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TETRANORTRITERPENOIDS—III[1]

6-HYDROXY- AND 6-ACETOXY- METHYL ANGOLENSATE FROM THE HEARTWOOD OF *KHAYA GRANDIFOLIOLA*

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Abstract—Two new tetranortriterpenoids from the heartwood of *Khaya grandifoliola* are shown to be methyl 6-hydroxy- and methyl 6-acetoxy- angolensate, by analysis of their NMR spectra, using single and double irradiation.

WE HAVE isolated from the heartwood of *Khaya grandifoliola* in addition to methyl angolensate[2] (I), a new alcohol II, $C_{27}H_{34}O_8$, m.p. 235–238°, $[\alpha]_D$ −85°, and its acetate (III), $C_{29}H_{36}O_9$, m.p. 172–174, $[\alpha]_D$ −82°. A detailed analysis of the NMR spectra of the new alcohol and its acetate leads us to conclude that the alcohol is methyl 6-hydroxy angolensate (II).

Comparison of the NMR spectra at 100 MHz of methyl angolensate, I (Fig. 1), the alcohol II (Fig. 2) and its acetate III (Fig. 3) at once reveals suggestive similarities; the presence in the three compounds of two α- and one β-furanic protons, the H-17 proton, α to the furan ring, two vinyl proton singlets at ~τ 5, characteristic of the vinylidene group exocyclic to a cyclohexane ring, two doublets (J = 14 Hz), each one proton, assignable to the isolated geminal protons at C-15, and five sharp three-proton singlets, attributable to one methyl ester and four quaternary methyls. The region between τ 6·3 and τ 8·0 becomes strikingly simplified in the alcohol II and its acetate III when compared with the corresponding region in methyl angolensate (I), as would be anticipated upon removal of the complex multiplet arising in the latter from the two C-6 protons.

We now discuss in turn the NMR spectra of the alcohol II and its acetate III. The alcohol (Fig. 2) loses upon exchange with D_2O a broad singlet at τ 6·87 which is therefore attributable to the alcoholic –OH proton. The two H-15 protons form an AB quartet centred at τ 7·08 and 7·44 (J = 18 Hz) and the H-5 proton appears as a slightly broadened singlet at τ 7·25. There remains in the τ 6–8 region a clearly discernible ABX system arising from the three protons attached to C-1 and C-2. The H-1 (A) signal is a quartet, centred at τ 6·42 whose couplings with the two C-2 protons (B, X) (*J* = 5·8 and 3·0 Hz) are supported by double irradiation (see below). Both H-2 protons form quartets, that centred at τ 6·89 (H_{2B}) having *J* = 14, 5·8 Hz, the other, centred at τ 7·63 (H_{2X}) having *J* = 14, 3 Hz. Double irradiation in turn at A, B and X (see Fig. 1) simplifies the signals from the other two protons in accordance with

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[1] Part II: J. D. Connolly, R. McCrindle, K. H. Overton and J. Feeney, *Tetrahedron* **22**, 891 (1966).

[2] C. W. L. Bevan, J. W. Powell, D. A. H. Taylor, P. Toft, M. Welford, W. R. Chan, B. S. Mootoo and T. G. Halsall, *Chem. & Ind.* 1751 (1964).

expectation. Complete decoupling of A when irradiating B (and the reverse) was not readily accomplished since $W^{\frac{1}{2}}$ for B (22 Hz) is almost one half of $\delta\Delta$ A, B (47 Hz).

Double irradiation also confirmed the assignments of the H-5 and H-6 resonances. Irradiation at τ 7·25 (H-5) sharpened the broad singlet at τ 5·57 (H-6). It was further possible to locate the C-13 methyl group at τ 8·55, since irradiation at this frequency sharpened the singlet at τ 4·45 (H-17), by removing the ^4J coupling between these groups.

The unresolved region between τ 7·6 and 8·5 contains the signals from the five protons attached to C-9, C-11 and C-12 and it is interesting to note that three of these protons are situated below τ 8.

The single and double resonance spectra of the acetate III (Fig. 3) are self explanatory and do not require additional comment.

We do not feel that the information available from these studies allows decisions concerning the configurations at either C-6 or C-1. The latter, indeed, remains undefined in methyl angolensate.

EXPERIMENTAL

For general experimental see Part II.[1]

Extraction of the heartwood of Khaya grandifoliola. The wood used in this work was obtained from the Forestry Division, Kumasi, Ghana, through the good offices of Mr. A. G. Kenyon, Tropical Products Institute, London, to whom we here express our gratitude.

The powdered heartwood (7 kg) was continuously extracted with AcOEt in a Soxhlet extractor. The resulting extract was evaporated to 1 l., mixed with $CHCl_3$ (2 l.) and filtered from insoluble material. After removal of solvent from the filtrate, the residue was chromatographed in benzene on alumina [Spence Grade H deactivated with 5% AcOH : water (1 :9)]. The terpenoid material obtained (6·6 g) was further purified by preparative TLC on Kieselgel G (Merck). Subsequent crystallizations yielded, inter alia, *methyl 6-acetoxy angolensate* (III; 180 mg), needles from MeOH–water, m.p. 172–174°, $[\alpha]_D$ $-82°$ (*c*, 1·60). $\nu_{max}^{CCl_4}$ 1750 (δ-lactone, α-acetoxy-methyl ester, acetate) and 1725 (cyclohexanone) cm^{-1}. (Found: C, 65·64; H, 7·03. $C_{29}H_{36}O_9$ requires: C, 65·89; H, 6·87%) and *methyl 6-hydroxy angolensate* (II; 1·62 g), needles from MeOH- water, m.p. 235–238°, $[\alpha]_D$ $-85°$ (*c*, 0·95). $\nu_{max}^{CCl_4}$ 3600 (free OH), 3510 (bonded OH), 1730 (δ-lactone, methyl ester, cyclohexanone) cm^{-1}. (Found: C, 66·51; H, 6·92. $C_{27}H_{34}O_8$ requires: C, 66·65; H, 7·04%.)

Alkaline hydrolysis of methyl 6-acetoxy angolensate (III). It was found convenient to separate III from the methyl angolensate also present in the extract by hydrolysis of a mixture of the two followed by separation and reacetylation of methyl 6-hydroxy angolensate (II). A mixture of methyl angolensate and III (2·1 g) was dissolved in a 2% soln of KOH in MeOH : water (99 : 1; 50 ml) and left at 20° for 3 hr. Water (50 ml) was added, the soln acidified with 6N HCl and extracted into $CHCl_3$. Separation of the products by preparative TLC yielded methyl angolensate (1·2 g) and III (600 mg).

Acetylation of methyl 6-hydroxy angolensate (II). Compound II (100 mg) was dissolved in pyridine (5 ml) and Ac_2O (5 ml) and the soln left at 60° for 18 hr. Water (120 ml) was added and the soln extracted into $CHCl_3$. The product was purified by preparative TLC to afford III (68 mg). This was identical with acetate obtained from the extract as above by column and TLC as judged by m.p., m.m.p., NMR and IR.

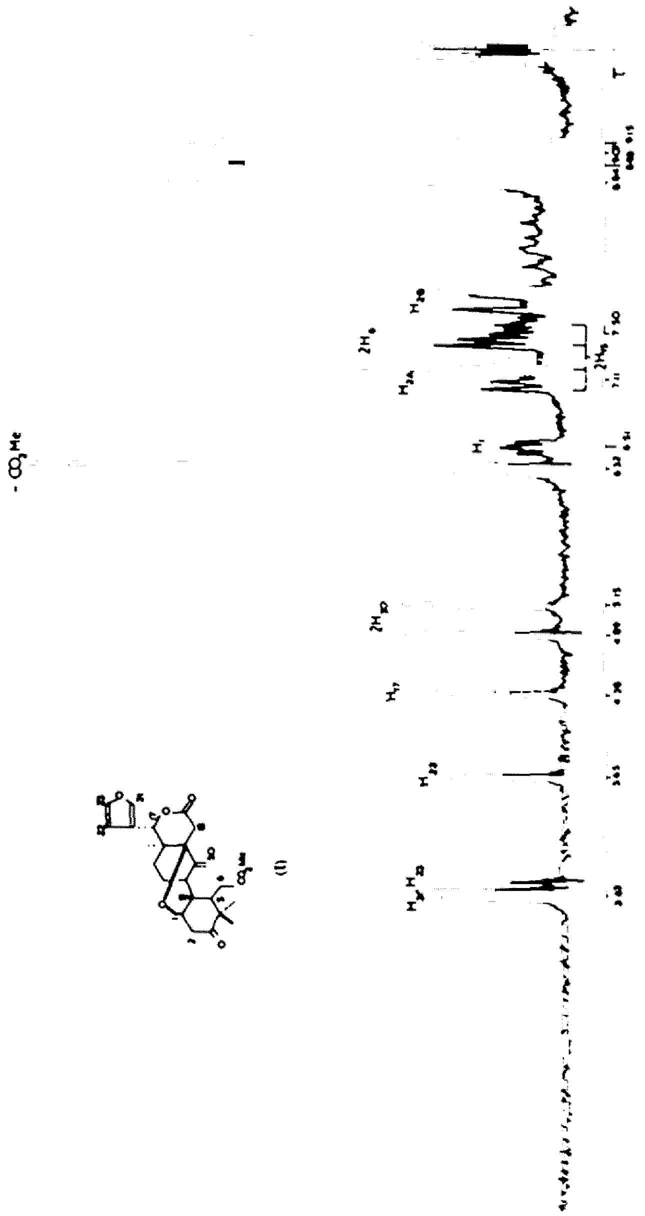

FIG. 1 NMR spectrum at 100 MHz of Methyl angolensate.

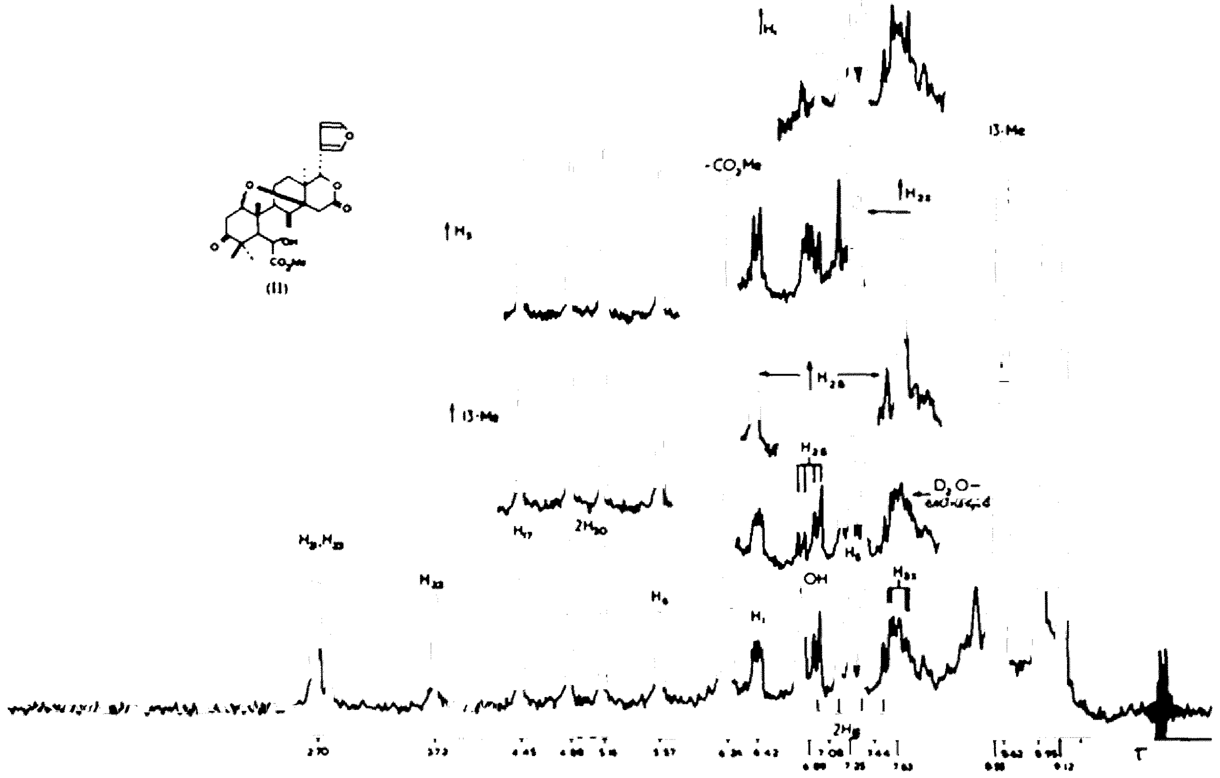

FIG. 2 NMR single and double resonance spectra at 100 MHz of Methyl 6-hydroxyangolensate.

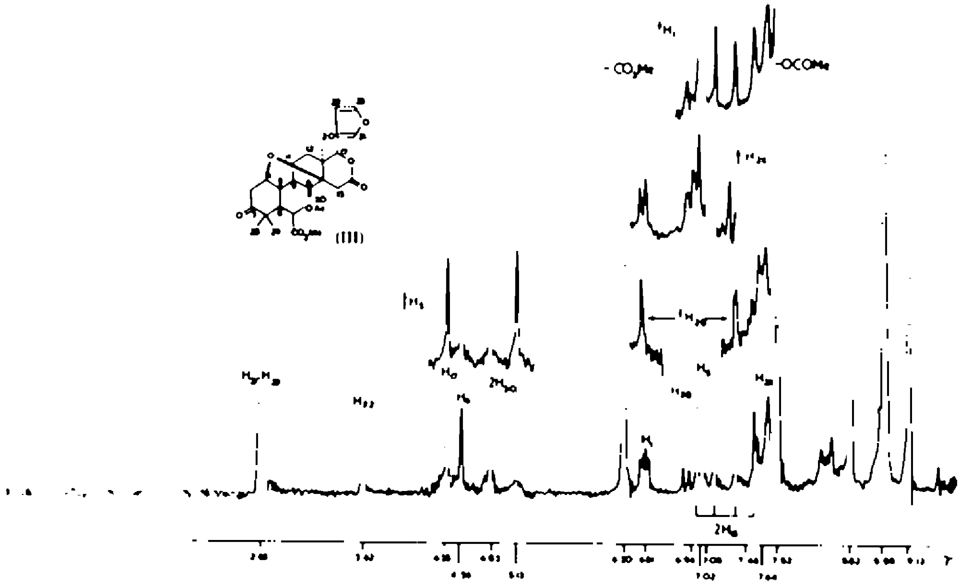

FIG. 3 NMR single and double resonance spectra at 100 MHz of Methyl 6-acetoxyangolensate.