led to the conclusion that picrasin D has the structure I.

Picrasin E, mp 293—295°, has the composition $C_{22}H_{30}O_7$ (M^+ at m/e 406 in MS). The functional groups are similar to those of picrasin D. Thus the presence of an α,β-disubstituted, α,β-unsaturated carbonyl in a six- or larger-membered ring (λ_{max} 262 nm, ν_{max} 1700, 1637 cm^{-1}, δ 5.18 ppm, $[\theta]_{342}$ -1070), a δ-lactone (ν_{max} 1715 cm^{-1}, δ 4.74 ppm), a methoxyl (δ 3.46 ppm), a methylene dioxy ring, (δ 5.11, 5.26 ppm ($J=1$ Hz)), two secondary methyls (δ 0.90, 1.26 ppm) and two tertiary methyls (δ 1.31, 1.46 ppm) are indicated. Analysis of the NMR spectrum has demonstrated that picrasin E also possesses the same part structures (a and b). Further, the chemical shifts and splitting patterns of certain NMR signals and ORD and CD data of picrasin E are in good accord with those of picrasin D, indicating that picrasin E is a derivative of picrasin D.

Picrasin E differs from picrasin D in having one extra tertiary hydroxyl (ν_{max} 3530 cm^{-1}, no carbinyl proton signal), which can only be accommodated as at C-14. This assignment was confirmed by the appearance of signals at δ 2.91 and 3.22 ppm due to a $\geqslant C-CH_2-CO-$ moiety, and by the downfield shift (-0.57 ppm) of the C-7 hydrogen signal in comparison with that of picrasin D, the latter fact confirming also the β-orientation of the hydroxyl.[7]

Based on the above evidence, it is concluded that picrasin E is represented by formula II.

From the biogenetic viewpoint, it is assumed that the C-12 methoxyl and the neighboring C-11 hydroxyl of nigakilactone B (III) are subjected to an oxidative cyclization to give picrasin D (I) which on further hydroxylation furnishes picrasin E (II).

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[7] W. Stöcklin and T.A. Geisman, *Tetrahedron Letters*, **1968**, 6007.

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A Tetracyclic Compound as a New Coloring Matter of the Reaction of Acetone with 1,3,5-Trinitrobenzene

In a previous paper,[1] the mechanism of the color reaction of acetone with a large amount of 1,3,5-trinitrobenzene (TNB) was discussed by isolating a Meisenheimer type compound[2] (I) and a bicyclic compound[3] (II) as the main coloring matters of the reaction.

In the course of study on the spectral behaviors of I and II, we found that their color intensities much increased as twice when the aqueous solution of I or II was treated with excess

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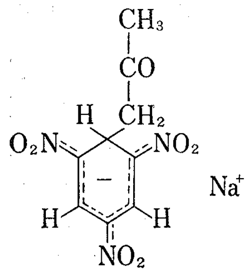
[1] K. Kohashi, Y. Ohkura and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **18**, 2151 (1970).

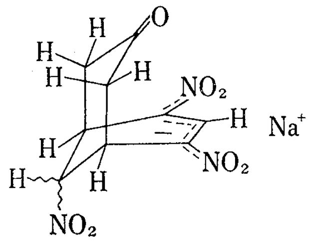
[2] M. Kimura, *Yakugaku Zasshi*, 73, 1219 (1953); R. Foster and C.A. Fyfe, *Rev. Pure and Appl. Chem.*, **16**, 61 (1966).

[3] T. Momose, Y. Ohkura and K. Kohashi, *Chem. Pharm. Bull.* (Tokyo), **17**, 858 (1969); R. Foster, M.I. Foreman and M.J. Strauss, *Tetrahedron Letters*, **1968**, 4949; M.I. Foreman, R. Foster and M.J. Strauss, *J. Chem. Soc.* (*C*), **1969**, 2112; M.J. Strauss and H. Schran, *J. Am. Chem. Soc.*, **91**, 3974 (1969); M.J. Strauss, T.C. Jensen, H. Schran and K.O' Conner, *J. Org. Chem.*, **35**, 383 (1970).

TNB more than equimolar amount to I or II under the similar conditions of the improved spot test.[4] This fact suggested that another type of compound might be also formed as a main coloring matter in the spot test reaction of acetone. Thus, a new compound (III) was separated in a crystalline form from the reaction mixture by thin-layer chromatographic technics (adsorbent: Wakogel B-5, solvent system: *n*-BuOH saturated with 3% ammoniumhyaroxide).

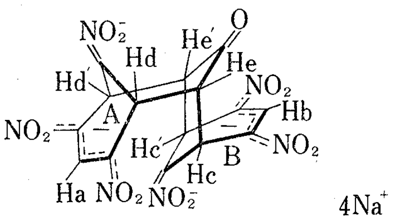


I

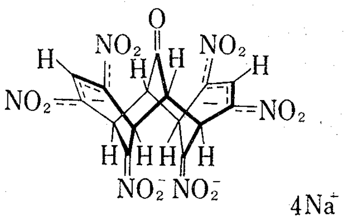


II

The compound (III) [dark crimson plates (from acetone and benzene), $Rf=0.20$ (thin-layer chromatographic conditions described above), IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1730, 1635, 1550, 1480, 1435, 1350, 1320, 1190, 1110, 755] showed no melting point and exploded when ignited or heated rapidly. Its aqueous solution gave a similar absorption curve to that of the color reaction mixture of acetone with excess TNB, showing two absorption maxima at 267 and 475 mμ and a shoulder at 310 mμ. The elemental analyses (*Anal.* Calcd. for $C_{15}H_8O_{13}N_6Na_4$: C, 31.48; H, 1.39; N, 14.68; Na, 16.07. Found: C, 31.67; H, 1.49; N, 14.56; Na, 16.00) were consistent with a structure containing four sodium, two moieties of TNB and one carbonyl group and led us to postulate two structural isomeric forms (IIIa and IIIb).



IIIa



IIIb

The above observations on the increase of absorption intensities could be well explained by the introduction of another dinitropropenide group in II. Then, the structure of III might be IIIa from the following nuclear magnetic resonance assignments (solvent: D_2O, internal standard: DSS): Two singlets at δ (ppm) 8.50 and 8.55 were assigned to a proton (Ha) on the dinitropropenide portion of A ring and a proton (Hb) on that of B ring respectively. Two doublets at δ 4.90 (2H, $J=2.9$ cps) and 4.20 (2H, $J=3.0$ cps) were assigned to two protons (Hd and Hd') on A ring and two protons (Hc and Hc') on B ring respectively and a poorly resolved triplet at δ 3.0 was assigned to two protons (He and He') adjacent to a carbonyl group. The above two doublets turned to two singlets by the irradiation of the triplet at δ 3.0.

Further details and studies of the color reaction mechanisms of acetone and other active methylene compounds with TNB under the improved spot test procedure[4] will be published in the near future.

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[4] T. Momose, Y. Ohkura and K. Kohashi, *Chem. Pharm. Bull.* (Tokyo), **11**, 301 (1963).