Isovitexin (*C. divergens*), R_f: TBA, 0·61; 15% HOAc, 0·49; Color appearance: UV, dark purple; UV/NH_3, yellow-green. λ_{max} in nm, MeOH: 271, 336; NaOMe: 279, 330, 400; $AlCl_3$: 265 sh, 305, 352, 382 sh; $AlCl_3$–HCl: 260 sh, 280, 301, 345, 375; NaOAc: 279, 305, 396; NaOAc–H_3BO_3: 272, 348, 403 sh.

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GYMNOSPERMAE

PINACEAE

ω-HYDROXY FATTY ACIDS AND FATTY ALCOHOLS FROM *PSEUDOTSUGA MENZIESII* BARK*

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Key Word Index—*Pseudotsuga menziesii*; Pinaceae; Douglas-fir; bark; fatty alcohols; ω-hydroxy acids.

Plant. Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco]. *Source.* From the George T. Gerlinger State Experimental Forest, located near Blackrock, Oregon, U.S.A. and operated by the School of Forestry, Oregon State University, in cooperation with the State Forestry Department of Oregon. *Uses.* Wood—lumber, pulp. Bark—garden mulch, fuel.

Previous work. On benzene-soluble, hexane-insoluble extract of whole bark,[1–4] of the cork fraction,[5] of the bast fibers,[6] on hexane-soluble extracts.[3–7]

Part examined. Bark—the benzene-soluble, hexane-insoluble extract.

Extraction of the bark and isolation by TLC of the hydroxy methyl esters and of the fatty alcohols from the saponified benzene-soluble, hexane-insoluble extract was described earlier.[1]

Alcohols. 1-Hexadecanol (trace), 1-octadecanol (4%), 1-eicosanol (4%), 1-docosanol (45%), and 1-tetracosanol (48%). (Relative abundances were calculated from peak areas.)

* Part III in the series "Douglas-fir Bark Extractives". For Part II see P. M. LOVELAND and M. L. LAVER, *Phytochem.* **11**, 430 (1972).

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Identification was by co-GLC (SE30 and Carbowax 20M) of the free alcohols with authentic compounds, and by co-GLC (SE30) of the acetates, methyl ethers, and trimethylsilyl ethers with the respective derivatives prepared from authentic alcohols. The C_{22} and C_{24} alcohols and their acetates were collected, and their IR spectra (KBr) were compared with those of authentic compounds; m.m.ps of the alcohols were not depressed.

ω-Hydroxy acids. GLC (SE30) of TLC *spot* 3,[1] containing the ω-OH Me esters, yielded a series of peaks for which a plot of chain-length vs. log R_t was a straight line; these peaks were identified as Me esters of 16-hydroxyhexadecanoic (26%), 18-hydroxyoctadecanoic (7%), 20-hydroxyeicosanoic (18%), 22-hydroxydocosanoic (24%), and 24-hydroxytetracosanoic (6%) acids. Other peaks not identified, (19%). (Relative abundances were calculated from peak areas.) Individual ω-OH Me esters and ω-MeO Me esters were collected by prep. GLC for analysis: ω-OH C_{16} gave white crystals, m.p. 54–55° (benzene) (lit. 54·5–55·5°);[8] IR (CCl_4) cm^{-1}: 3620 (absent in spectrum of ω-MeO Me ester); IR(KBr): 3400 with shoulder *ca.* 3320 (OH stretch), 2920 and 2850 (alkyl), 1740 (ester carbonyl), 1470, 1463, 1435, 1362, 1340, series of 6 small bands 1300–1190 (–CH_2– wag and twist), 1160 (Me ester C–O), 1060, 1045, 880, and 730 and 720 (–$(CH_2)_n$–rock), spectrum similar (not identical) to published spectrum of C_{18} homolog;[9] GLC–MS of ω-MeO C_{16}, *m/e*: 300 (M+) 285 (M-15), 270 (M-30), 269 (M-31), 268 (M-32), 253 (M-47), 241 (M-59), 236 (M-64), 208, (M-92), 143, 129, 115, 101, 87, 74, 55 and 45 ($CH_3OCH_2^+$, base peak). Treatment of ω-OH C_{16} with HI and red P followed by Zn and HCl[10] gave hexadecanoic acid (co-GLC and GLC–MS of Me ester). Oxidation (CrO_3 in HOAc)[11] of ω-OH C_{16} gave product whose Me ester was shown to be that of hexadecanedioic acid (co-GLC and GLC–MS). Found: C, 71·5; H, 12·0. Calc. for $C_{17}H_{34}O_3$: C, 71·3; H, 12·0%.

The other homologs had m.ps (hexane) identical to values reported in the literature.[12,13] IR (KBr) of ω-OH C_{18} was identical to a published spectrum,[9] and of the other homologs were similar; for each increase of –$(CH_2)_2$–, one additional band appeared in the region 1315–1180 cm^{-1}. Reduction[10] and oxidation[11] of the C_{20} and C_{22} homologs yielded the corresponding mono- and di-carboxylic acids. MS of ω-MeO C_{18} was identical to a published spectrum,[14] and spectra of C_{20} and C_{22} homologs yielded analogous fragments in the high *m/e* region; the region *m/e* 143 and below was identical in the spectra of the four homologs examined.

The unidentified peaks included a peak thought to be 26-hydroxyhexacosanoate (1%) (R_t), but no attempt was made to collect this peak for further verification. A peak emerging slightly before ω-OH C_{18} and only partially resolved from it (SE 30) (7%) was liquid at room temp.; its MeO derivative gave two major peaks on EGSS-X. Two peaks (2 and 8%) emerged well before ω-OH C_{16} (SE 30).

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