to freeze-drying to afford 0.8 g of colorless powder (92.7%), recrystallization of which was not successful. After drying over P_2O_5 at 60° for 24 hr *in vacuo* it had mp 105—125° (decomp.), $[\alpha]_D^{22.5}$ $-77.8°$ ($c=1.0$). *Anal.* Calcd. for $C_{14}H_{17}O_8N$: C, 51.38; H, 5.24; N, 4.28. Found: C, 51.03; H, 5.59; N, 4.11. The infrared spectrum is identical with that of synthetic I (Fig. 1).

Synthesis of I——a) Methyl (*p*-Aminophenyl 2,3,4-Tri-O-acetyl-*β*-D-glucopyranosid) uronate (VI): A solution of methyl (*p*-nitrophenyl 2,3,4-tri-O-acetyl-*β*-D-glucopyranosid)uronate (V) (3 g) in MeOH (150 ml) was shaken with H_2 in the presence of a catalyst prepared from activated charcoal (1.5 g) and $PdCl_2$ (75 mg) After the uptake of H_2 ceased, the catalyst was removed by filtration and the filtrate was evaporated *in vacuo*. The residue was recrystallized from EtOH to give 2.3 g (82.1%) of IV as colorless needles, mp 154—156°, $[\alpha]_D^{15}$ $-24°$ ($c=5.0$ in $CHCl_3$). *Anal.* Calcd. for $C_{19}H_{23}O_{10}N$: C, 53.65; H, 5.45; N, 3.29. Found: C, 54.07; H, 5.66; N, 3.36.

b) Methl (*p*-Acetamidophenyl 2,3,4-Tri-O-acetyl-*β*-D-glucopyranosid)uronate (II): VI (2.3 g) was dissolved in pyridine (10 ml) and to the solution was added Ac_2O dropwise under cooling with ice. After standing overnight, colorless needles deposited was collected by filtration and the filtrate was poured into ice-water (80 ml) to afford further crystals. Recrystallization from EtOH gave 2.25 g (89.0%) of colorless needles, mp 210—211°, $[\alpha]_D^{15}$ $-22.0°$ ($c=5.0$ in $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{25}O_{11}N$: C, 53.96; H, 5.39; N, 3.00. Found: C, 54.03; H, 5.45; N, 3.28.

c) Synthesis of I by Deacetylation of II: II (2.14 g) was dissolved in MeOH (100 ml) under gentle warming and to the solution was added a mixture of Na (75 mg) and MeOH (15 ml). Allowing to stand the mixture for 48 hr at room temperature, the solvent was evaporated *in vacuo* below 30°. The pale yellow residue was dissolved in water (10 ml) and submitted to a column chromatography of Dowex 50W-X8 (50—100 mesh, H-form, 100 ml) developing with water. The acidic eluate (pH 2—4) was evaporated to dryness *in vacuo* below 30° to leave pale yellow powder, which was purified from MeOH to give 0.94 g (62.7%) of colorless crystals. After drying over P_2O_5 at 60° for 24 hr *in vacuo*, it gave mp 132—133° (decomp.), $[\alpha]_D^{27.5}$ $-79.6°$ ($c=2.5$). *Anal.* Calcd. for $C_{14}H_{17}O_8N$: C, 51.38; H, 5.24; N, 4.28. Found: C, 51.33; H, 5.76; N, 3.63. The infrared spectrum is shown in Fig. 1.

Benzylamine Salt (III): Prepared as in the literature.[5a] mp 195—197°, $[\alpha]_D^{13.5}$ -38.0 ($c=1.0$). *Anal.* Calcd. for $C_{21}H_{26}O_8N_2$: C, 58.06; H, 6.03; N, 6.45. Found: C, 58.03; H, 6.17; N, 6.07.

Thin-Layer Chromatography——The procedure was as in the literature.[7] Silica gel HF_{254} according to Stahl was spread about 250 μ thick and dried at 110° for 1.5 hr. The solvent system was AcOH–H_2O–MeOH–AcOEt (1:9:30:60). All the compounds examined were revealed as dark spots against fluorescent background under ultraviolet light and the compounds containing free amino group were also detected by Ehrlich's reagent. *Rf* values of the compounds are as follows: *p*-aminophenyl-*β*-D-glucopyranosiduronic acid (IV), 0.2; *p*-acetamidophenyl-*β*-D-glucopyranosiduronic acid (I), 0.4; *p*-hydroxyacetanilide, 0.8; *p*-aminophenol, 0.85.

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Terpenoids. XVII.[1] Chemical Conversion of Trichokaurin into Isodocarpin *via* a Direct Pathway

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We have been investigating on diterpenoids of *Isodon* species. All of them belong to kaurene- and B-secokaurene-types. The former is biogenetically regarded as the precursor

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[1] Part XVI: E. Fujita, T. Fujita, and H. Katayama, *J. Chem. Soc.* (*C*), **1970**, **1681**.

[2] Location: *Uji, Kyoto.*

of the latter. Previously, we[3] converted trichokaurin(I), a kaurenoid, into dihydro-derivative (IV) of isodocarpin, a B-secokaurenoid. Recently, the dihydro-derivative of isodocarpin was chemically transformed into isodocarpin (V).[1] Thus, a chemical conversion of trichokaurin into isodocarpin has been accomplished. The route, however, takes a roundabout way as shown in Chart 1 (I→II→III→IV→V). Now, we report another chemical conversion *via* a more convenient route with much less steps.

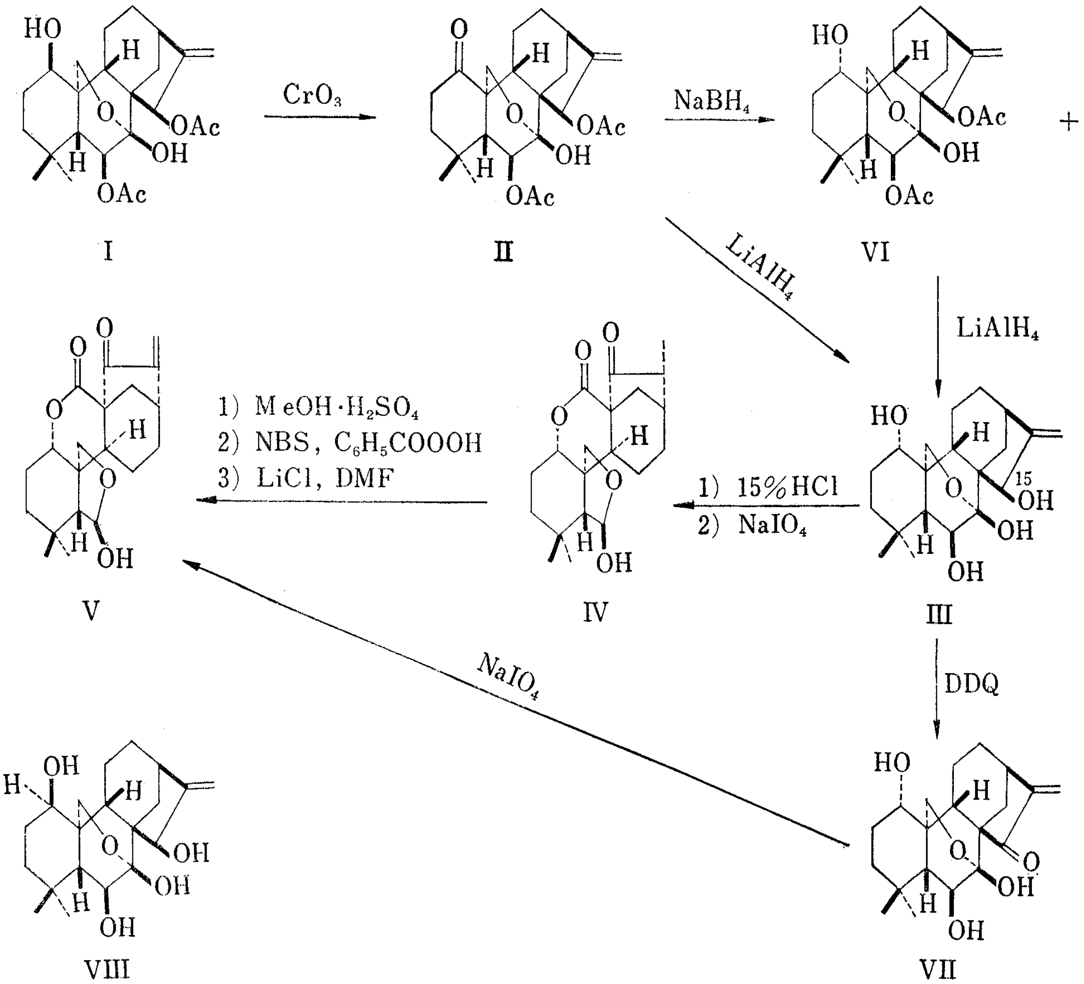

Chart 1

Trichokaurin (I) was subjected to Jones' oxidation to give the known ketone (II),[3] which was reduced by sodium borohydride in tetrahydrofuran to afford a new 1α-alcohol (VI) and trichokaurin (I) with a ratio of about 10:1. Treatment of VI with lithium aluminum hydride gave the known alcohol (III), which has been prepared directly from II by treatment with lithium aluminum hydride.[3] Alcohol (III) on reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[4] in tertiary butanol gave a new α,β-unsaturated ketone (VII). The latter was oxidized with metaperiodate to afford the desired isodocarpin (V) in a good yield. Compound (VII) is biogenetically expected to be a close precursor of isodocarpin. Compound (III) might be also considered as a possible precursor, although C-15 epimer seems to be more attractive to us as a precursor of isodocarpin.

We carried out reduction of II with sodium borotritide to prepare 1α-tritio-trichokaurin and 1β-tritio-(VI). The former was treated with lithium aluminum hydride to give the

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[3] E. Fujita, T. Fujita, and Shibuya, *Chem. Comm.*, **1967**, 466; E. Fujita, T. Fujita, M. Shibuya, and T. Shingu, *Tetrahedron*, **25**, 2517 (1969).

[4] S.H. Burstein and H.J. Ringold, *J. Am. Chem. Soc.*, **86**, 4952 (1964).

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corresponding C-1α labelled tetraol (VIII). The 1β-tritium-labelled (III and VII) were derived from the latter through the same route as described above. The details about these labelled compounds together with the results of their feeding experiments will be published elsewhere.

Experimental[5]

Reduction of II with $NaBH_4$——Trichokaurin 1-dehydro-derivative (II) (580 mg) was dissolved in tetrahydrofuran (13 ml), and a solution of $NaBH_4$ (120 mg) in tetrahydrofuran (2 ml)–water (3 drops) was dropwise added to the above solution under ice–cooling and stirring. The mixture was stirred for 1 hr, then a small excess of 10% cold HCl was added to acidify. The mixture, after addition of H_2O, was extracted with CH_2Cl_2, and the organic layer was washed with H_2O. After drying over $MgSO_4$, the solvent was evaporated off to give a gummy residue (643 mg), which was chromatographed on silica gel (10 g) column using CH_2Cl_2 for elution to isolate two fractions. The first crystalline eluate (42 mg) was recrystallized from ether to yield colorless needles, mp 182—184°. The substance was proved to be identical with trichokaurin by direct comparison and identity of IR spectra and their *Rf* value (7.8) on TLC (Silica gel, CH_2Cl_2–acetone (4:1)). The second eluate gave a crude crystalline substance (445 mg), which was recrystallized from ether to yield colorless needles (350 mg), mp 202—204°. *Anal.* Calcd. for $C_{24}H_{34}O_7 \cdot \frac{1}{2}H_2O$: C, 65.01; H, 7.90. Found: C, 65.00; H, 7.90. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3450, 3060, 1725, 1660, 1225. NMR δ ($CDCl_3$): 0.84, 1.13 (each 3H, s), 2.04, 2.17 (each 3H, s), 3.48—3.83 (1H, m, C-1-$\underline{H}$, it changes to a quartet at 3.65, $J=7.5$, 10 Hz with D_2O.), 4.05, 4.31 (2H, AB-type, $J=10$ Hz, C-20 $\underline{H}_2$), 4.91 (1H, d, $J=2.0$ Hz, C-17-$\underline{H}$), 5.03 (1H, d, $J=2.0$ Hz, C-17-$\underline{H}$), 5.18 (1H, d, $J=8.0$ Hz, C-6-$\underline{H}$), 6.30 (1H, t, $J=2.0$ Hz, C-15-$\underline{H}$).

Reduction of VI with $LiAlH_4$——To a suspension of 1α-alcohol (VI) (250 mg) in anhydrous ether (30 ml) an ethereal solution (2 ml) of $LiAlH_4$ (150 mg) was added, and the mixture was refluxed for 3 hr. The reaction mixture was added to AcOEt (100 ml), and washed with saturated NaCl solution, then 10% HCl and at last H_2O. After drying over $MgSO_4$, the solvent was evaporated off to give crude crystals (100 mg), which were recrystallized from MeOH to afford colorless needles (65 mg), mp 242—243°. The substance was proved to be identical with the known alcohol (III)[3] by direct comparison with an authentic sample (mmp, IR, TLC).

Oxidation of Alcohol (III) with DDQ——To a solution of DDQ (120 mg) in *t*-butanol (20 ml) alcohol (III) (120 mg) was added and the mixture was stirred for 9 hr at room temperature. Ethane dichloride (100 ml) was added to the reaction mixture and the solution was washed with 1% cold aq. NaOH, 10% cold HCl, and a saturated aq. NaCl. After drying over $MgSO_4$, the solvent was evaporated off to give a crystalline residue (125 mg), which was recrystallized from MeOH to yield colorless prisms (42 mg) of VII, mp 244—247°. *Anal.* Calcd. for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.95; H, 8.31. Mass Spectrum m/e: 348 (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3250, 1703, 1635. UV $\lambda_{\max}^{\mathrm{MeOH}}$ 242 mμ (ε 9230). NMR δ (in D_5-pyridine–D_2O): 1.07, 1.23 (each 3H, s), 1.40 (1H, d, $J=6.5$ Hz, C-5-$\underline{H}$), 3.68 (1H, t, $J=8$ Hz, C-1-$\underline{H}$), 4.24 (1H, d, $J=6.5$ Hz, C-6-$\underline{H}$), 4.36, 4.68 (each 1H, AB type, $J=10$ Hz, C-20 $\underline{H}_2$), 5.42, 6.00 (each 1H, s, C-17 $\underline{H}_2$).

Oxidative Cleavage of VII with $NaIO_4$ to Isodocarpin (V)——Ketone (VII) (20 mg) was suspended in MeOH (2 ml) and $NaIO_4$ (80 mg) in H_2O (2 ml) was added to it. The mixture was stirred overnight at room temperature. After a saturated aq. NaCl was added, it was extracted with AcOEt. The extract, after drying over $MgSO_4$, was evaporated off to give a redisue, which was passed through a silica gel column using CH_2Cl_2–acetone (3:2). The eluate gave crude solid (15 mg), which was recrystallized from MeOH to afford colorless prisms (10 mg), mp 288—290°. The substance was proved to be isodocarpin[1] by mixed melting point test, IR and TLC comparison.

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[5] Melting points were measured on a Yanagimoto micromelting point determination apparatus, and uncorrected. NMR spectra were taken on a Varian A-60 spectrometer with TMS as internal standard. Kieselgel 0.05—0.2 mm (Merck) and Kieselgel G nach Stahl (Merck) was used for column chromatography and TLC, respectively.