in the molecular rotation between II and 3 β ,9 α -dihydroxypregn-5-en-20-one [3]