

detected by acid hydrolysis and chromatography. Alkaline hydrolysis of the phlobaphenes (obtained by acid hydrolysis) showed the presence of hydroquinone and catechol, and pyrolysis the presence of catechol, pyrogallol, and gallic acid. The leucoanthocyanidins were isolated by repeated reprecipitation from a methanolic extract with ether [2]. The yield of leucoanthocyanidins from the roots was 2.8% and from the rhizomes 0.86%.

Dynamic Accumulation of Tanning Substances, % of the Absolutely Dry Weight

Growth phase	Organs					
	roots	rhizomes	leaves	stem	flower-stalk	fruit
Before flowering	15.4	7.84	14.9	3.8	—	—
Flowering	25.8	16.44	16.09	5.83	8.6	—
Milky maturity of the fruit	22.8	9.3	14.25	5.06	—	5.05

When the total leucoanthocyanidins were fused with a 50% solution of caustic potash and the products were chromatographed, catechol, phloroglucinol, and gallic acid were found. From the components obtained, the substance can be identified as leucodelphinidin.

The catechins in extracts of the raw material were studied chromatographically [3, 6]. 1-Epigallocatechin, d, 1-gallocatechin, d, 1-catechin, and epicatechin gallate were found in the leaves. In addition to the substances mentioned, epigallocatechin gallate was found in the hypogeeal organs, while 3, 1-gallocatechin was absent.

Thus, the polyphenolic complex of *Agrimonia asiatica* consists of derivatives of catechol and pyrogallol in association with benzoic and gallic acids, leucodelphinidin, and catechins.

A substance with an astringent action was obtained from the hypogeeal organs (from concentrated aqueous extracts after the addition of an electrolyte, sodium chloride) [4]. The product contained catechol tanning agents (73.19%) and pyrogallol tanning agents (8.91%) [5].

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21 February 1965

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#### REPIN, A NEW SESQUITERPENE LACTONE FROM ACROPTILON REPENS

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*Khimiya Prirodnikh Soedinenii*, Vol. 2, No. 4, p. 290, 1966

A crystalline combination of substances with mp 143°-160° C has been isolated from the leaves and flower heads of Acroptilon repens (L). D. C. collected in the region of Kirovobad in May 1964.

Fractional crystallization or chromatography on alumina of this mixture gave two colorless crystalline substances with mp 154°-156° C (from alcohol),  $R_f$  0.29 [in a thin layer of neutral alumina (activity grade IV) in the petroleum

ether-benzene-chloroform-methanol (5:4:2:1) system, spots revealed with a 0.5% solution of  $\text{KMnO}_4$  in 0.5%  $\text{H}_2\text{SO}_4$ ] and mp  $196^\circ\text{--}198^\circ\text{C}$  (from alcohol),  $R_f$  0.19. The present paper gives the results of a study of the substance with mp  $154^\circ\text{--}156^\circ\text{C}$ ,  $[\alpha]_D^{20} +101.2^\circ$  (c 2.57; chloroform),  $\text{C}_{19}\text{H}_{22}\text{O}_7$ .

The IR spectrum exhibits absorption bands in the  $3480\text{ cm}^{-1}$  region (OH group), and at  $1770$  ( $\gamma$ -lactone),  $1745$  ( $\text{C}=\text{O}$  of an ester grouping or a cyclopentanone), and  $1660$  and  $1640\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  bond).

The presence of a lactone ring in this substance is also confirmed by its solubility in alkalis on heating. In this process two moles of caustic soda are consumed, which shows the presence of another saponifiable grouping in addition to the lactone ring.

Hydrogenation of the substance both in the presence of a Raney Ni catalyst and in the presence of a small amount of Pt catalyst led to the absorption of two moles of hydrogen; the tetrahydro derivative was obtained in the form of a colorless glassy mass which could not be crystallized and had the composition  $\text{C}_{19}\text{H}_{26}\text{O}_7$ . Dehydrogenation of the tetrahydro derivative at  $280^\circ\text{--}310^\circ\text{C}$  for 40 min gave a viscous blue oil-an azulene giving a trinitrobenzene derivative mp  $128^\circ\text{--}130^\circ$  (from alcohol), which corresponds to the analogous derivative of chamazulene.

By comparing the results obtained with literature data, we concluded that the substance isolated is a new sesquiterpene lactone, which we have called repin.

4 January 1966

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#### SESQUITERPENE COMPOUNDS OF THE ESSENTIAL OIL OF THE FRUIT OF DAUCUS CAROTA

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Khimiya Prirodnykh Soedinenii, Vol. 2, No. 4, pp. 290-291, 1966

In the sesquiterpene fraction of the essential oil of Daucus carota L. (wild carrot) growing in the Armenian SSSR, we have identified, in addition to the hydrocarbon daucene isolated previously [1],  $\beta$ -bisabolene and, apparently, farnesene.

We used fractional vacuum distillation and repeated chromatography on alumina (activity grade III, eluant-petroleum ether with bp  $40^\circ\text{--}70^\circ\text{C}$ ) to isolate the sesquiterpene hydrocarbons. The separation of the mixture was followed by means of the IR spectra of the individual fractions.

Daucene  $[\alpha]_D +23.32^\circ$ ,  $d_4^{20}$  0.8936,  $n_D^{18}$  1.4918, MR 66.31, calc. for two double bonds MR 66.14.

$\beta$ -Bisabolene bp  $110^\circ\text{C}$  (8 mm),  $[\alpha]_D -34.2^\circ$ ,  $d_4^{20}$  0.8735,  $n_D^{20}$  1.4900, MR 67.63, calc. for three double bonds MR 67.88,  $\text{C}_{15}\text{H}_{24}$ .

A trihydrochloride with mp  $78.5^\circ\text{--}80^\circ\text{C}$  was obtained, which in admixture with an authentic sample of the trihydrochloride of  $\beta$ -bisabolene gave no depression of the melting point.

The reduction of  $\beta$ -bisabolene in ethyl alcohol in the presence of platinum black gave hexahydrobisabolene (bisabolane) with bp  $99^\circ\text{C}$  (8 mm),  $[\alpha]_D -3.0^\circ$ ,  $d_4^{20}$  0.8267;  $n_D^{20}$  1.4538;  $\text{C}_{15}\text{H}_{30}$ .

The third hydrocarbon, apparently farnesene, could not be separated completely from the  $\beta$ -bisabolene because of its small amount. The fraction containing the farnesene had  $n_D^{20}$  1.4930 (for farnesene  $n_D^{20}$  1.4870 [2]).

The hydrogenation of this fraction in glacial acetic acid in the presence of platinum black gave octahydrofarnesene (farnesane) with  $n_D^{20}$  1.4410.

The IR spectra of the sesquiterpene hydrocarbons that we have isolated and the products of the hydrogenation were identical with the IR spectra of  $\beta$ -bisabolene [3], farnesene, bisabolane, and farnesane [4].

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