

ISOLATION OF A NEW TRITERPENE, ROTUNDIC ACID,
FROM ILEX ROTUNDA

Tomoko Oyama, Hiromu Aoyama, Kazutoshi Yamada*,
Tatsuo Mitsuhashi** and Noboru Sugiyama***

Department of Chemistry, Tokyo Kyoiku University,
Otsuka, Tokyo, Japan

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From an ethereal extract of the seeds of *Ilex rotunda*, a new triterpene acid (Ia) has been isolated. We have named this new triterpene, rotundic acid.

The crude extract was esterified with diazomethane, and the resulted product was worked up on silica gel chromatography. This procedure yielded methyl oleanolate and methyl rotundate (Ib), $C_{31}H_{50}O_5$, m.p. 257° , $[\alpha]_D^{24} +38^\circ$. Methyl oleanolate was identified by comparison with an authentic sample (mixed m.p.; IR identical). Acetylation of Ib gave the diacetate (Ic), $C_{35}H_{54}O_7$, m.p. $100-102^\circ$, $[\alpha]_D^{24} +51^\circ$. The IR spectrum of Ic revealed the presence of a hydroxyl group (3500 cm^{-1}) which was presumed to be tertiary since it resisted acetylation and oxidation.

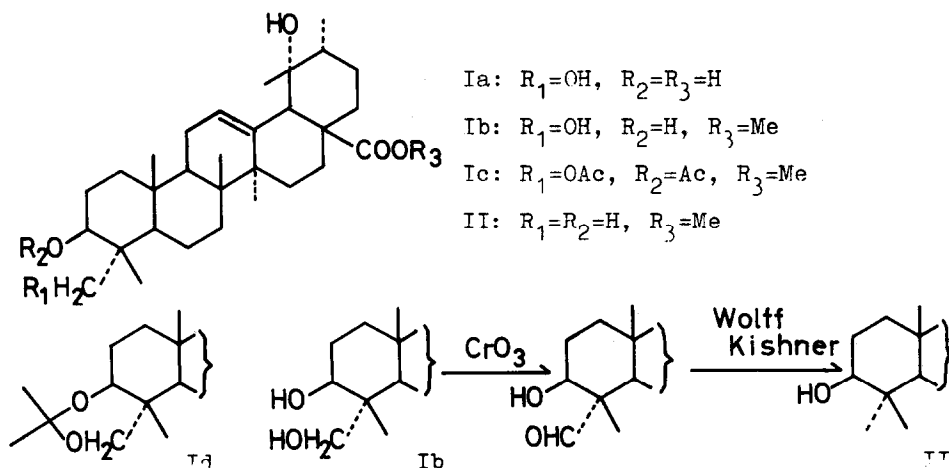
The mass spectrum of Ic demonstrated the retro Diels-Alder fragments at m/e 278 (a) and $307 (b)^{1)}$, characteristic of an α -or β -amyrine structure, together with a molecular ion at m/e 586. It follows that ring A and/or B in Ic possesses two acetoxyl groups, whereas the carbomethoxyl and tertiary hydroxyl groups are located in rings D and/or E. The NMR spectrum of Ic showed the presence of a carbomethoxyl group, singlet at τ 6.38 (3H) and indicated its

* Present address: Department of Synthetic Chemistry, Chiba University, Yayoi-cho, Chiba, Japan.

** Department of Chemistry, Tokyo University of Liberal Arts, Nukuikita-machi, Koganei, Tokyo, Japan.

*** To whom inquiries concerning this paper should be addressed.

position at C-28****. Two singlet signals at τ 7.96 and τ 7.92 showed two acetoxy groups. On biogenetical ground, it is highly probable that one of the acetoxy group was at 3β . This configuration was also supported by the triplet at τ 5.23 (1H, 3α H). The singlet at τ 6.23 (2H, methylene proton) suggested that the other acetoxy group possesses a primary structure. The formation of the acetonide (Id), $C_{34}H_{54}O_5$, m.p. 96° , from Ib, indicated that the position of the primary hydroxyl was at 23 or 24 position. The hydroxyl methyl group was further revealed to be in an equatorial configuration since the methylene proton in the $-CH_2OAc$ in Ic appeared as a broad singlet at τ 6.23^{2,4)}. Thus the primary hydroxyl has been placed at the 23-position.



The NMR spectrum also showed the presence of the methyl group to be on the C-atom which bears the OH (τ 8.77, 3H). This shows that the triterpene has an α -amyrine structure and the position of the tertiary hydroxyl group is at C-19 or C-20. The position of the hydroxyl group was established as follows. Methyl rotundate (Ib) was partially oxidized with CrO_3 in pyridine, followed by Wolff-Kishner reduction, which gave the known compound methyl $3\beta, 19\alpha$ -dihydroxy-urs-12-en-28-oate (II), m.p. $125-126^\circ$, $[\alpha]_D^{24} +38^\circ$ (lit. m.p. $126-128^\circ$, $[\alpha]_D^{20} +38.5^\circ$ ⁵⁾). Based on the above partial synthesis and the observed

**** The highest methyl group peak at τ 9.30 indicates the presence of a C-28 carbomethoxyl group^{2,3)}.

physical-chemical properties, the structure of rotundic acid was assumed to be 3 β ,19 α ,23-trihydroxy-urs-12-en-28-oic acid.

The analyses of all the compounds mentioned were satisfactory. If not otherwise stated, the optical activities were determined in CHCl₃, the NMR spectra in CDCl₃ with TMS as internal standard.

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