

PROTON MAGNETIC RESONANCE SPECTRA OF PHYTOXANTHONES

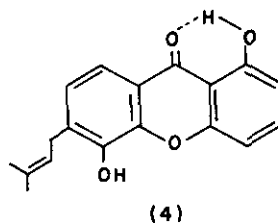
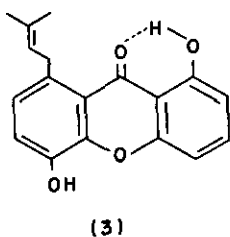
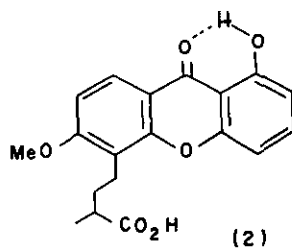
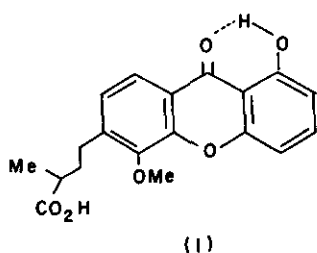
M. Afzal and J.M. Al-Hassan\*

Biochemistry Department, University of Kuwait,

P.O. Box 5969, Kuwait.

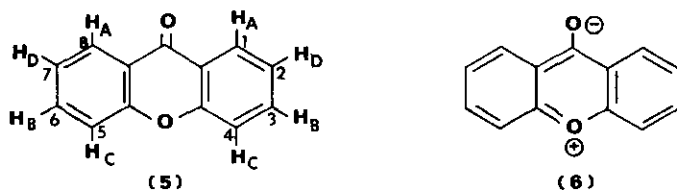
Proton magnetic resonance spectra of phytoxanthones with particular reference to structural elucidation has been discussed.

Pmr and cmr spectroscopy has been of immense use in determining the structure of natural xan-  
thones. Substitution patterns are usually determined on the basis of chemical shift and spin  
coupling data for the aromatic protons<sup>1</sup>. Thus in structures (1) and (2) for scriblitifolic  
acid, a metabolite of Callophyllum scriblitifolium Hend & Wyatt Smith, the chemical shifts of  
aromatic protons favoured structure (1) for this compound, although the position of aromatic  
protons in (1) and (2) remain unchanged. Also in guanandin (4) and isoguanandin (3), where  
the oxygenation pattern is the same, differentiation between the two metabolites has been made  
by careful interpretation of the chemical shifts of the aromatic protons<sup>2</sup>.



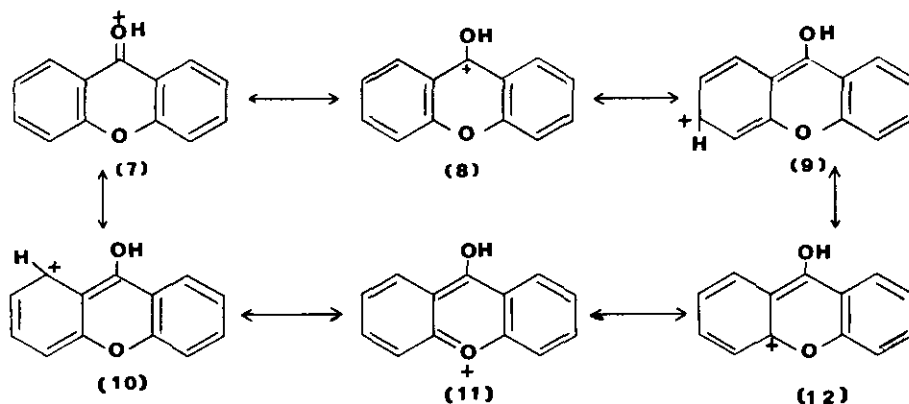
In order to predict the substitution and oxygenation pattern of xanthenes, it is now possible to calculate the chemical shifts of the aromatic protons of any xanthone containing hydroxy, alkoxy, alkyl and even fused ring substituents. This has been made possible by finding out the fundamental parameters for xanthone itself<sup>3</sup>.

Martin et al<sup>4</sup> have reported that the protons at the C-1 and C-8 positions of xanthone skeleton (5) are deshielded by the anisotropic effect of the ortho carbonyl group. These



workers have assigned chemical shifts to the other six protons. Scheinmann and co-workers<sup>3</sup> have reaffirmed the chemical shifts of H-1 and H-8 in xanthone nucleus. These workers have also measured the chemical shifts of xanthone, in different solvents and were able to assign the other six protons along with protons at C-1 and C-8, by collecting the data obtained through first order analysis of spectra at 60,100 and 220 MHz instruments.

From a graphical correlation of chemical shifts of H-1, H-2, H-3 and H-4 in various solvents (Fig.1), H-1 appeared anomalous, but H-2, H-3 and H-4 the signals were deshielded with increasing dielectric constants of the solvent<sup>5</sup>. The anomaly for H-1 has been explained in terms of solvation in deuterioacetone and deuteriodimethyl sulphoxide, which favours separation of charge typified by canonical form (6), resulting in diminished diamagnetic anisotropy of the carbonyl group. This results in shielding of H-1 as compared with measurements in deuteriochloroform. A similar effect has been demonstrated when trifluoroacetic acid is used as solvent, in which relative deshielding of hydrogen is maximum at C-1 and C-3 and minimum at C-2 and C-4. Use of pentadeuterio pyridine (dielectric constant 12.5) as solvent, has also been suggested to make solvent - solute collision complex<sup>6</sup> at the ring carbonyl group, thus resulting in deshielding at C-1 and shielding at other positions when compared with corresponding measurements in deuteriochloroform.



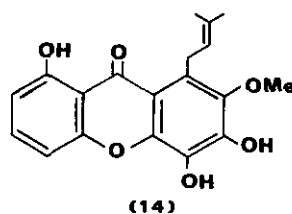
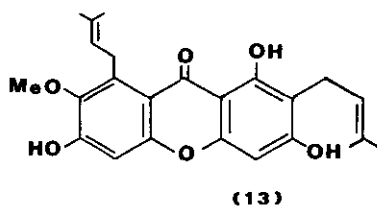
(Fig. 1)

Coupling constants are also suggested to be solvent dependent. It has been observed that ortho-coupling increases with increasing dielectric constant of the solvent and regular changes occur with meta- and para-coupling constants.

The fundamental parameters of the A, B, C and D protons of xanthone (5) in various solvents have been measured by Schienmann and co-workers and the effect of oxygen substituent on these parameters has also been measured in these solvents. The magnitude of increments on chemical shift of the protons at C-1, C-2, C-3 and C-4, caused by ortho-, meta- and para-hydroxy- or alkoxy- substituent has been calculated by subtracting the spectrum of xanthone from the spectrum of reference compounds with a mono-oxygenated ring. The additive shielding parameters for various aromatic protons in mono- and dioxygenated xanthenes are in good agreement with the experimental values. Although the diamagnetic effect of hydroxy- and alkoxy groups on neighbouring aromatic protons is reported<sup>7</sup> to be identical, irrespective of the relative location of the oxygenated site and the proton. Scheinmann *et al*<sup>3</sup> have shown that a slight but consistent paramagnetic shift of the proton signal occurs upon methylation of ortho and para-hydroxy groups in xanthenes. This effect is specially pronounced for the signal due to H-4 upon methylation of a 1-hydroxy group.

The effect of a variety of C-substituents on the chemical shift of the protons on the xanthone nucleus has been shown to be less significant. The variations around the mean calculated values have been attributed to purely steric effects. The chemical shifts of the methylene groups adjacent to the xanthone nucleus in mangostin<sup>8</sup> (13) a metabolite of mangosteen tree,

Garcinia mangostana, and celebixanthone (14) have been suggested<sup>9</sup> to depend whether the side chain was attached to an electron poor site (C-1 or C-3) or to a relatively electron rich site (C-2). Whereas Scheinmann et al<sup>10</sup> have shown that the chemical shifts of the benzylic methylene group in 5-allyl-1,6-dihydroxy and 6-allyl-1,5-dihydroxyxanthone derivatives are the same, if the side chain was para - or meta- to the xanthone carbonyl group. Thus these workers have suggested that the low chemical shift of the methylene group attached to C-1 or C-8 in mangostin (13) and celebixanthone (14) was because of the close proximity of the xanthone carbonyl group which causes deshielding largely by anisotropic effect<sup>11</sup> in preference to electrostatic effects<sup>12</sup>.



Similarly the position of side chain and oxygenation pattern of a large number of natural xanthones has been established with the help of proton magnetic resonance spectroscopy.

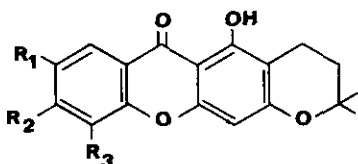
Arends and Helboe<sup>13,14</sup> have described a supplementary method based upon measurement of the chemical shifts in DMSO- $d_6$  of the hydroxyl protons of oxygenated xanthones, for structure elucidation. These workers have established the substitution pattern on xanthone nucleus by measuring the chemical shift of the hydroxyl protons present, either isolated or in conjunction with other hydroxy/prenyl groups in the same ring of xanthone nucleus.

Benzene induced solvent shifts for isolated OMe groups have been particularly useful in establishing the positions of these groups. It has been shown<sup>15-17</sup> that isolated OMe groups are selectively solvated in benzene relative to chloroform or carbon tetrachloride. The resonances of such OMe groups suffer a 20-40  $H_z$  upfield shift in benzene relative to comparatively "inert" solvent, such as carbon tetrachloride or deuteriochloroform<sup>18-20</sup>. The potential of such solvent shifts for structure elucidation in the coumarin and flavones has also been emphasised<sup>20,21</sup>. Use of this techniques has been made by Scheinmann et al for structure elucidation of xanthones. Thus the solvent induced shifts ( $\Delta$ ) in hexadeuteriobenzene relative to deuteriochloroform have been recorded according to the definition<sup>21,22</sup>.

$$\Delta \text{ (p.p.m.)} = \tau_{C_6D_6} - \tau_{CDCl_3}$$

The  $\Delta$ -values for C-2 protons vary from -0.30 to 0.12 p.p.m. depending upon the nature of the other substituents and for C-4 protons, the values vary from -0.15 to +0.30 p.p.m. These workers have further suggested that this spread of the values for the 2- and 4- protons resulting from variation in xanthone substitution pattern indicates a collision complex of hexadeuteriobenzene not only with ring carbonyl but also with certain ring substituents. These workers have recorded benzene induced solvent shifts for a number of substituted xanthenes. Dreyer<sup>23</sup> has made use of this technique for structure elucidation of four natural xanthenes.

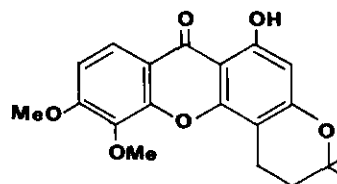
Scheinmann and co-workers<sup>24,25</sup> have also examined dimethyl ethers of dihydrojacareubin and dihydroisojacareubin, to establish  $\Delta$  - values for linear and angular isomers (15) and (16) respectively. Under identical conditions, the benzylic methylene group in (15) had a lower  $\Delta$ -value (0.07 p.p.m.) than that in the angular isomer (16), (0.22 p.p.m.).



(15)  $R_2 = R_3 = OMe$ ;  $R_1 = H$

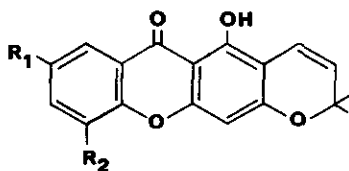
(17)  $R_2 = R_3 = H$ ;  $R_1 = OMe$

(18)  $R_1 = R_2 = H$ ;  $R_3 = OMe$



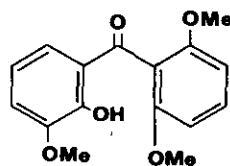
(16)

The  $\Delta$ -values, for the benzylic methylenes in the monomethyl ethers of dihydro-osajaxanthone (17) ( $\Delta = 0.08$  p.p.m.) and dihydro-6-deoxyjacareubin (18) ( $\Delta = 0.09$  p.p.m.), have supported<sup>26</sup> the linear pyranoxanthone structures for osajaxanthone (19) and 6-deoxyjacareubin (20), metabolites of *Calophyllum scriblitifolium* Hend & Wyatt-Smith.



(19)  $R_1 = OH$ ;  $R_2 = H$

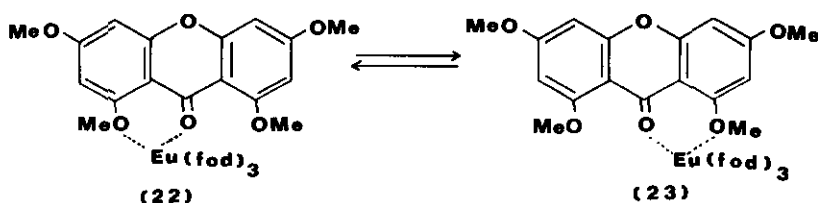
(20)  $R_1 = H$ ;  $R_2 = OH$



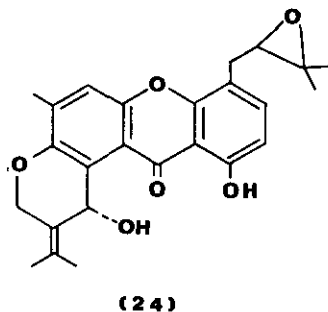
(21)

Structure (21) for 2-hydroxy-2',3-6'-trimethoxybenzophenone, an intermediate in the synthesis of 1,5-dihydroxy and 5-hydroxy-1-methoxyxanthenes was proved<sup>27</sup> by benzene induced shifts. Thus the n.m.r. spectra of (21) in deuteriochloroform and in hexadeuteriobenzene were shifted by about 0.5 p.p.m. in aromatic solvent<sup>5,16</sup>.

The effects of  $\text{Eu}(\text{fod})_3$ , tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato europium III), on the Pmr spectra of xanthenes has also been studied<sup>28,29</sup>. The shifts of protons attached to C-2 of the xanthenes are shown to be greater than those attached to C-4, indicating that the  $\text{Eu}^{3+}$  atom coordinates with the carbonyl oxygen and the methoxyl oxygen of the 1- and 8- methoxyxanthenes. However, in the case of 1,8-dimethoxyxanthenes the  $\Delta \text{Eu}$  values of the H-2 are shown<sup>30</sup> to be much smaller than those of 1-methoxyxanthenes indicating that the  $\text{Eu}^{3+}$  co-ordinates to both the carbonyl oxygen atom and the neighbouring methoxy-oxygens (22,23) in which the co-ordination number<sup>31</sup> of  $\text{Eu}^{3+}$  is 8



<sup>13</sup>C Nuclear magnetic resonance spectroscopy has also been used for structural elucidation of naturally occurring complex xanthenes<sup>32</sup>. Thus valuable structural information has been obtained by using <sup>13</sup>C n.m.r. in case of tajixanthone (24) and other metabolites of *Aspergillus varieocolor*<sup>33</sup>. The <sup>13</sup>C n.m.r. has also been recorded for arugosin A,B,C, the metabolites of *Aspergillus rugulosus*<sup>34</sup>. The reported proton magnetic resonance spectra of the phyto-xanthenes are reproduced in the forthcoming tables.



Compound	Solv	PMR Values	Ref.
<u>Mono-oxygenated Xanthenes</u>			
2-Hydroxy	a	1.48, br.d (J 7.OH <sub>2</sub> ), 8-H; 1.76-2.75, m, 1, 3-7H	30,35-42
2-Methoxy	b	1.76, q, 8-H; 2.4, d, 1-H; 2.4, t, 3 & 6-H; 2.6-2.9,m, 4-, 5- & 7-H; 6.20, s, OMe.	42-45,74
<u>Dioxygenated Xanthenes</u>			
3-Hydroxy-2-methoxy	a	1.98, s, 1-H; 1.28, br.d (J 7H <sub>2</sub> ), 8-H; 1.48-2.28, m, 5-, 6-, & 7-H;2.50, s, 4-H; 5.76, s, OMe.	35
3-Hydroxy-4-methoxy	c	1.86, q(J 8 & 1H <sub>2</sub> ), 8-H; 2.19,t(J 8 & 8H <sub>2</sub> ), 6-H; 2.21, d(J 8H <sub>2</sub> ), 1-H; 2.35, q(J 8 & 1H <sub>2</sub> ), 5-H; 2.57, t(J 8 & 8H <sub>2</sub> ), 7-H; 3.01, d(J 8H <sub>2</sub> ), 2-H; 6.08, s, OMe.	42,46
1,5-Dihydroxy	c	-2.40, -0.24 exchangeable with D <sub>2</sub> O; 2.19-3.49, m; 6H.	30,36,40, 42,47-52
5-Hydroxy-1-methoxy	c	0.0, br. s, 5-OH (exchangeable), 2.1-2.1, m, Ar-H; 6.03, s, OMe.	27,51,53
1-Hydroxy-5-methoxy	b	-2.79, s, 1-OH; 2.11, q, 8-H; 2.31, t, 3-H; 2.70, m, 7-H; 2.92, d, 4-H; 3.15, d, 2-H; 5.93, s, 5-OMe.	
1,2-Dihydro-6-hydroxy-3,3-dimethylpyrano-(2,3- $\alpha$ ) xanthene-12(3H)-one. (Cardato-oblongu-xanthone)	c	1.85, q(J 8 & 1H <sub>2</sub> ), 8-H; 2.31, t(J 8 & 8H <sub>2</sub> ) 6-H; 2.32, s, 3-H; 2.46, t(J 8 & 8H <sub>2</sub> ), 7-H; 2.87, q(J 8 & 1H <sub>2</sub> ), 5-H; 6.24, t(J 7 & 7H <sub>2</sub> ), Ar-CH <sub>2</sub> ; 8.0, -CH <sub>2</sub> -; 8.60 and 8.67, 2s, Me <sub>2</sub> .	46
6-(3,3-Dimethylallyl)-1,5-dihydroxy, (Guanandin; calophyllin B)	d	3.23, q(J 8.5 & 1.OH <sub>2</sub> ), 2-H; 2.32, t(J 8.5H <sub>2</sub> ), 3-H; 2.97,q(J 8.5 & 1.OH <sub>2</sub> ), 4-H; 2.78, d(J 8.5H <sub>2</sub> ), 7-H; 2.33, d(J 8.5H <sub>2</sub> ), 8-H; 4.58,	2,27,47, 54-58

Compound	Solv	PMR Values ( $\tau$ )	Ref.
Dehydrocycloguanandin	b	t(J 7.0H <sub>2</sub> ), :CH-; 6.45, d(J 7H <sub>2</sub> ), -CH <sub>2</sub> -; 8.23, s, Me <sub>2</sub> 3.22, q(J 8.3 & 1.1H <sub>2</sub> ), 2-H; 2.4, t(J 8.3H <sub>2</sub> ), 3-H; 2.73, q(J 8.3 & 1.1H <sub>2</sub> ), 4-H; 3.0, d(J 8H <sub>2</sub> ), 7-H; 2.24, d(J 8.0H <sub>2</sub> ), 8-H; 3.56, d(J 9.8H <sub>2</sub> ), :CH-; 4.17, d(J 9.8H <sub>2</sub> ), :CH-; 8.44, s, Me <sub>2</sub> .	2,27,59
6-(4-Hydroxy-3-methylbutanyl)- 1,5-dihydroxy	b	-2.62, 1-OH; 2.06, d(J 8.5H <sub>2</sub> ), 8-H; 2.83, d(J 8.5H <sub>2</sub> ), 7-H; 3.22, q(J 8.5 & 1.5H <sub>2</sub> ), 2-H; 3.03, q(J 8.5 & 1.5H <sub>2</sub> ), 4-H; 2.43, t(J 8.5H <sub>2</sub> ), 3-H; 6.45, d(J 6.0H <sub>2</sub> ), 4'-CH <sub>2</sub> ; 7.18, t(J 7.0 & 2.0H <sub>2</sub> ), 1'-CH <sub>2</sub> ; 8.3, m, 2'- CH <sub>2</sub> - & 3'-CH; 8.4, br., 4'OH; 8.97, d(J 6.0H <sub>2</sub> ), 3'OMe.	54
Scriblitifolic acid	b	-2.61, br., s, 1-OH; 3.20, md, 2-H; 2.40, t, 3-H; 3.02, md, 4-H; 2.79, d, 7-H; 2.04, d, 8-H; 6.02, s, OMe; 7.20, t, 1'- CH <sub>2</sub> -; 8.12, m, 2'-CH <sub>2</sub> -; 8.75, d, 3'-Me; 7.5, m, 3'-CH-.	15,46,55, 57
4,8-Dihydroxy-1-(3',3'-di- methylallyl) (Isoguanandin)	d	3.25, q(J 8.3 & 1.1H <sub>2</sub> ), 2-H; 2.33, t(J 8.3H <sub>2</sub> ), 3-H; 3.01, q(J 8.3 & 1.1H <sub>2</sub> ), 4-H; 2.70, d(J 8.3H <sub>2</sub> ), 6-H; 2.9, d(J 8.3H <sub>2</sub> ), 7-H; 4.58, t(J 7.0H <sub>2</sub> ), :CH-; 6.01, d(J 7.0H <sub>2</sub> ), -CH <sub>2</sub> -; 8.25, s, 2Me; 1.14, 5-OH; -2.97, s, 1-OH.	2,27,58
1,7-Dihydroxy (Euxanthone)	d	-2.41, 1-OH; 1.05, 7-OH; 2.1-3.19, complex Ar-H.	30,38,40, 47,49,50,55 60-79
1-Hydroxy-7-methoxy	b	-2.41, 1-OH; 2.39-3.50, A-H; 6.20, s, OMe.	38,42,44, 49,66
<u>Trihydroxyxanthenes</u>			
1-Methoxy-2,3-dihydroxy	b	-1.41, s, 3-OH; 1.77, octet (J 8.5 & 2.0H <sub>2</sub> ), 8-H; 2.80-2.25, m, 5-, 6- & 7-H; 3.40, br., 2-OH; 3.51, s, 4-H; 5.98, s, OMe.	80-82
3-Hydroxy-1,2-dimethoxy	a	1.43, octet (J 7.5 & 1.8H <sub>2</sub> ), 8-H; 1.74, m(J 8.5 6.5 & 1.8H <sub>2</sub> ), 6-H; 2.06, q(J 8.5 & 1.5H <sub>2</sub> ), 5-H;	80,81,83, 84



Compound	Solv	PMR Values ( $\tau$ )	Ref.
2,3,4-Trihydroxy	d	2.16, m(J 7.5, 6.5 & 1.5H <sub>2</sub> ), 7-H; 2.66, s, 4-H; 5.39, s, 1-OMe; 5.85, s, 2-OMe.	25,35
3,4-Dihydroxy-2-methoxy	d	1.71, q, 8-H; 2.15-2.65, m, 5-, 6-, & 7-H; 2.7, s, 1-H; 6.02, s, OMe.	25,43,44
4-Hydroxy-2,3-dimethoxy	a	1.80, octet, 8-H; 1.95-2.75, m, 5-, 6- & 7-H; 2.82, s, 1-H; 5.81, s, 3-OMe; 6.03, s, 2-OMe	25,36,37, 43,44,80, 81,84,85
3-Hydroxy-2,4-dimethoxy	b	1.53, d, 8-H; 2.15-2.60, m, 5-, 6- & 7-H; 2.40, s, 1-H; 3.48, br., 3-OH; 5.85 & 5.95, 2s, OMe	25,36,37, 80,82,86, 87
4-Methoxy-2,3-methylenedioxy	a	2.59, s, 1-H; 1.80-2.55, m, 5-, 6-, & 7-H; 1.62, octet, 8-H; 5.67, 4-OMe; 3.76, s, -O-CH <sub>2</sub> -O-	43,44,64, 84,86,87
Globuxanthone	b	-2.62, s, 1-OH; 1.0-2.0, br., OH; 2.51, s, 3-H; 2.65-2.92, m, 6-, & 7-H; 2.17, q, 8-H; 3.73, q, :CH-; 4.82, t, :CH <sub>2</sub> ; 8.51, s, 2xMe.	88,89
2,8-Dihydroxy-1-methoxy	a	2.30, t(J 8.0H <sub>2</sub> ), 6-H; 2.41, d(J 10.0H <sub>2</sub> ), 3-H; 2.60, d(J 9.5H <sub>2</sub> ), 4-H; 2.91, q(J 8.0 & 1.0H <sub>2</sub> ), 5-H; 3.08, q(J 8.0 & 1.0H <sub>2</sub> ), 7-H; 5.90, s, OMe.	38,55,61, 85,90,91
1,2-Dimethoxy-8-hydroxy	a	2.30, t(J 8.5H <sub>2</sub> ), 6-H; 2.36, d(J 9.5H <sub>2</sub> ), 3-H; 2.62, d(J 10.0H <sub>2</sub> ), 4-H; 3.0, q(J 8.5 & 1.0H <sub>2</sub> ), 5-H; 5.81 & 5.96, 2s, 2xOMe.	90,91
2-Hydroxy-1,8-dimethoxy	c	1.58, s, 2-OH; 2.31, t(J 8.4H <sub>2</sub> ), 6-H; 2.68, d(J 8.4H <sub>2</sub> ), 3-H; 2.80, d(J 8.4H <sub>2</sub> ), 4-H; 2.98, d(J 8.4H <sub>2</sub> ), 7-H; 3.08, d(J 8.4H <sub>2</sub> ), 5-H; 6.15, s, 2xOMe	55

Compound	Solv.	PMR Values ( $\tau$ )	Ref.
1,5,6- Trihydroxy (Mesuaxanthone B)	d	-2.71, 1-OH, 2.04, d(J 9.OH <sub>2</sub> ), 8-H; 2.54, t(J 9H <sub>2</sub> ), 3-H; 2.72, d(J 9H <sub>2</sub> ), 4-H; 3.19, d(J 9.OH <sub>2</sub> ), 7-H; 3.19, d(J 9.OH <sub>2</sub> ), 2-H; 4.58, br., 5- & 6-OH.	25,62,35, 42,46,50- 52,55,56, 61,64,69, 70,71,182.
1,6-Dihydroxy-5-methoxy (Buchanaxanthone)	c	-2.84, 1-OH; 2.18, d(J 9H <sub>2</sub> ), 8-H; 2.33, t, 3-H; 2.99, d(J 9H <sub>2</sub> ), 7-H; 2.99, md, 4-H; 3.23, md, 2-H; 6.04, s, OMe.	46,52,55, 61,62
1,6,7-Trihydroxy	c	2.45, t(J 9H <sub>2</sub> ), 3-H; 2.53, s, 8-H, 3.12, md(J 9 & 3H <sub>2</sub> ), 4-H; 3.10, s, 5-H; 3.33, md(J 9 & 3H <sub>2</sub> ), 2-H; 4.1, br., 6- & 7-OH.	63,64,68, 93
Tovoxanthone	b	-3.1, s, 1-OH; 2.05, d(J 10.OH <sub>2</sub> ), 4'-H; 2.55, t(J 8.OH <sub>2</sub> ), 3-H; 3.20, s, 5-H; 3.23, dd(J 1.0 & 8.OH <sub>2</sub> ), 4-H; 3.33, dd(J 1.5 & 8.OH <sub>2</sub> ), 2-H; 4.22, d(J 10.OH <sub>2</sub> ), 5'-H; 8.51, s, 2xMe.	94,95
6-Deoxyjacareubin		2.35, q(J 7 & 3H <sub>2</sub> ), 8-H; 2.7, m, 6- & 7-H; 3.61, s, 4-H; 3.33, d(J 9.OH <sub>2</sub> ) and 4.27, d(J 9.OH <sub>2</sub> ), CH:CH (chromen); 8.54, s, 2xMe.	2,15,48, 55,57,58, 61,85,97- 100,102, 103.
1,5-Dihydroxy-3-methoxy (Mesuaxanthone A)	a	3.20, d(J 2.5H <sub>2</sub> ), 2-H; 2.92, d(J 2.5H <sub>2</sub> ) 4-H; 2.20-2.60, m, 6- & 7-H; 2.02, q(J 6.5 & 3.5H <sub>2</sub> ), 8-H; 5.70, s, 1-OMe; 5.90, s, 3-OMe.	36,43,44, 69,81,84, 101,104
1,5,6-Trihydroxy (Mesuxanthone)	d	-2.71, 1-OH; 2.04, d(J 9H <sub>2</sub> ), 8-H; 2.54, t(J 9H <sub>2</sub> ), 3-H; 2.72, d(J 9H <sub>2</sub> ), 4-H; 3.19, d(J 9H <sub>2</sub> ), 7-H; 3.19, d(J 9H <sub>2</sub> ), 2-H; 4.58, br., 5- & 6-H.	15,25,35, 42,46,50, 52,56,61, 62,64,69- 71,182

Compound	Solv.	PMR Values ( $\tau$ )	Ref.
1,3,5-Trihydroxy-4-(3-methylbut-2-enyl) xanthene-9-one.	d	-3.02, 1-OH; 3.53, d(J 2.5H <sub>2</sub> ), 7- & 8-H; 2.74, m, 6-H; 3.63, s, 2-H; 4.80, t, :CH-; 6.71, d, -CH <sub>2</sub> -; 8.26, s, Me; 8.38, s, Me.	53
6,11-Dihydroxy-3,3-dimethyl-pyrano-(2,3-c) xanthene-7-(3H)-one.	d	-2.95, s, 6-OH; 2.43, q, 8-H; 2.8, m, 9- & 10-H; 3.92, s, 5-H; 3.06, d(J 10H <sub>2</sub> ), 1-H; 4.35, d(J 10H <sub>2</sub> ), 2-H; 8.58, s, 2xMe.	105
8-Deoxygartanin	b	-3.16, 1H, s; 0.25, 1H, s; 0.95, 1H, s; 2.42, 1H, q; 2.7-2.95, 2H, m; 4.76, 2H, br; 6.40-6.60, 4H, br; 8.18 & 8.34, 12H, S's.	96,106, 107
5,10-Dihydroxy-2,2-dimethyl-12-(3-methylbut-2-enyl)-pyrano(3,2-b)-xanthene-6(2H)-one (Trapezifolixanthone)	b	2.25, q(J 8 & 3H <sub>2</sub> ), 7-H; 2.61, m, 8- & 9-H; 3.24, d(J 10H <sub>2</sub> ), 4-H; 3.60-4.00, m, 10-OH; 4.38, d(J 10H <sub>2</sub> ), 3-H; 4.73, m, :CH; 6.51, d(J 7H <sub>2</sub> ), Ar-CH <sub>2</sub> ; 8.12 & 8.27, s, :CMe <sub>2</sub> ; 8.51, s, CMe <sub>2</sub> -3.25, s, 5-OH.	99,107, 108
Morellin		-2.77, s, 1-OH; 0.37, s, -CHO; 2.4, d(J 7H <sub>2</sub> ), 8-H; 3.35, d(J 10H <sub>2</sub> ), 14-H; 4.43, d(J 10H <sub>2</sub> ), 15-H; 3.9, t(J 8H <sub>2</sub> ), 30-H; 4.75, t, (J 7.5H <sub>2</sub> ), 20-H; 6.4, 7-H; 6.6-6.7, d, 19- & 29-H; 7.35, q, 24-H; 7.7, d(J 4.5H <sub>2</sub> ), 25-H; 8.2, 23-Me; 8.25, 33-Me; 8.3, 22-Me; 8.47, 17- & 18-Me; 8.5, 27-Me; 8.67, 28-Me.	109-111
Gambogic acid	e	-0.92, br.s, -CO <sub>2</sub> H; -2.55, s, 1-OH; 1.35, m, <u>o</u> -H pyr; 2.25, m, <u>p</u> -H pyr; 2.62, m, <u>m</u> -H pyr; 2.42, d(J 7H <sub>2</sub> ), 8-H; 3.37, d(J 10.2H <sub>2</sub> ), 14-H; 3.88, t(J 7.3H <sub>2</sub> ), 30-H; 4.61, d(J 10.2H <sub>2</sub> ), 15-H; 4.89, t(J 7H <sub>2</sub> ), 35 & 20-H; 6.53, q(J 7.3 & 4.6H <sub>2</sub> ), 7-H; 6.72, d(J 7H <sub>2</sub> ), 19-H; 6.95, d (J 7.2H <sub>2</sub> ), 29-H; 8.27, s, 33-H; 8.28, s, 22- & 37-H; 8.34, s, 23- & 38-H; 8.44, s, 18-H; 8.64, s, 27-H; 8.71, s, 28-H.	6,112-125

Compound	Solv	PMR Values ( $\tau$ )	Ref.
1,7-Dihydroxy-3-methoxy (Gentisin)	c	2.35-2.65, m, 5-, 6- & 8-H; 3.40, d(J 3H <sub>2</sub> ), 4-H; 3.62, d(J 3H <sub>2</sub> ), 2-H; 6.09, s, OMe.	36,49,58, 64,126-133
1-Hydroxy-3,7-dimethoxy (Methylgentisin)	b	-2.94, 1-OH; 3.58, d(J 2.5H <sub>2</sub> ), 4-H; 3.70, d(J 2.5H <sub>2</sub> ), 2-H; 2.41, q, 8-H; 2.68, m, 5- & 6-H; 6.08, s, 3-OMe; 6.11, s, 7-OMe.	1,128
2-(3,3-Dimethylallyl)-1,3,7- trihydroxy	b	-3.33, 1-OH; 0.82, br; 3- & 7-OH; 3.48, s, 4-H; 2.34, m, 8-H; 2.54, m, 5- & 6-H; 4.65, br. t, :CH-; 6.58, d, CH <sub>2</sub> ; 8.28 & 8.33, 2xMe.	15,73,134, 135
Mbarraxanthone (as it's dimethylether)	b	-2.50, s, 1-OH; 2.43, d(J 2.4H <sub>2</sub> ), 8-H; 2.65- 2.80, m, 5- & 6-H; 3.45, s, 2-H; 4.47, t, :CH-; 6.0, s, 2xOMe; 6.45, d, Ar-CH <sub>2</sub> ; 8.13, s, & 8.32, s, & 8.32, s,:CMe <sub>2</sub> .	11,88,89
Calabaxanthone	b	-3.70, s, 5-OH; 2.75, s, 9- & 10-H, 3.25, d(J 9.6H <sub>2</sub> ), 4-H; 4.34, d(J 9.6H <sub>2</sub> ), 3-H; 3.75, s, 12-H; 4.76, t, :CH-; 5.85, d, -CH <sub>2</sub> -; 6.12, s, 8-OMe, 8.15 & 8.34, s, :CMe <sub>2</sub> ; 8.54, s, CMe <sub>2</sub> .	47,55,99, 136
Thwaitesixantnone	b	-3.53, s, 13-OH; 1.98, d(J 10.2H <sub>2</sub> ), 1-H; 2.83, s, 5- & 6-H; 3.26, d, (J 10.2H <sub>2</sub> ), 12-H; 4.19, d(J 10.2H <sub>2</sub> ), 2-H; 4.41, d(J 10.2H <sub>2</sub> ), 11-H; 3.72, s, 8-H; 8.52 & 8.52, s, 3- & 10-Me <sub>2</sub> .	47
1-Methoxy-3,5-dihydroxy	c	2.48, q(J 6 & 4H <sub>2</sub> ), 8-H; 2.8, m, 6- & 7-H; 3.45, d(J 3H <sub>2</sub> ), 4-H; 3.6, d(J 3H <sub>2</sub> ), 2-H; 6.12, s, OMe	26
3-O-Rutinosyl-1-methoxy-5- hydroxy	c	2.42, q, 8-H; 2.78, m, 6- & 7-H; 3.46, d(J 3H <sub>2</sub> ), 4-H; 3.62, d(J 3H <sub>2</sub> ), 2-H; 5.0, br., glucosyl 1-H; 5.78, d, (J 2H <sub>2</sub> ), rhamnosyl 1-H; 6.12, s, OMe; 6.4, rhamnoglucosyl-H; 9.15, m, rhamnosyl- Me.	26
1,3-Dihydroxy-7-methoxy (Iso- gentisin)		-1.56, 1-OH; -0.22, 3-OH; 5.90, 7-OMe	60,128,137, 169

Compound	Solv	PMR Values ( $\tau$ )	Ref.
1,3,7-Trimethoxy		6.06, 1-OMe; 6.13, 3- & 7-OMe.	1,60,25,128 137
<u>Tetraoxygenated Xanthenes</u>			
1,3,6,7-Tetrahydroxy (Norathyriol)	c	-3.3, s, 1-OH; 1.03(-0.28), br, 3-, 6-, & 7-OH; 3.0, s, 5-H; 3.55, d(J 2H <sub>2</sub> ), 4-H; 3.73, d(J 2H <sub>2</sub> ), 2-H; 2.65, s, 8-H	25,35,51, 53,65,70, 73,76,143- 152,92
1,7-Dihydroxy-3,6-dimethoxy	c	-3.07, s, 1-OH; 2.63, s, 8-H; 3.14, s, 5-H; 3.51, & 3.72, 2 d(J 2H <sub>2</sub> ), 2- & 4-H; 6.14 & 6.17, s, 2xOMe.	57
6,7-Dihydroxy-1-methoxypyrano- (2',3':3,4) xanthone (Lorostemin)	d	2.06, s, 8-H; 2.33, s, 5-H; 3.35, s, 2-H; 3.17, d(J 10.3H <sub>2</sub> ), 4'-H; 4.10, d(J 10.3 H <sub>2</sub> ), 5'-H; 6.0, s, OMe; 8.41, s, 2xMe.	153
Normangostin ( $\gamma$ - Mangostin)	b+c	-3.92, 1H, s; 3.25, 1H, s; 3.65, 1H, s; 4.75, 2H, br; 5.92, 2H, br; 6.75, 2H, br; 8.25, 8.35, 12H, s.	106,154
$\beta$ - Mangostin	b	-3.38, 1H, s; 3.26, 1H, s; 3.63, 1H, br; 3.76, 1H, s; 4.8, 2H, m; 5.95, 2H, d(J 7H <sub>2</sub> ); 6.16, 3H, s; 6.24, 3H, s; 6.68, 2H, d(J 7H <sub>2</sub> ); 8.20, 8.22, 6H; 8.34, 6H.	
Tovopyrifolin-A 6-O-methyl ether	b	-3.33, s, 1-OH; 2.46, s, 8-H; 3.24, d(J 10H <sub>2</sub> ), 4'-H; 3.36, s, 4-H; 4.40, d(J 10 H <sub>2</sub> ), 5'-H; 4.80, t(J 7.5 H <sub>2</sub> ), :CH; 6.01, s, 2xOMe; 6.39, d(J 7.5H <sub>2</sub> ), 5-CH <sub>2</sub> ; 8.11, s, Me; 8.31, s, Me; 8.51, s, 2xMe.	155
Tovophyllin-A	b	-3.33, s, 1-OH; 1.95, d(J 10H <sub>2</sub> ), 4'-H; 3.68, s, 4-H; 4.25, d(J 10H <sub>2</sub> ), 5'-H; 4.78, t(J 7.5H <sub>2</sub> ), 2x:CH; 6.02, s, OMe; 6.05, s, OMe; 6.40, d(J 7.5H <sub>2</sub> ), 5-CH <sub>2</sub> ; 6.62, d(J 7.5H <sub>2</sub> ), 2-CH <sub>2</sub> ; 8.10, s,	155,156

Compound	Solv	PMR Values ( $\tau$ )	Ref.
Tovophyllin-B	b	Me; 8.20, s, Me; 8.30, s, 2xMe; 8.50, s, 6'-2xMe -3.68, s, 1-OH; 1.97, d(J 10H <sub>2</sub> ), 4'-H; 3.24, d(J 10H <sub>2</sub> ), 4''-H; 3.69, s, 4-H; 4.24, d(J 10H <sub>2</sub> ), 5'-H; 4.41, d(J 10H <sub>2</sub> ), 5''-H; 4.78, t(J 7.5H <sub>2</sub> ), :CH; 6.10, s, OMe; 6.43, d(J 7.5H <sub>2</sub> ), CH <sub>2</sub> ; 8.11, s, Me; 8.35, s, Me; 8.46, s, 2xMe; 8.49, s, 2xMe.	155,156
Pentadesmaxanthone	d	-3.2 to -3.3, 11-OH; 2.0, d(J 10 H <sub>2</sub> ), 1-H; 3.74, s, 10-H; 4.16, d(J 10H <sub>2</sub> ), 2-H; 4.7, t(J 7.4H <sub>2</sub> ), :CH; 6.4, m, Ar-CH <sub>2</sub> ; 8.22, s, & 8.36, s, :CMe <sub>2</sub> ; 8.56 & 8.66, s, - (-O)CMe <sub>2</sub>	157,158,
1,3,5,6-Tetrahydroxy	b	-2.8, s, 1-OH; 2.04, d(J 9H <sub>2</sub> ), 8-H; 3.01, d(J 9H <sub>2</sub> ), 7-H; 3.55, d(J 9H <sub>2</sub> ), 4-H; 3.72, d(J 9 H <sub>2</sub> ), 2-H	8, 25, 35, 60,71,182, 101,145, 149,159-161
3,5,6-Trihydroxy-1-methoxy	b	-1.00, br, OH; 2.13, d(J 9H <sub>2</sub> ), 8-H; 2.89, d(J 9H <sub>2</sub> ), 7-H; 3.7, d(J 9H <sub>2</sub> ), 4-H; 4.10, d(J 9H <sub>2</sub> ), 2-H; 6.48, s, OMe.	25,60,162
3-Hydroxy-1,5,6-trimethoxy	b	3.73, d(J 2.5H <sub>2</sub> ), 2-H; 3.63, d(J 2.5H <sub>2</sub> ), 4-H; 3.04, d(J 9H <sub>2</sub> ), 7-H; 2.02, d(J 9H <sub>2</sub> ), 8-H; 5.87, 6.00 & 6.05, s, 3xOMe.	84,162,163
Cudraniaxanthone	c	-4.03, s, 1-OH; 2.45, d(J 10H <sub>2</sub> ), 8-H; 3.10, d(J 10H <sub>2</sub> ), 7-H; 3.40, s, 4-H; 3.70, m, :CH; 5.15, 5.35, 2d, :CH <sub>2</sub> ; 8.47, s, 2xMe.	164,165
2-(3,3-Dimethylallyl)-1,3,5,6-tetrahydroxy	d	-3.5, s, 1-OH; 0.97, br., -OH; 2.35, d(J 9H <sub>2</sub> ), 8-H; 3.02, d(J 9H <sub>2</sub> ), 7-H; 3.47, s, 4-H; 4.69, t, :CH; 6.62, d, > CH <sub>2</sub> ; 8.21, s, 2xMe.	15,60-63, 97,98,134, 145,92
Jacareubin	d	-3.61, s, 1-OH; 1.2, br., -OH; 2.40, d(J 9H <sub>2</sub> ), 8-H; 3.06, d(J 9H <sub>2</sub> ), 7-H; 3.70, s, 4-H; 3.38, d, 48,55,58	2,15,46-

Compound	Solv	PMR Values ( $\tau$ )	Ref.
		:CH; 8.56, s, 2xMe	60-62,85, 97,98,134, 145,157,160 166-170,92
4-(3,3-Dimethylallyl)-1,3,5,6-tetrahydroxy (Ugaxanthone)	b	-2.45, s, 1-OH; 2.01, d(J 8.5H <sub>2</sub> ), 8-H; 3.02, d(J 9H <sub>2</sub> ), 7-H, 3.61, s, 2-H; 4.70, t, :CH; 6.0, s, 2xOMe; 6.08, s, OMe; 6.45, d(J 9H <sub>2</sub> ), CH <sub>2</sub> ; 8.12, s, Me; 8.31, s, Me.	88,89,165
Macluraxanthone (trimethylether)	b	1.99, d(J 9.4H <sub>2</sub> ), 8-H; 3.04, d(J 9.4H <sub>2</sub> ), 7-H; 3.21, d(J 10.OH <sub>2</sub> ), :CH; 4.30, d(J 10.OH <sub>2</sub> ), :CH; 3.54, 5.09 & 5.18, (J <sub>ax</sub> 17.9, J <sub>bx</sub> 10.0 & J <sub>ab</sub> 10.OH <sub>2</sub> ), vinyl group; 6.01, 6.06, 6.07, s, 3xOMe; 8.28, s, 2xMe; 8.59, s, 2xMe (chromene)	85,159,162, 171
10-O-Methylmacluraxanthone	b	-3.58, s, 5-H; 2.10, d(J 9H <sub>2</sub> ), 7-H; 3.04, d(J 9H <sub>2</sub> ), 8-H; 3.26, d(J 10H <sub>2</sub> ), 4-H; 3.68, q(J 18 & 10H <sub>2</sub> ), X of ABX system, :CH; 4.43, d(J 10H <sub>2</sub> ), 3-H; 5.11 & 5.16, 2d(J 18 & 10H <sub>2</sub> ), AB of ABX system; 6.06, s, 10-OMe; 8.28, s, 2xMe; 8.54, s, 2xMe (chromene)	172-174
Alvaxanthone (triacetate)	b	-2.45, s, 1-OH; 2.97, s, 7-H; 3.53, s, 4-H; 4.62, t(J 6.6H <sub>2</sub> ), :CH; 5.09, 5.13, 3.72, (J <sub>ax</sub> 10.8 & J <sub>ab</sub> 1.2H <sub>2</sub> ) vinyl group; 5.96, d(J 6.6H <sub>2</sub> ), CH <sub>2</sub> ; 7.62, 7.67, 7.78, s, 3xOAc; 8.25, s, 2xMe; 8.41, s, 2xMe.	160,175
1,3,5,8-Tetrahydroxy-2,4-(3,3-dimethylallyl) (Gartanin)	b	-2.16, 1-H, s; -1.33, 1H, s; 0.67, 1H, s; 2.78, 1H, d(J 9H <sub>2</sub> ), 3.48, 1H, d(J 9H <sub>2</sub> ); 4.75, 2H, br; 6.35-6.65, 4H, br; 8.20 & 8.30, 12H, s.	96,106,176
1,3,5-Trihydroxy-2-methoxy (Tovopyrifolin)	d	-3.06, s, 1-OH; 2.35, q, 8-H; 2.74, m, 6- & 7-H; 3.49, s, 4-H; 6.12, s, 2-OMe	48,55,157, 172,177

Compound	Solv	PMR Values ( $\tau$ )	Ref.
1,5-Dihydroxy-2,3-dimethoxy	c	-2.68, s, 1-OH; 2.30-2.98, m, 6-, 7-, & 8-H; 3.22, s, 4-H; 6.03 & 6.22, s, 2- & 3-OMe.	47
Kayeaxanthone	b	2.05, d(J 9H <sub>2</sub> ), 6-H; 2.90, d(J 9H <sub>2</sub> ), 5-H; 3.46, d(J 10H <sub>2</sub> ), 4-H; 3.51, q(J 20 & 12H <sub>2</sub> ), X of ABX system, :CH; 4.32, d(J 10H <sub>2</sub> ), 3-H; 5.01, q(J 20 & 1.2H <sub>2</sub> ), and 5.15, q(J 12 & 1.2H <sub>2</sub> ), AB of ABX system, CH <sub>2</sub> ; 6.00, 6.33, 2s, 8- & 10-OMe; 8.25, s, 2xMe; 8.41, s, 2-Me <sub>2</sub> .	172
1,2-Dimethoxy-3,8-dihydroxy	c	-3.25, 1-OH; 2.42, t(J 9.OH <sub>2</sub> ), 6-H; 3.13, md(J 9.0 & 1.OH <sub>2</sub> ), 5-H, 3.33, md(J 9.0 & 1.OH <sub>2</sub> ), 7-H; 6.08 & 6.16, s, 2xOMe.	48
1,3,8-Trihydroxy-7-methoxy	c	-1.9 to 1.54, br. s, 1-, 3-, & 8-OH; 2.58, d(J 9.1H <sub>2</sub> ), 6-H; 3.72, d(J 2.1H <sub>2</sub> ), 4-H; 3.12, d(J 9.1H <sub>2</sub> ), 5-H; 3.86, d(J 2.1H <sub>2</sub> ), 2-H; 6.23, s, OMe.	80,101
1,4,7-Trihydroxy-3-methoxy	d	- 2.34, s, 1-OH; 1.0, br, 4- & 7-OH; 2.35-2.60, m, 5-, 6- & 8-H; 3.70, s, 2-H; 6.06, s, OMe.	64
1,5-Dihydroxy-6,7-dimethoxy	a	2.13, 5(J 8.5H <sub>2</sub> ), 3-H; 2.59, s, 8-H; 2.68, q(J 8.5 & 1.5H <sub>2</sub> ), 4-H; 2.94, q(J 8.5 & 1.5H <sub>2</sub> ), 2 H; 5.76, s, OMe; 5.93, s, OMe.	25,178
3,4,8-Trihydroxy-1-(3,3-di- methylallyl)-2-methoxy (Celebixanthone)	b	-3.16, s, 8-OH; 1.28, br; 3- & 9, 4-OH; 2.59, t(J 8H <sub>2</sub> ), 6-H; 3.25, d(J 8H <sub>2</sub> ), 5-H; 3.49, d(J 8H <sub>2</sub> ), 7-H; 4.80, t(J 6H <sub>2</sub> ), :CH; 6.03, d(J 6H <sub>2</sub> ), CH <sub>2</sub> ; 6.15, s, OMe; 7.1, s, Me; 8.33, s, Me.	9,179-181
4-(1,1-Dimethylallyl)-1,2,5,6- tetrahydroxy (Symphoxanthone)	d	-3.0, s, 1-OH; 1-2, br., OH; 2.63, s, 3-H; 2.95, d(J 9H <sub>2</sub> ), 7-H; 2.29, d(J 9H <sub>2</sub> ), 8-H; 8.30, s, Me <sub>2</sub> ; 3.53, q, :CH; 4.89, t, :CH <sub>2</sub>	88,89



Compound	Solv	PMR Values ( $\tau$ )	Ref.
1-Hydroxy-2,3,5-trimethoxy	f	-2.65, 1H, s; 2.22, 1H, q; 2.74, 2H, m; 3.44, 1H, s; 6.02, 3H, s; 6.06, 3H, s; 6.16, 3H, s.	1,43,138
1-Hydroxy-2,3,7-trimethoxy	f	-2.65, 1H, s; 2.45, 1H, q; 2.73, 2H, m; 3.59, 1H, s; 6.07, 3H, s; 6.12, 3H, s; 6.16, 3H, s.	1,177
1,8-Dihydroxy-3,5-dimethoxy (Methylbellidifolin, Swerchirin)	b	-1.96, -1.33, 1- & 8-OH; 3.16/3.22, 7-H; 2.60/2.76, 6-H; 3.36/3.40, 4-H; 3.58/3.63, 2-H; 6.0/6.05, 2xOMe.	1,139-142, 176,177, 183,14
1,3-Dihydroxy-4,5-dimethoxy	c	2.32, 1H, q; 2.56, 2H, m; 3.70, 1H, s; 6.0, 3H, s; 6.12, 3H, s.	177,183, 184
1,3,4,7-Tetramethoxy	f	2.42, 1H, q; 2.72, 2H, m; 3.61, 1H, s; 6.04, 3H, s; 6.06, 3H, s; 6.15, 6H, s.	25,177
1,3,4,5-Tetramethoxy	f	2.25, 1H, q; 2.80, 2H, m; 3.57, 1H, s; 5.99, 3H, s; 6.01, 3H, s; 6.06, 3H, s, 6.10, 3H, s.	177,215
1-Hydroxy-3,7,8-trimethoxy (Decussatin)	b	-3.30, 1-OH; 2.70, d(J 9.2H <sub>2</sub> ), 5-, & 6-H; 3.65, s, 2- & 4-H; 5.99, 6.04, 6.12, s, 3xOMe.	101,142, 183,185 195
1,7-Dihydroxy-3,8-dimethoxy (Gentianacaulin)	b	-3.2, 1-OH; 2.59, 6-H; 2.8, 5-H; 3.61, 2- & 4-H; 5.92, 6.20, s, OMe.	186-188, 194
3,8-Dihydroxy-1,7-dimethoxy (Isogentiacaulin) (diacetate derivative)	b	2.61, 6-H; 2.89, 5-H; 3.30, 2-H; 3.49, 4-H; 6.10, 1-OMe; 6.15, 7-OMe; 7.55, 8-OCOMe; 7.69, 3-OCOMe.	169,186, 190
1,8-Dihydroxy-3,7-dimethoxy (Swertiaperennine, Methyl- swertianin)	c	2.20-2.35, d, 6-H; 2.9-3.05, d, 5-H; 3.4-3.45, d, 4-H; 3.67-3.72, d, 2-H; 6.05, 6.1, s, 2xOMe.	142,186, 191,194,196
1,3,7,8-Tetrahydroxy (Norswertianin) (as tetra- acetate derivative)	b	2.50, 2.69, (J 9.5H <sub>2</sub> ), 5- & 6-H; 2.79, 3.22 (J 2.5H <sub>2</sub> ), 2- & 4-H; 7.6 & 7.7, 4xOCOMe.	101,142,188 187,191,192 196

Compound	Solv	PMR Values ( $\tau$ )	Ref.
1,3,5,8-Tetrahydroxy (Desmethylbellidifolin) (as tetraacetate derivative)	b	3.18, d, 2.78, d, (J 2.5H <sub>z</sub> ), 2- & 4-H; 3.07, d, 2.55, d(J 9.5H <sub>z</sub> ), 6- & 7-H; 7.67, 7.58, 4XOCOMe.	139,142, 191,192, 197,198
1,5,8-Trihydroxy-3-methoxy (Bellidifolin)	c	-3.5, br., 1- & 8-H; 3.25/3.4, 7-H; 2.62/2.78, 6-H; 3.42/3.46, 4-H; 3.68/3.71, 2-H; 6.1, OMe.	139,142, 196,198,199
1,3,8-Trihydroxy-5-methoxy (Isobellidifolin)	c	-3.45, br., 1-OH; 3.26/3.41, 7-H; 2.67/2.83, 6-H; 3.42/3.45, 4-H; 3.70/3.74, 2-H; 6.0, OMe.	26,141,142, 190,192,14
1-Hydroxy-3,5,8-trimethoxy		-3.33, 1-OH; 3.12/3.28, 7-H; 2.60/2.76, 6-H; 3.35/3.40, 4-H; 3.52/3.57, 2-H; 6.0/6.05, 3xOMe.	139,142, 191
1,3,5-Trihydroxy-6-methoxy	c	2.05/221, d, 8-H; 3.07/3.23, d, 7-H; 3.52/3.58, d, 4-H; 3.68/3.73, d, 2-H; 6.05, OMe.	60,101, 200
1,5,6-Trihydroxy-3-methoxy	c	-3.1, 1-OH; 2.4, d(J 10H <sub>z</sub> ), 8-H; 3.12, d(J 10H <sub>z</sub> ), 7-H; 3.5, d(J 3H <sub>z</sub> ), 4-H; 3.62, d(J 3H <sub>z</sub> ), 2-H; 6.05, OMe.	149,201
3,7,8-Trimethoxyxanthone-1-O- primeveroside (Decussatin-O- primeveroside)	b	2.82, 2.95, (J 9.5H <sub>z</sub> ), 5- & 6-H; 3.28, 3.42, (J 2.5H <sub>z</sub> ), 2- & 4-H; 6.08, 3H; 6.13, 3H; 6.15, 3H, OMe.	187,202- 204
7-Hydroxy-3,8-dimethoxy- xanthone-1-O-primeveroside (Gentiabavaroside) (as acetate derivative)	b	2.72, 2.92 (J 9.5H <sub>z</sub> ), 5- & 6-H; 3.30, 3.40 (J 2.5H <sub>z</sub> ), 2- & 4-H; 6.10, 6H, 2xOMe; 7.69, 3H, OCOMe.	187,202
1,8-Dihydroxy-3-methoxy- xanthone-7-O-acetyl-rutinoside (Gentiabavarutinoside)	b	2.59, 2.64 (J 9.5H <sub>z</sub> ), 5- & 6-H; 3.33, 3.50 (J 2.5H <sub>z</sub> ), 2- & 4-H; 6.14, 3H, OMe; 7.57, 6H, OCOMe.	187,205
7,8-Dihydroxy-3-methoxy- xanthone-1-O-primeveroside (Isogentiakochianoside) (Diacetate derivative)	b	2.65, 2.76 (J 9.5H <sub>z</sub> ), 5- & 6-H; 3.37, 3.47 (J 2.0H <sub>z</sub> ), 2- & 4-H; 6.11, 3H, OMe, 7.52, 7.71, 6H, OCOMe.	187,202

Compound	Solv	PMR Values ( $\tau$ )	Ref.
3,6-Dihydroxy-1,7,8-trimethoxy	c	2.96, 5-H; 3.53, 4-H; 3.64, 2-H; 6.16, 7- & 8-OMe; 6.4, 1-OMe.	42
1,2,3,5,8-Pentamethoxy	f	2.93, d(J 9H <sub>2</sub> ), 1H; 3.29, s, 1H; 3.37, d(J 9H <sub>2</sub> ), 1H; 6.10, s, 3H; 6.12, s, 3H; 6.15, s, 3H; 6.18, s, 3H; 6.21, s, 3H.	177
1,3-Dihydroxy-4,5,8-trimethoxy	b	-2.74, 1-OH; 2.85, d(J 9H <sub>2</sub> ), 6-H; 3.22, d(J 9H <sub>2</sub> ), 7-H; 3.6, s, 2-H; 5.98-6.05, 3xOMe.	183
1,3,8-Trihydroxy-4,5-dimethoxy (4,5-Di-O-methylcorymbin)	c	-1.6, -1.3, 1- & 8-OH; 2.45, 2.6, 6-H; 3.18, 3.7, 7-H; 3.6, 2-H; 6.06, 6.13, 2xOMe.	176,216
4,7-Dimethoxy-1,3,8-trihydroxy (4,7-Dimethoxybellidin)	c	-2.18, -1.73, 1- & 8-OH; 2.48, 2.6, 6-H; 2.8, 3.0, 5-H; 3.5, 2-H; 6.03, 6.06, 2xOMe.	176
1-Hydroxy-3,4,7,8-tetramethoxy	b	-3.04, 1-OH; 5.98-6.06, 3xOMe; 3.6, s, 2-H; 2.95, d(J 9H <sub>2</sub> ), 5-H; 2.72, d(J 9H <sub>2</sub> ), 6-H.	191,192
1-Hydroxy-3,5,7,8-tetramethoxy	b	3.60, d(J 1.5H <sub>2</sub> ), 2-H; 3.45, d(J 1.5H <sub>2</sub> ), 4-H; 2.96, s, 6-H; 5.98, OMe; 6.02, 2xOMe; 6.10, OMe.	199
1-Hydroxy-2,3,4,5-tetramethoxy	b	-2.55, 1H, s, 2.20, 1H; q; 2.62, 2H, m; 5.86, 3H, s; 5.96, 3H, s; 6.00, 3H, s; 6.09, 3H, s.	1,138,177
1,4-Dihydroxy-2,3,4,7-trimethoxy	b	-2.66, 1-OH; 2.12, q, 8-H; 2.66, m, 6- & 7-H; 5.9-6.08, 4xOMe.	1,177,183
1,4-Dihydroxy-2,3,7-trimethoxy	b	-2.05, 1-OH; 2.37, q, 8-H; 2.54, m, 6- & 7-H; 5.88-5.98, 3xOMe.	183
1-Hydroxy-2,3,4,7-tetramethoxy	f	-2.62, 1H, s; 2.39, 1H, q; 2.55, 2H, m; 5.86, 3H, s; 6.04, 3H, s; 6.09, 6H d.	1,138,177
1,2,3,4,7-Pentamethoxy (Polygalaxanthone B)	g	2.3, d(J 3H <sub>2</sub> ), 8-H; 2.5, d(J 9H <sub>2</sub> ), 5-H; 2.7, q(J 9 & 3H <sub>2</sub> ), 6-H; 5.80, 5.90, 5.95, 5xOMe.	23,217
	h	5.75, 5.91, 6.00, 6.38, 5xOMe.	

Compound	Solv	PMR Values ( $\tau$ )	Ref.
3,7,8-Trihydroxyxanthone-1-O-glucoside (Norswertianin-1-O-glucoside)(Triacetate derivative)	b	2.6, 2.72 (J 9.5H <sub>2</sub> ), 5- & 6-H; 3.04, 3.25 (J 2.5H <sub>2</sub> ), 2- & 4-H; 7.51, 7.63, 7.70, 3xOCOMe.	187,206
1,3,5-Trihydroxyxanthone-8-O- $\beta$ -D-glucopyranoside (Desmethylbellidifolin-8-O-glucoside)(Triacetate derivative)	b	3.22, d, 2.85, d(J 2.5H <sub>2</sub> ), 2- & 4-H; 3.04, d, 2.69, d(J 9.5H <sub>2</sub> ), 6- & 7-H; 7.70, 7.62, 7.52, 3xOCOMe.	198
1,5-Dihydroxy-3-methoxy-xanthone-8-O- $\beta$ -D-glucopyranoside. (Bellidifolin-8-O-glucoside; Isoswertianolin)	c	-3.18, br., s, 1-OH; 2.85, d(J 9H <sub>2</sub> ), 7-H; 2.67, d(J 9H <sub>2</sub> ), 6-H; 3.45, d(J 3H <sub>2</sub> ), 4-H; 3.62, d(J 3H <sub>2</sub> ), 2-H; 5.02, C <sub>1</sub> -H of $\beta$ -glucoside; 6.5, six glucosyl protons & H <sub>2</sub> O.	101,198, 201,207
5,8-Dihydroxy-3-methoxy-xanthone-1-O-glucoside (Swertianolin)	c	-2.95, br.s, 8-OH; 2.70, d(J 9H <sub>2</sub> ), 6-H; 3.32 d(J 9H <sub>2</sub> ), 7-H; 3.40, d(J 3H <sub>2</sub> ), 4-H; 3.48, d(J 3H <sub>2</sub> ), 2-H; 5.0, m, C <sub>1</sub> -H of $\beta$ -glucoside, 6.50, six glucosyl protons & H <sub>2</sub> O	208-210
3,5,8-Trihydroxyxanthone-1-O-glucoside (Norswertianolin)	c	2.72, d(J 9H <sub>2</sub> ), 6-H; 3.35, d(J 9H <sub>2</sub> ), 7-H; 3.42, d(J 3H <sub>2</sub> ), 4-H; 3.56, d(J 3H <sub>2</sub> ), 2-H; 5.08, m, C <sub>1</sub> -H of $\beta$ -glucoside, 6.5, six glucosyl protons & H <sub>2</sub> O	142,208, 211-214
<u>Pentaoxygenated Xanthenes</u>			
1,8-Dihydroxy-2,3,7-trimethoxy	d	-3.2, s, 1-OH; -0.3, br.s, 8-OH; 2.55, d(J 9H <sub>2</sub> ), 6-H; 2.85, d(J 9H <sub>2</sub> ), 5-H; 3.37, s, 4-H; 6.07, 6.15 & 6.25, s, 2-, 3- & 7-OMe.	55
1,7-Dimethoxy-2,3,8-trihydroxy	d	-1.27, s, 1-OH; 2.67, d(J 9H <sub>2</sub> ), 6-H; 3.43, d(J 9H <sub>2</sub> ), 5-H; 3.55, s, 4-H; 6.18, s, OMe; 6.23, s, OMe.	115
1,3,6-Trihydroxy-7,8-dimethoxy	c	-2.91, 1-OH; 3.82, 2-H; 3.42, 4-H; 2.94, 5-H; 6.14, 7-OMe; 6.12, 8-OMe.	42

Compound	Solv	PMR Values ( $\tau$ )	Ref.
7-Hydroxy-1,2,3,4-tetramethoxy	a	1.8, s, Ar-H; 5.25, 5.57, 5.67, 4xOMe.	23,177,217
1-Methoxy-2,3,6,7-dimethylene- dioxy	a	2.1, s, 8-H; 2.5, s, 4-H; 2.65, s, 5-H; 3.43, s, -O-CH <sub>2</sub> -O; 5.2, s, OMe.	23
	b	2.38, s, 8-H; 3.18, s, 4-H; 3.38, s, 5-H; 3.87, 3.92, s, methylenedioxy, 5.8, s, OMe.	
	h	4.52, & 4.72, methylenedioxy, 5.99, OMe.	
1,2,3-Trimethoxy-6,7-methylene- dioxy (Polygalaxanthone A)	b	2.17, s, 8-H; 3.15, s, 4-H; 3.25, s, 5-H; 3.85, s, methylenedioxy; 5.90, 5.97, 6.01, OMe.	23,217
	h	5.83, 6.13, 6.67, OMe.	
1,2,3,4,6,7-Hexamethoxy	b	2.5, s, 8-H; 3.3, s, 5-H; 5.78, 5.80, 5.85, 5.88, 5.9, 6xOMe.	23
	h	5.75, 5.93, 6.01, 6.06, 6.42, 6.56, 6xOMe.	

## Solvents mentioned in the tables:-

- a = Trifluoroacetic acid;      b = Deuteriochloroform;  
 c = Dimethyl sulphoxide - d<sub>6</sub>      d = Diuterioacetone;  
 e = Pyridine salt      f = Methylene chloride;  
 g = Carbon tetrachloride      h = Benzene

### References

1. G.H. Stout, E.N. Christensen, W.J. Balkenhal and K.L. Stevens, Tetrahedron, 1969, 25, 1961.
2. O.R. Gottlieb, M. Taveira Magalhaes, M. Ottoni de Silva Pereira, A.A. Lins Mesquita, D. de Barros Correa and G.G. de Oliveira, Tetrahedron, 1968, 24, 1601.
3. D. Barraclough, H.D. Locksley, F. Scheinmann, M. Taveira Magalhaes and O.R. Gottlieb, J. Chem. Soc. (B), 1970, 603.
4. R.H. Martin, N. Defay, F. Geerts-Evrard, P.H. Given, J.R. Jones and R.W. Wedel, Tetrahedron, 1965, 21, 1833.
5. J. Ronayne and D.H. Williams, J. Chem. Soc. (B), 1967, 540, and references cited therein.
6. N.H. Dyson and W. Rigby, J. Chem. Soc., 1963, 1858.
7. J.A. Ballantine and C.T. Pillinger, Tetrahedron, 1967, 23, 1691.
8. P. Yates and G.H. Stout, J. Am. Chem. Soc., 1958, 80, 1691.
9. G.H. Stout, V.F. Stout and M.J. Welsh, Tetrahedron, 1963, 19, 667.
10. B. Jackson, H.D. Locksley and F. Scheinmann, J. Chem. Soc. (C), 1967, 785
11. L.J. Haynes and D.R. Taylor, J. Chem. Soc., 1966, 1685.
12. L.M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, 1959, p. 124.
13. P. Arends and P. Helboe, Acta. Chem. Scand., 1976, 26, 4180.
14. S.R. Dalal and R.C. Shah, Chem. & Ind., 1956, 140.
15. B. Jackson, H.D. Locksley and F. Scheinmann, J. Chem. Soc. (C), 1967, 2500.
16. P.J. Garrat, F. Scheinmann and F. Sondheimer, Tetrahedron, 1967, 23, 2413.
17. F. Scheinmann, Chem. Comm. 1967, 1015.
18. J.H. Bowie, J. Ronayne and D.H. Williams, J. Chem. Soc. (B), 1966, 785.
19. J.H. Bowie, D.W. Cameron, P.E. Schutz and D.H. Williams, Tetrahedron, 1966, 22, 1771.
20. R.G. Willson, J.H. Bowie and D.H. Williams, Tetrahedron, 1968, 22, 1407.
21. R. Grigg, J.A. Knight and P. Roffey, Tetrahedron, 1966, 22, 3301.
22. J. Ronayne and D.H. Williams, Chem. Comm. 1966, 712.
23. D.L. Dreyer, Tetrahedron, 1969, 24, 4415.
24. A. Prox. Tetrahedron, 1968, 24, 3697.
25. A.J. Quillinan and F. Scheinmann, J. Chem. Soc. Perkin I, 1973, 1329.
26. S. Ghosal, R. Ballava, P.S. Chauhan, K. Biswas and R.K. Chaudhuri, Phytochemistry, 1976, 15, 1041.
27. A.J. Quillinan and F. Scheinmann, J. Chem. Soc. Perkin I, 1972, 1382.

28. M. Okigawa, N.U. Khan, N. Kawano and W. Radhman, Chem. and Ind. (London), 1974, 14, 575.
29. M. Okigawa, N.U. Khan and N. Kawano, J. Chem. Soc. Perkin I, 1975, 1563.
30. R.A. Finnegan and J.K. Patel, J. Chem. Soc. Perkin I, 1972, 1896.
31. Y. Ikeshiro and M. Kanoshima, Tetrahedron Letters, 1972, 4383.
32. R.D. Knapp, Diss. Abstr. Int.; 1975, 35, 3247.  
Chem. Abstr., 1975, 82, 177741 m.
33. S.E. Holker, R.D. Lapper and T.J. Simpson, J. Chem. Soc. Perkin I, 1974, 2135.
34. J.A. Ballantine, V. Ferrito, C.H. Hassall and M.L. Jenkin, J. Chem. Soc. Perkin I, 1973, 1825.
35. J.D. Locksley and I.G. Murray, Phytochemistry, 1971, 10, 3179.
36. I. Carpenter, H.D. Locksley and F. Schienmann, Phytochemistry, 1969, 8, 2031.
37. O.R. Gottlieb, A.A. Lins Mesquita and T.J. Nagem, Phytochemistry, 1971, 10, 2253.
38. O.R. Gottlieb and G.M. Stefani, Phytochemistry, 1970, 9, 453.
39. R.A. Finnegan and P.L. Bachman, J. Pharm. Sci., 1965, 54, 633.
40. R.A. Finnegan, K.E. Merkel and J.K. Patel, J. Pharm. Sci., 1973, 62, 483.
41. D.J. Ringshaw and H.J. Smith, Chem. and Ind., 1965, 1383.
42. S.P. Gunasekera, S. Ramachandran, S. Selliah and M.U.S. Sultanbawa, J. Chem. Soc. Perkin I, 1975, 2447.
43. O.R. Gottlieb, M. Taveira Magalhaes, M. Camey, A.A. Lins Mesquita and D. De Barros Correa, Tetrahedron, 1966, 22, 1777.
44. M.A. Coelho Kaplan, O.R. Gottlieb, B. Gilbert, I. Salignac De Souza Guimaraes and M. Taveira Magalhaes, Ann. Acad. Brasil Cienc., 1966, 38, 269.
45. L. Crombie, D.E. Games and A. Mc Cormick, J. Chem. Soc. (C), 1967, 2545, 2553.
46. S.P. Gunasekera and M.U.S. Sultanbawa, J. Chem. Soc. Perkin I, 1975, 2215
47. M. Dahanayake, I. Kitagawa, R. Somanathan and M.U.S. Sultanbawa, J. Chem. Soc. Perkin I, 1974, 2510.
48. T.R. Govindachari, P.S. Subramaniam, B.R. Pai, P.S. Kalyanaraman and U.R. Rao, Indian J. Chem., 1971, 9, 772.
49. Y.L. Chow and H.H. Quon, Phytochemistry, 1968, 7, 1871
50. W.M. Bandaranayake, S.S. Selliah and M.U.S. Sultanbawa, Phytochemistry, 1975, 14, 265.
51. I. Carpenter, H.D. Locksley and F. Scheinmann, J. Chem. Soc. (C), 1969, 2421.
52. B. Jackson, H.D. Locksley, I. Moore and F. Scheinmann, J. Chem. Soc. (C), 1968, 2579.
53. P.J. Owen and F. Scheinmann, J. Chem. Soc. Perkin I, 1974, 1018.
54. B. Jackson, H.D. Locksley and F. Scheinmann, Tetrahedron, 1968, 24, 3059.

55. R. Somnathan and M.U.S. Sultanbawa, J. Chem. Soc. Perkin I, 1972, 1935.
56. T.R. Govindachari, B.R. Pai, P.S. Subramaniam, U.R. Rao and N. Muthukumaraswamy, Indian J. Chem., 1968, 6, 57.
57. V. Kumar, S. Ramachandran and M.U.S. Sultanbawa, Phytochemistry, 1976, 15, 2016.
58. M. Ottoni Da Silva Pereira, O.R. Gottlieb and M. Taveira Magalhaes, Ann. Acad. Brasil. Cienc, 1966, 38, 425.
59. M. Ottoni Da Silva Pereira, O.R. Gottlieb and M. Taveira Magalhaes, Ann. Acad. Brasil. Cienc, 1967, 39 (2), 255.
60. B. Jackson, H.D. Locksley and F. Scheinmann, J. Chem. Soc. (C), 1966, 178.
61. H.D. Locksley and I.G. Murray, J. Chem. Soc. (C), 1969, 1567.
62. F.S. Al-Jeboury and H.D. Locksley, Phytochemistry, 1971, 10, 603.
63. S. Bhanu, F. Scheinmann and A. Jefferson, Phytochemistry, 1975, 14, 298.
64. B. Jackson, H.D. Locksley and F. Scheinmann, J. Chem. Soc. (C), 1969, 2201.
65. W.M. Bandaranayake, S.S. Selliah, M.U.S. Sultanbawa and W.D. Ollis, Phytochemistry, 1975, 14, 1878.
66. L.D. Antonaccio, L.G. Fonseca de Silva, D. Barros Correa, O.R. Gottlieb and M. Taveira Magalhaes, Ann. Acad. Brasil Cienc, 1965, 37, 229.
67. G.A.L. Ferreira, O.R. Gottlieb, A.A. Lins Mesquita, Phytochemistry, 1972, 11, 1512.
68. E. Ritchie and W.C. Taylor, Tetrahedron Letters, 1964, 1431.
69. T.R. Govindachari, B.R. Pai, P.S. Subramaniam, U.R. Rao and N. Muthukumaraswamy, Tetrahedron, 1967, 23, 243.
70. H.D. Locksley, I. Moore and F. Scheinmann, J. Chem. Soc. (C), 1966, 430.
71. H.D. Locksley, I. Moore and F. Scheinmann, Tetrahedron, 1967, 23, 2229.
72. D.B. Spoelstra and M.J. Van Royen. Rec. Trav. Chem., 1929, 48, 370.
73. H.D. Locksley and I.G. Murray, J. Chem. Soc. (C), 1971, 1332.
74. I. Crombie, D.E. Games and A. McCormick, Tetrahedron Letters, 1966, 145.
75. K.S. Pankajamani and T.R. Seshadri, J. Sci. Ind. Res. India, 1954, 13B, 396.
76. J.E. Atkinson and J.R. Lewis, J. Chem. Soc. (C), 1969, 281.
77. M. Nierenstein, Ber., 1913, 46, 649.
78. A.L. Van Scherpenberg, Chem. Weekblad, 1919, 16, 1146.
79. F. Ullmann and L. Panchaud, Annalen, 1906, 350, 108.
80. O.R. Gottlieb, A.A. Lins Mesquita, G.G. De Oliveira and M.T. De Mello, Phytochemistry, 1970, 9, 2537.
81. G.G. De Oliveira, A.A. Lins Mesquita, O.R. Gottlieb, and M. Taveira Magalhaes,



- Ann. Acad. Brasil. Cienc., 1966, 38, 421.
82. L.G. Fonseca E. Silva, O.R. Gottlieb and M. Taveira Magalhaes, Ann. Acad. Brasil. Cienc., 1968, 40, 29.
83. G.G. De Olivera, A.A. Lins Mesquita, O.R. Gottlieb and M. Taveira Magalhaes, Ann. Acad. Brasil. Cienc., 1968, 40, 29.
84. D. De Barros Correa, L.G.F.E. Silva, O.R. Gottlieb and S.J. Goncalves, Phytochemistry, 1970, 9, 447.
85. O.R. Gottlieb, A.A.L. Mesquita, E.M. Da Silta and M.T. De Mello, Phytochemistry, 1969, 8, 665.
86. A. Pimenta, A.A.L. Mesquita, M. Camey, O.R. Gottlieb and M.T. Magalhaes, Ann. Acad. Brasil. Cienc., 1964, 36, 39.
87. A. Pimenta, A.A. Lins Mesquita, M. Camey, O.R. Gottlieb, and M. Taveira Magalhaes, Ann. Acad. Brasil. Cienc., 1964, 36, 283.
88. H.D. Locksley, I. Moore and F. Scheinmann, J. Chem. Soc. (C), 1966, 2265.
89. H.D. Locksley, I. Moore and F. Scheinmann, J. Chem. Soc. (C), 1966, 2186.
90. L.D. Antonaccio, G.M. Stephani, O.R. Gottlieb and M. Taveira Magalhaes, Ann. Acad. Brasil. Cienc., 1965, 37, 231.
91. O.R. Gottlieb, M. Taveira Magalhaes and G.M. Stephan, Tetrahedron, 1966, 22, 1785.
92. A.R. Jefferson and F. Scheinmann, Nature, 1965, 207, 1193.
93. H.D. Locksley and I. G. Murray J. Chem. Soc. (C), 1970, 392.
94. S.J. Gabriel and O.R. Gottlieb, Phytochemistry, 1972, 11, 3035.
95. G. Cardillo, R. Cricchio and L. Merlini, Tetrahedron, 1968, 24, 4825.
96. S.M. Anand and A.C. Jain, Tetrahedron, 1972, 28, 987.
97. B. Jackson, H.D. Locksley and F. Scheinman, Phytochemistry, 1969, 8, 927.
98. F. Scheinmann and Nuan-Among Sripong, Phytochemistry, 1971, 10, 1331.
99. R. Somanathan and M.U.S. Sultanbawa, J. Chem. Soc. Perkin I, 1974, 2515.
100. D. de Barros Correa, O.R. Gottlieb and M.T Magalhaes, Ann. Acad. Brasil. Cienc., 1966, 38, 296.
101. R.K. Chaudhuri and S. Ghosal, Phytochemistry, 1971, 10, 2425.
102. G.G. De Oliveira, A.A. Lins Mesquita, O.R. Gottlieb and M. Taveira Magalhaes, Ann. Acad. Brasil. Cienc., 1965, 37, 231.
103. J.R. Lewis and J.R. Reary, J. Chem. Soc. (C), 1970, 1662
104. V.V.Kane, A.B. Kulkarni and R.C. Shah, J. Sci. Ind. Res. (India), 1959, 18 B, 28.

105. H.O. House and G.H. Rasmusson, J. Org. Chem., 1961, 26, 4278.
106. T.R. Govindachari, P.S. Kalyanaraman, N. Muthukumaraswamy and B.R. Pai, Tetrahedron, 1971, 27, 3919.
107. S.M. Anand and A.C. Jain, Indian J. Chem., 1973, 11, 504.
108. R. Somanathan and M.U.S. Sultanbawa, Abs. VIII, IUPAC Symposium, New Delhi, 1972, 80.
109. C.G. Karanjaonkar, P.M. Nair and K. Venkatraman, Tetrahedron Letters, 1966, 687.
110. G. Kartha, G.N. Ramchandran, H.B. Bhat, P. Madhavan Nair, V.K.V. Raghavan and K. Venkatraman, Tetrahedron Letters, 1963, 459.
111. R.L. Alimchand and A.N. Meldrum, J. Chem. Soc., 1920, 117, 964.
112. W.D. Ollis, M.V.J. Ransay, I.O. Sutherland and S. Mongkolsuk, Tetrahedron, 1965, 21, 1453.
113. Braconnot, Trommsdorfs Journal der Pharmaz, 1809, 18, 164.
114. R. Christison, Ann. Pharm., 1837, 23, 173.
115. P. Buchner, Ann. Chem. Pharmaz, 1843, 45, 71.
116. J.F.W. Johnson, Phil. Trans., 1839, 281.
117. H. Hlasiwetz and L. Barth, Ann. Chem. Pharmaz, 1866, 138, 68.
118. P.R. Liechti, Arch. Pharm., 1891, 229, 434.
119. G. Tassinari, Gazzetta, 1896, 26, 248.
120. K.H. Bauer and W. Trumplet, Pharm. Zentralhalle, 1941, 82, 289, 301, 313.
121. M. Lang and A. Katz, Pharm. Acta. Helv., 1949, 24, 387.
122. M. Amorosa, Ann. Chim. Italy, 1955, 45, 40.
123. M. Amorosa and L. Lipparini, Ann. Chim. Italy, 1955, 45, 977.
124. V.S. Gupta, P.L. Narasimha Rao, S.N. Vaid and S. Ramaseshan, Chem. and Ind., 1962, 1469.
125. H. Auterhoff, H. Fraudendrof, W. Liesenklas and C. Schwanndt, Angew. Chem. (Inter. Ed.); 1962, 1, 455.
126. Henry and Caventou, J. Pharm. Chim., 1821, 7, 178.
127. L. Gononica and F. Pelizzoni, Gazz. Chim. Itali, 1955, 85, 1007.
128. J.E. Atkinson, P. Gupta and J.R. Lewis, Tetrahedron, 1969, 24, 1507.
129. H. Kostenecki and J. Tambor, Monatsh, 1894, 15, 1.
130. H. Kostenecki and J. Tambor, Ber., 1894, 27, 190.
131. A.G. Perkin, J. Chem. Soc., 1898, 73, 1028.
132. N. Anand and K. Venkataraman, Proc. Ind. Acad. Sci., 1947, 438.
133. A.M. Verney, P. Ozenda and Mrs. A.M. Debelmas, Bull. Trav. Soc. Pharm. Lyon, 1972, 16, 3.

134. I. Carpenter, H.D. Locksley and F. Scheinmann, J. Chem. Soc. (C), 1969, 486.
135. A.C. Jain, V.K. Khanna and T.R. Seshadri, Tetrahedron, 1969, 25, 2787.
136. M.L. Wolfrom, W.D. Harris, G.F. Johnson, J.E.M. Mahan, S.M. Moffatt and B.S. Wildi, J. Am. Chem. Soc., 1946, 68, 406.
137. P.K. Grover, G.D. Shah and R.C. Shah, J. Chem. Soc., 1955, 3982.
138. G.H. Stout and J.L. Fries, Phytochemistry, 1970, 9, 235.
139. K.R. Markham, Tetrahedron, 1964, 20, 991.
140. K.R. Markham, Tetrahedron, 1965, 21, 1449.
141. S.R. Dalal and R.C. Shah, Chem. and Ind., 1957, 140, 1956, 664.
142. S. Ghosal, P.K. Sharma, R.K. Chaudhuri and S.K. Bhattacharya, J. Pharm. Sci., 1973, 62, 926.
143. A.V. Rama Rao, M.R. Sarma, K. Venkataraman. and S.S. Yemul, Phytochemistry, 1974, 13, 1241.
144. D.M. Holloway and F. Scheinmann, Phytochemistry, 1975, 14, 2517.
145. A. Jafferson and F. Scheinmann, J. Chem. Soc. (C), 1966, 175.  
Nature, 1965, 207, 1193.
146. M.L. Wolfrom and H.B. Bhat, Phytochemistry, 1965, 4, 765.
147. A. Ueno, Yakugaku Zasshi, 1962, 82, 1482, 1486.
148. O.R. Gottlieb, R.A. De Lima, P.H. Mendes and M. Taveira Magalhaes, Phytochemistry, 1975, 14, 1674.
149. S. Ghosal and R.K. Chaudhuri, Phytochemistry, 1973, 12, 2035.
150. Fa. C. Chen, Y.M. Lin, J.C. Hung, Phytochemistry, 1975, 14, 300.
151. J. Shinoda, J. Pharm. Soc. Japan, 1928, 48, 214,
152. A. Ueno, Yakugaku Zasshi, 1962, 82, 1479.
153. R.B. Filho, M. De J. Coutinho Lemos and O.R. Gottlieb, Phytochemistry, 1973, 12, 947.
154. A. Jefferson, A.J. Quillinan, F. Scheinmann and K.Y. Sim, Austral. J. Chem., 1970, 23, 2539.
155. A.A. Lins Mesquita, W.G. De Oliveira, R.M.T. Neiva and O.R. Gottlieb, Phytochemistry, 1975, 14, 803.
156. P. De P.J. Dias, O.R. Gottlieb and Lins Mesquita, Phytochemistry, 1974, 13, 1953.
157. S.P. Gunasekara, K. Silvapan and M.U.S. Sultanbawa, J. Chem. Soc. Perkin I, 1977, 11.
158. J.B. Harborne, Chem. and Ind., 1954, 1142.
159. M.L. Wolfrom, F. Komitsky Jr., G. Fraenkel, J.H. Looker, E.E. Dickey, P. McWain, A. Thompson, P.M. Mundell and O.M. Windrath, J. Org. Chem., 1964, 29, 692.

160. F.E. King, T.J. King and L.C Manning, J. Chem. Soc., 1953, 3923.
161. A. Pictet and A. Goleznoff, Ber., 1903, 36, 2219.
162. M.L. Wolfrom, E.E. Dickey, P. McWain, A. Thompson, J.H. Looker, O.M. Windrath and F. Komitsky (Jr), J. Org. Chem., 1964, 29, 689.
163. D. De Barros Correa, O.R. Gottlieb and M. Taveira Magalhaes, Ann. Acad. Brasil. Cienc., 1968, 307.
164. V.V.S. Murti, T.R. Seshadri and S. Sivakumaran, Phytochemistry, 1972, 11, 2089.
165. E.D. Burling, A. Jefferson and F. Scheinmann, Tetrahedron, 1965, 21, 2653.
166. M.U.S. Sultanbawa, J. Natl. Sci. Council, Sri Lanka, 1973, 1, 123.
167. F.E. King, J.T. King and L.C. Manning, J. Chem. Soc., 1957, 563.
168. A. Jefferson and F. Scheinmann, Tetrahedron Letters, 1964, 1289.
169. J.C. Robert, Chem. Rev., 1961, 61, 591.
170. H.B. Bhat and K. Venkataraman, Tetrahedron, 1963, 19, 77.
171. M.L. Wolfrom, F. Komitsky Jr., G. Fraenkel, J.H. Look, E.E. Dickey, P. McWain, A. Thompson, P.M. Mundell and O.M. Windrath, Tetrahedron Letters, 1963, 749.
172. S.P. Gunasekera, S. Selliah and M.U.S. Sultanbawa, J. Chem. Soc. Perkin I, 1975, 1539.
173. A. Arnone, G. Cardillo, L. Merlini and R. Mondelli, Tetrahedron Letters, 1967, 4201.
174. W.D. Ollis and I.O. Sutherland, "Recent Developments in the Chemistry of Phenolic Compounds", ed. E.D. Ollis, Pergamon London, 1961, p. 74.
175. M.L. Wolfrom, F. Komitsky Jr. and P.M. Mundell, J. Org. Chem., 1965, 30, 1088.
176. K.R. Markham, Tetrahedron, 1965, 21, 3687.
177. G.H. Stout, E.N. Christensen, W.J. Balkenhol and K.L. Stevens, Tetrahedron, 1969, 25, 1947.
178. R.A. De Lima and O.R. Gottlieb, Phytochemistry, 1972, 11, 2307.
179. G.H. Stout, V.F. Stout, M.J. Welsh and L.H. Jenson, Tetrahedron Letters, 1962, 13, 541.
180. G.H. Stout and L.H. Jensen, Amer. Cryst. Assoc. Abstr., 1964, 24.
181. A.J. Quillinan and F. Scheinmann, J. Chem. Soc. Perkin I, 1975, 241.
182. G.D. Shah and R.C. Shah, J. Sci. Ind. Res. India, 1956, 15 B, 630.
183. S. Ghosal, P.V. Sharma and R.K. Chaudhuri, Phytochemistry, 1975, 14, 2671.
184. H. Inouye, S. Ueda, M. Inada and M. Tsujii, Takugaku Zasshi, 1971, 91, 1022.
185. M. Guyot, J. Massicot and P. Rivaille, C.R. Acad. Sc. Paris, 1968, 267, 423.
186. P. Rivaille, J. Massicot, M.G. et Victor Plouvier and M. Massias, Phytochemistry, 1969, 8, 1533.
187. K. Hostettmann, R. Tabacchi and A.J. Guillardmod, Helv. Chim. Acta , 1974, 57, 294.

188. K. Hostettmann, and A.J. Guillardmod, Phytochemistry, 1977, 16, 481.
189. S.R. Dalal, Sethna and R.C. Shah, J. Ind. Chem. Soc., 1953, 30, 457, 463.
190. A. Sarada, V. Narayanswami, Leather Sci. Madras, 1973, 20, 132.
191. S. Ghosal, P.V. Sharma and R.K. Chaudhuri, Phytochemistry, 1975, 14, 1393.
192. S. Ghosal, P.V. Sharma, R.K. Chaudhuri, and S.K. Bhattacharya, J. Pharm. Sci., 1975, 64, 80.
193. G.H. Stout, B.J. Reid and G.D. Breck, Phytochemistry, 1969, 8, 2417.
194. P.J. Chapelle, Planta Med., 1974, 26, 301.
195. D.A. Okorie, Phytochemistry, 1976, 15, 1799.
196. M. Komatsu, T. Tomimori, and M. Mikuriya, Chem. Pharm. Bull. Japan, 1969, 17, 155.
197. T. Tomimori, M. Yoshizaki and T. Nanba, Yakugaku Zasshi, 1974, 94, 647.
198. M. Kaldas, K. Hostettmann and A. Jacot-Guillardmod, Helv. Chim. Acta, 1974, 57, 2557.
199. S. Ahmad, M. Ikram, I. Khan and M.N. Galbraith, Phytochemistry, 1973, 12, 2542.
200. B. Jackson, H.D. Locksley and F. Scheinmann, Tetrahedron, 1965, 21, 2653.
201. S. Ghosal, R.K. Chaudhuri and A. Nath, J. Pharm. Sci., 1973, 62, 137.
202. K. Hostettmann and A.J. Guillardmod, Helv. Chim. Acta, 1974, 57, 1155.
203. P. Rivaille and D. Raulais, C.R. Acad. Sc. Paris, 1969, 269-D, 112.
204. J. Carbonnier, M. Massias, M.C. Jarreau-Carbonnier and D. Molho, Travaux Lab. de la Jaysinia, 1972, 169.
205. H. Rosler, T.J. Mohry, M.F. Cranmer and T. Kagan, J. Org. Chem., 1965, 30, 4346.
206. T. Tomimori, M. Yashizaki and T. Nanba, Yakugaku Zasshi, 1973, 93, 442.
207. S.K. Battacharya, A.K. Sanyal and S. Ghosal, Naturwissenschaften, 1972, 59, 651.
208. S. Ghosal, P.V. Sharma and R.K. Chaudhuri, J. Pharm. Sci., 1974, 63, 1286.
209. Y. Asahiana, J. Asano and Y. Uyeno, Bull. Chem. Soc. Japan, 1942, 17, 104.
210. T. Nakaoki and Y. Hida, J. Pharm. Soc. Japan, 1943, 63, 554.
211. M. Komatsu and T. Tomimori, Japan, 1972, 16676.
212. T. Tomimori and M. Komatsu, Yakugaku Zasshi, 1969, 89, 1276; C.A. 1972, 77, 8578.
213. R.N. Chopra, S.L. Nayar and I.C. Chopra, "Glossary of Indian Medicinal Plants", C.S.I.R. New Delhi, India, 1956, p. 49.
214. K.R. Kirtikar and B.D. Basu "Indian Medicinal Plants", Vol. III, Allahabad, India, 1933, p. 1664.
215. T.J. Mabry, K.R. Markham and M.B. Thomas, "The Systematic Identification of Flavonoids", Springer-Verlog, New York, 1970, p. 271.

216. D.J. Ross, N.Z.J. Sci. & Tech., 1950, 32, 39.
217. J. Moron, J. Polonsky and H. Pourrat, Bull. Soc. Chim. Fr., 1967, 130.

Received, 12th December, 1978