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 $[\eta] = 0.0612$ ml/g, $k = 4.30$, $c_{crit} = 0.0029$ g/ml; for fir lignin $[\eta] = 5.41$ ml/g, $k = 5.65$, $c_{crit} = 0.0028$ 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.

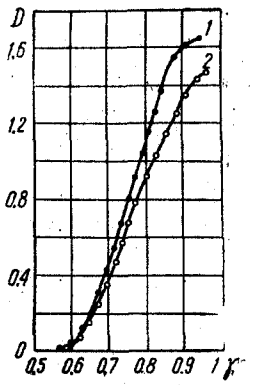

Fig. 2. Curves of the turbidimetric titration of solutions of the Björkmann lignins from larch (1) and fir (2).

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.

4 November 1966

Novosibirsk Institute of Organic Chemistry, Siberian Division, AS USSR

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

T. K. Chumbalov and G. M. Nurzalieva

Khimiya Prirodnykh Soedinenii, Vol. 3, No. 2, p. 144, 1967

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

glucose. The IR spectrum (KBr) had absorption bands at 1670, 1630, and 1585 cm^{-1}, and the UV spectrum (methanol) had λ_{max} 257 and 410 mμ (log ε 4.01, 3.60). A pentaacetate with mp 187° C was obtained.

From its physical constants and its behavior on chromatograms in systems 1-8, the substance was identified as a monoglucoside of chrysophanic acid (chrysophanein) [1, 3].

The substance with mp 190° C was hydrolyzed, giving emodin and glucose (1:1). The IR spectrum (KBr) showed absorption bands at 1672, 1631 and 1589 cm^{-1}, and the UV spectrum (methanol) had λ_{max} 284 and 423 mμ (log ε 3.98, 3.76). It gave a hexaacetate with mp 205° C.

The constants given and the chromatograms in systems 1-8 agree well with the data for glucoemodin [1, 2, 4].

The substances with mp 258° and 198° C were identified by mixed melting points with authentic emodin and chrysophanic acid and also from their R_f values in solvent systems 1-8.

Thus, the seeds of Rheum tataricum contain chrysophanein (1.01%), glucoemodin (1.07%), chrysophanic acid (0.20%), and emodin (0.34%) and the leaves the same anthraquinone derivatives in amounts of 0.05%, 0.2, 0.10, and 0.03%, respectively.

REFERENCES

1. H. Wagner and L. Hörhammer, Z. Naturf., 18b, 89, 1963.
2. O. E. Schultz and G. Mayer, Arzneimittel Forsch., 6, 334-342, 1956.
3. A. S. Romanova and A. I. Ban'kovskii, Med. prom. SSSR, no. 10, 18, 1964.
4. A. S. Romanova, et al., KhPS [Chemistry of Natural Compounds], 83-85, 1966.

18 March 1966

Kazakh State University, Alma-Ata

A STUDY OF THE CHEMICAL COMPOSITION OF BUPLEURUM AUREUM

A. T. Troshchenko and T. I. Limasova

Khimiya Prirodnykh Soedinenii, Vol. 3, No. 2, pp. 145-146, 1967

We have studied the epigeal part of the plant Bupleurum aureum Fisch collected in the environs of Novosibirsk.

The air-dry material was ground and subjected to systematic extraction with petroleum ether, benzene, and methanol. By chromatography on alumina, the petroleum ether extract was separated into three fractions with mp 67°-71°, 76°-79°, and 126°-135° C.

The first fraction, after repeated recrystallization from petroleum ether, was obtained in the form of lamellar crystals with mp 73°-74° C. From its melting point, a mixed melting point, and a mixed thin-layer chromatogram the substance was identified as 10-nonacosan-one. Literature data: mp 74°-74.5° C [1]. The plant contains 0.1% of this substance.

After repeated recrystallization from methanol the second fraction was obtained in the form of colorless acicular crystals with mp 78.5°-80° C. On the basis of its IR spectrum, it was established that the compound is a long-chain alcohol; its acetate had mp 63°-63.5° C. Literature data for hexacosyl acetate: mp 65° C [2]. A direct comparison of these alcohols and their acetates showed the identity of both compounds. The content of 1-hexacosan-ol in the plant is 0.04%.

The third fraction was rechromatographed on alumina and recrystallized from methanol. Colorless lustrous crystals with mp 168°-170° C deposited. Literature data for α-spinasterol: mp 172° C [3]. The IR spectra showed that the substance was an alcohol of the sterol series. It gave an acetate with mp 183°-183.5° C (literature data: mp 185° C [4] and 187° C [5]), a benzoate with mp 197°-198° C (literature data: mp 196°-197°C [6] and 201° C [7]), and a nitrobenzoate with mp 210°-211° C (literature data: mp 211°-212° C). Consequently, the alcohol was identified as α-spinasterol.

The chromatography of the benzene extract on alumina gave very small amounts of 10-nonocosan-one and 1-hexacosan ol.

When the methanolic extract was left to stand, a yellow granular precipitate deposited which gave a positive reaction for flavones. The chromatography of this precipitate on kapron powder gave a pure flavone glycoside with mp 188°-200° C (decomp.). An authentic sample of rutin was used as a reference sample for thin-layer chromatography on a fixed layer of silica gel. The chromatography showed that the substance was rutin. This was confirmed by hydrolysis, yielding quercetin, rhamnose, and glucose.