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STIZOLICIN—A NEW SESQUITERPENE LACTONE FROM STIZOLOPHUS CORONOPIFOLIUS

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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° (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 pmm—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.

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MICROBIOLOGICAL OXIDATION OF PREGNENOLONE

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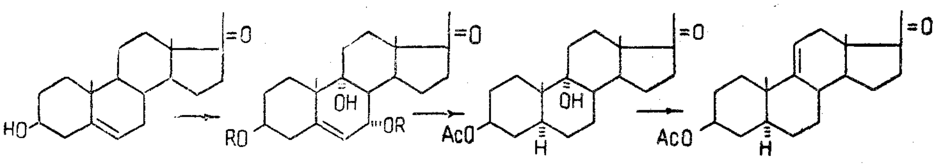
We have studied the microbiological hydroxylation of pregnenlone by means of a strain of Circinella muscae. Two grams of pregnenolone (I) was added to a growing culture of the fungus, and after fermentation 1.8 g of product (II) was obtained.

Compound II, $C_{21}H_{32}O_4$, had mp 234–235° C, $[\alpha]_D^{25}$ −38.4° (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° (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 3β,9α-dihydroxy-5α-pregnan-20-one 3-acetate (IV) [3] with mp 183–185° C, $[\alpha]_D^{25}$ +64.9° (c 1.54; chloroform). The treatment of the pregnanediol IV with thionyl chloride in pyridine gave 3β-hydroxy-5α-pregn-9(11)-en-20-one 3-acetate (V) [4], with mp 125–129° C, $[\alpha]_D^{24}$ +77.8° (c 0.77; chloroform).

It follows from this that the newly introduced tertiary hydroxyl group is present at C_9 and a secondary hydroxyl group at C_7. The increment in the molecular rotation between II and 3β,9α-dihydroxypregn-5-en-20-one [3]

($\Delta[M]_D$ − 81.9°) and that between their acetate ($\Delta[M]_D$ − 499.0°) shows the α-configuration of the hydroxyl at C_7. Consequently, compound II is 3β,7α,9α-trihydroxypregn-5-en-20-one.



I

II R=H

III R=Ac

IV

V

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A CHALCONE FROM COTTON PLANT FLOWERS

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In a study of the flowers of the cotton plant of the thin-fibered type 5094I growing in the south of Uzbekhistan we have isolated a chalcone glycoside with the composition $C_{21}H_{21}O_{13}$.

The chalcone crystallizes from aqueous ethanol in two forms: with mp 202–203° C (decomp.) and with mp 228–229° C (decomp). The substance apparently has cis and trans forms.

On a paper chromatogram in the butan-1-ol—acetic acid—water (4 : 1 : 5) system a single clear spot with R_f 0.22 is found. The two forms give identical UV spectra with additives: λ_{max}, mμ, 385, 248, 260 (C_2H_5OH); 395, 265, (+CH_3COONa); 395, 265 (+H_3BO_3); 443, 270 ($AlCl_3$).

The complete splitting off of the sugar from the aglycone was achieved by heating the substance with concentrated hydrochloric acid in the boiling water bath for 10 min. This gave 65.4% of aglycone and 35.4% of glucose (1 : 1).

The aglycone, with the composition $C_{15}H_{11}O_8$, mp 308–309° C (decomp.), R_f 0.43 (BAW), crystallizes in the form of orange needles with a green tinge. When a paper chromatogram is sprayed with a 2% solution of sodium bicarbonate, the spot of the aglycone is colored dirty green.

UV spectrum of the aglycone with additives, λ_{max}, mμ, 380, 277, 260 (C_2H_5OH); 395, 270 mμ (+CH_3COONa); 390, 270 mμ (+H_3BO_3); 440, 270 mμ ($AlCl_3$).

The following derivatives were obtained: pentaacetal derivative $C_{29}H_{25}O_{15}$, mp 226–227° C (reaction with $AlCl_3$ negative); pentamethyl ether $C_{22}H_{25}O_8$ with mp 166° C (reaction with $AlCl_3$ negative).

The sugar formed after acid and enzymatic (Aspergyllus oryzae) hydrolyzes was identified as glucose by paper chromatography in the ethyl acetate—pyridine—water (2 : 1 : 2) system.

Qualitative reactions for a glucoside: no coloration with Mg and HCl and with Zn and HCl; brown-green coloration ethanolic $FeCl_3$ solution; dark red solution with a green fluorescence with concentrated H_2SO_4; red-orange solution with concentrated aqueous sodium hydroxide; bright yellow coloration with aqueous $SbCl_3$ solution. On paper chromatography, in ordinary light the spot was yellow and in UV light it was dark brown.

The properties of the chalcone glycoside are close to those of gossypin and gossypitrin and its aglycone is similar to the gossypetin previously isolated from the flowers of the cotton plant [1–3].