

FURTHER STUDY ON THE DITERPENES OF ARALIA SPP.

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Previously, the occurrence of (-)kaur-16-en-19-oic acid(I)¹⁾ and a new diterpenic acid, (-)pimara-8(14),15-dien-19-oic acid(II) in the roots of Aralia cordata(Japanese name: Udo) and A. racemosa was reported²⁾. The present paper deals with the further study on the related diterpenes of Aralia spp. It has been found that the stems and the leaves of the above plants also contain I and II. From the acidic fraction of the ether-extract of the roots of A. cordata, the following compounds have now been obtained as minor constituents³⁾: Acid A C₂₀H₃₂O₄, mp 260-262°; /α/D -85.0°(pyridine), IR ν_{max}^{KBr} 3365 and 1696cm⁻¹. Acid B C₂₀H₃₀O₃, mp 292-294°(decomp), /α/D -70.4°(pyridine, IR ν_{max}^{KBr} 3360 and 1697cm⁻¹. Acid C C₂₀H₂₈O₃, mp 241-245°; /α/D -54.2°(pyridine), IR ν_{max}^{KBr} 1717, 1699, and 1667cm⁻¹. Acid D C₂₀H₃₀O₃, mp 218°; /α/D -62.8°(pyridine), IR ν_{max}^{KBr} 3480 and 1680cm⁻¹.

Acid A was proved to be identical with 16,17-dihydroxy-16β-(-)kauran-19-oic acid(III), which was already isolated from Beyeria spp⁴⁾.

Acid B(IV) afforded an oily methyl ester(V), /α/D -64.5°(CHCl₃), IR ν_{max}^{CCl₄} 3625 and 1730cm⁻¹. As shown in Table I, the NMR spectra of IV and V indicated the presence of a trisubstituted double bond and a vinyl group. In the NMR spectra determined for CDCl₃ solution as well as for pyridine-d₅ solution, three tertiary methyl signals of IV and V appeared at the almost same positions as those of II and its methyl ester(VI), respectively²⁾. These results and the co-occurrence of II in the same plant led to suggest that acid B(IV) would be an analogue of II

Table I. The NMR Chemical Shifts(ppm from TMS at 100MHz)[†]

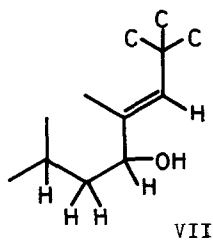
Compound	Solvent	20-Me	18-Me	17-Me	14-H($\frac{h}{2}$)	15-H and 16-H ₂ ($J_{trans}, J_{cis}, J_{gem.}$)	0-Me	7-H
II	C ₅ D ₅ N*	0.98	1.37	1.03	5.27br,s(4.5)	5.82sext 4.83-5.11quint**	----	----
	CDCl ₃	0.66	1.27	1.00	5.16br,s(4.5)	5.72sext 4.81-5.00quint**	----	----
VI	C ₅ D ₅ N*	0.67	1.22	1.04	5.24br,s(4.5)	5.82sext 4.83-5.13quint**	3.62	----
	CDCl ₃	0.57	1.21	1.01	5.14br,s(4.5)	5.72sext 4.80-4.98quint**	3.63	----
Acid B(IV)	C ₅ D ₅ N	0.97	1.40	1.10	6.22br,s(4.5)	5.83q 5.03q,4.95q(17.5, 10.5, 2.0)	----	4.34oct(11.5, 6.0, 1.5)
V	C ₅ D ₅ N	0.71	1.21	1.08	6.15br,s(5.0)	5.82q 4.99q,4.97q(17.5, 10.0, 3.0)	3.51	4.23oct(12.0, 5.0, 2.5)
	CDCl ₃	0.54	1.21	1.05	5.57br,s(***)	5.72q 4.89q,4.93q(17.5, 11.0, 2.0)	3.62	3.92oct(12.0, 6.5, 2.0)
Acid C(IX)	C ₅ D ₅ N	0.94	1.31	1.08	6.76br,s(4.5)	5.71q 4.79q,4.98q(17.0, 10.5, 2.0)	----	----
VIII	C ₅ D ₅ N	0.72	1.16	1.09	6.22br,s(5.0)	5.71q 4.80q,5.02q(17.0, 10.0, 2.0)	3.58	----
	CDCl ₃	0.70	1.21	1.14	6.60br,s(5.5)	5.71q 4.77q,5.00q(17.5, 10.5, 2.0)	3.66	($\frac{h}{2}$)
Acid D(XII)	C ₅ D ₅ N	0.96	1.46	0.98	5.51br,s(4.0)	5.77sext 4.84-5.03quint**	----	4.57br,s(5.5)
XI	C ₅ D ₅ N	0.68	1.27	0.95	5.42br,s(5.0)	5.72q 4.90q,4.98q(17.0, 10.5, 2.0)	3.58	4.41br,s(6.5)
	CDCl ₃	0.55	1.22	1.06	5.44br,s(4.5)	5.74q 4.86q,4.97q(17.0, 11.0, 2.0)	3.53	4.28br,s(6.0)
X	C ₅ D ₅ N	0.88	1.26	0.99	5.32br,s(5.5)	5.77q 5.03q,5.01q(17.5, 10.0, 2.0)	3.63	----
	CDCl ₃	0.67	1.22	1.04	5.27br,s(4.5)	5.68sext 4.79-4.98quint**	3.63	----

[†] Abbreviation: s=singlet, q=quartet, quint=quintet, sext=sextet, oct=octet, br=broad. Coupling constants and half widths expressed in Hz are listed in parentheses.

* These spectra were measured by a 60MHz spectrometer.

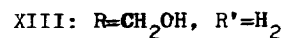
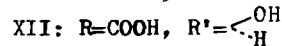
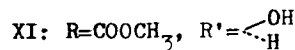
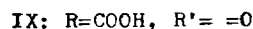
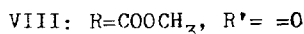
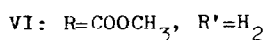
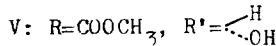
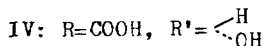
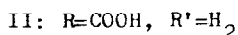
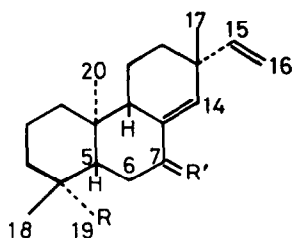
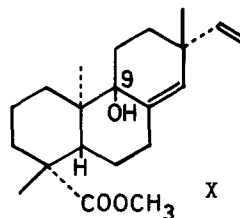
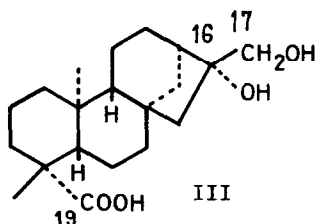
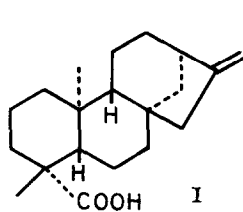
** ABC type splitting(R. M. Carman, *Aust. J. Chem.*, **16**, 1104(1963)).

*** The accurate value of the half width can not be obtained because of overlapping with 15-H signal.



having one hydroxyl group on its ring system.

The presence of the partial structure(VII) in IV was inferred from the following evidences. The NMR spectra of IV and V(Table I) indicated the presence of a secondary hydroxyl group. Allylic coupling between the trisubstituted olefinic proton and the carbinyll proton was secured by double irradiation experiment. The equatorial orientation of the secondary hydroxyl group was defined by the coupling shape of the carbinyll proton signal. On oxidation with MnO_2 in benzene, V gave an α,β -unsaturated ketone(VIII), mp 96-99°; $[\alpha]_D^{25} -75.0^\circ (CHCl_3)$, UV $\lambda_{max}^{EtOH} 249m\mu (\epsilon 8,200)$, IR $\nu_{max}^{CCl_4} 1733$ and $1688cm^{-1}$, NMR in $CDCl_3$; a pair of ABX type quartets at $\delta 3.13$ (1H, $J_{AX}=13.0Hz$, $J_{AB}=19.0$ Hz) and $\delta 2.79ppm$ (1H, $J_{BX}=5.5$ Hz, $J_{AB}=19.0$ Hz) (H^1-CH_2-CO-) and a broad singlet at $\delta 6.60ppm$ (1H) ($-CO-C=CH-$). It has been found that this ketone(VIII) is identical with the methyl ester derived from acid C(IX). Accordingly, it follows that acid B(IV) and acid C(IX) would be represented by 7 α -hydroxy-(-)-pimara-8(14),15-dien-19-oic acid and its 7-keto derivative, respectively. This formulation is also supported by the downfield shift of the trisubstituted olefinic proton signal of IV in comparison with that of II(Table I), since the equatorial hydroxyl



group at C-7 lies on the same plain as that of the 8(14)-double bond and is expected to have the deshielding effect on the signal of the proton at C-14.

The structures of acid B(IV) and acid C(IX) including the stereochemistry were finally established by their chemical correlations with II. Oxidation of VI with SeO_2 in ethanol at room temperature gave two hydroxylated products, mp 114.5-115.5°(X), $[\alpha]_D -135.3^\circ(\text{CHCl}_3)$ and mp 181-182°(XI), $[\alpha]_D -50.0^\circ(\text{CHCl}_3)$. The former(X) assumed to be methyl 9 β -hydroxy-(-)pimara-8(14),15-dien-19-oate by its IR($\nu_{\text{max}}^{\text{CCl}_4}$ 3625 and 1730 cm^{-1}) and NMR (Table I, no proton signal due to a carbinyll proton) spectra. The latter alcohol(XI)(IR $\nu_{\text{max}}^{\text{CCl}_4}$ 3625 and 1732 cm^{-1}), whose NMR spectra(Table I) indicated the presence of an axial hydroxyl group, was subjected to oxidation with MnO_2 affording a ketone, mp 97-99°, which was proved to be identical with the methyl ester(VIII) of acid C. Reduction of VIII with NaBH_4 gave the methyl ester(V) of acid B.

The alcohol(XI), an epimer of V, was confirmed to be identical with the methyl ester of acid D leading to the formulation of acid D(XII) as 7 β -hydroxy-(-)pimara-8(14),15-dien-19-oic acid.

Besides the above four acidic diterpenes, an alcohol(XIII), mp 109-110°; $[\alpha]_D -96.0^\circ(\text{CHCl}_3)$ has been isolated by repeated chromatography of the neutral fraction of the ether-extract of *A.cordata* (roots). This alcohol(XIII) was identified to be (-)pimara-8(14),15-dien-19-ol, which was already prepared from VI by reduction with LiAlH_4 ²⁾.

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References

- 1) After submitting the previous communication²⁾, the purification of I has been achieved, establishing its identification by comparison with the authentic sample including the optical rotation.
- 2) S.Shibata, M.Mihashi, and O.Tanaka: Tetrahedron Letters, 1967, 5241.
- 3) Molecular formulae of these compounds were obtained by high resolution mass spectrometry.
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