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# TETRANORTRITERPENOIDS—II[1]

## HEARTWOOD CONSTITUENTS OF *CARAPA GUIANENSIS* Aubl.

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**Abstract**—Two new tetranortriterpenoids, obtained from the trunkwood of *Carapa guianensis*, are shown to be 11$\beta$-acetoxygedunin (I) and 6$\alpha$,11$\beta$-diacetoxygedunin (II) by a detailed analysis of their NMR spectra and their base-catalysed conversion respectively into the lactones III and IV.

CONTINUING our investigations of the tetranortriterpenoid constituents of members of the Meliaceae, we have obtained from the trunkwood of *Carapa guianensis* Aubl. two crystalline substances in major amount. They are uniquely defined as 11$\beta$-acetoxy gedunin (I) [diacetate A] and 6$\alpha$, 11$\beta$-diacetoxy gedunin (II) [triacetate B] by a detailed study of their NMR spectra and their conversion on treatment with alkali respectively into the lactones (III and IV), which is entirely analogous to the parallel transformations of limonin,[2] gedunin,[3] and khivorin.[4]

Diacetate A (I), m.p. 176–178°, $[\alpha]_D$ +33°, and triacetate B (II), m.p. 184–188°; 248–251°, $[\alpha]_D$ +120° had the following common structural features:

(1) an $\alpha\beta$-unsaturated ketone, whose substitution is characteristic of a ring-A 1-ene-3-one, as in gedunin (V) [$\lambda_{max}$ 218 m$\mu$ ($\varepsilon$ 10,100) (A), 218 m$\mu$ ($\varepsilon$ 10,600) (B); $\nu_{max}^{CCl_4}$ 1677 cm$^{-1}$ (A), 1681 cm$^{-1}$ (B); $\tau_{H1}$ 2·93, $\tau_{H2}$ 4·17, J = 10 c/s (A); $\tau_{H1}$ 2·91, $\tau_{H2}$ 4·09, J = 10 c/s (B). Gedunin:[5] $\lambda_{max}$ 215 m$\mu$ ($\varepsilon$ 13,200); $\tau_{H1}$ 2·93, $\tau_{H2}$ 4·19].

(2) A $\beta$-substituted furan ring [$\tau_{H21,23}$ 2·65, $\tau_{H22}$ 3·74 (A); $\tau_{H21,23}$ 2·66, $\tau_{H22}$ 3·74 (B). Gedunin: $\tau_{H21,23}$ 2·62. $\tau_{H22}$ 3·69]

(3) The NMR signals from $H_{15}$ [$\tau$ 6·47 (A), $\tau$ 6·37 (B)]. and $H_{17}$ [$\tau$ 4·45 (A), $\tau$ 4·46 (B)] are consonant with the presence of an $\alpha\beta$-epoxy-$\delta$-furyl-$\delta$-lactone as in gedunin ($H_{15}$ $\tau$ 6·51, $H_{17}$ $\tau$ 4·43), and this is borne out by the products III and IV formed on alkaline hydrolysis (see below).

(4) Five quaternary methyl groups [$\tau$ 8·89 (2), 8·80, 8·67, 8·59, (A); $\tau$ 8·87, 8·82, 8·78, 8·62 and 8·57 (B)]. The two methyls at lowest field [$\tau$ 8·59, (A), 8·57 (B)] are deshielded compared with the lowest methyl signal in gedunin ($\tau$ 8·75) by the $C_{11}$ $\beta$-acetoxyl group.

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[1] Part I. J. D. Connolly, R. Henderson, R. McCrindle, K. H. Overton and N. Bhacca, *J. Chem. Soc.* In the press.

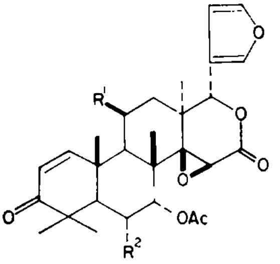
[2] A. Melera, K. Schaffner, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **40**, 1420 (1957).

[3] A. Akisanya, C. W. L. Bevan, T. G. Halsall, J. W. Powell and D. A. H. Taylor, *J. Chem. Soc.* 3705 (1961).

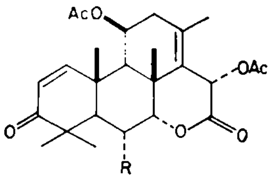
[4] C. W. L. Bevan, T. G. Halsall, M. N. Nwaji and D. A. H. Taylor, *J. Chem. Soc.* 768 (1962).

[5] W. Welford, Ph.D. Thesis, Oxford 1964. We thank Professor Bevan and Dr. Halsall for permission to quote the NMR data on gedunin contained in Dr. Welford's Thesis.

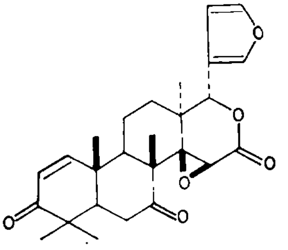
When these common elements between compounds A and B are accounted for, there remain two secondary acetoxyl groups in the case of compound A and three in compound B to be distributed between positions 6, 7, 11 and 12 of rings B and C. The following analysis of the NMR single and double resonance spectra at 100 Mc/s, based on the assumption of a gedunin structure, presents a unique solution.



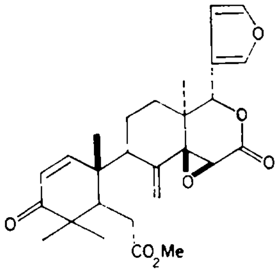
I R¹=OAc, R²=H
II R¹=R²=OAc
V R¹=R²=H



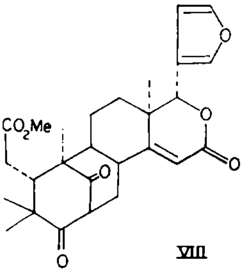
III R=H
IV R=OAc



VI



VII



VIII

*Diacetate* A (I) Fig. 1. The $>C\underline{H}OAc$ protons are centered at τ 4·26 (quintuplet, $W^{1/2}$ 21 c/s[6]) and τ 5·46 (broadened singlet, $W^{1/2}$ 5 c/s). These protons are not situated on adjacent carbon atoms since double irradiation at either proton leaves the other unaffected. The proton at τ 4·26, since it is a quintuplet, must have more than two neighbouring protons and is therefore at $C_6$ or $C_{11}$. To be at $C_6$ in a chair ring B, it would have to be axial (observed $W^{1/2}$ 21 c/s) and would then be flanked by two

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[6] A. Hassner and C. Heathcock, *J. Org. Chem.* 29, 1350 (1964).

axial and one equatorial neighbour. The observed multiplicity (quintuplet, separation 4·5 c/s) does not fit this situation. The proton whose resonance is centered at $\tau$ 4·26 must therefore be placed at $C_{11}$ (ring C boat as in gedunin) and be equatorial ($\alpha$), and the following experiments support this assignment. Upon irradiation at $\tau$ 4·26 (i) $H_9$ at $\tau$ 7·51 (1H doublet, J = 5 c/s) collapses to a singlet, and (ii) one $H_{12}$ proton at $\tau$ 7·71 (quartet, J = 13 and 10 c/s) collapses to a doublet (J = 13 c/s; residual geminal coupling). Only the lower field doublet of the other proton at $C_{12}$ can be seen; the upper doublet is obscured by the methyl resonance at $\tau$ 8·59. However, the visible doublet (J = 7 c/s) collapses to a singlet on irradiation at $H_{11}$. The observed coupling constants of $H_{11}$ with its neighbours are met by a twist-boat conformation of ring C, in which $C_{11}$ rotates downwards to minimize interaction between the $C_{11}\beta$ (axial) acetate and the two axial methyl groups at $C_{10}$ and $C_8$. The second proton ($>C\underline{H}OAc$ $W^{1/2}$ 5 c/s) is unlikely to have three neighbouring protons and must therefore be placed equatorially at $C_7$ and this assignment appears to be borne out by the facile base-catalysed loss of the furan residue (see below) for which a $C_7$ axial ($\alpha$) hydroxyl group appears to be a prerequisite. Upon irradiation at $\tau$ 8·04 ($C_6$, 2H), the broadened singlet at $\tau$ 5·46 ($H_7$) collapses to a sharp singlet.

*Triacetate* B (II) Fig. 2. The $>C\underline{H}OAc$ protons are centred at $\tau$ 4·23 (quintuplet, $W^{1/2}$ 21 c/s), $\tau$ 4·66 (pair of doublets, J = 3 and 12 c/s) and $\tau$ 5·11 (doublet, J = 3 c/s). The protons at $\tau$ 4·66 and $\tau$ 5·11 are mutually coupled since on irradiation at $\tau$ 5·11 the quartet at $\tau$ 4·66 collapses to a doublet (J = 12 c/s). This situation is met uniquely if the third acetate is placed, additionally to the acetates in the diacetate A, equatorially ($\alpha$) at $C_6$. In agreement with this, upon irradiation at $H_5$ ($\tau$ 7·54), $H_6$ ($\tau$ 4·66) collapses to a doublet (J = 3 c/s; residual coupling to $H_7$), while in the reverse experiment the doublet at $\tau$ 7·68 collapses to a singlet. Irradiation at $H_{11}$ ($\tau$ 4·66) produces the same changes in the signals from $H_9$ and $H_{12}$ as in the diacetate A.

Hydrolysis of diacetate A and triacetate B under the conditions which effect the limonol → merolimonol change,[2] afforded after acetylation respectively the diacetate (III), m.p. 233–235°, $[\alpha]_D$ +115°, and the triacetate (IV), m.p. 210–212°, $[\alpha]_D$ +167°. The compositions of these compounds and their spectroscopic properties are in accord with the expected structures. Thus in the NMR spectrum the signals from the furanic and epoxide protons are absent, the $C_1$ and $C_2$ vinyl protons are retained [$\tau$ 2·88, 4·17 (A); $\tau$ 2·89, 4·04 (B), J = 10 c/s] while in addition to four quaternary methyls [$\tau$ 8·91, 8·86, 8·70, 8·49 (A); $\tau$ 8·80, 8·70, 8·69, 8·40 (B)] there is now one vinyl methyl [$\tau$ 8·17 (A); 8·14 (B)]. $H_{15}$ appears as an unresolved multiplet [$\tau$ 3·90 (A); 3·97 (B)]. The positions and multiplicities of $H_7$ and $H_{11}$ in the diacetate and $H_6$, $H_7$ and $H_{11}$ in the triacetate correspond to those in the parent compounds. In the infra-red ($CCl_4$) there is a band [1784 $cm^{-1}$ (A); 1788 $cm^{-1}$ (B)] characteristic of an $\alpha$-acetoxy-$\delta$-lactone in addition to bands for the acetates [1744 and 1760 $cm^{-1}$ (A) and (B)] and enone [1677 $cm^{-1}$ (A) and 1680 $cm^{-1}$ (B)] functions.

Three other tetranortriterpenoids previously obtained from *Carapa spp.* have structures which fall in a neat biogenetic sequence. They are 7-deacetoxy-7-keto-gedunin (VI),[7] andirobin (VII),[7] both from the seeds of *Carapa guianensis* and carapin (VIII)[8] from the trunkwood of *Carapa procera*.

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[7] W. D. Ollis and A. D. Ward, *Tetrahedron Letters* No. 37, 2607 (1964).

[8] E. O. Arene, C. W. L. Bevan, J. W. Powell and D. A. H. Taylor, *Chem. Comm* 302 (1965).

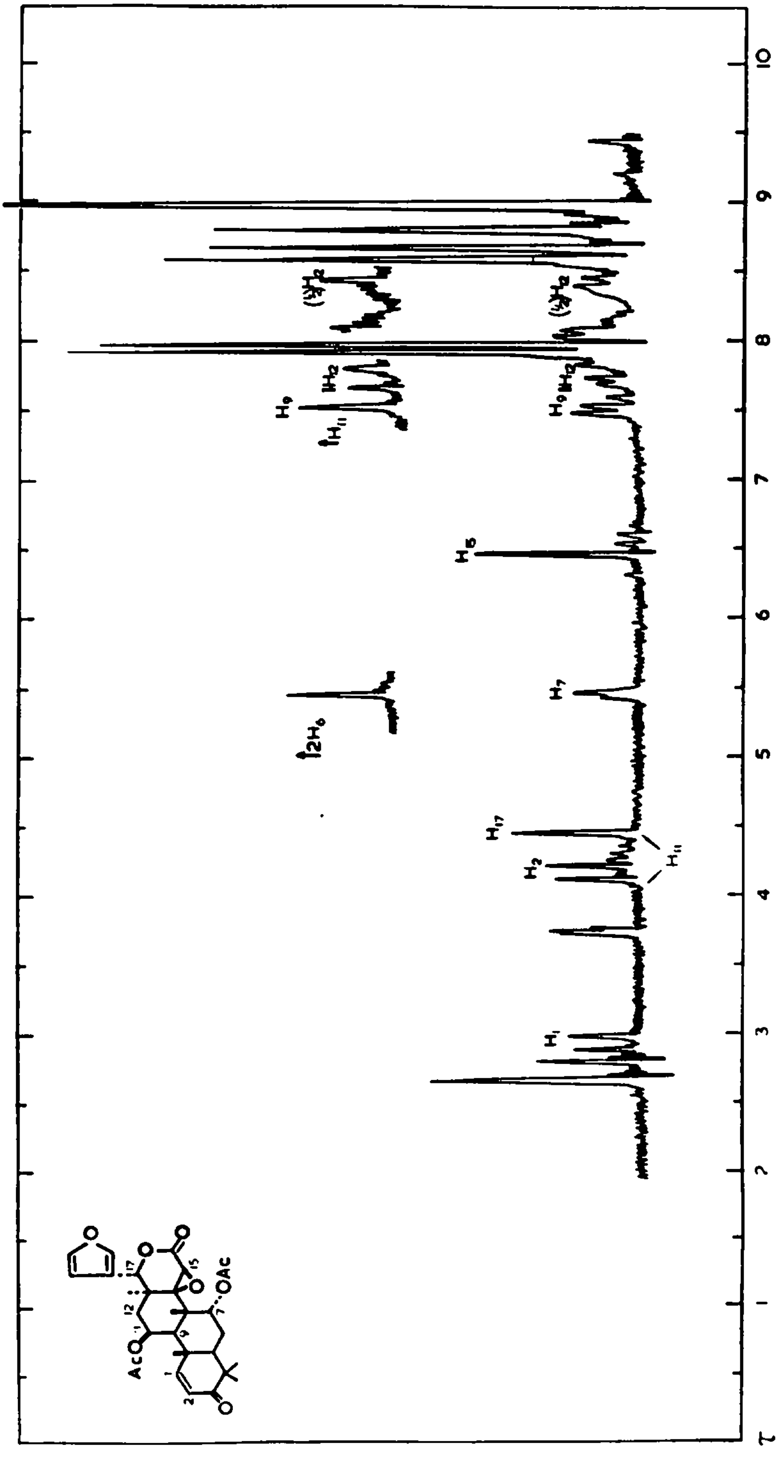

FIG. 1. NMR Single and Double Resonance Spectra at 100 Mc/s of Diacetate (I).

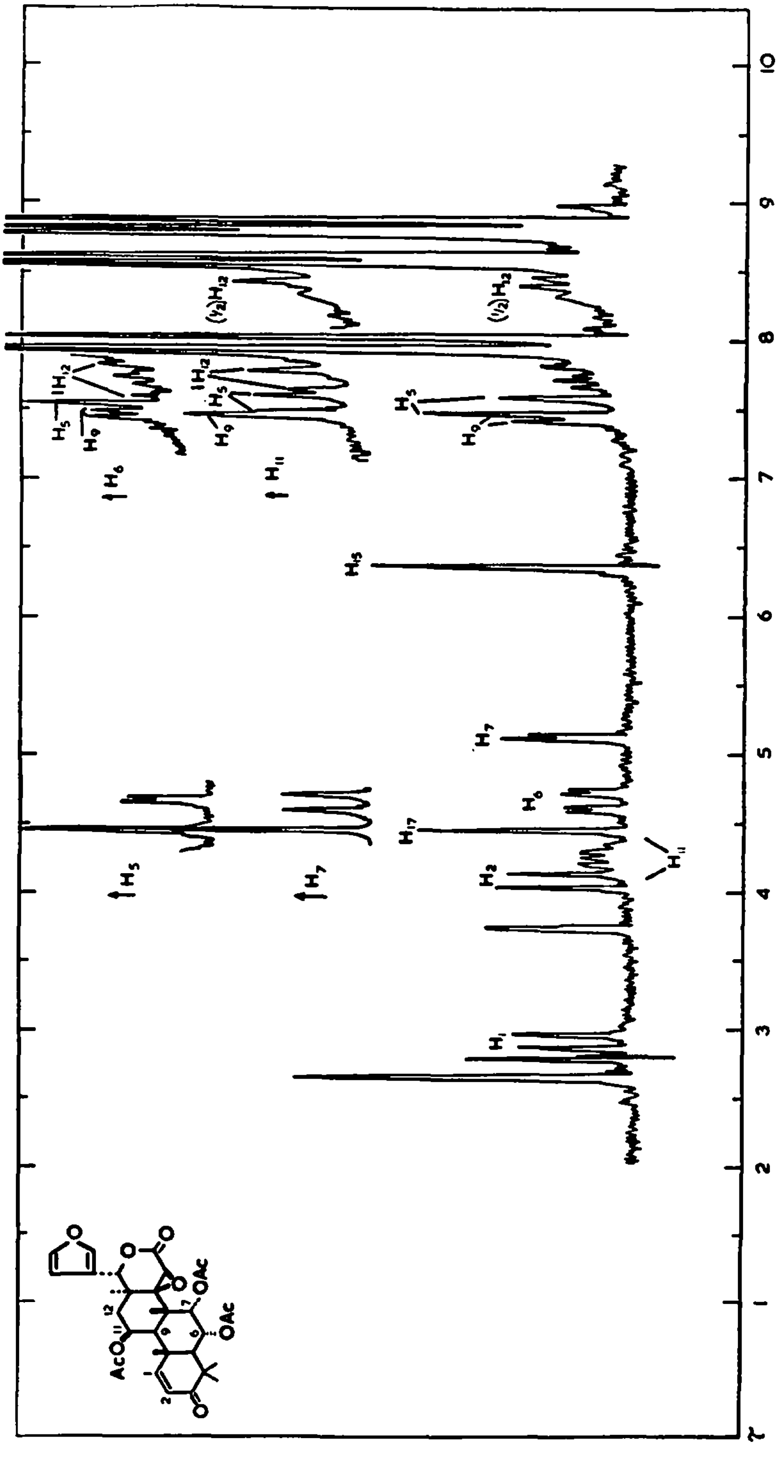

FIG. 2. NMR Single and Double Resonance Spectra at 100 Mc/s of Triacetate (II).

## EXPERIMENTAL

M.ps were taken on the Kofler Block. Specific rotations refer to $CHCl_3$ solutions. IR spectra were taken on the Unicam SP 100 IR spectrophotometer by Mrs. F. Lawrie. NMR spectra were obtained on the Varian HA 100 and Perkin–Elmer R 10 spectrometers, using approximately 0·3 M solutions in $CDCl_3$ with tetramethylsilane as internal standard. Microanalyses are by Mr. J. M. L. Cameron, B.Sc. and his staff, Glasgow. Chromatoplates both for analytical and preparative use were made by the method of Stahl, using Kieselgel G (Merck).

*Extraction of the heartwood of Carapa guianensis.* The wood used in this investigation was obtained through the courtesy of Mr. W. S. Chalmers, Assistant Conservator of Forests, Port of Spain, Trinidad, whose help we acknowledge with pleasure. The powdered heartwood (6 kg) was continuously extracted in a Soxhlet extractor with ethyl acetate. The extract obtained was concentrated to 1 l. mixed with 2 l. $CHCl_3$ and the insoluble material removed by filtration. The residue obtained after removal of solvent from the filtrate, was chromatographed in benzene on alumina [Spence Grade H deactivated with 6% of water-acetic acid (9:1)]. This initially yielded a mixture of diacetate A and triacetate B and β-sitosterol. The latter was almost completely removed by crystallization of the mixture from MeOH. The residue from the mother liquors (2·3 g) was then separated into its two components by a combination of column chromatography on deactivated alumina (see above) and preparative TLC on Kieselgel G. Several crystallizations from the specified solvent mixtures then afforded 11β-acetoxygedunin (diacetate A) (980 mg), fine needles from chloroform–ether–light petroleum, m.p. 176–178°, $[\alpha]_D$ +33° (*c*, 1·2). (Found: C, 66·5; H, 6·95. $C_{30}H_{36}O_9$ requires: C, 66·65; H, 6·7%), and 11β,6α-*diacetoxy-gedunin* (triacetate B; 920 mg) rods from acetone–ether–light petroleum, m.p. 184–188°; 248–251°; $[\alpha]_D$ +120° (*c*, 1·46). (Found: C, 63·85; H, 6·3. $C_{32}H_{38}O_{11}$ requires: C, 64·2; H, 6·4%.)

*Alkaline hydrolysis of compounds* A *and* B. Compound A (100 mg) dissolved in EtOH (10 ml) containing KOH (400 mg) was heated on the steam bath for 1 hr. The reaction product obtained in the usual way, was dissolved in pyridine (3 ml) and acetic anhydride (3 ml) and kept at 18° for 16 hr. The major product was separated by preparative TLC to afford the *lactone diacetate* (III) (35 mg) rods from chloroform–ether–light petroleum, m.p. 233–235°; $[\alpha]_D$ +115° (*c*, 0·74). (Found: C, 67·6; H, 7·5. $C_{25}H_{32}O_7$ requires: C, 67·55; H, 7·25%.) Compound B (105 mg), dissolved in a mixture of MeOH (5 ml) and 4N KOH (5 ml) was heated on the steam bath for 1 hr. The major product obtained after extraction and acetylation as for compound A afforded the *lactone triacetate* (IV; 35 mg), needles from ether–light petroleum, m.p. 210–212°, $[\alpha]_D$ +167°, (*c*, 1·33). (Found: C, 64·7; H, 6·85. $C_{27}H_{34}O_9$ requires: C, 64·55; H, 6·8%.)