were combined (1 g) and recrystallized from hexane, mp 211–213° $[\alpha]_D^{22}$ + 70°, PMR signals (270 MHz) at 7.69 (*d*) and 6.47 (*d*, *J* = 16 Hz, H-2′ and H-3′), 7.53, (2H, *m*) and 7.38 (3H, *m*, aromatic protons), 5.41 (*br*, H-15), 5.20 and 5.07 (*br*, H-17), 2.82 (*br*, H-13), 1.21 (C-4 methyl) and 0.99 ppm (C-10 methyl). (Calc. for $C_{29}H_{36}O_4$: C, 77.68; H, 8.03; MW, 448.2612. Found: C, 77.47; H, 8.18%; MW (MS), 448.2617). A soln of 0.20 g **1a** in 5 ml 10% aq. NaOH was heated at 100° for 1 hr, cooled, neutralized and extracted with Et_2O. The washed and dried Et_2O extract was evapd and separated by PLC (EtOAc–C_6H_6, 2:1) into two fractions. Fraction A was cinnamic acid (35 mg), mp 133°, identical with an authentic sample. Fraction B (**1b**, 75 mg) on recrystallization from EtOAc had mp 228–230°, $[\alpha]_D^{24}$ − 117.6° ($CHCl_3$, *c* 1.15), NMR signals at 5.20 and 5.07 (*br*, H-17), 3.80 (*br*, H-15), 2.72 (*br*, H-13), 1.25 (C-4 methyl) and 0.95 ppm (C-10 methyl). (Calc. for $C_{20}H_{30}O_3$: MW, 318.2194. Found: MW (MS), 318.2171). The substance was identical with an authentic sample of grandifloric acid [7, 9]. We wish to thank Professor Tanaka for supplying the sample.

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TRITERPENES FROM THE SEED OF *ENTANDROPHRAGMA* SPECIES

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Key Word Index—*Entandrophragma*; Meliaceae; limonoid; sapelin.

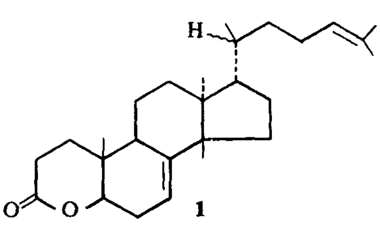
Abstract—The seeds of *Entandrophragma angolense* and *E. utile* contained no limonoids, but protolimonoids were isolated and identified.

INTRODUCTION

The genus *Entandrophragma* is the source of sapele, and other important West African timbers. These contain considerable amounts of limonoids [1], *E. angolense* contains the simple limonoid gedunin [2], while other species contain more complex compounds such as utilin [3]. In a more extensive examination of the timber of *E. cylindricum*, Chan *et al.* [4] have isolated as well as limonoids the sapelins, which are highly oxidised triterpenes, probably acting as metabolic precursors of the limonoids. These have been termed protolimonoids, and similar compounds have been isolated from other related plants. In many genera of the Meliaceae we have found the seed to be a richer source of liminoids than the timber, but with *Entandrophragma* this is not the case. We now report a more extensive investigation of the seed, which has yielded no limonoids, but certain compounds in the protolimonoid and triterpene groups which are probably metabolic precursors of the limonoids.

RESULTS AND DISCUSSION

We have investigated the seed of *E. angolense* and *E. utile*, representative of species giving simple and complex limonoids in the timber. The seeds were ground and extracted in the usual way, and the extracts chromatographed on Si gel columns. *E. angolense* gave a compound $C_{30}H_{48}O_2$, mp 125–8°, $[\alpha]_D - 94°$. The ^{13}C NMR spectrum of this compound, which we name entandrolide, showed that it was the ester of a tertiary alcohol (C=O, 175.4*s*; C—O, 86.2*s*). The ^1H and ^{13}C-NMR spectra also showed the presence of two double bonds, each carrying one vinyl proton, five quarternary methyl groups, and two methyl groups on a double bond. Two of the quarternary methyl groups appeared in the ^1H-NMR spectrum at chemical shifts (δ 1.45, 1.58) which suggested that they were attached to a carbon atom bearing oxygen, which must be the lactone oxygen. This, and the absence of any other oxygen atoms, suggested the presence of a triterpenoid ring A



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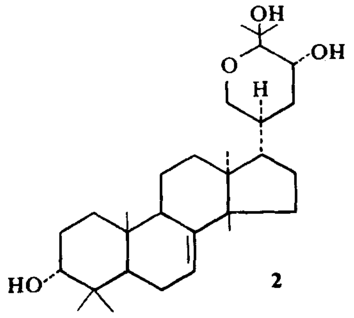

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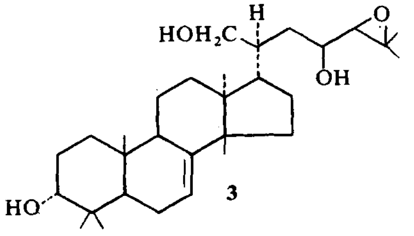

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lactone, produced by biological Baeyer–Villiger type oxidation of a ring A ketone. Biogenetic considerations [5] suggest a relation to euphane, and the spectral evidence is consistent with the presence of this nucleus. We therefore propose for entandrolide the structure **1**; there is no evidence to show whether the configuration at C-20 is *R* or *S*.

The seeds of *E. utile* did not yield entandrolide, but instead two other compounds. One of these was identical with a sample of sapelin A (**2**) supplied by Dr. D. R. Taylor, the second was isomeric and very similar, but showed slightly different spectral properties. In particular the C—O region of the ^{13}C-NMR spectrum was different. In the spectrum of sapelin A there is a singlet at δ 74.1 corresponding to the carbon of a tertiary hydroxyl, that at C-25. This was missing in the new compound, and was replaced by a singlet at δ 59.2, a position characteristic of a fully substituted ethylene oxide. This suggested that the compound might be the epoxy triol (**3**), which is the hypothetical biogenetic precursor of sapelin A. The other spectral properties were consistent with this hypothesis.

This compound has been prepared but not characterised by Lyons and Taylor (personal communication from Dr. D. R. Taylor) by borohydride reduction of 3-epimelianol, and cyclised with boron trifluoride to sapelin A. Following the conditions of Lyons and Taylor (cf. the cyclisation of the 3-epimer [6], also personal communication from Dr. D. R. Taylor) our new compound cyclised to sapelin A, thus confirming its structure.

EXPERIMENTAL

Isolation of entandrolide. The seed of *E. angolense* was minced and extracted with petrol in a Soxhlet extractor. The extract was chromatographed on Si gel, yielding entandrolide mp 125–8° (from MeOH–CH_2Cl_2) $[\alpha]_D^{20}$-94° [Found: C, 81.8; H, 10.7; M^+440. $C_{30}H_{48}O_2$ requires C, 81.77; H, 10.9%] ^{13}C-NMR: δ 175.4*s*, 146.2*s*, 130.9*s*, 125.2*d*, 117.6*d*, 86.2*s*, 52.9*d*, 52.5*d*, 51.3*s*, 47.0*d*, 43.3*s*, 38.3*s*, 36.2*d*, 35.9*t*, 34.1*t*, 33.6*t*, 33.6*q*, 33.3*t*, 32.0*t*, 28.2*t*, 27.9*t*, 27.3*q*, 25.7*q*, 25.0*t*, 23.0*q*, 29.8*q*, 18.3*q*, 18.3*q*, 18.3*t*, 13.3*q*.

Extraction of E. utile. In a similar manner, the seed of *E. utile* gave sapelin A (**2**), mp 211–212° (hexane–CH_2Cl_2), identical in mmp, ^{1}H-NMR and TLC with a sample provided by Dr. D. R. Taylor; ^{13}C-NMR 145.8*s*, 118.2*d*, 86.5*d*, 76.3*d*, 74.1*s*, 70.2*t*, 64.7*t*, 51.4*s*, 48.7*d*, 48.7*d*, 44.8*d*, 44.6*d*, 43.4*s*, 37.4*s*, 36.5*t*, 34.8*s*, 33.9*t*, 33.1*t*, 31.3*t*, 28.4*t*, 27.8*q*, 27.4*q*, 27.3*q*, 25.5*t*, 24.0*q*, 24.0*t*. 22.3*q*. 21.9*q*, 17.0*t*, 13.0*q* and the epoxytriol (**3**); mp 195–198° $[\alpha]_D^{20} - 34$ (hexane–CH_2Cl_2) [Found: C, 75.8; H, 10.4; M^+ 474. $C_{30}H_{50}O_4$ requires C, 75.9; H, 10.6%] ^{13}C-NMR 145.7*s*, 118.2*d*, 76.2*d*, 71.3*d*, 68.3*d*, 64.6*d*, 59.2*s*, 51.3*s*, 49.1*d*, 48.6*d*, 44.5*d*, 43.4*d*, 37.4*s*, 36.7*t*, 34.7*s*, 33.9*t*, 33.2*t*, 31.2*t*, 28.4*t*, 27.8*q*, 27.3*q*, 25.4*t*, 24.9*q*, 23.9*t*, 22.0*q*, 21.8*q*, 19.4*q*, 18.0*t*, 13.0*q*.

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