# A NEW PHENOL FROM <u>PINUS SYLVESTRIS</u>

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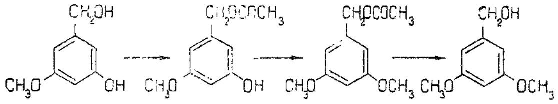
Continuing a study of the extractive substances of the wood of Pinus sylvestris (Scotch pine) growing in Siberia [1], we have isolated a white crystalline substance $C_{10}H_8O_3$ (I) with mp 85–86° C, readily soluble in acetone and alcohols. It gives a positive reaction with Pauli's reagent, absorbs at 278 mμ, and has one methoxyl group.

The IR spectrum shows the presence in this substance of a 1, 3, 5-substituted (710, 840 $cm^{-1}$) benzene ring (1510, 1602 $cm^{-1}$) and there are also two well-resolved bands of the stretching vibrations of hydroxyl groups (3460 and 3220 $cm^{-1}$).

In view of the fact that the substance undergoes the azo coupling reaction, it may be assumed that it contains a phenolic hydroxyl group with a free ortho- or para position with respect to it. The second hydroxyl group is probably aliphatic in nature.

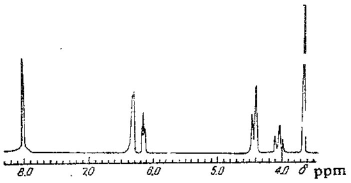
Since a phenolic hydroxyl, unlike an alcoholic hydroxyl, is not esterified by organic acids at moderate temperatures, we carried out selective acetylation and obtained an acetate (II) giving a positive reaction with diazotized sulfanilic acid. The IR spectrum of this compound retained the band at 3230 $cm^{-1}$, but that at 3460 $cm^{-1}$ had disappeared. The methylation of II gave compound III, containing no free hydroxyl groups. After hydrolytic cleavage of the latter, substance IV was obtained of which the IR spectrum again had the band of stretching vibrations at 3450 $cm^{-1}$. Consequently, the initial substance I does in fact contain two hydroxyl groups, one of which is phenolic (3220 $cm^{-1}$) and the other aliphatic (3450 $cm^{-1}$). The transformations described may be represented by the following scheme:



I II III IV

The results obtained permit the conclusion that substance I has the structure of 3-hydroxy-5-methoxybenzyl alcohol, and we have called it "sylvopinol."

The proposed structure of this compound is confirmed by proton magnetic resonance (PMR). The PMR spectrum of this compound is shown in the figure. The singlet in the strong field (δ 3.62 ppm) belongs to the protons of a methoxyl group and that in the weak field (δ 8.06 ppm) to the protons of a phenolic hydroxyl group. The signal of the protons of the methylene group is expressed by a doublet (δ 4.42 ppm) and the proton of a hydroxyl group attached to a methylene link by a triplet (δ 4.05 ppm). Since we used acetone as solvent, the form of the signals of the $CH_2OH$ group can be explained by the fact that acetone, forming a strong hydrogen bond with the hydroxyl proton, retards exchange to such an extent that spin-spin coupling of the benzyl and hydroxyl protons, giving a $A_2B$ system, appears in the spectrum. As a consequence of this, the signals of the protons of the $CH_2OH$ group included in the $A_2B$ system form a multiplet [2].



NMR Spectrum of sylvopinol in acetone.

A triplet (δ 6.18 ppm) and a poorly-resolved doublet in the 6.30–6.40 ppm region correspond to the protons of the benzene ring. Taking into account the relative integral intensities of the triplet and the doublet (1 : 2), the spin-

spin coupling constant in benzene derivatives [3], and the distance between the doublet and the triplet, it may be considered that the doublet and the triplet do not contain the resonance lines of the signal from the same proton, i. e., the signal of one of the benzene protons is represented by the triplet and those of the other two by the doublet. The proton responsible for the triplet is present in the meta position with respect to the two other protons. Consequently, its signal has a triplet structure, which is explained by spin-spin coupling with two protons having the same coupling constant ($J_{meta}$ 2.5 Hz). Hence, the substituents in the benzene ring are located in the meta-position with respect to one another.

However, if the triplet structure of one of the signals of an aromatic proton is the result of the averaging of two spin-spin coupling constants [2], the arrangement of the substituents may be different. A comparison of the PMR spectra of benzene, anisole, benzyl alcohol, and phenol [3, 4] shows that a $CH_2OH$ group does not in fact change the position of the signal of the protons of the benzene ring. By making use of the rule of the additivity of the influence of substituents on the position of the aromatic protons in disubstituted benzene [5] we have evaluated the relative position of the resonance lines of the protons as a function of the positions of the OH, $OCH_3$, and $CH_2OH$ groups. It was found that only where they have the meta arrangement in the ring does the PMR spectrum of the aromatic protons correspond to the spectrum that we have described. It follows from this that the triplet (δ6.18 ppm) is due to the protons located between the hydroxyl and methoxyl groups.

## EXPERIMENTAL

The UV absorption was measured in ethanol on an SF-4A spectrophotometer, the IR spectra on a UR-10 spectrophotometer (tablets with KBr and film), and the PMR spectrum on a JNM-4H-100 spectrometer.

**Isolation of sylvopinol.** By preparative chromatography on a polyamide sorbent with elution by the carbon tetrachloride–methanol (95 : 5) system, an acetone extract of dust of Scotch pine heartwood previously extracted with petroleum ether gave fractions enriched in sylvopinol. Rechromatography on polyamide in the 1 N acetic acid system followed by three recrystallizations from chloroform yielded 130 mg of a white crystalline substance with mp 85–86° C and mass 154 (mass spectrometry). UV spectrum: $\lambda_{max}$ ethanol) 278 mμ (log ε 3.32) and $\lambda_{min}$ 250 mμ (log ε 2.35).

Found, %: C 62.02; H 6.48; $OCH_3$ 19.10. Calculated for $C_8H_{10}O_3$, %: C 62.31; H 6.54; $OCH_3$ 20.1.

**Acetylation of sylvopinol.** A solution of 60 mg of sylvopinol in 5 ml of 50% acetic acid was heated at 60° C for 8 hr. After the usual working up and recrystallization from carbon tetrachloride (three times), 50 mg of sylvopinol monoacetate (II) with mp 87–88° C, mass 196 (mass spectrometry) was obtained. UV spectrum: $\lambda_{max}$ (in ethanol) 280 mμ (log ε 2.63) and $\lambda_{min}$ 250 mμ (log ε 1.74). The IR spectrum showed a band at 1710 $cm^{-1}$.

**Methylation of sylvopinol monoacetate (II).** A solution of 30 mg of II in 2 ml of ether was treated several times in the course of 1 hr with a freshly-prepared ethereal solution of diazomethane. After the elimination of the ether, the reaction products were chromatographed on a column (15 × 15 cm) of polyamide. On elution with chloroform, the first five fractions contained a substance which, after recrystallization from methanol, deposited in the form of a white flocculent precipitate. After drying in vacuum, it had the form of a transparent film. The yield of substance III was 15 mg.

**Saponification of III.** To 10 mg of substance III was added 10 ml of 30% KOH and the mixture was heated at 50° C for 8 hr. After the mixture had been neutralized with 20% $H_2SO_4$ it was extracted with ethyl acetate. The ethyl acetate extract yielded 5 mg of 3, 5-dimethoxybenzyl alcohol.

The mass spectra were recorded by O. S. Chizhov.

## CONCLUSIONS

From the extractive substances of Scotch pine a phenolic compound has been isolated for which the structure of 3-hydroxy-5-methoxybenzyl alcohol has been established; it has been given the name "sylvopinol."

## REFERENCES

1. M. F. Shostakovskii, N. A. Tyukavkina, V. I. Lutskii, and N. M. Borodina, KhPS [Chemistry of Natural Compounds], 5, 48, 1969.

2. B. I. Ionins and B. A. Ershov, NMR Spectroscopy in Organic Chemistry [in Russian], Leningrad, 29, 33, 248, 1967.
3. NMR Spectra Catalog, Varian Associates, Palo Alto, California, Spectrum, no. 161, 162, 1962.
4. J. C. Shug and J. C. Deck, J. Chem. Phys., 37, 2618, 1962.
5. J. Emsley, J. Feeney, and L. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 2 [Russian translation], Moscow, 85, 1969.

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