The stereochemical studies are presently under investigation.

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Biosynthesis of Lichen Substances. II. Participation of C_1-Unit to the Formation of β-Orcinol Type Lichen Depside

Previously, we reported1) that the lichen depsides, lecanoric acid and atranorin were formed by "head to tail" condensation of acetate, while formate took part as a source of methyl and aldehyde groups of atranorin type depsides.

In the present study, tritium labeled orsellinic and β-orcinolcarboxylic acids which were obtained by the hydrolysis of lecanoric acid and atranorin, respectively with tritiated acid, were administered to fresh *Parmelia tinctorum* Despr. by the same technique as previously reported. From the result as shown in Table I, it was recognized that orsellinic acid and β-orcinolcarboxylic acid afforded smoothly lecanoric acid and atranorin, respectively. However, the incorporation of tritiated orsellinic acid into atranorin or tritiated β-orcinolcarboxylic acid into lecanoric acid was not observed. These results showed that the participation of formate (or C_1-unit) to form β-orcinolcarboxylic acid should occur before the formation of the aromatic ring of orsellinic acid.

Table I. Incorporation of ^{3}H-Phenolcarboxylic Acids into the Depsides in *Parmelia tinctorum*

Precursor / Compound	Specific radioactivity (d.p.m./mM)	
	Orsellinic acid-^{3}H	β-Orcinolcarboxylic acid-^{3}H
Lecanoric acid	5.0×10^5	0
Atranorin	0	1.2×10^5
Chloroatranorin	0	4.2×10^4

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Further Characterization of Triterpenoids of Migrated Hopane and Arborane Groups from Gramineae Plants

Arundoin, one of the two major triterpenoids[1] from rhizomes of *Imperata cylindrica* P. Beauv. var. *media* Hubbard (チガヤ) (Gramineae), has been proved to be identical[2] with the triterpene from *Arundo conspicua* (Gramineae)[3] and the structure has been revised to 3β-methoxyfern-9(11)-ene (Ia).[2] The other triterpene, named cylindrin, has been characterised[1] as methyl ether (Ⅱ) of isoarborinol.[4] Considerations on biogenesis[5] of migrated hopane, *i.e.* fernane, and arborane derivatives from present knowledges on triterpene chemistry,[6] and the similarity of mass spectral fragmentation,[5] which would be much influenced by the stereochemical relations of the double bond and the rings D and E,[4,7] of fern-9(11)-ene and arbor-9(11)-ene derivatives, lead to our proposal[2] of the most probable structure (Ⅲ) for arbor-9(11)-ene derivatives. This has now been proved to be correct by X-ray analysis of 2α-bromoarborinone (Ⅳ).[8]

Further examinations on the minor constituents of the same plant afforded three triterpenoids of rearranged hopane and arborane groups: simiarenol(adian-5-en-3β-ol) (Ⅴa),[9] m.p. 209~211°, acetate, m.p. 216~217°, $[\alpha]_D$ +70° ($CHCl_3$); a new triterpene (Ib), m.p. 192~193°, $[\alpha]_D$ −19° ($CHCl_3$), acetate, m.p. 222~223°, $[\alpha]_D$ −9° ($CHCl_3$); and isoarborinol (arbor-9(11)-en-3β-ol) (Ⅲb),[4,10] m.p. 295~300°, acetate, m.p. 296~298°, in respective yields of 0.001, 0.0005, and 0.0005%. Identification of Ⅴa and Ⅲb has been made by the direct comparison with the authentic specimens.[*1]

Although simiarenol (Ⅴa) has been correlated with adian-5-ene (Ⅴb),[11] placement of the hydroxyl group at 3β-position has based on ORD and NMR data; thus the acid

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