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Note

A simple method for the isolation of crystalline D-hamamelose

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Isolation of D-hamamelose from the bark of witch-hazel (*Hamamelis virginiana* L.) according to the procedure of Freudenberg and Bluemmel[1] gives a syrupy product. Crystalline D-hamamelose has been prepared by chemical synthesis[2]; however, for large-scale preparations, the procedure is rather complicated.

We now report a simple method for the isolation of crystalline D-hamamelose in good yield from the bark of witch-hazel.

EXPERIMENTAL

Preparation of hamamelitannin. — The yield of hamamelitannin could be raised to 4–7% (depending on the bark) by combining the methods of Freudenberg and Bluemmel[1] and of Anderson[3] with a more exhaustive extraction procedure.

Dry bark (2 kg) was powdered and extracted with acetone (3 × 4 litres) at room temperature. The extracts were combined and concentrated under reduced pressure, and the residue was suspended in 100–200 ml of water and extracted with benzene. The aqueous solution was concentrated and lyophilized.

To a solution of the brown residue in the minimum volume of acetone, 5 vol. of ethyl ether was added with vigorous stirring to extract the tannin. After 48 h at 20°, the suspension was filtered and the residue was twice extracted as described above. The combined extracts were concentrated and a suspension of the residue in water was stirred into 2 litres of water at 60°. The solution was kept overnight at room temperature and then for 2–3 days at 2°. Hamamelitannin crystallized in small needles, m.p. 145–147° (*cf.* ref. 4). Recrystallization was unnecessary.

Hydrolysis of hamamelitannin. — Hamamelitannin (60 g) was treated with 750 ml of M hydrochloric acid for 60 h at 65°. The hydrolysate was concentrated *in vacuo* at 30° to half its volume and kept overnight at 2°. Crystallized gallic acid was removed, and the filtrate was partially neutralized with 30 g of sodium carbonate and concentrated to 150–200 ml at 30°. After 12 h at 2°, a second portion of crystalline gallic acid was removed, and the filtrate was exactly neutralized with sodium carbonate

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and concentrated under reduced pressure at 50°. The syrupy residue was dried by the distillation of 1-butanol (100 ml) therefrom.

Isolation of hamamelose. — Hamamelose was extracted from the residue with boiling, dry methanol. The extract was concentrated to a syrup (20 g) which was dissolved in water saturated with 1-butanol (60 ml). Portions (24 ml) of this solution were chromatographed[5] on a column (6-cm diam.) of acid-washed Celite (500 g). After 6–7 litres of the solvent had passed through the column, hamamelose appeared in the eluate (paper chromatography, detection with alkaline silver nitrate).

The fractions containing hamamelose (0.8–1.2 litre) were combined and concentrated, and a solution of the resulting dry syrup in dry methanol (20–30 ml) was treated at room temperature with charcoal (0.3 g). The solution was filtered and concentrated to ~5 ml; these operations must be performed in a dry atmosphere. The solution was saturated with light petroleum (b.p. 35–40°) and kept saturated at room temperature for 2–3 days. The hamamelose (1.5–2 g per column) was collected, washed with ice-cold dry methanol, and dried *in vacuo* at 50°. It had m.p. 110° (corr.), $[\alpha]_D$ $-6.7 \pm 0.5°$ (equil., water), and was identical with the synthetic product[2,6].

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