STEROLS AND NAPHTHOQUINONES FROM *DIOSPYROS GRACILESCENS*

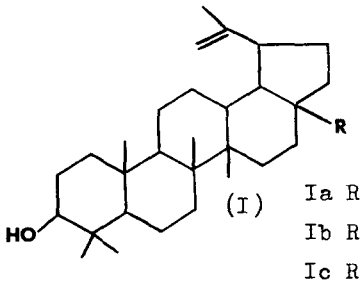
C.N. Mbi, P.G. Waterman, Department of Pharmaceutical Chemistry, University of Strathclyde, Glasgow G1 1XW, Scotland

Diospyros L. (Ebenaceae) is a large pan-tropical genus renowned for its hard woods and edible fruits (Hutchinson, 1964). Chemically the genus has been shown to be a rich source of triterpenes and dimeric forms of 7-methyljuglone (Hegnauer, 1966; van der Vijver & Gerritsma, 1976). We now wish to report the results of an investigation of the stem bark of *D. gracilescens* Gurke (Voucher: Waterman & McKey 851/884 at Kew), a large forest tree common in west Cameroon (Letouzey & White, 1970).

Extraction of the bark with chloroform followed by column chromatography over silica gel gave, on elution with cyclohexane/diethyl ether (1:1) containing increasing amounts of benzene (to a maximum of 10%), six bands (A-F). Direct comparison (mixed m.p., ir, mass spect., tlc) of B and E with authentic samples showed them to contain lupeol (Ia) and sitosterol respectively.

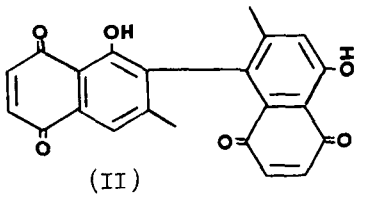
Band D on recrystallisation from 50% aq. acetone yielded needle crystals ($C_{30}H_{50}O_2$), m.p. 249°. Spectral analysis (ir, nmr, mass spect.) showed it to be an hydroxy-methyl derivative of lupeol. Both m.p. and optical rotation were in close accord with those required for betulin (Ib). Band F proved difficult to crystallise and gave no definite m.p. Accurate mass measurement showed $C_{30}H_{48}O_3$ with facile loss of CO_2. This together with bands in the ir spectrum for carboxylic acid and vinyl methylene substituents indicated this third triterpene was betulinic acid (Ic) which, like lupeol and betulin, has proved to be a common constituent of *Diospyros* species.

On concentration band C yielded a red solid ($C_{22}H_{14}O_6$), m.p. 231°. Spectral data (uv, ir, mass spect.) were all typical of a dimer of 7-methyljuglone (Fallas & Thomson, 1968). The positions at which dimerisation had occurred were resolved from the pmr spectrum (60MHz, deuterochloroform) which showed resonances for two phenolic hydroxyl protons (δ 12.10, 12.46) and two methyl groups (δ 2.04) typical of 6,8 coupling (Lillie & Musgrave, 1977). The major naphthoquinone of *D. gracilescens* must therefore be isodiospyrin (II). Band A, which contained small amounts of a second naphthoquinone, is still under investigation.



(I)

Ia R = CH_3
Ib R = CH_2OH
Ic R = COOH



(II)

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