1676, 1620, 1386, 1360, 1252, 1212, 1168, 983 cm^{-1}. NMR (60 MHz, $CDCl_3$): τ 9·12 (*q*, 6H), 8·41 (*s*, 3H), 7·87 (*d*, 3H *J* 1·0 Hz), 7·84 (*s*, 3H), 7·75 (*s*, 3H), 3·1–5·0 (4H). The physical data compares closely with those published for the synthetic material.[1] *Isomer*-A was a yellow oil. (Found: C, 78·52; H, 10·50. $C_{20}H_{32}O_2$ requires: C, 78·89; H, 10·59%.) UV λ_{max}^{EtOH} 229 nm (ϵ 17 700). IR ν_{max} (NaCl disc). 1686, 1672, 1615, 1384, 1356, 1252, 1168, 982 cm^{-1}. NMR (60 MHz, $CDCl_3$): τ 9·10 (*q*, 6H), 8·38 (*s*, 3H), 8·13 (*d*, 3H *J* 1·5 Hz), 7·85 (*s*, 3H), 7·75 (*s*, 3H), 3·1–5·0 (4H).

Stereochemistry of isomers-A *and* -B. The 7,8-double bonds in both isomers are assigned the *trans* configuration, that is, by applying Bates' observations to the NMR data.[3] The disubstituted 12,13-double bond is also of *trans* form.[1] The location of the peak for the methyl group at τ 7·87 in the isomer-*B* and at τ 8·13 in the isomer-*A* suggests that the 3,4-double bond is *cis* in isomer-*A* and *trans* in isomer-*B*. Analogy is drawn from chemical-shift data for *cis-trans* pairs of unsaturated esters where the deshielding of the protons of a *cis* methyl group by an alkoxy-carbonyl group is fairly constant, being of the order of 0·25 Hz.[4]

EXPERIMENTAL

Dark-fired and aged tobacco (U.S. Department of Agriculture Types 22 and 23) were wetted with H_2O to produce a 40–43% moisture content. The leaves were ground to a 6-mm size and stored at 23–25° in thin, opaque polyethylene bags. Once a week the bags were uncovered for about 5 min aeration. The progress of the fermentation was followed by GLC (OV-101) by sampling the tobacco at 8-day intervals. After 50 days the tobacco was air-dried, ground and extracted with cold hexane. The extract was chromatographed on silicic acid columns. The desired materials were found in the 10% Et_2O–C_6H_6 fractions. Compound II, which preceded I off the column, was further purified and separated into two stereo forms (*A* and *B*) on a florisil column using 50% Et_2O–C_6H_6.

Isomerization of isomers-A *and* -B. Distillation of isomer-*B* at 170° 0·2 mm Hg pressure produced about equal amounts of isomer-*B* and isomer-*A*. Similarly, the distillation of isomer-*A* produced about equal amounts of the two isomers. MS of *A* and *B* were identical.

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SIMIARENONE FROM *TREMA ORIENTALIS*[*]

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Repeated chromatographic fractionation on alumina of the neutral fraction of the light petrol. extract of the stem-bark of *Trema orientalis* gave a crystalline ketone (0·04% based

[*] L. OGUNKOYA, O. O. OLUBAJO and D. S. SONDHA, *Phytochem.* **11**, 2361 (1972).

on the air-dried powdered bark) which was identified as simiarenone[1] m.p. 209° $[\alpha]_D$ +19·4° (*c* 1·6, $CHCl_3$) (lit. 207–208°, +20°). Its IR spectrum (Nujol) showed bands at 1705 (carbonyl) and 843 cm^{-1} (trisubstituted d.b.). Its NMR (60 MHz, $CDCl_3$) showed a signal at 4·30 (broad band, 1 vinyl proton), and five signals at 8·78 (broad), 8·99, 9·06, 9·15 and 9·20 τ (24 hydrogens). The methyl region of the NMR spectrum appeared unusually simple with the five signals appearing as singlets with no obvious sign of the coupling expected from an isopropyl or secondary methyl groups. This fact had earlier led us to make erroneous deductions as to the structural possibilities of this ketone.

However, its MS gave M^+ *m/e* 424 ($C_{30}H_{48}O$) with strong peaks at *m/e* 274 (base), 259 (274 − Me) and particularly 231 (274 − C_3H_7) which are consistent with 5,(6) double bond, 3-oxo and an isopropyl group, the base peak arising from a straight-forward retro-Diels–Alder fission of the 5(6) double bond. The MS is virtually identical with that recorded on the ketone obtained by Jones oxidation of simiarenol.[2] Simiarenone forms a crystalline 2,4-dinitrophenylhydrazone m.p. 277–279° (lit. 275°). Reduction with either $LiAlH_4$ or $NaBH_4$ gave a pair of epimeric alcohols (in the approximate ratio 1 : 8) which were oxidized back by Jones reagent to simiarenone. The major, more polar (TLC), alcohol was identified as episimiarenol m.p. 195°, $[\alpha]_D$ +46·3° (*c* 0·58, $CHCl_3$) (lit. 197–198°, +46·8°) which gave a crystalline acetate m.p. 188–189° $[\alpha]_D$ +33° (*c* 0·51, $CHCl_3$) (lit. 188–189°, +48°). The minor, less polar alcohol was identified as simiarenol m.p. 209–211° $[\alpha]_D$ +47·7° (*c* 0·79, $CHCl_3$) (lit. 209°, +50·8°) which also gave a crystalline acetate m.p. 210° $[\alpha]_D$ +67·1° (*c* 0·64, $CHCl_3$) (lit. 209°, +73·9°). Alpin *et al.*[1] reported the isolation of only episimiarenol from the reduction of this ketone with $LiAlH_4$. Treatment of simiarenol with PCl_5 gave a conjugated diene (UV, IR) m.p. 238° (lit. 228°). These two alcohols gave virtually identical MS with M^+ *m/e* 426 ($C_{30}H_{50}O$) and strong signals at *m/e* 274 (base), 259 and 231. The MS of these 5,(6) unsaturated pentacyclic triperpenoid compounds possess an interesting common feature. In all of them (see also alnusenone), the most abundant high-mass fragments are due to ions which result from direct retro-Diels–Alder fission in which the charge remains with the monoalkene and not the diene as might have been anticipated.[3]

EXPERIMENTAL

Powdered stem bark (1 kg) was extracted with light petrol. The extract (9·8 g) was fractionated into a neutral and an acidic fraction using NaOH. The neutral fraction (6·7 g) was chromatographed over alumina III eluted with light petrol. The latter fractions were combined (TLC control) and rechromatographed over alumina II. Careful elution with light petrol.–C_6H_6, 1 : 1 gave simiarenone (380 mg) as pure white crystals (repeated recrystallisation from $CHCl_3$–MeOH) m.p. 209°.

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