コムギにおけるN-(5-chloro-4-methyl-2-thiazolyl) propanamide (CMPT)のヒドロキシル化反応

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Short Communication

Hydroxylation of N-(5-Chloro-4-methyl-2-thiazolyl)-propanamide (CMPT) in Wheat*

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CMPT (Select®, N-(5-chloro-4-methyl-2-thiazolyl)propanamide) had been used as a selective herbicide for the control of a wide range of weeds in wheat. Several investigations have been carried out to elucidate the selective toxicity among genera and/or the metabolism of CMPT in plants.[1,2]

In this paper we report on new metabolites of CMPT in wheat. Seeds of wheat (*Triticum aestivum* L.) were germinated and allowed to grow in Kasugai's nutrient solution in a greenhouse. The foliage at the three-leaf stage was dipped in an aqueous solution containing 400 ppm of ^{14}C-CMPT (prepared from $NH_2{}^{14}CS$-NH_2 and ^{14}C-labeled at C-2′ position; specific radioactivity, 0.39 μCi/mg) for one hour. The treated plants were grown for another five days and harvested. They were then washed with water, divided into foliage and roots, homogenized with 50% aqueous acetone (v/v), and filtered. The filtrate was concentrated to remove acetone under reduced pressure. The remaining aqueous solution was extracted three times with diethyl ether and the combined ether layer was dried over anhydrous magnesium sulfate. Ether and aqueous layers were concentrated respectively, and subjected to chromatography on plates coated with silica gel 60 F_{254} (0.5 mm thick, E. Merck).

The chromatogram of foliar ether extract developed with the solvent system A (shown in Table 1) was analyzed by a *tlc* radioscannograph. Three major peaks of metabolites besides that of CMPT were recognized as shown in Fig. 1, and designated as OM-1 (*Rf* 0.05), OM-2 (0.18) and OM-3 (0.37), respectively. OM-1 coincided in position with the authentic samples of thiourea and 5-chrolo-4-hydroxymethyl-2-thiazolamine (CHMAT), and *Rf* values of OM-2 and OM-3 coincided with those of authentic N-(5-chloro-4-hydroxymethyl-2-thiazolyl)propanamide (CHMPT) and 5-chloro-4-methyl-2-thiazolamine (CMAT), respectively.

The spot of OM-3 was scraped off the plate and extracted with ethanol. This ethanol extract was concentrated and analyzed by a mass spectrometer and the mass spectrum (EI) of OM-3 agreed reasonably with that of authentic CMAT.

The mass spectra (EI) of OM-2 and authentic CHMPT are shown in Fig. 2. Although impurities (*m/z* 149, 71, 69, 57, 43, 41) are also included, the characteristic ion peaks of OM-2, *m/z* 222 ($M^+ + 2$), 220 (M^+), 166, 164 (M^+-CH_3CH=C=O), 137 and 135 are the same kind and of nearly the same relative intensity (ratios to the ion peak of *m/z* 164) as those of authentic CHMPT. Although OM-1 was similarly analyzed, no definite evidence was obtained. It seems that the ethanol extract of MO-1 spot contains thiourea, CHMAT and many other compounds from wheat plants.

The chromatogram of the aqueous layer of foliar extract developed with the solvent system C (shown in Table 1) was similarly analyzed by a *tlc* radioscannograph. Three main peaks of metabolites were recognized as shown in Fig. 3, and designated as AM-1 (*Rf*

* Metabolism and Selectivity of CMPT in Plants (Part 1)

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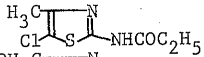
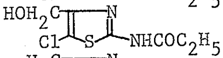
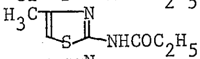
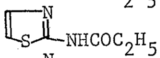
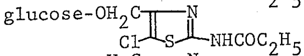
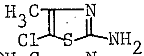
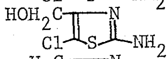
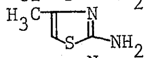
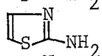
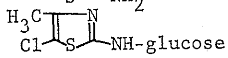
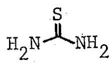
Table 1 *Rf* values of CMPT and related compounds on *tlc*.

Compounds		Solvent systems A	B	C
	CMPT	0.62	0.78	0.84
	CHMPT	0.14	0.26	0.81
	MPT	0.46	0.74	—
	PT	0.40	0.68	—
	CHMPT–glucose	0.00	0.00	0.30
	CMAT	0.37	0.46	0.80
	CHMAT	0.08	0.09	—
	MAT	0.22	0.37	—
	AT	0.16	0.30	—
	CMAT–glucose	0.00	0.00	0.26
	thiourea	0.05	0.05	0.72

Adsorbent: Silica gel.
Solvent systems; A: $CHCl_3$–AcOEt–MeOH (140 : 60 : 5, v/v), B: $CHCl_3$–MeOH (95 : 5, v/v), C: AcOEt–iPrOH (65 : 35, v/v).

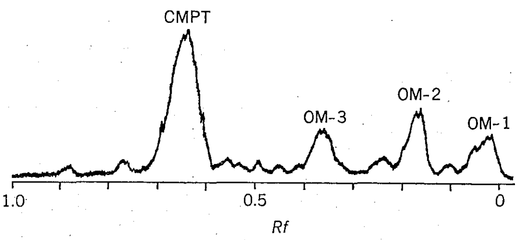


Fig. 1 Radioscannogram of the ether layer of foliar extract.
Tlc was developed with system A.

0.05), AM–2 (0.31) and AM–3 (0.81), respectively.

The spot of AM–2 was scraped off the plate and extracted with ethanol. This ethanol extract was then concentrated and gave characteristic ions, *m/z* 405 and 407 under mass spectrometric analysis (FD). The former ion corresponded to the Na^+–cluster ion of a CHMPT glucoside and the latter to its isotope ion. We have found CHMPT and its glucoside as new metabolites of CMPT in wheat. The finding of hydroxylation of a methyl group bound to aromatic rings in plants is rather unique, only a few examples have been reported in plants.[3,4]

Recently we have found that although CHMPT is a major metabolite of CMPT in wheat, CMAT is a major one in rice plant.[5] Further investigations to clarify the detailed metabolic pathway of CMPT and its selective toxicity among genera are now in progress.

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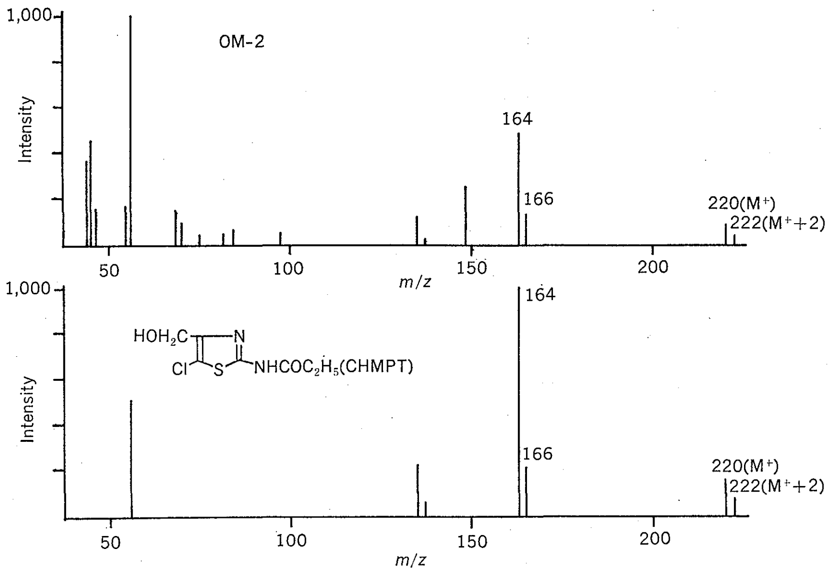

Fig. 2 Mass spectra of OM–2 and authentic CHMPT.

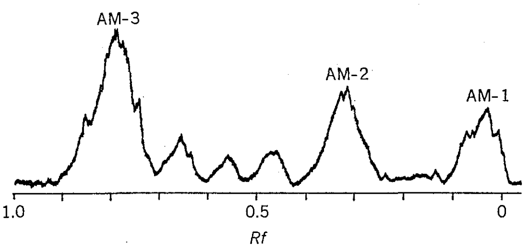

Fig. 3 Radioscannogram of the aqueous layer of foliar extract.
Tlc was developed with system C.

要　　約

コムギにおける *N*-(5-chloro-4-methyl-2-thiazolyl)propanamide (CMPT) のヒドロキシル化反応*

吉田英実，田原哲士，水谷純也

著者らは除草剤 CMPT の属間選択性を解明する目的で，^{14}C-CMPT を用いてコムギ体内における代謝を調べた．水耕法により生育した三葉期のコムギの地上部を ^{14}C-CMPT 水溶液 (400 ppm) に1時間浸した後，さらに5日間栽培した．茎葉のエーテル画分から，主要な代謝産物として *N*–(5–chloro–4–hydroxymethyl–2–thiazolyl)propanamide (CHMPT) と 5–chloro–4–methyl–2–thiazolamine (CMAT) を，標品の *tlc* および MS データと比較することにより確認した．また，水層から主要な代謝産物として，CHMPT glucoside を MS (FD) から推定した．植物における芳香環に置換したメチル基のヒドロキシル化はまだ例が少なく，選択毒性の観点から興味深い．

* 植物における CMPT の代謝および選択性 (第1報)