# FREE AND GLUCOSYLATED MONOTERPENE ALCOHOLS IN THE PETALS OF *Rosa gallica*

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The essential oil of the rose contains the monoterpene alcohols linalool (I), citronellol (II), nerol (III), and geraniol (IV), which can be found in the α and β isomeric forms.

In order to determine their structure in detail, we have isolated these alcohols from the essential oil by preparative gas–liquid chromatography in a Khrom-3 instrument (metal column 5 m long and 8 mm in diameter containing as solid support Chesasorb, 0.31-0.50 mm and as the stationary liquid phase polybutanediol succinate in an amount of 15% with a rate of flow of the carrier gas, helium, of 200 ml/min, thermostat temperature 150°C, flame-ionization detector, sample volume 0.2-0.3 ml) and have studied their IR spectra. The following absorption bands were found ($cm^{-1}$), for (I): 1850, 1650, 1415, 995, 925 (terminal vinyl group), 1675, 840 (C–C), 1125, 1380 (tertiary OH groups); for (II): 1670, 828 (C=C), 1040, 1235 (primary OH groups); for (III): 1665, 820, 1040, 1235, 1100 (doublet); and for (IV): 1670, 830, 1010, and 1245, which show that all the monoterpenol alcohols are present in the β-isomeric form [1-4].

It has been shown previously that rose petals contain glucosides of (II), (III), and (IV) [5].

On acid hydrolysis and enzymatic hydrolysis with β-glucosidase in acetate buffer, pH 5.0, of aqueous-ethanolic extracts obtained after steam distillation from the leaves of the rose of the varieties Krymskaya krasnaya (*Rosa gallica* L.) and Michurinka (*R. damascena* Mill. × *R. gallica* L.) we established by gas chromatography the presence of the monoterpene alcohols (I-IV) in the hydrolysis products. From an aqueous ethanolic extract of petals of the rose Krymskaya krasnaya, by preparative chromatography on silica gel in the water-saturated ethyl acetate + 4% ethanol system we isolated the total monoterpene glycosides which scarcely differed from one another in chromatographic mobility and had $R_f$ 0.30-0.36. As markers we used glucosides of the alcohols (I) and (II) synthesized by the Koenigs–Knorr method [6]. The IR spectra of the glucosides isolated had the absorption bands characteristic for a α-D-glucopyranose ring (900, 1030, 1055, 1080, 925 $cm^{-1}$) and for monoterpenoids (1670, 830, 1860, 1650, 1415, 1235 $cm^{-1}$). After the acid hydrolysis of the total monoterpene glycosides, only D-glucose was found in the hydrolyzate chromatographically. The aglycones were extracted with hexane and, after purification on a column of silica gel, their IR spectrum was taken, which showed absorption bands completely identical with the spectra of the monoterpene alcohols of the essential oils.

The ratio of free and glucosylated monoterpene alcohols in the petals of open flowers of the rose Krymskaya krasnaya was determined by chromatography of the essential oil and of the products of enzymatic hydrolysis from the area of the peaks.

The ratio of terpenoids was as follows (%):

| Alcohol | Free | Glucosylated |
|---|---|---|
| I | 4,9 | 19,9 |
| II | 14,1 | 5,9 |
| III | 38,8 | 4,1 |
| IV | 42,2 | 70,1. |

The free and the β-D-glucosylated monoterpene alcohols (I-IV) in the rose leaves were present in the β-isomeric form and had the usual isopropylidene structure, which shows their

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possible metabolic interrelationship.

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# THE MONOTERPENE FRACTION OF THE ESSENTIAL OIL OF *Nepeta transcaucasica*

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*Nepeta transcausica* is an endemic essential-oil plant growing in Azerbaidzhan. Individual specimens of the species differ considerably in the composition of the essential oil. In addition to aromatic oils containing citral, geraniol, citronellol, and their esters, unpleasant-smelling components are frequently found [1, 2].

We have studied the composition of the essential oil of *N. transcaucasica*, collected in the environs of the town of Krasnaya Sloboda, Kuba region. The oil content of the air-dry plants in the flowering period was 0.95%. The oil is a light colorless liquid with an unpleasant smell. On the basis of the constants of the oil ($n_D^{20}$ 1.4664; acid No. 11.7; ester No. 24.21; ester No. after acetylation 66.0), it was concluded that the oil contained an insignificant amount of oxygen-containing components. This was also confirmed by the results of gas-chromatographic analysis. Good results were obtained with a column filled with 5% of polypropylene glycol adipate on Celite-545 (1.4 × 0.4 cm). The temperature of the column was programed from 100 to 180°C at the rate of 8°/min. The rate of flow of helium was 18.5 ml/min. Under these conditions the oil was separated into 11 components, 5 of which were hydrocarbons, making up the bulk of the oil.

By fractional vacuum distillation (pressure 5 mm Hg, temperature 46-48°C), the oil was separated into a monoterpene fraction and a high-boiling residue. The monoterpenehydrocarbons amounted to 84.2%. They were separated in a Pye preparative chromatograph. The column (5 m × 0.8 cm) was filled with 10% of polypropyleneglycol adipate on Spherochrome, its temperature was 150°C, and the pressure of helium at the inlet to the column was 0.8 atm.

On the basis of retention times and the increases in the sizes of the peaks when known substances were added, the following components were identified in the essential oil: α-pinene (2.2%), β-pinene (11.8%), myrcene (0.5%), limonene (7.4%), and γ-terpinene (7.81%) [sic]. The main component of the oil — γ-terpinene — was isolated and was also identified by its IR spectrum.

Thus, the essential oil of *N. transcaucasica* is characterized by an exceptionally high content of one component, and we are the first to have reported this.

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