TABLE 2—PHYSICAL DATA OF 4-THIAZOLIDINONE DERIVATIVES (2, 3)*

Sl. no.	R	R'	R''	Mol. formula	M.p. °C	Yield %
1.	CH_3	H	H	$C_{24}H_{24}N_4O_4S_2$	220	53
2.	CH_3	NO_2	H	$C_{24}H_{22}N_6O_8S_2$	215	57
3.	CH_3	Br	H	$C_{24}H_{22}N_4O_4S_2Br_2$	212	60
4.	C_6H_5	H	H	$C_{34}H_{28}N_4O_4S_2$	222	65
5.	C_6H_5	NO_2	H	$C_{34}H_{26}N_6O_8S_2$	230	60
6.	C_6H_5	Br	H	$C_{34}H_{26}N_4O_4S_2Br_2$	238	55
7.	CH_3	H	CH_3	$C_{26}H_{28}N_4O_4S_2$	205	50
8.	CH_3	NO_2	CH_3	$C_{26}H_{26}N_6O_8S_2$	227	55
9.	CH_3	Br	CH_3	$C_{26}H_{26}N_4O_4S_2Br_2$	242	55
10.	C_6H_5	H	CH_3	$C_{36}H_{32}N_4O_4S_2$	260	60
11.	C_6H_5	NO_2	CH_3	$C_{36}H_{30}N_6O_8S_2$	225	63
12.	C_6H_5	Br	CH_3	$C_{36}H_{30}N_4O_4S_2Br_2$	232	57
13.	CH_3	H	CH_2COOH	$C_{28}H_{28}N_4O_8S_2$	280	45
14.	CH_3	NO_2	CH_2COOH	$C_{28}H_{26}N_6O_{12}S_2$	287	47
15.	CH_3	Br	CH_2COOH	$C_{28}H_{26}N_4O_8S_2Br_2$	275	55
16.	C_6H_5	H	CH_2COOH	$C_{38}H_{32}N_4O_8S_2$	293	60
17.	C_6H_5	NO_2	CH_2COOH	$C_{38}H_{30}N_6O_{12}S_2$	270	57
18.	C_6H_5	Br	CH_2COOH	$C_{38}H_{30}N_4O_8S_2Br_2$	227	60

*All compounds gave satisfactory elemental analyses.

(0 02 mol) in presence of anhydrous $ZnCl_2$ (0.5 g) at 160° for 30 min. The resulting solid was dissolved in sodium bicarbonate, reprecipitated with acid and crystallised from ethanol as pale yellow needles (**4a** ; 45%), m p. 280° (Found : C, 52.12 ; H, 4.30 ; N, 8.63. $C_{28}H_{28}O_8S_2$ requires : C, 52.17 ; H, 4.34 ; N, 8.69%) ; ν_{max} (KBr) (O–H) (broad) stretching at 3 080 br (OH), 1 595 (N–C), 1 405, 1 330 and 1 175 (1,3,4-thiadiazole ring system), 1 730 and 1 772 cm^{-1} (C=O for thiazolidinone ring system) ; λ_{max} (MeOH) 212 (log ϵ 30.13), 350 (3 40) and 395 (3 27).

Similarly, other substituted 4-thiazolidinone derivatives were prepared (Table 1).

2,5-Bis(α-methyl-3'-chloro-4'-(2''-hydroxy-5''-methyl)-2'-azetidinone-1'-yl)-1,3,4-thiadiazole (**4a**) : A mixture of **1a** (1.0 mol) and triethylamine (1.0 mol) in dioxan (25 ml) was stirred well by gradual dropwise addition of monochloroacetyl chloride (0.015 mol) at room temperature. The mixture was stirred for 5 h and left at room temperature for 3 days. The precipitates of triethylamine hydrochloride was filtered and washed with dioxan. The filtrate was treated with anhydrous magnesium sulphate and the solvent removed under reduced pressure. The resulting solid was crystallised from ethanol to get **5a** (60%), m.p. 190° (Found : C, 54.00 ; H, 4.07 ; N, 10.43. $C_{34}H_{28}N_4O_4SCl_2$ requires : C, 54 03 ; H, 4.12 ; N, 10.50) ; ν_{max} (KBr) 2 905 br (OH), 1 670 (C–O), 1 760 (β-lactum ring system), 1 450, 1 320 (1,3,4-thiadiazole ring system), 1 190 and 700 cm^{-1} (C–Cl) ; λ_{max} (MeOH) 310 (log ϵ 3.51) and 390 (3.70).

Similarly, other substituted 2-azetidinone derivatives were prepared (Table 3).

Antibacterial activity : The Schiff bases and their 2-azetidinone and thiazolidinone derivatives were screened for antibacterial activity by cup-plate method[6] using gram-positive bacterium

TABLE 3—PHYSICAL DATA OF 2-AZETIDINONE DERIVATIVES (4)*

Sl. no.	R	R'	Mol. formula	M.p. °C	Yield %
1.	CH_3	H	$C_{24}H_{22}N_4O_4SCl_2$	190	60
2.	CH_3	NO_2	$C_{24}H_{22}N_6O_8SCl_2$	185	55
3.	CH_3	Br	$C_{24}H_{20}N_4O_4SCl_2Br_2$	200	65
4.	C_6H_5	H	$C_{34}H_{26}N_4O_4SCl_2$	205	62
5.	C_6H_5	NO_2	$C_{34}H_{24}N_6O_8SCl_2$	211	60
6.	C_6H_5	Br	$C_{34}H_{24}N_4O_4SCl_2Br_2$	218	55

*All compounds gave satisfactory elemental analyses.

S. aureus and gram-negative bacteria, *E. coli* and *S. typhoso*. The testing was carried out in dioxan at a concentration of 10 mg ml^{-1}. The compounds were active at concentration of 10 mg ml^{-1} which is however a low activity. The ditails of assay reports are not reported.

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Structure and Stereochemistry of Mollugogenol-G – A Triterpenoid Sapogenin from *Mollugo hirta*

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A number of triterpenoid saponins and sapogenins have earlier been reported from this laboratory from *Mollugo hirta*[1] and *Mollugo spergula*[2]. The present communication reports the isolation of a new triterpenoid sapogenin called mollugogenol-G, the structure of which has been established as 3β,16β,22-trihydroxy-21α-H-hop-5-ene (**1a**). The

structure **1a** for mollugogenol-G was proposed in an earlier communication on the basis of ^{13}C nmr studies only[8].

Mollugogenol-G, $C_{30}H_{50}O_3$ (**1a**), gave pink→violet colour in the Lieberman–Burchard test. It also gave pale yellow colour with tetranitromethane indicating the presence of unsaturation. It showed end-absorption at 211 nm (log ε 3.4) for a trisubstituted double bond.

On treatment with Ac_2O and Py at 0°, **1a** yielded a diacetate (**1b**). The ease of acetylation indicated that both the secondary hydroxyl groups in **1a** must be equatorial in nature. The ir, mass, ^1H nmr and ^{13}C nmr spectra[8] of **1b** were in conformity with the structure assigned. Its ^1H nmr spectrum showed a signal at δ 5.55 for the vinyl proton at C-6 which is in perfect conformity with the location of a double bond at 5,6-position[4-6]. That mollugogenol-G is a 21α-H-hopane derivative like its congeners mollugogenol-A, -E etc. isolated from *M. hirta*, was proved by hydrogenolysis experiment. Mollugogenol-G (**1a**) on hydrogenation in HOAc solution in presence of Adam's catalyst gave only unreacted starting material which indicated **1a** to be a 21α-H-hopane derivative[7]. It should be mentioned here that the 5,6-double bond in pentacyclic triterpene is inert to hydrogenation[8].

On oxidation with CrO_3/Py complex, **1a** furnished a hydroxydiketone (**1c**) and a dihydroxyketone (**1d**) both of which gave Zimmermann colour reaction characteristic of 3-keto group in triterpenes[9].

On treatment with ethanolic HCl, **1a** yielded a product (not isolated in pure state) which showed a triple absorption maxima at 243, 251 and 261 nm which is very characteristic of hopa-15,17(21)-diene[10]. The course of the reaction was followed by tlc. The prolonged acid treatment required for the formation of the diene is reminiscent of 21α-H-hopane derivative (cf. methyl isoleucotylate[11]). The compound **1c** on refluxing with ethanolic HCl furnished a α,β-unsaturated–ketone (not isolated in pure state due to poor yield). Its uv spectrum showed absorption maximum at 255 nm. Similar α,β-unsaturatedketone was also obtained by treatment of mollugogenol-A triketone[10] with ethanolic HCl and the product showed absorption maximum at 255 nm. On the basis of the above observations **1a** was considered as a 21α-H-hopane derivative having hydroxyl groups at C-16 and C-22 positions.

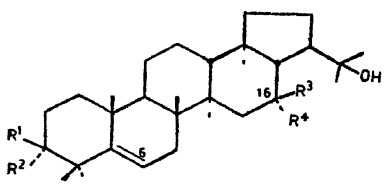
A comparative study of the ^1H nmr spectra of **1b** with the related compounds mollugogenol-A triacetate[10], spergulagenol triacetate[2] and spergulagenin-A triacetate[2] was made. The signals for the 3α-H and 16α-H of all the above compounds were found to be very similar. The signal for the 22-OH appeared at around δ 3.5 in all the above acetates excepting spergulagenin-A triacetate as there is no 22-OH group in it.

On the basis of the above data the structure **1a** is assigned to mollugogenol-G.

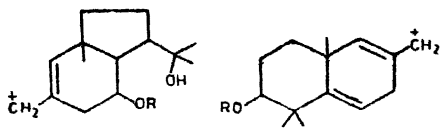
Experimental

M.ps. are uncorrected. Mass spectra were taken on a AEI MS-30 instrument and ^1H nmr spectra on a Varian EM 390 spectrometer. Silica gel (B.D.H.; 60–120 mesh) and silica gel G (B.D.H.) were used for cc and tlc, respectively. Plant material was collected from suburbs of Calcutta during June–August, 1980 when in full leaf, and identified by the Keeper, National Botanical Garden, Howrah.

Isolation of mollugogenol-G: Concentrated ethanolic extract of the defatted air-dried crushed plant material (3 kg, whole plant excluding the roots) was treated with excess diethyl ether and the precipitated crude saponin was hydrolysed by refluxing with ethanolic HCl (5%) for 2 h. The resulting aglycone (sapogenins) was extracted with $CHCl_3$ and the extract washed with aqueous KOH (1%). The neutral sapogenins thus obtained was subjected to cc (500 g) and eluted with solvents of increasing polarity. Benzene–ether (8 : 1) eluted fraction showing three spots in tlc was resolved by preparative tlc (thickness 0.35 mm; solvent system: C_6H_6–$CHCl_3$–MeOH, 32 : 14 : 4, v/v; I_2 vapour used for detection of the spots). The major component was repeatedly crystallised from $CHCl_3$–petrol and finally from MeOH to yield mollugogenol-G (13 mg), m.p. 242° (Found: C, 78.28; H, 11.12. $C_{30}H_{50}O_3$ requires: C, 78.55; H, 10.9%); M^+ 458; ν_{max} (KBr) 3 400 and 3 280 cm^{-1}; *m/z* 458 (55%, M^+), 440 (40, $M-H_2O$), 422 (90, $M-2H_2O$), 404 (15, $M-3H_2O$), 382 (90, $M-H_2O-CH_3COCH_3$), 364 (18, *m/z* 382–H_2O), 223 (9, **a**), 205 (20, **c**) and 187 (45, **a**–$2H_2O$ or **c**–H_2O).



1a, $R^1=R^3=OH$, $R^2=R^4=H$
1b, $R^1=R^3=OAc$, $R^2=R^4=H$
1c, R^1, $R^4=O$, R^2, $R^4=O$
1d, R^1, $R^3=O$, $R^2=OH$, $R^4=H$



a, R=H
b, R=Ac

c; R=H
d, R=Ac

Mollugogenol-G diacetate (**1b**): Mollugogenol-G (150 mg) in pyridine (2 ml) and Ac_2O (3 ml) was

left overnight at 0°. Usual work-up gave a product which was repeatedly crystallised after charcoalisation from MeOH to yield **1b**, m.p. 228° (Found : M^+ 542. $C_{34}H_{54}O_5$ requires : 542) ; ν_{max} (nujol) 3 560 (free OH), 1 733 and 1 245 cm^{-1} (acetoxy groups) ; *m/z* 542 (15%, M^+), 524 (20, $M-H_2O$), 482 (25, $M-CH_3COOH$), 424 (40, $M-CH_3COOH-CH_3COCH_3$), 422 (10, $M-2CH_3COOH$), 404 (25, $M-2CH_3COOH-H_2O$), 364 (30, *m/z* 424-CH_3COOH), 265 (7, **b**), 247 (7, **d**), 187 (78, **b**$-H_2O-CH_3COOH$ or **d**$-CH_3COOH$) and 59 (^+OH ‖ CH_3CCH_3) ; δ (90 MHz, $CDCl_3$) 5.55 (1H, t, *J* 4Hz, 6-H), 4.89 (1H, br m, $W_{1/2}$ 24Hz, 16α-H), 4.49 (1H, m, $W_{1/2}$ 16Hz, 3α-H), 3.50 (1H, s, disappeared on D_2O exchange, OH), 2.02, 2.01 (3H each, s, 2×$OCOCH_3$), 1.20, 1.20, 1.20, 1.17, 1.12, 1.07, 1.03, 0.73 (3H each, s, 8× *tert*-CH_3). For ^{13}C nmr data vide Ref. 3.

Oxidation of mollugogenol-G with CrO_3/Py complex : Ice-cold mollugogenol-G (100 mg) in pyridine (2.5 ml) was treated with a slurry of CrO_3–pyridine complex (prepared from 300 mg CrO_3 and 5 ml pyridine) at 0° with stirring and left overnight. Usual work-up afforded a mass showing two spots in tlc. Cc and repeated crystallisations from MeOH furnished **1c**, m.p. 232–35° (Found : C, 78.98 ; H, 10.43. $C_{30}H_{46}O_3$ requires : C, 79.25 ; H, 10.20%) ; M^+ 454 ; and **1d**, m.p. 226–27° (Found : C, 78.61 ; H, 10.82. $C_{30}H_{48}O_3$ requires : C, 78.90 ; H, 10.59%) ; M^+ 456.

Treatment of **1a** *with ethanolic HCl :* Compound **1a** (5 mg) in dry EtOH (1 ml) was treated with dry ethanolic HCl (10%, 1 ml) and refluxed on a steam-bath for 3 h. Crushed ice was poured into the reaction mixture and the precipitate was filtered and washed with water. The product (diene) showed triple absorption maxima at 243, 251 and 261 nm and a shoulder at 290 nm.

Treatment of the monohydroxydiketone (**1c**) *with ethanolic HCl :* The monohydroxydiketone (**1c** ; 5 mg) in dry EtOH (1 ml) was refluxed with dry ethanolic HCl (10% ; 1 ml) on a steam-bath for 3 h. Work-up as above afforded a product (α,β-unsaturated-ketone) which showed λ_{max} (EtOH) at 255 nm.

Hydrogenation of mollugogenol-G (**1a**) *:* Adam's catalyst (15 mg) suspended in glacial acetic acid was shaken in an atmosphere of hydrogen for 1 h at room temperature and pressure. Mollugogenol-G (15 mg) in glacial acetic acid (4 ml) was added to it and the mixture shaken in an atmosphere of hydrogen for 30 h at room temperature and pressure. On working up in the usual way only unreacted mollugogenol-G was recovered.

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Chemical Examination of *Cassia pumila* Lam.

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IN connection of our works on *Cassia*[1] species, the chemical investigation of *Cassia pumila* Lam. (*Leguminosae*) on which no phytochemical works seems to have been reported so far, has been undertaken. *C. pumila*[2] is a plant growing abundantly throughout India and is commonly used as purgative.

The air-dried powdered whole plant of *C. pumila* was extracted successively with petrolium ether (b.p. 60–80°) and chloroform. The concentrated petroleum ether extract was chromatographed over silica gel. Elution of the column with petroleum ether (b.p. 60–80°)–benzene (1 : 1) mixture furnished a white crystalline solid, m.p. 88–90°, ν_{max} (KBr) 3 440 cm^{-1} (OH) ; δ 0.65 (3H, t, CH_3), 1.40 (64H, s, 32×CH_2) and 3.50 (2H, CH_2OH) ; *m/z* 494 (M^+), 476 and 463. It was identified as tetratriacontanol by the usual comparison (m.m.p., co-tlc and co-ir) with an authentic sample.

The concentrated chloroform extract of the defatted whole plant was subjected to chromatographic separation over silica gel with solvents of increasing polarity. The benzene elute afforded a solid crystallised from light petrol (b.p. 60–80°), $C_{14}H_{14}O_3$ (M^+ 230), m.p. 123–25° ; λ_{max} (EtOH) 220, 272 and 330 nm ; ν_{max} (KBr) 1 715 (coumarin lactone), 1 625, 1 485 (aromatic unsaturation) and 1 140 cm^{-1} (C–O–C). The spectral data suggest that the compound is a coumarin derivative. The ^1H nmr spectrum (90 MHz, $CDCl_3$) is also consistent with the above view and displayed signals at δ 7.45