

## THE NATURE OF ROSMARICINE FROM ROSMARINUS OFFICINALIS. III

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We have previously reported the isolation of an alkaloid rosmarinine from Rosmarinus officinalis L. (rosemary) [1]. An additional study of the dichloroethane extracts of this plant has given, in addition to rosmarinine, base 2 with the composition  $C_{20}H_{27}NO_4$  having mp  $197^{\circ}$ - $198^{\circ}$  C (decomp., from toluene),  $[\alpha]_D^{20} + 36^{\circ}$  (c 1.48; dioxane). In contrast to rosmarinine, the sulfate of this substance, with mp  $188^{\circ}$ - $190^{\circ}$  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  $214$ - $216^{\circ}$  C (decomp., water), containing no methoxy or methylenedioxy groups but with a  $\gamma$ -lactone grouping (IR spectrum:  $1760\text{ cm}^{-1}$ ), 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  $291^{\circ}$ - $292^{\circ}$  C (decomp.,  $CH_3OH$ ), IR spectrum:  $1685$ ,  $1780\text{ cm}^{-1}$ ;  $HNO_2$  gave a deaminohydroxy derivative  $C_{20}H_{26}O_5$  with mp  $178^{\circ}$ - $180^{\circ}$  C (decomp., ether), and heating with selenium at  $340^{\circ}$  C yielded 6-hydroxy-1-methyl-7-isopropylphenanthrene, identified by direct comparison with an authentic sample [2].

Further investigation showed that rosmarinine 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-methylrosmarinine  $C_{21}H_{29}NO_4$  with mp  $192^{\circ}$ - $194^{\circ}$  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  $169^{\circ}$ - $172^{\circ}$  C (decomp., ether).

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

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

### REFERENCES

1. L. D. Yakhontova and M. I. Anisimova, ZhOKh, 32, 1337, 1962.
2. L. D. Yakhontova and A. D. Kuzovkov, ZhOKh, 33, 308, 1963.

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## L-CANADINE $\beta$ -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  $\beta$ -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  $\beta$ -allocryptopine, a quaternary base  $C_{21}H_{24}O_4NCl$  (I) with mp  $191^{\circ}$ - $193^{\circ}$  C (decomp.) and  $[\alpha]_D - 158^{\circ}$  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  $\beta$ -methochloride, the  $\alpha$ -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  $110^{\circ}$ - $111^{\circ}$  C. The anhydro base of L-canadine  $\alpha$ -methochloride has mp  $111^{\circ}$ - $112^{\circ}$  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  $166^{\circ}$ - $168^{\circ}$  C, was inactive and the second, with mp  $133^{\circ}$  C, was optically