

SYNTHESIS OF D:A-FRIEDO-LUP-19-ENE AND ITS
CONVERSION INTO METHYL TRINORSHIONANOATE

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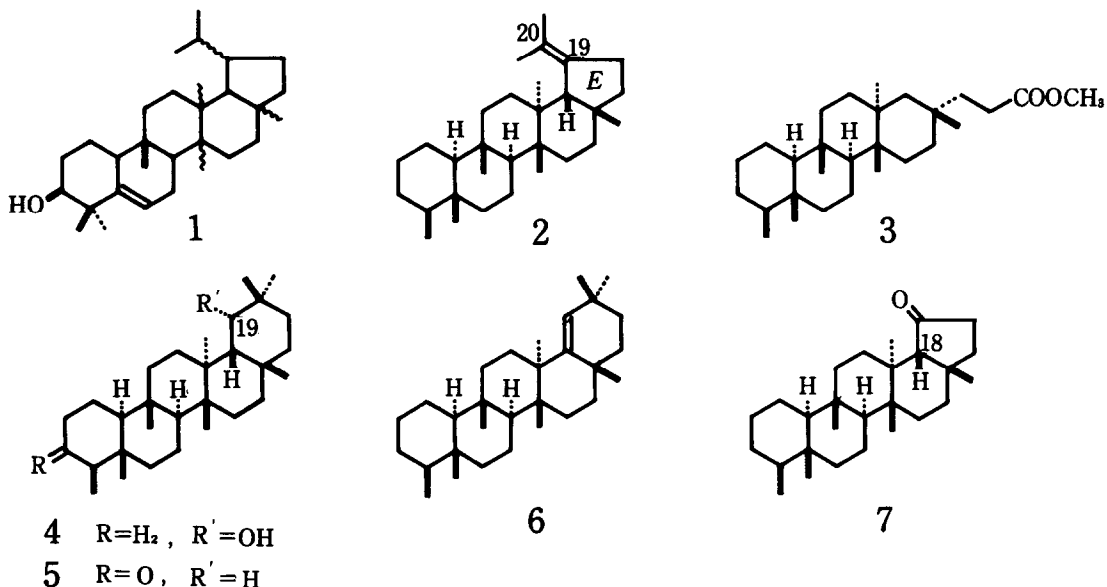
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Guimarenol (1), a pentacyclic triterpene alcohol isolated from Ceropegia dichotoma, has been described to have a novel rearranged lupane (D:B-friedo-lupane) skeleton.¹⁾ However, no isolation nor synthesis of a triterpene with D:A-friedo-lupane framework has yet been recorded. We wish to report a synthesis of D:A-friedo-lup-19-ene (2) and its conversion into methyl trinorshionanoate (3).

Friedelan-19 α -ol (4)²⁾ derived from friedelin (5) was treated in toluene with phosphorus pentachloride to give a mixture of olefins, which was separated by column chromatography (SiO₂ impregnated with AgNO₃) to yield a ring-E contracted olefin (2; yield: 44%), C₃₀H₅₀,³⁾ mp 181.5-182.5°; IR (Nujol) no ν_{OH} absorption; PMR (CDCl₃) δ 0.78 - 0.90 (6 X CH₃) and δ 1.64 (6H, s; (CH₃)₂C=C<) (absence of olefinic proton); mass spectrum m/e 410 (M⁺) and m/e 121 (base peak), together with friedel-18-ene (6; y: 3%).⁴⁾ Oxidation of 2 with ruthenium tetroxide⁵⁾ in carbon tetrachloride (at room temperature) afforded a ketone with five-membered ring (7; y: 54%), C₂₇H₄₄O,³⁾ mp 217-218°; IR (Nujol) 1725 cm⁻¹; PMR (CDCl₃) δ 0.77 - 1.00 (6 X CH₃), δ 2.18 (2H, m; -CH₂-CO-), and δ 2.20 (1H, s; -CH-CO-); CD (dioxane, c, 0.0014)⁶⁾ (θ)₃₀₂ +7570, (θ)₃₁₃ +7710, and (θ)₃₂₅ +4190; mass spectrum m/e 384 (M⁺) and m/e 109 (base peak). A five-membered ring nature for the ring-E of 2 was therefore received support.

The ketone (7) in methanol was irradiated under nitrogen using a 100 W high pressure mercury lamp. The mixture, after separation by column chromatography (SiO₂), gave an ester (3; y: 49%),⁷⁾ mp 122-123.5°, which proved to be identical (mp, mixed mp, IR, PMR, mass spectrum, and TLC) with the known methyl trinorshionanoate (3).⁸⁾

A transformation of friedelin (5) into methyl trinorshionanoate (3) via D:A-friedo-lupane-type compound (2) was thus shown.



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- 6) An 188-H configuration was suggested for **7**. cf. e.g. 3 α ,11 α -Diacetoxy-(13 β -H)-fusidan-17-one showed a positive Cotton effect, while its (13 α -H)-isomer a strong negative maximum: W. O. Godtfredsen, W. von Daehne, S. Vangedal, A. Marquet, D. Arigoni, and A. Melera, *Tetrahedron*, **21**, 3505 (1965).
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