hydride. Compound C, $C_{30}H_{50}O$, is an alcohol and was converted to Compound B by chromic acid oxidation. Their melting points and specific rotations are very similar to those of taraxerol and the derivatives as shown in the Table I.

Final confirmation was made by the infrared spectra of Compound C and taraxerol*6 which were superimposable and, therefore, Compound A and B are taraxeryl acetate and taraxerone, respectively.

Experimental

Extraction and Chromatographic Separation——The dried and powdered root and stem (8.5 kg.) were refluxed in petr. ether (b.p. 40~100°) for 2 hr. three times to give 14.8 g. of a crude mixture. A portion (790 mg.) of the sample that was recrystallized once from petr. ether was chromatographed on 35 g. of silicic acid with chloroform, and several fractions were checked by IR spectrum and thin-layer chromatography. Compound A (400 mg.), B (50 mg.), and C (300 mg.) were eluted in turn and then recrystallized from a small amount of chloroform.

Compound A——Colorless needles. *Anal.* Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18; mol. wt., 468.7. Found: C, 82.02; H, 10.74; mol. wt., 473.

Compound B——Colorless plates. *Anal.* Calcd. for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 85.09; H, 11.39.

Compound C——Colorless needles. *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.17; H, 11.83.

Hydrolysis of Compound A——Compound A (100 mg.) was hydrolyzed with refluxing 0.06*N* NaOH in ethanol (15 ml.) for 4 hr. to yield Compound C (68 mg.).

Reduction of Compound B——Reduction of Compound B (50 mg.) with excess $LiAlH_4$ in ether was carried out according to the usual procedure giving 37 mg. of Compound C.

Oxidation of Compound C——Compound C (190 mg.) was oxidized in the usual manner using CrO_3 (130 mg.)//pyridine (8 ml.) complex to give Compound B (160 mg.).

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*6 The authors wish to thank Professor T. Takemoto, Tohoku University, for providing a copy of the infrared spectrum of taraxerol.

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Shun-ichi Yamada, Takayuki Shioiri, Taisuke Itaya, Takeshi Hara, and Rei Matsueda: Ind.-N-Alkylation of Tryptophan and Synthesis of 1-Alkyltryptophan Hydrazides.

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During the course of an investigation of the synthetic approaches to the indole alkaloids, it became desirable to obtain 1-alkyltryptophans,*2 some of which were synthesized by rather troublesome methods.[1~3]

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*2 DL-form, unless otherwise stated.

1) *a*) H. Wieland, W. Konz, H. Mittasch: Ann., **513**, 1 (1934). *b*) H. R. Snyder, E. L. Eliel: J. Am. Chem. Soc., **70**, 3855 (1948). *c*) T. Matsuura, K. Matsui, K. Ichikawa: Med. J. Osaka Univ., **4**, 449 (1954); C. A., **49**, 6222 (1955).

2) E. Leete: J. Org. Chem., **23**, 631 (1958).

Our starting material for the synthesis of 1-alkyltryptophans was tryptophan*2 (I) because of its being produced cheaply in recent years. The general method employed consisted of preparing the disodium salt of tryptophan in liquid ammonia and then allowing it to react with alkyl halides. Tryptophan was selectively alkylated at the position of indole-N under this condition. This procedure is essentially analogous to that of Potts and Saxton.[4] But in this case, one atom of sodium was not enough to conduct the reaction and led to the recovery of the starting material (I).

First, the methylation of tryptophan (I) with methyl iodide smoothly proceeded to give the 1-methyl derivative (IIa) in nearly quantitative yield. Since the alkylation of indole derivatives under the above condition appeared to have the possibility of alkylation of both 1- and 3-positions[5] and of the amino group of the amino acid moiety,[6] the product (IIa) was acetylated by the usual procedure in order to confirm the structure of the alkylated material (IIa). The N-acetyl derivative thus obtained was identified with the authentic N-acetyl-1-methyltryptophan[7] (IIa) through admixture and infrared spectra. By this alkylation procedure, 1-ethyl-,[2] 1-allyl- and 1-benzyltryptophans[3] (IIb~d) were respectively synthesized in good yields.

The structure proof of these ind.-N-alkyltryptophans was also obtained from positive ninhydrin color test (purple) and spectral data. The infrared spectra of these amino acids have no characteristic absorption band near 3400 cm^{-1} which is ascribed to ind.-NH stretching vibration.[8] The ultraviolet spectra of indole and its alkyl derivatives in neutral solution, in general, exhibit a strong maximum near 220 mμ (log ε 4.0~4.5) and a maximum of lower intensity near 280 mμ (log ε 3.6~4.0), usually flanked by two maxima (270 and 290 mμ). The same tendency was observed on the ultraviolet spectra of 1-alkyltryptophans thus obtained. But as a significant spectral difference, each fourth

Table I. Ultraviolet Spectra of 1-Alkyltryptophans[a]

Compound	Solvent[b]	λ_{max} mμ (log ε)	λ_{min} mμ (log ε)	$\lambda_{sh.}$ mμ (log ε)	λ_{max} mμ (log ε)	$\lambda_{sh.}$ mμ (log ε)
I	A	220 (4.51)	243 (3.08)	274 (3.69)[c]	282 (3.71)	290 (3.64)[c]
	B	219 (4.52)	245 (3.33)	273 (3.73)[c]	280 (3.74)	289 (3.67)[c]
IIa	A	223 (4.52)	246 (3.05)	277 (3.72)	286 (3.76)	296 (3.68)
	B	222 (4.54)	248 (3.29)	277 (3.77)	285 (3.81)	296 (3.71)
IIb	A	223 (4.53)	245 (2.99)	278 (3.71)	287 (3.76)	297 (3.67)
	B	223 (4.53)	246 (3.22)	277 (3.74)	286 (3.78)	296 (3.70)
IIc	A	222 (4.60)	245 (3.17)	276 (3.78)	284 (3.82)	295 (3.76)
	B	221 (4.61)	246 (3.31)	275 (3.81)	284 (3.84)	295 (3.77)
IId	A	223 (4.55)	246 (3.36)	277 (3.76)	286 (3.80)	296 (3.73)
	B	221 (4.56)	248 (3.45)	276 (3.80)	284 (3.83)	295 (3.75)

a) The UV spectra were measured with a Cary Model 11.
b) A: in 90% aq. EtOH. B: in 90% aq. EtOH-35% aq. HCl (5:1).
c) λmax

*3 Although indoles constitute an important group of natural products, little attention has been paid to the effect of alkyl substituents on the ultraviolet absorption properties. S. Ghosal [J. Sci. Ind. Res., **20B**, 412 (1961)] and H. Bader and W. Oroshnik [J. Am. Chem. Soc., **79**, 5686 (1957)] reported 2-alkyl substitution produces bathochromic displacement for all the selective absorption bands, but their studies on the alkyl effects are not extensive.

3) J. W. Cornforth, R. H. Cornforth, C. E. Dalgliesh, A. Neuberger: Biochem. J., **48**, 591 (1951).
4) K. T. Potts, J. E. Saxton: J. Chem. Soc., **1954**, 2641; Org. Syntheses, **40**, 68. cf. H. Plieninger: Chem. Ber., **87**, 127 (1954); J. W. Cook, J. D. London, P. McClosky: J. Chem. Soc., **1952**, 3904.
5) M. Nakazaki, S. Isoe: Nippon Kagaku Zasshi, **76**, 1159 (1955); M. Nakazaki: Bull. Chem. Soc. Japan, **32**, 838 (1959).
6) V. du Vigneaud, O. K. Behrens: J. Biol. Chem., **117**, 27 (1937).
7) H. R. Snyder, E. L. Eliel: J. Am. Chem. Soc., **71**, 663 (1949).
8) A. R. Katritzky (Ed.): "Physical Methods in Heterocyclic Chemistry," Vol. II, 211 (1963), Academic Press, New York and London.

absorption peak near 290 mμ became merely a shoulder and was shifted bathochromically by 5~6 mμ as shown in Table I. This spectral change by the substitution of the 1-alkyl group would distinguish N-alkylindoles from the N-unsubstituted compounds.*3

Numerous attempts to prepare the 1-isopropyl and 1-*tert.*-butyl derivatives by alkylation with isopropyl and *tert.*-butyl iodide were unsuccessful. When isopropyl iodide was used, a mixture of 1-isopropyltryptophan (Rf 0.80) and the starting material (I) (Rf 0.58) was obtained, but the isolation of the former failed. This incomplete alkylation seemed to be due to the steric hindrance of alkyl groups.

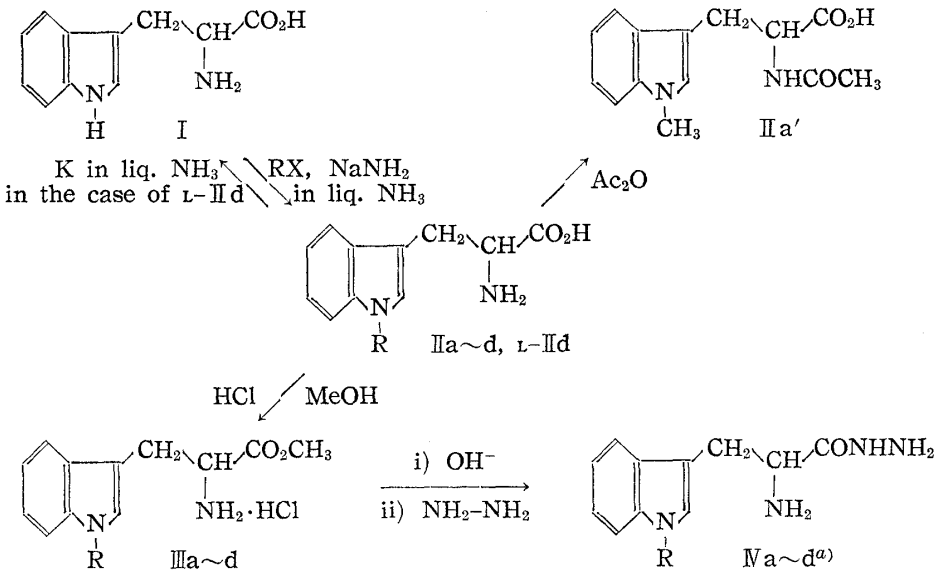

Chart 1.

When an optically active isomer (D or L-I) is used as a starting material, it comes into problem whether any racemization may take place in this ind.-N-alkylation. To examine it, L-tryptophan (L-I) was allowed to react with benzyl chloride and the resultant optically active L-1-benzyltryptophan (L-IId) ($[\alpha]_D^{17}$ −21.5°, DMF) was subjected to debenzylation by metallic sodium in liquid ammonia according to the method of Julia, *et al.*[9] In contrast to their satisfactory results on the debenzylation, our results were found to be unsatisfactory owing to incomplete reaction by infrared spectra and paper chromatography. However, replacement of sodium by potassium gave the expected L-tryptophan (L-I) in good yield, whose optical activity was retained completely. The success of benzylation and debenzylation is of interest because no racemization occurred in these two reactions.

In order to test the enzyme inhibition of the 1-alkyltryptophan hydrazides (IV), the synthesis of them from the 1-alkyltryptophans (II) was carried out. The amino acids (II) were refluxed in 10 w/v % methanolic hydrogen chloride to give the hydrochlorides (III) of methyl esters in good yields. The free bases of methyl esters seemed to be easily converted to the diketopiperazines, so the crude bases were subjected to hydrazinolysis by hydrazine in ethanol. The characteristic absorption bands of the infrared spectra of the hydrazides are in accord with the data published for aliphatic hydrazides.[10]

9) M. Julia, P. Manoury, J. Igolen : Compt. rend., **251**, 394 (1960); cf. reference 6).
10) M. Mashima : Bull. Chem. Soc. Japan, **35**, 1882 (1962); *Idem* : *Ibid.*, **36**, 210 (1963) and references therein.

The preparations of the 1-alkyltryptophans and their hydrazides have now become very convenient and their biochemical investigations and the synthetic scheme starting from them are now under progress.

Experimental*4

Ind.-N-Alkylation of Tryptophan (I)*5

1-Methyltryptophan (IIa)——Metallic Na (32 g., 1.4 atom) was added with stirring in small pieces to liquid NH_3 (ca. 4,500 ml.) containing ferric nitrate nonahydrate (2 g.). After dissolution was complete, tryptophan (I) (123 g., 0.60 mole) suspended in anhyd. Et_2O (appropriate amount) was added to the stirred mixture. After 30 min., MeI (114 g., 0.80 mole) was added dropwise over 15 min., and stirring was continued to evaporate NH_3. Water (350 ml.) was added to the residue and the mixture was heated to dissolve, filtered and adjusted to pH 5.0 with glac. AcOH (ca. 60 ml.) while hot, followed by the addition of EtOH (350 ml.). The mixture was allowed to stand in a refrigerator overnight. The resultant white precipitates were collected and washed successively with H_2O (400 ml.), 50% aq. EtOH (400 ml.), EtOH (400 ml.), Et_2O (400 ml.), showing m.p. 256~257.5° (decomp.), yield 126 g. (96.3%). Recrystallizations from 50% aq. EtOH afforded colorless scales, m.p. 269° (decomp.). (Reported m.p. 289°,[1a] 223~225°,[1b] 285°,[1c] 250~251°[2]). *Anal.* Calcd. for $C_{12}H_{14}O_2N_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 66.20; H, 6.75; N, 12.77. IR ν_{max}^{KBr} cm^{-1}: 3026, 2590, 2360 (NH_3^+), 1655 (NH_3^+), 1582 (COO^-), 1405 (COO^-), 728 (*o*-disubstituted benzene). Rf 0.67.

1-Ethyltryptophan (IIb)——Tryptophan (I) was alkylated with EtBr as above, and the product obtained as colorless plates (yield, 81%) from 50% aq. EtOH, m.p. 228~229° (decomp.). (Reported m.p. 225~226°[2]). *Anal.* Calcd. for $C_{13}H_{16}O_2N_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.07; H, 7.42; N, 12.23. IR ν_{max}^{Nujol} cm^{-1}: 2656, 2300 (NH_3^+), 1645 (NH_3^+), 1612 (COO^-), 726 (*o*-disubstituted benzene). Rf 0.71.

1-Allyltryptophan (IIc)——Allyl bromide was used under the same condition as above. Yield 71.8%. Recrystallizations from 80% aq. EtOH furnished colorless plates, m.p. 203~204° (decomp.) (dried over P_2O_5 *in vacuo* at 100~110° for 20 hr.). *Anal.* Calcd. for $C_{14}H_{16}O_2N_2 \cdot \frac{1}{2}H_2O$: C, 66.38; H, 6.77; N, 11.06. Found: C, 66.31; H, 6.83; N, 11.04. IR ν_{max}^{Nujol} cm^{-1}: ca. 3600 (H_2O), 2690, 2300 (NH_3^+), 1643 (C=C), 1590 (broad) (NH_3^+, COO^-), 1525 (NH_3^+), 991, 905 (CH_2=CH-), 744 (*o*-disubstituted benzene). Rf 0.75.

1-Benzyltryptophan (IId)——The reaction was carried out as above, from benzyl chloride and I. The product (yield, 71.9%) was purified from 80% aq. EtOH to colorless minute needles, m.p. 209~210° (decomp.) (dried over P_2O_5 *in vacuo* at 90~100° for 20 hr.). (Reported m.p. 214° as monohydrate[3]). *Anal.* Calcd. for $C_{18}H_{16}O_2N_2 \cdot \frac{1}{2}H_2O$: C, 71.26; H, 6.31; N, 9.24. Found: C, 71.51; H, 6.44; N, 8.98. IR ν_{max}^{Nujol} cm^{-1}: ca. 3600 (H_2O), 2705 (NH_3^+), 1588 (NH_3^+, COO^-), 1534 (NH_3^+), 743, 721, 705 (benzene). Rf 0.81.

L-1-Benzyltryptophan (L-IId)——L-Tryptophan (L-I) ($[\alpha]_D^{17}$ −33.3°, c=0.82, H_2O) was used. Yield, 92.8%. Colorless minute needles from 80% aq. EtOH, m.p. 211~212° (decomp.) (dried as IId). $[\alpha]_D^{17}$ −21.5° (c=0.06, DMF). *Anal.* Calcd. for $C_{18}H_{16}O_2N_2 \cdot \frac{1}{2}H_2O$: C, 71.26; H, 6.31; N, 9.24. Found: C, 70.96; H, 6.46; N, 9.39. IR ν_{max}^{Nujol} cm^{-1}: ca. 3600 (H_2O), 2700, 2600 (NH_3^+), 1627 (NH_3^+), 1605 (COO^-), 1403 (COO^-), 748, 722, 691 (benzene). Rf 0.81.

The IR spectrum of the L-isomer in Nujol was not superimposable with that of the racemate (IId).

N-Acetyl-1-methyltryptophan (IIa')——The amino acid (IIa) (1.0 g.) was dissolved in an approximately *N* NaOH (10 ml.). To this solution was added dropwise Ac_2O (3 ml.), with vigorous shaking over a period of an hour, followed by cooling with ice-water. The resultant white precipitates were filtered, washed successively with H_2O, 1% aq. HCl, 10% aq. HCl, and H_2O, showing m.p. 165~168°, yield 1.2 g. (nearly quantitative). Recrystallizations from a mixture of Me_2CO and benzene afforded colorless crystalline aggregates, m.p. 168~170°. (Reported m.p. 171~172°,[1b,7] 169.5~170.5°[2]). The mixed melting point with the authentic IIa' (m.p. 168~169°, prepared according to the method of Snyder, *et al.*[7]) showed no depression. The IR spectra were virtually identical. IR ν_{max}^{Nujol} cm^{-1}: 3430 (NH), 1730 (COOH), 1608 (Amide I), 1533 (Amide II), 736 (*o*-disubstituted benzene).

Debenzylation of L-1-Benzyltryptophan (L-IId)

L-Tryptophan (L-I)——The L-isomer of IId (3.5 g., 0.017 mole) was dissolved in liquid NH_3 (ca. 300 ml.) with stirring, to which K (2.65 g., 0.068 atom) was added in small pieces to give rise to a permanent blue

*4 All melting points are uncorrected. The IR absorption spectra were measured with a Koken Model DS-301 spectrophotometer equipped with NaCl optics. A Yanagimoto Photo-Magnetic polarimeter Model OR-20 was used for the measurement of optical rotation. Paper chromatography was carried out on Toyo Roshi No. 50 filter paper using a solvent of BuOH–AcOH–H_2O (4 : 1 : 2.5). Spots were detected as usual by spraying with 5% solution of ninhydrin in Me_2CO.

*5 1-Methyl series are described as typical examples.

color. After Amberlite IR-120 (NH_4^+-form*6) (15.6 g.) was added to the mixture with stirring, NH_3 was allowed to evaporate. The resin and the residue were washed thrice with hot H_2O (100 ml., 100 ml., 50 ml.), filtered, and the filtrate was washed with Et_2O, concentrated to 20 ml., and made pH 5.9 with AcOH. After the addition of EtOH (5 ml.) and kept standing in a refrigerator overnight, the brownish white precipitates (yield, 1.73 g., m.p. 238~244°(decomp.)) were collected, and recrystallized from 65% aq. EtOH (charcoal) to give colorless leaflets, m.p. 248~249°(decomp.). $[\alpha]_D^{17}$ −33.1° (c=0.14, H_2O). *Anal.* Calcd. for $C_{11}H_{12}O_2N_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.79; H, 6.08; N, 13.86. IR ν_{max}^{KBr} cm^{-1}: 3470 (ind.-NH), 3027, 2600 (NH_3^+), 1671 (NH_3^+), 1596 (COO^-), 1411 (COO^-), 743 (*o*-disubstituted benzene). Rf 0.58.

The IR spectrum was superimposable with that of L-tryptophan.

Esterification of 1-Alkyltryptophans (II)*5

1-Methyltryptophan Methyl Ester Hydrochloride (IIIa)——The amino acid (IIa: 113 g., 0.52 mole) in 10 w/v% MeOH-HCl (850 ml.) was gently refluxed at 80~90° (bath temp.) for 5 hr., and the mixture was allowed to stand in a refrigerator overnight. The crystals precipitated were collected and washed with MeOH (100 ml.), MeOH-Et_2O (1 : 1) (100 ml.), Et_2O (200 ml.), showing m.p. 225°(decomp.), yield 132 g. (94.5%). Recrystallizations from MeOH afforded colorless needles, m.p. 227.5°(decomp.). *Anal.* Calcd. for $C_{13}H_{16}O_2N_2 \cdot HCl$: C, 58.10; H, 6.00; N, 10.42. Found: C, 58.20; H, 6.04; N, 10.25. IR ν_{max}^{Nujol} cm^{-1}: 3000, 2630, 2370 (NH_3^+), 1745 ($COOCH_3$), 1577, 1501 (NH_3^+), 1241 ($COOCH_3$), 727 (*o*-disubstituted benzene).

1-Ethyltryptophan Methyl Ester Hydrochloride (IIIb)——Esterification was carried out as above from IIb. Yield, 68.8%. Recrystallizations from benzene-MeOH (5 : 1) gave colorless needles, m.p. 203~204°(decomp.). *Anal.* Calcd. for $C_{14}H_{18}O_2N_2 \cdot HCl$: C, 59.47; H, 6.77; N, 9.91. Found: C, 59.58; H, 6.39; N, 9.56. IR ν_{max}^{Nujol} cm^{-1}: 2610 (NH_3^+), 1749 ($COOCH_3$), 1514 (NH_3^+), 1262 ($COOCH_3$), 733 (*o*-disubstituted benzene).

1-Allyltryptophan Methyl Ester Hydrochloride (IIIc)——The amino acid (IIc) was esterified in a yield of 87.1% as described above. Recrystallization from MeOH gave colorless needles, m.p. 195° (decomp.). *Anal.* Calcd. for $C_{15}H_{18}O_2N_2 \cdot HCl$: C, 61.11; H, 6.50; N, 9.50. Found: C, 60.87; H, 6.64; N, 9.12. IR ν_{max}^{Nujol} cm^{-1}: 3065, 2610 (NH_3^+), 1747 ($COOCH_3$), 1645 (C=C), 1517 (NH_3^+), 1260 ($COOCH_3$), 994, 925 (CH_2=CH-), 735 (*o*-disubstituted benzene).

1-Benzyltryptophan Methyl Ester Hydrochloride (IIId)——The methyl ester hydrochloride was obtained in 92.2% yield, and recrystallized several times from MeOH-benzene as colorless scales, m.p. 198~198.5° (decomp.). *Anal.* Calcd. for $C_{19}H_{20}O_2N_2 \cdot HCl$: C, 66.18; H, 6.14; N, 8.12. Found: C, 66.31; H, 6.30; N, 7.83. IR ν_{max}^{Nujol} cm^{-1}: 2620, 2540 (NH_3^+), 1752 ($COOCH_3$), 1609 (NH_3^+), 1500 (NH_3^+), 1249 ($COOCH_3$), 750, 725, 706 (benzene).

Isolation of the Free Bases of Methyl Esters from the Hydrochlorides (III)*5

1-Methyltryptophan Methyl Ester——The hydrochloride (IIIa) (8.03 g., 0.03 mole) suspended in cold Et_2O (160 ml.) was vigorously shaken with 20 w/v% aq. K_2CO_3 (42 ml., 0.06 mole). After dissolution was complete, the aqueous layer was separated and extracted with Et_2O (4×20 ml.). The combined Et_2O layer was washed with H_2O (2×10 ml.) and satd. aq. NaCl (2×10 ml.), dried over Na_2SO_4, and evaporated *in vacuo* to give a yellow viscous transparent oil (6.50 g., 93.3%). It distilled at 196~197°/3 mm. Hg (IR $\nu_{max}^{Cap.}$ cm^{-1}: 3375, 3320 (NH_2), 1729 ($COOCH_3$), 1213, 1170 ($COOCH_3$), 737 (*o*-disubstituted benzene)) with the formation of a considerable amount of the diketopiperazine.

In the case of 1-benzyl derivative (IIId, m.p. 179~180°(decomp.)) dil. NaOH was used on behalf of aq. K_2CO_3, because aq. K_2CO_3 layer became gelatinous and the separation of Et_2O- and aq. K_2CO_3-layers was difficult.

Hydrazinolysis of 1-Alkyltryptophan Methyl Esters*5

1-Methyltryptophan Hydrazide (IVa)——A mixture of the crude 1-methyltryptophan methyl ester (5.0 g., 0.022 mole) and hydrazine hydrate (1.2 g., 0.024 mole) in EtOH (1 ml.) was refluxed at 115~125° (bath temp.) for 3 hr., and evaporated *in vacuo* to dryness. Recrystallization of the residue from benzene (0.1 g. of IIa was obtained as an insoluble solid) gave slightly yellow plates of m.p. 86~89°, yield 4.85 g., 97%. It was recrystallized from benzene, after purification in benzene-$CHCl_3$ through Al_2O_3, to colorless scales of m.p. 88~90°. *Anal.* Calcd. for $C_{12}H_{16}ON_4$: C, 62.05; H, 6.94; N, 24.12. Found: C, 61.90; H, 7.18; N, 23.55. IR ν_{max}^{Nujol} cm^{-1}: 3365, 3320, 3240 (NH_2), 1643 (Amide I), 1603 (NH_2), 1529 (Amide II), 733 (*o*-disubstituted benzene).

1-Ethyltryptophan Hydrazide (IVb)——1-Ethyltryptophan methyl ester was subjected to hydrazinolysis as above. The product (yield, nearly quantitative) was recrystallized from benzene to give colorless pillars, m.p. 111.5~112.5°. *Anal.* Calcd. for $C_{13}H_{18}ON_4$: C, 63.39; H, 7.37; N, 22.75. Found: C, 63.62; H, 7.08; N, 22.59. IR ν_{max}^{Nujol} cm^{-1}: 3345, 3315, 3240 (NH_2), 1650 (Amide I), 1620 (NH_2), 1532 (Amide II), 730 (*o*-disubstituted benzene).

1-Allyltryptophan Hydrazide (IVc)——Anhyd. hydrazine was used in the case of 1-allyltryptophan methyl ester. Yield was nearly quantitative. Recrystallizations from benzene afforded colorless small

*6 The Amberlite IR-120 resin (200~400 mesh) was washed successively with *N* HCl, H_2O, *N* NH_3, H_2O, and dried at 70°. cf. J. M. Swan, V. du Vigneaud: J. Am. Chem. Soc., **76**, 3110 (1954).

pillars, m.p. 100.5~101°. *Anal.* Calcd. for $C_{14}H_{18}ON_4$: C, 65.09; H, 7.02; N, 21.69. Found : C, 65.55; H, 7.26; N, 21.68. IR ν_{max}^{Nujol} cm^{-1} : 3360, 3320, 3230 (NH_2), 1650 (broad) (Amide I, NH_2), 1523 (Amide II), 990, 910 (CH_2=CH-), 730 (*o*-disubstituted benzene).

1-Benzyltryptophan Hydrazide Sulfate (IVd)——The hydrazide was synthesized from 1-benzyltryptophan methyl ester and anhyd. hydrazine in EtOH, but failed to crystallize. IR $\nu_{max}^{Cap.}$ cm^{-1} : 3345 (broad) (NH_2), 1670 (broad) (Amide I), 1613 (NH_2), 1555 (Amide II), 740 (broad), 699 (benzene).

Sulfate was obtained from equivalent molecules of the crude hydrazide and 95% aq. H_2SO_4 in EtOH-Et_2O (1:2). Yield was quantitative. Recrystallizations from 30% aq. EtOH (charcoal) afforded colorless granules, showing m.p. 222° (decomp.). *Anal.* calcd. for $C_{18}H_{20}ON_4 \cdot H_2SO_4$: C,53.19; H, 5.46; N, 13.79. Found: C, 53.24; H, 5.53; N, 13.50. IR ν_{max}^{Nujol} cm^{-1} : 3200~2600 (broad) (NH_3^+), 1708 (Amide I), 1609 (NH_3^+), 1549 (Amide II), 1111, 1064, 1030 (SO_4^{--}?), 732, 700 (benzene).

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Summary

A convenient method for the synthesis of 1-alkyltryptophans is described. The proof of ind.-N-alkylation was obtained from several data. Effect of 1-alkyl substitution of indole was observed on the ultraviolet spectra of 1-alkyltryptophans. It was confirmed by debenzylation of L-1-benzyltryptophan in liquid ammonia that no racemization had occurred in the alkylation. 1-Alkyltryptophans were converted to hydrazides *via* methyl ester hydrochlorides in good yields.

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Yutaka Fujise, Takashi Toda, and Shô Itô : Isolation of Trifolirhizin from *Ononis spinosa* L.

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In an attempt to isolate α-onocerin from material identified as *Ononis spinosa* L., Professor Stork at Columbia University obtained an acetate, m.p. 188~189°, which on alkaline hydrolysis afforded a compound, m.p. 223°, different from α-onocerine, m.p. 202~203°. Described in this paper is a chemical investigation of these compounds, generously provided by Professor Stork, which has shown them to be identical with trifolirhizin (maackiain glucoside) and its tetraacetate.

We have encountered some difficulty in obtaining constant figures for the elementary analyses of the compound of m.p. 223° (I) because of its great tendency to occlude solvent molecules. The melting point of the compound also varied considerably depending on the state of dryness. Finally, after for a long time at an elevated temperature, constant analytical values were obtained to establish the molecular formula as $C_{22}H_{22}O_{10}$. On the other hand, micro analysis of the acetate (II) presented no difficulty and gave constant figures for a molecular formula of $C_{30}H_{30}O_{14}$ when the molecular weight as determined by osmotic method and the Rast method is taken into consideration. An acetoxyl determination showed the presence of four acetoxyl groups. The infrared spectrum of compound (I) had hydroxyl absorption but none dues to carbonyl groupings, whereas that of the acetate

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