V₁ is the volume of the total acetone extract, ml; 
V₂ is the volume of extract deposited on the plate, ml; 
P is the weight of the raw material, g; and 
h is the loss in weight on the drying of raw material, %.

SUMMARY

A procedure has been developed for the selective quantitative determination of the triterpene saponins in hawthorn fruit (haws) with the aid of chromatophotodensitometry. The relative error does not exceed ±5.1%.

LITERATURE CITED


TOTAL SYNTHESIS OF THE RACEMIC ALKALOID DIPTOCARPAMINE

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A route for the synthesis of racemic diptocarpamine from hex-5-enoic acid has been developed.

Continuing work on the total synthesis of the alkaloid of Diphythocarpus strictus [1-3], we have developed a short method of obtaining diptocarpamine (VIII) [4]. Our main attention was devoted to the synthesis of the key 7-thiaoctylamine (VI), which we had used previously in the preparation of the racemic alkaloids diptocarpidine and diptocarpiline [5].

Starting from hex-5-enoic acid, 7-thiaoctanoic acid (I) was prepared with quantitative yield by the thiylation reaction with methyl mercaptan. Its methyl ester (II) was converted under the action of lithium tetrahydroaluminate into the corresponding alcohol (III). The

*The hex-5-enoic acid was supplied by E. K. Starostin.


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reaction of the latter with phosphorus tribromide in the presence of pyridine gives 7-thia-octyl bromide (IV). When compound (IV) was heated with sodium azide, 7-thiaoctyl azide (V) was obtained and the reduction of this led to the key amine (VI). Isopropyl isocyanate was prepared from isobutyryl chloride via the corresponding azide [6], and the reaction of this with the amine (VI) gave the sulfide precursor (VII). Its oxidation completed the synthesis of racemic diptocarpamine (VIII).

\[
\text{\begin{align*}
\text{\text{III}} & \quad \text{\text{VII}} \\
\text{\text{IV}} & \quad \text{\text{VIII}}
\end{align*}}
\]

In the electron-impact mass spectra of compounds (VII) and (VIII) the peaks of molecular ions were recorded with mass numbers corresponding to the empirical formulas \(C_{11}H_{24}N_2O_2S\) (measured 232.1610; calculated 232.1609) and \(C_{11}H_{24}N_2O_2S\) (measured 248.1582; calculated 248.1559). The characteristic ions \(M - \text{CH}_3\)\(^+\), \(M - \text{CH}_3\text{S(O)}\)\(^+\), \(M - \text{CH}_3\text{S(O)}\text{CH}_2\)\(^+\), \(M - \text{CH}_3\text{S(O})\text{CH}_2\text{SH})\(^+\), and \(M - \text{CONH-C}_3\text{H}_7\)\(^+\) in the mass spectra of (VII) and (VIII) are formed, according to [7] by simple bond cleavage. For example, the origin of the peak of the \(M - 100\)\(^+\) ions is due to the successive splitting out of a methyl radical and isopropyl isocyanate:

**EXPERIMENTAL**

IR spectra were taken on a UR-20 instrument in Nujol or in a thin layer. PMR spectra were obtained on a Tesla BS-567B instrument with a working frequency of 100 MHz, and \(^13\)C NMR spectra were recorded on a JEOL FX-90 Q instrument with a working frequency of 22.5 MHz. TMS was used as internal standard, and CDCl\(_3\) as solvent. The positive-ion mass spectra were obtained on a MKh-1320 instrument with a temperature of the ionization chamber of 30-50°C and energies of the ionizing electrons of 70 and 16 eV, using a SVP-5 direct-introduction system. Accurate values of the mass numbers of the ions were measured on a Varian MAT CH-5 instrument with an energy of the ionizing electrons of 70 eV and an ionization chamber temperature of 250°C. Negative-ion mass spectra were obtained on a MI-1201 mass spectrometer reequipped for recording negative ions [8]. The electron energy of the scale was calibrated from the curves of the effective yields of \(\text{SF}_6^-\) from \(\text{SF}_6\) and of \(\text{NH}_2^-\) from ammonia. The products of synthesis were separated by column chromatography on silica gels L40/100 and L 100/160 (Czechoslovakia). Commercial isobutyryl chloride with a purity of not less than 99.9% was used in the synthesis.

7-Thiaoctanoic Acid (I). A quartz-glass flask was charged with 3.65 g (3.2\cdot10^{-2} \text{ mole}) of hex-5-enoic acid and 0.03 g of azoisobutyronitrile and was cooled to \(-10^\circ\text{C}\). Then 3.54 ml (6.4\cdot10^{-2} \text{ mole}) of methyl mercaptan was added carefully in one portion. The flask was tightly sealed and, with stirring and cooling (\(-20^\circ\text{C}\)), the reaction mixture was illuminated.