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ISOLATION AND STRUCTURE OF SURANGIN A AND SURANGIN B, TWO NEW COUMARINS FROM *MAMMEA LONGIFOLIA* (WIGHT) PLANCH AND TRIANA*

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Abstract—From the roots of *Mammea longifolia* (wight) Planch and Triana two new 4-alkylated coumarins designated as surangin A and surangin B have been isolated. They have been constituted as II and III, on the basis of evidence largely resting on a combination of UV, IR, NMR and mass spectral data.

Mammea longifolia (Wight) Planch. and Triana (Syn. *Ochrocarpus longifolius* (Wt.) Benth. and Hook. f. ex T. Anders.) (Fam. Gurriferae) (*Sanskrit*—Surangi) is a large tree growing in the Western Ghats of India. The roots gave on hexane extraction a viscous oil having high *in vitro* antibacterial activity. Chromatographic separation of the oil on silica gel led to the isolation of two new coumarins designated surangin A, m.p. 85° and surangin B, m.p. 100° in 0·06 and 0·54% yields respectively.

Surangin A analyses for the formula $C_{27}H_{36}O_5$ (mol. wt. by mass spec. 440) and forms colourless needles. $[\alpha]_D$ −1·6°; R_f 0·6 (Silica gel; benzene–Chf. 1:1). Surangin B is slightly more polar having R_f 0·4 and differs from surangin A by a $C_2H_2O_2$ unit, mol. wt. by mass spec. 498, $[\alpha]_D$ −30°.

The structure determination of the two compounds is based on a combination of spectroscopic data and no degradative experiments have been carried out. Both the compounds give a blue ferric chloride coloration indicating chelated phenolic OH groups. The UV spectra of surangin A λ_{max}^{EtOH} 222, 296 and 325 (infl) mμ; log ε 4·44, 4·32 and 4·21 respectively and surangin B λ_{max}^{EtOH} 222, 295 and 329 mμ; log ε 4·43, 4·29 and 4·24 respectively are extremely similar to those reported for a number of 5,7-dioxygenated coumarins (I).[1,2] The IR spectrum of surangin A exhibits bands characteristic of OH (3300), coumarin CO (1730), chelated acyl (1605) and aromatic (1600, 1560 cm^{-1}) groups. Surangin B showed in addition, the C—O stretching band at 1240 cm^{-1} due to an acetate group.

The NMR spectra of both the compounds are exceptionally useful in arriving at the structures, since the environment of every proton in the molecule is unambiguously defined. Surangin A (Table 1) showed sharp peaks at 14·6 and 6·92 δ (1H each) which disappeared on deuteration. The low field signal is clearly due to the chelated OH at 7 position and the upfield signal at 6·92 is due to the unchelated OH at position 5 of the coumarin nucleus. The 7-OH group is chelated by an 8-acyl and not a 6-acyl group.[3,4] This conclusion is also supported by the changes in the UV spectrum of Surangin A (Table 2) by the addition of acid and alkali.[3–5]

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TABLE 1. NMR SPECTRUM OF SURANGIN A (II)
(60 Mc; $CDCl_3$, TMS)

Chemical shift (δ)	Proton count	Assignment	Shape of peaks
1·0	6	f, j	Triplet (J = 7 c/s)
1·25	3	h	Doublet (J = 7 c/s)
1·58	3	q or r	Singlet (slightly split)
1·65	3	q or r	Singlet (slightly split)
1·4–1·8	4	e, i	Multiplet
1·82	3	m	Singlet
2·1	4	n, o	Doublet
2·92	2	d	Triplet (J = 7 c/s)
3·5	2	k	Doublet (J = 7 c/s)
3·9	1	g	Quartet (J = 7 c/s)
5·05	1	p	Multiplet
5·2	1	l	Triplet (J = 7 c/s)
6·0	1	a	Singlet
6·92	1	b	Singlet
14·6	1	c	Singlet

TABLE 2. UV DATA OF SURANGING A AND SURANGIN B

Surangin A	λ_{max}^{EtOH} (log ε_{max})		
N/100 HCl	222 (4·46)	295 (4·35)	325 (4·21)
N/100 KOH	225 (4·25)	257 (4·01)	332 (4·45)
Surangin B			
N/100 HCl	222 (4·53)	295 (4·33)	325 (4·16)
N/100 KOH	225 (4·25)	258 (4·06)	333 (4·52)

The appearance of a high field singlet at 6·0 δ (1H) due to the C-3 proton indicated that the C-4 position of surangin A is substituted.[2] On phytochemical considerations it is consistent to attach an n-propyl chain at C-4. A triplet at 2·92 δ (2H; J = 7 c/s) is due to the methylene protons attached to the ring B while the terminal Me is seen as a triplet at 1·0 δ (3H; J = 7 c/s). The other methylene protons appear between 1·4–1·8 δ. The 8-acyl side chain is composed of $-CO-\underset{\displaystyle Me}{\underset{|}{CH}}-CH_2-CH_3$ as in mammea B/BB[3] and ferruol A[4]. A 10-carbon unit is attached at the 6-position of the coumarin nucleus as a geranyl chain. The chemical shifts and the probable assignments given in Table 1 indicate that suranging A must be represented by structure II.

The UV shifts in acid and alkali (Table 2) show a closely resembling pattern of substitution in surangin B. On methylation with dimethyl sulphate and potassium carbonate in acetone, surangin B gave an oily dimethyl ether. The NMR spectrum of surangin B is almost identical with that of suranging A (Fig. 1) except for the absence of the methylene triplet at 2·92 and instead having an additional one proton quartet at 6·5 and a singlet Me signal at 2·2 δ. The quartet at 6·5 δ is due to the proton *d* in formula III and the peak at 2·2 δ could be ascribed to the acetate Me group.

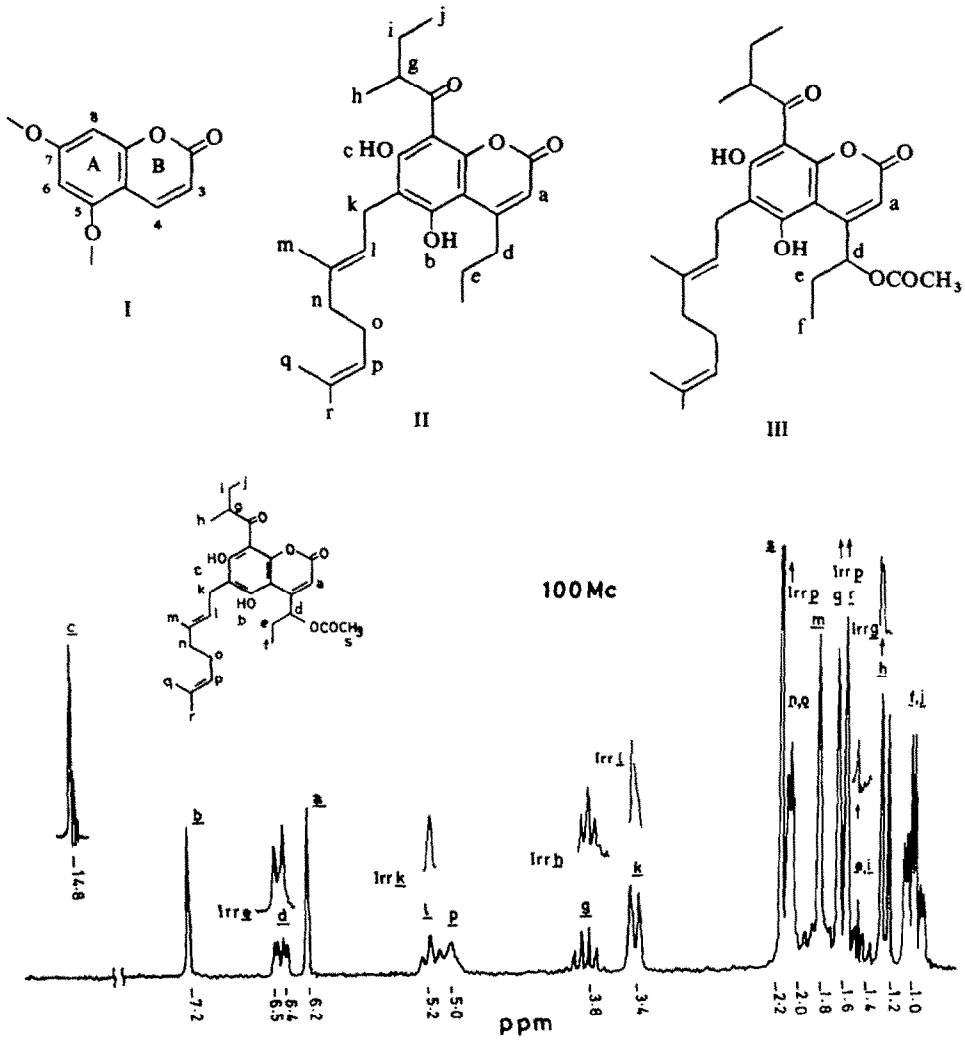
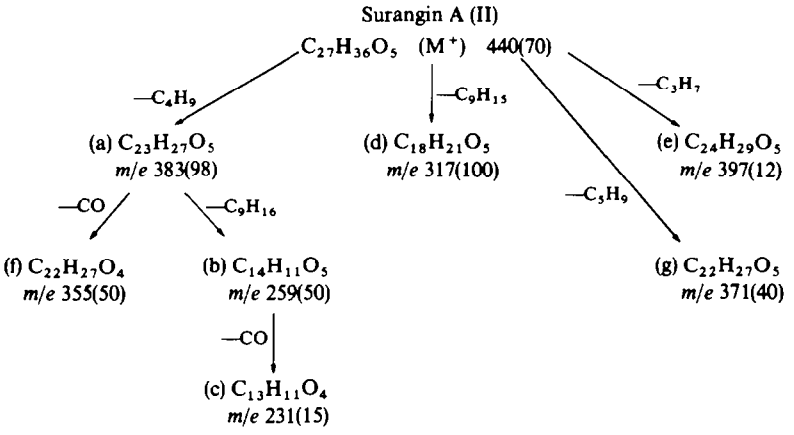


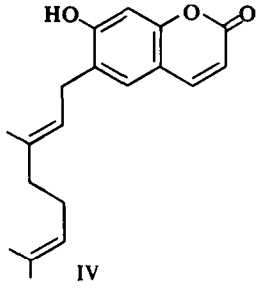
FIG. 1 NMR Spectrum of surangin B (III).

Surangin B can therefore be constituted as III. The quartet at 6·5 δ has been shown to be coupled with the adjacent methylene *e* at 1·73 δ by double resonance experiments. In addition, double resonance experiments of surangin B have shown that the proton *g* is coupled with the Me *h* and the methylene *i*, the proton *l* with the benzylic methylene *k* and the proton *p* with the methylene protons at *o* with sharpening of the methyls *q* and *r*.

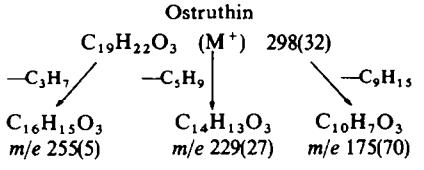
Mass spectra of surangin A and surangin B are consistent with the proposed structures. The major fragmentation pattern of surangin A is shown in Scheme I. The 2-methylbutyryl substituent in position 8 loses a butyl radical to give fragment (a) followed by the elimination of a C_9H_{16} moiety from the geranyl chain giving (b). Loss of carbon monoxide from fragments (a) and (b) would give rise to the ions (f) and (c) respectively. These fragmentations are analogous to similarly substituted



SCHEME I

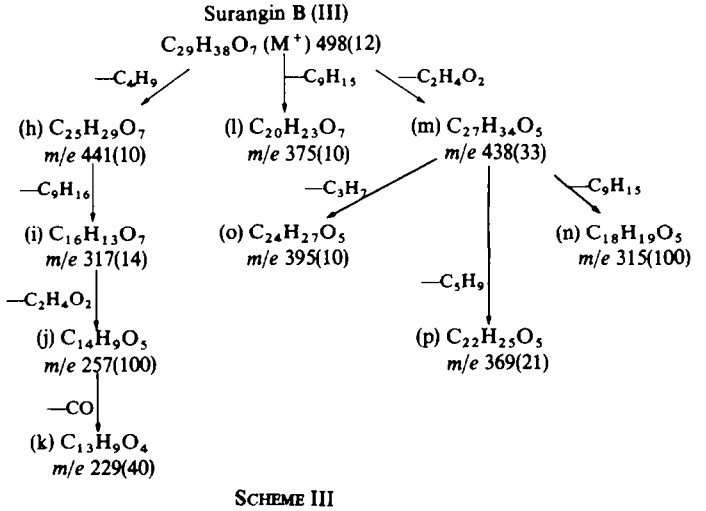


IV



SCHEME II

coumarins, e.g. mammea B/BB, mammea B/BA and ferruol A[3,4]. The base peak in the spectrum appears at *m/e* 317 (d) due to loss of a C_9H_{15} radical from the geranyl chain. Another mode of fragmentation of surangin A is loss of a propyl (M-43) and



SCHEME III

1,1-dimethyl-Δ^1-propenyl (M-69) radicals to give (e) and (g) respectively. Evidence that the (M-123) peak is due to the loss of C_9H_{15} radical from the geranyl side chain is obtained from the mass spectrum of ostruthin (IV; Scheme II). The spectrum shows the breakdown of the geranyl side chain. Surangin B shows loss of butyl radical (M-57) to give (h) (Scheme III) from which the C_9H_{16} moiety is expelled to give the peak at *m/e* 317 (i). Loss of acetic acid from the C-4 side chain gives an intense peak at *m/e* 257. Contrary to surangin A, the ion (1) having *m/e* 375 obtained by the direct loss of C_9H_{15} from surangin B is not abundant. As would be expected, elimination of acetic acid (M-60) gives rise to the peak (m) at *m/e* 438. The most intense peak in the spectrum is seen at *m/e* 315 (n), due to the loss of C_9H_{15} ion from (m). Other fragments such as (o) and (p) are obtained by loss of a propyl and 1,1-dimethyl-Δ^1-propenyl radicals from (m).

EXPERIMENTAL

UV and IR spectra were determined on Beckmann DK-2A and Perkin–Elmer model 421 spectrophotometers. NMR spectra were taken on Varian A-60 or HR-100 spectrophotometers in $CDCl_3$ solution with TMS as internal reference standard. M.ps are uncorrected.

Extraction of the roots of Mammea longifolia. The powdered roots (12 kg) were extracted by percolation with hexane (3 × 30 l) at room temp. The extract on evaporation under reduced press gave a viscous oil (360 g). On examination by TLC, this showed four distinct spots, R_f. 0·6, 0·55, 0·4 and 0·07 (Sigel, benzene–Chf, 1:1). A separation was effected by column chromatography.

Isolation of surangin A, surangin B and taraxerol. The oil (360 g) was dissolved in hexane (1200 ml) and chromatographed on a column of Si gel (0·05–0·2 mm; 3·6 kg) in hexane. 500 ml fractions were collected and the course of the chromatography followed by TLC.

Fractions	Eluent	Eluate	R_f TLC on Si gel in benzene–Chf (1:1)
1–30	Hexane	—	—
31–50	Hexane–Benzene (1:1)	—	—
51–80	Hexane–Benzene (1:1)	20 g, oil	0·6
81–115	Benzene	20 g, oil + crystals	0·6
116–125	Benzene	10 g, oil + crystals	0·55
126–135	Benzene	13 g, oil	0·4
136–350	$CHCl_3$	142 g, oil + crystals	0·4
351–500	$CHCl_3$	40 g, oil	0·4
501–580	$CHCl_3$–MeOH (3:1)	106 g, thick residue	0·07

(i) Fractions 51–115 were pooled and the solvent removed. The oily residue was diluted with hexane and left overnight at room temp. The crude crystalline mass was separated by filtration and purified by recrystallization from hexane to give *surangin A* (6 g), m.p. 83–85°, $[\alpha]_D^{26°}$ −1·6° (*c*, 0·3, $CHCl_3$), UV λ_{max}^{EtOH} 222, 296 and 325 (inflexion) mμ (log ε 4·44, 4·32 and 4·21); IR (CH_2Cl_2) 3300, 1730, 1605, 1600, 1560, 1380, 1190, 1140, 1115, 930 and 350 cm^{-1}. (Found: C, 73·7; H, 8·2. Mol. wt. by mass spectrum 440. $C_{27}H_{36}O_5$ requires: C, 73·6; H, 8·2%. Mol. wt. 440).

(ii) Fractions 116–125 were combined and the solvent evaporated. The residue on dilution with hexane gave a small amount of crystalline substance (100 mg), m.p. 278°. This compound was identified as *Taraxerol* by comparison of m.p., mixed m.p., TLC and IR with an authentic sample.

(iii) Fractions 126–500 were pooled, freed of the solvent, diluted with hexane and left at room temp overnight. The crude crystalline mass was isolated by filtration and further purified by recrystallization

from CH_2Cl_2–hexane to give *surangin B* (50 g), m.p. 98–100°, $[\alpha]_D^{24°}$ −30°; UV λ_{max}^{EtOH} 222, 295 and 329 mμ (log ε 4·43, 4·29 and 4·24); IR (CH_2Cl_2): 3300, 1742, 1610, 1560, 1400, 1330, 1240, 1195, 1140, 1108, 1048, 1020, 975, 932 and 865 cm^{-1}. (Found: C, 69·6; H, 7·8. Mol. wt. by mass spectrum 498. $C_{29}H_{38}O_7$ requires: C, 69·8; H, 7·7%, Mol. wt. 498).

Methylether of surangin B. A mixture of surangin B (4·8 g), anhyd K_2CO_3 (18 g), Me_2SO_4 (6 ml) and dry acetone (180 ml) was refluxed on a waterbath overnight. Acetone was distilled off, the residue diluted with water, left at room temp overnight and then extracted with ether. The ether extract was washed with $NaHCO_3$, water, dried over anhyd Na_2SO_4, and the solvent removed. A thick oil (5 g) was obtained.

This was purified by dissolving in hexane (15 ml) and chromatography over a column of Sigel (0·05–0·2 mm, 50 g) in hexane. The initial hexane eluates gave only negligible waxy matter and the next benzene eluates afforded the methyl ether as a gummy solid (3·6 g); TLC on Si gel (R_f 0·25, benzene–Chf. 1:1); UV λ_{max}^{EtOH} 210, 224 and 300 mμ (log ε 4·51, 4·50 and 4·17); IR (CH_2Cl_2): 1742, 1710, 1620, 1595, 1460, 1395, 1320, 1285, 1100, 1048, 1020, 988, 970, 928, 885 and 868 cm^{-1}. (Found: C, 70·5; H, 8·2, Mol. wt. by mass spectrum 526. $C_{31}H_{42}O_7$ requires: C, 70·7; H, 8·0%. Mol. wt. 526).

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