Since it has been shown that many lipid constituents of forest soil derive from decomposed tree leaves,[5] we put forward the suggestion that the above-mentioned triterpenes found in some mosses could have been derived from chestnut leaves.[2] This hypothesis was also supported by the fact that amyrin or lupane derivatives have never been found in ferns,[6] which instead are rich in hopane derivatives.

In the light petroleum extract of the dead leaves of *Castanea sativa*, Mill., collected in autumn, the following constituents have been found: *waxes*, λ_{CO} 5·8 μ, 0·1%; *ursolic acid* ((m.p. 283–286°), $[\alpha]_D$ +65°), 0·2%; *lupeol* ((m.p. 208–210°), $[\alpha]_D$ +25°, benzoate (m.p. 270–273°), $[\alpha]_D$ +55°), 0·4%; *betulin* ((m.p. 252–255°), $[\alpha]_D$ +22°, diacetate (m.p. 220–223°), $[\alpha]_D$ +23°), 0·1%; *aliphatic hydrocarbons*, 0·04%; % composition (GLC), C_{23} 0·5, C_{25} 0·5, C_{27} 13·0, C_{29} 66·0, C_{31} 19·0; *fatty acids*, 1·58%; % composition (determined by GLC on the corresponding Me esters), lauric 1·4, tridecanoic 1·8, myristic 3·5, pentadecanoic 1·0, pentadecenoic 0·5, palmitic 24·8, palmitoleic 0·9, eptadecanoic 0·6, stearic 5·0, oleic 13·7, linoleic 13·0, linolenic + arachidic 21·5, monocosanoic 2·5, behenic 4·5, tricosanoic 0·7, lignoceric 4·6.

These results strengthen our belief that both ursolic acid and lupeol are not constituents of the mosses studied, but were derived from the decomposed chestnut leaves.

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JUGLANDACEAE

POLYPHENOLS OF *JUGLANS NIGRA*

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Key Word Index—*Juglans nigra*; Juglandaceae; juglone; dihydrojuglone-4-glucoside; myricitrin; sakurenin; neosakuranin.

Plant. Juglans nigra L. (bark, sapwood and heartwood). *Source.* North Central Forest Experimental Station, St. Paul, Minn., U.S.A. *Other species.* Juglone,[2] α-hydrojuglone-4-β-D-glucoside[3] and sakurnetin[4] were isolated from *Juglans regia.*

Present work. The concentrate of the acetone extract of the powdered stem-bark (600 g was defatted with light petroleum and then extracted with Et_2O (Fraction 1). The Et_2O-insoluble part was redissolved in minimum quantity of acetone and diluted with Et_2O.

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The acetone–Et_2O solution was decanted from the precipitated gum (*M*) and let stand. After 2 days, a brownish-yellow solid separated (Fraction 2) and the mother-liquor yielded, on evaporation, a dark coloured solid (Fraction 3).

Fraction 1 on chromatography over silica gel using C_6H_6–EtOAc mixtures furnished three compounds *A*, *B* and *C*. Compound *A* formed orange–red needles from hexane (10 mg), identified as juglone by comparison with an authentic sample (TLC, UV and IR). Compound *B* was obtained as colourless needles from benzene (50 mg), m.p. 147–148°: λ_{max}^{MeOH} 335 (inflex.) 287 and 228 nm; + $AlCl_3$, 306, 290 (sh) and 225 (sh) nm. It was identified as sakuranetin[5] and confirmed by comparison with an authentic sample. Compound *C*, yellow needles from EtOH (200 mg), m.p. >350° (acetate m.p., 212–214°), was found to be a flavonol from its colour reactions and UV spectrum: λ_{max}^{MeOH} 377, 302 (inflex) and 255 nm. It was identified as myricetin[6] and confirmed by direct comparison.

Fraction 2 was chromatographed on polyamide (EtOH) yielding a pale yellow crystalline solid, compound *D*, from EtOH (2 g), m.p. 187–190° λ_{max}^{MeOH} 356, 210 (inflex) and 258 nm. Acid hydrolysis yielded myricetin and rhamnose. NMR spectrum of its acetate (m.p. 120–121°) indicated that compound *D* is a monorhamnoside of myricetin. Methylation with Me_2SO_4 in acetone–K_2CO_3 medium gave myricetin hexamethyl ether (m.p. 159–160°). However, methylation with CH_2N_2 followed by hydrolysis with 2% aq. H_2SO_4 gave 5,7,3′,4′,5′-penta-*O*-methylmyricetin, m.p. 228–230°; λ_{max}^{EtOH} 357 and 249 nm; +$AlCl_3$, 417 and 271 nm, thus proving that the sugar was in the 3-position and compound *D* is myricitrin.

Fraction 3 was separated into three compounds *E*, *F* and *G* by chromatography on silica gel ($CHCl_3$–MeOH) and then on polyamide (aq. EtOH). Compound *E* formed buff coloured needles from $CHCl_3$–MeOH (500 mg), m.p. 195°. Its IR spectrum showed the absence of carbonyl function and the UV spectrum, λ_{max}^{MeOH} 225, 305 (inflex) and 340 (inflex) nm was characteristic of a naphthalene derivative. Acid hydrolysis gave glucose, juglone (artefact by oxidation) and α-hydrojuglone. NMR spectrum of its acetate (m.p. 144–145°) showed that the compound *E* is a monoglucoside of α-hydrojuglone. Methylation and hydrolysis furnished 4,8-dimethoxy-1-naphthol, m.p. 150–152°, identical with an authentic sample. Thus, compound *E* is 1,4,5-trihydroxynaphthalene-4-*O*-glucoside.[3,8]

Compound *F*, colourless needles from EtOAc–MeOH (200 mg), m.p. 214–216°, was found to be a flavanone glycoside from its colour reactions and UV spectrum; λ_{max}^{MeOH} 315 (sh), 278 and 235 nm. It gave sakuranetin and glucose on hydrolysis. Absence of a shift in UV spectrum with $AlCl_3$ indicated that the compound could be sakuranetin-5-glucoside (sakurenin);[5] this was confirmed by comparison with an authentic sample.

Compound *G*, orange–yellow needles from aq. MeOH, (*ca.* 10 mg.); λ_{max}^{MeOH} 369 nm; +NaOMe, 400 nm; +$AlCl_3$, 420 nm; +$AlCl_3$ +HCl, 420 nm; it was identified as the chalcone glucoside, neosakuranin[9] by comparison with sample obtained by alkali-treatment of sakuranin followed by acidification in the cold. The alcohol extract of the bark and the gum (*M*) which separated from the acetone extract were found by TLC to contain small amounts of myricitrin, α-hydrojuglone-4-glucoside and sakuranin.

Examination of the alcohol extracts of the sapwood and heartwood indicated they contained appreciable quantity of gallic acid while the compounds present in the bark

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appeared to be absent. The heartwood extract contained a dark violet coloured polymeric substance, but it has not been possible to obtain it pure.

Conclusion. Apart from juglone, the bark of *J. nigra* contains α-hydrojuglone-4-glucoside, myricetin, myricitrin, sakuranetin, sakuranin and neosakuranin. This appears to be the first report of the occurrence of myricetin or its derivative in the genus *Juglans*. These compounds appear to be absent in the sapwood and heartwood.

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LABIATAE

TERPENOID COMPOSITION OF SOME CANADIAN LABIATAE

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The chemical composition of the essential oils of a number of Canadian Labiatae have been examined chromatographically. In each case the oil, which was obtained by microhydrodistillation of partially dried leaves, was analysed by a combination of techniques described previously.[1,2] All components identified were characterized by a combination of relative retention, time data and IR spectroscopy. Voucher specimens of each plant studied can be found in the herbarium at the University of Waterloo.

Plant. Agastache nepetoides (L.) Kuntze. *Source.* Galt, Ontario. *Uses.* Not known. *Previous work.* None. *Terpenoid Composition.* Germacrene D (48·3%), caryophyllene (18·4%) and *trans*-ocimene (3·6%).

Plant. Collinsonia canadensis L. *Source.* Glen Morris, Ontario. *Uses.* Roots used medicinally.[3] *Previous work.* The composition of the resin[4] has been examined.

Terpenoid Composition. Germacrene D (46·0%), caryophyllene (5·3%), elemicin (3·6%) and β-elemene (3·3%).

Plant. Glechoma hederacea L. *Source.* Fredericton, New Brunswick. *Uses.* Leaves used in herb tea.[3] *Previous work.* None.

Terpenoid Composition. Germacrene D (19·4%), germacrene B (13·9%), *cis*-ocimene (9·2%), β-elemene (8·9%), 1,8-cineol (6·2%), α-pinene (3·7%), myrcene (3·4%), β-pinene

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