

Triterpene Methyl Ethers from Gramineae Plants: Lupeol Methyl Ether, 12-Oxoarundoin, and Arborinol Methyl Ether

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THREE new triterpene methyl ethers (I), (II), and (III) have been isolated from Gramineae plants.

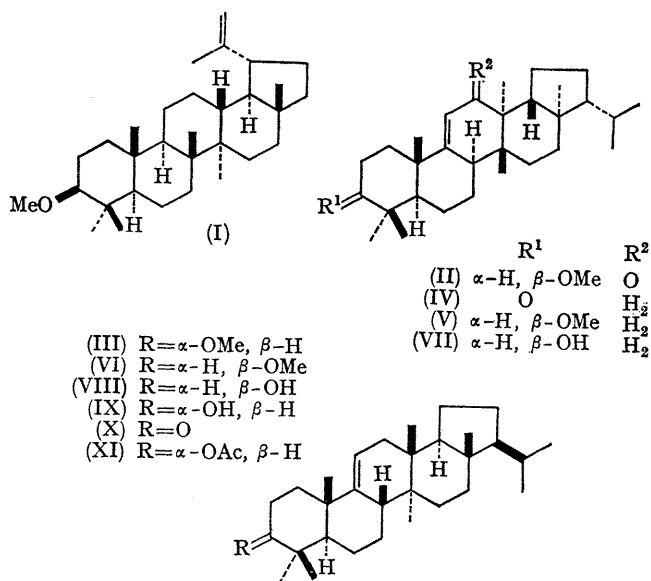
Lupeol methyl ether (I), obtained from the neutral portion of a saponified hexane extract of culms and blades of *Paspalum dilatatum* Poir. by chromatography on alumina, had m.p. 250–251°, $[\alpha]_D^{25} + 35.6^\circ$ (CHCl_3). From the molecular formula $\text{C}_{31}\text{H}_{52}\text{O}$ and the presence of an isopropenyl group and a methoxy-group [ν_{max} . (KBr) 1620, 874, 1103 cm^{-1} ; τ (CDCl_3) 8.32 (3H, br. s), 5.37 (2H, m); 6.67 (3H, s), 7.44 (1H, m)] the compound appeared to be lupeol methyl ether. This view was confirmed by the synthesis of the latter from lupeol and the identity of the synthetic and natural product was established by mixed m.p., i.r. spectra, v.p.c., and t.l.c.

The hexane extract of whole herb of *Zoysia matrella* Merr. gave two new natural products; fern-9(11)-en-3-one¹ (IV) and 12-oxoarundoin [3β -methoxyfern-9(11)-en-12-one]¹ (II). The latter, m.p. 291°, $[\alpha]_D^{25} - 5.2^\circ$ (CHCl_3), was identical with a specimen prepared by chromic acid oxidation of arundin (V).

The rhizomes of *Imperata cylindrica* var. *koenigii* contain (V), cylindrin (VI), fernenol (VII), isoarborinol (VIII), and simiarenol.¹ The culms and blades have now been shown to contain (V), (VI), (VIII), arborinol² (IX), arborinone² (X), friedelin, and a new triterpene methyl ether (III), m.p. 284–285°, $[\alpha]_D^{25} + 11.5^\circ$ (CHCl_3), having a tri-substituted double bond [ν_{max} . (KBr) 1606, 807, and 793 cm^{-1} ; τ (CDCl_3) 4.74 (1H, m) and an axial methoxy-group [ν_{max} . (KBr) 1101 and 1093 cm^{-1} ; τ (CDCl_3) 6.68 (3H, s), 7.14 (1H, t, J 7 c./sec.)]. Demethylation of (III) with hydrobromic acid, phenol, and acetic anhydride gave arborinol acetate (XI) and arborinol (IX). Hydrolysis of

(XI) gave (IX) and methylation of (IX) gave the methyl ether (III), identical with the natural product.

Ten triterpene methyl ethers have so far been characterized from Gramineae plants.^{1,3,4} Since the wide occurrence of the compounds has been confirmed for about fifty species⁴ they are assumed to be a chemotaxonomical characteristic of the family.



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⁴ T. Ohmoto, *Shoyakugaku Zasshi*, 1966, **20**, 67; 1967, **21**, 115, 120; 1968, **22**, 110; *J. Pharm. Soc. Japan*, 1969, **89**, in the press. The summary of the results and chemotaxonomical discussion will be submitted to *Phytochemistry*.