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ACROPTILIN — A NEW SESQUITERPENE LACTONE FROM ACROPTILON REPENS

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Two crystalline substances have been isolated from the leaves and flower heads of Acroptilon repens (L.) DC. A new sesquiterpene lactone — repin — has been reported previously [1].

We give the results of a study of a second substance having the composition $C_{21}H_{24}O_9$ [1] with mp 196–198° C (from ethanol), $[\alpha]_D^{20}$ +92.3° (c 0.688; alcohol); it contains $2H_{lab}$; on chromatography in a thin layer of neutral alumina (activity grade IV) in the petroleum ether–benzene–chloroform–methanol (5:4:2:1) system it had R_f 0.29, in the benzene–ethanol (9:1) system R_f 0.44, and in ethyl acetate R_f 0.74; revealing agent a 0.5% solution of potassium permanganate in 0.5% sulfuric acid.

The IR spectrum has absorption bands in the 3470 region (OH group) and the 1743 cm^{-1} region (C=O) and a weak band at 1665 cm^{-1} (C=C). In the UV spectrum above 209 mμ there are no maxima characteristic for conjugated systems.

When the substance was heated with an ethanolic solution of alkali, three equivalents of caustic potash was consumed. However, the saponification products did not separate out. In the cold, the substance dissolves slowly in 5% caustic potash solution. From the neutral fraction obtained on saponification was obtained a colorless crystalline substance (II) with the composition $C_{15}H_{20}O_6$, mp 184–186° C (decomp). The IR spectrum of (II) has a well-defined peak at 3550 cm^{-1} (OH group), a broad band at 3440–3280 cm^{-1} (adjacent OH groups), and bands at 1775 (γ-lactone) and 1645 cm^{-1} (C=C). The IR spectrum of its acetyl derivative (III) has absorption bands at 3510 cm^{-1} (OH group), 1780 (γ-lactone), 1740 and 1255 ($OCOCH_3$), and 1650 cm^{-1} (C=C).

On hydrogenation, I consumed 3 moles of hydrogen per mole, and when it was dehydrogenated over selenium at 240–260° C for 2.5 hr guaiazulene was obtained.

These results show that the second substance isolated from Acroptilon repens is also a new sesquiterpene lactone; we have called it acroptilin.

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TURCOMANIC ACID FROM JUNIPERUS TURCOMANICA

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Juniperus turcomanica B. Fedtsch. was collected in November 1965 on Mount Dushak close to Kheirabad in the Geok-Tepe region, TurkmSSR.

When an acetonic extract of the needles (after the elimination of acetone) was shaken in ethereal solution with a 2% solution of sodium carbonate, a solid suspension formed at the boundary between the two layers. The solution was filtered and the residue was washed with ether. After recrystallization from ethanol, colorless crystals with mp 356–357° C were isolated. The crystals were dissolved in water and the aqueous solution was acidified with dilute sulfuric acid. A colorless precipitate readily soluble in diethyl ether deposited.

Recrystallization from ethanol gave colorless crystalline needles with a stable mp of 218° C. Yield 0.2% (of the dry acetone extract of the needles).

Found, %: C 75.55, 75.42; H 9.67, 9.72. Calculated for $C_{20}H_{30}O_3$, %: C 75.47; H 9.43; mol. wt. 318 (by mass spectroscopy).

The UV spectrum had no maximum whatever (between 400 and 220 mμ). The IR spectrum of the substance had the following bands: 3440 cm^{-1} (OH group), 1700 (CO in a carboxy group), 1640 and 900 cm^{-1} (double bond, possibly of the $CH_2 =$ type). Thus, we had obtained a hydroxy acid with a composition relating it to the diterpenes.

Many workers [1–5] have isolated resin acids of the pimaric acid group from plants of the genus Juniperus and other genera of the family Cupressaceae.

The closest to the hydroxy acid that we isolated is hydroxysandaracopimaric acid [3], but it has mp 270° C.

Evidently the hydroxy acid $C_{20}H_{30}O_3$ that we found is a new one, at least for junipers; we have called it turcomanic acid.

The IR spectra (on a UNICAM SP.200 spectrometer) and the mass spectra of turcomanic acid were taken in the Institute for the Chemistry of Natural Compounds AS USSR.

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ALKALOIDS OF GLAUCIUM FLAVUM

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A study of the alkaloid composition of Glaucium flavum Grantz. has led to the isolation of, in addition to the alkaloids known for this genus, a base with the composition $C_{19}H_{21}NO_4$, mp 125–126° C (benzene), $[\alpha]_D^{20}$ +60° (c 0.9591; ethanol); hydrochloride $C_{19}H_{21}NO_4 \cdot HCl$ with mp 260–262° C (decomp., aqueous ethanol); picrate with mp 194–196° C (decomp., aqueous ethanol).

When the base $C_{19}H_{21}NO_4$ was compared with a sample of the alkaloid d-aurotensine (I), kindly given to us by I. Slavik, their IR spectra were found to coincide and there was no depression of the melting point of a mixture. However, our alkaloid contains a N-methyl group and two mobile hydrogens, and on treatment with acetic anhydride it formed a triacetyl derivative $C_{25}H_{27}NO_7$ with mp 165–167° C (alcohol), which possessed no basic properties and was optically inactive.

The production of a triacetyl derivative which, according to the IR spectrum, contains not only a O-acetyl but also a N-acetyl group (1770, 1648 cm^{-1}), can be explained by the rupture of the C–N bond during acetylation with simultaneous N-acetylation which is characteristic for the aporphine alkaloids. In actual fact, the methylation of the base that we had isolated with diazomethane gave its di-O-methyl derivative, which proved to be identical with d-glaucine. The results of the investigations carried out show that our base $C_{19}H_{21}NO_4$ is identical with authentic d-aurotensine from G. flavum. This base is bis-O, O-demethylglaucine.

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