To decide this question, ervinidine was reduced with sodium borohydride in methanol. This gave an amorphous base, ervinidinol, with R_f 0.43 [thin-layer chromatogram on silica gel, ethylacetate—methanol (9:1)], and 0.89 [paper chromatogram, butan-1-ol—acetic acid—water (100:5:100)]. The UV spectrum of ervinidinol had one maximum: λ_{max} 288 m μ (log ϵ 3.44) and a small break at 254 m μ (log ϵ 3.60) characteristic for an indole derivative.

The IR spectrum exhibited a broad band at 3350-3460 cm⁻¹ (NH and OH), 1740, 1620, 1260 cm⁻¹ (COOCH₃), and had no band in the 1660 cm⁻¹ region (CO). The acetylation of ervinidinol gave an O-acetyl derivative (1760 cm⁻¹) although ervinidine does not acetylate. On the basis of these results, ervinidine can be assigned to the alkaloids of the 2-acylindole group. The structure of ervinidine is apparently close to that of picraphylline [7]. The UV and IR spectra and some chemical properties of the second base—ervinidinine are similar to those of ervinidine.

REFERENCES

- 1. P. Kh. Yuldashev, V. M. Malikov, and S. Yu. Yunusov, DAN UzSSR, no. 1, 25, 1960.
- 2. V. M. Malikov, P. Kh. Yuldashev, and S. Yu. Yunusov, DAN UZSSR, no. 4, 21, 1963.
- 3. S. Yu. Yunusov and P. Kh. Yuldashev, DAN UzSSR, no. 9, 23, 1956.
- 4. V. M. Malikov, P. Kh. Yuldashev, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 388, 1966.
 - 5. W. G. Kump and H. Schmid, Helv. Chim. Acta., 44, 1503, 1961.
 - 6. J. A. Weisbach and B. Douglas, Chem. and Ind., 15, 623, 1965.
 - 7. J. Levy, G. Ladouble, J. LeMen, and M. M. Janot, Bull. Soc. chim. Fr., 8, 1917, 1964.
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A COMPARISON OF THE BJÖRKMANN LIGNINS FROM LARCH AND FIR WOODS

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The attempts that have been made repeatedly to investigate the chemical composition of larch lignin, in particular by Shorigina and Elkin [1], have shown that it is very similar to the lignins of other coniferous species of wood (in elementary composition and amount of functional groups). We have determined some physicochemical properties of larch lignin having a direct relationship with the processes of the delignification of the wood. We have studied the Björkmann lignin from Larix sibirica (OCH₃ 15.04%, OH 13.10%, yield 20.9% for the Klason lignin in the wood). The material for comparison was a similar sample of lignin from Picea obovata (OCH₃ 15.20%, OH 12.67%, yield 21.7%).

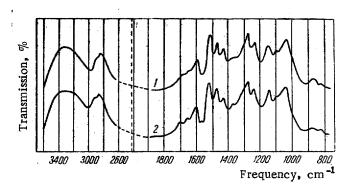


Fig. 1. IR spectra of the Björkmann lignins from larch (1) and fir (2).

The IR spectra of samples (KBr tablets) were taken on a ISK-14 double-beam spectrophotometer. The spectra of the lignins of larch and fir (Fig. 1, curves 1 and 2 respectively), are practically identical. The IR spectra for lignins of different origins, including those from larch and fir, have been published previously [2]. In the present work, questions of the interpretation of the spectra are not considered. We mention only that the results obtained do not contradict the opinion that the chemical structures of the lignins of larch and fir are similar.

Viscosimetric measurements were carried out in a suspended-level viscometer at 25° C with aqueous dioxane (1:9 by volume) solutions of the lignin (concentration 0.001-0.01 g/ml). At concentrations of 0.01-0.003 g/ml, there was a linear relationship between the reduced viscosity and the concentration. When the solutions were diluted further, an anomalous increase in the viscosity appeared which was preserved when the solution was acidified with hydrochloric acid. The characteristic viscosity was determined by extrapolation to infinite dilution in accordance with the Huggins equation. The following values of the characteristic viscosities, Huggins constants, and the critical concentrations were found; for larch lignin [η] = 0.0612 ml/g, k = 4.30, $c_{\rm crit}$ = 0.0029 g/ml; for fir lignin [η] = 5.41 ml/g, k = 5.65, $c_{\rm crit}$ = 0.0028 g/ml. The calculations carried out from the viscosimetric measurements showed that the mean viscosimetric molecular weight of the Björkmann lignin of the larch was 1.5 times higher than that of the analogous fir lignin.

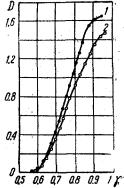


Fig. 2. Curves of the turbidimetric titration of solutions of the Björkmann lignins from larch (1) and fir (2).

The turbidimetric titration of 0.04% solutions of the lignins in dioxane was carried out with water at 25° C (Fig. 2). The results obtained show the similarity of the molecular weight distributions of the samples studied.

REFERENCES

- 1. N. N. Shorygina and V. V. Elkin, Izv. AN SSSR, Ser. khim., 7, 1279, 1965.
- 2. Yu. S. Pilipchuk, R. Z. Pen, and A. V. Finkel'shtein, Tr. Sibirskogo tekhnologicheskogo instituta, Krasnoyarsk, no. 38, 20, 1966.

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ANTHRAQUINONE PIGMENTS OF THE SEEDS AND LEAVES OF RHEUM TATARICUM. III

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We have studied the anthraquinone pigments of the seeds and leaves of Rheum tataricum L. fil. collected in May 1964 in the Syugata valley, Alma-Ata Oblast.

The anthraquinone pigments were extracted from the air-dry raw material with methyl alcohol. The alcoholic extract was concentrated to small bulk and chromatographed on a kapron column. The column was washed with distilled water to eliminate the mono- and oligosaccharides. Elution with 60% ethanol and subsequent crystallization from 70% ethanol gave two products with mp 245° and 190° C. The eluate from the zone desorbed from the column with 95% ethanol was evaporated to dryness. The solid residue was dissolved in chloroform and treated with 3% sodium carbonate solution. Acidification of the carbonate layer gave a curdy precipitate, which was recrystallized from 95% ethanol and then had mp 258° C.

From the chloroform layer, a substance was isolated which, after repeated recrystallization, had mp 198° C.

The compounds obtained were chromatographed on paper in eight systems of solvents: 1) toluene; 2) petroleum ether saturated with methanol; 3) 2% acetic acid; 4) butan-1-ol-acetic acid-water (4:1:5); 5) ethyl acetate-formic acid-water (10:2:3, upper layer); 6) n-propanol-ethyl acetate-water (4:3:3); 7) petroleum ether-toluene-xylene-methanol (4:1:1:2); and 8) water-acetone-benzene (2:1:4, lower layer).

Acid hydrolysis of the substance with mp 245° C formed a molecule of chrysophanic acid and one molecule of