

with *n*-hexane-EtOAc, 4:1 or 9:1) as described previously,⁹ 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).

Acknowledgements—The authors thank Dr. F. Bohlmann for providing dehydrongaione. The first author expresses his thanks to Mr. T. Hasegawa, President of his Junior College and Professor M. Hiura for giving him the opportunity to study at the Laboratory of Biochemistry, Department of Agricultural Chemistry, Nagoya University.

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

Phytochemistry, 1974, Vol. 13, pp. 522 to 523. Pergamon Press. Printed in England.

ALKANES AND TRITERPENOIDS OF *QUERCUS GLAUCA*

TAKAYUKI SUGA and SHIGEHARU KONDO

Department of Chemistry, Faculty of Science, Hiroshima University, Higashiesenda-machi, Hiroshima 730, Japan

(Received 6 September 1973. Accepted 1 October 1973)

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.¹

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 H₂O 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*. C₂₉H₅₀O; m.p. 138–139°; $[\alpha]_D^{25} -32.1^\circ$ (c 0.78, CHCl₃); ν_{\max} (Nujol) 3400 (OH), 1640 (C=C), 1050 cm⁻¹ (C–O); δ_{ppm} (CDCl₃) 5.35 (m, 1H, >C=C<^H), 3.5 (m, 1H, >CH(OH)); direct comparison (TLC, IR, NMR, and m.p.) with an authentic sample. *Stigmast-4-en-3-one*. C₂₉H₄₈O; m.p. 89–90°; $[\alpha]_D^{25} +86.2^\circ$ (c 4.12, CHCl₃); *m/e* 412.3753 (M⁺, calcd. 412.3705); ν_{\max} (KBr) 1660 (conjugated C=O), 1620 cm⁻¹ (C=C); λ_{\max} (EtOH) 245 nm (log ε 4.3), 240 (sh.), (Isooctane) 238 (3.95), 244 (sh.); δ_{ppm} (CDCl₃) 5.72 (s, 1H, >C=C<^H), 2.30 (m, 2H, –CO–CH₂–). 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.p.) prepared² from sitosterol by the Oppenauer oxidation.

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

² 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-wood, giving in order normal alkanes (56 mg; $C_{15} \sim C_{31}$), β -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%. β -Amyrin acetate. $C_{32}H_{52}O_2$; m.p. 244–245°; $[\alpha]_D^{25} + 53.9^\circ$ (*c* 1.34, $CHCl_3$); ν_{max} (KBr) 1730 (ester C=O), 1640 (C=C), 1390, 1370 (gem-dimethyl), 1250 cm^{-1} (ester C–O); δ_{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, $CHCl_3$); ν_{max} (KBr) 1710 (C=O), 1390, 1375 cm^{-1} (gem-dimethyl); δ_{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^+); ν_{max} (Nujol) 3610 (free OH), 3450 cm^{-1} (OH); δ_{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.³ *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^+); ν_{max} (Nujol) 3400 (OH), 1390, 1370 cm^{-1} (gem-dimethyl); δ_{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, $CHCl_3$).

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

Phytochemistry, 1974, Vol. 13, pp. 523 to 525. Pergamon Press. Printed in England.

ENANTIO-8(17),13(16),14-LABDATRIEN-18-OIC ACID FROM TRUNK RESIN OF KENYAN *HYMENAEEA VERRUCOSA*

SUSAN S. MARTIN and JEAN H. LANGENHEIM

Division of Natural Sciences, University of California, Santa Cruz, CA 95060, USA

(Received 3 September 1973. Accepted 20 September 1973)

Key Word Index—*Hymenaea verrucosa*; *Trachylobium verrucosum*; Leguminosae; resin acid; enantio-8(17),13(16),14-labdatrien-18-oic acid.

Plant and source. Trunk resin of *Hymenaea verrucosa* Gaertn., formerly known as *Trachylobium verrucosum*.¹ 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.

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