

Terpenoids and Related Compounds. Part XVII† : Neutral Constituents of *Michelia lanuginosa* Wall. Structures, Absolute Configuration and Conformation of Three New Germacranolides. A Novel Rearrangement of Lanuginolide

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Dihydroparthenolide and lanuginolide, two new sesquiterpene lactones of germacrane type, isolated from the trunk bark of *Michelia lanuginosa* Wall, and 11,13-dehydrolanuginolide—another new germacranolide isolated along with parthenolide (4) and a new natural aldehyde sinapaldehyde (17) from the less mature trunk bark of the same plant, are shown to possess stereostructures 1, 5 and 12 respectively on the basis of spectral and chemical evidence. The relative and absolute configurations as well as the molecular conformation of these sesquiterpenes were derived from detailed PMR analyses and substantiated by molecular rotation difference studies. The mass spectral fragmentation patterns of the germacranolides and their derivatives were also rationalised for the first time. The plausible mechanism of a novel rearrangement of lanuginolide (5) under the influence of Adam's catalyst has been discussed. Isolation of sinapaldehyde is biogenetically significant. ¹³C NMR signals of acetylsinapaldehyde are also reported.

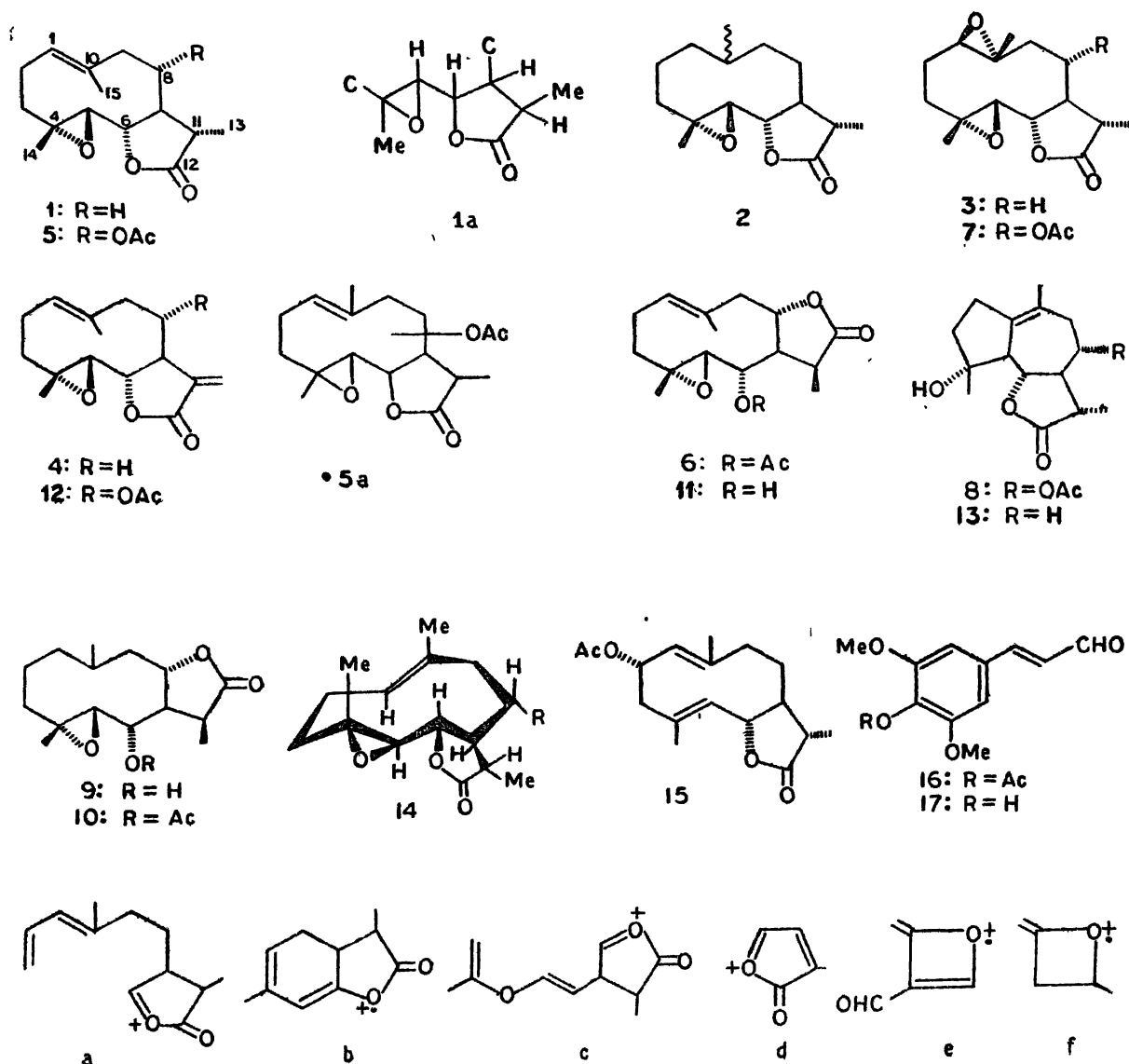
RECENT years have witnessed a tremendous surge of interest on sesquiterpene lactones particularly germacranolides because a number of them has been shown to possess potential physiological activity. Germacranolides seem to be plentiful in the Compositae although isolated instances of their occurrence in other plant families, e.g. Magnoliaceae (*Michelia champaca*¹, *Liriodendron tulipifera*²), Umbelliferae (*Laser trilobum*³) and Leguliflorae (*Urospermum dalechampii*⁴) are coming to light. We have studied the Magnoliaceae plant *Michelia lanuginosa* from which, in addition to some aporphine and oxoaporphine alkaloids⁵, parthenolide and three new germacranolides dihydroparthenolide, lanuginolide and 11,13-dehydrolanuginolide and a new natural aldehyde sinapaldehyde have been isolated. The present communication deals with their isolation and structure along with the elaboration of the absolute stereochemistry and molecular conformation of the new germacranolides.

The minor neutral constituent 1 exhibited IR absorption bands for unconjugated γ -lactone, epoxy ring and cyclic trisubstituted double bond. The PMR spectrum (Table 1) revealed the presence of one $\text{CH}-\text{CH}_3$, and $\text{O}-\text{C}-\text{CH}_3$ and one $\text{HC}=\text{C}-\text{CH}_3$, and an epoxy proton (H-5) coupled with a lactone methine proton (H-6). These observations indicate the presence of the system 1a. The presence of a double bond in 1 was confirmed by its ready hydrogenation (PtO_2 , EtOH) to the dihydroderivative 2, as well as by epoxidation⁶ with $\text{C}_6\text{H}_5\text{CO}_3\text{H}$ to an epoxy derivative 3. Both 2 and 3 showed the absence of IR bands for trisubstituted double bond. Their PMR spectra (Table 1) were also in agreement with the above

findings. The absence of any UV absorption maxima above 200 nm region in 1 indicated the isolated nature of its double bond. Thus the germacranolide structure 1 (or its $\Delta^{9,10}$ isomer) was derived for this natural lactone. Literature survey indicated that this lactone has similar physical constants and spectral characteristics as those reported for dihydroparthenolide [lit.¹ m.p. 137°, $[\alpha]_D - 62^\circ$ (CHCl_3) having the same gross structure as 1], a product obtained earlier by partial hydrogenation of parthenolide (4). Its identity with dihydroparthenolide has since been established by direct comparison (mmp, TLC, IR, $[\alpha]_D$, PMR) with an authentic sample of dihydroparthenolide prepared by us by partial hydrogenation of parthenolide. The isolation of dihydroparthenolide (1) constitutes the first report of its natural occurrence⁷.

The second sesquiterpene lactone lanuginolide (5) also showed no UV absorption maximum above 200 nm. The bands for unconjugated γ -lactone, acetate, epoxy ring and trisubstituted double bond are clearly discernible in its IR spectrum. In addition to the signals for a $\text{O}-\text{C}-\text{CH}_3$, a $\text{CH}-\text{CH}_3$ and a $>\text{C}=\text{C}(\text{CH}_3)$, a OCOCH_3 signal is also present in its PMR spectrum (Table 1). The signals, 1H each, at δ 2.63 (d, $J=9$ Hz) and 3.94 (t, $J=9$ Hz) indicated, as in the case of 1, the presence of the grouping 1a in 5. The spectrum also showed two complex signals at δ 5.25 (1H) and 4.85 (1H) which are assigned to a $-\text{HC}=(\text{CH}_3)$ and a $\text{CH}-\text{OAc}$ respectively. All the foregoing observations and the comparable physical properties of 5 and 1 are in agreement with the presence of a germacranolide skeleton 5a. The evidence for the location of the acetoxyl function at C-8 was secured

† Part XVI : S. K. Talapatra, R. Chakravarty and B. Talapatra, *Indian J. Chem.*, 17B, (1979), in press.



by alkaline hydrolysis of **5** followed by acetylation of the resulting oily product to afford, along with the minor amount of **5**, the lactone rearrangement product isolanuginolide (**6**). The latter showed absorption bands for γ -lactone, acetate and trisubstituted double bond. The PMR spectrum of **6** exhibited the signals for the different characteristic protons as are present in that of the parent compound **5**, but the appearance of a triplet (1H, $J=9$ Hz) at δ 5.0 (CH-OAc) and a multiplet (1H) at 4.20 (lactone methine proton) suggested that the positions of the acetoxy and the γ -lactone linkages (compared to that in **5**) have been interchanged and consequently the acetoxy function in **5** should be located⁷ at C-8.

The formation of the epoxide **7** (showing all IR bands excepting those for the trisubstituted double bond) with $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ also supported the presence of

a double bond in **5**. The PMR spectrum of **7** lacked the signals for any vinyl methyl and vinyl proton; two epoxy methyls appeared at δ 1.40 and 1.43; signals for other characteristic protons are listed in Table 1.

The presence of an epoxy ring in **5** was indicated by its transannular cyclisation with acidic reagents (BF_3 or dry HCl gas) to furnish a tertiary alcohol derivative **8**. Its IR spectrum exhibited bands for $-\text{OH}$, γ -lactone and acetate functions but no band for epoxy ring and trisubstituted double bond. Its PMR spectrum showed signals for a $\text{O}-\text{C}-\text{CH}_3$, a $>\text{C}=\text{C}(\text{CH}_3)$ and an OH in addition to those for a $\text{CH}-\text{CH}_3$, a OCOCH_3 , a lactone methine proton and a $\text{CH}-\text{OAc}$; the signals for the vinyl and epoxy protons were absent. Its inert behaviour towards Ac_2O and pyridine, indicated the tertiary nature of the OH.

TABLE 1—PMR SIGNALS* OF DIHYDROPARTHENOLIDE (1), LANUGINOLIDE (5), 11, 13-DEHYDROLANUGINOLIDE (12) AND THEIR DERIVATIVES IN δ (PPM).

Compound**	H-1	H-5	H-6	H-8	H-13	H-14	H-15	Miscellaneous
Dihydroparthenolide (1)	5.25, m	2.70, d, 9	3.84, t, 9	—	1.27, d, 6.5	1.28	1.72	
Tetrahydroparthenolide (2)	—	2.95, d, 9	3.83, t, 9	—	1.25, d, 6.5	1.50	0.88, d, 6	
Dihydroparthenolide epoxide (3)	—	2.86, d, 9	3.98, t, 9	—	1.27, d, 6.5	1.28	1.39	
Lanuginolide (5)§	5.25, m	2.63, d, 9	3.94, t, 9	4.85, m	1.41, d, 6	1.28	1.80	C ₈ -OCOCH ₃ , 2.09
Isolanuginolide (6)	5.33, m	2.67, d, 9	5.0, t, 9	4.20, m	1.37, d, 6.5	1.30	1.80	C ₈ -OCOCH ₃ , 2.11
Lanuginolide epoxide (7)	—	2.78, d, 9	4.12, t, 9	4.97, m	1.35, d, 6	1.43	1.40	C ₈ -OCOCH ₃ , 2.10
<i>t</i> -Alcohol derivative (8)	—	—	3.94, t, 9.5	4.88, m	1.32, d, 6.5	1.30	1.68, d, 2.5	C ₈ -OCOCH ₃ , 2.80 C ₄ -OH, 2.16
Deacetyldihydroisolanuginolide (9)	—	2.87, d, 9.5	3.53, t, 9.5	4.25, m	1.48, d, 7	1.47	0.98, d, 6	C ₈ -OH, 2.67, b
Dihydroisolanuginolide (10)	—	2.87, d, 9.5	5.0, t, 9.5	4.30, m	1.31, d, 7	1.47	0.93, d, 7	C ₈ -OCOCH ₃ , 2.11
Dehydrolanuginolide (12)	5.30, m	2.63, d, 9.5	4.25, dd, 9.5, 7.5	4.59, m	5.75, d, 3 6.37, d, 3	1.28	1.81	C ₈ -OCOCH ₃ , 2.0 H-7, 3.27, m
Parthenolide (4)	5.30, m	2.70, d, 9	3.89, t, 9	—	5.58, d, 6.31, d, 3.5 each	1.28	1.72	

* d, doublet; t, triplet; m, multiplet; the number after multiplicity denotes coupling constant in Hz.

** for numbering see structure 1.

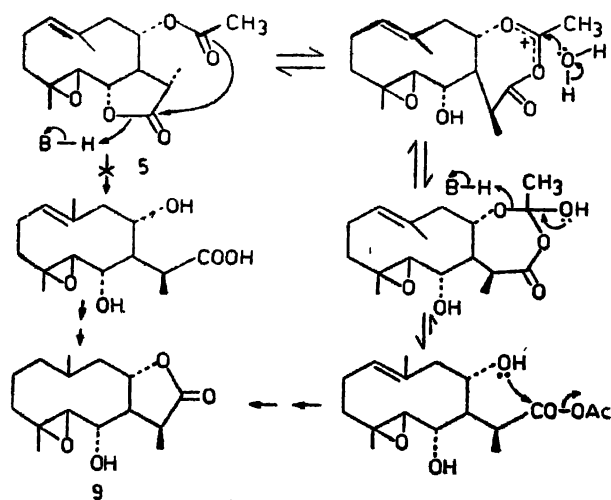
§ Spectrum run in a JEOL Machine.

Lanuginolide (5) is quite resistant to hydrogenation. No consumption of H₂ took place even after stirring its EtOH soln for 4 hr in the presence of PtO₂ (1/4th amount by weight) and 5 was mostly recovered unchanged. Prolonged exposure (12 hr) of 5 to H₂ in the presence of an equal amount of PtO₂ in EtOH solution brought about an unusual hydrogenative deacetylation to yield along with a small amount of lanuginolide, deacetyldihydroisolanuginolide (9) which showed IR absorption bands for OH, γ -lactone and epoxy ring—bands for acetate and trisubstituted double bond being absent. The PMR spectrum of 9 (Table 1) showed the absence of any signal for acetate methyl and the appearance of a signal for an —OH function (δ 2.67, b, exchangeable with D₂O). Further, the multiplicities of the lactone methine proton (δ 4.25, m) and the carbinyl proton (3.53, t, $J = 9.5$ Hz) suggested that an unusual rearrangement of the lactone function took place. On treatment with Ac₂O/Py 9 afforded dihydroisolanuginolide (10). The IR spectrum of 10 exhibited signals for γ -lactone, epoxy ring and acetate function. The PMR spectrum of 10 (Table 1) is quite revealing. The multiplicities of the lactone methine proton (δ 4.30, m) and the acetate methine proton (5.0, t, $J = 9.5$ Hz), when compared to those in lanuginolide, indicated that the sites of their location have been interchanged in conformity with structure 10 for dihydroisolanuginolide. The structure 9 and 10

received further confirmation from the following experiment. Hydrogenation of isolanuginolide (6) in EtOH solution in the presence of PtO₂ afforded 10, identified though undepressed mmp, TLC and IR spectral comparison.

The novel rearrangement of 5 to 9 during catalytic hydrogenation took place on the catalyst surface and probably involved internal nucleophilic attack on the lactone carbonyl by the neighbouring carbonyl oxygen of the acetate moiety (this appeared to be quite feasible from the study of the molecular conformation of 5) leading to the original lactone ring opening (Scheme 1). Subsequent hydrolysis of the resulting resonance stabilized incipient carbonium ion, followed by the original acetate acyl-oxygen bond cleavage to form an unstable mixed anhydride and rapid relactonisation of the latter by internal nucleophilic attack by 8-OH with concomitant expulsion of OAc would then lead to 9. Alternatively, the dihydroxy acid generated by the reversible hydrolysis of both the acetate and the γ -lactone may undergo irreversible relactonisation with the 8-OH [the dihydroxy acid has already been shown⁷ (*vide supra* 5→6) to cyclise exclusively in the direction of C-8]. Though in 95% EtOH protons are almost certainly available for reversible deacetylation and opening of the lactone ring to the dihydroxy acid (however small the rate may be), this possibility is excluded in view of the

fact that no rearrangement of 5 to deacetylsolanuginolide (11) occurred when stirred with 95% EtOH alone for several days. The formation of the more stable lactone involving C-8 OH (less rigid and less strained since the saturated C-6 separates two strained rings, viz. the epoxy and the lactone) seems to be the driving force for this novel rearrangement. Again, dihydrolanuginolide could not be isolated from the reaction mixture and the yield of the rearranged product (9) was fairly high. The C-8 acetate function of 5 in its preferred conformation thus appears to make the double bond inert by shielding it on the exposed face of the molecule. Hydrogenation thus occurred at any stage after the opening of the lactone ring in 5 making the molecule more flat and exposed (Scheme 1).



Scheme-1

From the less mature trunk bark of the same plant two thermally somewhat unstable germacranolides were isolated. One of them, showing λ_{max} 215 nm (log ϵ 4.02) and characteristic IR bands for conjugated γ -lactone, epoxy ring and trisubstituted double bond was found to be identical (mmp, TLC, IR) with parthenolide (4), isolated from *M. champaca* L. Controlled catalytic hydrogenation (10% Pd-C) of this lactone in EtOH soln furnished 1, identical with the natural specimen. The other lactone (12), showed λ_{max} 215 nm (log ϵ 3.82) and characteristic IR bands for α, β -unsaturated γ -lactone, acetate, epoxy ring and trisubstituted double bond. The appearance of the characteristic pair of doublets (slightly broad) at δ 5.75 (1H, $J=3$ Hz) and 6.37 (1H, $J=3$ Hz) for conjugated methylene, an epoxy methyl signal (δ 1.28, s), an epoxy proton doublet (2.63, $J=9.5$ Hz), a lactone methine double doublet (4.25, $J=9.5$ and 7.5 Hz), a vinyl methyl singlet (1.81), a vinyl proton (5.30, m), and signals (2.0, s; 4.59, m) for CH_3OCOCH_3 in its PMR spectrum are in conformity with the structure 12 which received confirmation⁸ through its conversion to lanuginolide (5) by catalytic hydrogenation.

The absence of the more stable lactones 6 and 11, 13-dehydrosolanuginolide in this plant suggests that the oxygenation at C-8 must have followed the lactonisation step in the plant cells. Costunolide⁹ and hence 4 may thus be regarded as the most probable biogenetic precursors of 12 and 5. The co-occurrence of 4 and 12, 1 and 5 provides circumstantial evidence in support of this postulate. The occurrence of 1 and 5 in the mature trunk bark of *M. languinosa* and of 4 and 12 in the trunk bark of less mature plant is biogenetically significant. It appears that hydrogenation of the 11, 13-double bond in 4 and 12 takes place only when the plant attains certain maturity.

The stereochemistry at C-6, C-7 and C-11 in 1 was determined¹⁰ by direct conversion of dihydrocostunolide of known stereochemical structure to 1 through selective monoepoxidation with $C_6H_5CO_3H$. However, there seems to be no report on the stereochemistry of the epoxy ring at C-4 and C-5. A careful examination of the PMR spectra of 1 and 2 (Table 1) throws much light on the stereochemistry of these centres as well as on the molecular conformation of the former. Since H-6 and H-7 are *trans*¹⁰, the appearance of the triplet H-6 and the doublet H-5 with $J=9$ Hz in each case indicates that the H-5 should also be *trans* and so α -oriented with respect to the β H-6. Again epoxidation takes place on the *trans* 4, 5-double bond of costunolide¹¹ necessitating the *trans* orientation of 4- CH_3 and H-5 (α -) and hence 4- CH_3 should be β -oriented. Consequently epoxy linkage at C-4 is α -oriented as shown in 1. The co-occurrence of 1 and 5 and the close similarity with regard to chemical shifts, multiplicities and coupling constants of their PMR signals (Table 1) indicate their same relative stereochemistry; so by analogy, the absolute configuration of 5 at C-4, C-5, C-6, C-7 and C-11 may be represented as shown. The comparable molecular rotation difference values (Table 2) between 1 and 4 ($[M]_D - [M]_4 = +47^\circ$) and between 5 and 12 ($[M]_5 - [M]_{12} = +119^\circ$) also suggest their same relative stereochemistry at C-11. Again the formation of 6 from 5 (by alkaline hydrolysis followed by acetylation) suggests that the oxygen functions at C-6 and C-8 of 5 are *cis* and so H-8 is β as shown. The transformation of the C-6 lactone exclusively to C-8 lactone during alkaline hydrolysis is in keeping with the independent findings that similar compound with lactonisable α -hydroxyls at C-6 and C-8 lactonises exclusively to the C-8 product¹².

The formation of transannular cyclisation products of similar structure under the action of BF_3 or dry HCl gas from 1 and 5 indicate the same steric relationship of the participating epoxy ring and the double bond. This is supported by the comparable molecular rotation difference values between 1 and its cyclised product 13 ($[M]_{13} - [M]_1 = +155^\circ$) and between 5 and 8 ($[M]_8 - [M]_5 = +120^\circ$). Similar stereochemistry around the double bonds in 1 and 5 are also suggested by the comparable changes in molecular rotations on conversions to the corresponding epoxides 3 and 7 respectively ($[M]_3 - [M]_1 = -50^\circ$; $[M]_7 - [M]_5 = -77^\circ$).

TABLE 2—MOLECULAR ROTATIONS OF DIHYDROPARTHENOLIDE (1), LANUGINOLIDE (5), DEHYDROLANUGINOLIDE (12) AND THEIR DERIVATIVES.

Compound	$[\alpha]_D$	$[M]_D$	Molecular rotation difference
Dihydroparthenolide (1)	-68.5°	-171°	
Tetrahydroparthenolide (2)	-35°	-88°	$[M]_1 - [M]_4 = +47°$
Dihydroparthenolide epoxide (3)	-83°	-221°	$[M]_5 - [M]_{13} = +119°$
Parthenolide (4)	-88°	-218°	
Lanuginolide (5)	-57°	-176°	$[M]_8 - [M]_1 = -50°$
Isolanuginolide (6)	+38°	+117°	
Lanuginolide epoxide (7)	-78°	-253°	$[M]_7 - [M]_5 = -77°$
Tertiary alcohol (8) from lanuginolide	-18°	-56°	
Deacetyldihydroisolanuginolide (9)	+17°	+46°	$[M]_8 - [M]_5 = +120°$
Dihydroisolanuginolide (10)	+50°	+155°	$[M]_{18} - [M]_1 = +155°$
Dehydrolanuginolide (12)	-96.5°	-295°	
Tertiary alcohol 13 ¹ from dihydroparthenolide	-6.5°	-16°	

It is interesting to note (Table 1) that H-5 and 4-CH₃ protons in 1 are significantly shielded by 0.25 and 0.22 ppm respectively relative to those of its dihydroderivative (2), indicating that these protons lie in the shielding cone associated with the π -electrons of the 1,10-double bond. The H-5 and H-8 and 4-CH₃ protons in 5 are significantly shielded (by 0.12–0.15 ppm) (Table 1) relative to those of its epoxide 7 indicating that these protons lie in the shielding cone associated with the π -electrons of the double bond (i.e. above its plane) in the preferred conformation of the 10-membered ring. It has also been observed that H-6 in 5 is also shielded by 0.18 ppm relative to that of its epoxide 7 (cf. H-6 of 1 is shielded by 0.14 ppm relative to that of its epoxide 3). On the other hand no change in chemical shift has been observed for H-6 of 2 when compared with that of 1, indicating that H-6 in 1 does not lie in the shielding cone associated with the π -electrons of the 1,10-double bond. Compound 6 shows shielding of H-5, H-8 and 4-CH₃ protons (by 0.20, 0.10 and 0.17 ppm respectively) relative to 10 suggesting that in the rearranged lactone these protons and not H-6 lie over the plane of the double bond. 5 and 1 should thus have the preferred molecular conformation 14 in keeping with the above geometry as revealed by careful examination of their Dreiding models. Since epoxidation of 1 and 5 can take place only from outside the cage of the medium ring, the stereochemistry of the corresponding epoxides is suggested as shown in 3 and 7 respectively. So 5 should exist in this preferred conformation 14 (R = OAc) which indicates that (i) the plane of the 1,10-double bond is approximately orthogonal to the medium ring, (ii) the epoxide ring is more or less in the plane of the medium ring, (iii) 4-CH₃ and 10-CH₃ groups are

syn-oriented having the same direction in space as the β -oriented H-6 or H-8 and hence the 8-OAc is α -oriented and (iv) 1,10-double bond and 4, 5 single bond (of the epoxide ring) have crossed and not parallel orientation. 1, 4 as well as 12 should, therefore, also have the same molecular conformation 14 (with appropriate substitution at C-8 and C-11) consistent with the PMR data, stated earlier. A similar conformation has been reported for dihydrotamaulipin-A acetate (15), determined with the aid of nuclear Overhauser effects¹⁵.

The mass spectral fragmentation patterns of 5, 12, 4, 1 and all their derivatives are in accord with their structures. Most of the fragmentations in the mass spectra of these compounds are formed by well established routes^{14,15} involving allylic cleavage, α -fission, expulsion of CO₂ from the lactone moiety, etc. It was observed that lactones having 1,10-double bond or 1,10-epoxy ring showed a general fragmentation behaviour. In the cases of 5, 12 and 7 the most significant pathway involved the loss of the elements of AcOH from the parent ion to form the M⁺-AcOH ion having a double bond at 7, 8 or 8, 9 position. Subsequent fragmentations occurred through the ion generated by the elimination of the H-2 with simultaneous cleavages of 3-4 and 5-6 bonds. 4, 1 and 3 also showed similar fragmentation. 6 showed similar fragmentation after isomerisation of the 6, 7 double bond of M⁺-AcOH ion. 6, 9 and 10 showed a common facile fragmentation involving cleavages of 2-3 and 8-9 bonds with simultaneous loss of OAc radical followed by the cleavage of the epoxy C-C bond. M⁺⁺ and (M - CO)⁺⁺ peaks were most significant in the mass spectrum of 2.

From the trunk bark of the less mature plant was also isolated a phenolic compound as an acetyl derivative, $C_{18}H_{14}O_5$ (M^+ 250) crystallising in prisms, m.p. 140° ; λ_{max} 322 nm ($\log \epsilon$ 3.78); IR absorption bands for conjugated carbonyl (1658 cm^{-1}), aryl acetate (1749 and 1248), benzene ring (1585, 1500) and conjugated double bond (1610). The 100 MHz PMR spectrum (HA-100D, $CDCl_3$) revealed the details of its structure in such a way as to permit its formulation as 16. The spectrum showed signals for an aldehyde proton at δ 9.69 (d, $J=7.5$ Hz), two vinyl protons at δ 6.66 (dd, $J=15.5$ Hz and 7.5 Hz) and 7.42 (d, $J=15.5$ Hz). Decoupling of the aldehyde proton signal resulted in the collapse of the signal at δ 6.66 to a doublet ($J=15.5$ Hz) indicating the presence of *trans*- $CH=CHCHO$ side chain in 16. The spectrum also showed signals for an acetate (δ 2.34, s) on benzene ring, two equivalent methoxys (3.85, s) and two equivalent aromatic protons (6.82, s). The ^{13}C NMR spectrum (25.15 MHz, $CDCl_3$) exhibited signals assignable to all carbons of the formulation 16, viz. at δ 20.4 (CH_3COO), 56.2 (3- OCH_3 and 5- OCH_3), 105.0 (C-2 and C-6), 128.7 (α -C), 130.5 (C-4), 132.2 (C-1), 152.1 (β -C), 152.5 (C-3 and C-5), 168.2 (CH_3COO) and 193.2 (CHO). Supporting evidence for the orientation of the oxygen functions and the side chain in the aromatic ring, as shown in 16, was obtained as follows. Alkaline hydrolysis of 16 furnished the parent compound sinapaldehyde (17), m.p. 108° which on methylation with Me_2SO_4 and alkali gave an oily product. Alkaline $KMnO_4$ oxidation of the latter gave trimethylgallic acid, m.p. $166-8^\circ$, identical with an authentic sample (mmp, TLC, IR). This is the first report of the isolation of sinapaldehyde from natural source, the presence of which is biogenetically significant since such phenyl propane derivatives are lignan precursors.

Experimental

All m. ps were determined in open capillaries and are uncorrected. Light petrol refers to b. p. $60-80^\circ$. The UV spectra were measured in a Carl Zeiss Spectrophotometer (Model VSU-1, manual) using 95% aldehyde free EtOH. The IR spectra were examined in KBr pellets with a Perkin Elmer Infrared Grating Spectrophotometer. The PMR spectra were measured in $CDCl_3$ using TMS as the internal standard with a Varian A 60 D Spectrometer (unless otherwise stated) and the ^{13}C NMR spectra were run in a 25.15 MHz JEOL PSFT 100 Spectrometer; chemical shift and degree of protonation of each carbon were determined by noise decoupling and single frequency off-resonance decoupling experiments respectively; the δ -values are expressed in ppm. The rotations were measured in $CHCl_3$ solutions with a Hilger Watts M-511 Microoptic Photoelectric Polarimeter. The mass spectra were run in an A.E.I., MS-9 Mass Spectrometer operating at 70 e.v. and using direct insertion probe. SiO_2 gel (Gouri Chemical, Calcutta) was used in all chromatographic experiments. TLC experiments were carried out using SiO_2 gel G as adsorbent and $CHCl_3$: MeOH (97:3) mixture as developer. The spots were detected with iodine vapour. Crystallisations were carried out with $CHCl_3$ -Petrol unless otherwise stated. The analytical samples were routinely dried in *vacuo* over P_2O_5 at 65° for 8 hrs.

Isolation of dihydroparthenolide (1) and lanuginolide (5). Air-dried and milled trunk bark of *Michelia lanuginosa* (1.3 Kg) collected in Darjeeling district was extracted with light petrol in a Soxhlet apparatus for about 40 hr. The petrol extract on concentration afforded a thick oil. The extract showing negative Dragendorff's test for alkaloid was chromatographed. The residue from the earlier $C_6H_6-CHCl_3$ (1:1) eluate fractions was repeatedly chromatographed. The concentrated $CHCl_3$ eluate fractions afforded dihydroparthenolide (1), crystallising in beautiful needles (yield 0.012%), m.p. 138° , R_f 0.66, $[\alpha]_D -68.5^\circ$ (c 0.98); showed yellow colour with TNM and no UV absorption maximum; ν_{max} 1760, 1230, 1170 cm^{-1} (γ -lactone), 1255, 890, 803 (epoxy ring), 860, 828 (trisubstituted double bond); showed m/e 250 (M^+ , 15%), 235 ($M-CH_3$, 5%), 222 ($M-CO$, 3%), 207 ($M-CO-CH_3$, 9%), 206 ($M-CO_2$, 9%), 193 (ion a formed from M^+ after cleavage of 3-4 and 5-6 bonds and loss of H, 15%), 192 (m/e 193-H, 27%), 177 (m/e 222- CH_3CHO-H , 21%), 165 (m/e 193-CO, 21%), 133 (39%), 119 (54%), 95 ($CH_2=CHCH=C(CH_3)CH_2CH_2^+$, 58%), 81 ($CH_2=CHCH=C(CH_3)CH_2^+$, 65%), 69 ($CH_2=CHC^+(CH_3)_2$, 28%), and 43 ($CH_3C\equiv O^+$, 100%). (Found: C, 72.08; H, 8.77. $C_{15}H_{22}O_3$ requires: C, 71.97; H, 8.86%).

The residue obtained from the later $C_6H_6-CHCl_3$ (1:1) fractions was repeatedly chromatographed. The concentrated $CHCl_3$ eluate fractions afforded lanuginolide (5) (0.043% yield) crystallising in fine needles, m.p. 185° , R_f 0.64, $[\alpha]_D -57^\circ$ (c 0.70). 5 gave yellow colour with TNM and showed no UV absorption; ν_{max} 1775, 1180 cm^{-1} (γ -lactone), 1737, 1240 (acetate), 892, 800 (epoxy ring) and 860, 828 ($>C=C<_H$); m/e 308 (M^+ , 3%), 266 ($M-CH_2CO$, 1%), 242 ($M-CH_3COOH$ or m/e 266- H_2O , 35%), 233 (m/e 248- CH_3 , 2%), 200 (m/e 248-CO, 9%), 205 (m/e 220- CH_3 or m/e 233-CO, 7%), 191 (fission of 3-4 and 5-6 bonds of m/e 248 and loss of H-2, 6%), 190 (m/e 191-H, 13%), 175 (m/e 220- CH_3CHO-H , 7%), 163 (m/e 191-CO, 8%), 95 (14%), 68 (45%), 55 (14%), and 43 (100%). (Found: C, 66.12; H, 7.80. $C_{17}H_{24}O_5$ requires: C, 66.21; H, 7.84%).

Isolation of parthenolide (4) and dehydrolanuginolide (12). Air-dried powdered trunk bark (2 Kg) of the same plant (less mature), collected in the same region as before, was extracted with $CHCl_3$ at room temperature by percolation. The extract on concentration afforded a thick oil from which the basic fraction was separated off in the usual way. The non-basic fraction was chromatographed as before. The earlier $C_6H_6-CHCl_3$ (1:1) eluates upon concentration furnished a gummy residue from which parthenolide (4) was obtained after rechromatography and crystallisation of the residue from $CHCl_3-C_6H_6$ (3:1) eluates from CH_2Cl_2 -petrol in flakes, m.p. 115° , R_f 0.74, $[\alpha]_D -88^\circ$ (c 0.54); λ_{max} 215 nm ($\log \epsilon$ 4.02); ν_{max} 1765, 1647 cm^{-1} (conjugated γ -lactone), 890, 810 (epoxy ring), 855, 828 (trisubstituted double bond); m/e 248 (M^+ , 2%), 233 ($M-CH_3$, 3%), 220 ($M-CO$, 2%), 205 (m/e 233-CO or m/e 220- CH_3 , 8%), 191 (ion obtained by cleavage of 3-4 and 5-6 bonds and

subsequent loss of H-2, 32%), 190 (*m/e* 191-H, 80%), 163 (*m/e* 191-CO, 56%), 95 (72%), 81 (52%), 67 ($\text{CH}_2=\text{CHC}(\text{CH}_3)\text{CH}_2^+$, 45%), 55 (45%) and 43 (100%). (Found: C, 72.48; H, 8.21. $\text{C}_{15}\text{H}_{20}\text{O}_3$ requires: C, 72.55; H, 8.12%).

The residue obtained from the later $\text{C}_6\text{H}_6-\text{CHCl}_3$ (1:1) eluates was rechromatographed. The $\text{CHCl}_3-\text{C}_6\text{H}_6$ (3:1) eluates furnished a residue from which dehydrolanuginolide (12) crystallised in flakes, m.p. 168°d, R_f 0.71, $[\alpha]_D -96.5^\circ$ (*c* 0.74). It gave yellow colour with TNM; λ_{max} 215 nm ($\log \epsilon$ 3.82); ν_{max} 1779, 1647 cm^{-1} (conjugated γ -lactone), 1733, 1233 (acetate), 901, 806 (epoxy ring), 855, 822 (trisubstituted double bond); *m/e* 306 (M^+ , 0.5%), 264 ($\text{M}-\text{CH}_2\text{CO}$, 5%), 246 ($\text{M}-\text{CH}_2\text{COOH}$, 65%), 231 (*m/e* 246- CH_3 , 5%), 218 (*m/e* 246-CO, 8%), 203 (*m/e* 231-CO, 22%), 189 (ion formed by fission of 3-4 and 5-6 bonds of *m/e* 245 with subsequent loss of H-2, 45%), 188 (*m/e* 189-H, 100%), 175 (*m/e* 218-H- CH_2CO , 38%), 161 (*m/e* 189-CO, 58%), 95 (68%), 81 (66%), 68 (84%), 55 (63%) and 43 (100%). (Found: C, 66.77; H, 7.15. $\text{C}_{17}\text{H}_{22}\text{O}_5$ requires: C, 66.65; H, 7.24%).

Isolation of sinapaldehyde as acetylsinapaldehyde (16). The concentrated EtOH extract of the marc from the above was freed from the basic constituents in the usual way. The nonbasic residue was chromatographed. The CHCl_3 eluate furnished further quantities of dehydrolanuginolide (55 mg) upon usual processing. The residue from the CHCl_3 -MeOH (19:1) eluates, although showed single spot in TLC (R_f 0.45), could not be freed from the gummy matter through several rechromatography or attempted crystallisations. The residue was then left with Ac_2O and fused NaOAc for 24 hr. After usual work-up the acetylated material was chromatographed. From the $\text{C}_6\text{H}_6-\text{CHCl}_3$ (1:1) eluate fractions was isolated acetylsinapaldehyde (16) (55 mg) crystallising in prisms, m.p. 142°, $[\alpha]_D \pm 0^\circ$ (*c* 0.82); showed λ_{max} 322 nm ($\log \epsilon$ 3.78); showed absorption bands at 1749, 1658, 1610, 1585, 1500 and 1248 cm^{-1} ; *m/e* 250 (M^+ , 10%), 208 ($\text{M}-\text{CH}_2\text{CO}$, 100%), 180 (*m/e* 208-CO, 31%), 177 (*m/e* 208- $\text{CH}_2\text{O}-\text{H}$, 17%), 165 (*m/e* 180- CH_3 , 19%), and 137 (*m/e* 165- CO , 7%). (Found: C, 62.23; H, 5.57. $\text{C}_{18}\text{H}_{14}\text{O}_8$ requires: C, 62.39; H, 5.64%).

Hydrogenation of dihydroparthenolide (1) to tetrahydroparthenolide (2). A solution of 1 (50 mg) in EtOH (5 ml) was stirred in H_2 atm. sphere under atmospheric pressure at 30° for 3 hr using PtO_2 (15 mg) as catalyst. The reaction mixture was filtered and evaporated. The residue upon crystallisation afforded pure 2 (35 mg), m.p. 148°, R_f 0.67, $[\alpha]_D -35^\circ$ (*c* 0.62); ν_{max} 1765, 1255, 1175, 895 and 788 cm^{-1} ; *m/e* 252 (M^+ , 1%), 237 ($\text{M}-\text{CH}_3$, 7%), 209 ($\text{M}-\text{CH}_3-\text{CO}$, 10%), 195 (ion formed by the cleavage of 3-4 and 5-6 bonds followed by loss of H-2, 13%), 179 ($\text{M}-\text{CH}_2\text{CHCOO}-\text{H}$, 11%), 168 (*m/e* 195-CO+H, 20%), 126 (M^{++} , 100%), 112 ($\text{M}-\text{CO}^{++}$, 88%), 95 (52%), 81 (59%), 59 (57%), 55 (100%) and 43 (100%). The compound gave no yellow colour with TNM. (Found: C, 71.31; H, 9.50. $\text{C}_{18}\text{H}_{24}\text{O}_8$ requires: C, 71.39; H, 9.59%).

Dihydroparthenolide epoxide (3). 1 (50 mg in 1 ml CHCl_3) was added to a CHCl_3 solution (12 ml) of $\text{C}_6\text{H}_5\text{CO}_2\text{H}^+$ and the mixture was kept at 0° for 4 days. The CHCl_3 solution was washed with NaHCO_3 solution and then with NaCl solution, dried and concentrated in *vacuo*. The resulting residue was chromatographed. The CHCl_3 -eluted material on crystallisation from CH_2Cl_2 -petrol afforded 3 in heavy needles (38 mg), m.p. 176°, R_f 0.54, $[\alpha]_D -83^\circ$ (*c* 0.92); no colour with TNM; ν_{max} 1770, 1260, 1180, 900 and 805 cm^{-1} ; *m/e* 266 (M^+ , 1%), 251 ($\text{M}-\text{CH}_3$, 0.5%), 223 (*m/e* 251-CO, 2%) 222 ($\text{M}-\text{CO}_2$, 4%), 209 (ion formed by the cleavage of 3-4 and 5-6 bonds and loss of H-2, 3%), 207 (*m/e* 222- CH_3 , 3%), 179 (*m/e* 223- CH_2CHO , 7%) 164 (ion b formed through RDA cleavage involving both epoxide C-C bonds, 59%), 71 (27%), 69 (56%), 55 (78%) and 43 (100%). (Found: C, 67.77; H, 8.39. $\text{C}_{18}\text{H}_{22}\text{O}_4$ requires: C, 67.55; H, 8.33%).

Isolanuginolide (6) from lanuginolide (5). 5 (150 mg) was refluxed with 0.2N methanolic KOH (12 ml) for about 40 minutes. The solution was cooled and 1N HCl (2 ml) was added to make the solution faintly alkaline. MeOH was removed under section, the solution was diluted with water (5 ml), cooled and then acidified with 1 ml 1N HCl and extracted with CHCl_3 (10 ml $\times$ 3). The washed and dried CHCl_3 layer on evaporation afforded an uncrystallisable viscous mass. The residue was then treated with pyridine (1 ml) and Ac_2O (0.5 ml) and kept overnight. The reaction mixture was treated with ice-cold dilute acid (15 ml 0.5N HCl) and extracted with CHCl_3 . The washed and dried CHCl_3 extract on evaporation afforded a mass which on chromatographic resolution afforded 6 crystallising in needles (44 mg), m.p. 154°, R_f 0.68, $[\alpha]_D +38^\circ$ (*c* 0.73), along with the original compound 5 (10 mg). The isomeric compound gave yellow colour with TNM and showed IR absorption bands at 1780, 1738, 1238, 1180, 885, 828 and 803 cm^{-1} ; *m/e* 308 (M^+ , 1%), 293 ($\text{M}-\text{CH}_3$, 2%), 266 ($\text{M}-\text{CH}_2\text{CO}$, 4%), 249 ($\text{M}-\text{CH}_2\text{COO}$, 8%), 248 ($\text{M}-\text{CH}_2\text{COOH}$, 6%) 233 (*m/e* 248- CH_3 , 5%), 220 (*m/e* 248-CO, 7%). 205 (*m/e* 220- CH_3 or *m/e* 233-CO, 12%), 190 (formed by isomerisation of double bond in *m/e* 248 followed by cleavage of 3-4 and 5-6 bonds and of loss H-2 and H-9, 14%), 181 (ion c formed by 2-3 and 8-9 bond cleavages and loss of OAc with subsequent epoxy C-C bond cleavage, 36%), 68 (100%), 55 (57%) and 43 (100%). (Found: C, 66.36; H, 7.73. $\text{C}_{17}\text{H}_{24}\text{O}_8$ requires: C, 66.21; H, 7.84%).

Lanuginolide epoxide (7). 5 (60 mg) dissolved in CHCl_3 (1 ml) was added to a CHCl_3 solution (20 ml) of $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ and the mixture was kept at 0° for 4 days. The CHCl_3 solution was washed with NaHCO_3 solution followed by NaCl solution and dried and concentrated. The resulting residue was chromatographed. The CHCl_3 eluate fractions gave 7 on crystallisation as microcrystalline solid (34 mg), m.p. 214°, R_f 0.59, $[\alpha]_D -78^\circ$ (*c* 0.63); ν_{max} 1775, 1730, 1240, 1182, 892 and 802 cm^{-1} ; *m/e* 324 (M^+ , 1%), 281 ($\text{M}-\text{CH}_2\text{CO}$, 1%), 264 ($\text{M}-\text{CH}_2\text{COOH}$, 1%), 249 (*m/e* 264- CH_3 , 1%), 220 (*m/e* 249-CO-H, 7%), 179 (3-4 and 5-6 bond cleavages of *m/e* 264-CO-H, 11%),

97 (ion d, 21°/o), 71 (29°/o), 69 (31°/o), 55 (36°/o) and 43 (100°/o). The compound gave no yellow colour with TNM. (Found : C, 63.11; H, 7.39. $C_{17}H_{24}O_6$ requires : C, 62.95; H, 7.46°/o).

Trans-annular cyclisation of 5: formation of the tertiary alcohol 8. (i) *With dry HCl gas.* Dry HCl gas was passed in a slow stream through a dry Et_2O solution (15 ml) at 0° of 5 (50 mg) for one hr. To the red solution, diluted with further 25 ml of Et_2O , crushed ice (50g approx.) was added. The Et_2O layer was separated and the aqueous layer was extracted with Et_2O . The combined Et_2O extract was washed with cold aqueous $NaHCO_3$ solution and then with NaCl solution and dried. The residue left after removal of Et_2O , on chromatographic purification afforded the tertiary alcohol (8) crystallising in fine needles (25 mg), m.p. 165°, R_f 0.61, $[\alpha]_D -18^\circ$ (c 0.86); showed yellow colour with TNM; ν_{max} 3520, 1777, 1737, 1250, 1192 cm^{-1} ; m/e 308 (M^+ , 1%), 293 ($M - CH_3$, 6%), 248 ($M - CH_3COOH$, 25%), 230 (m/e 248 - H_2O , 28%), 203 (m/e 248 - $CO - OH$, 15%), 202 (m/e 230 - CO or m/e 203 - H , 14%), 190 (m/e 243 - $CH_3C(OH)=CH_2$, 85%), 187 (m/e 202 - CH_3 , 31%), 175 (m/e 248 - $CH_3CH - COO^- - H$, 99%), 159 (m/e 175 + $H - OH$, 19%), 157 (m/e 175 - H_2O , 19%), 145 (m/e 190 - $CO_2 - H$, 28%), 133 (formed from M^+ by the cleavage of 5-6 and 7-8 bond followed by loss of $HOAc$ and OH , 18%), 131 (formed from M^+ by the cleavage of 5-6 and 7-8 bond and loss of $HOAc$, H_2O and H , 21%), 43 (100%). (Found : C, 66.11; H, 7.80. $C_{17}H_{24}O_8$ requires : C, 66.21; H, 7.84%).

(ii) *With BF_3 .* To a solution of 5 in dry Et_2O (10 ml), $BF_3 - Et_2O$ (1 ml, BDH) was gradually added and the solution was left at room temperature for 1/2 hr. The Et_2O layer was washed successively with water, $NaHCO_3$ and NaCl solutions, dried and evaporated to afford a gummy residue. The latter was chromatographed. The $CHCl_3$ eluates crystallised in fine needles (15 mg), m.p. 164-65°, identified through m.m.p. (undepressed) and TLC behaviour (same spot) with the tertiary alcohol (8) obtained by the action of dry HCl gas on 5. The compound remained unchanged even on keeping with Ac_2O/Py for 24 hr.

Deacetyldihydroisolanuginolide (9). A solution of 5 (150 mg) in 95% EtOH (15 ml) was hydrogenated under atmospheric pressure at 30° for 12 hr using PtO_2 (150 mg) as catalyst. Evaporation of the filtrate of the reaction mixture furnished a residue which was chromatographed carefully. The $C_6H_6 - CHCl_3$ (1:3) eluated material on crystallisation from Et_2O -hexane afforded 9 as beautiful transparent stout needles (88 mg), m.p. 114°, R_f 0.51, $[\alpha]_D +17^\circ$ (c 0.91); ν_{max} 3460, 1780, 1190, 890 and 805 cm^{-1} ; m/e 268 (M^+ , 1%), 253 ($M - CH_3$, 2%), 250 ($M - H_2O$, 2%), 225 (m/e 253 - CO , 6%), 209 (m/e 253 - CO_2 , 5%), 181 (c, 40%), 139 (RDA of m/e 268 - $CH_3C(=CH_2)O - CO_2$, 16%), 123

(m/e 268 (RDA) - $CH_2=C-CH_2-CO_2-OH$, 11%), 96 (ion e, 54%), 84 (ion f, 24%), 55 (75%) and 43 (100%).

(Found : C, 67.22; H, 8.92. $C_{18}H_{24}O_4$ requires : C, 67.14; H, 9.01%).

Dihydroisolanuginolide (10) A solution of 9 (30 mg) in pyridine (0.3 ml) was treated with freshly distilled Ac_2O (0.2 ml) and left at room temperature for 24 hr. The reaction product in 1 ml EtOH was poured into ice-cold water containing few drops of HCl and then extracted with $CHCl_3$. The washed and dried $CHCl_3$ layer on evaporation afforded a crystalline residue which on twice recrystallisation afforded 10 in plates (26 mg), m.p. 164°, R_f 0.69, $[\alpha]_D +50^\circ$ (c 0.74); showed IR bands at 1765, 1730, 1245, 1180, 898 and 803 cm^{-1} ; m/e 310 (M^+ , 1%), 295 ($M - CH_3$, 1%), 268 ($M - CH_3CO$, 21%), 251 ($M - CH_3COO$, 16%), 250 ($M - CH_3COOH$, 15%), 225 (m/e 268 - $CH_3 - CO$, 6%), 181 (c, 22%), 165 (RDA of $M - HOAc - CH_3C(=CH_2)O^-$, 15%), 137 (m/e 165 - CO , 36%), 119 (m/e 181 - $CO_2 - H_2O$, 44%), 96 (84%), 95 (68%), 55 (97%) and 43 (100%). (Found : C, 65.66; H, 8.53. $C_{17}H_{24}O_5$ requires : C, 65.78; H, 8.44%).

Hydrogenation of isolanuginolide (6). A solution of 6 (15 mg) in EtOH (2 ml) was hydrogenated at 30° for 4 hr using PtO_2 (5 mg) as catalyst. Evaporation of the filtrate of the reaction mixture furnished a residue which crystallised from $CHCl_3$ -petrol to afford a compound (8 mg), m.p. 163°, identical (m.m.p., TLC, IR) with dihydroisolanuginolide (10).

Hydrogenation of parthenolide (4). 4 (50 mg) in 5 ml 95% EtOH was hydrogenated at 30° in presence of 10% Pd-C (upto 1 mole H_2 uptake) for nearly 10 minutes. The solution was filtered from the catalyst. Evaporation of the filtrate furnished a crystalline material which was recrystallised thrice to yield pure 1 (32 mg), m.p. 137°, $[\alpha]_D -64.5^\circ$ (c 0.84). This showed no depression in m.p. with dihydroparthenolide (1), isolated from *Michelia lanuginosa* Wall. The IR spectra and TLC behaviour were also identical.

Hydrogenation of dehydrolanuginolide (12) to lanuginolide (5). A soln of 12 (15 mg) in 95% EtOH (3 ml) was hydrogenated at 30° for 15 minutes using 10% Pd-C (3 mg) as catalyst. Evaporation of the filtrate of the reaction mixture furnished a residue which crystallised to afford crystals (5 mg), m.p. 182-3°, identical with lanuginolide (m.m.p. determination, co-TLC and superimposable IR spectra).

Hydrolysis of acetylsinapaldehyde (16) to sinapaldehyde (17). 16 (35 mg) was refluxed with 1 ml 0.2N methanolic KOH for about 45 minutes. The solution was cooled, neutralised to faint alkalinity. MeOH was removed under suction. The residue after dilution with water, acidification with 0.2 N HCl was extracted with $CHCl_3$ (10 ml x3). The residue from the $CHCl_3$ layer after usual work up afforded 17 (25 mg) crystallising from in EtOH needles, m.p. 108°.

KMnO₄ oxidation of O-methylsinapaldehyde : Isolation of trimethylgallic acid. Sinapaldehyde (20 mg) in dry CH₃COCH₃ (5 ml) was refluxed with (CH₃)₂SO₄ (0.4 ml) in presence of anhydrous K₂CO₃ (1 g). The oily residue obtained after usual work up was refluxed with KMnO₄ (70 mg) and Na₂CO₃ (15 mg) in 3 ml water for about 1 hr. Addition of Na₂SO₃ (80 mg) to the cold reaction mixture, acidification with dilute H₂SO₄, extraction with CHCl₃ and subsequent work up furnished an acid, m.p. 166-8° identical with an authentic sample of trimethylgallic acid (m.m.p. TLC, IR)

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