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NEUTRAL CONSTITUENTS OF *LARIX DECIDUA* BARK

TORBJÖRN NORIN* and BJÖRN WINELL†

Forest Products Research Laboratory, P.O.B. 5604, S-114 86 Stockholm, Sweden

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Key Word Index—*Larix decidua* Mill., Pinaceae; larch; bark; alkanes; waxes; triglycerides; fatty alcohols; polyprenol esters; sitosterol; 13-epimanool; torulosyl acetate; torulosol; torulosal; 19-acetoxylabda-12,14-dien-8-ol.

Plant. Larix decidua Mill. *Uses.* Timber and pulp. *Source.* Royal College of Forestry, experimental forest at Bogesund near Stockholm. *Previous work.* Wood,[1] wood resin[2-4] and needles.[5-7]

Bark. Powdered bark (4·2 kg) was extracted with CH_2Cl_2. The extract (231 g) was divided into light petroleum soluble (167 g) and insoluble (64 g) parts. A portion (47 g) of the petrol. soluble part was separated into neutral (22·6 g) and acidic (24·4 g) fractions. A part (6 g) of the neutral fraction was chromatographed on a silica gel column. Increasing concentrations of ether in petrol. eluted the following compounds or groups of compounds.

Alkanes (1·0% of neutral fraction) characterized by IR, NMR and argentative TLC and *terpenoid hydrocarbons* (1·7%), not further examined.

Waxes (11·0%) composed of sitosterol, fatty alcohols and fatty acids (TLC, GLC, IR and NMR).

Polyprenol esters (0·5%) IR, characteristic bands at 3020, 1750, 1670 and 840 cm^{-1}; NMR ($CDCl_3$, τ), 4·9 (18 H, *b m*, olefinic protons), 5·5 (2 H, *d*, *J* 7 Hz, $-CH_2-O$), 7·95 and 8·00 (68 H, allylic CH_2), 8·27, 8·34 and 8·42 (57 H, Me-groups on double bonds), 8·75 (30 H, methylenes of fatty acids), 9·1 (*m*, Me of fatty acids).

The NMR indicate[8] the presence of three methyl groups *cis*-located to their vicinal olefinic protons and 15 *trans*-located methyl groups. The polyprenol esters were saponified with methanolic alkali under N_2. The NMR spectrum of the polyprenols thus obtained showed close similarities to that of the esters except that the signals at τ 8·75 and 9·1 were missing and the doublet at τ 5·5 had moved upfield to τ 5·95. The MS of the crude polyprenol fraction exhibits groups of peaks rather than distinct peaks which has been interpreted as thermal destruction.[9,10] A peak at *m/e* 1242 is assigned to the major

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* Present address: Royal Institue of Technology, Department of Organic Chemistry, P.O.B., S-100 44 Stockholm 70, Sweden.

† Present address: National Food Administration, P.O. Box, S-104 01 Stockholm 60, Sweden.

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component ($C_{90}H_{146}O$). A minor peak at *m/e* 1310 is due to the presence of the next higher homologue ($C_{95}H_{154}O$). There are also peaks at *m/e* 1174, 1106 and 1038 which are assigned to the presence of the lower homologues $C_{85}H_{138}O$, $C_{80}H_{130}O$ and $C_{75}H_{122}O$.

The fatty acid fraction from the saponification of the polyprenol esters was found (GLC) to consist of a homologous series of *n*-acids (C_{12}–C_{20}) with myristic (8%), palmitic (29%), palmitoleic (10%), stearic (20%) and oleic (15%) acids as main components.

Triglycerides (22·0%) characterized by IR and NMR. Saponification gave the following *fatty acids* as main components (GLC, argentative TLC): oleic, linoleic and linolenic acids. *Fatty alcohols* (4·7%) characterized by GLC, IR and NMR. *Sitosterol* (5%). *13-Epimanool* (11·4%) $[\alpha]_D$ +52° (*c* 1·0, $CHCl_3$). *Terpenoid alcohols* (6·7%) not further examined.

Torulosyl acetate (11·6%), *torulosal* (2·8%) and *torulosol* (6·7%). Torulosyl acetate and torulosal did not separate by silica gel TLC. NMR, IR and MS of the mixture showed the presence of acetate and aldehyde groupings. Saponification in methanolic alkali under N_2 yielded torulosol ($[\alpha]_D$ + 33; *c* 1·9 in $CHCl_3$; m.p. and m.m.p. 110–110·5°)[11] and torulosal ($[\alpha]_D$ +32; *c* 0·3, $CHCl_3$)[11] which was identified by reduction[11] to torulosol also present in the bark extract.

A *diterpene alcohol ester* (0·2%): $[\alpha]_D$ +31° (*c* 1·0, $CHCl_3$); IR characteristic bands at 3500, 3080, 1730, 1640, 1240, 940 and 900 cm^{-1}; NMR ($CDCl_3$, τ), 2·4–5·0 (4 H, olefinic protons with a pattern identical to that of abienol),[12] 6·0 (2 H, *q*, *J* 10·7 Hz, $-CH_2-OAc$), 8·0 (3 H, *s*, acetate), 8·23 (3 H, *bs*, methyl on a double bond), 8·85 (3 H, *s*, methyl vicinal to hydroxyl), 9·05 and 9·16 (two *s*, each 3 H, angular methyl groups). The signal at τ 6·0 due to the carbinol protons indicates that the compound possesses an axial (C-19) acetoxy methylene group similar to that of torulosyl acetate. MS of the compound showed a very small molecular ion at *m/e* 348 and large peaks at *m/e* 330 ($M-H_2O$), 270 ($M-H_2O-MeCOOH$) indicating the presence of hydroxyl and acetate groupings. The spectral data strongly indicate that the compound is 19-acetoxy-12,14-labdadien-8-ol(19-acetoxyabienol). Owing to lack of material no more efforts were made to settle the structure of this acetate.

The rest (14·7%) of the neutral fraction was mainly a complex mixture of oxygen-containing compounds which have not been further investigated.

Comments. Triterpenes of serratene type have been isolated from the bark of *Pinus* and *Picea* species.[13–15] No such triterpenes could be detected in the bark of *Larix decidua*. Diterpenes with labdane skeleton were main terpenoid constituents of the bark. However, the characteristic wood resin constituents, larixol and larixyl acetate,[2–4] were not detected. The occurrence of polyprenol esters in the bark is of interest especially since the average number of isoprene units in the polyprenol part is 18. Polyprenols have been found in many other plants[16] and the number of isoprene units usually varies from 6 to 14. Thus the polyprenols of *L. decidua* bark represents higher homologues and are related to those isolated from the needles of *Pinus strobus* L.[17] The number of isoprene

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units are in the same range as those of the dolichols (C_{70}–C_{115})[16] which, however, possess a saturated isoprene end unit.

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FRIEDELAN-3,28-DIOL AND A TETRA-*O*-METHYLMORIN FROM *MORTONIA PALMERI*

Xorge A. Dominguez and A. Yepes Meneses

Departmento de Química, Instituto Tecnológico y de Estudios Superiores de Monterrey,
Sucursal Correos "J", Monterrey, N.L., México

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Key Word Index—*Mortonia palmeri*; Celastraceae; friedelan-3,28-diol; 3,7,2′4′-tetramethoxy-5-hydroxy-flavone.

Plant. Mortonia palmeri. Uses. None. *Source.* San Roberto, Coah., October 1970, Voucher Specimen 7243. *Previous work.* Only on sister species, *M. gregii*,[1] sesquiterpenoid lactones.

Present work. The dried aerial part (1500 g) was extracted with light petrol. (b.p. 30–60°). On evaporation of the solvent, 79 g of resinous paste were left. 30 g of this residue were chromatographed on silica gel and eluted with petrol., followed by C_6H_6, $CHCl_3$, acetone and EtOAc. The C_6H_6–$CHCl_3$ eluted friedelan-3,28-diol recrystallized from MeOH, m.p. 270–272°, $C_{30}H_{52}O_2$, M^+444; soln Chl. $[\alpha]_{589}$ +1·08°; $[\alpha]_{578}$ +1·06°; $[\alpha]_{546}$ +1·00; $[\alpha]_{436}$ −11·0; $[\alpha]_{365}$ −58·4°; $[\alpha]_{316}$ −53·0°. IR, UV, NMR, singlet at δ 3·25 (2H), MS[2] *m/e* (abundance %). M + 1 445 (11·8), M^+444 (29·9), 429 (26·2) 426 (17·4), 411 (14·8), 395 (3·6), 390 (12·5), 277 (25), 276 (32), 275 (72), 249 (25), 248 (34), 231 (55), 206 (43), 203 (26), 195 (96), 189 (36), 179 (37), 177 (100), 109 (54), 83 (95), 69 (76), 55 (56). Diacetate, m.p. 250–253°, $C_{34}H_{56}O_4$, soln Chl. $[\alpha]_{589}$ + 18·1°; $[\alpha]_{578}$ +19·4°; $[\alpha]_{546}$ +21·6°; $[\alpha]_{436}$ +36°; $[\alpha]_{365}$ +53·8°; $[\alpha]_{316}$ +60·3°. *IR, UV, NMR*, two singlets at δ 2·01, 2·05.

The $CHCl_3$ eluted 3,7,2′,4′-tetramethoxy-5-hydroxyflavone as yellow crystals, m.p. 141–143° $C_{19}H_{18}O_7$ M^+ 358; Shinoda, $FeCl_3$ and Wilson tests were positive. UV in MeOH, MeOH–$AlCl_3$, MeOH–$AlCl_3$–HCl, MeOH–AcONa showed the expected absorptions and shifts,[3] ν 3300, 2900–2840, 1640, 1600, 1580, 1500, 1150, 1020, 900, 870 cm^{-1}. NMR δ 12·5 (*d*, 1H), 7·4 (*s*, 1H), 7·0 (*d*, 1H), 6·5 (*d*, 1H), 6·4 (*d*, 1H), 3·9–4·02 (4*s*, 12H). Acetate $C_{21}H_{20}O_8$, m.p. 167–169°, UV, the IR and NMR, showed the presence of monoacetate. On KOH fusion, 2,4-dimethoxybenzoic acid was isolated, IR, m.m.p. Identification was confirmed

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