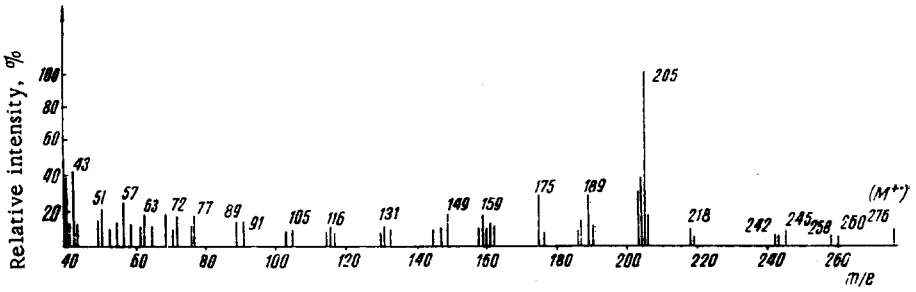

Fig. 2. Mass spectrum of lophopterol.

Structure (Ib) is also confirmed by the results of the oxidation of the substance in acetone with chromium trioxide in an acid medium (20% H_2SO_4), which gave the known acetonide (III), $C_{18}H_{20}O_6$, with mp 121-121.5°C, obtained previously in the study of angelol [6].

Thus, lophopterol has the structure of 6-(1'-hydroxy-2',3'-epoxy-isopentyl)-7-methoxycoumarin (Ib), and in it the H-1' and H-2' protons have the trans configuration, since the value of their SSCC are characteristic for such protons with the trans configuration [7].

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ACETYLCYNAROSIDE, A NEW ACYLATED FLAVONOID FROM *Campanula patula*

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We have continued a study of the flavonoids of the epigeal part of *Campanula patula* L., from which luteolin, cynaroside, and patuloside have previously been isolated [1]. The raw material was extracted with 70% ethanol, the aqueous ethanolic extracts were evaporated in vacuum, and the aqueous residue was treated successively with chloroform and ethyl acetate. The combined flavonoids from the ethyl acetate extract were separated on a column of polyamide. On elution with mixtures of ethanol and chloroform (5:95 → 30:70), a new glycoside with the composition $C_{23}H_{22}O_{12}$ was isolated, which we called *acetylcynaroside*.

Acetylcynaroside has mp 249-251°C (MeOH), $[\alpha]_D^{18}$ −126° (c 0.29; MeOH—DMFA, 8) 2), $\lambda_{max}^{C_2H_5OH}$ 257, 268 sh., 355 nm (log ε 4.09, 4.04, 4.09). Its IR spectrum shows an absorption band at 1730 cm^{-1}, which is characteristic for an ester grouping.

The products of the acid hydrolysis of the substance under investigation (5% H_2SO_4, 100°C, 2 h) were found to contain D-glucose and luteolin (mp 327-328°C, M^+ 286). Emulsin and rhamnodiastase do not cleave the glycoside.

UV spectra with diagnostic reagents showed the presence of a substituent in position 7 of the luteolin. Alkaline saponification of the glycoside gave cynaroside (luteolin 7-O-β-D-

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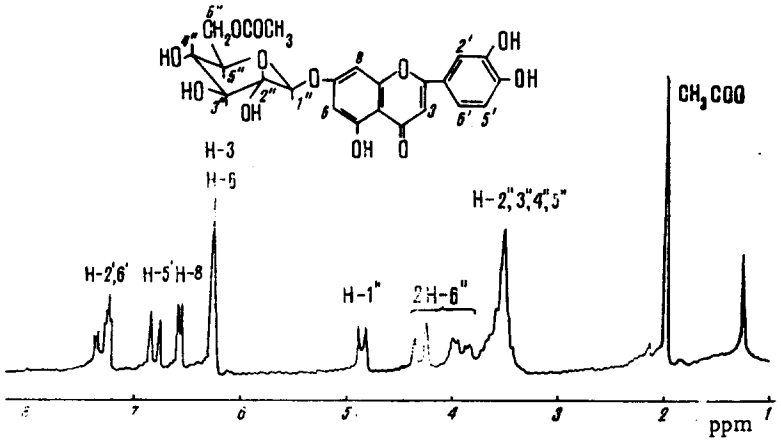

Fig. 1. NMR spectrum of the TMS ether of acetylcynaroside in CCl_4 (internal standard TMS).

glucopyranoside) and acetic acid. The latter was shown by the preparation of its hydroxamate derivative and its comparison with a marker by paper chromatography [2].

Acetylation of the glycoside gave an acetate with the composition $C_{35}H_{34}O_{18}$, mp 241-243°C, ν_{CO} 1650, 1760, 1785 cm^{-1}. The NMR spectrum of the acetate showed the singlets of three aromatic acetoxy groups (δ 2.42, 2.37, 2.35), and four aliphatic acetoxy groups resonated in the form of three singlets at 2.07 ppm (3 H), 2.05 ppm (6 H), and 2.03 ppm (3 H). A comparison of the heptaacetate obtained with the full acetate of cynaroside showed the identity of their compositions, melting points, and IR and NMR spectra.

The position of attachment of the acetyl group in the compound under investigation was shown by the NMR spectrum of the trimethylsilyl derivative (Fig. 1). The signal of the anomeric proton (doublet at δ 4.85 with J = 6.5 Hz) showed a β-link with the aglycone and the Cl conformation of the D-glucopyranose. A triplet of a hemiacyl methine proton was absent in the weak field, and consequently the acetyl group is present in position 6 of the glucose. The signals of the proton of the hemiacyl methylene group form a broadened doublet (δ 4.28; J_{gem} = 12 Hz) and a quartet with a poorly resolved structure (δ 3.9 ppm). The other glucose protons resonate in the 3.2-3.7-ppm region, and the acetoxy group gives a singlet at 1.95 ppm, while the aromatic protons of luteolin form a characteristic group of signals in the 6.2-7.3-ppm region.

Thus, acetylcynaroside has the structure of 3',4',5-trihydroxyflavone 7-O-(6"-O-acetyl-β-D-glucopyranoside) (see Fig. 1).

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