

with *n*-hexane-EtOAc, 4:1 or 9:1) as described previously,<sup>9</sup> followed by GLC, using a column (2 m × 3 mm) of 10% 1,4-butanediol-succinate on shimalite (60–80 mesh) at 185°, with He gas (60 ml/min).

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<sup>9</sup> OGUNI, I., OSHIMA, K., IMASEKI, H. and URITANI, I. (1969) *Agr. Biol. Chem.* **33**, 50.

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## ALKANES AND TRITERPENOIDS OF *QUERCUS GLAUCA*

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**Key Word Index**—*Quercus glauca*; Fagaceae; oak; alkanes; phytosterols; triterpenoids.

**Plant.** *Quercus glauca* Thunb. (Fagaceae) (Japanese name, arakashi). **Source.** Hiroshima Prefecture, Japan. **Uses.** Timber. **Previous work.** D-mannitol from the wood.<sup>1</sup>

**Present work.** The *n*-hexane soluble constituents of trunk-wood and leaves of the plant have been examined.

**Trunk-wood.** The chipped trunk-wood (22.8 kg) was extracted with MeOH (100 l.) at room temp. for 4 months. A part (5 l.) of the extract was concentrated to dryness to give a dark viscous oil (30.2 g), which was suspended over H<sub>2</sub>O and extracted with *n*-hexane. The *n*-hexane soluble fraction (4.2 g) was chromatographed on a silica gel column with *n*-hexane-EtOAc as eluent with increasing EtOAc concentration, giving in order normal alkanes (417 mg), sitosterol (86 mg), and stigmast-4-en-3-one (82 mg).

**n-Alkanes.** GLC indicated the alkanes to be composed of alkanes having less carbon atoms than those of the leaves. **Sitosterol.** C<sub>29</sub>H<sub>50</sub>O; m.p. 138–139°; [ $\alpha$ ]<sub>D</sub><sup>25</sup> −32.1° (c 0.78, CHCl<sub>3</sub>);  $\nu_{\text{max}}$  (Nujol) 3400 (OH), 1640 (C=C), 1050 cm<sup>−1</sup> (C—O);  $\delta_{\text{ppm}}$  (CDCl<sub>3</sub>) 5.35 (m, 1H, >C=C<<sup>H</sup>), 3.5 (m, 1H, >CH(OH)); direct comparison (TLC, IR, NMR, and m.m.p.) with an authentic sample. **Stigmast-4-en-3-one.** C<sub>29</sub>H<sub>48</sub>O; m.p. 89–90°; [ $\alpha$ ]<sub>D</sub><sup>25</sup> +86.2° (c 4.12, CHCl<sub>3</sub>);  $m/e$  412.3753 (M<sup>+</sup>, calcd. 412.3705);  $\nu_{\text{max}}$  (KBr) 1660 (conjugated C=O), 1620 cm<sup>−1</sup> (C=C);  $\lambda_{\text{max}}$  (EtOH) 245 nm (log ε 4.3), 240 (sh.), (Isooctane) 238 (3.95), 244 (sh.);  $\delta_{\text{ppm}}$  (CDCl<sub>3</sub>) 5.72 (s, 1H, >C=C<<sup>H</sup>), 2.30 (m, 2H, −CO−CH<sub>2</sub>−). These data suggested the conjugated carbonyl compound to be stigmast-4-en-3-one; this was confirmed with an authentic specimen (co-TLC, IR, NMR, MS, and m.m.p.) prepared<sup>2</sup> from sitosterol by the Oppenauer oxidation.

<sup>1</sup> MINAMI, K. and HANASHI, Y. (1962) *Nippon Mokuzai Gakkaishi* **8**, 258; (1963) *Chem. Abstr.* **59**, 5361.

<sup>2</sup> EASTHAM, J. F. and TERANISHI, R. (1955) *Organic Syntheses* (CAIRNS, T. L., ed.) Vol. **35**, p. 39. Wiley, New York.

*Leaves.* Leaves (1.8 kg) were extracted with MeOH (8 l.) at room temp. for 3 months. Removal of the solvent gave a dark-green residue (443 g), which was then extracted with *n*-hexane. The *n*-hexane soluble fraction (29.6 g) was chromatographed on a silica gel column with the same solvent as in the case of trunk-wook, giving in order normal alkanes (56 mg;  $C_{15} \sim C_{31}$ ),  $\beta$ -amyrin acetate (45 mg), friedelin (32 mg), epi-friedelanol (43 mg), and glutinol (42 mg). Identity of each compound, as indicated by their physical data shown below, was established by direct comparison (co-TLC, IR, NMR, and MS) with respective authentic samples.

*n-Alkanes.* GLC indicated  $n-C_{27}H_{56}$  18.7% and  $n-C_{29}H_{60}$  19.3%.  $\beta$ -Amyrin acetate.  $C_{32}H_{52}O_2$ ; m.p. 244–245°;  $[\alpha]_D^{25} + 53.9^\circ$  (*c* 1.34,  $CHCl_3$ );  $\nu_{max}$  (KBr) 1730 (ester C=O), 1640 (C=C), 1390, 1370 (gem-dimethyl), 1250  $cm^{-1}$  (ester C–O);  $\delta_{ppm}$  ( $CDCl_3$ ) 5.2 (*t*, 1H,  $>C=C<^H$ ), 4.5 (*m*, 1H,  $>CH(OAc)$ ), 2.02 (*s*, 3H,  $-O-CO-CH_3$ ). Friedelin.  $C_{30}H_{50}O$ ; m.p. 267.5–268°;  $[\alpha]_D^{25} - 23.6^\circ$  (*c* 1.06,  $CHCl_3$ );  $\nu_{max}$  (KBr) 1710 (C=O), 1390, 1375  $cm^{-1}$  (gem-dimethyl);  $\delta_{ppm}$  ( $CDCl_3$ ) 2.30 (*m*, 2H,  $-CO-CH_2-$ ). *epi*-Friedelanol.  $C_{30}H_{52}O$ ; m.p. 284.5–286.5°;  $[\alpha]_D^{25} + 27.5^\circ$  (*c* 0.2,  $CHCl_3$ ); *m/e* 428 ( $M^+$ );  $\nu_{max}$  (Nujol) 3610 (free OH), 3450  $cm^{-1}$  (OH);  $\delta_{ppm}$  ( $CDCl_3$ ) 3.75 [*m*,  $>CH(OH)$ ]; the acetate, m.p. 293–295°,  $[\alpha]_D^{25} + 49.0^\circ$  (*c* 0.11,  $CHCl_3$ ). An authentic sample of *epi*-friedelanol was prepared from friedelin by the  $NaBH_4$  reduction, following the method reported in a literature.<sup>3</sup> Glutinol.  $C_{30}H_{50}O$ ; m.p. 212–213°;  $[\alpha]_D^{25} + 72.9^\circ$  (*c* 0.55,  $CHCl_3$ ); *m/e* 426 ( $M^+$ );  $\nu_{max}$  (Nujol) 3400 (OH), 1390, 1370  $cm^{-1}$  (gem-dimethyl);  $\delta_{ppm}$  ( $CDCl_3$ ) 5.65 (*t*, 1H,  $>C=C<^H$ ), 3.45 (*m*, 1H,  $>CH(OH)$ ); the acetate, m.p. 195.5–196.5°;  $[\alpha]_D^{25} + 90.4^\circ$  (*c* 0.22,  $CHCl_3$ ).

<sup>3</sup> KAMANO, Y., TACHI, Y., OTAKE, T. and KOMATSU, M. (1968) *Yakugaku Zasshi* **88**, 1246.

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## ENANTIO-8(17),13(16),14-LABDatrien-18-OIC ACID FROM TRUNK RESIN OF KENYAN HYMENAEA VERRUCOSA

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*Plant and source.* Trunk resin of *Hymenaea verrucosa* Gaertn., formerly known as *Trachylobium verrucosum*.<sup>1</sup> Collections were from the region of Kwale, Kenya (J. H. Langenheim No. 5521) and the Mida-Gede Forest, Jilore Forest Station, Kenya (JHL No. 5522). Upon conclusion of a detailed study of the genus *Hymenaea* now in progress, documentary specimens will be deposited in the herbarium of the University of California, Berkeley.

<sup>1</sup> LANGENHEIM, J. H. and LEE, Y. T. (1973) *Brittonia* **25**, in press.