

## <sup>13</sup>C Nuclear Magnetic Resonance Spectra of Some Limonoids. Part I. The Structure of Procerin, an Extractive from *Carapa procera*

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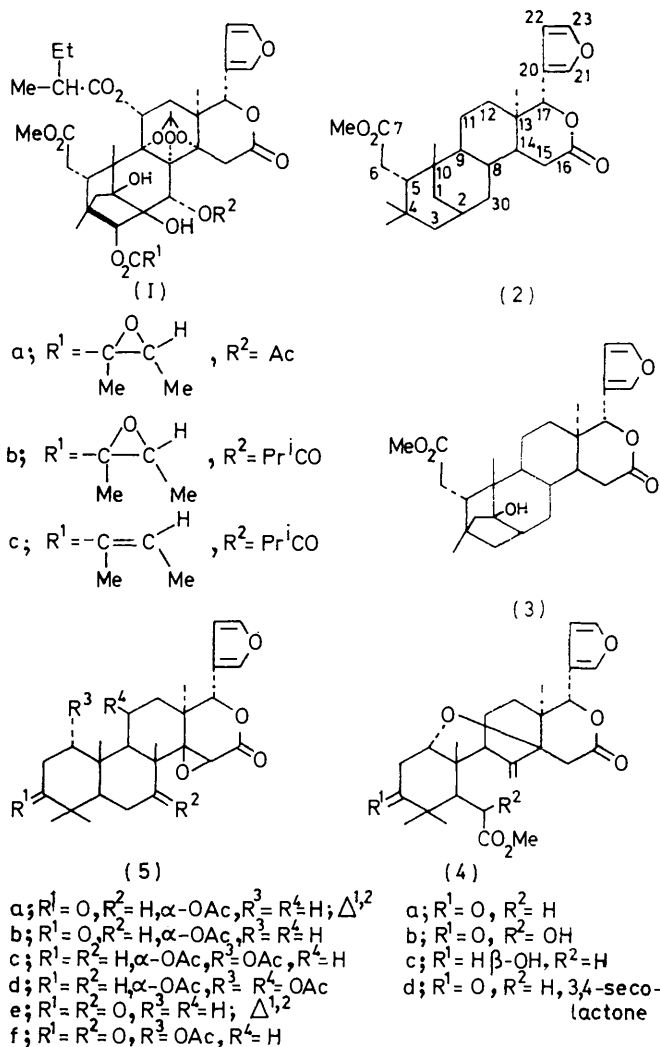
The structure (8) is suggested for procerin, a limonoid of the utilin group extracted from the timber of *Carapa procera* (Meliaceae), on the basis of chemical and spectroscopic properties, including <sup>13</sup>C n.m.r. spectra. Tables are given of the <sup>13</sup>C n.m.r. spectra of a number of other limonoids.

DURING studies in Ibadan on extractives from the Meliaceae, many compounds have been obtained which are too complex, or obtained in too small quantities, for us to have been able to determine their structures by chemical and spectroscopic means, including <sup>1</sup>H n.m.r. One method of dealing with such problems is direct crystallographic analysis, without a heavy atom. The determination of the structure of utilin (1a)<sup>1</sup> is an example. Unfortunately this method is not generally applicable; even when it is, it requires an able crystallographic collaborator.

It was hoped that application of <sup>13</sup>C n.m.r. methods might answer at least some of these problems, and for this purpose a collection of spectra of limonoids of known structure has been made. The carbon resonances in these were assigned on the basis of the residual splitting in off-resonance decoupled spectra, data from the literature, and the comparison of the spectra of closely related compounds. The spectra of a number of derivatives of methyl meliacate (2) are given in Table 1 (for nomenclature see ref. 2). Table 2 contains the spectra of some more complex compounds with the 1,29-cyclo-meliacate structure (3) typical of utilin. Some derivatives of methyl angolensate (4) are listed in Table 3, and derivatives of meliacolide (5) (for nomenclature see ref. 3) in Table 4. In some cases where resonances of the same multiplicity have similar chemical shifts, there is no certain basis for assignment, and the Tables in these cases give probable assignments only. Some of these data have been used already to reach a decision between two structural proposals for fissionolide.<sup>4</sup>

This paper reports the use of <sup>13</sup>C n.m.r. in structural diagnosis of procerin, an extractive first obtained in Ibadan from the bark of *Carapa procera*.<sup>5</sup> The <sup>13</sup>C n.m.r. spectrum showed resonances due to 41 carbon atoms. Integration of the <sup>1</sup>H n.m.r. spectrum indicated 52 hydrogen atoms. The highest mass peak in the mass spectrum (*m/e* 848·3099) corresponds to the formula C<sub>41</sub>H<sub>52</sub>O<sub>19</sub>. The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra showed the presence of two methoxycarbonyl groups, the usual β-substituted furan ring, and one tertiary hydroxy-group. Quantitative hydrolysis gave 8 mol of acid per mol of procerin, and since the <sup>13</sup>C spectrum showed only seven carbonyl carbon atoms this suggests the presence of a hydrolysable orthoester system, as in

utilin. This was confirmed by the presence of a <sup>13</sup>C resonance at 118·6 p.p.m., characteristic of an orthoester carbon atom (*cf.* utilin, 119·3; bussein, 119·1) and a resonance due to an orthoacetate methyl group at δ 1·82 in the <sup>1</sup>H spectrum (*cf.* utilin, 1·72; bussein 1·63). The <sup>1</sup>H spectrum also shows four acetate methyl groups



[δ 2·05, 2·15 (6H), and 2·36], three nuclear methyl groups (δ 1·26, 1·16, and 0·82), and a primary methyl group (δ 1·15). Analysis of the volatile acids from the

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<sup>1</sup> H. R. Harrison, O. Hodder, C. W. L. Bevan, D. A. H. Taylor, and T. G. Halsall, *Chem. Comm.*, 1970, 1388.

<sup>2</sup> E. K. Adesogan and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1968, 1974.

<sup>3</sup> N. S. Ohochuku and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1969, 864.

<sup>4</sup> D. A. H. Taylor and F. W. Wehrli, *J.C.S. Perkin I*, 1973, 1599.

<sup>5</sup> C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1963, 980.

hydrolysis (by  $^1\text{H}$  n.m.r.<sup>6</sup>) identifies this as due to a propionic acid residue.

Together, these oxygen functions, two methoxycarbonyl groups, one furan ring, one tertiary hydroxy-group, four acetates, one propionate, and one orthoacetate, account for all the oxygen atoms in procerin. Together

present has been opened as in C.O.C. (6a), a transformation product of mexicanolide.<sup>7</sup>

The  $^1\text{H}$  n.m.r. spectrum of procerin shows four signals downfield of those due to the methoxycarbonyl groups, in addition to those due to the furan ring. These are all singlets ( $\delta$  5.35, 5.64, 5.80, and 6.74). Since the  $^{13}\text{C}$

TABLE 1  
Derivatives of methyl meliacate (2);  $^{13}\text{C}$  n.m.r. spectra (solvent  $\text{CDCl}_3$ ;  $\delta_{\text{C}}$  values;  $\text{Me}_4\text{Si}$  standard)

Substituents in methyl meliacate (2)																			
Carbon atom	1,3-Dioxo- $\Delta^8(14)$	1,3-Dioxo- $\Delta^{14}(15)$	1,3-Dioxo-2-hydroxy- $\Delta^{14}(15)$	1,3-Dioxo- $\Delta^8(9), 14(15)$	$3\beta$ -Acetoxy-1-oxo- $\Delta^8(14)$	$3\beta$ -Acetoxy-1-oxo- $\Delta^8(9), 14(15)$	$3\beta$ -Acetoxy-1-oxo- $\Delta^8(9), 14(15)$	$3\beta$ -Acetoxy-2-hydroxy-1-oxo- $\Delta^8(14)$	$3\beta$ -Acetoxy-2-hydroxy-1-oxo	$3\beta$ -Acetoxy-1-oxo- $\Delta^8(9)$	$3\beta$ -Acetoxy- $3\beta$ -Isobutyryloxy-1-oxo	$3\beta$ -Acetoxy-8,30-epoxy-1-oxo	6-Hydroxy-1,3-dioxo- $\Delta^8(14)$	$3\beta$ -Acetoxy-6-hydroxy-1-oxo- $\Delta^{14}(15)$	1-Hydroxy-3-oxo- $\Delta^{14}(15)$	1-Oxo- $3\beta$ -tigloyloxy- $\Delta^8(9)$ (swietenine)	C.O.C. acetate (6b)		
1	212.7	213.0	212.9	210.6	217.6	213.3	214.0	217.4	218.6	216.8	217.0	214.0	213.2	212.7	79.2	216.5	218.9		
2	58.0	57.1	81.7	55.3	52.3	48.9	53.8	78.0	77.3	56.5	56.4	55.8	57.8	49.4	44.0	57.6	56.5		
3	210.9	211.4	108.6	209.8	78.4	78.2	78.4	85.7	85.9	77.4	79.2	78.8	210.0	80.3	219.8	78.5	77.4		
4	49.4	50.0	41.9	48.9	38.2	37.4	38.7	39.0	38.7	38.1	38.7	39.2	49.4	38.4	46.3	39.0	38.1		
5	50.5	48.8	53.3	45.4	48.0	46.7	48.9	52.2	47.1	48.4	48.7	48.6	53.4	46.5	50.2	49.0	47.7		
6	32.3	32.6	32.5	31.9	33.4	32.3	32.7	33.3	33.1	32.0	32.7	33.4	73.2	73.6	33.8	72.8	33.4		
7	173.5	173.5	174.4	173.4	174.1	173.8	173.7	174.0	174.2	174.1	174.0	174.2	174.9	175.7	174.8	175.9	173.8		
8	133.8	33.1	53.3	124.6	131.7	125.5	136.2	133.0	57.8	138.4	50.1	60.4	134.1	34.9	35.0	138.3	133.8		
9	40.2	40.0	41.5	150.9	40.8	151.9	40.5	40.9	41.6	41.6	41.4	42.5	44.4	44.9	40.3	45.5	41.1		
10	54.3	52.2	52.3	52.6	52.9	51.2	52.0	52.2	50.7	49.9	49.2	48.2	54.5	51.2	42.8	50.4	51.7		
11	18.6	18.6	19.6	21.9	18.8	22.3	21.6	18.8	19.9	22.4	19.2	19.4	18.6	18.6	17.5	21.2	20.1		
12	28.8	26.8	32.0	30.1	29.2	30.9	33.0	29.2	30.0	30.1	29.9	33.0	28.7	26.8	27.1	29.6	35.7		
13	37.8	38.2	36.9	36.9	38.1	36.9	37.6	38.3	35.2	36.8	36.9	36.4	38.1	38.2	38.1	36.7	43.1		
14	125.3	164.2	165.6	157.6	127.7	158.1	160.6	125.7	45.4	45.2	45.2	45.9	126.0	164.3	164.8	45.1	133.7		
15	32.9	113.9	118.6	111.3	33.9	109.9	112.4	33.5	33.1	34.4	33.9	33.7	33.1	113.0	113.2	34.6	35.5		
16	169.7	168.3	166.5	165.2	170.1	165.4	164.9	169.9	170.2	170.8	169.4	172.0	169.5	170.2	170.1	168.5	172.0		
17	80.6	81.0	81.1	80.4	80.6	80.7	79.7	80.6	76.7	77.5	77.0	77.0	80.6	81.2	81.2	76.7	79.0		
20	120.4	119.9	119.9	119.8	120.6	120.0	120.2	120.5	120.8	120.7	120.7	120.7	120.4	119.9	119.9	121.4	123.9		
21*	142.7	143.0	143.1	143.0	142.7	143.0	143.1	142.9	143.1	142.9	142.9	143.1	142.9	143.1	142.9	143.1	143.0		
22	109.8	109.8	110.0	109.8	109.8	110.0	110.2	109.8	109.8	109.7	109.7	110.2	109.7	109.8	109.8	109.2	110.7		
23*	141.5	141.2	141.4	141.2	141.6	141.2	141.4	141.8	141.6	141.8	142.0	141.0	141.2	141.2	141.2	140.5	142.1		
30	36.4	37.7	47.0	34.0	33.4	30.2	128.8	44.2	35.1	122.8	56.7	63.6	36.4	35.4	35.7	123.6	34.2		
$\text{OCH}_3$	52.1	52.2	52.0	52.2	51.9	52.0	52.0	52.2	52.2	52.2	52.1	52.3	52.1	53.3	51.9	53.2	56.2, 51.8, 51.7		
MeCO					169.6	169.6	170.1	169.6	170.0	169.6	168.7	169.8		169.8		166.9	170.4		
$\text{CCCH}_3$	21.9	22.0	22.6	24.5	23.2	25.9	22.2	22.7	23.6	22.4	21.8	26.2	21.0	23.8	27.7	23.0	23.7		
	17.8	19.0	21.7	21.4	21.1	25.2	22.0	21.2	22.2	22.0	( $\times 3$ ) 20.7	22.5	20.5	23.1	25.6	22.8	21.1		
	17.8	18.6	18.8	16.0	20.5	20.7	21.2	19.9	20.7	20.4	18.6	20.7	17.6	20.7	21.7	21.2	20.8		
	17.4	18.0	16.8	15.4	18.0	16.7	20.7	18.1	19.9	20.4	15.7	20.7	17.6	18.4	17.9	16.5	19.4		
					16.7	16.0	15.6	16.8	17.7	15.8		16.6		17.1		14.6	16.6		
Other (extra nuclear)											22.4					11.6	139.0		
											(d)					(d)	(s)		
																127.7			

\* These rows may be interchanged.

with the normal  $\text{C}_{28}$  nucleus of a limonoid, they also account for all the carbon atoms.

It is significant that procerin contains no lactone system. Either therefore it belongs to the carbocyclic-ring-D group of limonoids, or else the lactone ring usually

n.m.r. spectrum shows no double bonds (except those in the furan ring), these must correspond to the carbinol protons of four secondary ester groups, the other oxygen functions being tertiary.

Similar carbinol singlets are characteristic of sub-

<sup>6</sup> D. H. Calam and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1966, 949.

<sup>7</sup> E. K. Adesogan, C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1966, 2127.

stituents in the bicyclononane system of methyl meliacate derivatives (e.g. 2-hydroxyfissinolide<sup>8</sup> and utilin<sup>1</sup>) and they are not known to be produced by any other nucleus. We therefore assume as a working hypothesis the presence

TABLE 2

Derivatives of methyl 1,29-cyclomeliacate (3); <sup>13</sup>C n.m.r. spectra (solvent CDCl<sub>3</sub>; δ<sub>C</sub> values; Me<sub>4</sub>Si standard)

Carbon atom	Utilin (1a)	Bussein hydrolysis product acetate methyl ester (7b)	Bussein (7a)	Procerin (8)
1	84.2	83.9	84.3	84.2
2	74.9	77.7	79.6	83.1
3	84.1	82.9	83.0	79.1
4	51.1	45.6	44.9	46.4
5	41.0	42.4	43.6	37.0
6	34.1	33.5	33.3	33.3
7	174.3	172.5	172.7	172.6
8	89.6	85.8	90.8	89.0
9	87.2	85.1	84.9	88.2
10	44.1	45.6	45.7	45.9
11	64.6	69.3	70.0	22.8
12	30.1	68.7	68.9	27.8
13	38.7	38.5	45.7	44.8
14	84.5	36.4	41.4	85.7
15	37.5	27.5	176.2	61.9
16	168.9	169.2	168.7	171.8
17	77.1	76.7	73.9	78.4
20	120.6	121.3	122.0	122.9
21*	142.3	143.2	142.7	142.6
22	110.1	109.8	109.9	109.7
23*	141.4	140.6	141.3	141.2
29	40.0	39.9	39.9	38.6
30	70.0	70.1	70.0	71.1
OCH <sub>3</sub>	51.6	51.7	51.8	52.1, 51.5
CO <sub>2</sub> R	170.5	170.5	170.5	170.9, 169.6
	172.4	170.5	169.2	169.4, 169.2
	168.0		168.4	168.1
MeCO <sub>3</sub>	119.3	119.5	119.1	118.6
MeC(OH)O <sub>2</sub>		77.1	77.1	
Other (extra nuclear)	57.8(s)		183.3(s)	27.0(t)
	57.8(d)		36.9(d)	
	40.3(d)		30.3(d)	
	25.1(t)		26.5(t)	
CCH <sub>3</sub>	20.3	21.1		21.4
	18.7	21.0	20.7	21.4
	17.7	20.7	20.7	21.0
	17.0	19.9	20.3	21.0
	16.6	15.8	19.7	18.4
	16.4	15.6	18.4	16.4
	15.1	14.2	17.8	13.4
	13.4		16.8	11.5
	11.3		15.9	8.6
			14.2	
			11.6	

\* These rows may be interchanged.

of a bicyclononane system. The partial synthesis of mexicanolide,<sup>9</sup> which is believed to follow the biochemical route, depends for the formation of the bicyclononane system on the presence of a lactone ring D. It therefore seems unlikely that we have a bicyclononane containing a carbocyclic ring D, and more likely that procerin has an opened lactone ring similar to that in C.O.C. (6a). This conclusion is supported by the <sup>1</sup>H n.m.r. spectrum of procerin. In the <sup>1</sup>H n.m.r. spectra of all the ring D

<sup>8</sup> E. K. Adesogan and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1970, 1710.

<sup>9</sup> J. D. Connolly, I. M. S. Thornton, and D. A. H. Taylor, *Chem. Comm.*, 1971, 17.

TABLE 3  
Derivatives of methyl angolensate (4); <sup>13</sup>C n.m.r. spectra (solvent CDCl<sub>3</sub>; δ<sub>C</sub> values; Me<sub>4</sub>Si standard)

Carbon atom	Methyl angolensate (4a)	Methyl 6-hydroxy-angolensate (4b)	Methyl 3β-hydroxy-angolensate (4c)	Methyl ivorensate (4d)
1	77.8	79.2	75.0	73.4
2	40.4	40.1	37.7	41.5
3	212.7	212.2	72.5	169.5
4	49.0	49.8	50.0	83.8
5	50.9	51.9	50.5	51.9
6	33.7	73.3	34.0	34.1
7	174.3	177.1	174.6	173.3
8	146.4	146.6	146.6	145.7
9	43.9	48.5	32.5	43.4
10	45.0	45.7	43.9	47.6
11	24.7	25.1	24.0	24.0
12	30.1	29.7	29.6	32.0
13	42.4	42.4	39.8	41.6
14	81.1	81.3	80.0	81.3
15	34.5	34.5	37.7	35.7
16	170.4	170.5	170.4	170.0
17	80.2	80.3	80.0	79.3
20	121.6	121.6	121.0	120.7
21*	143.3	143.3	142.7	142.6
22	110.7	110.7	109.9	109.9
23*	141.4	141.3	140.7	140.9
30	112.3	112.3	110.8	111.9
OCH <sub>3</sub>	52.9	54.2	51.9	55.2
CCH <sub>3</sub>	26.5	25.9	27.1	28.8
	22.6	24.9	22.0	22.5
	22.6	24.5	14.4	22.0
	14.8	15.0	13.9	13.8

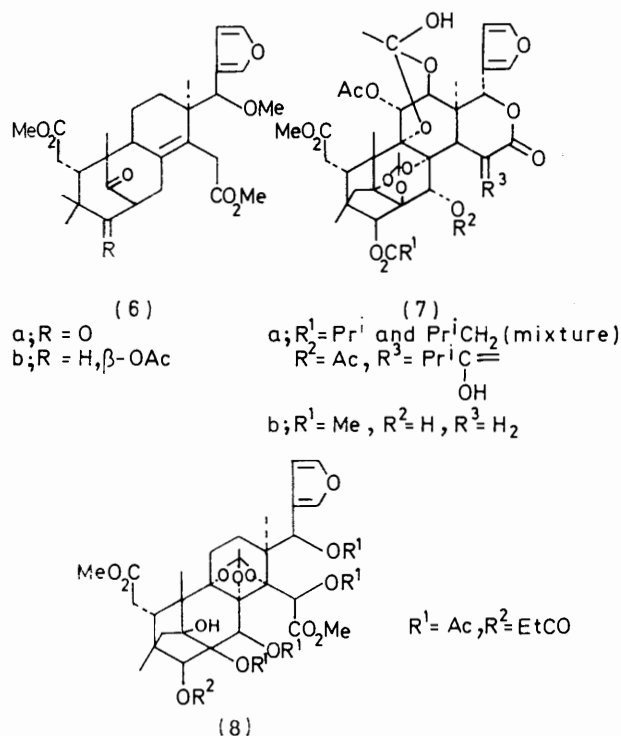
\* These rows may be interchanged.

TABLE 4  
Derivatives of meliacolide (5); <sup>13</sup>C n.m.r. spectra (solvent CDCl<sub>3</sub>; δ<sub>C</sub> values; Me<sub>4</sub>Si standard)

Carbon atom	Gedunin (5a)	Dihydro-gedunin (5b)	Khivorin (5c)	11β-Acetoxy-khivorin (5d)	7-Oxo-gedunin (5e)	7-Oxo-khivorin (5f)
1	157.0	33.7	72.3	75.1	156.0	72.5
2	125.9	47.8	25.6 †	25.2 †	126.3	25.8 †
3	203.8	215.7	75.9	75.5	203.2	75.8
4	44.0	46.6	35.9	36.0	45.2	37.3
5	39.5	38.9	37.0	37.8	47.6	45.8
6	14.9 †	15.0 †	22.3 †	22.9 †	36.7 †	35.7 †
7	73.2	73.7	73.8	73.0	208.3	209.4
8	42.6	42.0	42.2	41.9	53.4	52.9
9	46.0	44.0	36.3	39.7	53.7	44.4
10	40.0	37.4	40.7	41.5	40.0	40.5
11	17.7 †	17.4 †	14.4 †	87.0	17.1 †	15.9 †
12	18.3 †	23.8 †	26.1 †	37.5	32.1 †	32.2 †
13	38.7	38.8	38.8	37.8	37.7	37.3
14	69.8	69.8	69.7	68.7	65.7	65.4
15	56.9	56.7	56.4	54.7	54.5	53.3
16	167.4	167.6	167.6	167.1	166.9	167.3
17	78.2	78.4	78.4	78.3	78.0	78.2
20	120.5	120.5	120.5	120.0	120.3	120.4
21*	143.0	142.9	143.0	143.3	143.1	143.7
22	109.8	109.8	109.9	109.8	109.8	109.8
23*	141.4	141.1	141.1	141.2	141.0	141.0
MeCO	169.8	169.8	169.9	169.9	169.5	169.5
			169.7	169.6	170.1	
			169.6	(× 2)		
CCH <sub>3</sub>	27.2	26.1	27.4	27.4	27.0	26.9
	26.0	25.9	21.6	21.8	20.9	21.1
	23.3	21.1	21.3	21.6	20.7	21.1
	21.7	20.9	21.1	21.4	19.7	20.8
	21.0	18.0	21.1	21.2	17.4	20.8
	19.7	15.7	18.3	21.2		16.9
			17.3	20.1		16.8
			16.4	17.6		
				(× 2)		

\* These rows may be interchanged. † Assignment doubtful.

lactones of the limonoid group, and of C.O.C. (6a), the resonance due to H-17 is characteristically broadened<sup>10</sup> in comparison with other singlets in the same spectrum. The band at  $\delta$  5.80 in the spectrum of procerin is broadened in this way, and could correspond to H-17, the other



singlets being much sharper. There is no signal detectable in the  $\delta$  3–4 region which can be assigned to H-17 in a carbocyclic ring D. The chemical shift of  $\delta$  5.80 assigned to H-17 is similar to that in the lactones, and requires an acyloxy-substituent at C-17, not an ether as in C.O.C. (6a)

Derivatives of the methyl meliacate group containing the bicyclononane system normally have a 1-oxo-group. The <sup>13</sup>C n.m.r. spectrum of procerin shows that no ketone is present. The only known natural bicyclononanes without a 1-ketone are members of the group of 1,29-cyclo-compounds, which so far contains utilin (1a),<sup>1</sup> entandrophragmin (1b),<sup>1</sup> candollein (1c),<sup>11,12</sup> bussein (7a),<sup>13</sup> and the closely related phragmalin.<sup>14</sup> The presence of this bridge in procerin is suggested by the fact that only three nuclear methyl groups are shown by the <sup>1</sup>H n.m.r. spectrum, instead of the usual four in methyl meliacate. It is supported by the <sup>13</sup>C n.m.r. spectrum of procerin, which is similar in detail to those of utilin and of bussein hydrolysis product acetate methyl ester (7b), and in particular shows a triplet at 38.6 p.p.m. which may be ascribed to C-29 in this bridged ring structure (cf. utilin, 40.0; bussein, 39.9 p.p.m.). A doublet of doublets ( $\delta$  3.04 and 2.74, *J* 13 Hz) in the <sup>1</sup>H n.m.r. spectrum may be ascribed to the two C-29 protons in

this structure (utilin,  $\delta$  2.77 and 2.17, *J* 10 Hz; bussein,  $\delta$  3.15 and 2.55, *J* 10 Hz). The doublet of doublets which commonly arises from the 15-protons has a larger coupling constant, typically 19 Hz. We therefore consider that these further observations strongly support the hypothesis that procerin contains a bicyclononane system, and that this is present in a 1,29-cyclomeliacate skeleton (3), which has been modified by the opening of ring D to give a  $\delta$ -acyloxy-methyl ester. To identify procerin completely, it is necessary to locate in this nucleus the oxygen functions already mentioned, *i.e.* four secondary esters (including that already located at C-17), one tertiary ester, an orthoacetate, and a tertiary hydroxy-group.

Normally, orthoacetates are resistant to alkaline hydrolysis, as in bussein. The orthoacetate in procerin is hydrolysed, as shown by the results of total acid titration. The orthoacetate in utilin is similarly hydrolysed; this is because one of the points of attachment is C-14,  $\beta$  to the lactone carbonyl group, where it can be lost by elimination to give an  $\alpha\beta$ -unsaturated ester and a hemi-orthoacetate, which is hydrolysed by alkali. We therefore assign one oxygen of the orthoacetate in procerin to C-14, to allow the same mechanism to operate in this case. We consider the other points of attachment to be C-8 and C-9, as in utilin, since this is known to give a stable, naturally occurring group.

We assign two of the secondary esters to C-3 and C-30, in accord with the usual substitution pattern. For these to give rise to <sup>1</sup>H n.m.r. carbinol singlets, it is necessary for tertiary oxygen atoms to be located at C-2 and C-9, and a tertiary oxygen atom is also expected at C-1, resulting from the ring A bridging. From comparison with bussein, the singlets at  $\delta$  5.35 and 5.64 may be ascribed to H-3 and H-30, respectively.

This leaves one secondary ester group to be located. Three lines of evidence suggest that this is at C-14. (a) This is the only location left in the nucleus where an ester would give rise to a carbinol singlet, except C-29 which is believed to be unsubstituted. (<sup>1</sup>H and <sup>13</sup>C n.m.r.; see above). (b) The chemical shift of the remaining singlet ( $\delta$  6.74) is unusually large, suggesting location next to a carbonyl group. (c) The usual C-15 proton n.m.r. signals (utilin,  $\delta$  3.35 and 2.53, *J* 19 Hz) are absent in procerin, although this might also be due to the opening of the lactone ring.

An alternative possibility is that the ester is at C-6, as in many known limonoids. This substitution normally gives rise to a broad H-6 singlet, owing to weak coupling with H-5. The singlet at  $\delta$  6.74 is much sharper than this, showing no sign of weak coupling. Further, there is a two-proton doublet at  $\delta$  2.26 (*J* 7 Hz) and what appears to be a one-proton triplet at  $\delta$  2.88 (*J* 7 Hz). Although these have not been shown to be coupled, and one band of the supposed triplet is obscured by the AB

<sup>10</sup> K. Wragg, unpublished results.

<sup>11</sup> R. Hanni and Ch. Tamm, *J.C.S. Chem. Comm.*, 1972, 1253.

<sup>12</sup> N. S. Ohochuku and J. W. Powell, *Chem. Comm.*, 1966, 422.  
<sup>13</sup> G. A. Adesida and D. A. H. Taylor, *Phytochemistry*, 1967, **6**, 1429.

<sup>14</sup> R. R. Arndt and W. H. Barschers, *Tetrahedron*, 1972, **28**, 2333.

system ascribed to 29-H<sub>2</sub>, these correspond to the positions of the 6-H<sub>2</sub>, 5-H system in the spectra of many methyl meliacate derivatives.

We consider that the tertiary acetate is more likely to be at C-2, leaving the tertiary hydroxy-group at C-1, on grounds of steric hindrance, and because 2-acetyl derivatives are known, *e.g.* 2-acetoxifissinolide.<sup>8</sup>

There is no evidence to show where the propionate ester system is situated. In view of the number of natural products with more complex ester groups at C-3 and acetates at other positions (*e.g.* utilin, bussein, and methyl 30-acetoxy-3 $\beta$ -isobutyryloxy-1-oxomeliacate<sup>15</sup>) it is perhaps more likely that the propionate is at C-3. We therefore consider that procerin is represented by the structure (8), in which the acyl groups are most probably distributed as shown. Assignments of the <sup>13</sup>C n.m.r. spectrum of procerin, based on this structure, are included in Table 2.

#### EXPERIMENTAL

*Isolation of Procerin.*—The milled bark of *Carapa procera* (10 kg) was extracted with refluxing light petroleum (b.p. 60–80°). The solid which precipitated from the cold, concentrated extract was recrystallised from methanol to give a mixture (130 mg), m.p. 260–270°, not separated on further crystallisation. This (70 mg) was kindly separated by t.l.c. by Dr. J. D. Connolly, to give procerin (43 mg) and a second compound (24 mg). Previous extractions of *Carapa* bark had given only procerin.<sup>5</sup>

Crystallised from methanol, procerin had m.p. 296–301°,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>; 60 and 100 MHz) 7.64 and 7.39 (m, 2  $\times$   $\alpha$ -furan), 6.74(s), 6.46 (m,  $\beta$ -furan), 5.80(s), 5.64(s), 5.35(s), 3.9 (s, OH), 3.72(s) and 3.66(s) (2  $\times$  OMe), 3.04 and 2.74 (dd, *J* 13 Hz), 2.86 (t, *J* 8 Hz), 2.26 (2H, d, *J* 8 Hz), 2.36, 2.15 (6H), 2.05, 1.82, 1.26, and 0.82 (all s, 8  $\times$  CMe tert.), and 1.15 (t, *J* 7.5 Hz, CMe primary) (Found: *M*<sup>+</sup>, 848.3099. Calc. for C<sub>41</sub>H<sub>52</sub>O<sub>19</sub>: *M*, 848.3103). The second compound, m.p. 285–288°, had *M*<sup>+</sup> 424 (probably C<sub>26</sub>H<sub>32</sub>O<sub>6</sub>).

*Quantitative Hydrolysis of Procerin.*—Procerin (13.7 mg) was dissolved in methanol (10 ml) and aqueous 0.1N-sodium hydroxide (10 ml) and refluxed for 0.5 h. Titration against aqueous 0.1N-hydrochloric acid (phenolphthalein; 8.7 ml required) revealed the production of 8.06 mol of acid per mol of procerin. The solution was treated with more 0.1N-hydrochloric acid (total 10 ml) and distilled to dryness. The residue was treated with water (10 ml) and distilled to dryness again. Titration of the combined distillates with 0.01N-sodium hydroxide (phenolphthalein) required 8.1 ml, equivalent to the production of 5.01 mol of volatile acid for every mol of procerin. The neutralised solution from the titration was evaporated to dryness, and the residue was dissolved in D<sub>2</sub>O. <sup>1</sup>H N.m.r. spectroscopic examination of the solution showed the presence of acetic and propionic acids in the ratio 10 : 1.

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<sup>15</sup> D. A. H. Taylor, *J. Chem. Soc. (C)*, 1969, 2439.