

where  $p$  is the weight of the raw material, g;  $h$  is the moisture content of the raw material, %;  $E$  is a gram-equivalent of cnicin (190.22);  $V_1$  is the volume of alkali taken for saponification, ml;  $V_2$  is the volume of the ethanolic solution in which the total lactones were dissolved, ml;  $V_3$  is the volume of the solution deposited on the chromatogram, ml;  $N_{acid}$  is the normality of the acid solution; and  $N_{alk}$  is the normality of the solution of alkali.

A control titration and elution was performed in parallel. The amount of cnicin in plant raw material (1975 harvest) was determined by the method developed and was found to be 0.8% on the weight of the raw material. The maximum deviation on the mean value for six determinations did not exceed  $\pm 3\%$ .

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### THE STRUCTURE OF THE SOLUBLE FRACTIONATION OF AMBER

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Information on the chemical structure of amber is given in the literature [1-4], and Rottländer et al. [5, 6] have shown that amber consists predominantly of a polyester the basis of which is hydroxydiabetic acid and they consider a suggested mechanism of the formation of succinite.

Our aim was to refine the structure of the fraction of amber soluble in ethanol or acetone. By exhaustive extraction of succinite in a Soxhlet apparatus with ethanol we isolated a soluble fraction of amber (I) - a resinous dark-colored substance - with a yield of about 25%. Resin (I) was hydrolyzed with 10% KOH in a mixture of ethanol and tetrahydrofuran (1:1) in the cold for several hours. Treatment of the hydrolyzate with HCl gave the light yellow acid form of the product (II), which was dried at room temperature in vacuum. The acid numbers of (I) and (II) were determined by titration with 0.5 N ethanolic KOH and their molecular weights by the isopiestic method on a Hitachi instrument (Table 1). The IR spectra were taken on a UR-20 spectrophotometer in the 400-4000  $\text{cm}^{-1}$  region using the substances in the form of pastes with paraffin oil (see Table 1).

The molecular weight of the hydrolyzed resin (II) (590) gives grounds for assigning the bulk of it to diabetinic acid and its derivatives (molecular weight of diabetic acid 604). The presence of an acid is also shown by the acid numbers and by absorption bands at 1690 and 1710  $\text{cm}^{-1}$  in the IR spectra (see Table 1).

TABLE 1. Physicochemical Properties of the Resins (I) and (II)

Resin	Acid No.	mol. wt. (in dimethylformamide)	Characteristic absorption bands in the IR spectrum and their most probable assignments			
			$\nu$ C-O	$\nu$ C=C	$\nu$ C=O (in COOR)	$\nu$ C=O (in COOH)
I	95	100	1055 m 1030 m	1645 sh 1640 m	1690 s 1710 s	1735 s
II	145	590	1065 sh		1690 s 1705 s	—

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The decrease in the acid number of the soluble and then of the hydrolyzed fraction of amber (II) in comparison with diabetinic acid the theoretical acid number of which is 185 by about 20% shows the presence of an acidic substance in the resin (II) (~80%).

The presence of an absorption band at  $1730\text{ cm}^{-1}$  in the IR spectrum of the resin (I) and its disappearance after hydrolysis with the simultaneous appearance of a band at  $1030\text{ cm}^{-1}$  in resin (II) shows the existence of ester groups in resin (I). This is also indicated by the change in the acid number during the hydrolysis of the soluble fraction. The molecular weight of the resin (I) (700) suggests the presence of a second component of the soluble amber in the form of a low-molecular-weight polyester based on diabetinic acid. The numbers of acid and ester groups in the soluble amber (I) was determined from the ratio of the acid numbers of the soluble (I) and the hydrolyzed (II) fractions (see Table 1) (2:1).

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#### TRITERPENE AND STEROID GLYCOSIDES OF *Rosa gallica*

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Free triterpenoids and sterols have been isolated from the flowers of *Rosa gallica* previously [1-3].

From rose flowers by essential-oil extraction with aqueous ethanol we obtained three crystalline glycosides called in order of increasing polarity gallicosides A, B, and C with mp  $280-282^{\circ}\text{C}$  (decomp.),  $[\alpha]_{\text{D}}^{20} +12.1^{\circ}$  (c, 1.6; water); mp  $250-254^{\circ}\text{C}$  (decomp.),  $[\alpha]_{\text{D}}^{20} -10.4^{\circ}$  (c, 2.0; water); and mp  $209-211^{\circ}$  (decomp.),  $[\alpha]_{\text{D}}^{20} +15.2^{\circ}$  (c 0.8; water), respectively. They were separated preparatively on silica gel in the ethyl acetate-ethanol-water (7:3:3) system.

To determine the nature of the aglycones and the monosaccharide compositions of the glycosides they were subjected to acid hydrolysis (5% sulfuric acid,  $100^{\circ}\text{C}$ , 5 h). The aglycones of gallicosides A and B that were isolated were identified as oleanolic acid from their chromatographic mobilities in the chloroform-methanol (9:1) system and also by the melting points of the aglycones themselves and their acetates. The aglycone of gallicoside C was identified by its chromatographic behavior, melting point, and absence of a depression of a mixture with an authentic sample as  $\beta$ -sitosterol. By paper chromatography and gas-liquid chromatography we found glucose in the carbohydrate fraction of gallicoside A, glucose and ribose, gallicoside B, and in galactose and glucose in gallicoside C. The results of the alkaline saponification of glycosides A and B show the absence of a carbohydrate chain at the carboxy group of the oleanolic acid.

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