

SHORT COMMUNICATIONS

A NEW LIMONOID, AMOORININ FROM THE STEM BARK OF *AMOORA ROHITUKA* WALL

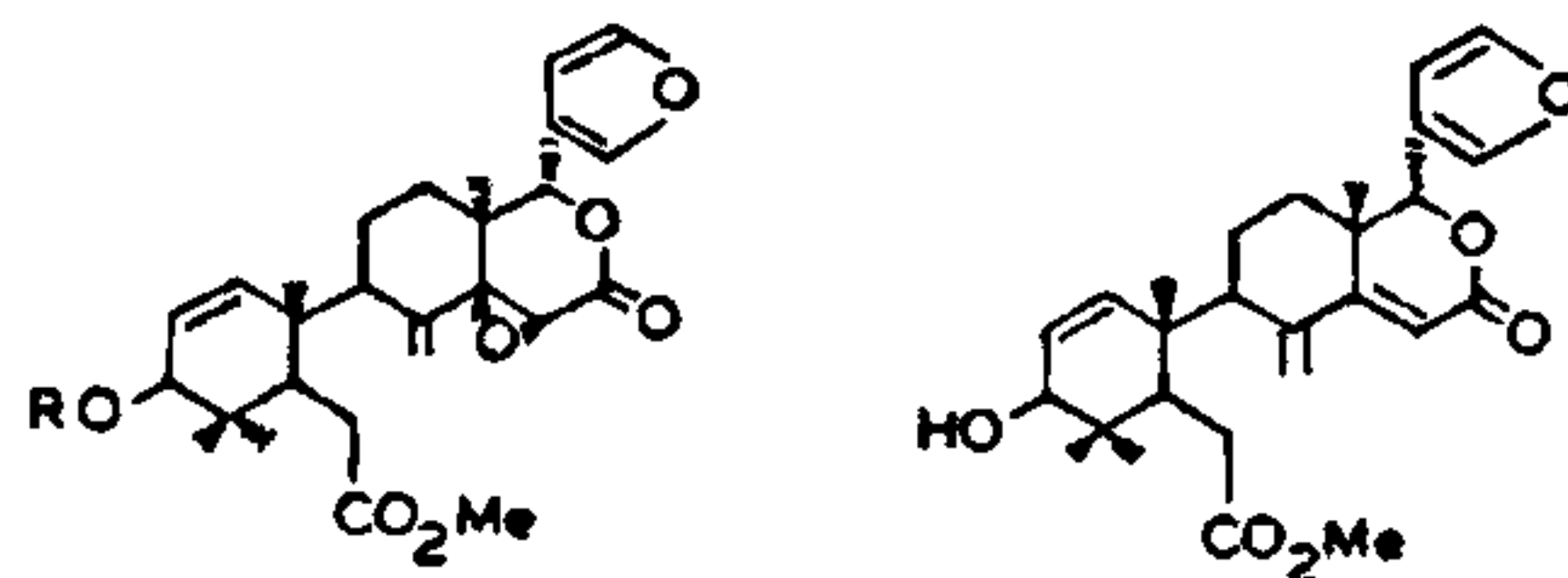
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AMOORA ROHITUKA (syn. *Aphanamixis polystachya*, N. O. Meliaceae) has disclosed the presence of aphanamixinin¹ and sterol, saponins, flavanone and anthraquinone glycosides². Further study of this plant has now led to the isolation of one congener which biogenetically links a class of limonoid, andirobin. We report here the isolation and characterization of a new limonoid, amoorinin (1) on the basis of spectral and chemical methods.

Compound (1), C₂₇H₃₄O₇, mp. 172-174° (M⁺470), (α)_D²⁵-105° (CHCl₃, c, 0.14) exhibited IR spectrum characteristic for hydroxyl (3450), δ-lactone (1735), ester (1725), trisubstituted double bond (1640, 825), furan (1510, 875), epoxide (1285) and exocyclic methylene group (910 cm⁻¹). The ¹H-NMR spectrum suggests that compound (1) is closely related to aphanamixin in [1] and similar compounds³ except in ring-A which displayed signals at δ 6.15 (d, J = 10 Hz, H-1), 5.90 (dd, J = 6 and 10 Hz, H-2), 3.65 (d, J = 6 Hz, H-3) and 3.20 (s, OH, exchangeable with D₂O) characteristic for an allylic alcohol type grouping in (1). Compound (1) formed mono-methyl ether (Me₂SO₄/K₂CO₃), 2, mp. 160-163°, C₂₈H₃₆O₇ (¹H-NMR, δ 3.75, 3H) and an acetate (Ac₂O/C₅H₅N), 3, mp. 140-143°. The ¹H-NMR of 3 exhibited signals at δ 2.0 (1 × OAc) and δ 4.80 (d, J = 6 Hz, H-3) indicating the presence of a secondary OH group in 1. CrO₃/C₅H₅N oxidation⁴ afforded a product, mp. 195-196°, C₂₇H₃₂O₇ identical to andirobin in its spectral data⁵ (lit. mp. 195-197°). Compound (1) undergoes facile reduction with chromous chloride to furnish, 4, mp. 170-172°, C₂₇H₃₂O₆, which on CrO₃/C₅H₅N oxidation yielded a known compound deoxyandirobin⁵⁻⁷, mp. 170-173° (lit. mp. 171-174°). Thus the structure of the new compound was assigned as 1.

The melting points were determined on a Toshniwal apparatus and were uncorrected. Optical rotation was taken on a Perkin-Elmer 141 polarimeter at room temperature. IR spectra were determined on a Perkin-Elmer model 157 spectrophoto-



1 R=H 2 R=Me 3 R=Ac

4

meter. ¹H-NMR spectra were recorded in CDCl₃ at 90 MHz on a Varian EM 360 L spectrometer with TMS as an internal standard and chemical shifts recorded in δ units. The mass spectra were taken with Hitachi RMU-6E mass spectrometer fitted with direct inlet system and operating at 70 eV.

The powdered stem bark of *A. rohituka* (5 kg) procured from the United Chemicals and Allied Products, Calcutta (India) was exhaustively extracted with ethanol under reflux on a water bath for 200 hr. The ethanol from the percolates (20 l) was removed under pressure to make the volume 500 ml and kept at room temperature for a few days during which a dirty white mass was deposited. This was separated by filtration and passed through a column of neutral Al₂O₃. Elution with C₆H₆: CHCl₃ (1:1) and crystallization from CHCl₃ afforded colourless needles of (1) (yield 900 mg) (Found C; 68.87, H: 7.18; C₂₇H₃₄O₇ required C; 68.93; H: 7.23%); (α)_D¹⁵⁰-150° (CHCl₃). ¹H-NMR: 0.95, 1.00, 1.08, 1.10 (each s, 12H, 4 × CH₃) 1.20-1.90 (complex pattern, CH₂ and CH), 3.20 (s, 1 × OH), 3.65 (d, J = 6 Hz, 1H, H-3), 3.75 (s, 3H, 1 × COO CH₃), 3.80 (s, 1H, H-15), 4.90 and 5.10 (each s, 2H, >C = CH₂), 5.65 (s, 1H, H-17), 5.90 (dd, J = 6 and 10 Hz, 1H, H-2), 6.15 (d, J = 10 Hz, 1H, H-1), 6.40, 7.20 and 7.39 (each m, 3H, furan-H); MS: 470 (M⁺), 457, 452, 437, 411, 403, 402, 389, 263 and 245. Compound (1) formed a methyl ether (2) (100 mg 1 + 4 ml Me₂SO₄ + 2 g K₂CO₃, yield 60 mg); ¹H-NMR: 0.90, 1.00, 1.05, 1.09, 1.20-1.90, 3.65, 3.72, 3.80, 4.90, 4.00 (s, 3H, 1 × OCH₃) 5.10, 5.65, 5.90, 6.12, 6.39, 7.20 and 7.40 and an acetate (3) (100 mg 1 + 5 ml Ac₂O + 5 ml C₅H₅N, yield 80 mg); IR: 1725; ¹H-NMR: 0.95, 1.00, 1.08, 1.10, 1.20-1.90, 2.00, 3.75, 3.80, 4.80, 4.90, 5.10, 5.65, 5.95, 6.15, 6.40, 7.20 and 7.39.

The compound (1) (300 mg) in Me₂CO (10 ml) and AcOH (10 ml) was added to excess of CrCl₂ in HCl. The mixture was stored in CO₂ for 5 days. The

product (4) was extracted with ether and crystallized as colourless plates from Et₂O: CHCl₃ mixture (yield 250 mg) (Found C; 71.59, H: 7.00; C₂₇H₃₂O₆ required C; 71.68, H: 7.07%); IR: 3445, 1735, 1722, 1640, 1510, 910, 875 and 822; ¹H-NMR: 0.93, 1.00, 1.05, 1.08, 1.20-1.90, 3.25, 3.65, 3.70, 4.90, 5.10, 5.60, 6.15, 6.39, 6.90, 7.20 and 7.40.

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1. Chatterjee, A., Kundu, A. B., Chakraborty, T., Chandrasekharan, S., *Tetrahedron*, 1970, 1859.
2. Srivastava, S. K., Agnihotri, V. K., *Curr. Sci.*, 1984, 53, 1288; 1985, 54, 38.
3. Srivastava, S. K. and Gupta, H. O., *Indian J. Chem.*, 1985, 24, 166.
4. Poos, G. I., Arth, G. E., Beylor, R. E. and Sarrett, L. H., *J. Am. Chem. Soc.*, 1953, 75, 422.
5. Ollis, W. D., Ward, A. D., Zelnik, R., *Tetrahedron Lett.*, 1964, 37, 2609.
6. Adesogan, E. K. and Taylor, D. A. H., *Chem. Ind.*, 1967, 1365.
7. Ekong, D. E. U. and Olagbemi, E. O., *J. Chem. Soc.*, 1966, 944.

CLAY-CATALYSED KNOEVENAGEL CONDENSATION

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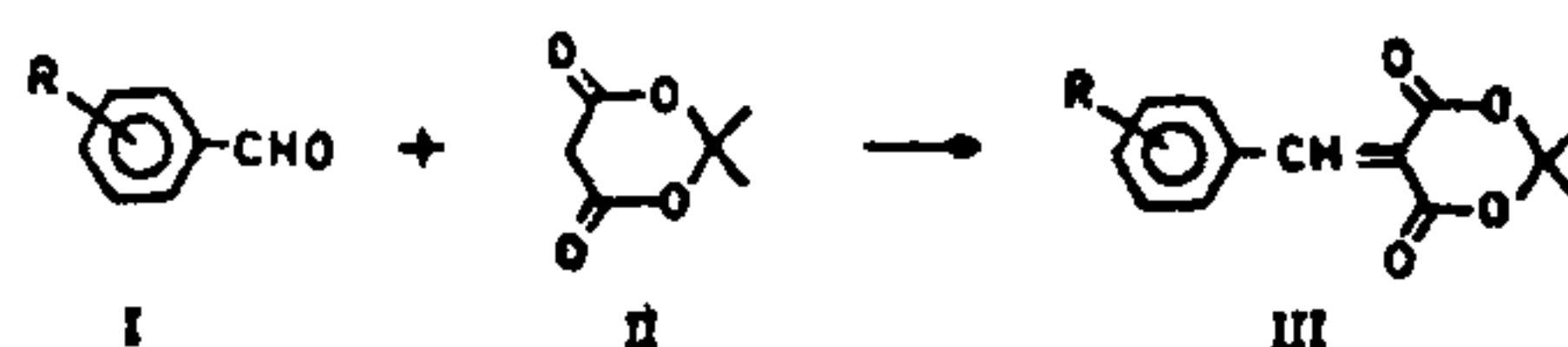
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MELDRUM'S acid (2,2-dimethyl-1,3-dioxan-4,6-dione) is an attractive alternative to acyclic esters in organic synthesis¹ and it has a strong tendency to undergo bis-alkylation². Meldrum's acid is a good source of malonate carbanion and has an acidity (pK = 4.83) very close to that of acetic acid which is used with acetate as a catalyst in Knoevenagel and related condensations. In continuation of our work on solid-supported reactions³⁻⁶, and in view of the importance of alkylated Meldrum's acid in phar-

maceuticals, we report here a simple method for a Knoevenagel condensation of Meldrum's acid with aldehydes in the presence of clay, Kaolin (Kaylene Chemicals Ltd., London) at room temperature, in the absence of a solvent. The advantage of the method is its simplicity and high yields of the pure product.

An equimolar mixture of aldehydes (I) and Meldrum's acid (II) was melted and adsorbed on kaolin at room temperature without the use of solvent. It was observed that complete condensation took place within 20-25 hr after mechanical stirring.



General procedure for condensation

An aldehyde or ketone (I) was mixed with Meldrum's acid (II) in equimolar (0.01 mol each) quantity. This mixture whether it contained solid or liquid carbonyl compound, was carefully melted and adsorbed on 4 g of kaolin and mechanically stirred for 20-25 hr at room temperature. The product (III) was eluted by dichloromethane (3 × 30 ml). Evaporation of the solvent under reduced pressure generally gave a pure crystalline product. Purity was assured by TLC. If necessary, the product was crystallized from an appropriate solvent, i.e. CH₂Cl₂, CHCl₃ or benzene. Products were characterized by PMR, IR and compared with authentic samples.

Kaolin gave a good result similar to basic alumina⁷ (Merck 1076) and chromatographic neutral alumina⁷ (Woelm-N, 2087) and more active

Table 1 Condensation of Meldrum's acid with aldehydes

Aldehyde (I)	Yield (III) (%)	m.p (°C)
Benzaldehyde	89	85
Cinnamaldehyde	80	109
<i>m</i> -hydroxybenzaldehyde	80	175
<i>p</i> -hydroxybenzaldehyde	85	197
<i>p</i> -methoxybenzaldehyde	91	126
<i>p</i> -N-dimethylamino- benzaldehyde	95	174
Vanillin	85	129
<i>p</i> -methylbenzaldehyde	87	159
<i>p</i> -chlorobenzaldehyde	82	182