REFERENCES

1. I. F. Makarevich, M. Ya. Tropp, and D. G. Kolesnikov, Farmatsevt. zh. 4, 36, 1960; DAN SSSR, 136, 3, 617, 1961; Med. prom. SSSR, 7, 38, 1961; DAN SSSR, 147, 4, 849, 1962.
2. I. F. Makarevich, et al., Med. prom. SSSR, 7, 23, 1963.
3. N. P. Maksyutina, ZhOKh, 28, 1383, 1958.
4. I. F. Makarevich and I. G. Zoz, Med. prom. SSSR, 5, 19, 1964.
5. Z. Kowalewski, Helv. Chim. Acta, 43, 1314, 1960.

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THE CRYSTALLINE SUBSTANCE FROM CARPESIUM EXIMIUM C. WINKLER

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Two sesquiterpene lactones have previously been isolated from Carpesium abrotanoides L.: carpesialactone [1, 2] with bp 200-202/5 mm and composition $C_{15}H_{20}O_3$, and carabrone with mp 90-91°, $[\alpha]_D + 116.9°$ and empirical formula $C_{15}H_{20}O_3$ [3].

The sesquiterpene lactone content of other representatives of the genus Carpesium has not been investigated.

We have studied Carpesium eximium C. Winkler (C. macrocephalum Franch. et Sav.). It has been established provisionally that the leaves of this plant contain γ-lactones. The Carpesium eximium was collected in July 1964 in the south of Primorskii Krai.

Aqueous extraction of the leaves and flower heads [4] gave a colorless crystalline substance with mp 155-157.5°. The thin-layer chromatography of this substance, as well as of its mother liquor, on alumina in the petroleum ether–benzene–chloroform–methanol (5 : 4 : 1 : 2) system gave only one spot with R_f 0.74.

The IR spectrum of the compound obtained had absorption bands of an OH group (3450 cm^{-1}), an α, β-unsaturated γ-lactone (1745, 1672 cm^{-1}), and a double bond (1647 cm^{-1}). Found, %: C 74.20, 74.29; H 8.14, 8.08; mol. wt. 284. Calculated for $C_{17}H_{22}O_3$, %: C 74.45, 8.02; mol. wt. 274.

The presence of a lactone ring was confirmed by the solubility of the substance in alkalies on heating. This substance is readily soluble in alcohol and ether.

On comparing the results obtained for the substance isolated with literature data, we came to the conclusion that it is probably a new, previously unreported sesquiterpene lactone.

REFERENCES

1. T. Karlyone and N. Kawano, Chem. Abst., 44, 1918, 1950.
2. S. Naito, Chem. Abst., 50, 891, 1956.
3. H. Minato, S. Nasaka, and I. Horibe, Proc. Chem. Soc., Apr., 120, 1964.
4. K. S. Rybalko, A. N. Ban'kovskaya, and R. I. Evstratova, Med. prom. SSSR, 3, 13, 1962.

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INVESTIGATION OF THE ALKALOIDS OF PEDICULARIS OLGAE

The Structure of Plantagonine and Indicaine

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We have previously isolated plantagonine and indicaine from the epigeal part of Pedicularis olgae [1]. In the present communication the structure of these alkaloids is considered. Indicaine is a cyclic aminoaldehyde, and oxidation converts it into plantagonine.

The UV spectrum of plantagonine has one maximum at 270 mμ (lg ε 3.12), which is characteristic of alkaloids of the pyridine series [2].

Since in the NMR spectrum of plantagonine, the signals of the protons of the methyl group give a doublet (δ = 1.15 ppm), the latter must be adjacent to a tertiary carbon atom.

The oxidation of plantagonine with alkaline potassium permanganate consumes 10 atoms of oxygen giving an amino acid with mp 310-312° which forms a methyl ester with mp 83-84°.

The IR spectrum of the amino acid exhibits stretching vibrations of two carboxyl carbonyl groups (1600, 1740 cm^{-1}) and of a pyridine nucleus (1520, 1580, 1625 cm^{-1}).

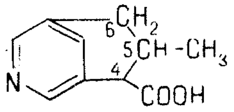
When the amino acid is heated at 320°, decarboxylation takes place with the formation of nicotinic acid. These results agree with the properties of pyridine-3, 5-dicarboxylic acid [3].

We have carried out the synthesis of pyridine-3, 5-dicarboxylic acid by the sulfonation of piperidine. Heating piperidine with fuming sulfuric acid (1:4) at 300° gave pyridine-3, 5-disulfonic acid [4]. Fusion of the latter with potassium hexacyanoferrate gave 3, 5-dicyanopyridine, and hydrolysis of this with hydrochloric acid yielded pyridine-3, 5-dicarboxylic acid.

The results of a direct comparison of the acid isolated in the oxidation of plantagonine with synthetic pyridine-3, 5-dicarboxylic acid (mixed mp test, paper and thin-layer chromatography, and the IR spectra of the methyl esters) showed their complete identity.

The production of pyridine-3, 5-dicarboxylic acid indicates that the residue $C_3H_4(CH_3)(COOH)$ is attached to the pyridine ring in the C_3 and C_5 positions, and forms a second six-membered ring.

The value of the chemical shift for the protons of the methyl group (δ = 1.15 ppm) shows that it must be in the γ position with respect to the pyridine ring, and consequently occupies the position at C_5, while the equivalent positions C_4 and C_6 remain for the carboxyl group. Thus, the following structure is proposed for plantagonine:



Substance	M+	M—CH_3	M—CO_2 M—CO	M—CH_3 M—CO_2 Or CO	118—CH_2=CH	91—CH_2
Plantagonine	177	162	133	118	91	77
Indicaine	161	146	133	118	91	77

The mass spectrum of plantagonine has an intense molecular ion at 177 m/e, 162 ($M^+ - CH_3$), 133 ($M^+ - CO_2$), 118 ($M - CH_3 - CO_2$) ions, and peaks at 91 and 77 m/e.

The 91 ion is formed from the 118 ion by the elimination of a fragment of mass 27, which is assigned to the CH CH_2=CH group, and the 77 ion from the 91 ion by the elimination of a CH_2 group.

The results of a comparison of the mass spectra of plantagonine and indicaine confirm this type of decomposition (table).

The formation of intense ions with m/e values of 162, 146, and 133 by the elimination of the functional groups confirms their location in the hydrogenated part of the molecule.

REFERENCES

1. Kh. Ubaev, P. Kh. Yuldashev, and S. Yu. Yunusov, Uzb. khim. zh., no. 3, 33, 1963.
2. Fu Feng-Yung and Sun Nan-Chum, C. A., 8310, 1959.
3. Dictionary of Organic Compounds [in Russian], 1, 970, 1949.
4. W. Koenigs and R. Geigy, Ber., 17, 589, 1884.

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