2 hr), left in the refrigerator overnight, filtered and solvent removed A small portion of the Et_2O-soluble fraction when submitted to TLC [*n*-hexane–Et_2O (2 1), 2 developments] gave **1** which was purified by further TLC (same solvent system) Another portion of the Et_2O-soluble fraction when submitted to Silica gel CC (120 g packed in *n*-hexane) gave nine fractions 1 [*n*-hexane–Et_2O (2 1)], 2–4 [*n*-hexane–Et_2O (1 1)], 5–8 (Et_2O) and 9 [CH_2Cl_2–MeOH (1 1)], from which **2–4** were isloated as follows

Fraction 1, which contained **2**, was initially submitted to Silica gel CC and the fraction eluted with *n*-hexane–Et_2O (4 1) gave **2** on further TLC [*n*-hexane–Et_2O–AcOH (25 10 1)]

Fractions 6–7 gave **3** when submitted to TLC [*n*-hexane–$CHCl_3$-AcOH (10 10 3), 1 development]

TLC of Fr 2 [*n*-hexane–Et_2O–AcOH (15 9 1), 2 developments] gave **4**, ^{13}C NMR (δ, $CDCl_3$) (for C-1 to C-20, in order) 27 1, 64 1, 135 8, 144 4, 37 9 or 38 3, 35 2, 27 1, 36 0, 37 9 or 38 3, 41 1, 38 6, 17 4, 125 6, 142 4, 111 0, 138 3, 172 2, 18 6 or 18 8, 15 7 and 18 6 or 18 8, in accord with the structure

The spectral properties of **1–4** are described in the text

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A NEW CLERODANE DERIVATIVE FROM *TINOSPORA CORDIFOLIA*

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(*Revised received* 21 *August* 1987)

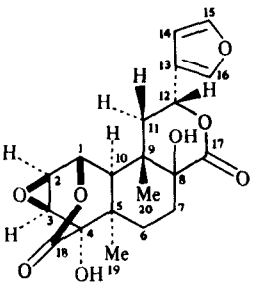
Key Word Index—*Tinospora cordifolia*, Menispermaceae, new clerodane diterpenoid

Abstract—A new clerodane diterpenoid has been isolated from the stems of *Tinospora cordifolia* Its structure was established by spectroscopic means and by comparison with closely related clerodane derivatives

INTRODUCTION

Chemical investigation of *Tinospora cordifolia* has led to the isolation of a phenolic lignan and one diterpenic furano lactone which were reported earlier [1, 2] In the present paper the isolation and structure of a new clerodane derivative, isolated from the same plant is reported The structure (**1**) was deduced mainly with the help of ^1H NMR, spin-decoupling and ^{13}C NMR studies along with the comparison of the spectral data of closely related clerodane diterpenoids such as 6-hydroxy arcangelisin (**2**) [3], fibraurin (**3a**) [4], 6-hydroxy fibraurin (**3b**) [3, 4], palmarin (**4**) [5–7] and 8-hydroxy columbin (**5**) [8]

*Author to whom correspondence should be addressed



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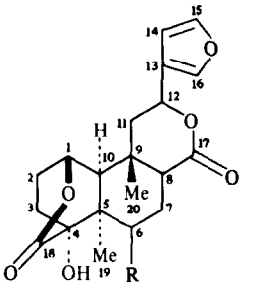
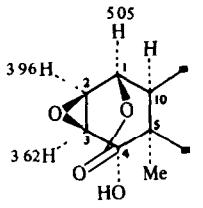


2 R = OH, 2,3 - epoxide
3a R = H, 2,3 - epoxide, 7,8 - dehydro
3b R = OH, 2,3 - epoxide, 7,8 - dehydro
4 R = H, 2,3 - epoxide
5 R = H, 8 hydroxy, 2,3 - dehydro

RESULTS AND DISCUSSION

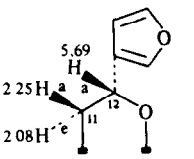
The molecular formula $C_{20}H_{22}O_8$ for the terpene was established from its mass spectrum $[M]^+$, *m/z* 390 and elemental analysis. The IR spectrum (Table 1) showed characteristic absorption for hydroxyl groups (3500, 3480 cm^{-1}), two lactone carbonyls (1750, 1720 cm^{-1}), a furan ring (3180, 1510, 1020, 880 cm^{-1}, positive Ehrlich test) and an epoxide ring (3160, 1210 cm^{-1} symmetrical stretchings, 950–850 and 860–740 cm^{-1} asymmetrical stretchings)

The ^1H NMR spectrum of the new compound was very similar to that of other furanoditerpenoids and the assignments are given in the Table 2. The signals at δ7.71 (1H, *br s*), δ7 67 (1H, *br s*) and δ6 55 (1H, *br s*) were assigned to two α- and one β-protons of a β-substituted furan moiety Two angular methyl groups were observed as singlets at δ1.06 and 1 11 (3H each). Two D_2O exchangeable singlets at δ6 29 and 6 08 (1H each) were observed and assigned to two tertiary hydroxyl groups The signals at δ5 69 (1H, *dd*, $J_1 = 11\,8$, $J_2 = 5\,1$ Hz), δ2 25 (1H, *dd*, $J_1 = 14\,3$, $J_2 = 12\,0$ Hz) and δ2 08 (1H,



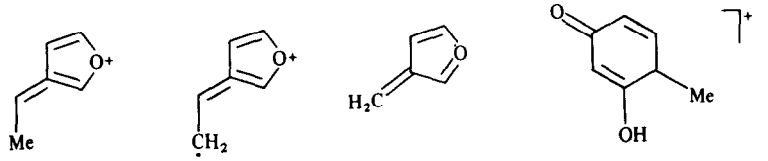
$J_{1,2}$ = 1 9 Hz
$J_{2,3}$ = 4 1 Hz

A



$J_{11a,12a}$ = 1 2 Hz
$J_{11e,12a}$ = 5 1 Hz
$J_{11a,11e}$ = 14 3 Hz

B



a b c d

Table 1 Infrared spectral data of diterpenoid furanolactones

Functional groups	1	2	3a	3b	4	5
OH	3500 3480	3300	3460	3500 3400	3470	3500 3450 3400
δ-Lactones	1750 1720	1780 1705	1766 1690	1773 1717	1771 1700	1750 1735 1705
Furan ring	3180 1510 1020 880 800	1508 1022 875 812	3120 1600 1505 1021 874 815	1507 873 810	1504 881	
Epoxide	3160 1210 950–850 860–740				3150	

* Absorption frequencies are in cm^{-1}, recorded in Nujol

Table 2 ^1H NMR spectral data of diterpenoid furanolactones

H	1*	2	3a	3b	4	5
1	5 05 (*d*, $J = 1$ 9)	5 00	5 08	5 10	4 93	5 54
2	3 96 (*dd*, $J_1 = 4$ 1 $J_2 = 1$ 9)	3 88	3 87	3 91	3 80	6 68
3	3 62 (*d*, $J = 4$ 1)	3 67	3 65	3 74	3 60	6 42
6	1 60 (*dd*, $J_1 = 14$ 8, $J_2 = 8$ 9)	-	1 71 and	4 33		1 50–1 65
6	1 51 (*dd*, $J_1 = 14$ 4, $J_2 = 8$ 9)	3 92	2 30			
7	2 85 (*m*)	2 07	7 25	6 86		3 06
7	1 34 (*m*)	1 65				1 50–1 65
8	—	2 97	-		2 74	-
10	1 95 (*br s*)	1 78	1 74	1 90	1 60	1 86
11	2 25 (*dd*, $J_1 = 14$ 3, $J_2 = 12$ 0)	1 88 and	1 97 and	2 04 and		2 25
11	2 08 (*dd*, $J_1 = 14$ 3, $J_2 = 5$ 1)	2 31	2 30	2 29		2 40
12	5 69 (*dd*, $J_1 = 11$ 8 $J_2 = 5$ 1)	5 46	5 60	5 68	5 46	5 76
14	6 55 (*br s*)	6 65	6 64	6 64	6 63	6 69
15	7 67 (*br s*)	7 68	7 67	7 69	7 62	7 63
16	7 71 (*br s*)	7 75	7 76	7 76	7 70	7 77
19	1 11 (*q*)	1 26	1 06 1 15	1 16	1 18	1 20
20	1 06 (*q*)	1 05		1 18	1 04	1 00
4-OH	6 29 (*br s*)	6 06	6 38	6 34	6 24	5 16
6-OH	–	5 54	-	5 51		
8-OH	6 08 (*br s*)	—	-	-	-	4 83

*At 500 MHz, chemical shifts are in δ values from TMS, coupling constants (J) in Hz, in DMSO-d_6 solution

dd, $J_1 = 14.3$, $J_2 = 5.1$ Hz) were assigned to an 'ABX' system as given in the part structure 'B' (C-11, C-12). Two multiplets were observed at δ2.85 and 1.34 (1H each) which were assigned to protons at C-7. The down field signal at δ2.85 was assigned to an axial proton on C-7 which experiences the anisotropic effect of the lactone carbonyl group. The signals at δ5.05 (1H, *d*, $J = 1.9$ Hz), δ3.96 (1H, *dd*, $J_1 = 4.1$, $J_2 = 1.9$ Hz) and δ3.62 (1H, *d*, $J = 4.1$ Hz) could be explained by considering an epoxide ring in the part structure 'A'. The presence of partial structures 'A' and 'B' were confirmed on the basis of 100 MHz ^{1}H NMR spin-decoupling experiments.

On irradiating the signal at δ5.05 (H-1), the signal at δ3.96 (H-2) was collapsed into a doublet ($J_{2,3} = 4.1$ Hz). On irradiating the signal at δ3.96 (H-2), the signals at δ5.05 (H-1) and δ3.62 (H-3) were collapsed into two clean singlets. These observations supported the presence of partial structure 'A'.

When the signal at δ5.69 (H-12, X of ABX) was irradiated, the signals at δ2.25 and 2.08 (H_a-11 and H_e-11, AB of ABX) collapsed into two doublets ($J_{AB} = 14.3$ Hz). Irradiation of the signal at δ2.25 (H_a-11, B of ABX), caused the signals at δ5.69 and 2.08 (H_a-12 and H_e-11, AX of ABX system) to collapse into two doublets ($J_{AX} = 5.1$ Hz). These observations suggested a partial structure 'B' having an axial proton at C-12 and vicinal methylene protons at C-11. A broad singlet was observed for H-10 showing a very small coupling constant between the vicinal axial-equitorial protons (H-1, H-10) [9]. This clearly indicated the *trans* diaxial relationship of the C-1 lactone oxygen and H-10.

The stereochemistry of the epoxide is deduced from the coupling constant values between H-1, H-2 and between H-2, H-3. For β-epoxides these values are of the order of 2-3 Hz and 4.2 Hz, respectively (Table 3). In compound (**1**) the coupling constants between H-1, H-2 and H-2, H-3 are 1.9 and 4.1 Hz, respectively. Hence, the epoxide group present in the compound could be β.

Table 3. Coupling constants between H-1, H-2 and H-2, H-3 in the 2,3-β epoxide moiety of diterpenoid furanolactones

	$J^*_{1,2}$	$J^*_{2,3}$	Ref
Fibraurin	2.9	4.2	[4]
A derivative of fibraurin	2.2	4.2	[4]
Palmarin	3.0	4.2	[7]
A derivative of palmarin	2.0	4.0	[7]
Compound (**1**)	1.9	4.1	—

*Coupling constants (J) in Hz.

The noise decoupled and single frequency off-resonance ^{13}C NMR spectrum contained signals arising from two methyl carbons (*q*, δ 20.1 and 22.8), three methylene carbons (*t*, δ 26.1, 26.6 and 34.5), five methine carbons (*d*, δ45.6, 49.2, 51.1, 69.9 and 70.6), three furanoid carbons (*d*, δ109.1, 140.1 and 143.9), five quaternary carbons (*s*, δ 39.0, 40.5, 71.7, 80.4 and 125.5) and two lactone carbonyl carbons (*s*, δ171.6 and 173.1). These values compared well with the values reported for clerodane derivatives (Table 4).

Manbe and Nishino [10] reported the usefulness of ^{13}C chemical shifts of angular methyls to distinguish between *cis* and *trans* A/B-ring junction in clerodane diterpenes. In the case of *cis* clerodanes, the C-19 methyl carbon atom resonates in a region above δ20 and in corresponding *trans* compounds it resonates in the region δ11–19. The C-19 methyl signal of compound (**1**) was found at δ22.8, and hence it is concluded that the A/B-ring junction is *cis*.

Table 4. ^{13}C NMR chemical shifts of diterpenoid furanolactones

C	1*	2	3a	3b	4	5
1	69.9 *d*	69.2 *d*	69.7 *d*	69.9 *d*	69.4 *d*	73.1 *d*
2	49.2 *d*	49.1 *d*	49.5 *d*	49.4 *d*	49.2 *d*	130.3 *s*
3	51.1 *d*	50.5 *d*	51.6 *d*	51.1 *d*	50.9 *d*	136.5 *s*
4	80.4 *s*	82.7 *s*	80.0 *s*	82.0 *s*	80.3 *s*	80.6 *s*
5	38.9 *s*	34.8 *s*	35.2 *s*	35.2 *s*	40.4 *s*	37.0 *s*
6	26.1 *t*	69.3 *d*	31.2 *t*	70.2 *d*	25.3 *t*	26.6 *t*
7	26.6 *t*	27.3 *t*	142.1 *d*	145.8 *d*	16.5 *t*	26.7 *t*
8	71.7 *s*	43.1 *d*	133.7 *s*	131.1 *s*	41.8 *d*	72.2 *s*
9	40.5 *s*	43.4 *s*	44.8 *s*	48.7 *s*	34.6 *s*	39.5 *s*
10	45.6 *d*	55.5 *d*	54.0 *d*	55.1 *d*	53.0 *d*	46.5 *d*
11	34.5 *t*	43.2 *t*	42.0 *t*	42.0 *t*	43.2 *t*	34.7 *t*
12	70.6 *d*	71.3 *d*	70.6 *d*	71.0 *d*	70.9 *d*	70.6 *d*
13	125.5 *s*	125.2 *s*	125.0 *s*	124.8 *s*	125.0 *s*	125.5 *s*
14	109.1 *d*	109.1 *d*	109.1 *d*	109.0 *d*	108.8 *d*	109.1 *d*
15	140.1 *d*	140.4 *d*	140.4 *d*	140.4 *d*	139.9 *d*	140.2 *d*
16	143.9 *d*	143.8 *d*	143.9 *d*	143.9 *d*	143.4 *d*	143.8 *d*
17	173.1 *s*	171.7 *s*	171.5 *s*	171.1 *s*	172.0 *s*	174.5 *s*
18	171.6 *s*	171.4 *s*	163.2 *s*	169.1 *s*	172.9 *s*	171.2 *s*
19	22.8 *q*	17.2 *q*	25.0 *q*	21.3 *q*	23.6 *q*	24.0 *q*
20	20.1 *q*	18.4 *q*	20.7 *q*	18.4 *q*	17.4 *q*	19.8 *q*

*Chemical shifts are in δ values from TMS at 125 MHz, in DMSO-d_6 solution.

The proposed structure (**1**) as a diterpenoid furano lactone clearly satisfied the above spectral data The mass fragmentation pattern also supported the structure (**1**) The mass spectrum gave peaks at m/z 390 $[M]^+$, 346 $[M-CO_2]^+$, 95, 94 and 81 which are due to the fragments 'a', 'b' and 'c', respectively, in accord with similar diterpenoid furano lactones [4, 11] A characteristic and base peak at m/z 124 is assigned to the ion 'd' which arises by the retro-Diels–Alder type fragmentation of ring B

EXPERIMENTAL

Mps. uncorr. IR spectra were recorded in Nujol. The proton spin-decoupling NMR expts were carried out at 100 MHz

Extraction and isolation of (**1**). Stems of *T. cordifolia* Miers. (26 kg) were collected from IIT Campus, Bombay and identified by Dr. Agarkar, Institute of Science, Bombay. The stems were dried, finely powdered and extd with $CHCl_3$ (60 l) in a Soxhlet for 48 hr Repeated CC over silica gel with 70% EtOAc–petrol (60–80°) (7:3) afforded (**1**) which was recrystallized from MeOH (6·8 g, 3·8 × 10^{-3}%); as cubic crystals, mp. 231–233° (decomp.); $[\alpha]_D^{20} = +28.2$° (DMSO, c 0.62). IR ν_{max}^{nujol} cm^{-1} (Table 1), UV λ_{max}^{MeOH} log ε 207.8 nm (3.8). ^{1}H NMR (500 MHz, DMSO-d_6), (Table 2), ^{13}C NMR (125 MHz, DMSO-d_6), Table 4, MS. m/z 390 $[M]^+$ (0.5%), 346 $[M-CO_2]^+$ (1), 291 (1), 252 (25), 199 (2), 125 (24), 124 (100), 95 (38), 94 (32), 93 (12), 91 (25), 81 (33), Anal. calcd. for $C_{20}H_{22}O_8$: C, 61.53; H, 5.68. Found: C, 61.29; H, 5.54%.

Acknowledgement– The use of facilities provided by the 500 MHz FT-NMR National Facility at T I F R, Bombay are gratefully acknowledged

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A SOYASAPOGENOL-B GLUCOSIDE FROM THE SEEDS OF *PHASEOLUS VULGARIS*

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Key Word Index—*Phaseolus vulgaris* Leguminosae triterpenoid glucoside soyasapogenol B-24-*O*-β-D-glucopyranoside

Abstract—A new triterpenoid glucoside has been isolated from the seeds of *Phaseolus vulgaris* and characterized as 3β,22β-dihydroxy olean-12-en-24-*O*-β-D-glucopyranoside

INTRODUCTION

Seeds of *Phaseolus vulgaris* Linn (French bean) are a rich source of saponins [1]. Crude extracts of the seeds show antifertility activity [2] and are known to contain phytosterols, triterpenoids and triterpenoid saponins [3–6]

RESULTS AND DISCUSSION

The new triterpenoid glucoside (**1**) was isolated from a methanolic extract of the seeds by column chromatography and purified by droplet counter current chromatography (DCCC)