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THE STRUCTURE OF A NEW TRITERPENE, MOMORDIC ACID, OBTAINED FROM MOMORDICA COCHINCHINENSIS SPRENGER

T. Murakami[*1], M. Nagasawa[*1], H. Itokawa[*2], Y. Tachi[*3], and K. Tanaka[*1].
(Department of Pharmacy, Tokyo College of Science[*1])

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The Chinese crude drug "Mubiezi", Japanese name "Mokubessi", the seeds Momordica cochinchinensis Sprenger, which occurs in Southeast Asia has been used in the treatment of tumor, mastopathy, malignant skin diseases and tubercular cervical lymphadenitis. A sterol[1] and oleanolic acid[2] which was obtained by acid hydrolysis of rhizomesaponins have been isolated as constituents of this drug.

In the course of further investigation of this drug, we have isolated some free amino acids[3] and a new triterpene, momordic acid, obtained by acid hydrolysis of the saponin fraction. We report in this communication the elucidation of the structure of momordic acid (I), the first example of a triterpenic acid having a 1-oxo group in the oleanane series.

Momordic acid has been obtained as colourless needles, λ_{max}^{EtOH} 203mμ ($\log\varepsilon = 3.79$), 295mμ($\log\varepsilon = 1.39$), $C_{30}H_{46}O_4$, m.p.274-276°, ν_{max}^{KBr} 3400cm^{-1} (-OH), 1717cm^{-1}(six membered ring ketone), 1700cm^{-1}(-COOH). The compound

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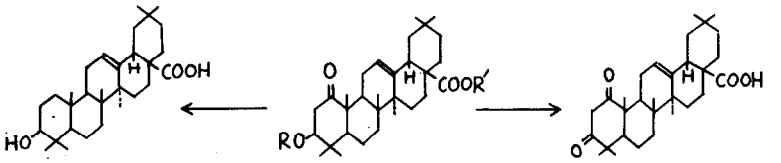
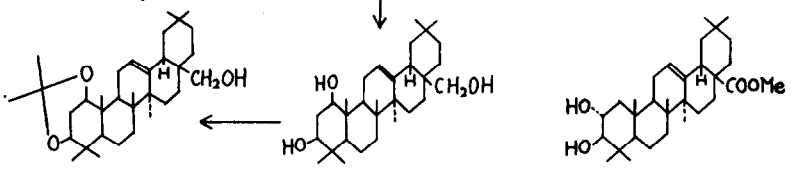
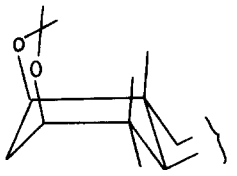
*1 Funagawara-cho, Shinjuku-ku, Tokyo.
*2 Present address, Tokyo College of Pharmacy, Shinjuku-ku, Tokyo.
*3 Present address, Research Laboratory, Taisho Pharmaceutical Co., Ltd. Toshima-ku, Tokyo.



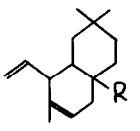
(IV) (I) R=R'=H (II) R=H; R'=Me (III) R=Ac; R'=H (V)



(VII) (VI) (VIII)



(IX)



(a) m/e=248; R=COOH
(b) m/e=203 (248-R)

forms a monooxime $C_{30}H_{47}O_4N$, m.p.274-276°, a monomethylester (II) $C_{31}H_{48}O_4$, m.p.217-220° and a monoacetate (III) $C_{32}H_{48}O_5$, m.p.179-180°.

The mass spectrum of momordic acid showed the molecular weight to be 470 and indicated that it was a pentacyclic triterpene since there was no peak corresponding to the loss of a side chain and from the peaks at m/e 248 (a) and m/e 203 (b) no substituents were found in rings C, D, E[4].

The NMR spectra of (II) and (III) showed seven methyl groups at 0.61-1.11ppm. (III) had a carboxyl proton (9.3ppm) and a signal (3H) due to an acetyl group (1.98ppm), and (II) had a signal (3H) due to a methylester (3.56ppm).

A Wolff-Kishner reduction converted momordic acid into a compound (IV), $C_{30}H_{48}O_3$, m.p.308-310°, which was subsequently identified as oleanolic acid. This suggested that (I) was an oxo-derivative of oleanolic acid.

By oxidation with chromic acid (I) was converted to a diketone (V), $C_{30}H_{44}O_4$, m.p.177-180°, ν_{max}^{KBr} 1730cm^{-1}, 1770cm^{-1}(shoulder), 1700cm^{-1}, 1660cm^{-1}, the U.V. spectrum of (V), λ_{max}^{EtOH} 252mμ(log ε = 3.61), suggesting to be an α- or β- diketone (maybe present as an enol form). By $LiAlH_4$ reduction of (I), a triol (VI) $C_{30}H_{50}O_3$, m.p.262-263°, was obtained. Compound (VI) formed an isopropylidene derivative (VII) $C_{33}H_{54}O_3$, m.p.129-131°, the NMR spectrum of which showed two methyl signals at 1.45 and 1.42ppm respectively due to the protons of the isopropylidene group. The triol (VI) did not consume periodic acid, although methylmaslinate (VIII) used as a reference compound, consumed one mole. This indicates that the hydroxyl group formed by $LiAlH_4$ reduction of (I) was located at C_1 rather than at C_2. The ORD curve of (I) showed a positive Cotton Effect and was also very similar to the curves of 1-oxo-steroids.[5]

These results demonstrate the presence of an oxo-group at C_1 and the A-ring in (VII) must have the boat conformation as (IX).

Momordic acid is thus shown to be 1-oxo-3β-hydroxyolean-12-en-28-oic acid (I).

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