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CARAPOLIDE A, A NOVEL HEXANORTRITERPENOID AND CARAPOLIDES B AND C, NOVEL TETRANORTRITERPENOIDS FROM THE SEEDS OF CARAPA PROCERA (MELIACEAE)[1]

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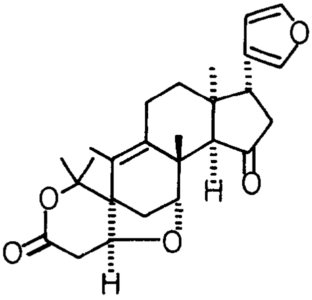
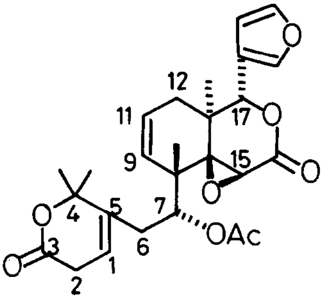
Summary : Carapolide A, a novel hexanortriterpenoid, and carapolides B and C, novel tetranortriterpenoids have been isolated from the seeds of *Carapa procera* and have been assigned structures (2), (10) and (11) respectively on the basis of chemical and spectroscopic evidence.

Previous investigations of the bark of *Carapa procera* DC resulted in the isolation of Carapa spirolactone (1)[2], evodulone[4] and the complex tetranortriterpenoid, procerin[3]. We have now examined the seeds of *C. procera*, collected in the University Garden in Yaounde and have obtained three new compounds, carapolides A (2), B (10) and C (11), whose structures have been assigned on the evidence below. Carapolide B and C are the first representatives of a new group of tetranortriterpenoids with a novel C-9, C-10 - cleaved carbon skeleton. Carapolide A is a related hexanortriterpenoid arising by subsequent cleavage of the C-5, C-10 bond and loss of two carbon atoms.

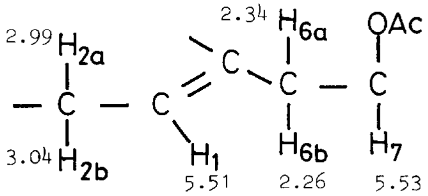


(1)



(2)

Carapolide A (2), $C_{26}H_{30}O_8$, mp 194-6°, $\{\alpha\}_D^{20}$ -31.5° (c, 1.7 in $CHCl_3$), m/z 470, has resonances in its ^1H and ^{13}C nmr spectra ($CDCl_3$)[5] consistent with the presence of a β-substituted furan, a ring D epoxylactone {δ_H 3.88 (s, H-15) and 5.59 (s, H-17)}, four tertiary methyl groups {δ_H 1.47, 1.45, 1.16 and 0.92}, a secondary acetate {δ_H 2.02 (3H, s), 5.53 (dd, J 11.0, 2.7 Hz, H-7)}, two non conjugated double bonds with one trisubstituted {δ_H 5.51 (tt, J 4,1 Hz, H-1) ; δc 118.4 (d, C-1) and 136.6 (s, C-5)} and the other cis-disubstituted {δ_H 5.52 (ddd, J 10.3, 2.7, 1.2 Hz, H-9) and 5.73 (ddd, J 10.3, 6.0, 2.2 Hz, H-11) ; δc 130.9 (d, C-9) and 123.4 (d, C-11)} and a second lactone {δ 168.8 (s, C-3) and 84.9 (s, C-4)}. The presence of an acetate indicates that carapolide A has a C-24 skeleton and is therefore a hexanortriterpenoid. Thus two carbons including a methyl group have been lost from the normal tetranortriterpenoid nucleus. Double resonance experiments at 360 MHz permitted the construction of the part structures (3) and (4), which together with the β-substituted furan and ring D epoxylactone, can be reasonably assembled to give structure (2) for carapolide A. The C-7 acetoxyl group is assumed to have the usual α-configuration.



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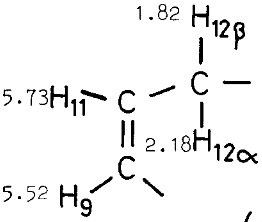


(4)

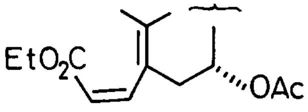
J(Hz) 2a, 2b: 22.2 ; 2a, 3 4 ; 2b, 3 4
2a, 6a 1.5 ; 2a, 6b 1 ; 2b, 6a 1.5
2b, 6b 1 ; 3, 6a 1 ; 3, 6b 1.0
6a, 6b 15.1 ; 6a, 7 3 ; 6b, 7 11.0

J(Hz) 9,11 10.3 ; 9,12β 2.7
9,12α 1.2 ; 11,12β 2.2
11,12α 6 ; 12α, 12β 16.8

In an attempt to move the trisubstituted double bond into conjugation with the ring A lactone carbonyl group carapolide A (2) was treated with methanolic KOH. The product lacked both acetate and hydroxyl absorption in its i.r spectrum. Its ^1H nmr spectrum ($CDCl_3$) indicated that it was a mixture of ethers with the gross structure (5), resulting from the migration of the double bond, hydrolysis of the acetate and addition of the resultant hydroxyl group to the ring A unsaturated lactone. The major isomer has resonances for 2H-2 {δ_H 2.90 (dd, J 18.1, 8.1 Hz) and 2.59 (dd, J 18.1, 2.9 Hz)}, H-1 (δ_H 4.56 (dt, J 2.9, 7.6 Hz)}, H-5 {δ_H 2.50 (ddd, J 10, 8, 6 Hz)}, 2H-6 {δ_H 2.00 (ddd, J 13.2, 9.5, 7.5 Hz) and 1.93 (ddd, J 13.2, 7.5, 6.0 Hz)} and H-7 {δ_H 4.18 (t, J 7.5 Hz)} consistent with the assigned structure.

Treatment of carapolide A (2) with ethanolic HCl afforded two isomeric diene ethyl esters (6) and (7) {λ_{max} 276 nm (ε 8,000)}. Both isomers have resonances ($CDCl_3$) for two vinyl methyl groups {δ_H 1.60 and 1.74 (6), 1.93 and 1.88 (7)}. In the cis-compound (6) the coupling constant between H-1 and H-2 {δ_H 6.63 and 5.78 (both d)} is 11.1 Hz whereas in the trans-isomer (7) {δ_H 7.74 and 5.74 (both d)} it is 15.8 Hz. As expected H-1 of the trans-isomer (7) is considerably deshielded with respect to (6).

In biogenetic terms carapolide A (2) can be derived from a spiro-precursor (8) as in scheme I. A retro-Prins reaction results in cleavage of the C-9, C-10 bond with formation of the ring C double bond and a methyl ketone as in (9). Subsequent vinylogous 1,3-dicarbonyl cleavage of (9) and protonation at C-2 then leads directly to carapolide A (2) with the loss of C-10 and C-19, presumably as ethanoic acid.



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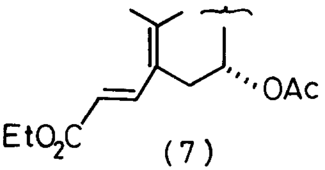

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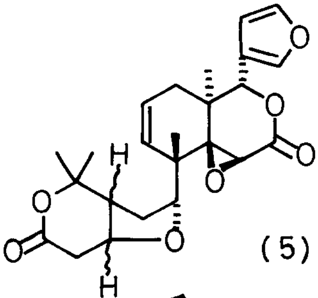

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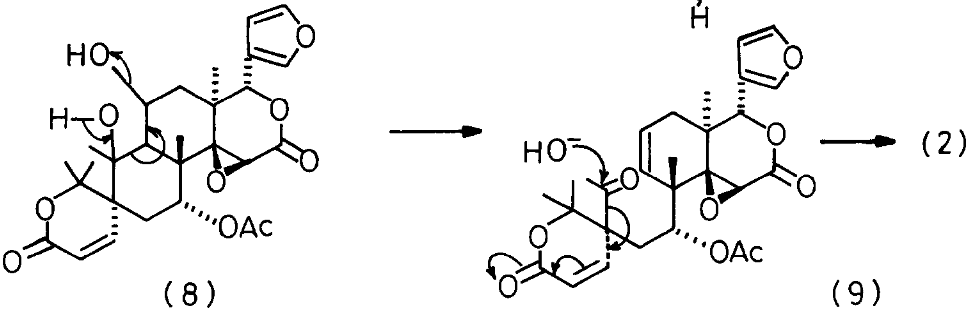
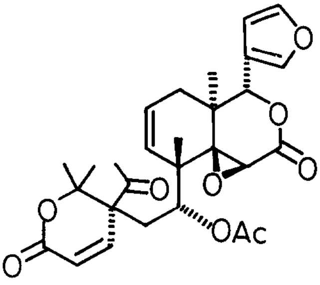


Scheme I

Support for a biogenetic pathway of this type was obtained by examining the minor constituents of the extract. Two new tetranortriterpenoids, carapolides B (10) and C (11), both containing methyl ketone functions, were isolated in minor amount. Carapolide B (10), $C_{28}H_{32}O_9$, νmax 1712, 1740, 1752 (sh) cm^{-1}, has resonances ($CDCl_3$) for a secondary acetate {δ_H 2.01 (3H, s), 5.07 (dd, J 11.7, 2.0 Hz, H-7)} flanked by an isolated methylene group 2H-6 {δ_H 2.69 (dd, J 13.9, 11.7 Hz) and 2.02 (dd, J 14, 2 Hz)}, a methyl ketone {δ_H 2.26 (3H, s)} and an αβ-unsaturated ring A lactone {δ_H 7.15 and 6.19 (both d, J 10.1 Hz, H-1 and H-2)} in addition to those arising from the same C,D-ring system as in (2). These data are consistent with structure (10). The configurations at C-5 and C-7 are assumed to be the same as in (1).

Carapolide C (11), $C_{26}H_{30}O_8$, νmax 1710, 1752 cm^{-1}, has the same C,D-ring system as (10) but lacks the acetate and the αβ-unsaturated lactone functionality. Its spectroscopic properties ($CDCl_3$) are indicative of a methyl ketone {δ_H 2.30 (3H, s) ; δc 28.6 (q, C-19), 206.3 (s, C-10)} and a saturated ring A lactone {δc 169.7 (s, C-3)} with a 1,7-ether {δc 75.8 (d, C-1) and 81.5 (d, C-7)} as in Carapa spirolactone (1)^2. Thus H-1 {δ_H 4.83 (dd, J 7.3, 2.2 Hz)} resonates as the X-part of an AMX system {2H-2 δ_H 3.03 (dd, J 18.2, 7.3 Hz) and 2.68 (dd, J 18.2, 2.2 Hz)} and H-7 {δ_H 4.17 (t, J 8.2, Hz)} as the X-part of an AA'X system {2H-6 δ_H 2.25 (d, J 8.2 Hz)}. These data support structure (11) for carapolide C.

Acknowledgement : We are grateful to the University of Yaounde Research Grants Allocation Committee for support of this investigation.



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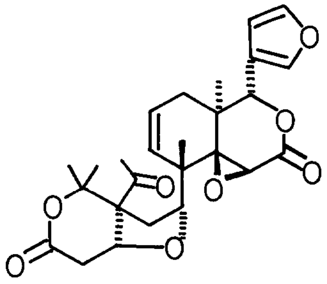

(11)

REFERENCES AND NOTES

1. Part of this work was presented in a plenary lecture delivered by one of us (JDC) at the PSE symposium on the Chemistry and Chemotaxonomy of the Rutales in Glasgow in April 1982.

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4. Sondengam, B.L., Kamga, C.S. and Connolly, J.D., (1979) Tetrahedron Letters, 1357.

5. The complete list of ^{13}C shifts of carapolides A and C appears in Table I in the following paper.

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