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## STUDY OF THE DYNAMICS OF THE ACCUMULATION OF PECTIN SUBSTANCES

IN THE FRUIT OF *Sorbus aucuparia*

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The fruit of the mountain ash contains 2% of pectin substances [1]. We have studied the dynamics of the accumulation of water-soluble pectins and of protopectin in the fruit of the mountain ash in dependence of the stage of its ripening. The fruit of *Sorbus aucuparia* (European mountain ash) was collected in 1978 in the Ryazan' province. Analysis was performed on the air-dry fruit. The substances were exhaustively extracted by a standard method [2] and were precipitated with 96% ethanol. The information given below shows that the pectin substances in them accumulate differently according to the stage of ripening of the fruit (% on the absolutely dry weight):

Color of the fruit	Total amount of pectin substances	Water-soluble pectins	Protopectin
Green (June 26)	12.02	0.32	11.70
Brown (July 8)	8.04	1.07	6.97
Orange (July 26)	7.80	1.27	6.53
Orange-red (August 20)	6.32	1.43	4.89

Green fruit contained only a small amount of water-soluble pectins. As the fruit ripened, their amount increased. The maximum amount of protopectin was found in the green-fruit stage, and then its amount fell and by the time of full ripeness it had decreased to less than half.

We also used the method of determining pectin substances by precipitation with calcium chloride. The pectin substances were extracted from the fruit with 0.3 N HCl, and precipitation was carried out in two variants: with calcium chloride and with ethanol. As statistical treatment of the results of the two experiments shows, the two methods are characterized by high reproducibility and high accuracy and they do not show great disagreements. The determination of the pectin substances by precipitation with ethanol proved to be simpler and quicker:

Repetition of the experiment	Amount of pectin substances (%) precipitated by		Reproducibility on precipitation by
	calcium chloride	ethanol	
1	3.78	4.04	Calcium chloride $\Sigma(X_{av} - X)^2 = 0.3754$ $S_n = 0.2042$ $E_{rel} = \pm 1.46$ Ethanol $\Sigma(X_{av} - X)^2 = 0.2558$ $S_n = 0.1686$ $E_{rel} = \pm 1.21$
2	4.03	3.86	
3	3.56	3.72	
4	3.53	3.98	
5	3.39	4.09	
6	3.78	3.66	
7	3.46	3.79	
8	3.53	3.62	
9	3.83	3.92	
10	3.49	3.68	
	$X_{av} = 3.64$	$X_{av} = 3.84$	

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Thus, the greatest amount of water-soluble pectins accumulates in the ripe fruit of the mountain ash, and the greatest amount of protopectin in the green fruit.

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#### SECOLIN — A NEW DIHYDROFUROCUMARIN FROM *Seseli mucronatum*

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By chromatography on silica gel in the petroleum ether-ethyl acetate system with a rising gradient of the latter, the roots of *Seseli mucronatum* (Schrenk) M. Pimen et Sdobn., collected in the Dzhetly-Oguz gorge (environs of Przheval'sk) have yielded an amorphous substance  $C_{18}H_{16}O_5S$ ,  $M^+$  346, mp 78-82°C,  $[\alpha]_D^{20} +233.5^\circ$  (c 2.36;  $CHCl_3$ ), which we have called secrolin.

The UV spectrum of secrolin in ethanol [ $\lambda_{max}$ , nm: 217 (infl.), 263 (infl.), 278, 328 (log  $\epsilon$  4.22, 4.15, 4.27, 4.07);  $\lambda_{min}$ , nm: 240, 305 (log  $\epsilon$  3.71, 3.95)] showed that it was a derivative of 7-hydroxycoumarin.

It follows from the PMR spectrum (Varian HA-100D,  $CDCl_3$ , 0 — HMDS, 20°C) that the compound isolated was an ester of an angular dihydrofurocoumarin [6.04 and 7.48 ppm, 1 H each, d, J = 9.5 Hz ( $H_3$ ,  $H_4$ ); 7.18 and 6.22 ppm, 1 H each, d, J = 8.5 Hz ( $H_5$ ,  $H_6$ ); 5.19 ppm, 1 H, t, J = 9.5 Hz ( $O-CH-CH_2$ ); 3.32 ppm, 2 H, d, J = 9.5 Hz ( $CH-CH_2-Ar$ ); 1.47 and 1.57 ppm, 3 H each, s ( $O-C(CH_3)_2$ ) — columbianetin [1] (zosimol [2]).

The IR spectrum (Fig. 1) contained absorption bands of an  $\alpha$ -pyrone  $C=O$ , of an ester group, and of the  $-C=C-$  bonds of a coumarin nucleus. In this compound, the esterifying component was methylthioacrylic acid [2.26 ppm, 3 H, s ( $-S-CH_3$ ); 7.44 and 5.48 ppm, 1 H each, d, J = 16 Hz ( $H_\alpha$  and  $H_\beta$ )] with the trans arrangement of the olefinic protons, while compounds consisting of esters of cis-methylthioacrylic acid have been found previously [3, 4].

In addition to secrolin, the sample of *S. mucronatum* investigated contained borneol trans-p-hydroxycinnamate [5], ostruthin, mp 118-119°C, and columbianadin (zosimin), mp 120-121°C, and differed from a sample of *S. mucronatum* collected in the valley of the R. Usek (Kazakhstan) [6], which contained anomalin, pteryxin, and ostruthin.

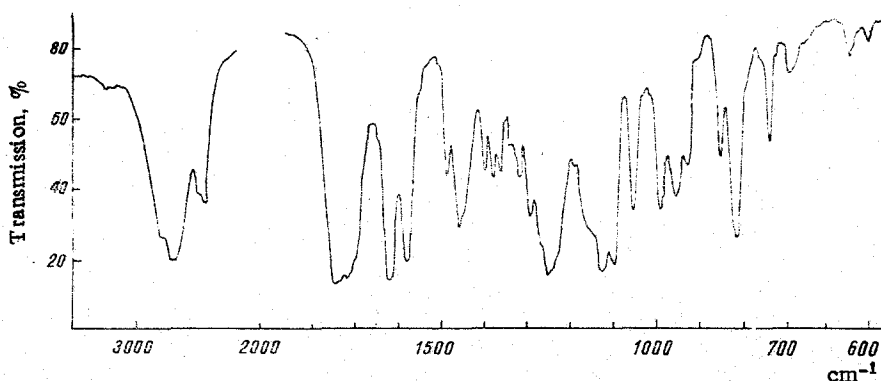


Fig. 1. IR spectrum of secrolin.

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