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#### PHENOLIC COMPOUNDS OF *Phaseolus vulgaris*

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UDC 547.592:635.652

Continuing an investigation of the phenolic compounds of the epigeal part of *Phaseolus vulgaris* L. (kidney bean) [1], we have studied the chloroform and ethyl acetate fractions obtained as the result of the treatment with chloroform and ethyl acetate of an evaporated 80% ethanolic extract.

When the material from the chloroform extract was separated on silica gel (with methylene chloride as eluent), substance (I) was isolated. The chromatography of the material from the ethyl acetate extract on Filtrak FN-1 paper in 2% acetic acid showed the presence of four substances which were assigned to the phenocarboxylic acids on the basis of qualitative reactions. The material of the ethyl acetate extract was separated on a column of polyamide. On elution with water with rechromatography of the fraction in 2% acetic acid, substances (II)-(V) were isolated.

Substance (I), with the composition  $C_{10}H_8O_4$ , mp 204-205°C,  $R_f$  0.34, has a blue fluorescence in UV light with  $\lambda_{max}$  (in ethanol) 256, 298, 340 nm. By comparison with an authentic sample, (I) was identified as scopoletin [3].

Substance (II), with the composition  $C_{16}H_{18}O_9$ , mp 200-204°C,  $R_f$  0.76, has a blue fluorescence in UV light with  $\lambda_{max}$  (in ethanol) 325, 240 nm, and was identified as chlorogenic acid [2].

Substance (III) with the composition  $C_{16}H_{18}O_9$ , amorphous,  $R_f$  0.69, showed a blue fluorescence in UV light with  $\lambda_{max}$  (in ethanol), 328, 245 nm. Compound (III) was shown to be identical with an authentic sample of neochlorogenic acid [2].

Substance (IV), with the composition  $C_{10}H_{10}O_4$ , mp 168-169°C,  $R_f$  0.32, gave a bright blue fluorescence in UV light with  $\lambda_{max}$  (in ethanol) 323 nm. Compound (IV) was identified by comparison with an authentic sample as ferulic acid.

Substance (V), with the composition  $C_9H_8O_4$ , mp 196°C,  $R_f$  0.29, had a blue fluorescence in UV light with  $\lambda_{max}$  (in ethanol) 325, 299, 235 nm. Compound (V) was identified as caffeic acid [2].

The epigeal part of *Phaseolus vulgaris* L. contained chlorogenic and neochlorogenic acids in the largest amounts.

This is the first time that scopoletin and phenolic acids have been isolated from the epigeal part of the kidney bean plant.

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#### HYDROGENATION AND DISPROPORTIONATION OF HYDROGEN IN 3-CARENE

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UDC 547.597:547.526

The hydrogenation of 3-carene (I) on Pt gives a mixture of cis- and trans-caranes together with very small amounts (2-5%) of 1,1,4-trimethylcycloheptane (II) [1]. Conversely, the hydrogenation of (I) on Pd gives (II) as the main product (74%) and smaller amounts of carenes [2]. Since the hydrogen disproportionation reaction in olefins may be considered as the combinations of two reactions — dehydrogenation and rehydrogenation — it must be expected that the products of the hydrogenation stage in the disproportionates obtained on Pt and Pd will be different.

In the present communication we give the results of a study of the hydrogen disproportionation reaction in (I) in Pt. The reaction was performed in sealed tubes with Pt/C (0.5% of Pt) as catalyst with a ratio of substrate to catalyst of 10:1 (by weight) at a temperature of 180-200°C, for 5-240 min. Analysis was performed by the GLC method [3].

With the complete conversion of the 3-carene, a disproportionate of the following composition was obtained: 2-carene, 5%; 1,4,4- and 1,4,5-trimethylcycloheptenes, 20% each; cis- and trans-caranes, 4%; p- and m-menthanes, 1%; p- and m-cyrenes, 25 and 15%, respectively; and p- and m-methylisopropenylbenzenes, 5% each. A mixture of similar composition has been obtained previously in the hydrogen disproportionation of (I) on Pd [2].

A study of the composition of the hydrogen disproportionation reaction products in (I) when it had undergone incomplete conversion showed that the disproportionates always contained small amounts (up to 4%) of 3,7,7-trimethylcyclohepta-1,3,5-triene (III). This gives grounds for assuming that the stage determining the transition to compounds with a cycloheptane ring is the dehydrogenation of the 2-carene formed under the conditions of this reaction [2] to cara-2,4-diene (IV). Compound (IV) is present in rapid equilibrium with its tautomer (III), the equilibrium being strongly shifted in the direction of the monocyclic compound [4]. The hydrogenation of (III) also gives products with a trimethylcycloheptane skeleton.

A similar scheme probably applies in the hydrogenation of (I), also, since Pd and Pt catalyze not only the forward but also the reverse reaction. Raising the temperature should favor the endothermic dehydrogenation reaction competing with the hydrogenation of (I), i.e., it should increase the yield of products with the cycloheptane skeleton. Such a situation is known for Pd [2]. We observed an analogous pattern when the hydrogenation of (I) was performed at elevated temperatures (70-100°C). The formation of different products in the hydrogenation of (I) on Pt and Pd at room temperature is most probably due to the high activation energy of dehydration on Pt as compared with the same reaction on Pd.

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Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Khimiya Prirodnkh Soedinenii, No. 2, pp. 259-260, March-April, 1982. Original article submitted December 14, 1981.