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A Terpenoid-based Gelator: The First Arjunolic Acid-derived Organogelator for Alcohols and Mixed Solvents

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A derivative of *arjunolic acid*, a naturally occurring chiral triterpenoid, formed gels efficiently with a variety of organic solvents. Electron microscopy images revealed the morphology of the gels consisting of fibers and strands as well as 'cabbage leaf' type sheets of micrometer dimensions.

Keywords: Organogel; Terpenoids; Self-assembly; Arjunolic acid

In recent years there has been growing interest in the development of low molecular mass gelators for aqueous and nonaqueous media because of their potential applications in photography, drug delivery, food processing, cosmetics, hydrometallurgy, lubrication industry, etc., and their importance in supramolecular chemistry [1–2]. A gelator, by definition, is capable of immobilizing a variety of solvents, usually at a low concentration. The gel should have a continuous structure with a 'solid-like' rheological behavior. Various noncovalent interactions, such as van der Waals, H-bonding and π-stacking interactions, have been suggested as the driving force for assembling the low molecular mass gelator molecules leading to the formation of a fibrous network [1–2]. The solvent molecules are then trapped inside the network leading to the formation of a gel.

Although studies of gelation by polymers, proteins and inorganic substances such as silica or clays are well documented [3–5], the study of the low molecular mass gelators has only recently become an active area of research. Cholesterol-based organogelators have been reported by Weiss [6–8] and Shinkai and colleagues [9–10]. Bile acid-based gelators of aqueous and nonaqueous media have been reported by Hishikawa *et al.* [11] and Maitra and coworkers [12–13]. However, according to our knowledge, there are no reports of low molecular mass gelators based upon terpenoids. Herein, we report the first gelation properties of a terpenoid-based organogelator.

Arjunolic acid (**1**) (Fig. 1), a pentacyclic trihydroxy-triterpenic acid, is the major component of extracts of the heavy wood powder of *Terminalia arjuna* [14]. While synthesizing various arjunolic acid-based molecular receptors for molecular recognition studies [15], we serendipitously discovered that compound **4** is an efficient gelator of a variety of organic solvents (Table I).

Synthesis of compound **4** was carried out as follows. Methyl arjunolate **2** on reaction with benzaldehyde in the presence of perchloric acid as a catalyst afforded the benzylidene derivative **3** in 87% yield. The 2-OH group of compound **3** was esterified with 3,5-dinitrobenzoyl chloride/triethylamine/DMAP to afford compound **4** in 90% yield. Selected data for **4**: ^{1}H NMR (500 MHz, CDCl3) δ: 9.17 (t, $J = 2.1$ Hz, 1H), 9.08 (d, $J = 2.1$ Hz, 2H), 7.44 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 2H), 7.33-7.28 (m, 3H), 5.59 (s, 1H), 5.52-5.47 (m, 1H), 5.28 (br, s, 1H), 3.99 (d, $J = 10.5$ Hz, 1H), 3.77 (d, $J = 10.4$ Hz, 1H), 3.63 (s, 3H), 3.58 (d, $J = 10.4$ Hz, 1H), 2.87 (dd, $J_1 = 13.9$ Hz, $J_2 = 3.9$ Hz, 1H), 2.26 (dd, $J_1 = 12.3$ Hz, $J_2 = 4.5$ Hz, 1H), 2.03-1.0 (m, terpenoid Hs, 19H), 1.32 (s, 3H), 1.19 (s, 3H), 1.17 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H, 0.76 (s, 3H). ^{13}C NMR (125 MHz, CDCl3) δ: 178.6, 162.5, 149.0, 144.4, 138.4, 134.8, 129.8, 129.4, 128.7, 126.5, 122.6, 122.1, 102.9, 87.3, 79.0, 72.1, 52.0, 51.6, 48.2, 47.1, 46.3, 45.0, 42.1, 41.7, 39.9, 39.2, 38.1, 34.3, 33.5, 32.7, 32.5, 31.1, 28.1, 26.4, 24.1, 23.8, 23.4, 18.0, 17.2, 14.8. FTIR (neat): 3044, 2928, 1722, 1700, 1653, 1542, 1507, 1457, 1343 cm^{-1}, $[\alpha]_D^{298} = -31.2$ (c 0.218, CHCl$_3$),

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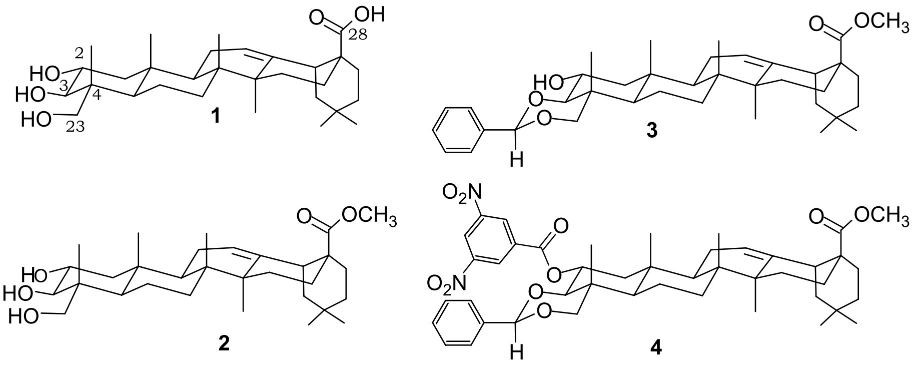

FIGURE 1 Arjunolic acid **1** and its derivatives.

HRMS (ESI): *m/z* calcd ($C_{45}H_{57}N_2O_{10}$) 785.4013, found 785.4021 [M + H].

Gelation experiments were carried out as follows: *ca.*5 mg of compound **4** contained in a vial was dissolved in a solvent by warming. The solution thus obtained was kept at room temperature and checked visually. When the vial could be turned upside down without significant flow of the medium, we called it a gel. Highly stable gels were obtained with aliphatic alcohols with <1wt% of the gelator. For instance, methanol could be gelated with only 0.5% of compound **4** indicating that one gelator molecule is capable of immobilizing more than 3500 solvent molecules. However, during solubilization of compound **4** in short-chain primary alcohols, such as methanol and ethanol, by heating, partial decomposition of **4** was observed due to alcoholysis of the 3,5-dinitrobenzoate group. Compound **4** was, however, very soluble in chlorinated solvents (Table I, entries 6 and 7), and gelation was not observed in these solvents. Hence, attempts were made to solubilize compound **4** in a minimum amount of the chlorinated solvents and then their gelation abilities were tested after mixing with the alcohols. Interestingly, in the mixed solvents **4** was also found to be an efficient gelator (entries 8-12) and no decomposition was observed. In most cases the gels were colorless and transparent. T_{gel} values, measured following the procedure of Takahasi *et al.* [16], were in the range 33–51°C (Table I). It is important to note that compound **3** did not form a gel with the liquids.

The morphologies of the gels were studied by scanning electron microscopy (SEM) after drying in vacuum. For these studies, a thin layer of a gel sample was taken on a glass plate, dried under reduced pressure for 4–6 h, and the dried sample sputter coated with gold. Significant SEM images were obtained for the gels in the mixed solvent systems (Fig. 2). Network structures composed of fibers (Fig. 2a) and strands (Fig. 2b) of micrometer dimensions were observed, respectively, for the gels in ethanol–chloroform (entry 10) and 2-propanol–chloroform (entry 12), characteristic of most low molecular mass gelators. The transparent gel in

TABLE I Results of gelation tests on **4**

Entry	Solvent	Conc. (g/100 mL)	State	T_{gel} (°C)
1	Methanol	0.50	G	38
2	Ethanol	0.66	G	46
3	*n*-Propanol	0.66	G	46
4	2-Propanol	0.66	G	51
5	1-Butanol	0.66	I	–
6	CH_2Cl_2	0.66	S	–
7	$CHCl_3$	0.66	S	–
8	Methanol–CH_2Cl_2 (3:1 v/v)	0.66	G	43
9	Ethanol–CH_2Cl_2 (6:1 v/v)	0.66	G	40
10	Ethanol–$CHCl_3$ (5:1 v/v)	0.66	G	37
11	2-Propanol–CH_2Cl_2 (8:1 v/v)	0.66	G	43
12	2-Propanol–$CHCl_3$ (6:1 v/v)	0.66	G	33
13	Cyclohexanol	2.50	G	43
14	Benzene	0.66	S	–
15	Cyclohexanone	0.66	S	–
16	Diethylene glycol	0.66	P	–
17	Triethylene glycol	0.66	P	–

Compound **4** was warmed with a solvent and the solution was kept at room temperature for several hours to allow gel formation. For mixed solvent systems, **4** was initially solubilized in the chlorinated solvent and then mixed with the alcohols. G, gel; S, solution; I, almost insoluble; P, precipitate. T_{gel} values were measured by using the 'ball drop method' [9].

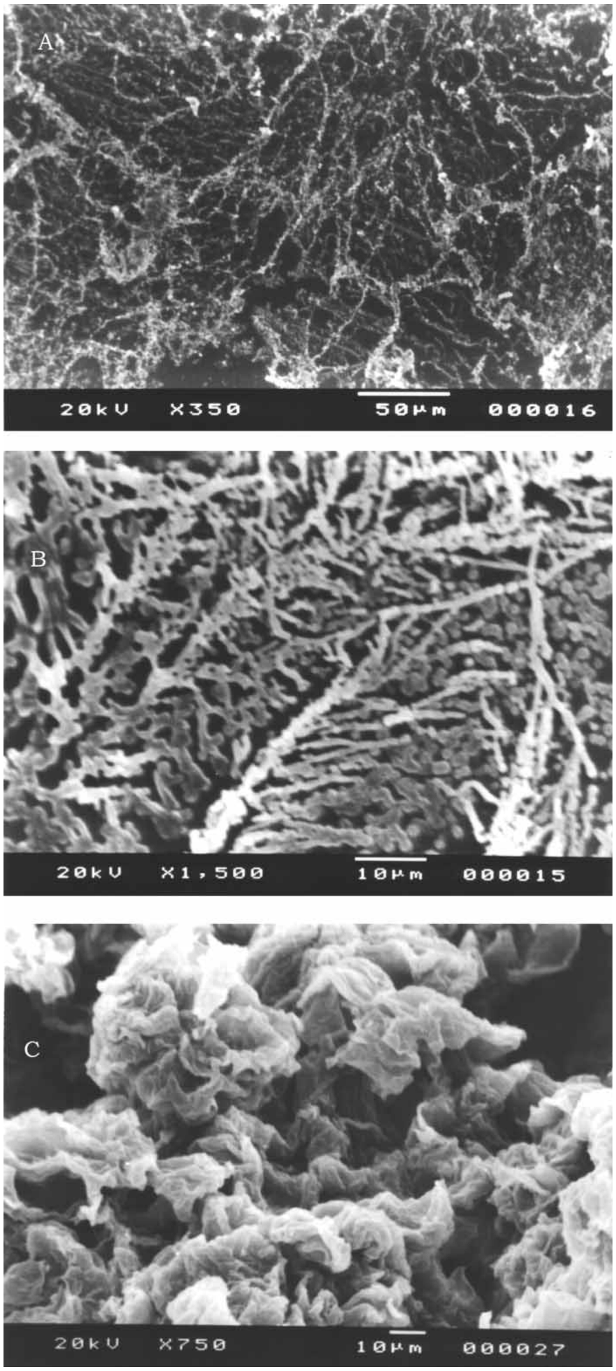

FIGURE 2 Scanning electron micrograph of dried gels obtained from compound **4** in: (a) ethanol–$CHCl_3$ (entry 10), (b) 2-propanol–$CHCl_3$ (entry 12), (c) ethanol–CH_2Cl_2 (entry 9).

ethanol–dichloromethane (entry 9) showed ‘cabbage leaf’ type sheets of micrometer dimensions (Fig. 2c).

In conclusion, we have demonstrated the first example of an efficient low molecular mass organogelator based upon the terpenoid, arjunolic acid. The role of the rigid triterpenoid backbone and the effects of the presence of substituents on the aromatic rings on gelation is not yet clear. Nevertheless, the morphologies revealed by SEM images are encouraging for further studies on this system that might result in newer molecular assemblies and nanomaterials.

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