

Supramolecular Gels: Materials with Self-Assembled Micro and Nano Fibrillar Networks

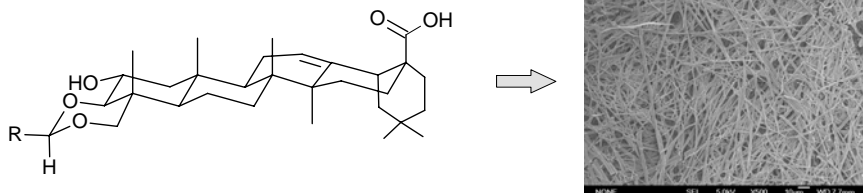
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ABSTRACT

Novel classes of supramolecular gelators are synthesized from arjunolic acid which is obtained from *Terminalia arjuna*. Self-assembly properties of the derivatives have been studied in a wide range of organic solvents. The supramolecular assembly of organogels was examined by microscopy. The importance of aromatic ring and carboxylic acid group on gelation are established. The SEM images of the xerogel of gelators reveal different types of morphology depending upon the solvent systems and concentration of gelator



Keywords: Terminalia arjuna, Low molecular mass Gelators, Supramolecular assembly, SEM images, micro and nano fibrillar networks.

1. Introduction

Supramolecular gels are formed by the self-assembly of *low molecular mass* organic compounds in a medium have attracted considerable attention in recent years and efficient gelation has been reported with compounds of wide structural diversities.¹⁻⁵ The studies in this area have been motivated not only to gain a better understanding of the self-assembly process in a medium but also because of their numerous technological applications.⁶ Self-assembly has proved to be a powerful strategy to develop molecularly defined and functional materials. The long range molecular order, obtained by self-assembly of the low molecular mass organic compounds through gelation, has recently been utilized to create self-assembled nanowires. Although there are many definitions of gels, none seems to encapsulate all of their properties. According to Flory, a gel has a continuous structure with macroscopic dimensions that is permanent on the time scale of

an analytical experiment and is solid-like in its rheological behavior below a certain stress limit. It is thermo-reversible, viscoelastic, materials and comprised of an organic solvents or water as the major component and a low concentration of an immobilizing agent, a “gelator”. Various noncovalent interactions, such as van der Waals, H-bonding and π - π stacking interactions, charge transfer interaction (CT)⁷⁻¹¹ have been suggested as the driving force for assembling the low molecular mass gelator leading to the formation of a fibrous network. The solvent molecules are then trapped inside the network leading to the formation of a gel.

The studies of gelation by polymers, proteins and inorganic substances such as silica or clays are well known, but the study of the low molecular mass self-assembling gelators has only recently become an active area of research. The low molecular mass gelators include long chain hydrocarbons, steroids, carbohydrates, peptides, alkoxy polycyclic aromatic hydrocarbons organic salts etc.¹²⁻¹⁶

Arjunolic acid **1**, a *triterpenoid*, is the major component of the extracts of the heavy wood powder of *Terminalia arjuna*. The chiral triterpenic acid has a rigid pentacyclic backbone with two equatorial hydroxyl and one equatorial hydroxymethyl groups attached at the “A” ring. The carbonyl group is attached at the ring junction of the *cis*-fused “D” and “E” rings. Arjunolic acid offers a great opportunity for the design of molecular receptors, supramolecular architectures and nano-materials.^{12, 17, 18, 19} The first arjunolic acid derived efficient organogelator have been reported.²⁰ Herein I report the facile synthesis of a new series of arjunolic acid derivative and the studies of their self assembling properties through gelation.

2. Experimental section

2.1. Synthesis of arjunolic acid derivatives

Compounds 2, 3, 4, 5, 7, 8 and 9 were synthesized from Arjunolic acid 1 (Figure1).²¹ Arjunolic acid on react with benzaldehyde, catalytic amount of perchloric acid and dichloromethane at room temperature produced compound 2 in 86% yield. Arjunolic acid on react with anthracene-9-aldehyde, catalytic amount of perchloric acid and dichloromethane at room temperature produced compound 3 in 60% yield. Arjunolic acid on react with acetone, perchloric acid at room temperature produced compound 4 in 92% yield. Arjunolic acid on react with anisaldehyde, perchloric acid, dichloromethane and molecular sieves at room temperature produced compound 5 in 74% yield. Compound 1 on react with *p*-nitro benzaldehyde, perchloric acid, dichloromethane and molecular sieves at room temperature produced compound 6 in 82% yield. Arjunolic acid on react with naphalene-1-aldehyde, catalytic amount of perchloric acid and dichloromethane at room temperature produced compound 7. Arjunolic acid 1 on esterification with diazomethane in ether produced methyl arjunolate as in 97% yield. Methyl arjunolate on react with benzaldehyde and a catalytic amount of perchloric acid at room temperature produced compound 8 in 87% yield. Methyl arjunolate on react with anthracene-9-aldehyde and catalytic amount of perchloric acid in benzene at room temperature produced compound 9 in 85% yield.

2.2. Gelation test

A typical procedure for the preparation of organogels was as follows. In a vial, approximately 0.2-0.5 mL solvent was added to 5 mg of powdered sample. The vial was closed and gently heated, in most cases until the mixture started to boil. When a clear solution was obtained, the mixture was allowed to cool at room temperature. Gelation was confirmed when a homogeneous transparent substance having no gravitational flow was observed. The stability of the gels were examined by inverted vials method and observed for couple of weeks at room temperature.

2.3. Gelation criteria and determination of T_{gel}

The inverted vial approach was used as a general criterion for gel formation. When the gel had a viscosity high enough to turn the vial upside down without damaging the structure, the gel transition temperature was determined by the inverted vial method. A glass bead was carefully placed on top of the gel and the vial was subsequently placed in a thermo stated water bath and heated slowly. The temperature at which the balls started to fall through the gel was denoted as gel transition temperature (T_{gel}).

2.4. Scanning electron microscopic studies

Morphological studies of the reported compound were investigated using scanning electron microscope (SEM). The scanning electron microscopic studies of the gels were done using a thin slice of gel on microscopic slides and drying under vacuum at room temperature for 18 hours. The dried sample was platinum coated and observed under the SEM apparatus.

3. Results and discussion

3.1. Gelation studies

5 mg of compound 2 taken in a vial was dissolved in a solvent by heating and the solution was kept at room temperature. When no significant flow of the material was observed visually on turning the vial upside down, we called it a gel. The gelation was confirmed by the inverted vial method (*Figure 5*). Compound 2 formed colorless gels mostly with aromatic solvents including toluene, o-xylene, m-xylene, p-xylene, chlorobenzene, bromobenzene, benzylchloride etc. (*Table 1*).²¹ The result of gelation was summarized in *Table 1*. In most of the aromatic solvents, gels were very stable for several weeks. The compound 2 was very efficient gelator at a very low concentration. For instance, toluene could be gelated with only 1.7% (w/v) of compound 2 indicating that a single gelator molecule is capable of immobilizing more than 423 solvent molecules. The efficiency of the gelator 2 was examined by the gelation studies in various aromatic solvents at various concentrations. Compound 3 gives gelation properties in most of organic liquids studies. The result of gelation shows in table 1. Interestingly it is found that compound 2 is more efficient gelators than the compound 3. Compound 5 gives gel in only benzyl chloride where 7 give gel in mesitylene.

3.2. Importance of aromatic ring and carboxylic acid group on gelation

In order to understand the importance of aromatic ring of both the compounds 2 and 3, compound 4 was synthesized in which aromatic group is replaced by aliphatic group and checked its gelation properties with organic solvents. But, compound 4 did not form gels with any of the solvents. This signifies the importance of aromatic ring of both the

compounds 2 and 3 on gelation. Probably intermolecular π - π interaction is the major driving force for the occurrence on gelation. In order to understand the importance of carboxylic acid group (-COOH) of both the compounds 2 and 3 on gelation, their carboxylic acid group was converted to methyl ester. The conversion of carboxylic acid group of both compounds 2 and 3 produce compounds 8 and 9 respectively and their gelation properties were carried out with various organic solvents. But, compounds 8 and 9 did not form gels with any of the solvents. This signifies the necessity of the carboxylic acid group of both compounds 2 and 3 on gelation.

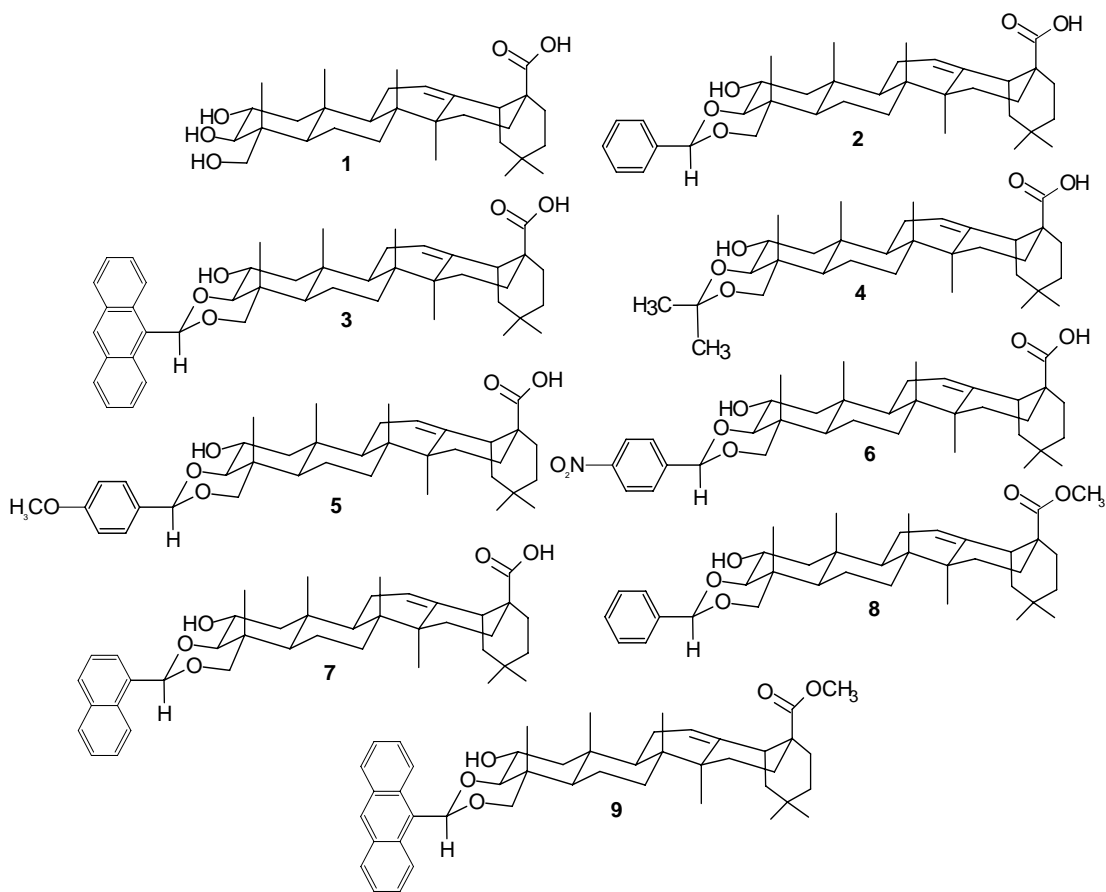


Figure 1: Arjunolic acid and its derivatives

To see the effect of electron releasing or withdrawing group on gelation of compound 2, a methoxy group (-OCH₃) or a nitro group (-NO₂) is introduced at the para position of benzene ring of compound 2. The introduction of electron releasing group (-OCH₃) and electron withdrawing group (-NO₂) at the para position of benzene ring of compound 2 produce compounds 5 and 6 respectively. Compound 5 gives gel in only benzyl chloride. The gelation studies of the compounds 5 and 6 indicate that they did not form gels with any of the organic solvents. The introduction of electron releasing group (-OCH₃) or

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electron withdrawing group (-NO₂) at the para position of benzene ring of compound 2 changes gelator to non gelator molecule.

| Solvents | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------------|-------|-------|-------|--------|-------|--------------|
| Benzene | G/1.4 | G/5.0 | S/1.0 | I/1.0 | I/1.0 | S/10 |
| Toluene | G/1.4 | G/2.0 | S/1.0 | I/1.0 | I/1.0 | G/10 |
| o-xylene | G/2.0 | G/4.0 | S/1.0 | P/2.0 | I/1.0 | S/10 |
| m-xylene | G/2.0 | G/9.0 | S/1.0 | I/1.0 | I/1.0 | G/2.5 |
| p-xylene | G/1.0 | G/5.0 | S/1.0 | I/1.0 | I/1.0 | PG/10 |
| Mesitylene | P/2.5 | P/4.0 | S/1.0 | S/2.0 | I/1.0 | G/0.9 |
| Chlorobenzene | G/2.0 | G/9.0 | S/2.0 | PG/2.2 | I/1.0 | PG/10 |
| Bromobenzene | G/1.7 | G/9.0 | S/2.0 | PG/5.0 | I/1.0 | PG/10 |
| Benzyl chloride | G/2.5 | G/10 | S/2.0 | G/5.0 | I/1.0 | PG/10 |
| nitrobenzene | G/10 | G/10 | G/6 | PG/5.0 | I/1.0 | PG/1 |
| o-dichloro benzene | P/5.0 | G/9.0 | S/2.0 | S/5.0 | I/1.0 | PG/10 |

G = gel; PG = partial gel; S = solution; P = precipitate; I = insoluble.

Table 1: Results of Gelation studies

3.3. Gel to sol melting temperature (T_{gel})

To determine the thermal stability of the gels, the gel to sol melting temperature (T_{gel}) was measured by the ball drop method. The thermal stabilities of the gels are increased upon increasing the concentration of the gelator. The gel to sol melting temperature (T_{gel}) of the gelator is increased with increasing in gelator concentration. T_{gel} values of the gelator 2 are plotted against the gelator concentration in bromobenzene, p-xylene and m-xylene solvent as shown in *Figure 2*, *Figure 3*, *Figure 4* respectively. The T_{gel} value of gelator 2 in xylene solvent is greater than the T_{gel} value in other solvents at same concentration. For example, T_{gel} value in p-xylene is 102°C at concentration 3.33% whereas it is 49°C in chlorobenzene solvent at the same concentration. The increase in T_{gel} with increasing gelator concentration indicates that self-assembly is driven by strong intermolecular interactions. When the concentration of the gelator in gelation increases, a large number of molecules are accommodated in aggregation, because of the packing of the gelator molecules become more pronounced due to enhanced π - π stacking interactions, van der waals interaction and other noncovalent interactions.

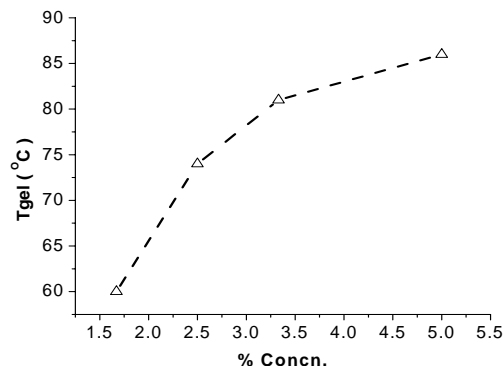


Figure 2: Plot of T_{gel} vs % concentration (w/v) of compound **2** in bromobenzene solvent.

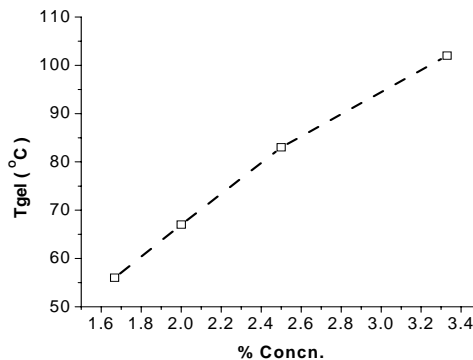


Figure 3: Plot of T_{gel} vs % concentration (w/v) of compound **2** in p-xylene solvent.

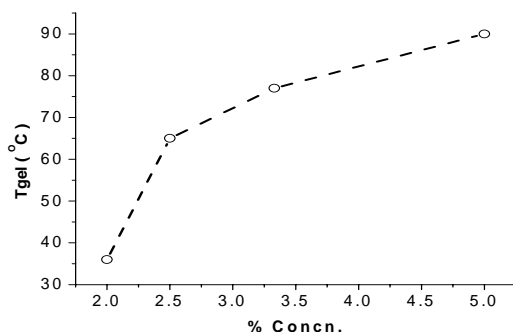


Figure 4: Plot of T_{gel} vs % concentration (w/v) of compound **2** in m-xylene solvent.

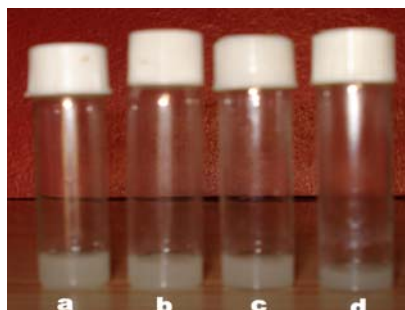


Figure 5: Vials containing gels obtained from **2** in: (a) toluene, (b) m-xylene, (c) p-xylene, (d) bromobenzene solvent.

3.4. Morphology of the gels

Molecular self-aggregation features can be observed by an electron microscope, since the initial stage of physical gelation is the self-assembly of gelator monomers. Figures 6-9 represent the scanning electron microscope (SEM) images of the organogels formed by **2** (Figure 6 a and b, 7 a and b, 8 c, d and e, 7) and **3** (Figure 7 c and d, 8 a and b). The images of their xerogels reveal different types of morphologies. The organogel formed in o-xylene solvent by compound **3** showed flowerlike (mari gold) morphology (Figure 7d and 8 a, b). The organogel of **2** in o-xylene solvent showed fibers morphology at microscopic level (Figure 6a). These fibers are entangled and formed a dense fibrous network that results in the immobilization of the solvent molecules. The SEM images of the xerogel of **2** also reveal different types of morphology depending upon the solvent systems. For example, the organogel of **2** in toluene solvent showed rod like (Figure 7a) or fibers (6a) morphology at microscopic level whereas in chlorobenzene solvent showed helical like morphology (Figure 8 and e). Analysis of these aggregates clearly showed

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that the individual fibers are 125-162 micrometer diameter and length is up to several micrometers and the rods are approximately 290-655 micrometer diameter.

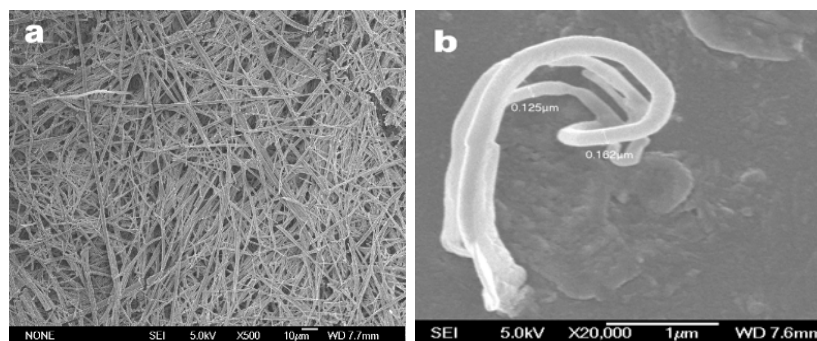


Figure 6: Scanning electron micrograph of the dried gel: (a) compound **2** in o-xylene (2 % w/v), (b) compound **2** in toluene (1.25 % w/v).

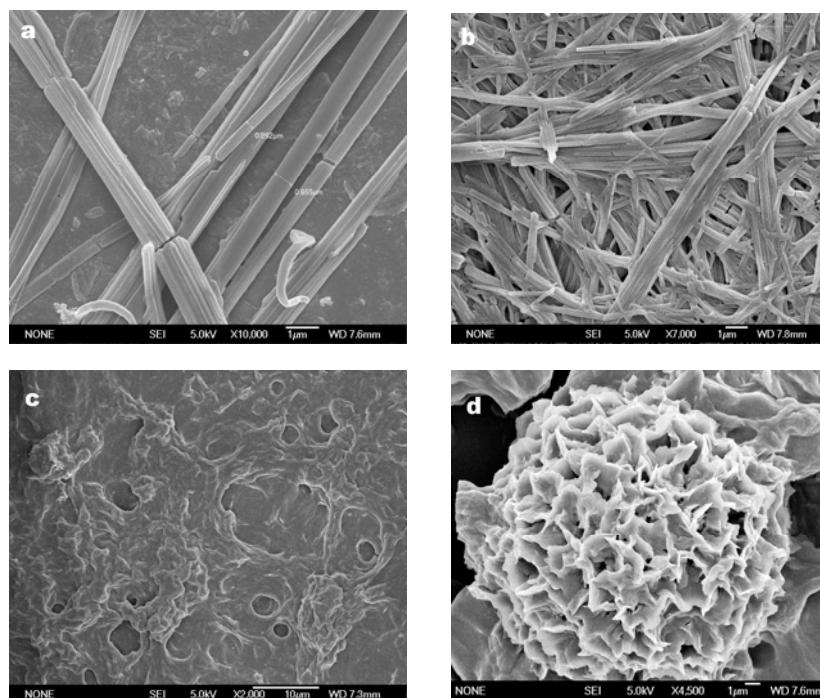


Figure 7: Scanning electron micrograph of the dried gel: (a) compound **2** in toluene (1.25 %) (b) compound **2** in bromobenzene (2.5 % w/v), (c) compound **3** in toluene (2.5 % w/v), (d) compound **3** in o-xylene (2.5 % w/v).

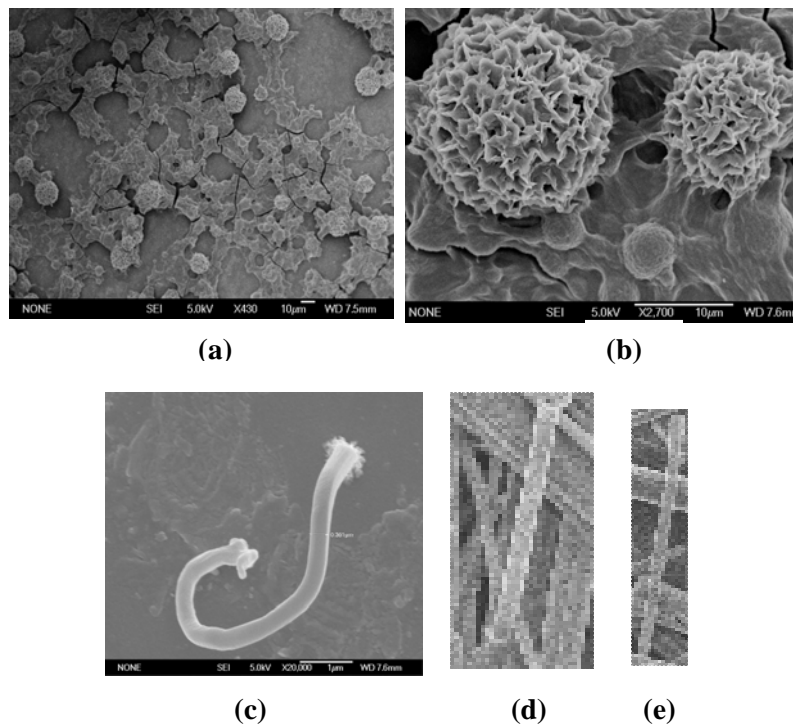


Figure 8: Scanning electron micrographs of the dried gels: (a, b) compound **3** in *o*-xylene (2.5% w/v), (c) compound **2** in toluene (1.25% w/v), (d, e) compound **2** in chlorobenzene solvent(5.0% w/v).

3.5. Conclusion

The facile syntheses and gelation test results of compounds **2**, **3**, **4**, **5**, **6**, **8**, and **9** have been reported. Compounds **2**, **3**, **5** and **7** are excellent gelators of varieties of organic solvents and especially aromatic solvents whereas compounds **4**, **6**, **8** and **9** are not. These are the first example of triterpene based gelators containing carboxylic acid group. The importance of carboxylic acid group as well as aromatic ring for gelation has been established but the role of triterpene backbone is yet to be undiscovered. Compounds **2** and **3** are self-assembled to form different types structure depending upon the solvent systems. The increase in T_{gel} values with increase in concentration of the gelator indicates stronger intermolecular interactions. Scanning electron micrographs of the xerogels formed by both compounds **2** and **3** revealed different types of morphologies. Organogel formed by compound **2** showed fibers morphology. The fibers formed by self-assembly of **2** are of micrometer and nanometer dimensions.

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