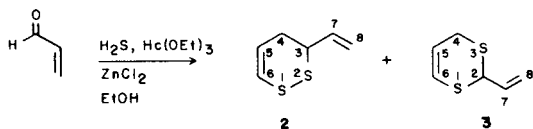


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Received January 19, 1982A simple synthesis of 3,4-dihydro-3-vinyl-1,2-dithiin (**2**) and 2-vinyl-4*H*-1,3-dithiin (**3**) is reported.*J. Heterocyclic Chem.*, **20**, 1753 (1983).

☆ Two thioacrolein dimers, 3-ethenyl-3,6-dihydro-1,2-dithiin (**1**) and 3-ethenyl-3,4-dihydro-1,2-dithiin (**2**) have been recently detected in the flavor components of cooked asparagus [1]. Compound **2** was also found in fresh garlic french salad dressing [2]. We previously showed that aliphatic conjugated thioketones dimerize exclusively into the kinetic isomer (4*H*-1,3-dithiin) which has been thermally converted into the thermodynamic isomer (3,4-dihydro-1,2-dithiin [3a,b]). We and others also reported the preparation of such 4*H*-1,3-dithiins involving the reaction of hydrogen sulphide with the parent α -ethylenic ketone [3b] and two aldehydes, 2-hexenal and 2-butenal [4]. The synthesis of compound **2** could be envisioned either by simple *in situ* dimerization of thioacrolein in spite of its propensity to polymerize into a linear polymer [5] or by reaction of hydrogen sulphide with acrolein in suitable acidic conditions; 3-formyl 4-hydroxytetrahydrothiopyran [6] and 2,4-dihydroxy 1,5-dithiocin [7] were formed respectively in neutral and basic medium.

Here we present a convenient synthesis of 3-ethenyl-3,4-dihydro-1,2-dithiin (**2**) and 2-ethenyl-4*H*-1,3-dithiin (**3**), the two expected dimers [3b]. We used the slightly modified procedure which successfully worked for the α,β -ethylenic thioketone dimers preparation [3b]. Thus a hydrogen sulphide stream (25 ml/minute) was passed through an ice-cooled solution of acrolein (0.1 mole) ethyl orthoformate (0.15 mole) and anhydrous zinc chloride (0.002 mole) in 50 ml of absolute ethanol. After 2.5 hours the reaction was complete. The usual work-up with pentane at 0° left a pale yellow oil. Silica gel chromatography with petroleum-ether as the eluant afforded the two products **2** and **3** (RF 0.24, 0.12 in pentane) in a 1/4 ratio with a 24% yield.

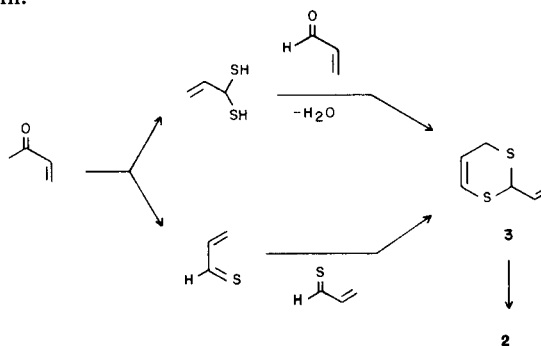


The structure of these two dimers was established from spectral data.

The mass spectrum of compound **3** is very similar to that reported for 3-ethenyl-3,6-dihydro-1,2-dithiin (**1**). Nevertheless there is no doubt about the 4*H*-1,3-dithiin

structure of **3** [11].

Two primary reactions may account for the formation of these two dimers, either sulfurization of acrolein to give thioacrolein which dimerize *in situ*, regioselectively [3] into 1,3-dithiin **3**, or addition of a *gem*-dithiol intermediate to a mole of acrolein as it is well known for the addition of a simple *gem*-dithiol [4,8] to α,β -unsaturated ketone [9]. Compound **2** may be then derived from **3** by the known thermal isomerization [3,4,10] of a 1,3-dithiin into a 1,2-dithiin.



Subsequent work to elucidate the mechanism of this reaction are needed and uses of such compounds, especially in food chemistry need to be explored. Some attention to similar dithiins has been paid recently [1,2]. This work supports the suggested origin of compound **2** in the aromatic components of cooked asparagus; its formation was assumed to involve reaction of hydrogen sulphide with acrolein resulting from thermal degradation of the *S*-methyl amino acid, methionine.

EXPERIMENTAL

3,4-Dihydro-3-vinyl-1,2-dithiin (**2**).

This compound had nmr (carbon tetrachloride): 2.3-2.7 (m, 2 allylic H), 3.62 (m, H in **3**), 5.10-6.5 (complex m, 5 ethylenic H); ¹³C nmr (deuteriochloroform): 30.55 (C4), 44 (C3), 117.5 (C8), 120.6 (C7), 126.0 (C5), 136.5 (C6); ir (film): 3095, 3008, 1634, 1610, 982, 920, 900, 760, 712, 675, 640, 630 cm⁻¹; ms: (70 eV) (dir) m/e 112 (M-32, 70%), 111 (M-33, 22%), 97 (M-47, 50%), 85 (M-59, 38%), 84 (M-60, 30%), 80 (M-64, 14%), 79 (M-65, base peak).

Anal. Calcd. for C₆H₈S₂: C, 49.95; H, 5.59; S, 44.49. Found: C, 49.41; H, 5.44; S, 44.66.

Our data including the mass spectrum agree with known 1,2-dithiin structure [3,4,10]. The only reported mass spectrum [1] shows some differences probably due to a different mode of introduction (coupled gas chromatography mass spectrography and direct introduction).

2-Vinyl-4*H*-1,3-dithiin (**3**).

This compound had nmr (carbon tetrachloride): 3.17-3.35 (m, 2 allylic H), 4.68 (d, $J = 5.5$, H in 2), 5.17-6.4 (complex m, 5 ethylenic H); ^{13}C nmr (deuteriochloroform): 25.1 (C4), 45.1 (C2), 117.2 (C8), 118.3 (C7), 122.2 (C5), 134.3 (C3); ir (film): 3095, 3005, 1634, 1605, 980, 965, 925, 710, 640 cm^{-1} ; ms: (70 eV) (dir) m/e 144 (M^+ , 36%), 111 (M-32, 29%), 103 (M-41, 7%), 97 (M-47, 19%), 72 (m/2 base peak).

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