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Determination of 3-keto-valproate in urine by metal capillary gas chromatography.

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A simple and rapid determination of 3-keto-valproate(3-keto-VPA) in urine is described by a metal capillary gas chromatography(GC). 3-keto-VPA was converted to 3-heptanone under acidic condition. 3-Keto-VPA-glucuronide was hydrolyzed to 3-keto-VPA by β-D-glucuronidase. 3-Heptanone formed was determined by GC. Suitable conditions for decarboxylation of 3-keto-VPA and hydrolysis of 3-keto-VPA ethyl ester were also investigated. The present procedure does not require any derivatization. Classificable determination of free 3-heptanone, free 3-keto-VPA and 3-keto-VPA-glucuronide were possible. A deactivated metal capillary column was applied for the determination of urinary 3-keto-VPA; its minimum detectable amount was about 0.1 μg/ml in urine.

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Comparison of derivatization of malonaldehyde with phenylhydrazines for HPLC.

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Malonaldehyde(MA) reacted with phenylhydrazines to form pyrazole derivatives. The behavior of the three hydrazines, 2,4-dinitrophenyl-(DNPH), p-nitrophenyl-(NPH) and phenyl-(PhH), in the reaction with MA was compared by HPLC. A Shimadzu LC-5A HPLC equipped with a UV detector(315 nm for DNPH-MA and NPH-MA, 265 nm for PhH-MA) was used for the analysis. A metal column (250×4.6 mm I.D.) was packed with ODS-5. Elution was carried out with CH_3CN-0.01M HCl(40:60, v/v) at a flow rate of 1.5 ml/min. The reaction of MA with DNPH required a strongly acidic condition, while NPH and PhH reacted well with MA in a weakly acidic medium. The highest peak of the three derivatives was observed from reation with NPH.

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New Description of the Substituent Effect on Electronic Spectra by Means of Substituent Constants. VI. Ultraviolet Spectra of 4-Substituted Pyridine *N*-Oxides and Blue Shifted Iodine Bands of Their EDA Complexes with Iodine.

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Electronic spectra of 4-substituted pyridine *N*-oxides and their EDA complexes with iodine were studied. The substituent effect on the near UV $^1A_1$ intramolecular CT bands of the *N*-oxides and on the blue shifted iodine bands caused by the CT complex formation are discussed in terms of a general equation, theoretically derived in order to describe the substituent effect on electronic spectra by means of substituent constants. The results are quite successful and supported by semiempirical SCFMO-CI calculations.