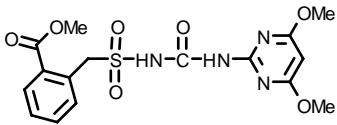


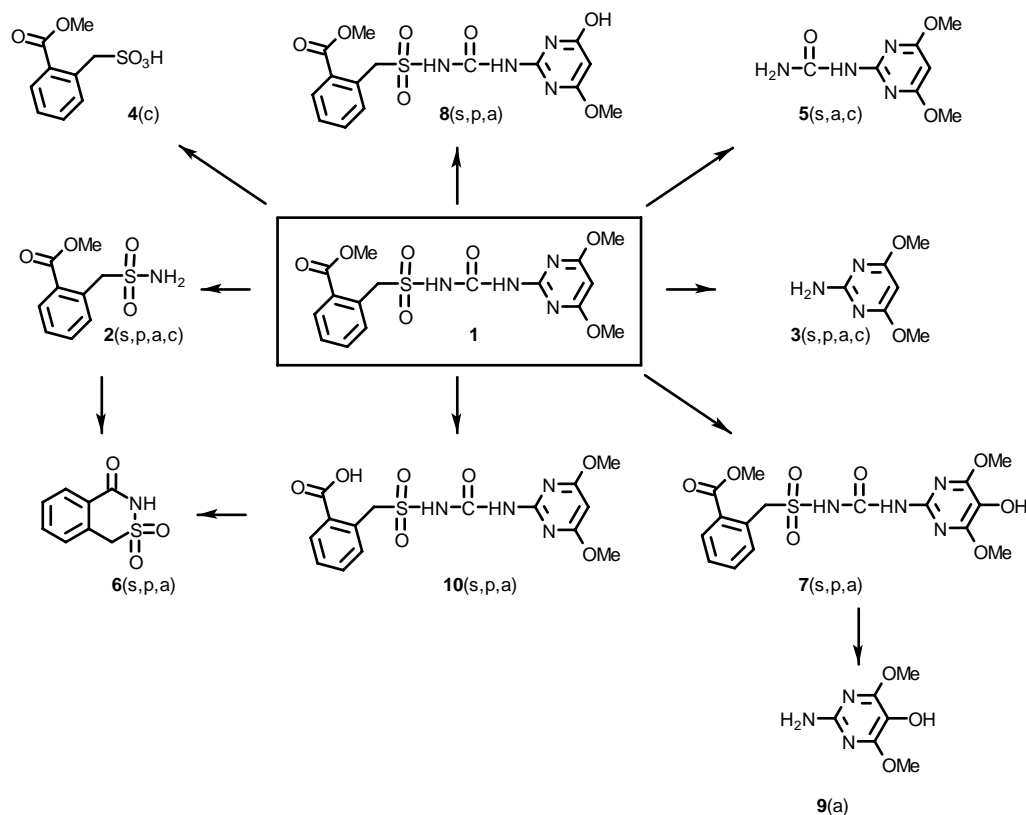
Bensulfuron methyl

Uses Bensulfuron methyl is a systemic sulfonylurea herbicide for the pre- and post-emergence control of annual and perennial broad-leaved and sedge weeds in rice.

Common name	Bensulfuron methyl
Chemical name (IUPAC)	Methyl 2-[(4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoylmethyl]benzoate
CASRN	83055-99-6
Molecular formula	C ₁₆ H ₁₈ N ₄ O ₇ S
Molecular weight	410.4
Chemical structure	 <p>The chemical structure of Bensulfuron methyl consists of a methyl benzoate group attached to a sulfamoyl group (-SO₂NH-), which is further attached to a carbamoyl group (-NH-C(=O)-NH-), and finally to a 4,6-dimethoxypyrimidin-2-yl ring. The pyrimidine ring has methoxy groups (-OMe) at the 4 and 6 positions.</p>
Water solubility	1.1 mg l ⁻¹ (pH 5), 80 mg l ⁻¹ (pH 7), 880 mg l ⁻¹ (pH 8, 25 °C)
K_{oc}	257-499
Vapour pressure	2.8 × 10 ⁻¹² Pa (25 °C)
Log K_{ow}	2.17 (pH 5), 0.78 (pH 7), -1.0 (pH 9, 25 °C)
pK_a	5.2

Metabolic pathways

The metabolic pathways of bensulfuron methyl in plants, soil, and animals are similar. Primary metabolic pathways include *O*-demethylation of the methoxypyrimidine moiety and cleavage of the sulfonylurea linkage. Minor metabolic pathways include the hydrolysis of the bensulfuron methyl ester to bensulfuron and hydroxylation of the pyrimidine ring. The metabolic pathways of bensulfuron methyl are presented in Scheme 1.



Scheme 1 Primary metabolic pathways of bensulfuron methyl.

Chemical degradation

Bensulfuron methyl (1) hydrolysed rapidly at pH 5 (DT_{50} of 11 days) but slowly at pH 7 and 9 at 25 °C (DT_{50} >150 days). Cleavage of the sulfonylurea linkage was the primary hydrolytic degradation pathway, yielding methyl 2-(aminosulfonylmethyl)benzoate (2) and 4,6-dimethoxy-2-aminopyrimidine (3) (Friedman, 1983).

Bensulfuron methyl was stable to direct photolysis in sterile buffer solutions (Horne, 1987), but degraded rapidly *via* cleavage of the sulfonylurea

linkage in natural water under sunlight to methyl 2-(sulfomethyl)benzoate (**4**) and (4,6-dimethoxypyrimidin-2-yl)urea (**5**), with a DT₅₀ of 3–4 days (Crosby, 1989).

Degradation in soils

In moist field soils, bensulfuron methyl was degraded *via* chemical hydrolytic degradation and microbial processes, with a DT₅₀ of 3–4 weeks. Compounds **2**, **3**, and **6** [1*H*-2,3-benzothiazin-4(3*H*)-one 2,2-dioxide] and CO₂ were detected (Yordy, 1987). Similar degradation products were also generated in flooded aerobic and anaerobic water–sediment systems (Hunt, 1986; Cadwgan and Ryan, 1986; Cadwgan and Oxenhorn, 1986). Other minor degradation reactions observed under flooded conditions included hydroxylation to yield methyl α -(4,6-dimethoxy-5-hydroxypyrimidin-2-ylcarbamoylsulfamoyl)-*o*-toluate (**7**) and *O*-demethylation to yield methyl α -(4-hydroxy-6-methoxypyrimidin-2-ylcarbamoylsulfamoyl)-*o*-toluate (**8**).

Metabolism in plants

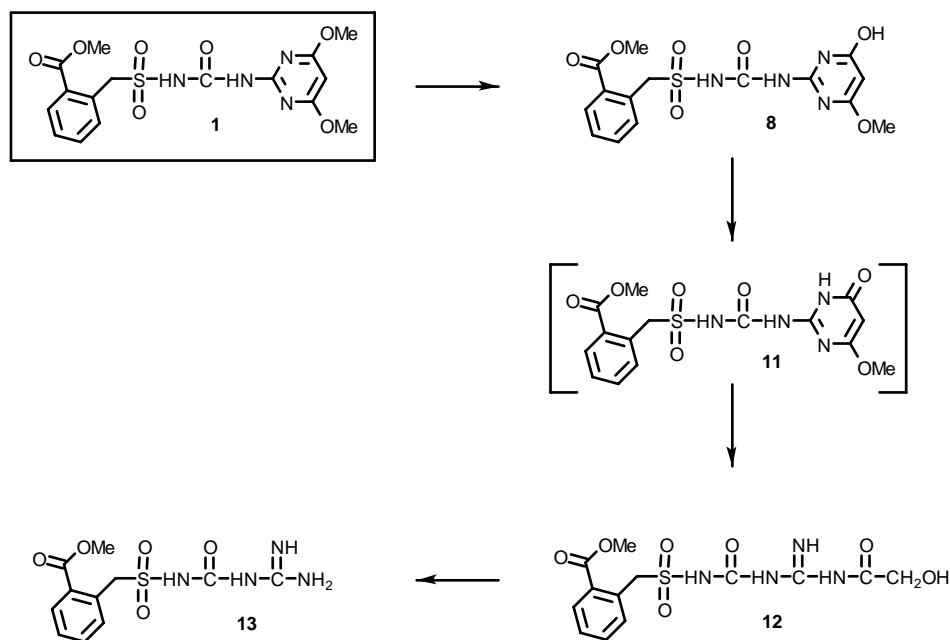
Plant metabolism studies were conducted with Indica (Priester, 1984; Priester, 1985), Japonica (Hunt and Berus, 1986), and Samgang (Kwon and Pyon, 1993) rice cultivars, as well as the weed *Cyperus serotinus* (Kwon and Pyon, 1993). The crop selectivity of bensulfuron methyl was due to a slower rate of translocation from roots to shoots in tolerant rice and, more importantly, an increased rate of metabolism in rice *vs.* weed species. For example, excised rice shoots metabolised bensulfuron methyl with a DT₅₀ of 4–6 hours while sensitive broad-leaved and sedge weeds did not appreciably degrade bensulfuron methyl (DT₅₀ >50 hours). A moderately sensitive weed (*Echinochloa crus-galli*) metabolised bensulfuron methyl at an increased rate (DT₅₀ 12 hours) (Takeda *et al.*, 1986).

Metabolism appeared to proceed initially through *O*-demethylation of the pyrimidine ring to yield **8** and the hydrolysis of the parent methyl ester to produce bensulfuron (**9**). Terminal metabolites included cleavage products **2**, **3**, **6**, and unextractable ¹⁴C-residues. Usui *et al.* (1993) observed a similar metabolic profile for bensulfuron methyl in both normal and tolerant carrot suspension-cultured cells to yield **2**, **6** and **8** as primary products.

Metabolism in animals

In mammals (rats and goats), bensulfuron methyl was metabolised and rapidly eliminated. The primary metabolic pathway included hydroxylation and *O*-demethylation yielding compounds **7** and **8**, respectively (Hundley and Hunt, 1984; Hunt, 1984; McCooey, 1986; Cornelissen *et al.*,

1987). Compound **10** (5-hydroxy-4,6-dimethoxy-2-aminopyrimidine), from the cleavage of the sulfonylurea linkage, was also observed as a major metabolite in rats. Cleavage and hydrolysis products such as **2**, **3**, **5**, and **6** were observed as minor metabolites. Several minor, unique metabolites were also isolated from the chicken excreta. These metabolites (**12** and **13**) were ring-opened products resulting from demethylation, oxidation, decarboxylation, and hydrolysis reactions *via* an intermediate (**11**) (Scheme 2, Reiser *et al.*, 1991). No significant bensulfuron methyl-equivalent residues were detected in the animal tissues, milk and eggs (Cheng, 1989).



Scheme 2 Pyrimidine ring-opening as a minor metabolic pathway of bensulfuron methyl in poultry.

References

- Cadwgan, G.E. and Ryan, T.W. (1986) Anaerobic Aquatic Metabolism of [2-¹⁴C-Pyrimidine]DPX-F5384 and [¹⁴C-Phenyl(U)]DPX-H6573 in Water. DuPont Internal Report, AMR 606-86.
- Cadwgan, G.E. and Oxenhorn, S. (1986) Anaerobic Aquatic Metabolism of [2-¹⁴C-Pyrimidine]DPX-F5384 and [¹⁴C-Phenyl]DPX-F5384 in Japanese Rice Paddy Sediments. DuPont Internal Report, AMR 472-86.
- Cheng, T. (1989) Metabolism Study of [¹⁴C]Bensulfuron Methyl in Laying Hens. DuPont Internal Report, AMR 1454-89.
- Cornelissen, K.S., Lewis, C. and Hopkins, R. (1987) [¹⁴C]Bensulfuron Methyl: Absorption, Distribution, Metabolism and Excretion in the Rat. DuPont Internal Report, AMR 964-87.

- Crosby, D.G. (1989) Annual Report of Comprehensive Research on Rice. Project No. RP-5. University of California-Davis, 48–56.
- Friedman, P. (1983) Hydrolysis of [¹⁴C]DPX-F5384. DuPont Internal Report, AMR 143-83.
- Horne, P. (1987) Photodegradation of [¹⁴C-Phenyl]DPX-F5384 and [2-¹⁴C-Pyrimidine]DPX-F5384 in Water (Conducted in Sunlight). DuPont Internal Report, AMR 899-87.
- Hundley, S.G. and Hunt, O.R. (1984) Metabolism of [¹⁴C]DPX-F5384 By Male and Female Rats. DuPont Internal Report, AMR 222-84.
- Hunt, O.R. (1984) Metabolism of [¹⁴C-Phenyl]DPX-F5384 in a Lactating Goat. DuPont Internal Report, AMR 219-84.
- Hunt, O.R. (1986) Aerobic Aquatic Metabolism of [¹⁴C-Phenyl]DPX-F5384 and [2-¹⁴C-Pyrimidine]DPX-F5384. DuPont Internal Report, AMR 475-86.
- Hunt, O.R. and Berus, J.S. (1986) Metabolism of [¹⁴C-Phenyl]DPX-F5384 and [2-¹⁴C-Pyrimidine]DPX-F5384 in Field-Grown Japonica Rice. DuPont Internal Report, AMR 473-86.
- Kwon, C.S. and Pyon, J.Y. (1993) *Korean J. Weed Science*, **13**, 75–80.
- McCooey, K.T. (1986) Metabolism of [2-¹⁴C-Pyrimidine]DPX-F5384 in Male and Female Rats. DuPont Internal Report, AMR 483-86.
- Priester, T. (1984) Metabolism of [¹⁴C-Phenyl]DPX-F5384 in a Rice Paddy Ecosystem. DuPont Internal Report, AMR 229-84.
- Priester, T. (1985) Metabolism of [2-¹⁴C-Pyrimidine]DPX-F5384 in Indica Rice Grown in a Rice Paddy Ecosystem. DuPont Internal Report, AMR 315-85.
- Reiser, R.W., Barefoot, A.C., Dietrich, R.F., Fogiel, A.J., Johnson, W.R. and Scott, M.T. (1991) *J. Chromat.*, **554**, 91–101.
- Takeda, S., Erbes, D.L., Sweetser, P.B., Hay, J.V. and Yuyama, T. (1986) *Weed Res. Japan*, **31**, 157–163.
- Usui, K., Suwanwong, S., Ohno, A. and Ishizka, K. (1993) *Zasso Kenkyu*, **38**, 7–11.
- Yordy, J.R. (1987) Aerobic Soil Metabolism of DPX-F5384. DuPont Internal Report, AMR 782-87.

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