Tetrahedron Letters,Vol.25,No.15,pp 1617-1620,1984
Printed in Great Britain
0040-4039/84 $3.00 + .00

CARAPOLIDES D, E AND F, NOVEL TETRANORTRITERPENOIDS FROM THE SEEDS OF CARAPA GRANDIFLORA (MELIACEAE)

S. Fon Kimbu, J. Foyere Ayafor, B. Lucas Sondengam*, E. Tsamo
Department of Organic Chemistry, University of Yaounde,
Yaounde, B.P. 812 Yaounde.

Joseph D. Connolly and David S. Rycroft
Deaprtment of Chemistry, University of Glasgow,
Glasgow G 12 8QQ, Scotland

Summary : Carapolides D and E, two new ring B cleaved tetranortriterpenoids, and carapolide F, a novel tetranortriterpenoid spirolactone, have been isolated from the seeds of Carapa grandiflora and have been assigned structures (1),(3) and (6) on the basis of their ^{1}H and ^{13}C spectroscopic properties.

In the preceding communication[1] we described the isolation of the novel hexanortriterpenoid, carapolide A, and two tetranortriterpenoids, carapolides B and C, from the seeds of Carapa procera. These compounds form a novel group of limonoids with a C-9, C-10 cleaved carbon skeleton. We have now examined the chloroform extract of C. grandiflora and have obtained two further members of this groups, carapolides D (1) and E (3) together with a tetranortriterpenoid spirolactone with an intact ring B, carapolide F (5), which has the sturctural requirements of the proposed[1] biogenetic progenitor of this group. The structures of carapolides D, E and F were assigned on the basis of the following evidence.

Carapolide D (1), mp 234-236°, $\{\alpha\}^{20}_{D}$ -362° (c 1.8;acetone), m/z 452.1844 ($C_{26}H_{28}O_7$ requires m/z 452.1833) has resonances for four tertiary methyl groups {δ_H 0.88, 1.11, 1.48 and 1.50}, a ring C double bond {δ_H 5.84 (dd, J 10.3, 2.5Hz, H-9), 5.77 (ddd, J 10.3, 6.0, 1.7Hz, H-11) ; δc 131.0 and 123.0 (both d, C-9 and C-11)}, a secondary oxygen-bearing carbon {δ_H 4.34 (dd, J 7.6, 8.7Hz, H-7) ; δc 81.2 (d, C-7)} coupled to an isolated methylene group {dH 1.85 (2H, d, J 8Hz, 2H-6)}, a ring A αβ-unsaturated δ-lactone {δ_H 6.58 and 5.98 (both d, J 9.7Hz, H-1 and H-2)}, δc 163.1 (s, C-3), 148.3 (d, C-1) and 118.3 (δ, C-2) together with the characteristic ring D epoxylactone and β-substituted furan ring. The remaining features of its ^{1}H and ^{13}C nmr spectra are an AB quartet {δ_H 4.17 and 4.49

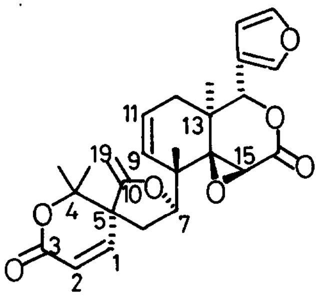
(J_{AB} 2Hz)} and two carbon resonances {δc 159.8(s) and 86.3(t)}. These data are consistent with the presence of a vinyl ether which can be readily accommodated in structure (1) for carapolide D. Strong support for this structure comes from the appearance in the mass spectrum of (1) of the base peak at m/z 193.0856 ($C_{11}H_{13}O_3$ requires m/z 193.0864) due to the fragment (2). The configuration at C-5 and C-7 in (1) are assumed to be the same as in carapolides B and C.

Carapolide E (3) mp 178-180°, $\{\alpha\}^{20}_{D}$ + 106° (c, 4.3 in acetone), m/z 470.1960 ($C_{26}H_{30}O_8$ requires m/z 470.1939), νmax ($CHCl_3$) 3598, 1735, 1720, 1600 cm^{-1}, is a hydrate of (1) and has five tertiary methyl group {δ 0.81, 1.08, 1.50, 1.52 and 1.63}, a tertiary hydroxyl group {δ 2.41(s)} and a hemiacetal carbon {δc 105.2(s)}. The remaining features of its ^1H and ^{13}C nmr spectra ($CDCl_3$, 360 MHz) are similar to those of (1) with the exception of the vinyl ether resonances. Thus carapolide E has structure (3). Direct correlation of C. grandiflora and C. procera was achieved by treatment of carapolide E (3) with ptsa to give the ether, carapolide C (4), previously isolated from C. procera[1]. As expected, reaction of carapolide E with acidic methanol yielded the methyl acetal (5).

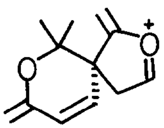
The spectroscopic properties of the third compound carapolide F (5), $C_{28}H_{34}O_8$, mp 238-240°, clearly indicate that it has an intact ring B and are consistent with the spirolactone structure (6). Thus it has in addition to a β-substituted furan and a ring D epoxylactone resonances{^1H ($CDCl_3$), ^{13}C ($CDCl_3$ + CD_3OD), 360 MHz} for five tertiary methyl groups {δ_H 1.16, 1.55, 1.59, 1.64, 1.65}, a ring A αβ-unsaturated δ-lactone {δ 6.78 and 5.91 (both d, J 10.2Hz, H-1 and H-2) ; δc 154.4 (d, C-1), 117.0 (d, C-2) and 165.2 (s, C-3)} and a secondary acetate δ_H 2.01 (3H, s), 4.55 (dd, J 2.3, 3.7Hz, H-7) ; δc 170.2(s) and 74.3(d), C-7)}. H-7 is coupled to an isolated methylene group 2H-6 {δ 2.63 (dd, J 15.2 and 2.3Hz) and 2.13 (dd, J 15.2, 3.7Hz)} showing that C-5 is fully substituted. There are two additional oxygenated carbons {δc 78.6 (s, C-10) and 65.4 (d, C-11) both bearing hydroxyl groups. H-11 appears as a multiplet {δ_H 4.85} and is coupled to H-9 {δ_H 2.50 (d, J 5.3Hz)} and the C-12 methylene group {δ_H 2.21 (dd, J 13.5, 9.4Hz, H-12β) and 1.79 (dd, J 13.5, 7.4Hz, H-12α)}. The coupling data suggest that the 11-hydroxyl group is pseudo-equatorial (β) with ring C, adopting a boat conformation and the C-7 acetoxyl group is axial in a chair ring B. There is no direct evidence for the configuration at C-10.

Treatment of carapolide F (6) with $SOCl_2$ in pyridine afforded two diastereoisomeric cyclic sulphites differing in the configuration at sulphur which were separated by preparative tlc. The ^1H nmr spectra of these derivatives are similar in chemical chifts and coupling constants to that of (6) apart from showing downfield shifts of H-11 and the C-10 methyl. The major differences between the spectra of the sulphites involve the shifts of H-11 (δ_H 5.49 and 5.78). H-9 (2.46 and 2.59) and the C-10 methyl group (δ_H 1.99 and and 2.20). The formation of these cyclic esters supports the assigned structure (6) for carapolide F.

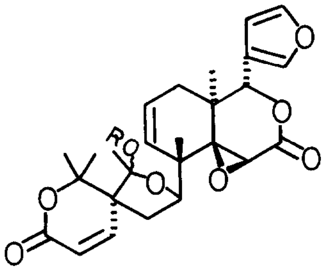
We thank Mr Mpom Benoit of the National Herbarium Yaounde, Cameroon, for the identification and collection of plant material and the S.E.R.C. University of Edinburgh MH 360 nmr Service for ^{1}H and ^{13}C spectra.



(1)

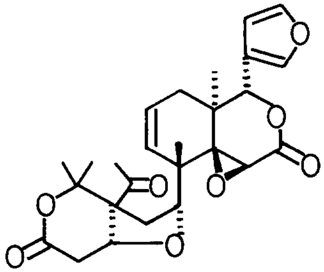


(2)

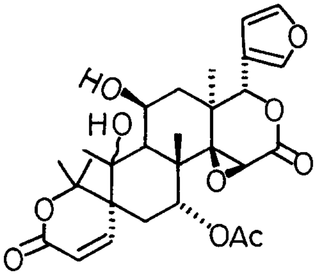


(3) R = H

(5) R = Me



(4)



(6)

TABLE 1

^{13}C nmr Shifts of Carapolide Compound ($CDCl_3$)

Carbon n°	A	C	D	E	F*
1	118.7	75.8	148.7	149.7	154.4
2	30.1	35.7	118.3	120.5	117.0
3	168.8	169.7	163.1	163.3	165.2
4	84.9	81.7	84.0	85.1	90.8
5	136.6	66.8	52.1	55.4	47.4
6	32.2	33.2	35.7	36.6	37.0
7	73.6	81.5	81.2	80.0	74.3
8	42.8	42.0	41.6	42.2	41.0
9	130.9	131.3	131.0	131.7	39.9
10	-	206.3	86.3	105.2	78.6
11	123.4	122.7	123.0	122.4	65.4
12	32.5	32.2	32.1	32.1	31.1
13	38.3	38.1	38.1	38.1	38.3
14	65.8	65.2	66.7	67.7	70.1
15	53.6	52.5	52.5	52.7	57.1
16	166.8	167.0	166.9	167.3	168.8
17	77.7	77.8	77.8	77.8	78.6
20	119.9	120.1	120.0	120.3	120.6
21	141.0	141.0	141.0	141.0	141.8
22	109.8	109.9	109.9	109.9	110.2
23	143.3	143.2	143.2	143.2	143.7
CMe	27.8	27.0	25.0	26.7	27.6(2)
	27.4	26.5	23.3	24.9(2)	26.1
	17.8	16.7	16.8	18.2	19.8
	16.3	16.1	16.1	16.1	16.3
		28.6(C-19)	159.8		
Ac	169.8				170.2
	20.8				21.1

* $CDCl_3 + CD_3OD$

REFERENCES

1. S.F. Kimbu, J.F. Ayafor, B.L. Sondengam, J.D. Connolly and D.S. Rycroft. Tetrahedron Letters (1984), · · · preceding paper.

(Received in UK 17 January 1984)