BRIEF COMMUNICATIONS

1,7-DIPHENYLHEPTANE-3,5-DIOL FROM ALNUS FRUTICOSA AND A. MANSHURICA

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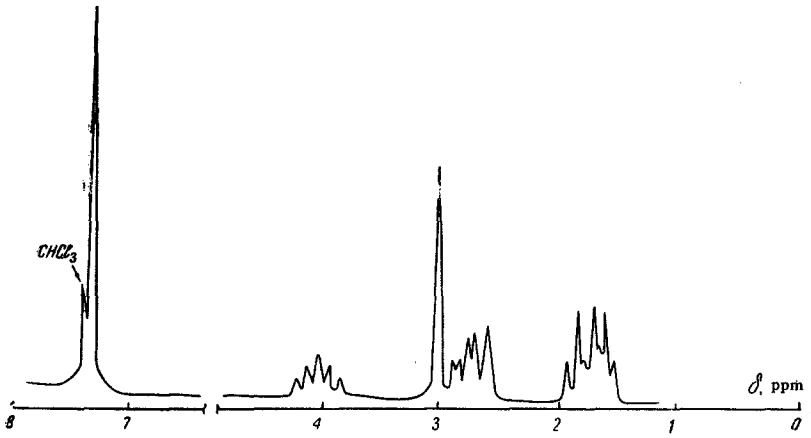
From ethereal extracts of the dry leaves of Alnus fruticosa (environs of Skovorodino, June–July, 1968) and A. manshurica (Maritime Territory, Shkotovo region, June, 1968) by chromatography on Al_2O_3 we have isolated a substance with the composition $C_{19}H_{24}O_2$, mp 94.5–95° C (ether), $[\alpha]_D^{20}$ −10° (c 2.13, $CHCl_3$).

Its IR spectrum has absorption bands in the 3625-, 3550-, 1610-, and 3000–3100-cm^{-1} regions, showing the presence in the molecule of hydroxyl groups, both free and bound by intramolecular hydrogen bonds, and of aromatic rings. The substance does not fluoresce in UV light and gives no coloration with $FeCl_3$ solution. Consequently, the hydroxyls in it are not attached to the aromatic rings. When the substance was boiled with a mixture of acetic anhydride and pyridine, a chromatographically homogeneous product was formed in the IR spectrum for which there were no absorption bands of hydroxyls, while an absorption band characteristic for carbonyl had appeared (1745 cm^{-1}). It was impossible to isolate the acetate in the crystalline state. The saponification of the acetate with 5% KOH solution in methanol led to the starting material.



The mass spectrum of the compound had a peak with m/e 284, corresponding to the molecular ion and agreeing with the calculated molecular weight. Peaks with m/e 266 and 248 correspond to the fragments (M − 18) and (M −36). This shows the presence of two hydroxyls in the molecule; fragments with m/e 77 ($C_6H_5^+$) and 91 ($C_6H_5CH_2^+$) confirm that the molecule of the substance under investigation contained monosubstituted aromatic nuclei.

The substance was not oxidized by periodate, and consequently it did not contain an α-glycol grouping. Oxidation of the diol with CrO_3 in pyridine (0–5° C) gave an oxoalcohol with the composition $C_{19}H_{22}O_2$, mp 51–52.5° C (petroleum ether), IR spectrum: 1715 and 3400–3600 cm^{-1}. Oxidation of the diol with $KMnO_4$ in boiling acetone led to the formation of a mixture of acids, in addition to the oxoalcohol. The action of diazomethane on the acids gave their esters, which were identified by the GLC method. By the addition of an internal standard and comparison of the relative retention times of authentic samples and of the mixture the latter was shown to contain methyl γ-phenylpropionate and methyl benzoate.

The benzoic acid may have been produced by further oxidation of the γ-phenylpropionic acid originally formed, under the reaction conditions, and its appearance unambiguously shows the presence in the diol of the fragment .

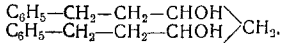
$C_6H_5—CH_2—CH_2—CHOH—$. The combination of all these facts shows that the substance has the structure of 1, 7-diphenylheptane-3, 5-diol.

A further confirmation of this structure follows from an analysis of the NMR spectrum of the diol (figure). The intensity of the signals at 7.2 ppm shows the presence in the molecule of two monosubstituted aromatic rings (10H). The quintet at 3.91 ppm (2H, τ = 6 Hz) shows the presence in the molecule of two symmetrically arranged secondary hydroxyl groups in the fragment $-CH_2-CHOH-CH_2-CHOH-CH_2-$.

The secondary nature of the hydroxyls is confirmed by the NMR spectrum of the acetate, in which the quintet has shifted downfield to 4.9 ppm.

The protons of the hydroxyl groups give a singlet (2H) at 3 ppm. This singlet disappears in the PMR spectra of the acetate and the diol taken in CD_3OD. The hydrogen atoms of the three methyl groups adjacent to CHOH form a multiplet at 1.50–1.95 ppm, and the protons of the two methylene groups adjacent to the benzene rings appear in the form of a multiplet (4H) at 2.55–2.90 ppm.

Thus, the structure of the diol isolated from Alnus is expressed by the following formula.



No diol of this structure has previously been isolated from the leaves and roots of species of the genus Alnus [1–6].

The samples of the leaves of A. fruticosa and A. manshurica were kindly given to us by P. G. Gorov and N. S. Pavlova.

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