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A New Triterpenoid Alcohol, 24-Methylenecycloartanol, as its Ferulate, from Rice Bran Oil

Recent reports[1] from this laboratory described the isolation of three phenolic substances, oryzanol-A, -B, and -C, from rice bran oil and the structure of oryzanol-A was determined as cycloartenyl ferulate. The structure of oryzanol-C has now been elucidated as 24-methylenecycloartanyl ferulate by the following experiments.

From the most insoluble fraction of oryzanol acetate mixtures, oryzanol-C acetate, m.p. 216~218°, $[\alpha]_D$ +39°[2] (*Anal.* Calcd. for $C_{43}H_{62}O_5$: C, 78.38; H, 9.48. Found : C, 78.18; H, 9.20), was obtained and deacetylated under weakly alkaline conditions to oryzanol-C, m.p. 162~164/193~194°, $[\alpha]_D$ +36°. U.V. : λ_{max}^{EtOH} 322 mμ (log ε 4.29) (*Anal.* Calcd. for $C_{41}H_{60}O_4$: C, 79.82; H, 9.80. Found : C, 79.59; H, 10.07). Drastic saponification of oryzanol-C gave ferulic acid and a new triterpenoid alcohol (I), m.p. 121~122°, $[\alpha]_D$ +43° (*Anal.* Calcd. for $C_{31}H_{52}O$: C, 84.48; H, 11.89. Found : C, 84.30; H, 11.66), characterised as its acetate (II), m.p. 116~117°, $[\alpha]_D$ +54° (*Anal.* Calcd. for $C_{33}H_{54}O_2$: C, 82.09; H, 11.27. Found : C, 82.48; 11.06), and its benzoate, m.p. 156~157°, $[\alpha]_D$ +62° (*Anal.* Calcd. for $C_{38}H_{56}O_2$: C, 83.77; H, 10.36. Found : C, 83.79; H, 10.49). Oppenauer oxidation of (I) afforded a ketone, m.p. 111~112°, $[\alpha]_D$ +20° (*Anal.* Calcd. for $C_{31}H_{50}O$: C, 84.86; H, 11.49. Found : C, 84.40; H, 11.66); oxime, m.p. 189~190°. (I) contains one double bond which was determined by oxidation of (II) with perbenzoic acid, and catalytic hydrogenation of (I) with platinum catalyst gave a dihydric alcohol, m.p. 135.5~136.5°, $[\alpha]_D$ +46.5°; acetate, m.p. 123~124°, $[\alpha]_D$ +54.5° (*Anal.* Calcd. for $C_{33}H_{56}O_2$: C, 81.75; H, 11.64. Found : C, 81.60; H, 11.64).

The infrared spectrum of (I) exhibits absorptions at 1045, 1020, 1005, and 988 cm^{-1} (in CS_2), and the acetate (II) at 1242, 1039, 1022, and 978 cm^{-1} (in CS_2), which can be interpreted as indicatiag the presence of cycloartane-type ring system.[3] Absorptions at 1639 and 887 cm^{-1} in the spectrum of (I) or (II) also suggest the presence of a vinylidene group, and the fact was confirmed by the formation of formaldehyde on ozonolysis of (II). The other product obtained by ozonolysis is an acetoxy-demethyl-oxo compound (III), m.p. 121~123°, $[\alpha]_D$ +52°; I.R. $\nu_{C=O}$ 1710 cm^{-1} (Nujol) (*Anal.* Calcd. for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81. Found : C, 79.17; H, 10.63); oxime, m.p. 192~194°, $[\alpha]$, +50°. (III) was not isomerised on treating with alkali, apart from hydrolysis of the acetoxyl group, and the fact, contrary to the case of oxonorcyclolaudanyl acetate,[4] shows the absence of

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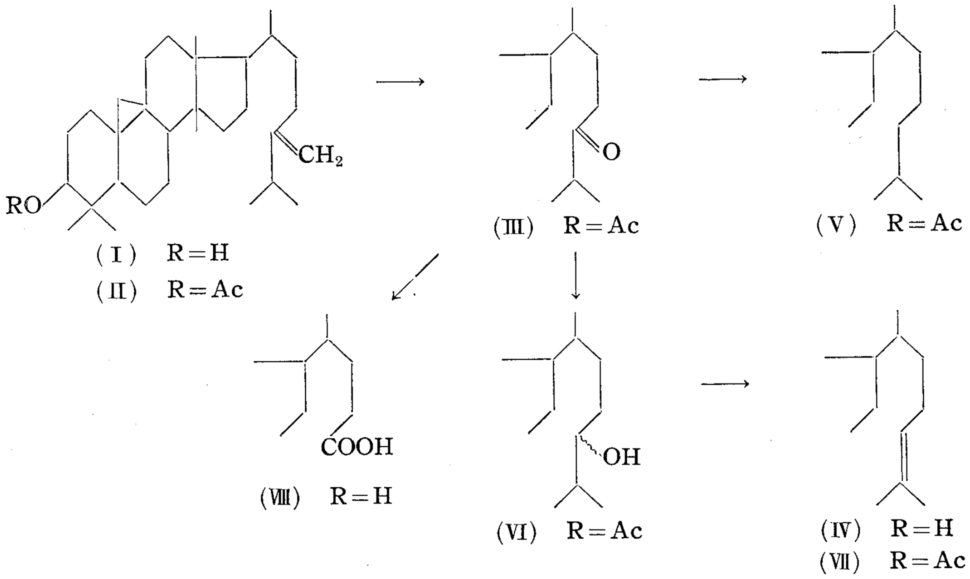
[1] M. Shimizu, *et al.* : This Bulletin, **5**, 36, 40(1957).
[2] Optical rotations were taken in $CHCl_3$ unless otherwise stated.
[3] cf. I.L. Allsop, *et al.* : J. Chem. Soc., **1956**, 4868.
[4] cf. J.A. Henry, *et al.* : *Ibid.*, **1955**, 1607.



asymmetric carbon atom adjacent to the carbonyl group. (III) was related to cycloartenol (IV) by the following reactions.

Wolff-Kishner reduction of (III), followed by acetylation, gave an acetoxy-demethyl compound, m.p. 132~133°, $[\alpha]_D$ +59° (*Anal.* Calcd. for $C_{32}H_{54}O_2$: C, 81.64; H, 11.56. Found: C, 81.82; H, 11.51), identical with cycloartanyl acetate (V). (III) was reduced with sodium borohydride to the corresponding alcohol (VI), m.p. 128~132°, $[\alpha]_D$ +27° (*Anal.* Calcd. for $C_{32}H_{54}O_3$: C, 78.96; H, 11.18. Found : C, 78.64; H, 10.87), which was treated with phosphoryl chloride in pyridine solution to give a halogenated compound and a dehydrated one. The latter, m.p. 121~123°, $[\alpha]_D$ +55° (*Anal.* Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18. Found : C, 81.97; H, 10.86), was found to be identical with cycloartenyl acetate (VII). Bayer-Villiger oxidation of (III) with 5% peracetic acid, followed by hydrolysis, gave a hydroxy acid (VIII), m.p. 220~222°, $[\alpha]_D$ +49° (in pyridine) (*Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.83; H, 10.65. Found : C, 77.91; H, 10.61); methyl ester, m.p. 131~132°, $[\alpha]_D$ +41°; methyl ester acetate, m.p. 121.5~122.5°, $[\alpha]_D$ +54°. (VIII) was proved to be identical with 3β-hydroxy-25,26,27-trisnorcycloart-24-oic acid derived from cycloartenyl acetate (VII) by standard methods. In these experiments identity was confirmed by mixed fusion and comparison of infrared spectra, and the structure of (I) was established as 24-methylenecycloartanol.

Detailed reports will be published in the near future.

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