mesh Gas-Chrom Q; 10% UC W-98 on 80/100 mesh Gas-Chrom S; 3% Hi-Eff 8 BP on 100/120 mesh Gas Chrom Q. All columns were stainless steel, 1/8 in. o.d. and 6 ft long. Typical conditions were: injection port 235°, detector 255°, column temp. held at 148° for 10 min, then programmed at 2°/min to 300°; helium flow rate 28 ml/min. In most cases the 'yellow band' eluate was injected directly into the GC but in some instances it was silylated[14] prior to injection.

Authentic samples of β-sitosterol and campesterol were subjected to GLC for comparison purposes, and small quantities were added to the 'yellow band' eluate for 'peak enhancement' studies.

GLC–MS. An F&M 810 GC was hooked in tandem to an Atlas MAT CH-4, Nier-type single focusing, 70 eV, MS. The 'yellow band' eluate was silylated,[14] and injected into the GC. An MS scan at the β-sitosterol peak showed *m/e* data at 486, 396, 381, 357, 255 and 129. A scan at the campesterol peak resulted in prominent *m/e* fragments at 129 and 255. MS scans of early peaks to elute from the GC showed prominent *m/e* fragments at 136, 121, 112, 93, 91, 80, 70, 69, 55, 43 and 41.

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ANGIOSPERMAE DICOTYLEDONAE

ANONACEAE

DITERPENES FROM *ANNONA SENEGALENSIS*

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Abstract—The bark of *Annona senegalensis* Pers. has yielded kauran-16α-ol, kaur-16-en-19-oic acid, kauran-19-al-17-oic acid, and 19-norkauran-4α-ol-17-oic acid.

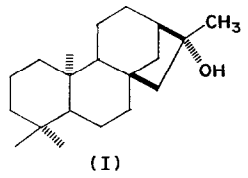
Annona senegalensis Pers. (Yoruba—abo) is a shrub common in the West African savannah. The bark is used in Nigeria for the treatment of convulsions in children.

Light petroleum extraction of the bark gave acidic and neutral fractions, the latter gave a solid m.p. 217°, which was identified as kauran-16α-ol[1](I). The acid fraction after chromatography over silica gel gave mainly kaur-16-en-19-oic acid[2](II) together with a little kauran-19-al-17-oic acid (IIIa).[2]

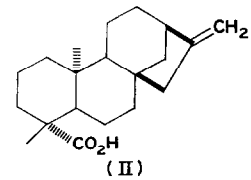
[1] L. H. BRIGGS, B. F. CAIN, R. C. CAMBIE, B. R. DAVIS, P. S. RUTLEDGE and J. K. WILMSHURST, *J. Chem. Soc.* 1345 (1963).

[2] C. A. HENRICK and P. R. JEFFERIES, *Austral. J. Chem.* **17**, 915 (1964).

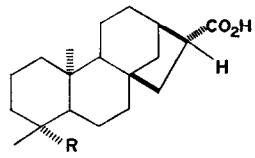
Chloroform extraction of the bark gave a further acid fraction, separated after chromatography to give more of acid (II) together with kauran-17,19-dioic acid (IIIb),[2] and a new acid, $C_{19}H_{30}O_3$ m.p. 274°; methyl ester m.p. 132°. This appeared to be a norditerpene hydroxy acid. The NMR spectrum showed two tertiary methyl groups, a very characteristic multiplet centred at δ 2·90, identical to one in (IIIa) and (IIIb) which is due to the proton adjacent to the carboxyl group, and an OH proton, disappearing on addition of D_2O. There was no resonance in the region δ 3–4 which might be due to CHOH protons. This evidence appears to demonstrate the compound is 19-norkauran-4α-ol-17-oic acid (IV).



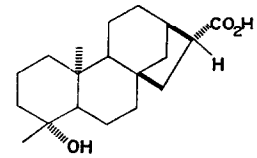
(I)



(II)



(III) (a) R=CHO
(b) R=CO_2H



(IV)

A similar nor-alcohol has been isolated before.[3] We have some doubts whether (IV) is a natural product or an artefact of isolation, since it is the expected oxidation product of (IIIa), and related aldehydes have been found to be unstable,[4,5] and to oxidize spontaneously.

EXPERIMENTAL

Extraction of bark. The dried, powdered, bark (1·5 kg) was extracted with refluxing light petroleum (b.p. 60–80°). The oily extract (25 g) with MeOH (150 ml) gave a solid (2·5 g) which appeared to consist of phytosterols. The MeOH-soluble portion was separated into acidic and neutral fractions with Na_2CO_3 solution. Chromatography of the neutral fraction on alumina gave more steroidal material and kauran-16α-ol[1] (1·1 g) m.p. 217° $[\alpha]_D^{20} = 56°$. Attempted acetylation of this caused dehydration to *iso*kaurene, m.p. 62°, identical with an authentic sample. The acidic fraction (7 g) was chromatographed over silica gel to give (a) kaur-16-en-19-oic acid[2] (4·5 g) (II) m.p. 176–177°, $[\alpha]_D$ −123° (methyl ester m.p. 86°) and (b) kauran-19-al-17-oic acid[2] (0·1 g) m.p. 204–5°, $[\alpha]_D$ −63°; (methyl ester m.p. 123–5°) (aldehyde proton,[2] δ 9·81).

The bark was then extracted with $CHCl_3$, the acidic fraction of the extract (3 g) was chromatographed on silica to give more of acid (II) (1·5 g), together with kauran-17,19-dioic acid[2] (IIIb) (0·2 g), m.p. 265–270° (methyl ester m.p. 105°) and 19-*norkauran-4α-ol-17-oic acid*, m.p. 274–5°, (methyl ester m.p. 132°). (M^+ 306, M^+ ester 320; IR shows OH band at 3500 cm^{-1}).

Acknowledgement—We thank Professor Jeffries for authentic specimens of kaurenoic acid and kaurandioic acid.

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[4] D. E. U. EKONG, Personal communication.
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