AN ESTER OF trans-DEC-8-ENE-4,6-DIYN-1-OL AND cis-3-METHYLTHIOACRYLIC ACID FROM THE ROOTS OF Seseli sessiliflorum

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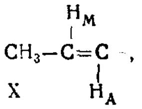
UDC 547.362/17.582.89

From the roots of Seseli sessiliflorum Schrenk – in addition to the coumarins floroselin [1, 5], seselifiorin [2, 5], and anomalin [3], the chromone seselirin [4, 5], and other compounds [3] isolated previously – we have obtained a compound with the composition $C_{14}H_{16}O_2S$ (M^+ 248), mp 71°C (from petroleum ether).

The UV spectrum of the substance [λ_{max}228, 240, 252, 266, 282 nm (log ε 3.46; 3.57; 3.57; 4.12; 4.39; 4.52)] is characteristic for systems with conjugated double and triple bonds – diynene chromophores [6]. The IR spectrum shows the presence of the following structural elements in it: $-C\equiv C-$ (weak band at 2140 cm^{-1}), an α,β-unsaturated ester (strong bands at 1690 and 1560 cm^{-1} due to C=O and C=C, respectively), and $-C=C-$ (weak band at 1630 cm^{-1}). A definitive answer to the question of the structure of the substance was obtained by means of the NMR spectrum (Fig. 1).

The molecule of the substance has the fragment  $\underset{X}{CH_3}-C=\overset{H_M}{\underset{H_A}{C}}$, the protons of which form an AMX_3 system: δ_A = 5.45 (1H), δ_M = 6.22 (1H), δ_X = 1.82 (3H); J_{AM} = 15.7 Hz, J_{AX} = 1.7 Hz, J_{MX} = 6.9 Hz. The existence of spin-spin coupling between these protons was established by double resonance. When the octet with δ 6.22 was irradiated, the signal of the X protons became a broadened singlet. The superposition of an additional frequency on the center of the quartet with δ 1.82 eliminated the coupling of AM and AX and the signal of the M proton became a doublet (J = 15.7 Hz) while the broadening of the doublet from proton A disappeared. The value of J_{AM} shows the trans configuration of the olefinic protons of the allyl fragment.

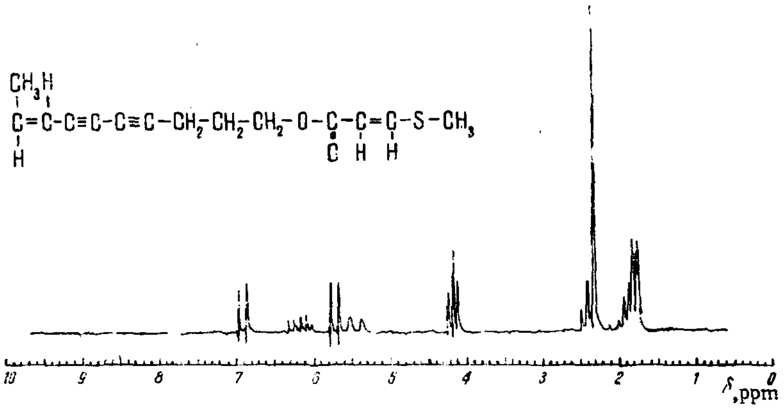
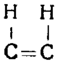
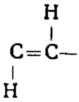


Fig. 1. NMR spectrum of the ester of trans-dec-8-ene-4,6-diyn-1-ol and cis-3-methylthioacrylic acid (HA-100 D, CCl_4, 0 – TMS).

All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 286-287, March-April, 1973. Original article submitted September 21, 1972.

One-proton doublets at 6.93 and 5.73 ppm, J = 10.0 Hz and a singlet at 2.37 ppm (3H) show the presence in the molecule of the compound under investigation of a cis-3-methylthioacrylic acid residue [1-5]. In agreement with this, the hydrolysis of the substance with 10% KOH in ethanol (boiling for 2 h) gave a mixture of the cis and trans forms of 3-methylthioacrylic acid (24 and 76%, respectively); cis-3-methylthioacrylic acid: CH_3 – 2.40 ppm, s, 3H;  $\overset{H}{C}=\overset{H}{C}$ at 5.82 and 7.19 ppm, d, J = 10.0 Hz; trans-3-methylthioacrylic acid: CH_3 – 2.36 ppm s, 3H;  $\underset{H}{C}=\overset{H}{C}-$ 5.61 and 7.83 ppm, d, J = 15.0 Hz.

Two-proton triplets at 4.19 ppm (J = 6.0 Hz) and 2.44 ppm (J = 7.0 Hz) and also a two-proton multiplet in the 1.6-2.1-ppm range are due to the $-C \equiv C-CH_2-CH_2-CH_2-OAc$ grouping. The assignment of the signals in this case is also confirmed by the results of double-resonance experiments.

What has been said enables a single possible variant of the structure to be proposed for the substance: trans-dec-8-ene-4,6-diyn-1-yl cis-3-methylthioacrylate. The cis form of dec-8-ene-4,6-diyn-1-ol has been isolated previously by Bohlmann from Chrysanthemum maximum [7]. The ester of the trans form of this alcohol and of cis-3-methylthioacrylic acid is a new natural compound.

LITERATURE CITED

1. A. A. Savina, M. E. Perel'son, A. I. Ban'kovskii, and G. K. Nikonov, Khim. Prirodn. Soedin., 517 (1970).
2. A. A. Savina, G. K. Nikonov, and A. I. Ban'kovskii, Khim. Prirodn. Soedin., 522 (1970).
3. A. A. Savina and M. G. Pimenov, Rast. Res., 8, 361 (1972).
4. A. A. Savina, M. E. Perel'son, A. I. Ban'kovskii, and G. K. Nikonov, Khim. Prirodn. Soedin., 412 (1970).
5. A. A. Savina and M. E. Perel'son, Khim. Prirodn. Soedin., 831 (1970).
6. J. Brand and G. Eglinton, Applications of Spectroscopy to Organic Chemistry, Oldbourne Press, London (1965).
7. F. Bohlmann, H. Moench, and U. Niedballa, Chem. Ber., 99 (2), 586 (1966).