AN INVESTIGATION OF THE ALKALOIDS OF *Thalictrum longipedunculatum*

THE STRUCTURE OF THALIXINE

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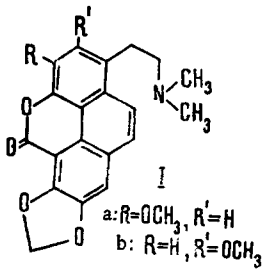
From the epigeal part of Th. longipedunculatum we have isolated thalidasine [1] and an alkaloid of unknown structure – thalixine – obtained previously from Th. simplex. On the basis of an elementary analysis and a determination of the molecular weight and of the halogens in the hydrochloride and methiodide, the structure $C_{21}H_{19}O_6N$ has been established for thalixine [2]. However, the mol. wt. determined mass spectrometrically agrees with the formula $C_{21}H_{19}O_5N$. UV spectrum (ethanol), λ_{max}: 237, 265, 313, 390 nm (log ε 4.22, 4.48, 3.96, 3.60). The IR spectrum has absorption bands at 1740 cm^{-1} (C=O) and 930 cm^{-1} (methylenedioxy group). The mass spectrum showed the peaks of ions with m/e 365 (M+, 44%), 320 (33%), 307 (27%), 305 (13%), 277 (10%), 58 (100%). NMR spectrum (in $CDCL_3$, τ scale): 7.69 ppm (singlet, 6H, $N\langle^{CH_3}_{CH_3}$), 6.03 ppm (singlet, 3H, OCH_3), 6.70-7.60 ppm (4H, $-CH_2-CH_2-$), and 3.78 ppm (singlet, 2H, methylenedioxy group), and in the weak field there are two one-proton singlets at 2.89 and 2.75 ppm and two one-proton doublets at 2.52 ppm (J=9 Hz) and 2.87 ppm (J=9 Hz). Since in the NMR spectrum taken in $CDCL_3$ the signals of the aromatic protons are poorly resolved, the spectrum was taken in CF_3COOH, in which the four aromatic protons give two clear one-proton doublets with J=9 Hz each and two one-proton singlets. An analysis of these results and a comparison of them with available literature material showed that thalixine is a derivative of dimethylaminoethylphenanthrene [3]. The absorption at 1740 cm^{-1} and the inert nature of the carbonyl group showed the presence of an α-pyrone system. The doublets at 2.52 and 2.87 ppm are due to the C_9 and C_{10} protons of the phenanthrene ring, and since the two remaining aromatic protons appear in the form of singlets, the methoxy and methylenedioxy groups are present in different rings. The downfield shift of the signals of the methylenedioxy group is due to the action of the carbonyl group. Consequently, the methylenedioxy group must be present at C_6-C_7 and the methoxy group at C_3 or C_2. The choice between them was made by comparing the properties of thalixine and thaliglucinone (Ia) isolated by N. M. Mollov et al. from Th. rugosum (see Table 1).

Since thalixine is not identical with thaliglucinone, it must have the structure (Ib).



I

a: R=OCH$_3$, R'=H

b: R=H, R'=OCH$_3$

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TABLE 1

Base	mp, °C	M	$N(CH_3)_2$	OCH_3	CH_2O_2	$-CH_2-CH_2-$	Aromatic protons
Thaliglucinone	126–128	365	7,60	6,00	3,70	6,50–7,50	2,50 d (1H, J=9 Hz); 2,70 d (1H, J=9 Hz), 2,80 d (2H)
Thalixine	193–194	365	7,69	6,03	3,78	6,70–7,60	2,52 d (1H, J=9 Hz); 2,87 d (1H, J=9 Hz), 2,89 d (1H), 2,75 d (1H).

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4. N. M. Mollov, Le Nyat Thuan, and P. P. Panov, Dokl. Bolg. Akad. Nauk, 24, No. 8, 1047 (1971).