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O-METHYL PERTYOL, A C_{33} TRITERPENE METHYL ETHER

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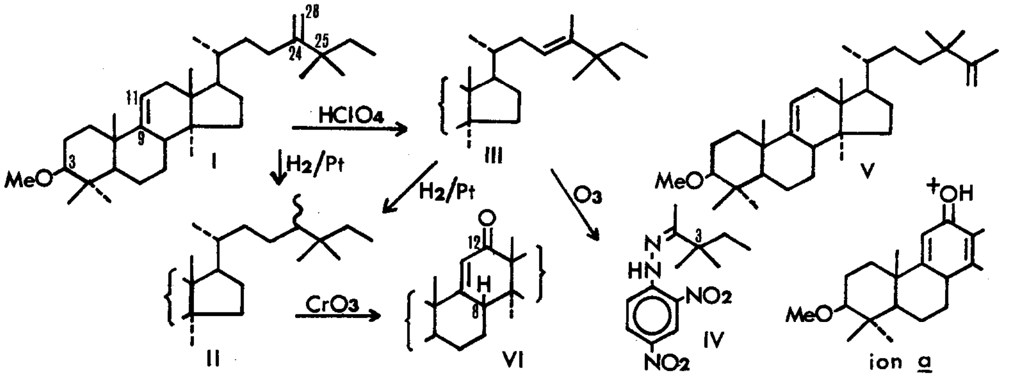
From the roots of *Pertya robusta* (Maxim.) Beauverd (*Macroclinidium robustum* Maxim.) (Compositae), there has been isolated a new triterpene methyl ether (I), designated as O-methyl pertyol, $C_{34}H_{58}O$, mp. 223-223.5°, $[\alpha]_D^{15}$ +101° (c=1.1, $CHCl_3$). Anal.Calcd. : C, 84.58; H,12.11. Found :C,84.64; H,11.91. Liebermann-Burchard color reaction : + (purple).

In the NMR spectrum**, O-methyl pertyol (I) shows signals at δ 0.66, 0.76, 0.81, 0.97, 1.06 (3H each,s), 1.02 (6H,s), 2.70 (1H,br,CH-O-CH_3)[1], 3.39 (3H,s,CH-O-CH_3), 4.79 (2H,br.s,C=CH_2), and 5.24 (1H,m,C=CH). Its IR spectrum** is also indicative of the presence of an ether linkage (ν_{max} 1100 cm^{-1}), a vinylidene group (ν_{max} 3090, 1625, 880 cm^{-1}), and a trisubstituted double bond (ν_{max} 3040, 855, 810 cm^{-1}) in the molecule. On catalytic hydrogenation I afforded a dihydro-derivative (II), $C_{34}H_{60}O$, mp. 207.5-209°, $[\alpha]_D^{19}$ +99.4° (c=1.1, $CHCl_3$), in which the trisubstituted double bond of I still remains.

On treatment with perchloric acid O-methyl pertyol (I) was isomerized to III, $C_{34}H_{58}O$, mp. 214-215°, $[\alpha]_D^{15}$ +87.5° (c=1.8, $CHCl_3$). The NMR spectrum of III suggested that the vinylidene group of I disappeared in III, and that another trisubstituted double bond (δ 5.17 (2H,m))[2] and a methyl group attached on a double bond carbon (δ 1.55 (3H,s)) were newly formed in III. On catalytic hydrogenation, III afforded a dihydro-derivative, mp. 208-209°, $[\alpha]_D^{15}$ +93.7° (c=1.1, $CHCl_3$), which was found to be identical with the dihydro-derivative (II) obtained directly from O-methyl pertyol (I), by mixed mp., TLC, GLC, IR, NMR, and mass spectrometry. After ozonolysis of III and reductive degradation of the resulted ozonide followed by steam distillation, 3,3-dimethyl-pentan-2-one was obtained as its 2,4-dinitrophenyl hydrazone (IV), mp. 114.5° (lit.[3], 112°). The NMR and mass spectral data of IV supported its structure.

The mass spectrum of I in direct comparison with that of 3β-methoxy-24,24-dimethyl-lanosta-9(11),25-diene (V)[4][5] suggested that I is a lanost-9(11)-ene with a novel side chain ; peaks at 482 (M^+), 467 (M^+-CH_3), and 435 (M^+-CH_3-CH_3OH) were observed at 14 (CH_2) higher mass numbers than the corresponding peaks of V ; peak at m/e 327 represents M^+-$C_{11}H_{21}$ (side chain)-2H[4][6] ; I is in accord with V in showing prominent peaks at m/e 287, 273, 261, 255, and 241, which are ascribable to fragment ions formed from the nucleus of lanost-9(11)-ene derivatives.[1][5][7] In order to confirm the lanost-9(11)-ene structure of I, the dihydro-derivative (II) was oxidized with chromic acid[8], affording an α,β-unsaturated ketone (VI), $C_{34}H_{58}O_2$, mp. 185-186°, $[\alpha]_D^{28}$ +58.1° (c=0.85, $CHCl_3$), IR ν_{max} 1670, 1590 cm^{-1}, UV λ_{max}^{EtOH} 242 nm (ε=10700)[1][7][9][10][11], mass spectrum m/e 498 (



CHART

M$^+$), 483, 451, 303 (ion a in CHART), 271, 175, 135.[12)] VI showed a one proton-doublet (J=2 Hz) at δ 5.60 in its NMR spectrum which is ascribable to C-11-H coupled with the allylic hydrogen located axially in C-8[1)7)13)], and exihibited a negative Cotton effect ($[\theta]$ -1.53×10^{4}) at 331 nm for $n-\pi^*$ transition and a positive one ($[\theta]$ $+5.52\times10^{4}$) at 243 nm for $\pi-\pi^*$ in its Circular Dichroism curve in EtOH.[1)14)15)]

From these findings and the biosynthetic hypothesis of triterpenoid[16)], 3β-methoxy-24-methyl-25-ethyl-lanosta-9(11),24(28)-diene (I in CHART) is proposed for the structure of O-methyl pertyol (I), the first C_{33} triterpene methyl ether to be reported.

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REFERENCES AND NOTES

**) NMR spectra (solvent : $CDCl_3$) were recorded on Hitachi R-20 (60 MHz) using tetramethylsilane as internal standard, and expressed in δ-value (ppm) from TMS. IR spectra were measured on KBr tablets.

1) The coupling pattern of the proton indicates that the methoxy group is β-oriented and equatorial. cf) a) S.Uyeo, J.Okada, S.Matsunaga, J.W.Rowe, Tetrahedron, 24, 2859 (1968) b) J.P.Kutney, N.D.Westcott, F.H.Allen, N.W.Isaacs, O.Kennard, W.D.S. Motherwell, Tetrahedron letters, 1971, 3463 c) H.Irie et al, Ibid., 1971, 3467

2) Signals ascribable to C-11-H and to C-23-H overlap each other in this region.

3) F.C.Whitmore, C.E.Lewis, J.Am.Chem.Soc., 64, 2964 (1942)

4) E.Ritchie, R.G.Senior, W.C.Taylor, Aust.J.Chem., 22, 2371 (1969)

5) W.H.Hui, K.Luk, H.R.Arthur, S.N.Loo, J.Chem.Soc.(C), 1971, 2826

6) S.G.Wyllie, C.Djerassi, J.Org.Chem., 33, 305 (1968)

7) H.Vorbrüggen, S.C.Pakrashi, C.Djerassi, Ann., 668, 57 (1963)

8) D.S.Irvine, J.A.Henry, F.S.Spring, J.Chem.Soc., 1955, 1316

9) H.R.Bentley, J.A.Henry, D.S.Irvine, F.S.Spring, J.Chem.Soc., 1953, 3673

10) S.K.Kundu, A.Chatterjee, Tetrahedron letters, 1966, 1043

11) Yong-Yeng Lin, H.Kakisawa, Y.Shiobara, K.Nakanishi, Chem.Pharm.Bull., 13, 986 (1965)

12) C.Djerassi, L.Tökés, J.Am.Chem.Soc., 88, 536 (1966)

13) T.A.Wittstruck, S.K.Malhotra, H.J.Ringold, J.Am.Chem.Soc., 85, 1699 (1963)

14) G.Snatzke, Tetrahedron, 21, 413 (1965)

15) C.Djerassi, R.Records, E.Bunnenberg, K.Mislow, A.Moscowitz, J.Am.Chem.Soc., 84, 870 (1962)

16) L.Ruzicka, Proc.Chem.Soc., 1959, 341