

acid derivative. Both mechanisms have the analogy in the experiment of internucleotidic linkage formation achieved by Todd⁵⁾ and Khorana.³⁾

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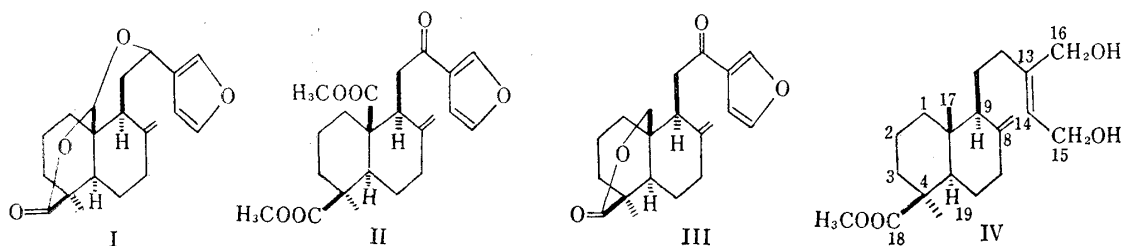
5) A. M. Michelson, A. R. Todd: J. Chem. Soc., 1955, 2632.

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Interrelation of Methyl Sciadopate with Communic Acid and Danielllic Acid

Three furanoid diterpenes, sciadin,¹⁾ dimethylsciadinonate, and sciadinone^{2,3)} obtained from the heartwood as well as the leaves of *Sciadopitys verticillata* SIEB. et ZUCC. have been shown to have the structures (I), (II), and (III), respectively. In contrast to these three diterpenes methyl sciadopate (IV), m.p. 108°, $[\alpha]_D^{25} +0.36$ ($c=2.5$, CHCl_3), UV: $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ m μ 202 ($\log \epsilon$ 4.202); IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3330, 1022, 1000 (OH), 3060, 1639, 884 ($>\text{C}=\text{CH}_2$), 847 ($-\text{CH}=\text{C}<$), 1735, 1222, 1150 (ester); $\text{C}_{21}\text{H}_{34}\text{O}_4$ *¹ obtained from the heartwood, but not from the leaves of the same plant, has no furan ring and its structure



(including absolute configuration) has been determined independently by Sumimoto, *et al.*⁴⁾ and the author.⁵⁾ Not only do these four diterpenes closely resemble each other structurally, but they all have so-called normal absolute configurations. The common carbon skeleton strongly suggests that they are biogenetically related quite closely.

A literature survey of diterpenoid chemistry indicates that methyl sciadopate (IV) is seemingly situated biogenetically at the mid-point between communic or agathadiene-dicarboxylic acid and the furanoid diterpenes mentioned above, since the *cis*-2-butene-

*¹ All the analytical values were in good agreement with molecular formula shown.

1) M. Sumimoto: Tetrahedron, **19**, 643 (1963).

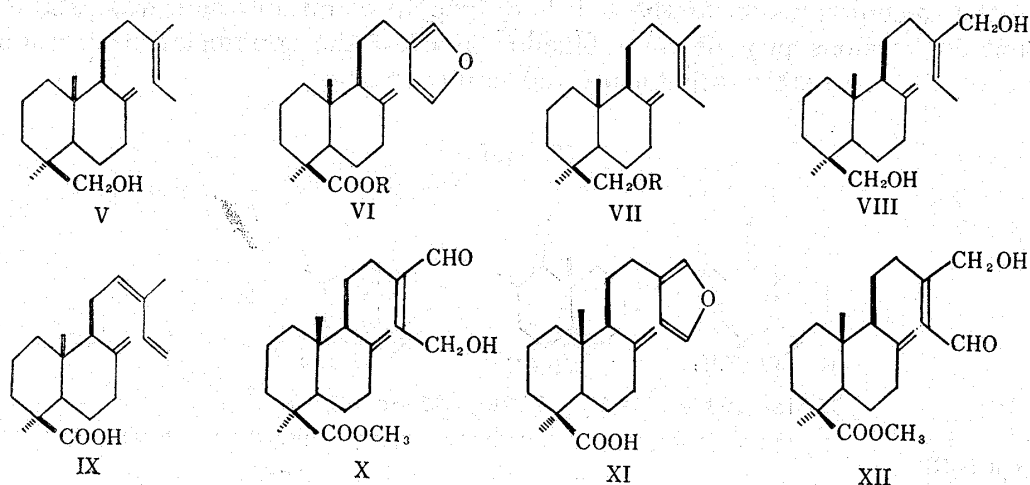
2) C. Kaneko, T. Tsuchiya, M. Ishikawa: This Bulletin, **11**, 271 (1963).

3) *Idem*: *Ibid.*, **11**, 1346 (1963).

4) M. Sumimoto, *et al.*: Abstract of papers, Symposium on the organic chemistry of natural products, Kyushu, Japan (1963), p. 243.

5) T. Miyasaka: *Ibid.*, p. 238.

1,4-diol grouping in IV seems to be the appropriate precursor convertible into the functional group about C-13 and C-16 in these furanoid diterpenes. The chemical transformation of IV into isodihydrocommunol (V) and into the antipode (VI; R=H) of daniellic acid under the quite mild condition recently performed in this laboratory seems to support these suppositions. Reduction of methyl sciadopate (IV) with lithium metal in liquid ammonia in the presence of ethanol gave after separation on silica gel chromatography two products, VII (R=H) and VIII. The former was identified as isodihydrocommunol (V) as 3,5-dinitrobenzoate of V, m.p. 109°, $[\alpha]_D^{25}$ 9.0° (CHCl₃), C₂₇H₃₆O₆N₂ which had been prepared from communin acid (IX) by Arya, *et al.*^{6,7)}



The formation of a furan ring in methyl sciadopate was accomplished using series of novel reactions described below. Stirring methyl sciadopate with 20%-palladized charcoal⁸⁾ in methanol, resulted in the oxidation of the allyl-alcohol group. The aldehyde-alcohol (X) (oil, IR cm⁻¹: 1735, 1698 (CCl₄), UV: $\lambda_{\max}^{\text{EtOH}}$ 227 m μ (ϵ 13,000)) thus obtained was transformed into the furan derivative (VI; R=CH₃) by warming in acetic acid. Melting point, polarity and other physical properties of VI (R=CH₃) revealed it to be an optical antipode of the methyl ester of daniellic acid (XII).⁹⁾ The methyl ester (VI) was saponified yielding the corresponding acid (VI; R=H), m.p. 129~130°, IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 1697, 1641, 890, 778. UV: 225 m μ (endabsorption ϵ 3,300). ORD: simple positive: $[\alpha]_{600}^{25} +56^\circ$, $[\alpha]_{589}^{25} +58^\circ$, $[\alpha]_{290}^{25} +262^\circ$ (c=0.48, MeOH), C₂₀H₂₈O₃, in boiling aqueous potassium hydroxide: propylene glycol.

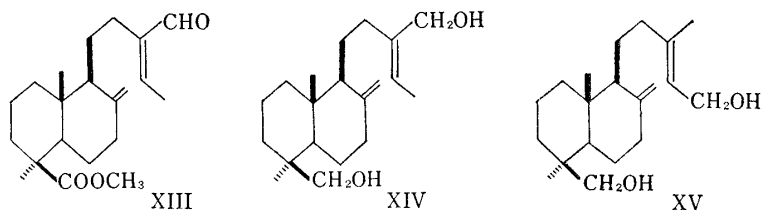
The structure of aldehyde-alcohol described above could be either X or XIII. Unambiguous choice of structure (X) for this compound was established through the following experiments. Acetylation of X with acetic anhydride, followed by reduction with zinc-acetic acid afforded the conjugated aldehyde (XIII) after chromatography over silica gel. Without further purification, XIII was reduced with lithium aluminum hydride in ether to give a dihydroxy compound (XIV), m.p. 83~84°. IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 1641, 894, C₂₀H₃₄O₂. This compound was identical with VIII by mixed melting point determination and by comparison with their infrared spectra. Nonidentity of VIII with agathadienediol (XV)⁹⁾ obtained from agathadienedicarboxylic acid, definitely excludes the alternate structure (XIII). Therefore the structure of above mentioned aldehyde-alcohol must be formulated as X.

6) V. P. Arya, H. Erdtman, T. Kubota: *Tetrahedron*, **16**, 255 (1961).

7) Cf., C. Enzell: *Acta Chim. Scand.*, **15**, 1303 (1961).

8) Cf., A. S. Pfau, P. A. Plattner: *Helv. Chim. Acta*, **23**, 781 (1940).

9) J. Haeuser, R. Lombard, F. Lederer, G. Ourisson: *Tetrahedron*, **12**, 205 (1961).



These chemical transformations gave not only the strong support of our supposition that *N* could be the precursor of both types of diterpenes as mentioned above, but also data for clarification of the stereochemistry of these diterpenes.

Since the α -configuration of the C-9 hydrogen in communic acid was established,^{6,7)} the present conversions provide unambiguous proof of the equatorial orientation of the side chain at C-9 in methyl sciadopate and daniellic acid.

TABLE I.

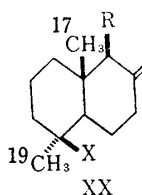
R						
	17 Me	19 Me	17 Me	19 Me	17 Me	19 Me
$-\text{CH}_2\text{CH}_2-\text{CH}_2\text{OH}$	9.52	8.83	(9.36)	(9.08) ^{a)}	9.30	9.05
$-\text{CH}_2\text{CH}_2-\text{CH}_2\text{OH}$						
$-\text{CH}_2\text{CH}_2-\text{CH}_3$	9.51	8.83	9.34	9.02	9.29	9.01
$-\text{CH}_2\text{CH}_2-\text{COOCH}_3$						
$-\text{CH}_2\text{CH}_2-\text{CH}_3$	—	—	9.37	9.08	9.30	9.03
$-\text{CH}_2\text{CH}_2-\text{CH}_3$						
$-\text{CH}_2\text{CH}_2-\text{CH}_2\text{OH}$	—	—	9.33	9.01		
$-\text{CH}_2\text{CH}_2-\text{CH}_3$						
$-\text{CH}_2\text{CH}_2-\text{O}$	9.50	8.83	—	—	—	—
mean	9.51	8.83	9.35	9.02	9.30	9.03
					$^{17}\Delta\text{COOCH}_3-\text{CH}_2\text{OAc}$	0.21
					$^{19}\Delta\text{COOCH}_3-\text{CH}_2\text{OAc}$	-0.20
$-\text{CH}_2\text{CH}_2-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$						
	9.33	8.82	9.17	9.04	9.14	9.06
	$\Delta F \sim \text{dihydro}$		$\Delta F \sim \text{dihydro}$		$\Delta F \sim \text{dihydro}$	
	0.19	0.01	0.19	-0.02	0.16	-0.03
					$^{17}\Delta\text{COOCH}_3-\text{CH}_2\text{OAc}$	0.19
					$^{19}\Delta\text{COOCH}_3-\text{CH}_2\text{OAc}$	-0.24

All the NMR spectra was measured on 5~15% solution in CDCl_3 or CCl_4 containing tetramethylsilane as an internal standard, with Japan Electron Optics Lab. 3H-60 NMR spectrometer or Varian A-60 spectrometer operating at a frequency of 60 Mc.p.s.

a) Dioxane was used as solvent.

The nuclear magnetic resonance spectra of these compounds, together with those obtained in the degradation investigation of methyl sciadopate seem to deserve a brief comment. The nuclear magnetic resonance spectrum of IV exhibited an angular methyl signal at a rather high field of 9.52. Spectral analyses of the related compounds enable one to attribute this high-field shift to the anisotropic effects of the carbonyl and the exocyclic methylene groups.

The proton resonance signal on C-17, together with the one on C-19 of methyl sciadopate and those of its related compounds are shown in Table I. Data in Table I indicate that the high field shifts of 0.2 p.p.m. of angular methyl signals are due to the anisotropic shielding of the carbonyl function axially oriented at C-4, and those of 0.15 p.p.m. are due to the exocyclic methylene function, compared to those of the compounds having the axial acetoxymethylene group and methyl group at C-4 and C-8 respectively in XX.



These observations of the angular methyl chemical shifts at C-10 should be useful for stereochemical problems of other diterpenes having the same carbon skeleton as XX.

More detail discussions concerning the anisotropic shielding effects of these functional groups on the angular methyl group will be published elsewhere, together with the complete set of data.

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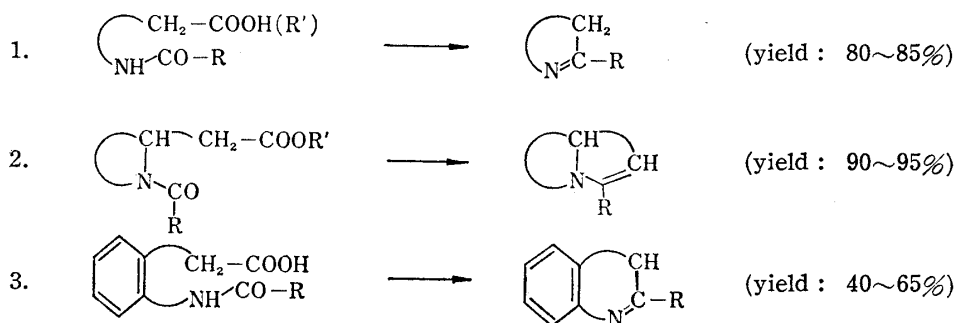
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Decahydropyrido[2,1,6-*de*]quinolizine (Decahydrocyclo[3.3.3]azine)*¹

We wish to report the synthesis of 1,2,3,3a,4,5,6,6a,7,8-decahydropyrido[2,1,6-*de*]quinolizine (VI).

In previous reports, we reported a new synthetic method for cyclic nitrogen compounds as shown by the general formulas below.



*¹ This work is a part of "a new synthetic method of cyclic nitrogen compounds by Isamu Murakoshi."