BRIEF COMMUNICATIONS

NAPHTHENIC DERIVATIVES OF Ligularia macrophylla

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Continuing an investigation of Ligularia macrophylla D. C. Prodz [1, 2] collected in the flowering period in Alma-Ata province, on the chromatographic separation of the petroleum extract of the roots we isolated a crystalline substance with the composition $C_{31}H_{60}O$, mp 78-79°C, M^+ 448, readily soluble in chloroform and ethanol, sparingly in petroleum ether, and insoluble in water, with a yield of 0.001%.

The mass spectrum of the substance contained peaks differing from one another by 14 mass units (21 of them) and characteristic for a saturated hydrocarbon chain. These peaks had mass numbers corresponding to $C_nH_{2n-1}^+$, and there were also the peaks of ions with m/z 69, 83, 97, 111, 125, and 139, which are characteristic for monocyclic naphthenes. The absence of a peak at 84 m.u. and the presence of strong peaks with m/z 420 ($M^+ - 28$) (15%) and 378 ($M^+ - 70$) (100%) unambiguously showed the presence of a five-membered ring [3].

According to its IR and PMR spectra, the substance contained no hydroxy groups, ether bonds, or oxide rings but did contain a carbonyl group (ν_{max} 1708 cm^{-1}). Peaks with m/z 43, 57, 71, and 83 m.u. permitted the substance to be assigned to the ketone group.

It is known that in the case of saturated ketones cleavage takes place of an α-bond in relation to the carbonyl group, as a result of which the peaks of the $R_1C{\equiv}O$ and R_2 ions and of the R_1 and $R_2C{\equiv}O$ ions are formed. From their values it appeared possible to determine the mass numbers of the radicals and thereby the position of the carbonyl group in the molecule of the substance under investigation.

The presence of the first fragment $(-CH_2)_{21}CH_3$ was confirmed by the appearance in the mass spectrum of the peaks of ions with m/z 309 (12.5%) and of $\underset{\underset{O}{\|}}{C}-(CH_2)_{21}CH_3$ with m/z 337 (55%).

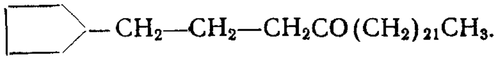
The second fragment, $C_5H_9-(CH_2)_3$ was confirmed similarly by the peaks of ions with m/z 111 (29.5%) and of $C_5H_9(CH_2)_3\underset{\underset{O}{\|}}{C}$ with m/z 139 m.u. (15%).

In addition, when three or more carbon atoms are present in the hydrocarbon chain the cleavage of a β-bond usually takes place with migration of the γ-atom of hydrogen to the positively charged fragment.

In the mass spectrum of the substance, the peaks of ions with m/z 354 (77.5%) and 154 (15%) were observed, which showed β-decomposition and confirmed the suggested structure.

In the PMR spectrum (in $CDCl_3$, δ scale), a triplet at 2.28 ppm, J = 6 Hz (4 H), corresponded to methylene protons adjacent to a carbonyl group, and a strong singlet at 1.2 ppm to the protons of the methylene groups of a hydrocarbon chain.

From these facts it is most likely that the substance under investigation has the following structure:



The second crystalline substance, with the composition $C_{26}H_{52}O$, mp 74-75°C, M^+ 380, was isolated from the epigeal part of the plant. By analogy with substance (I), its spectral characteristics likewise showed that it was a naphthene derivative (m/z 139, 125, 97,

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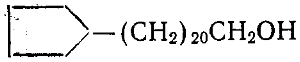
83, and 69). The presence of a peak with m/z 335 ($M^+ - 17 - 28$) (42.9%) stronger than a peak with m/z 293 ($M^+ - 17 - 70$) (23.0%) is characteristic for naphthenes with a five-membered ring. The substance was a primary alcohol [IR spectrum: ν_{max} 3580-3630 cm^{-1}; mass spectrum: peaks with m/z 380 ($M^+ - 17$) (9.6%); PMR spectrum: triplet at 3.53 ppm, J = 6 Hz, 2 H].

On the basis of what has been said, the most probable structure for substance (II) is the following



We are the first to have detected naphthenic derivatives in plants of the genus Ligularia.

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CARBOHYDRATES OF THE INFLORESCENCES OF Calendula officinalis

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The inflorescences of pot marigold Calendula contain a series of pharmacologically active substances relating to various classes of natural compounds [1, 2]. In the present communication we consider the results of an investigation of the polysaccharides of inflorescences of pot marigold Calendula isolated from raw material gathered in 1986.

Polysaccharides are attracting ever increasing attention at the present time as medicinal agents acting in various directions [3].

Fractions of carbohydrates from the raw material were isolated by the following scheme. The raw material was first defatted with chloroform, and then with carbohydrates were extracted: with 82% ethanol — the ethanol-soluble sugars (ESs); with water — the water-soluble polysaccharides (WSPSs); with a mixture of 0.5% solutions of oxalic acid and ammonium oxalic acid and ammonium oxalate — the pectin substances (PSs); and with 7 and 14% solutions of caustic potash — the hemicelluloses (HCs).

The ESs were freed from noncarbohydrate components with 10% lead acetate and sodium sulfate solutions. After filtration and concentration of the solution, the sugars were precipitated from a methanolic solution with acetone (1:3), and the precipitate was washed with anhydrous acetone and was dried with ether and over P_2O_5 in a vacuum desiccator. Free glucose, sucrose, and unidentified reducing oligosaccharides were detected in the ESs by paper chromatography in systems 1) butanol—pyridine—water (6:4:3), and 2) ethyl acetate—acetic acid—formic acid—water (18:3:1:4). The reducing sugars were revealed with aniline phthalate, and the nonreducing ones with Bonner's reagent [4].

The WSPSs and the PSs were freed from proteins by Sevag's method [5] and were precipitated with methanol (1:3). The HCs were neutralized with acetic acid and precipitated in the same way as the preceding fraction. The polysaccharides were determined by a gravi-

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