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NOVEL LIGNANS FROM A CINNAMOMUM SP. FROM BOUGAINVILLE

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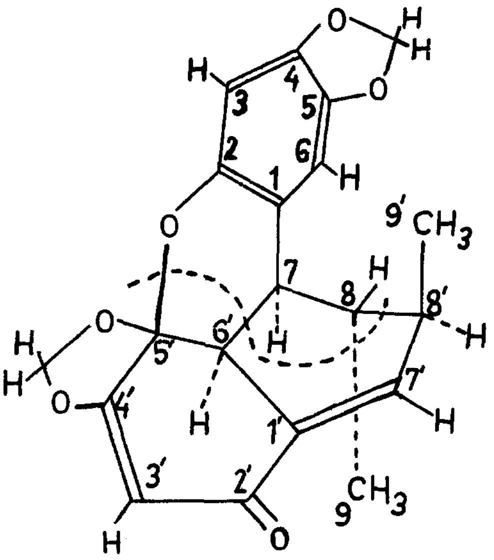
Light petroleum extracts of the bark of the Carpano tree, a Cinnamomum sp. of the Family Lauraceae, which is native to Bougainville, yielded, among other compounds[1], a colourless crystalline material, carpanone (I), m.p. 210-2°, which analysed for $C_{20}H_{18}O_6$, (M^+ 354), ir spectrum, ν^{KCl} no OH, 1657 cm^{-1}, uv spectrum (MeOH) λ_{max} 243 (log ϵ 3.93), 262 (4.04), 298 (3.71). The compound showed no optical activity (ORD measurement).

Hydrogenation of (I) over Pt in acetic acid yielded dihydrocarpanone (II), $C_{20}H_{20}O_6$, (M^+ 356), m.p. 189-90°, ir spectrum, ν^{KCl} no OH, 1680 cm^{-1}, uv spectrum λ_{max} 243 (log ϵ 4.25), 300 (3.79). Treatment of a solution of (II) in acetic anhydride with 96% sulphuric acid at room temperature for 30 minutes, followed by pouring into iced water and neutralising with bicarbonate yielded the diacetate (III), $C_{24}H_{24}O_8$, (M^+ 440), m.p. 135-6°, ir spectrum, ν^{KCl} no OH, 1750 cm^{-1}, uv spectrum (MeOH) λ_{max} 236 (sh) (log ϵ 3.96), 291 (3.88).

Proton nmr data, including the results of numerous spin decoupling experiments, for (I), (II) and (III) were obtained with Varian HA100 and HR220 instruments. The series of transformations described above, together with the spectroscopic data, enabled us to deduce the structures and relative stereochemistries (I), (II) and (III). In addition to (I), smaller quantities of two other compounds were isolated. The first of these is isocarpanone,

Carpanone (I)

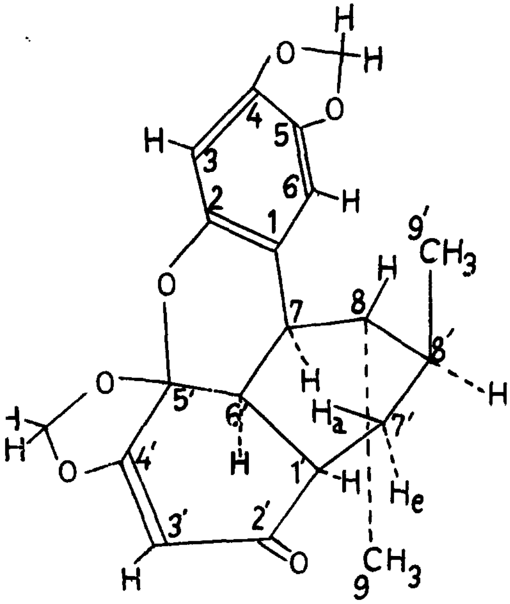


δ (p.p.m.)		J (Hz)	
H7'	7.01	6, 3	0.4
H6	6.81	6, 7	0.6
H3	6.32	7, 8	2.1
C4 and C5	5.88*	8, 9	7.0
H3'	5.68	8, 8'	1.0
C4' and C5'	5.66 and 5.62**	8, 7' 7, 8'	1.0 1.0
H6'	3.17	8', 9'	7.5
H7	3.27	8', 7'	5.0
H8'	2.21	8', 6'	2.3
H8	2.52	7', 6'	2.3
C9 Me	1.13	6', 7	7.5
C9' Me	0.70		

* AB quartet, $J_{AB}=1.5$
$\Delta AB = 0.03$ p.p.m.

**AB quartet, $J_{AB}=0.3$

Dihydrocarpanone (II)

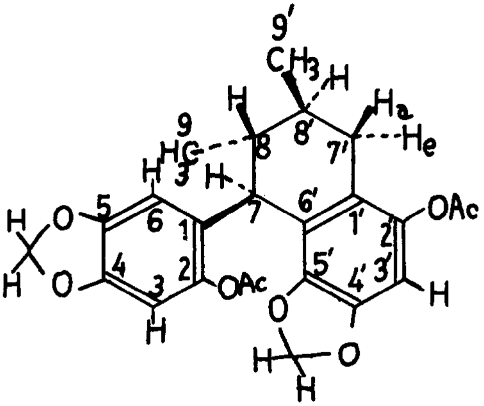


δ (p.p.m.)		J (Hz)	
H6	6.78	6, 3	≠ 0
H3	6.35	6, 7	0.4
C4 and C5	5.90*	7, 8	2.0
H3'	5.62	8, 9	7.4
C4' and C5'	5.61 and 5.58**	8, 8' 8', 9'	2.0 7.0
H7	3.20	8', $7'_a$	11.6
H6'	2.89	8', $7'_e$	7.0
H1'	2.66	$7'_a$, $7'_e$	13.4
H8	2.26	$7'_a$, 1'	13.5
H$7'_e$	2.05	$7'_e$, 1'	2.7
H8'	1.58	1', 6'	9.0
H$7'_a$	1.16	6', 7	8.4
C9 Me	1.23		
C9' Me	0.70		

* AB quartet, $J_{AB}=1.5$
$\Delta AB = 0.03$ p.p.m.

**AB quartet, $J_{AB}=0.3$

(III)

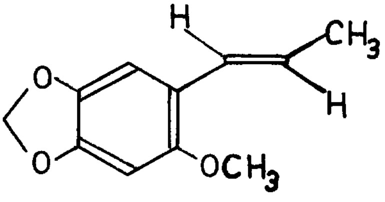


δ (p.p.m.)		J (Hz)	
H6	6.61	6, 3	$\neq$ 0
H3	6.52	6, 7	0.4
H3'	6.40	3', 7	0.8
C4 and C5	5.95*	7, 8	10.2
C4' and C5'	5.70and 5.57**	$7'_e$, 8'	4.1
		$7'_e$, $7'_a$	16.3
H7	3.58	$7'_a$, 7	1.3
$H7'_a$	2.63	$7'_a$, 8'	11.3
$H7'_e$	2.18	8, 9 and 8', 9' approx.	7
H8 and H8'	1.2-1.8		
C9 and C9'	1.07and 0.91		
MeCO	2.02and 2.30		

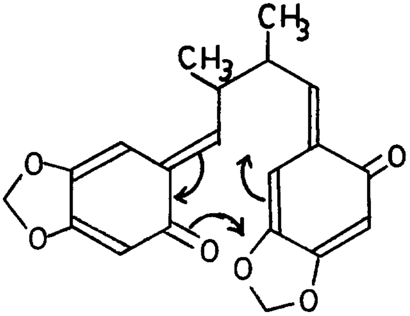
* Singlet

** AB quartet, J_{AB} = 1.3

$C_{20}H_{18}O_6$,(M$^+$ 354), m.p. 216-7°. We believe that, on the basis of nmr data, isocarpanone differs from carpanone only in the configuration at C7, C8 and C8'. The other compound, carpananone, $C_{20}H_{20}O_6$,(M$^+$ 356), m.p. 227-9°, has spectroscopic properties similar to those of (II) and we believe that these two compounds are configurational isomers.



(IV)



(V)

The structure of carpanone (I) indicates that it is a lignan[2]. Given the occurrence of a trioxygenated propenylbenzene, carpacin[1] (IV), in the same plant, carpanone and isocarpanone could arise from a ββ-phenolic coupling of demethylated carpacin to give (V) which by a simple rearrangement (arrows) gives carpanone-type products. The structure of (I) is further supported by the principal cleavage (dashed line in formula) in the mass spectrum which gives the base peak m/e 177 shown by accurate mass measurement to be $C_{10}H_9O_3$. This fragment could readily arise by a reverse Diels-Alder reaction followed by cleavage of a single bond, to give a conjugated allylic ion and a phenoxy radical.

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REFERENCES

1 J. Mohandas, M. Slaytor and T.R. Watson, Aust. J. Chem., 22, 1803 (1969).

2 R.S. McCredie, E. Ritchie, and W.C. Taylor, Aust. J. Chem., 22, 1011 (1969).