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ALNUSERRUDIOLONE, A NEW C_{31}-DAMMARANE-TYPE TRITERPENE FROM *ALNUS SERRULATOIDES* CALL.

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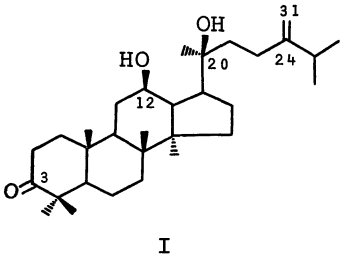
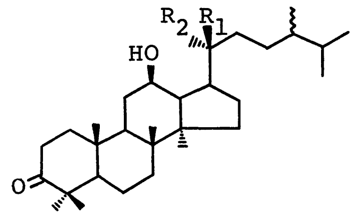
The structure of alnuserrudiolone, a new C_{31}-dammarane-type triterpene isolated from the male flowers of *Alnus serrulatoides* Call. (Betulaceae), has been elucidated to be (20*S*)-12β,20-dihydroxy-24-methylene-dammaran-3-one (I) by a combination of chemical and spectroscopic methods.

In connection with the biochemical studies on the plants of Betulaceae, we investigated the chemical constituents of the male flowers of *Alnus serrulatoides* Call. (Japanese name: Kawara-hannoki) and isolated a new C_{31}-dammarane-type triterpene, named as alnuserrudiolone (I), and here report evidence which led to the establishment of its structure.

Alnuserrudiolone (I) was isolated from the acetone extract of the male flowers (3.3 Kg) of the plants by column chromatography on silica gel with a mixture of *n*-hexane and ethyl acetate, as colorless needles (4.3 g), mp 174-175°, $[\alpha]_D^{25}$ +50.0°,

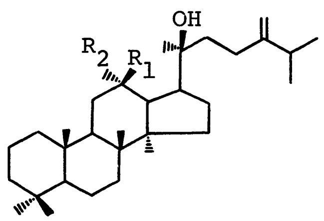


I



II: R_1=OH, R_2=CH_3

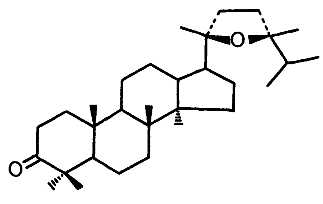
VI: R_1=CH_3, R_2=OH



III: R_1=OH, R_2=H

IV: R_1,R_2=O

V: R_1=H, R_2=OH



VII

(*c* 2.74, $CHCl_3$), $C_{31}H_{52}O_3$ [IR (0.005 M, CCl_4) 3610 (free OH), 3440 (intramolecularly hydrogen-bonded OH), 1710 (C=O), 3080, and 1640 cm^{-1} ($\gt C=CH_2$)].[1] The NMR spectrum in $CDCl_3$ indicated the presence of eight methyl groups (δ 0.90-1.10 ppm), a terminal methylene (2H, 4.74 ppm), and a hydrogen atom on the carbon bearing oxygen (1H, 3.60 ppm). Hydrogenation of I in the presence of platinum oxide yielded a dihydro-derivative (II), mp 156-157°, $[\alpha]_D^{25}$ +66.0° (*c* 0.38, $CHCl_3$), $C_{31}H_{54}O_3$ [IR (CCl_4) 3620, 3430, and 1705 cm^{-1}], which was characterized by the disappearance of the IR band and the NMR signal due to the terminal methylene. Huang-Minlon reduction of I gave a dihydroxy-compound (III), mp 167-168°, $[\alpha]_D^{25}$ +26.5° (*c* 0.77, $CHCl_3$), $C_{31}H_{54}O_2$ [IR (CCl_4) 3620 and 3430 cm^{-1}], which could be derived to a keto-alcohol (IV), mp 200-202°, $[\alpha]_D^{25}$ +56.4° (*c* 0.65, $CHCl_3$), $C_{31}H_{52}O_2$ [IR (CCl_4) 3610, 3450, 1705, and 1690 cm^{-1}] by Jones' oxidation. These facts demonstrate that the three oxygen atoms of I are involved in a carbonyl, a secondary hydroxyl, and a tertiary hydroxyl groups.

The ORD curve patterns of I and IV were quite similar to those of the previously documented 3-keto- and 12-keto-dammarane-type triterpenes[2-5] (Fig. 1). This similarity demonstrates that I possesses a 12-hydroxy-3-keto-dammarane-type skeleton. The fragments arising from the cleavages (a) and (b) in the mass spectrum of I (Fig. 2) indicate that the tertiary hydroxyl group is attached to C-20 and the terminal methylene is located in the side chain.[6] The presence of the tertiary hydroxyl group at C-20 was established by verifying the intramolecular hydrogen bonding between the tertiary hydroxyl and the C-12-hydroxyl groups in I. The mass spectrum of I exhibited resemblance to that of II except the m/e 436, m/e 421, and m/e 393 peaks generated by the elimination of two molecules of water from the molecular ion and by the further loss of a methyl and an isopropyl radical of the side chain from the dehydrated species. These peaks occurred at two mass units lower than the corresponding peaks of II.[6] These data suggest that the terminal methylene is situated at C-24. This is supported by the fact that in all the naturally occurring C_{31}-dammarane-type triterpenes described previously,[5,7] the 31st carbon is located at the C-24 carbon atom.

Reduction of the 12-keto-alcohol (IV) with lithium aluminum hydride gave exclusively a diol (V), which is an epimer of III with respect to C-12. Since it has already been established that the reduction of 12-keto-dammarane-type triterpenes yields the 12α-isomer stereospecifically,[3] the configuration of the 12-hydroxyl group of III should be β. Consequently, the C-12-hydroxyl group of I should also possess the β-configuration. It has been reported earlier that the C-20-hydroxyl group of the dammarane-type triterpenes, having a β-hydroxyl group at C-12, undergoes facile acid-catalyzed epimerization to yield an equilibrated mixture of 20*R*- and 20*S*-epimers with the predominance of the former.[8] Similar treatment of an aqueous ethanolic solution of the dihydro-derivative (II) with sulfuric acid afforded an equilibrated mixture of II and its epimer (VI) with the latter as the major product. Thus the chirality of C-20 in I appears to be *S*. This was evidenced by the observation that the IR spectrum of the 12-keto-alcohol (IV) exhibited both the free hydroxyl and the intramolecularly hydrogen-bonded hydroxyl bands (Fig. 3), which were in complete agreement with the previous IR spectral description[4] on hydroxyl bands of (20*S*)-3β-acetoxy-20-hydroxydammaran-12-one. In this connection, it is interesting to note

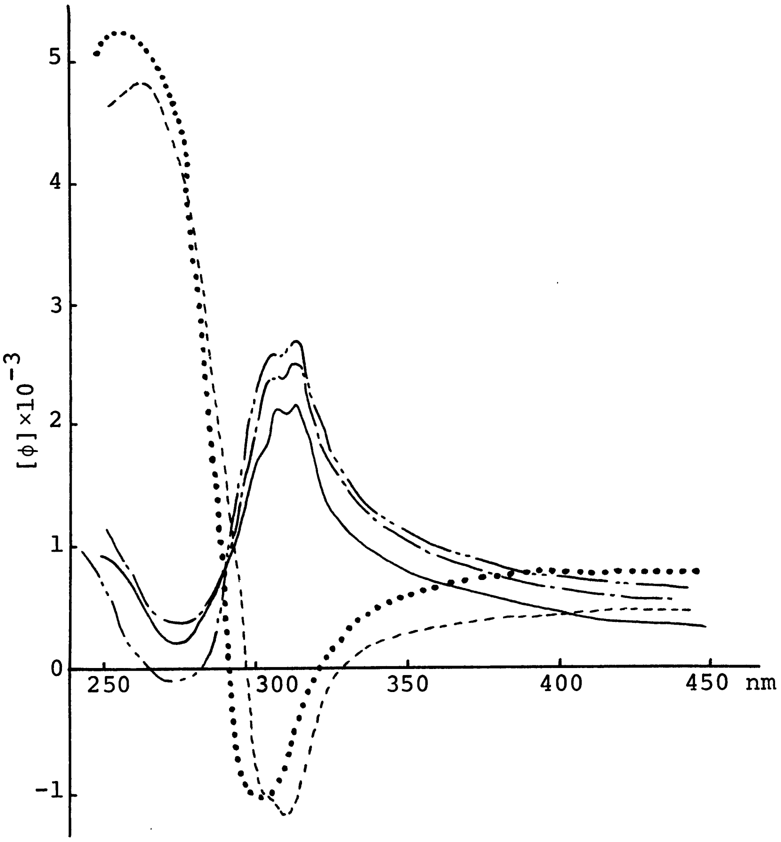


Fig. 1. ORD curves of 3-keto- and 12-keto-dammarane-type triterpenes (in dioxane, except (20*R*)-3β-acetoxy-20-hydroxydammaran-12-one which is in MeOH): ———, alnuserrudiolone (I); ————-——, alnincanone (VII); ——-·——, dipterocarpol;[2] -----, 12-keto-alcohol (IV); •••••, (20*R*)-3β-acetoxy-20-hydroxydammaran-12-one.[3,4]

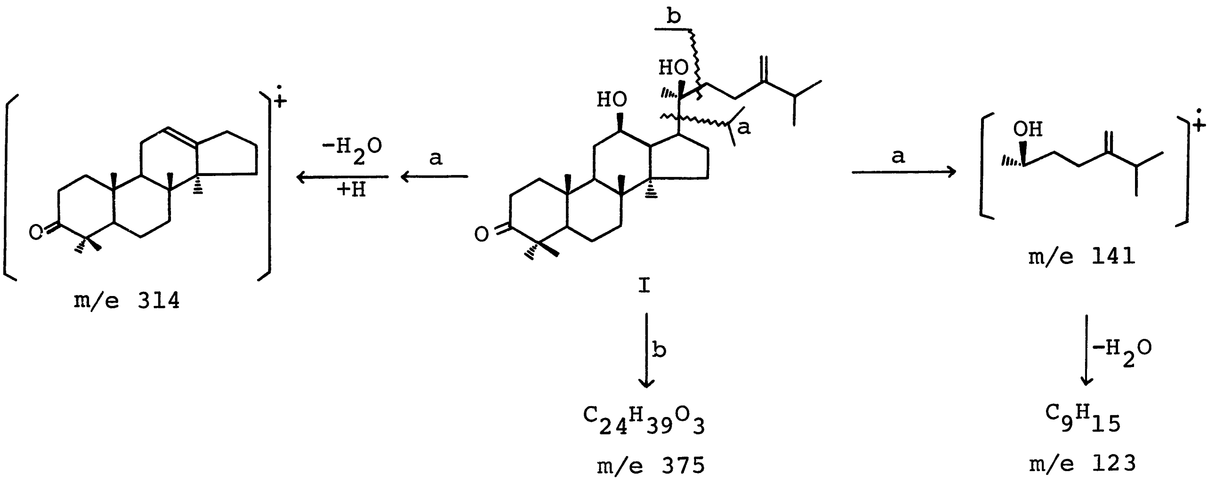


Fig. 2. Mass spectral fragmentation patterns of I.

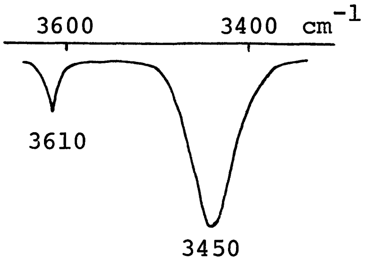


Fig. 3. IR spectrum of IV in CCl_4 (0.003 M).

that the chirality in all the C-20 oxygenated dammarane-type triterpenes occurring in the Betulaceae is *S*.[5,9,10]

Thus the structure of alnuserrudiolone has been elucidated to be (20*S*)-12β,20-dihydroxy-24-methylene-dammaran-3-one (I). Along with this dihydroxyketone (I), alnincanone (VII), a recently established triterpene,[5] has also been identified. Biogenetically, it is fascinating to note that the compound (VII) having a tetrahydrofuran ring probably might have originated by the cyclization of the side chain of I.

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References and Footnotes

1) Elemental analyses of all compounds described here were satisfactory.
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