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THE OCCURRENCE OF (-)PIMARANE-TYPE DITERPENE IN ARALIA CORDATA THUNB.

Shoji Shibata, Susumu Mihashi* and Osamu Tanaka
Faculty of Pharmaceutical Sciences, University of Tokyo, Japan.

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During a series of investigation of the oriental plant drugs, we isolated a new diterpenic acid (I) from the ethereal extracts of the roots of Aralia cordata Thunb. (Japanese name: Udo), one of the original plants of Chinese drug "Duhuo" (独活) (1). The diterpenic acid (I), $C_{20}H_{30}O_2$, colourless needles (from hexane), m.p. 163-164°, $[\alpha]_D^{16}$ - 120.6° ($CHCl_3$), afforded a methyl ester (II), $C_{21}H_{32}O_2$, m.p. 63-64.5°. The U.V. spectrum (in EtOH) of I, giving only an end absorption, revealed the absence of conjugated system. The I.R. spectrum (in CCl_4) of I showed absorption bands at 1695 cm^{-1} (carboxyl), 998, 917 cm^{-1} (monosubstituted double bond), 865 and 850 cm^{-1} (trisubstituted double bond). The N.M.R. spectrum (in $CDCl_3$) of I showed the presence of three tertiary methyls (τ 9.34, 9.00 and 8.73), one olefinic proton on a trisubstituted double bond (τ 4.85 (broad singlet)), and three olefinic protons on a monosubstituted double bond (τ 4.0-5.3 (ABC type coupling)), whose coupling pattern is quite similar to that of methyl (+)-pimarate (III) (2).

Reduction of the methyl ester (II) with $LiAlH_4$ yielded an alcoholic compound (IV), $C_{20}H_{32}O$, m.p. 109-110°. Tosylation of IV followed by reduction with $LiAlH_4$ gave an oily hydrocarbon (V), $[\alpha]_D^{20}$ - 115.5° ($CHCl_3$). Comparison of I.R. and N.M.R. spectra, thin layer and gas-liquid chromatograms, specific rotation, and O.R.D. curve of V with those of (+)pimara-8(14),15-diene (VI) (3) led to assign this hydrocarbon (V) as (-)pimara-8(14),15-diene (4).

The position of the carboxyl group of I has been established by the comparison of the methyl signals of N.M.R. spectrum of the original acid (I) in pyridine with those of its methyl ester (II). (see Table I)

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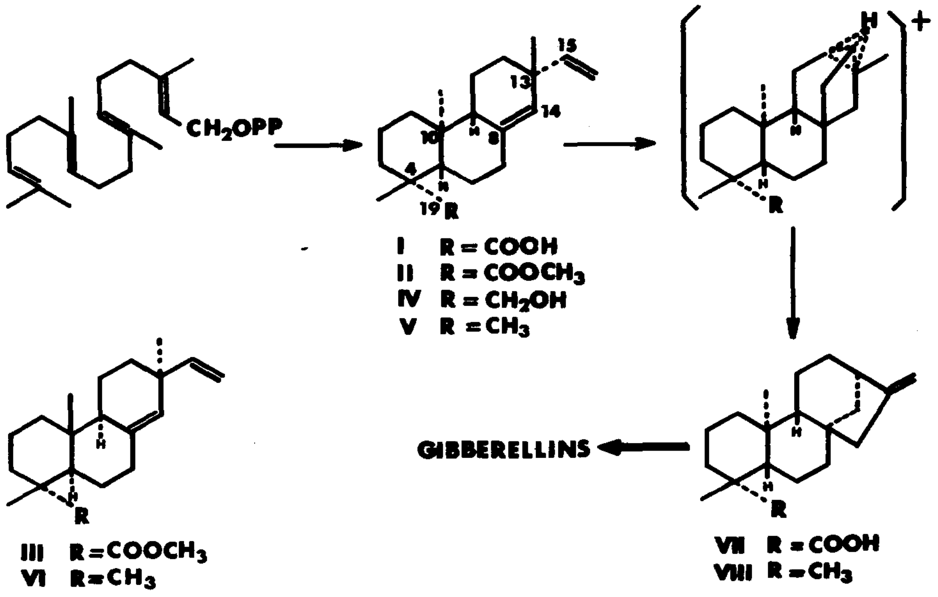
*Present address: Tokyo College of Pharmacy, Kashiwagi, Shinjuku-ku, Tokyo.

Table I

Methyl signals	Chemical shifts(cps) from TMS at 60 Mc.		Difference
	Compd. I	II	
a	54.0	40.0	+ 14.0
b	62.0	62.5	- 0.5
c	82.0	72.5	+ 9.5

Referring the report of Narayanan et al. (5), the signal a can be assigned to the methyl group which is located in a 1,3-cis diaxial disposition with the carboxyl or the carbomethoxyl group. The signal c can be assigned to the methyl group attached to the carbon atom bearing the carboxyl or carbomethoxyl group. The axial conformation of the carboxyl group of I is also demonstrated by the I.R. spectrum (KBr) of its methyl ester (II) (C-O bands at 1232 (strong), 1193, 1186 (weak), 1158 cm^{-1}(strong)) (6), and by the C$\underline{H}_2$OH signals of N.M.R. spectrum (in CDCl$_3$) of the corresponding alcohol (IV) (τ 6.13 and 6.58 doublets, J= 11.5 cps) (7). These evidences led to a conclusion that the carboxyl group of I must be present at C-4α (axial) of (-)pimara-8(14),15-diene (V), and the N.M.R. signals a, b and c should correspond to the methyl at C-10, C-13, and C-4β (equatorial), respectively.



Consequently, the diterpenic acid (I) can be formulated as (-)pimara-8(14), 15-dien-19-oic acid.

The co-occurrence of kau-16-en-19-oic acid (VII or its antipode) (8) in the root of this plant has been shown by the gas-liquid chromatography of its methyl ester. The isolation of I in a fairly good yield (0.2%) from *Aralia cordata* would be noticeable, since I or its homologues would be a significant precursor of the biosynthesis of (-)kaurene (VIII) derivatives and gibberellins. (9,10)

The methylated crude ethereal extracts of the roots of *Aralia racemosa* L. which is being used as a western folk medicine has been found to give the same pattern of gas-liquid and thin layer chromatograms with that of given by *Aralia cordata* Thunb., indicating the presence of I and VI (or its antipode).

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References

1. J. Sato:On the Chinese Medical Plants (Japan Society for Promotion of Sciences. 1959) pp.332.
2. E. Wenkert and P.Beak, *J. Am. Chem. Soc.*. **83**, 998 (1961); E. Wenkert, A. Afonso, P. Beak, R.W.J. Carney, P.W. Jeffs and J.D. McChesney, *J.Org. Chem.*, **30** 713 (1965).
3. E. Ireland and W. Scheirs, *J. Org. Chem.*, **28**, 6 (1963).
4. A.H. Kapadi, R.R. Sobti and Sukh Dev, *Tetrahedron Letters*, 2729 (1965).
5. C.R. Narayanan and N.K. Venkatasubramanian, *Tetrahedron Letters*, 3639 (1965).
6. S. Bory and M. Fétizon, *Bull.soc.chim.Fr.*, **1964**, 750.
7. A. Gaudemer, J. Polonsky and E. Wenkert, *Bull.soc.chim.Fr.*, **1964**, 407.
8. C.A. Henrick and P.R. Jefferies, *Aust. J.Chem.* , **17**, 915 (1964).
9. E. Wenkert, *Chem. and Ind.*, **1955**, 282.
10. B.E. Cross, R.H.B. Galt and J.R. Hanson, *J. Chem. Soc.*, **1964**, 295; J.E. Graebe, D.T. Dennis, C.D. Upper and C.A. West, *J. Biol. Chem.*, **240**, 1847 (1965); T.A. Geissman, A.J. Verbicar, B.O. Phinney and G. Cragg, *Phytochem.*, **5**, 933 (1966). A.J. Verbiscar, G. Cragg, T.A. Geissman and B.O. Phinney, *Phytochem.*, **6**, 807 (1967). C.D.Upper, C.A.West, *J.Biol.Chem.*, **242**, 3285 (1967). D.T.Dennis, C.A.West, *Ibid.*, **242**, 3292 (1967).