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LIMONOIDS FROM THE SEEDS OF *MELIA AZEDARACH*

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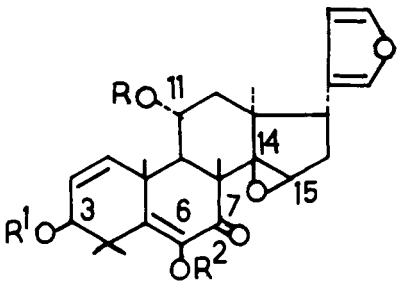
ABSTRACT.—Evidence is presented for the structure of a new limonoid glycoside, 6-acetoxy-11α-hydroxy-7-oxo-14β,15β-epoxymeliacin-1,5-diene-3-*O*-α-L-rhamnopyranoside, which occurs together with salannin and meldenin in the seeds of *Melia azedarach*. The glycoside shows antibacterial activity against four organisms.

Melia azedarach L. (Meliaceae) is a medicinal plant employed in the Indian indigenous system of medicine (1). As the result of an extensive study (2) of plants of this family, a large number of bitter principles have been isolated and classified as limonoids. *M. azedarach* has been found to contain santonum (3), meliantriol (4), sandolactone (5), ochinal and ochinine acetate (6), sandanol (7), melianone (8), mellanin A (9), and other limonoids (10), but it appears from the literature that no systematic chemical investigations has been made of the seeds. I report here the isolation and structure elucidation of a new limonoid glycoside **1** (11) as well as the isolation of the known limonoids salannin and meldenin from the seeds. The structure of the new limonoid glycoside has been established as 6-acetoxy-11α-hydroxy-7-oxo-14β,15β-epoxymeliacin-1,5-diene-3-*O*-α-L-rhamnopyranoside on the basis of chemical and spectroscopic data that are described herein. Compounds of such a structure occur rather rarely in nature. The isolate was found to exhibit antibacterial activity.

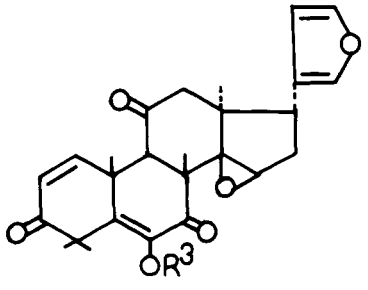
RESULTS AND DISCUSSION

Compound **1**, on repeated crystallization from MeOH-$CHCl_3$, furnished a colorless microcrystalline substance, mp 320-324° (dec), $C_{34}H_{44}O_{11}$ (M^+ at *m/z* 628), $[\alpha]^{30}D$ −70° (c=1.0 $CHCl_3$). It responded positively to the reactions characteristic of glycosides (12). The isolate showed strong uv absorption maxima at 239 (ε 8000) and 217 (ε 10000) nm, which are characteristic for diosphenol acetate and furan diene groups, respectively (13-16). The principal peaks in the ir spectrum of **1** indicated the presence of hydroxyl, enolic acetate, carbonyl, furan ring, and glycoside units. Compound **1** formed a methyl ether (Me_2SO_4/K_2CO_3), mp 122-124°, and a pentaacetate (Ac_2O/C_5H_5N), mp 140-142°. The ^{1}H-nmr spectrum of this pentaacetate displayed signals for the presence of the usual furan bands, rhamnose methyl and sugar protons, a one-proton doublet at δ 3.62, suggestive of H-15 in a 14β,15β-epoxide, three coupled allyl proton signals at δ 6.18, 6.90, and 3.95 in ring-A, and five acetate groups, respectively, which are indicative for the presence of a β-substituted furan ring, an allyl type grouping in ring-A, a diosphenol acetate group in ring-B, and an additional hydroxyl group in a meliacin skeleton (17,18).

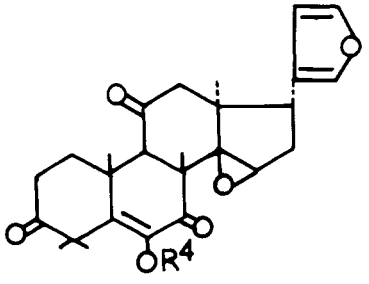
Acid hydrolysis of **1** afforded a genin **2**, mp 132-135°, and a sugar identified as L-rhamnose (co-pc and osazone formation). The genin **2** which analyzed for $C_{28}H_{34}O_7$ (M^+ at *m/z* 482) exhibited uv absorption bands characteristic for substituted diosphenol acetate and furan diene systems. The ir spectrum of **2** lacked the band for a glycoside unit. The ^{1}H-nmr spectrum of **2** showed absorptions for the presence of a furan and a 14β,15β-epoxide, an allyl alcohol type grouping in ring-A [δ 3.95, 6.18, 6.90, and 4.20 (exchangeable with D_2O)], a secondary acetate group (δ, 2.0), and an additional secondary hydroxyl group (δ, 3.64). Genin **2** was acetylated (Ac_2O/C_5H_5N) to yield a triacetate **3**, mp 128-130°, the ^{1}H-nmr spectrum of which displayed three singlets at δ 2.0, 2.05, and 2.10 for three OAc groups. Comparison of the ^{1}H-nmr spectra of **2** and **3** clearly indicated the presence of two OH functions and one OAc



1 R=H, R^1=L-Rhamnose, R^2=Ac
2 R=R^1=H, R^2=Ac
3 R=R^1=R^2=Ac
4 R=R^1=R^2=H
10 R=R^2=Ac, R^1=H



5 R^3=Ac
8 R^3=H



6 R^4=Ac
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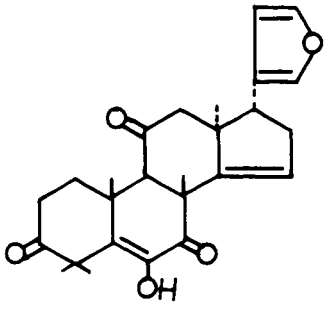

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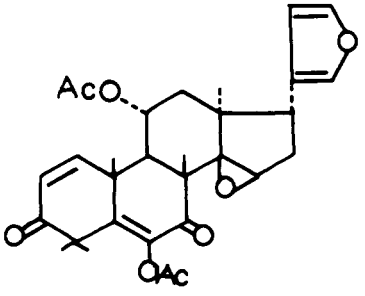

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group in **2**. Deacetylation (2 N NaOH) of **2** gave **4**, mp 140-142° (dec), which showed uv absorption at 280 nm (ε 11000), undergoing a bathochromic shift to 326 nm (ε 5000) in the presence of NaOH, thereby indicating the presence of a diosphenol function in **4**. The uv absorption maxima of **2** and **4** are consistent with the presence of a diosphenol acetate group in **2** in the ring-B of a tetracyclic triterpenoid similar to anthothecol (17). The CrO_3/C_5H_5N (19,20) oxidation of **2** afforded **5**, mp 161-162°, which showed a band at 1680 cm^{-1} in the ir spectrum characteristic of a cyclohexenone ring. The ^{1}H-nmr spectrum of **5** exhibited absorptions for two coupled vinyl protons at δ 5.90 and 7.25 (J=10 Hz) which agrees with the presence of a 4,4-dimethyl-3-oxo-Δ^1-triterpenoid nucleus as in anthothecol and gedunin (4,8,10,19), and accordingly, a secondary hydroxyl must be present at C-3 in **2**. Compound **5** on mild catalytic hydrogenation (Pd/C) or with Adams catalyst afforded **6**, mp 198-199° (dec), the ^{1}H-nmr spectrum of which did not display signals for coupled vinyl protons (as observed in **5**), indicating that saturation of the C-1,2 double bond had taken place. The structure of **2**

was confirmed by the following conversions to compounds of known structure. Thus, deacetylation of **6** (2 N NaOH) gave a known product **7**, mp 247-249°, identical to deacetyl dehydrodihydroanthothecol (lit. mp 248-250°) (17). The formation of **7** clearly placed the other hydroxyl group at the C-11 position in **2**. The correctness of the structure **7** was further confirmed by conversion into known derivatives by the following reactions. Compound **5** on deacetylation (2 N NaOH) yielded **8**, mp 202-203°, which was identical to deacetyldehydroanthothecol (lit. mp 203°) (17). Compound **7** on treatment with chromous chloride at room temperature afforded a known deoxy derivative **9**, mp 212-213° (lit. mp 214°) (17). The mass spectrum of **2** also supported the proposed structure of the genin.

Acid hydrolysis of the acetate of **1** afforded **10**, mp 169-170°. The ^{1}H-nmr spectrum of **10** showed signals for an allyl alcohol (δ 3.95, 6.18 and 6.90) and two acetate groups (δ 2.0 and 2.05). The δ values at 3.95, 6.18, and 6.90 are those expected for a C-1,2 double bond and a C-3 OH group in a limonoid (10). Oxidation of **10** with CrO_3/C_5H_5N gave **11**, mp 233-234°, identical with anthothecol diacetate (lit. mp 234°) (17). This clearly establishes the presence of an L-rhamnose unit attached to the hydroxyl group at C-3. Periodate oxidation (21) of **1** in 90% EtOH at room temperature consumed 2 moles of periodate with the liberation of 1 mole of HCOOH per mole of **1** after 80 h, indicating the presence of L-rhamnose in the pyranose form. Compound **1** on treatmnt with takadiastase solution (22) yielded **2** (mp, mmp, and co-tlc) and L-rhamnose (co-pc), indicating that an α-linkage was present. Thus, on the basis of the above results, the new genin and its glycoside were assigned the structures 6-acetoxy-3β,11α-dihydroxy-7-oxo-14β.15β-epoxymeliacin-1,5-diene (**2**) and 6-acetoxy-11α-hydroxy-7-oxo-14β,15β-epoxymeliacin-1,5-diene-3β-*O*-α-L-rhamnopyranoside (**1**) respectively.

EXPERIMENTAL

Mps were taken on a melting point apparatus (Toshniwal, India) and are corrected. Specific rotations were taken in $CHCl_3$ solution (c 1.0) at room temperature on a Perkin-Elmer 141 polarimeter. Ir spectra in KBr were recorded on a Perkin-Elmer 157 spectrophotometer (ν max in cm^{-1}). ^{1}H-nmr spectra were obtained on solutions in $CDCl_3$ at 90 MHz on a Varian EM 360L instrument using TMS as an internal standard. Chemical shifts are given in δ ppm. The mass spectra were obtained on a Perkin-Elmer Hitachi RMU GR instrument. Silica gel refers to Merck silica gel (mesh 0.05-0.2 mm). Petroleum ether refers to the fraction of bp 60-80°.

ISOLATION OF LIMONOIDS.—The powdered seeds of *M. azedarach* (5 kg) procured from the Himalaya company, Dehradoon (India), reference No. IFSS:A/Seeds/82-83, and authenticated by the Botanical Survey of India, Allahabad Circle (India), were extracted with EtOH under reflux conditions on a steam bath for 180 h. The EtOH extract (30 liters) was concentrated under reduced pressure to yield a dirty white mass that was then extracted successively with refluxing Et_2O and C_6H_6. The Et_2O extract was concentrated under reduced pressure. The resulting solid (tlc pure) crystallized from $C_6H_6/CHCl_3$ as colorless needles, mp 166-169°, and was shown to be identical with salannin (yield 550 mg), $[\alpha]^{30}D$ +165° [lit. $[\alpha]D$ +166° (10)] [mmp, co-tlc, and lit. mp 167-169° (10)]. The C_6H_6 extract was found by tlc examination to be a mixture of two substances. The C_6H_6 extract was concentrated and chromatographed over silica gel. The column was eluted successively with petroleum ether and C_6H_6. The petroleum ether eluate was concentrated and the purified product crystallized from $C_6H_6/CHCl_3$ as colorless needles, mp 240-243°. It was found to be identical with meldenin (yield 400 mg), $[\alpha]^{30}D$ +168° [mmp, co-tlc and lit. mp 240-244° (23)]. The C_6H_6 eluate was concentrated and the product repeatedly crystallized from $MeOH/CHCl_3$ to afford a colorless microcrystalline substance **1**, mp 320-324° (dec), (yield 2.950 g); tlc Rf 0.84 (C_6H_6-petroleum ether, 2:8) and 0.97 (C_6H_6-$CHCl_3$, 9:1); in ν max 3450 (hydroxyl), 1770, 1725-1730, 1230 (enolic acetate), 1680 (carbonyl), 2942, 1500, 860 (furan ring), and 825 (glycoside). *Anal.* calcd for $C_{34}H_{44}O_{11}$: C, 64.96; H, 7.05. Found: C, 64.32; H, 7.08.

ACETYLATION OF **1**.—The glycoside (400 mg) was acetylated with Ac_2O (20 ml) and C_5H_5N (20 ml) as usual under reflux condition for 6 h. The product was crystallized from C_6H_6 as colorless needles, mp 140-142° (yield 360 mg); ^{1}H nmr δ 0.78 (d, J=7 Hz, rhamnose Me); 0.97, 1.07, 1.09, 1.14, 1.18 (each s, 15H, 5×tert. Me); 1.20-1.90 (complex pattern, CH_2 and CH protons); 1.98 (s, 3H, 4′-OAc); 2.0 (s,

3H, 1×OAc); 2.03 (s, 3H, 2′-OAc); 2.05 (s, 3H, 3′-OAc); 2.10 (s, 3H, 1×OAc); 3.62 (d, J=1 Hz, 1H, H-15, 14β, 15β-epoxide); 3.70-3.90 (m, 4H, sugar protons); 3.95 (d, J=6 Hz, 1H, H-3); 4.64 (m, 1H, α-H in sec. OAc); 4.80 (d, J=6.5 Hz, 1H, H-1′, anomeric proton); 6.18 (d, J=10 Hz, 1H, H-1); 6.90 (dd, J=6 and 10 Hz, 1H, H-2) and 6.40, 7.20, 7.39 (each m, 3H, β-substituted furan ring) *Anal.* calcd for $C_{42}H_{52}O_{15}$: C, 63.31; H, 6.53. Found: C, 63.25; H, 6.45.

METHYLATION OF **1**.—The glycoside (100 mg) was methylated with Me_2SO_4 (6 ml) and K_2CO_3 (2 g) in Me_2CO (10 ml) by refluxing on a water bath for 8 h and worked up as usual. The product was crystallized from Et_2O as colorless needles, mp 122-124°. *Anal.* calcd for $C_{38}H_{52}O_{11}$: C, 66.66; H, 7.60. Found: C, 66.75; H, 7.58.

ACID HYDROLYSIS OF **1**.—A solution of **1** (2.2 g) in absolute EtOH (40 ml) and 7% H_2SO_4 (50 ml) was refluxed for 5 h, poured into ice-cooled H_2O (150 ml) and kept at room temperature for 24 h. The precipitated genin **2** was filtered off. The filtrate was neutralized ($BaCO_3$) and was found to contain L-rhamnose (co-pc and osazone).

GENIN **2**.—The genin was purified by chromatography over neutral alumina eluting with $CHCl_3$. Attempted crystallization from C_6H_6-petroleum ether furnished colorless needles, mp 132-135° (yield 1.8 g); tlc Rf 0.75 ($CHCl_3$-MeOH, 8:2) and 0.86 (C_6H_6-MeOH, 5:5); uv λ max 240 (ε 8000, substituted diosphenol acetate) and 218 nm (ε 10000, furan diene system); ir ν max 3450 (hydroxyl), 1770, 1728-30, 1230 (enolic acetate), 1679 (carbonyl), 2940, 1500, 860 (furan); ^{1}H nmr δ 0.98, 1.07, 1.09, 1.10, 1.18 (each s, 15H, 5×tert. Me); 1.20-1.90 (complex pattern, CH_2 and CH protons); 2.0 (s, 3H, 1×OAc); 3.60 (d, J=1 Hz, 1H, H-15); 3.95 (d, J=6 Hz, 1H, H-3); 3.64 (m, 1H, α-H in sec. OH); 4.20 (sbr, OH, exchangeable with D_2O); 6.18 (d, J=10 Hz, 1H, H-1); 6.90 (dd, J=6 and 10 Hz, 1H, H-2) and 6.39, 7.22, 7.39 (each m, 3H, β-substituted furan ring); ms *m/z* 482 (M^+), 467 (M^+-15), 464 (M^+-18), 423 (M^+-59), 415 (M^+-67), 414 (M^+-68), 401 (M^+-81), 387 (M^+-95), 358 (M^+-124), 333 (M^+-149), 319 (M^+-163), 265 (M^+-217), and 207 (M^+-275). *Anal.* calcd for $C_{28}H_{34}O_7$: C, 69.69; H, 7.10. Found: C, 70.0; H, 7.0.

ACETYLATION OF GENIN **2**.—Compound **2** formed an acetyl derivative, **3** (100 mg **2**, 5 ml Ac_2O, 4 ml C_5H_5N; 4 h on a water bath) which crystallized from Me_2CO/Et_2O as colorless needles, mp 128-130° (yield 85 mg); ^{1}H nmr δ 0.97, 1.05, 1.0, 1.10, 1.18 (each s, 15H, 5×tert. Me); 1.20-1.90 (complex pattern, CH_2 and CH protons); 2.0 (s, 3H, 1×OAc); 2.05 (s, 3H, 1×OAc); 2.10 (s, 3H, 1×OAc), 3.60 (d, J=1 Hz, 1H, H-15); 4.68 (m, 1H, H-11); 5.05 (d, J=6 Hz, 1H, H-3); 6.18 (d, J=10 Hz, 1H, H-1); 6.95 (dd, J=6 and 10 Hz, 1H, H-2) and 6.40, 7.20 and 7.39 (each m, 3H, furan-H). *Anal.* calcd for $C_{32}H_{38}O_9$: C, 67.84; H, 6.71. Found: C, 67.80; H, 6.69.

DEACETYLATION OF **2**.—The genin (100 mg) in MeOH (10 ml) was refluxed with 2 N NaOH (5 ml) for 30 min to give **4** as plates from $C_6H_6/CHCl_3$, mp 140-142° (dec), (yield 70 mg). Its ir spectrum lacked the band for an acetate group. *Anal.* calcd for $C_{26}H_{32}O_6$: C, 70.90; H, 7.27. Found: C, 70.75; H, 7.18.

SARETT OXIDATION OF **2**.—A portion (600 mg) of **2** in C_5H_5N (10 ml) was added with stirring to CrO_3 (600 mg, dried in vacuo over P_2O_5) and C_5H_5N (25 ml). After the usual workup, the product **5** crystallized from Et_2O as white needles, mp 161-162° (yield 300 mg), $[\alpha]^{30}D$ −60°. uv λ max 218 (ε 10000) and 240 nm (ε 8000); ir ν max 1680 (cyclohexenone); ^{1}H nmr δ 0.98, 1.07, 1.09, 1.10, 1.18 (each s, 15H, 5×tert. Me); 1.20-1.90 (complex pattern, CH_2 and CH protons) 2.0 (s, 3H, 1×OAc); 3.60 (d, J=1 Hz, 1H, H-15), 5.90 (d, J=10 Hz, 1H, H-2); 7.25 (d, J=10 Hz, 1H, H-1); 6.39, 7.20 and 7.39 (each m, 3H, β-furan ring). *Anal.* calcd for $C_{28}H_{30}O_7$: C, 70.29; H, 6.27). Found: C, 70.20; H, 6.23.

CATALYTIC HYDROGENATION OF **5**.—A portion of **5** (100 mg) in MeOH (10 ml) was hydrogenated over 5% Pd/C (6 mg) or Adams catalyst. The product, **6**, crystallized from PrOH as colorless needles, mp 198-199° (dec) (yield 70 mg); ^{1}H nmr δ 0.98, 1.07, 1.09, 1.10, 1.18 (each s, 15H, 5×tert. Me); 1.20-1.90 (complex pattern, CH_2 and CH protons); 2.0 (s, 3H, 1×OAc); 3.60 (d, J=1 Hz, 1H, H-15); 6.39, 7.20 and 7.39 (each m, 3H, furan-H). *Anal.* calcd for $C_{28}H_{32}O_7$: C, 70.0; H, 6.66. Found: C, 69.88; H, 6.58.

DEACETYLATION OF **6**.—A solution of **6** (50 mg) in MeOH (10 ml) and 2 N NaOH (4 ml) was refluxed for 30 min to yield **7** as colorless prisms from CH_2Cl_2/MeOH, mp 247-249° (yield 40 mg); $[\alpha]^{30}D$ −60° [lit. $[\alpha]D$ −61°] (17); uv max 217 (ε 8000) and 280 nm (ε 10000) [lit. λ max 211 (ε 8000) and 281 nm (ε 10000) (17)]. *Anal.* calcd for $C_{26}H_{30}O_6$: C, 71.23; H, 6.84. Found: C, 71.20; H, 6.79.

DEACETYLATION OF **5**.—A portion of **5** (50 mg) in MeOH (10 ml) was refluxed with 2 N NaOH (4 ml) for 40 min to give **8** as white needles from MeOH, mp 202-203° (yield 40 mg); $[\alpha]^{30}D$ −72° [lit. $[\alpha]D$

−74° (17)]; uv max 217 (ε 8000) and 280 nm (ε 10000) [lit. λ max 217 (ε 10000) and 279 nm (ε 12000) (17)]. *Anal.* calcd for $C_{26}H_{28}O_6$: C, 71.55; H, 6.42. Found: C, 71.43; H, 6.40.

REDUCTION OF **7** BY CHROMOUS CHLORIDE.—The compound **7** (30 mg) was dissolved in Me_2CO (10 ml) and HOAc (10 ml) in a 50 ml flask. The air was displaced by butane, and <20% aqueous chromous chloride added to fill the flask, which was then stoppered and left overnight. The contents were diluted with H_2O (50 ml) and $CHCl_3$ (50 ml), and the $CHCl_3$ layer was washed with Na_2CO_3 solution and with H_2O, and evaporated. The residue crystallized from MeOH to afford **9** as plates, mp 212-213° (yield 10 mg); $[\alpha]^{30}D$ −118° [lit. $[\alpha]D$ −118°] (17); uv max 215 (ε 10000) and 280 nm (ε 10000) [lit. λ max 206 (ε 10000) and 279 nm (ε 10000)] (17). *Anal.* calcd for $C_{26}H_{30}O_5$: C, 73.93; H, 7.10. Found: C, 73.85; H, 7.0.

HYDROLYSIS OF THE ACETYLATED COMPOUND **1**.—A solution of acetylated derivative of **1** (200 mg) in absolute EtOH (20 ml) and 7% H_2SO_4 (15 ml) was refluxed for 5 h, poured into ice-cooled H_2O (50 ml) and kept at room temperature for 24 h. The precipitated product, **10**, was filtered off and crystallized from Et_2O as colorless plates, mp 169-170° (yield 140 mg); uv λ max 218 (ε 10000) and 240 nm (ε 8000); ^1H nmr δ 0.97, 1.07, 1.08, 1.10, 1.18 (each s, 15H, 5×tert. Me); 1.20-1.90 (complex pattern, CH_2 and CH protons); 2.0 (s, 3H, 1×OAc); 2.05 (s, 3H, 1×OAc); 3.62 (d, J=1 Hz, 1H, H-15); 3.95 (d, J=6 Hz, 1H, H-3); 4.62 (m, 1H, α-H in sec. OAc); 6.18 (d, J=10 Hz, 1H, H-1); 6.90 (dd, J=6 and 10 Hz, 1H, H-2) and 6.40, 7.20, 7.39 (each m, 3H, furan-H). *Anal.* calcd for $C_{30}H_{36}O_8$: C, 68.70; h, 6.87. Found: C, 68.62; H, 6.85.

SARETT OXIDATION OF **10**.—A portion of **10** (100 mg) in C_5H_5N (5 ml) was added with stirring to CrO_3 (100 mg) and C_5H_5N (10 ml). After the usual workup, the product, **11**, crystallized from toluene as white needles, mp 233-234° (yield 40 mg); $[\alpha]^{30}D$ −66° [lit. $[\alpha]D$ −67° (17)]; uv λ max 217 (ε 10000) and 239 nm (ε 8000) [lit. λ max 230 nm (ε 10000) (17)]. *Anal.* calcd for $C_{30}H_{34}O_6$: C, 68.96; H, 6.51. Found: C, 68.95; H, 6.60.

ANTIBACTERIAL ACTIVITY OF **1**.—The antibacterial activity of **1** was assayed by the method of Maruzzella *et al.* (24) using streptomycin as a control for comparing the data with the compound **1**. A positive effect was observed on all the organisms tested (Table 1).

TABLE 1. Sensitivity of Some Bacteria to Different Concentrations of Compound **1**

Organisms[a]	Control[b]	Zone of inhibition (mm, including the size of the paper disc=6 mm)				
		10 mg/10 ml DMF[c]	concentration 8 mg/10 ml DMF	6 mg/10 ml DMF	4 mg/10 ml DMF	2 mg/10 ml DMF
Vibrio cholerae	12	20	18	17	15	13
Klebsiella pneumoniae . .	10	18	16	14	12	10
Salmonella typhimurium	9	16	15	13	12	11
Escherichea coli	8	15	14	12	11	10

[a]Deposited in the culture collection of the Department of Botany, University of Saugar, Sagar, India.
[b]Streptomycin in a concentration of 10 mg/10 ml DMF.
[c]Dimethylformamide.

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