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STRUCTURE OF ALNUSERIC ACID, THE FIRST REPORTED NATURALLY OCCURRING C_{31}-SECODAMMARANE-TYPE TRITERPENE FROM *ALNUS SERRULATOIDES* CALL.

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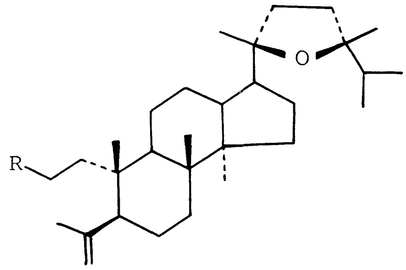
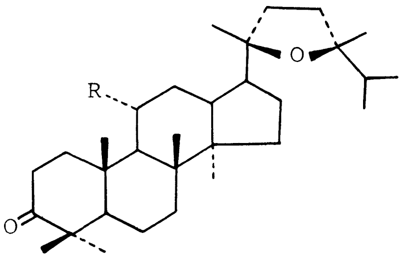
A novel C_{31}-3,4-secodammarane-type triterpene, alnuseric acid, was isolated from the male flowers of *Alnus serrulatoides* Call. (Betulaceae). Its structure was elucidated to be (20*S*,24*R*)-20,24-epoxy-24-methyl-3,4-secodammar-4(28)-en-3-oic acid (I) by a combination of chemical and spectroscopic methods.

In connection with the chemical and physiological studies of pollen,[1)] we have reported the triterpenoids and phytosterols of the male flowers of *Alnus serrulatoides* Call. (Japanese name: Kawara-hannoki).[2~4)] We now have isolated a new C_{31}-secodammarane-type triterpene, named alnuseric acid (I), from the male flowers. Naturally occurring triterpenes having a seco-form have been well documented,[5)] but as yet no C_{31}-seco-triterpene. We here report evidences which led to the establishment of its structure.

Column chromatography of the ether soluble fraction of the male flowers gave alnuseric acid (I) as colorless needles, mp 107~109°C, $[\alpha]_D^{25}$ +24.3° (*c* 0.21, MeOH),



I: R=COOH
IV: R=CN



II: R=H
III: R=OH

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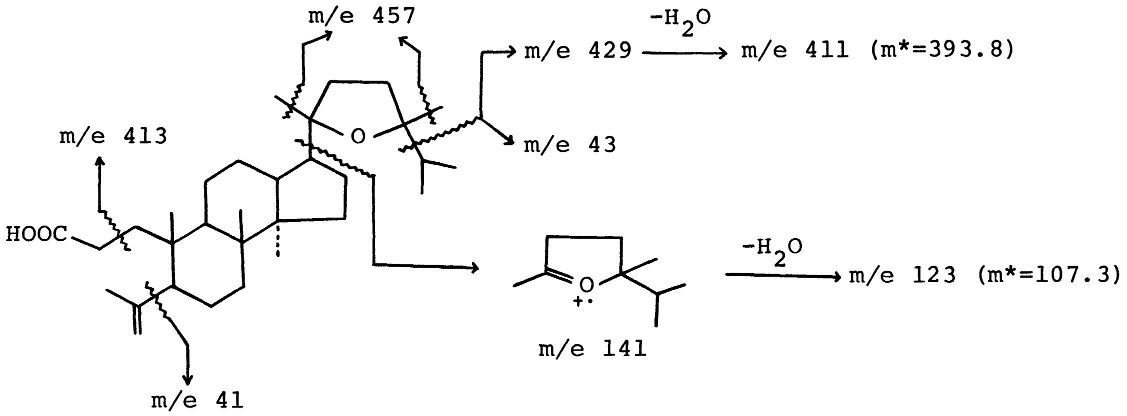
m/e 472 (M^+); $C_{31}H_{52}O_3$ (requires: C 78.76; H 11.09. found: C 79.06; H 11.01%). The IR spectrum showed absorption bands due to the end-methylene (ν_{max} (in Nujol) 3077, 1638 and 888 cm^{-1}) and the carboxyl groups (3300~2800 and 1708 cm^{-1}). The NMR and MS spectra demonstrated the presence of the isopropenyl group (δ_{ppm} (in $CDCl_3$) 1.75 (bs, 3H), 4.70 (bs, 1H) and 4.85 (bs, 1H); m/e 41). The ^{13}C-NMR spectrum in $CDCl_3$ also indicated the presence of the carboxyl (δ_{ppm} 180.2), the end-methylene (147.4 and 113.4) and the ether-ring carbons (85.8 and 85.3). The peaks at m/e 141 (base), 123 and 43 in the MS spectrum of alnuseric acid was quite similar to those in it of alnincanone (II), a naturally occurring dammarane-type triterpene with a tetrahydrofuran ring.[6,7] Ryabinin *et al.*[6] has proved the occurrence of such m/e 141, 123 and 43 peaks from the tetrahydrofuran ring of alnincanone (II). This has also been established in the MS spectra of alnuserol (III)[4] and various compounds[8,9] with a tetrahydrofuran ring. Therefore, the occurrence of these peaks in the MS spectrum of alnuseric acid (Scheme I) demonstrated that this acid possesses the side chain with a tetrahydrofuran ring similarly to II and III.



Scheme I. Mass spectral fragmentation pattern of alnuseric acid (I).

The other interesting feature of alnuseric acid is that it contains no carbonyl or hydroxyl group at C-3, though such functional groups appear almost without exception in plant triterpenoids. In addition, the molecular formula indicates that alnuseric acid has four rings whereas alnincanone (II) and alnuserol (III) have five rings. These structural features of alnuseric acid may result from the cleavage of a 3-keto-triterpenoid. To the alnuseric acid, we here propose a biogenetically acceptable structure (I)[5] probably derived from alnincanone or its derivatives by ring-opening at the 3,4-position. The proposed structure (I) possesses all the features necessary to explain the spectral data of alnuseric acid.

The structure (I) proposed for alnuseric acid was confirmed by its synthesis starting from alnincanone following the method established for ring-opening at the 3,4-position in the A ring of β-amyrenone.10) Alnincanone (II) was transformed to the corresponding ketoxime, which then was treated with *p*-toluenesulfonyl chloride in dry pyridine to yield the abnormal Beckmann rearrangement product (IV) with infrared bands (in Nujol) at 2240 (-C≡N) and 3075, 1632 and 899 cm^{-1} ($>C=CH_2$). The mild alkaline hydrolysis of the product (IV) gave (20*S*,24*R*)-20,24-epoxy-24-methyl-3,4-secodammar-4(28)-en-3-oic acid (mp 107~109°C; m/e 472 (M^+), 141 (base), 123, 43, 41; ν_{max} (in Nujol) 3300~2800, 3079, 1710, 1638, 890 cm^{-1}; δ_{ppm} (in $CDCl_3$) 1.75, 4.70, 4.85). Identity of naturally occurring alnuseric acid with this authentic acid was established by comparison of mixed mp, TLC, IR, NMR, and MS.

Thus, the structure of alnuseric acid (I) has been elucidated to be (20*S*,24*R*)-20,24-epoxy-24-methyl-3,4-secodammar-4(28)-en-3-oic acid. To our knowledge, the acid I is the first reported naturally occurring C_{31}-3,4-secodammarane-type triterpene. Along with the acid I, alnincanone (II) has also been found in the male flowers of *Alnus serrulatoides*. It is fascinating to note that II might be an intermediate for the biosynthesis of the new seco-triterpene I.

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