Previous work. Stem bark.[15]

Leaves and Stem. Benzene extract of EtOH extractive (chromatography over alumina) gave *hentriacontane*, *hentriacontanol* and *β-sitosterol.*

Plant

Pyrus pashia—Rosaceae.

Occurrence. Temperate Himalaya, Khasia Mountains at 5000 ft.

Previous work. Bark and leaves.[16]

Stem. Benzene soluble fraction of EtOH extractive (chromatographed over alumina) yielded *hentriacontanol, β-sitosterol, friedelin, α-amyrin* $C_{30}H_{50}O$ m.p. 180°, $[\alpha]_D$ +85° (m.p., mixed m.p., IR and acetate). Arborinol $C_{30}H_{50}O$ m.p. 275°, $[\alpha]_D$ + 39° (m.p. and IR), acetate $C_{32}H_{52}O_2$ m.p. 235°, $[\alpha]_D$ +18°.

Plant

Rhododendron niveum—Hook.f.—Ericaceae.

Occurrence. North East Himalaya.

Plant. Benzene soluble fraction of EtOH extractive (chromatographed over alumina) yielded *β-sitosterol* and *friedelin.*

[15] A. CHATTERJEE, C. P. DUTTA and S. BHATTACHARYA, *Sci. Cul. Calcutta* **33,** 371 (1967).

[16] D. CHAKRAVARTI, N. K. ROY and N. N. CHAKRAVARTI, *J. Ind. Chem. Soc.* **41,** 83 (1964).

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FAGACEAE

PHENOLICS OF *QUERCUS RUBRA* WOOD

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Abstract—Sixteen phenolics are positively identified in oak wood; seven had not been reported in oaks. Several additional phenolics are tentatively identified. Bark is briefly investigated. Lyoniside is shown to be lyoniresinol 2a-*O*-xyloside.

Plant. Quercus rubra L.—Fagaceae (northern red oak).

Uses. Timber.

Previous work. Tannin content of wood 1·8%.[1] Hamamelitannin in bark.[2]

Isolation. Extraction of the wood proceeded as shown in the following tabulation:

* Deceased. See *Phytochem.* **9,** 679 (1970). Reprint requests and correspondence should be addressed to Dr. John W. Rowe at the U.S. Forest Products Laboratory.

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‡ Maintained in cooperation with the University of Wisconsin.

[1] A. J. RUSSELL, *J. Amer. Leather Chem. Assoc.* **39,** 176 (1944).

[2] W. MAYER, W. KUNZ and F. LOEBICH, *Ann. Chem.* **688,** 232 (1965).

TABLE 1

Solvent	Extractive yield, %	
	Sapwood	Heartwood
Light petroleum	0·5	0·35
Chloroform	0·3	0·7
Acetone–water (95:5)	2 1	5·0
Acetone–water (1:1)	2·4	1·9
Water	0 9	0·2
Total	6·2	8 2

The last three extracts mentioned consisted mainly of tannins. All research was on the components of the acetone–water (95:5) extract that was concentrated on a rotary vacuum evaporator and freeze-dried to yield a pale tan powder. Two-dimensional paper chromatography using butanol–27% acetic acid (1·1) (BAW) followed by 6% acetic acid–acetone (95·5) gave the best fractionation of the extract, 90 or so distinguishable spots being present in each. It was found that the nontannin components of the acetone–water (95:5) extract could best be isolated by extracting the wood with chloroform–methanol (10:1) subsequent to the light petroleum and chloroform extractions. Extracts were chromatographed on silica and nylon. Individual compounds were positively identified by direct comparison with known compounds via several paper chromatographic systems, TLC, NMR, IR and UV.

Another spot was tentatively identified as *m*-digallic acid, and pinoresinol was tentatively identified in the sapwood. The sapwood but not the heartwood extract gave the pink butanol-extractable color characteristic of leucoanthocyanins after boiling with hydrochloric acid. No gallocatechin was detected although gallo- and ellagi-tannins predominate. Spots having low R_f in BAW and 0·2–0·6 in HOAc are apparently ellagitannins similar to those found in *Eucalyptus delegatensis* wood.[4] Neither flavonols nor their glycosides could be detected. However, color tests on the paper chromatograms suggested that several esters of hydroxycinnamic, vanillic, and syringic acids were present. Glucose, arabinose, and xylose were produced on hydrolysis of the extract.

A brief investigation of the phloem (inner bark) gave a pattern of extractives very different from either the sapwood or the heartwood. No gallic or ellagic acid was present, but tannin esters, catechin, flavonoids, and lyoniside were tentatively identified.

Structure of Lyoniside

Lyoniside has been proved to be lyoniresinol xyloside;[5] however, the point of attachment of the xylose had not been determined. In related compounds, the authors have observed that the 2a-hydroxyl has a band in the infra-red at 1020–1028 cm^{-1}, whereas the 3a-hydroxyl has a band at 1048–1060 cm^{-1}.[6] Lyoniside has a band at 1050 cm^{-1} suggesting a 2a-*O*-xyloside. This was confirmed by investigating the NMR of the hexa-acetate. In complete analogy to the NMR spectrum of the hexa-acetate of lyoniresinol-2a-*O*-rhamnoside,[6]

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[3] Not previously reported in *Quercus* spp.

[4] M. K. SEIKEL and W. E. HILLIS, *Phytochem.* **9**, 1115 (1970)

[5] M. YASUE and Y. KATO, *Yakugaku Zasshi* **80**, 1013 (1960).

[6] F D. HOSTETTLER and M K. SEIKEL, *Tetrahedron* **25**, 2325 (1969).

TABLE 2

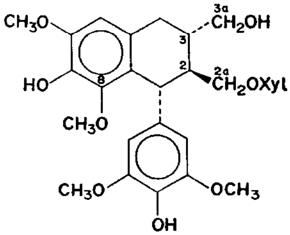
Results

Compound	Isolated from*
Ellagic acid	H and S
Hamamelitannin	H and S
Gallic acid	H and S
Sinapaldehyde	H and S
Coniferaldehyde	H and S
Catechin	S
Scopoletin	H
Syringaldehyde	H and S
Propioguaiacone (propiovanillone)[3]	H
Vanillin	H and S
Lyoniside[3,5]	H and S
rac-Lyoniresinol[3,6]	H
2,6-Dimethoxybenzoquinone[3,6]	H
Resorcinol[3]	H
Syringaresinol[3]	H and S
p-Hydroxybenzaldehyde[3]	S

* H, Heartwood; S = Sapwood.

Location on chromatograms unknown; probably masked under other spots.

the 8-methoxyl group at δ 3·35 in lyoniside hexa-acetate is split into a doublet because of inhibition of free rotation due to steric crowding by the 2a-*O*-triacetylxyloside. As expected, higher temperatures caused the doublet to collapse toward a singlet. Lyoniside is, therefore, lyoniresinol 2a-*O*-xyloside as shown:



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