

SUMMARY

An x-ray structural study has been made of 3β -acetoxy- $25R$ - 5α -spirostan-1-one. The bond lengths and valence angles are the usual ones for compounds of this type. All the six-membered rings have the chair conformation and the five-membered rings the envelope form. Rings A, B, C, and D are trans-linked and D and E are cis-linked.

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ISOLATION OF FRUTITSIN FROM THE SEEDS OF *Amorpha fruticosa*

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The conditions for the isolation and purification of frutitsin by various solvents and mixture of solvents have been studied. The proposed method for the isolation of frutitsin permits the yield of the substance to be increased.

In the Institute of the Chemistry of Plant Substances of the Academy of Sciences of the Uzbek SSR, an original drug, frutitsin, isolated from the seeds of the plant *Amorpha fruticosa* L. [1, 2] has been created, and it is recommended as a sedative in vegetative neuroses, neuroses of the cardiovascular system, and paroxysmal tachycardia [3]. A method for its production has been developed [4] in which ethanol-dichloroethane (1:1, by volume) is used as the extractant for the plant raw material. Dichloroethane has a fairly high toxicity (the MAC for dichloroethane in a working area is 10 mg/m^3), and therefore in large-tonnage manufacturers it is desirable not to use this solvent in the industrial process.

We have developed a new method of obtained frutitsin using less toxic solvents. We used the seeds of *Amorpha fruticosa* of the 1977 and 1978 harvests grown in the *Gazety "Pravda" sovkhoz*, Tashkent province.

In order to select the solvents for the extraction and subsequent purification of frutitsin, in model experiments we selected an extractant and studied the process of extracting fru-

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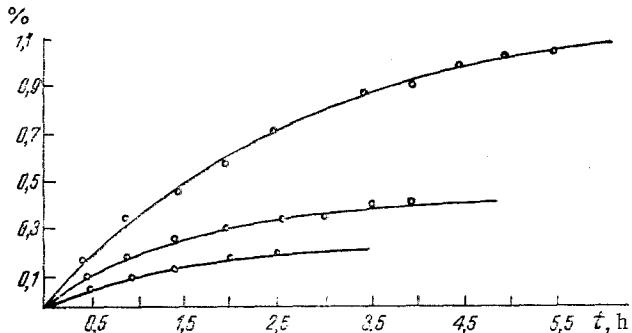


Fig. 1. Kinetics of the extraction of frutitsin.

titsin. At room temperature, frutitsin is practically insoluble in individual solvents and therefore as the extractant we used mixtures of chloroform and ethanol in various ratios by volume (1:2, 1:1, 2:1). Extraction was performed by the steeping method until the reaction for rotenoid glycosides was negative. The best result was obtained by using mixtures of chloroform and ethanol in ratios of 1:1 and 2:1, but it is undesirable to increase the proportion of chloroform in the mixture since a larger amount of ballast substances then passes into the extract, which interferes with the subsequent purification of the frutitsin. To establish the time of extraction, we studied the kinetics of the process of extracting frutitsin from the raw material. In each experiment, changes of solvent were made every 0.5 h until phase equilibrium had set in. Raw material containing 1.64% of frutitsin on the weight of the air-dry seeds was extracted. The results of the experiments are shown in Fig. 1.

It can be seen from Fig. 1 that the time necessary to establish phase equilibrium is 5.5 h on the first contact of the phases, 4 h on the second, and 2.5 h on the third. After three changes of solvent, about 95% of the frutitsin present in the raw material has passed into the extract. Extraction isotherms show that when using chloroform-ethanol (1:1) as extractant, with the impoverishment of the raw material the relative rate of extraction of the rotenoid glycosides rises.

When an extract is evaporated to approximately 1/10 of its initial volume, not only the glycosides deposit from the still residue but so also do the ballast substances. The elimination of the bulk of the ballast substances at this stage permits a considerable simplification of the subsequent purification of the preparation. With this aim, the precipitate was washed with acetone and chloroform. Comparative experiments showed that chloroform eliminates about 90% of the ballast substances and acetone 80%.

By using chloroform for purifying the combined glycosides, the nonpolar and weakly polar impurities, (fats, resins, pigments) were eliminated from the precipitate and a product containing 85-90% of glycosides was obtained. Qualitative analysis showed that after the precipitate had been treated with chloroform the only glycoside remaining was amorphin. To obtain a preparation containing not less than 95% of the active substance and to reduce the losses of amorphin to a minimum in the process, the following experiments were made using technical frutitsin containing 87% of the main substance. After recrystallization from ethanol, a product containing 91-92% of the main substance was obtained, the losses of frutitsin in this process amounting to 10-20%. After a second recrystallization of the product obtained from water, the purity of the frutitsin had risen to 96-97%, its losses in this stage amounting to 5-10%. The total losses of frutitsin on two successive recrystallizations, first from ethanol and then from water, amounted to 30%.

Recrystallization of the same initial technical frutitsin in a different sequence — first from water and then from ethanol — permitted the losses to be lowered to 15-20%; after the recrystallization from water a product with a purity of 94-97% was obtained, and after recrystallization from ethanol one with a purity of 97-101%.

Consequently, it may be assumed that the bulk of the ballast substances in technical frutitsin consists of polar impurities and it is therefore desirable in the preparation of the finished product to perform two recrystallizations: first from a more polar solvent — water — and then, to eliminate the residual less polar impurities, from ethanol.

EXPERIMENTAL

Extraction of the Rotenoid Glycosides. Seeds of the *Amorpha fruticosa* crushed in a roller mill (50 kg) were extracted with chloroform-ethanol (1:1) by the steeping method. Three changes of solvent were made. The first contact of the phase lasted 5.5 h, the second 4 h, and the third 2.5 h. The extracts were combined (a total of 210 liters of extract) and were evaporated in a vacuum-evaporating apparatus to 25 liters and left for a day.

Elimination of Weakly Polar and Nonpolar Impurities from the Deposit. After a day, the precipitate that had deposited was separated off on a suction filter, suspended three times in chloroform (3×8 liters), the solvent being removed by suction each time, and the product was well dried in a vacuum-drying chest.

Crystallization and Recrystallization of Frutitsin. With stirring, 850 g of technical frutitsin was dissolved in 128 liters of boiling water and the resulting solution was filtered through a heated pressure filter and was left for crystallization at room temperature. After 12-16 h, the precipitate was separated off on a suction filter and the moist product was recrystallized from 47 liters of ethanol. The yield of frutitsin was 500 g, or 1% on the weight of the raw material.

SUMMARY

1. The conditions for the isolation and purification of frutitsin by various solvents and mixtures have been studied.
2. A method for isolating frutitsin which increases the yield of the preparation is proposed.

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QUANTITATIVE DETERMINATION OF THE AGLYCONE OF THE TOTAL PATRINOSIDES IN THE ROOTS OF *Patrinia intermedia*

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A method has been developed for the quantitative determination of the aglycone of the total patrinosides present in the roots of *Patrinia intermedia*. The method comprises the extraction of the patrinosides from the raw material, their hydrolysis to oleanolic acid, and the potentiometric titration of the aglycone obtained.

The roots of *Patrinia intermedia* Roem. et Schult. contain a whole set of triterpene glycosides the main ones of which are patrinoside B, C and D. From 9 to 11 individual glycosides are found in different populations of the plant [1]. The structures of only two of the glucosides — patrinosides D and C — have been established, but it is known that they all have a common aglycone — oleanolic acid [2].

A densitometric method has been developed for evaluating introduced forms of *P. intermedia* for their content of the main patrinosides, B, C, and D [3]. The low accuracy of the method, the presence of other triterpene glycosides in the raw material, and also the necessity for using standard samples of the glycosides being determined do not permit its use for the

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