THE NATURE OF ROSMARICINE FROM ROSMARINUS OFFICINALIS. III

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We have previously reported the isolation of an alkaloid rosmaricine from Rosmarinus officinalis L. (rosemary) [1]. An additional study of the dichloroethane extracts of this plant has given, in addition to rosmaricine, base 2 with the composition $C_{20}H_{27}NO_4$ having mp 197°–198° C (decomp., from toluene), $[\alpha]_D^{20}$ +36° (c 1.48; dioxane). In contrast to rosmaricine, the sulfate of this substance, with mp 188°–190° C (decomp., aqueous CH_3OH), is insoluble in 5% sulfuric acid, and this property was used for its isolation.

Base 2 formed a hydrochloride with mp 214–216° C (decomp., water), containing no methoxy or methylenedioxy groups but with a γ-lactone grouping (IR spectrum: 1760 cm^{-1}), a $C-CH_3$ group, and four labile hydrogen atoms. Acetylation with boiling $(CH_3CO)_2O$ led to a N, O, O-triacetate with mp 291°–292° C (decomp., CH_3OH), IR spectrum: 1685, 1780 cm^{-1}; HNO_2 gave a deaminohydroxy derivative $C_{20}H_{26}O_5$ with mp 178°–180° C (decomp., ether), and heating with selenium at 340° C yielded 6-hydroxy-1-methyl-7-isopropylphenanthrene, identified by direct comparison with an authentic sample [2].

Further investigation showed that rosmaricine and base 2 are not native alkaloids but are formed in the extraction of the plant raw material with dichloroethane in the presence of ammonia. When, in the method described [1], the ammonia was replaced by methylamine, the process gave N-methylrosmaricine $C_{21}H_{29}NO_4$ with mp 192°–194° C (decomp., toluene), which did not contain an NH_2 group and gave with HNO_2 a N-nitroso derivative $C_{21}H_{28}N_2O_5$ with mp 169°–172° C (decomp., ether).

When the plant raw material was treated with dichloroethane in the presence of sodium carbonate, we isolated neither rosmaricine nor any other compound of a basic nature.

The substances forming the precursors of rosmaricine and base 2 are diterpene compounds and are characterized by high lability.

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L-CANADINE β-METHOCHLORIDE FROM THALICTRUM MINUS L. II

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It has previously been reported [1] that thalictrimine $C_{21}H_{23}O_5N$ isolated from the epigeal part of Thalictrum minus L. is identical with β-allocryptopine.

On continuing our investigation [1], we have made a detailed study of the subsidiary alkaloids of Th. minus, obtained in the form of a mixture of sulfates and reineckates. From the mixture of sulfates we have isolated, in addition to β-allocryptopine, a quaternary base $C_{21}H_{24}O_4NCl$ (I) with mp 191°–193° C (decomp.) and $[\alpha]_D$ − 158° in the form of the chloride, and from the crude reineckates we have obtained the same base in the form of a nitrate.

The physical and chemical properties of the chloride of the alkaloid (I) are similar to those of L-canadine β-methochloride, the α-isomer of which has been isolated from the plant Xanthoxylum brachyacanthum [2]. The reaction of the iodide of the base with silver oxide gave us the anhydro base $C_{21}H_{23}O_4N$ with mp 110°–111° C. The anhydro base of L-canadine α-methochloride has mp 111°–112° C [2].

When the iodide was heated with monoethanolamine, a mixture of two isomeric substances with the composition $C_{20}H_{21}O_4N$ was formed. One of them, with mp 166°–168° C, was inactive and the second, with mp 133° C, was optically active, $[\alpha]_D$ −305°.

According to the literature [3], the melting point of L-canadine $C_{20}H_{21}O_4N$ is 133° C and its $[\alpha]_D$ is −299°, while DL-canadine melts at 170° C. The results of a direct comparison of the two substances, that with mp 166°–168° C and a sample of DL-canadine that we synthesized from dihydroallocryptopine, showed that they were identical. The IR spectra, (taken in alcoholic solutions on a SF-4 instrument in the 215–315 mμ region) of the chloride of the quaternary base and the base $C_{20}H_{21}O_4N$ obtained from it are similar to the spectrum of DL-canadine [4], which is confirmed by the following data.

Alkaloid	λ_{max}, mμ	log ε	λ_{min}, mμ	log ε
Quaternary base from Th. minus, chloride	231 (inflection), 286	3.99; 3.69	260	2.97
Base $C_{20}H_{21}O_4N$	230 (inflection), 285	4.06; 3.71	252	2.75
DL-Canadine	209, 230 (inflection), 284	4.45; 4.07; 3.71	252	2.76

Thus, the subsidiary alkaloid from Th. minus is identical with L-canadine β-methochloride. Although the initial mixture of alkaloid sulfates gives four spots on a chromatogram, only two alkaloids were obtained from it: β-allocryptopine and L-canadine β-methochloride. It is likely that this is due to the presence of stereoisomeric salts (asymmetrical with respect to the nitrogen).

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ISOLATION OF ERVINIDINE AND ERVINIDININE FROM VINCA ERECTA

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It has previously been reported that the alkaloids vincamine, reserpinine, erectine, ervamine, ervine, and akuammidine have been isolated from the epigeal part of Vinca erecta Rgl. et Schmalh, growing in the Fergansk Oblast [1–4]. Erectine was subsequently identified with the known alkaloid kopsinine [5]. Continuing the separation of the remaining part of the total alkaloids, we have isolated two new alkaloids: ervinidine with the composition $C_{22}H_{26}N_2O_4$ having mp 283°–284° C (decomp., methanol), $[\alpha]_D$ −17.3° (chloroform), and ervinidinine, $C_{21}H_{24}N_2O_3$, mp 255°–258° C (decomp., methanol), [α] −160.6° (methanol).

Ervinidine contains a methoxy group and a $=N-CH_3$ group and also one atom of active hydrogen. When ervinidine was oxidized by a modified Kuhn–Roth method, acetic acid was obtained, which shows the presence of a $C-CH_3$ group in the substance. The IR spectrum showed bands of vibrations at 3310 cm^{-1} (N–H bond), 1230, 1610, 1720 (the grouping $O-\underset{|}{C}=\underset{|}{C}-COOCH_3$), 1660 cm^{-1} (carbonyl group of a 2-acylindole nature). The information given showed that ervinidine has the following analytical formula:

$$C_{18}H_{19}(=NH)(=N-CH_3)(COOCH_3)(CO)(-O-).$$

Its UV spectrum contained three maxima: λ_{max} 232, 302, and 340 mμ (log ε 4.10, 4.08, 4.30, respectively).

The nature of the UV and IR absorption curves of ervinidine permit the assumption that the base can be assigned to the group of α-methyleneindolines (I) or 2-acylindoles (II) [6].