ACTA CHEMICA SCANDINAVICA 13 (1959) 1395–1396

The Chemistry of the Natural Order Cupressales XXIII *

L-Arabinoic Acid from the Heartwood of *Austrocedrus chilensis* (D.Don), Florin et Boutelje

ANDERS ASSARSSON, BENGT LINDBERG and
HELMUT VORBRÜGGEN

Institutionerna för träkemi och organisk kemi, Kungl. Tekniska Högskolan, Stockholm, Sweden

L-Arabinoic acid was isolated in the form of the 1,4-lactone from the heartwood of *Austrocedrus chilensis.*

A water soluble carbohydrate fraction was isolated from the heartwood of *Austrocedrus chilensis* (natural order Cupressales) during the course of an investigation by one of us (H.V.) of the terpenoid and phenolic constituents **. A paper chromatographic investigation of this fraction revealed the presence of arabinose and galactose, which are generally found in these woods, and of smaller amounts of other reducing sugars, with both high R_F-values such as rhamnose and fucose, and with low R_F-values, similar to those of di- and trisaccharides. Indications were also found of the presence of several non-reducing carbohydrates, one of which seemed to occur in fairly large amount. This component was enriched by carbon column chromatography and obtained in a pure crystalline state by chromatography on a cellulose column; m.p. 97—99°, $[\alpha]_D$—72°. It gave a positive hydroxamate test for an ester, and the IR spectrum showed a strong peak at 1 760 cm^{-1}, the carbonyl frequency characteristic of a γ-lactone. This data agreed with that reported for L-arabino-1,4-lactone [1]. The m.p. was not depressed on admixture with an authentic sample of that substance and the IR spectra of the two substances were identical.

The 1,4-lactone is in equilibrium with the free acid and the 1,5-lactone, and spots due to these substances were also observed on paper chromatograms of the carbohydrate fraction. It is obvious that all three components occur in

---

* Part XXI, *Tetrahedron* 4 (1958) 361.
Part XXII, *Acta Chem. Scand.* 13 (1959) 1124.

** Sponsored by U.S. Army and Development Liaison Group under contract DA-91-508-ECU-288.

the wood, but the 1,4-lactone, being the most stable, was most easily isolated in a state of purity. The 1,4-lactone was isolated in a yield of about 0.01 % but the total percentage of L-arabinoic acid present both as lactones and as free acid is probably about twice this value.

L-Arabinoic acid has not been found in nature before. It is almost certainly formed by oxidation of L-arabinose, which is present in the wood in a fairly high concentration. Some bacteria [2], especially those of the genus *Pseudomonas*, are known to oxidise L-arabinose to L-arabinoic acid in the presence of air. The possibility that the L-arabinoic acid found in the heartwood of *Austrocedrus chilensis* is not a wood constituent but is formed by bacterial oxidation cannot be excluded but seems highly improbable since this extremely durable wood contains unusually large amounts of the highly toxic α-thujaplicin [3].

EXPERIMENTAL

Melting points are corrected.

Paper chromatography was done on Whatman No. 1 filter paper, using the solvent system (v/v): Ethyl acetate:acetic acid:water, 3:1:3 (upper phase).

The milled, airdried heartwood (40 kg), was extracted with acetone in a continuous extractor for two days. On concentration the extract separated into two layers, a brown oil and a yellow aqueous phase (1.5 l). On cooling, yellow crystals (52 g) separated from the aqueous phase, m.p. 240—241°, which were identified as taxifolin. The mother liquors were concentrated to about 200 ml, treated with decolourising carbon and concentrated to a thick syrup. On crystallisation from methanol this gave L-arabinose (70 g), m.p. 158°, $[\alpha]_D + 103°$.

The mother liquors, which still contained some phenolic material, were concentrated to dryness. The product obtained was disolved in 50 % aqueous ethanol (1 l) and half of this solution was shaken with decolourising carbon (200 g) for two hours. The carbon was filtered off and washed with the same solvent. Extraction of the carbon with boiling ethanol gave phenolic material (1.5 g) which was not further investigated. The decolourised solution was concentrated and deionised by filtration through columns of IR 120 and IR 4B resins. The acid material recovered from the resin (3.45 g) was found by chromatography to be mainly L-arabinoic acid and its lactones.

The deionised solution was concentrated to a syrup (18.4 g), adsorbed on the top of a carbon-Celite solumn and then eluted with aqueous ethanol, using gradient elution. The first fractions contained traces of cyclitols, and the next contained the majority of the reducing sugars. The fractions following that contained the component that was later found to be the arabino-1,4-lactone. They were combined (7.6 g) and rechromatographed on a cellulose column, using butanol, saturated with water as eluant. The fraction containing the 1,4-lactone crystallised on concentration and was recrystallised from propanol, m.p. 97—99°, $[\alpha]_D^{20} - 72°$ (water, *c*, 2).

Authentic L-arabino-1,4-lactone was isolated from the mixture of acid and lactones by chromatography on a cellulose column as above. It melted at 97—99°, alone or in admixture with the natural product.

The authors are indebted to Professor Holger Erdtman for his interest in this work.

REFERENCES

1. Fisher, E. and Piloty, B. *Ber.* **24** (1891) 4214.
2. Lockwood, L. B. and Nelson, G. E. N. *J. Bacteriol.* **52** (1946) 581.
3. Erdtman, H. and Pelchowicz, Z. *Acta Chem. Scand.* **9** (1955) 1728.

Received May 26, 1959.