

Effects of gamma radiation on polymer in solution. II. Poly (vinyl methyl ether). Ichiro Sakurada and Yoshito Ikada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 16 (1962).

Effects of gamma radiation on polymer in solution. III. Poly (vinyl alcohol) partially acetalized with glycoxylic acid. Ichiro Sakurada and Yoshito Ikada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 25 (1962).

Shrinkproofing of wool by permanganate / sodium chloride treatment. Masao Horio, Chikaaki Sakai, Takashi Kondo and Ken'ichi Sekimoto. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 351 (1962).

Comparison between the effect of permanganate / sodium chloride and that of permanganate / water upon wool. Masao Horio, Chikaaki Sakai, Takashi Kondo and Ken'ichi Sekimoto. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 358 (1962).

Theory of multi-coordination centered catalyst. A proposed mechanism of stereoregular polymerization. Junji Furukawa. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 130 (1962).

Stereoregular polymerizations of acrylic ester and its related monomers. Teiji Tsuruta and Junji Furukawa. *Bull. Inst. Chem. Res., Koto Univ.*, **40**, 151 (1962).

Preparation of polyether. Junji Furukawa and Takeo Saegusa. *Bull. Inst. Chem. Res., Koto Univ.*, **40**, 171 (1962).

Study on vulcanization promoters. Junji Furukawa, Shinzo Yamashita and Ryuzo Yamamoto. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 197 (1962).

Preparation of active calcium carbonate for reinforcing SBR. Junji Furukawa, Shinzo Yamashita, Hiroshi Niwa, Minoru Fukuda and Teizo Kotani. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 211 (1962).

Organic Chemistry

New addition reactions. II. Addition of aliphatic epoxides to Schiff bases. Ryohei Oda, Masaya Okano, Shohei Tokiura and Akira Miyasu. *Bull. Chem. Soc. Japan*, **35**, 1216 (1962).—See, this Bulletin, **40**, 406 (1962).

New addition reactions. III. Addition of aliphatic epoxides to nitriles. Ryohei Oda, Masaya Okano, Shohei Tokiura and Fujio Misumi. *Bull. Chem. Soc. Japan*, **35**, 1219 (1962).—See, this Bulletin, **40**, 406 (1962).

New addition reactions. IV. The addition of Schiff bases to diketene. Ryohei Oda, Shunichi Takashima and Masaya Okano. *Bull. Chem. Soc. Japan*, **35**, 1843 (1962).—See, this Bulletin, **41**, 223 (1963).

Studies of 2-oxazolidinones. I. A convenient synthesis of 3-substituted 2-oxazolidinones. Ryohei Oda, Masahiko Miyanoki and Masaya Okano. *Bull. Chem. Soc. Japan*, **35**, 1309 (1962).—See, this Bulletin, **41**, 222 (1963).

Studies of 2-oxazolidinones. II. Products of the pyrolysis of some 2-oxazolidinones. Ryohei Oda, Masahiko Miyanoki and Masaya Okano, *Bull. Chem. Soc. Japan*, **35**, 1910 (1962).—See, this Bulletin, **41**, 222 (1963).

Studies of 2-oxazolidinones III. Kinetics of the pyrolytic decarboxylation of 2-oxazolidinones. Ryohei Oda, Masahiko Miyanoki and Masaya Okano. *Bull. Chem. Soc. Japan*, **35**, 1915 (1962).—See, this Bulletin, **41**, 222 (1963).

Reaction of methylal with carbon monoxide under high pressure. Yoshimasa Takezaki, Nobuyuki Sugita, Sachio Yuasa and Tasuo Ota. *Koatsugasu Kyokai Shi*, **26**, 12 (1962).

Reaction of methyl radical with dimethyl disulfide. Masakazu Suama and Yoshimasa Takezaki. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 229 (1962).

The rates of reaction of sodium borohydride with some representative ketones. Herbert C. Brown and Katsuhiko Ichikawa. *J. Am. Chem. Soc.*, **84**, 373 (1962).—The rates of reaction of sodium borohydride with representative ketones in isopropyl alcohol have been determined at several temperatures, yielding values for the relative rates at 0°, and for the enthalpies and entropies of activation. The relative rates decrease from acetone (1.00), to diethyl ketone (0.101) to di-*n*-propyl ketone (0.0291). Further lengthening of the chain has little effect: di-*n*-butyl ketone (0.0403) and di-*n*-hexyl ketone (0.0300). Branching of the alkyl groups also results in a rate reduction: acetone (1.00), methyl ethyl ketone (0.417), methyl isopropyl ketone (0.195), methyl *t*-butyl ketone (0.0815). The presence of two branched alkyl groups decreases the rate considerably beyond that estimated from the effect of a single branched group: acetone (1.00), diethyl ketone (0.101), diisopropyl ketone (0.00551), di-*t*-butyl ketone (0.000191). The marked decrease accompanying the introduction of two bulky bulky groups is attributed to steric effects. A modest decrease is observed with chain branching in the phenyl alkyl ketones, with a sudden large increase in the phenyl *t*-butyl derivative: acetophenone (0.136), phenyl ethyl ketone (0.0756); phenyl isopropyl ketone (0.0709); phenyl isobutyl ketone (0.0111), phenyl *t*-butyl ketone (2.47). The effect of the *t*-butyl group is attributed to its large steric requirements which force the acyl group from its preferred configuration, coplanar with the aromatic ring, causing a reduction in the resonance interactions and permitting the phenyl group to exert its normal-I inductive effect. The data are compared with the rates of solvolysis of the related tosylates to test the proposal that the ketones may be taken as reasonable models for carbonium ions of related structures.

The kinetics of the reactions of β -acetoxyethylmercuric, β -acetoxypropylmercuric and β -acetoxy- β -phenylethylmercuric acetate with aromatic substance. Ka-

tsuhiko Ichikawa, Koichi Fujita and Osamu Itoh. *J. Am. Chem. Soc.*, **84**, 2632 (1962). The reaction rates of β -acetoxyethylmercuric, β -acetoxypropylmercuric and β -acetoxy- β -phenylethylmercuric acetate with aromatic substances have been studied in acetic acid-perchloric acid-water systems. The results showed that the reactivity order of various aromatics is the same with those in the usual electrophilic aromatic substitutions. The relative rates of the three mercurials mentioned above with anisole were 1.0, 1.3 and 710, respectively, under the same conditions. From these results, the mechanism is discussed as an electrophilic aromatic substitution. As a preliminary experiment for the rate study above, the stabilities of the mercurials in acetic acid containing perchloric acid have been studied and the stoichiometry, rates and mechanism of the decompositions are reported.

The reaction of lead tetraacetate with anethole: addition equilibria and kinetics. Katsuhiko Ichikawa, Yoshiichi Takeuchi and Osamu Itoh. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 317 (1962).

Studies on lactone formation in vapor phase. II. Synthesis of ϵ -caprolactone. Shinzaburo Oka. *Bull. Chem. Soc. Japan*, **35**, 562 (1962).—See, this Bulletin, **41**, 221 (1963),

Studies on lactone formation in vapor phase. III. Mechanism of lactone formation from diols. Shinzaburo Oka. *Bull. Chem. Soc. Japan*, **35**, 986 (1962).—See, this Bulletin, **41**, 221 (1963),

Direct synthesis of organotin compounds. III. Reaction of α -substituted benzyl halides with metallic tin. Keiiti Sisido, Yosiyuki Takeda and Hitosi Nozaki. *J. Org. Chem.*, **27**, 2411 (1962).—Wurtz condensation products, instead of organotin compounds, were obtained in the reaction of metallic tin powder with diphenylmethyl chloride, α -phenylethyl chloride, anethole hydrobromide, and benzaal chloride, respectively, in boiling toluene as a solvent. When the reaction was carried out in water suspension, hydrolysis occurred along with the condensation. Bis(diphenylmethyl) tin dichloride was prepared from diphenylbis(diphenylmethyl) tin by the preferential cleavage of phenyl groups, and the reaction of diphenylmethylpotassium or -magnesium bromide with stannic chloride was examined.

The stereochemistry of 9,10-dihydro-9,10-o-xylyleneanthracene derivatives. Keiiti Sisido, Ryozi Noyori and Hitoshi Nozaki. *J. Am. Chem. Soc.*, **84**, 3562 (1962).—Ten derivatives of 9,10-dihydro-9,10-o-xylyleneanthracene (I) substituted at the methylene group(s) (II-XI) have been prepared and the stereochemistry of these new compounds has been examined by means of their spectrographic properties. Attention is focused on the conformational equilibrium of three possible forms as exemplified by Ia, Ib and Ic. All four ketones (VIII-XI) show absorption spectra which are conceivable only by assuming coplanarity of the 9,10-bridging groups, for example, IXb being preferred to IXa. The *trans*-configuration is tentatively assigned to the diol VII and the process of substitution on the methylene group of I discussed

Cyclization of N-phenylcarbamates of ethynylcarbinols. Keiiti Sisido, Keisuke Fukuoka, Minoru Tuda and Hitosi Nozki. *J. Org. Chem.*, **27**, 2663 (1962).

Vinylogy in alkylation of *t*-butyl esters. Keiiti Sisido, Kacuo Sei and Hitosi Nozaki, *J. Org. Chem.*, **27**, 2681 (1962).

Aromatische Verbindungen aus Blätteralkoholen. Akikazu Hatanaka, Minoru Ohno und Yuzo Inouye. *Angew. Chem.*, **74**, 291 (1962)—Aromatische Verbindung, 2-Propyl-5-äthyl-benzylkohol wurde aus Blätteralkohl dargestellt.

Blätteralkohol. (X). Aromatische Verbindung aus dem Blätteralkohol. Minoru Ohno, Akikazu Hatanaka und Yuzo Inouye. *Agr. Biol. Chem.*, **26**, 460 (1962)—Durch Erhitzen von 3-*cis*-Hexen-1-ol (Blätteralkohol) mit Natrium wurde die aromatische Verbindung (2-Propyl-5-äthyl-benzylkohol) hergestellt und auch aus 3-*trans*-, 2-*cis*- oder 2-*trans*-Hexen-1-ol, oder aus 2-*trans*-Hexen-1-al (Blätteraldehyd) wurde die gleiche Verbindung erhalten. Durch eine gleiche Reaktion, wurde aus 3-Penten-1-ol die aromatische Verbindung (2-Äthyl-5-methyl-benzylkohol) und aus 2-*trans*-Buten-1-ol wurde 2-Methylbenzylalkohol erhalten. Wir möchten besonders diese interessante Reaktion, bei der aus $\alpha\beta$ - oder $\beta\gamma$ -ungesättigten, *n*-primären Alkoholen Benzylalkohole mit verschiedenen Substitutionen hergestellt werden, als „Blätteralkohol-Reaktion“ bezeichnen.

Blätteralkohol und Blätteraldehyd. Minoru Ohno und Akikazu Hatanaka. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 322 (1962).

Studies on the syntheses of the pyrethrin analogues and their biological activities. Saburo Takei. *Botyu-Kagaku*, **27**, 51 (1962), in Japanese.—See, this Bulletin, **40**, 409 (1962).

Studies on the syntheses of the pyrethrin analogues and their biological activities. II. Relationship between the stereochemistry and the biological activities. Saburo Takei, Yuzo Inouye, Minoru Ohno and Sankichi Takei. *Agr. Biol. Chem.*, **26**, 362 (1962).—See, this Bulletin, **40**, 410 (1962).

Partial asymmetric synthesis in the conjugate addition of a Grignard reagent to an α, β -unsaturated ester. Yuzo Inouye and H. M. Walborsky. *J. Org. Chem.*, **27**, 2706 (1962).—See, this Bulletin, **40**, 406 (1962).

Studies on the alkaloids of *Thalictrum Thunbergii* DC. IX. Structure of thalictrine and homothalictrine, the tertiary bases in the root. (1). Eiichi Fujita, Toshiaki Tominatsu and Yoko Kano. *Yakugaku Zasshi*, **82**, 311 (1962), in Japanese.—From the root of *Thalictrum Thunbergii* DC. (Japanese name "Akikaramatsu") growing in Tokushima, a new tertiary phenolic base, thalictrine, was isolated as colorless needles, m.p. 221~222°, $[\alpha]_D + 341.2^\circ$ (CHCl₃), and a new non-phenolic base, homothalictrine, as colorless cubic crystals, m.p. 235~236° (decomp.), $[\alpha]_D + 425.3^\circ$ (CHCl₃). O-Methylthalictrine, obtained by brief methylation of thalictrine with dia-

zomethane, was found to be identical with homothalictine, from its elemental analytical values, melting point, and infrared spectrum (in chloroform). Composition and empirical formula of thalictine agree with $C_{35}H_{38}O_6N_2 = C_{32}H_{25}O_3(OH)(OCH_3)_2(NCH_3)_2$ and those of homothalictine with $C_{37}H_{40}O_6N_2 = C_{32}H_{25}O_3(OCH_3)_3(NCH_3)_2$. The Hofmann degradation of thalictine dimethochloride and oxidation of its methylmethine with potassium permanganate afforded 4-methoxy-3,4'-oxydibenzoic acid (I). The same Hofmann degradation of O-ethylthalictine and permanganate oxidation of its methylmethine afforded an acid of m.p. 274~275°. In order to elucidate the structure of this acid, O-ethylberbamine (II) was submitted the same degradation and oxidation, and authentic sample of 4-ethoxy-3,4'-oxydibenzoic acid (V) thereby obtained was found to be identical with the foregoing acid of m.p. 274~275° in melting point and infrared spectrum (in Nujol). From these experimental evidences and ultraviolet spectra, the two bases here obtained were considered to be new bases of the biscoclaurine type. It was also proved that the phenolic hydroxyl in thalictine is in the position *ortho* to the ether bond connecting the two phenyl rings and *para* to the benzyl group.

Studies on the alkaloids of *Thalictrum Thunbergii* DC. X. Structure of thalictine and homothalictine. (2). Toshiaki Tominatsu and Yoko Kano. *Yakugaku Zasshi*, 315 (1962), in Japanese.—The presence of one cryptophenolic hydroxyl in each of the new bases, thalictine and homothalictine, was proved by the following facts. Homothalictine and its methylmethine are both insoluble in alkali hydroxide or Claisen solution but are positive to the Millon and ammonium phosphomolybdate reactions. Both have a sharp absorption at 3580cm^{-1} in their infrared spectra. Methylation of thalictine and homothalictine with excess diazomethane for two weeks gave identical O-methyl ether (O,O-dimethylthalictine or O-methylhomothalictine), in which two and one methoxyl group had been formed respectively in thalictine and homothalictine. Methylation only for a few days was found to give homothalictine from the former and recovery of the starting material from the latter. Cleavage reaction of O-methylhomothalictine (I) with metallic sodium in liquid ammonia was found to result in almost quantitative fission into two components, *d*-armepavine (II) and *l*-1-(4-methoxybenzyl)-2-methyl-6-hydroxy-7-methoxy-1,2,3,4-tetrahydroisoquinoline (III). From earlier experiments, the phenolic hydroxyl in the benzyl group of (II) should have been formed by severance of the ether-oxygen connecting the phenyl group with benzyl group and the phenolic hydroxyl in 6-position of (III) should have been formed by severance of ether-oxygen connecting the two phenyl groups. The other end of the ether bond in (III) was considered to be in 8-position of the isoquinoline ring, from analogy with biogenesis of this type of natural bases. Consequently, the chemical structure of thalictine and homothalictine would be a new base formed by substitution of one of the three methoxyls on the isoquinoline side in (VIII: R=H) and (VIII: R=CH₃) with cryptophenolic hydroxyl.

Studies on the alkaloids of *Thalictrum Thunbergii* DC. XI. Structure of thalictine and homothalictine. (3). Toshiaki Tominatsu and Yoko Kano. *Yakugaku Zasshi*, 82, 320 (1962), in Japanese.—In order to prove the position of cryptophenolic

hydroxyl present in the new bases, thalicrine and homothalicrine, cleavage reaction of O,O-diethylthalicrine (VI) with metallic sodium in liquid ammonia was carried out. It was thereby confirmed that the base is severed almost quantitatively into two parts, *d*-1-(4-hydroxybenzyl)-2-methyl-6-methoxy-7-ethoxy-1,2,3,4-tetrahydroisoquinoline (VII) and *l*-1-(4-ethoxybenzyl)-2-methyl-6-hydroxy-7-methoxy-1,2,3,4-tetrahydroisoquinoline (IX). It follows, therefore, that the cryptophenolic hydroxyl in thalicrine and homothalicrine is present in 7-position of the benzylisoquinoline ring on the left side of the formulae (XXI) and (XXII), which are proposed as the chemical structures of thalicrine and homothalicrine, by the summation of experimental evidences obtained to date. It goes without saying that the steric configuration (direction of optical rotation) of the two asymmetric centers in the two bases is (+, -) in both.

Studies on the alkaloids of *Thalictrum Thunbergii* DC. XII. Difference of quaternary bases by the grown district of plants. Toshiaki Tominatsu, Matao Matsui, Akira Uji and Yoko Kano. *Yakugaku Zasshi*, 82, 1560 (1962), in Japanese.—Experimental evidences suggest that the bases contained in *Thalictrum thunbergii* DC. (Japanese name "Akikaramatsu") differs slightly by its habitat. In order to elucidate this point, the root of this plant collected in Nagano Prefecture was processed and a comparatively large amount of magnoflorine (I) was obtained, while its leaves and stems yielded takatonine (II). The leaves and stems of the same plant collected in Kochi Prefecture yielded magnoflorine (I) and berberine (III).

Studies on the alkaloids of *Thalictrum actaeifolium* Sieb. et Zucc. I. On the quaternary base. (1). Matao Matsui, Toshiaki Tomimatsu and Eiichi Fujita. *Yakugaku Zasshi*, 82, 308 (1962), in Japanese.—A quaternary base, berberine (II), was isolated and identified from the whole herb of *Thalictrum actaeifolium* Sieb. et Zucc. (Japanese name "Shigin-karamatsu"). A quaternary base was also isolated from the root of the same plant growing in Gifu Prefecture but the base did not crystallize. It was identified by derivation to tetrahydroberberine (III) by reduction with zinc dust and acetic acid. Other quaternary bases are under investigation yet due to the minute amount available.

***l*-N-Norarmepavine.** S. Morris Kupchan, B. Dasgupta, Eiichi Fujita and M. L. King. *J. Pharm. Sci.*, 51, 599 (1962).—A new alkaloid was isolated from American lotus, *Nelumbo lutea* (Willd.) Pers. (*Nymphaeaceae*), and characterized as *l*-(*l*)-N-norarmepavine.

The tiglate ester as an alcohol blocking group in organic synthesis. S. Morris Kupchan, A. D. J. Balon and Eiichi Fujita. *J. Org. Chem.*, 27, 3103 (1962).—The effective use of the tiglate ester as an easily formed and readily cleaved alcohol blocking group is described.

Veratrum alkaloids L. Structure-activity relationship in a series of synthetic hypotensive analogs of the protoveratrine. S. Morris Kupchan, Eiichi Fujita, John

C. Grivas and Lawrence C. Weaver. *J. Pharm. Sci.*, **51**, 1140 (1962).—A study aimed at further elucidation of the relationship between hypotensive activity and structure among analogs of the protoveratrinines is reported. A series of synthetic protoverine tetraesters, which differ from each other only in the nature of the acid residue affixed at C₁₅, have been prepared and subjected to preliminary pharmacological evaluation. The results indicate that alteration in the structure of the ester affixed at C₁₅ in analogs of the protoveratrinines profoundly affects hypotensive potency.

Biochemistry

Syntheses of analgesics. XXVIII. Syntheses and pharmacological action of isoxazole derivatives. (1). Torizo Takahashi, Hajime Fujimura and Atsushi Asai. *Yakugaku Zasshi*, **82**, 474 (1962), in Japanese.—See, this Bulletin, **40**, 408 (1962).

Syntheses of analgesics. XXIX. Syntheses and pharmacological action of isoxazole derivatives. (2). Torizo Takahashi, Hajime Fujimura and Atsushi Asai. *Yakugaku Zasshi*, **82**, 481 (1962), in Japanese.—See, this Bulletin, **40**, 408 (1962).

Syntheses of analgesics. XXX. Indanamine derivatives. (1). Torizo Takahashi, Hajime Fujimura and Kentaro Okamura. *Yakugaku Zasshi*, **82**, 1597 (1962), in Japanese.—See, this Bulletin, **41**, 224 (1963).

Syntheses of 1-phenyl-2-thiobarbituric acid derivatives and their analgesic activity. Jutaro Okada, Hajime Fujimura and Yoshiko Ueda. *Yakugaku Zasshi*, **82**, 976 (1962), in Japanese.—See, this Bulletin, **40**, 407 (1962).

A pharmacological study of 6-hydroxy-4a, 10-trimethylene-1,2,3,4,4a,9,10,10a-octahydrophenanthridine. Hajime Fujimura, Norio Sugimoto and Goro Hayashi. *Japan. J. Pharmacol.*, **11**, 101 (1962).—See, this Bulletin, **40**, 194 (1962).

γ -L-Glutamyl-S-allyl-L-cysteine. A new γ -glutamyl peptide in garlic. Tomoji Suzuki, Michiyasu Sugii and Toshio Kakimoto. *Chem. Pharm. Bull.*, **10**, 345 (1962).—During the studies of the sulfur containing amino acid and the related compound in garlic, the present authors have isolated a new γ -glutamyl peptide in crystalline state and confirmed that the crystals are monoammonium salt of γ -L-glutamyl-S-allyl-L-cysteine. The new peptide showed R_f values of 0.61 (PhOH·0.08% NH₄OH=4:1) and 0.47 (BuOH·AcOH·H₂O=5:1:4). m.p. 187–188° (decomp.) [α]_D²⁰ -29.7 (in H₂O).

Metabolism of S-(2-carboxypropyl)-glutathione in rabbit. Tomoji Suzuki, Michiyasu Sugii and Toshio Kakimoto. *Chem. Pharm. Bull.*, **10**, 346 (1962).—A female rabbit was injected intravenously with S-(2-carboxypropyl)-glutathione (I) and the urine was analyzed. The result indicated that S-(2-carboxypropyl) cysteine and N-acetyl-S-(2-carboxypropyl) cysteine were formed from (I) *in vivo*.

Metabolic incorporation of L-valine-[¹⁴C] into S-(2-carboxypropyl)-glutathione and S-(2-carboxypropyl)-cysteine in garlic. Tomoji Suzuki, Michiyasu Sugii and