

of fused sodium acetate. No reaction took place and both the reactants were recovered as such.

**Method B:** A mixture of **4b** ( $R=R'=OCH_3$ ; 0.259 g, 0.001 mol) and **1** (0.158 g, 0.001 mol) in a dry test tube was heated in an oil-bath at  $160-70^\circ$  for 4 h. No reaction took place and the reactants were recovered as such.

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## Studies on Thiazolidinone. Part-XVIII. Synthesis of Thiazolidinone Derivatives from Benzosuberone and Cyclohexanone

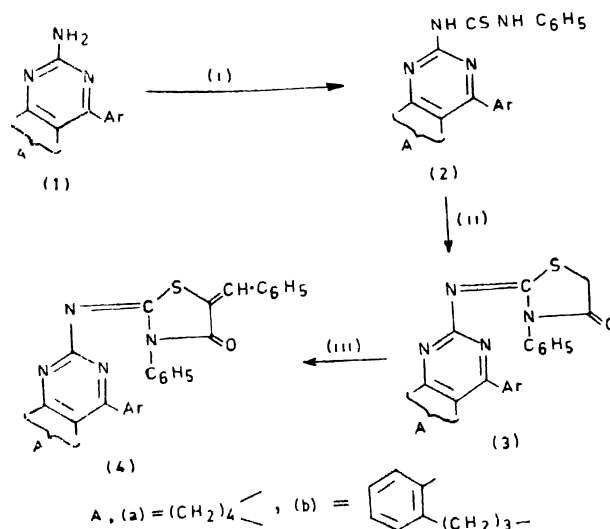
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IN continuation of our earlier work on thiazolidinone derivatives<sup>1</sup> as potential chemotherapeutic agents, the synthesis of two new series of thiazolidinones possessing alicyclic moieties as a part of the substituent have been made. 2-Amino-4-aryl-cyclohexa[1,2-d]pyrimidines (**1a**) were obtained in 50–80% yield by the reaction of free guanidine on 2-arylidene cyclohexanones by following the procedure reported for the synthesis of **1b**<sup>2,3</sup>. The amines (**1a** and **1b**) were smoothly converted into unsymmetrical thioureas (**2a** and **2b**) by reacting them with phenylisothiocyanate in rectified spirit. The condensation of monochloroacetic acid with thioureas furnished the thiazolidinones, the structures of which are confirmed as **3a** and **3b** since the hydrolysis of these compounds in alcoholic HCl gave 3-phenyl-2,4-thiazolidione in all cases along

with the respective amines (**2**). The thiazolidinones are highly soluble in dilute NaOH and reprecipitated by acetic acid. The ir spectra of the thiazolidinones (**3a** and **3b**;  $Ar=C_6H_5$ ) showed bands at 1710 and 1700  $cm^{-1}$  for the carbonyl groups whereas their benzylidene derivatives (**4a** and **4b**;  $Ar=C_6H_5$ ) gave bands at 1670 and 1675  $cm^{-1}$  respectively for their carbonyl groups. This is in good agreement with our earlier observation<sup>4</sup>, with other series of compounds. The bathochromic shifts in the absorption of carbonyl group are due to exocyclic conjugation<sup>5</sup>.



Scheme 1 Reagents: (i)  $C_6H_5NCS$ , EtOH,  $\Delta$ , (ii)  $ClCH_2COOH$ , NaOAc, AcOH, (iii)  $C_6H_5CHO$ , AcOH, NaOAc

### Experimental

Melting points are determined in open capillaries in sulphuric acid bath and are uncorrected. Ir spectra (KBr) were recorded on a Perkin-Elmer 293 spectrophotometer.

2-Amino-4-aryl-benzo[6,7]cyclohepta[1,2-d]pyrimidines (**1b**) were prepared according to Rayyes, *et al.*<sup>3</sup> by the reaction of 2-arylidene benzosuberones with guanidine carbonate and 2-arylidene cyclohexanones were synthesised by condensing cyclohexanone with aldehydes in alkali<sup>6</sup>.

**2-Amino-4-phenyl-cyclohexa[1,2-d]pyrimidine (1a;  $Ar=C_6H_5$ ):** To a solution of guanidine hydrochloride (3.6 g, 40 mmol) in ethanol (60 ml) was added a solution of NaOH (4 g in 100 ml of water) and stirred for 30 min. The precipitated NaCl was filtered off. The filtrate was added to a solution of 2-benzylidene cyclohexanone (1.9 g, 10 mmol) in ethanol (50 ml) and refluxed for 4 h. Excess solvent was then distilled off and the residue treated with water and warmed to make it soluble. The aqueous solution after filtration was acidified with dilute HCl (0.1N). The resulting solid was filtered, washed with warm ethanol and recrystallised from ethanol as a pale yellow solid (2.1 g, 65%, m.p.  $186^\circ$

TABLE 1—PHYSICAL AND ANALYTICAL DATA OF COMPOUNDS (1–3)

Ar	Amine (1) m.p. °C	M.P. °C	Thiourea(2) % Sulphur		M.P. °C	Thiazolidinone (3) % Sulphur		$\nu(\text{C}=\text{O})$ $\text{cm}^{-1}$
			Found	Calcd		Found	Calcd	
<i>p</i> -Chlorophenyl <sup>a</sup>	130	208	8.9	8.11	190	7.33	7.96	1 715
Furyl-2 <sup>a</sup>	186	142	9.10	9.14	170	8.23	8.21	1 700
Thienyl-2 <sup>a</sup>	152	168	17.45	17.49	116	15.78	15.76	1 700
<i>p</i> -Chlorophenyl <sup>b</sup>	148	185	7.02	7.00	142	6.41	6.45	1 720
<i>p</i> -Anisyl <sup>b</sup>	175	200	7.04	7.08	146	6.53	6.50	1 710

<sup>a</sup>Structure (a). <sup>b</sup>Structure (b).

(Found : C, 74.32 ; H, 6.32 ; N, 18.54.  $\text{C}_{14}\text{H}_{16}\text{N}_8$  requires : C, 74.66 ; H, 6.66 ; N, 18.46%).

$\text{N}_1$ -(4-Phenylcyclohexa[1,2-d]pyrimidino)- $\text{N}_2$ -phenylthiourea (**2a**;  $\text{Ar}=\text{C}_6\text{H}_5$ ): A solution of aminopyrimidine (**1a**; 2.25 g) and phenylisothiocyanate (1.5 g) in rectified spirit (40 ml) was refluxed for 3 h. The solid deposited on cooling was filtered and recrystallised from glacial acetic acid (2.4 g, 66%), m.p. 124° (Found : S, 8.64.  $\text{C}_{21}\text{H}_{20}\text{N}_4\text{S}$  requires : S, 8.88%;  $\nu_{\text{max}}$  3 400br (NH), 2 870 ( $\text{CH}_2$ ) and 1 610  $\text{cm}^{-1}$  (C–N).

$\text{N}_1$ -(4-Phenylbenzo[6,7]cyclohepta[1,2-d]pyrimidino)- $\text{N}_2$ -phenylthiourea (**2b**;  $\text{Ar}=\text{C}_6\text{H}_5$ ): It was prepared from a mixture of the aminopyrimidine (**1b**; 1.45 g) and phenylisothiocyanate (0.75 g) in rectified spirit (40 ml) by following the above procedure and recrystallised from ethanol as colourless solid (1.6 g, 80%), m.p. 124° (Found : C, 72.50 ; H, 5.28 ; N, 13.71.  $\text{C}_{28}\text{H}_{22}\text{N}_4\text{S}$  requires : C, 72.63 ; H, 5.47 ; N, 13.93%).

2-(4-Phenylcyclohexa[1,2-d]pyrimidino)imino-3-phenyl-4-thiazolidinone (**3a**;  $\text{Ar}=\text{C}_6\text{H}_5$ ): A mixture of the thiourea (**2a**; 1.8 g, 5 mmol), monochloroacetic acid (0.5 g, 6 mmol) and anhydrous NaOAc (0.2 g) in glacial acetic acid (10 ml) was refluxed for 4 h with occasional shaking. The excess acetic acid was distilled off and the residue was triturated with water. The pale yellow solid deposited was filtered, washed with hot water, dried and recrystallised from ethanol (1.2 g, 60%), m.p. 105° (Found : C, 68.93 ; H, 4.82 ; N, 14.18.  $\text{C}_{28}\text{H}_{20}\text{N}_4\text{SO}$  requires : C, 69.00 ; H, 5.00 ; N, 14.00%;  $\nu_{\text{max}}$  2 900 ( $\text{CH}_2$ ), 1 710 (C=O) and 1 540  $\text{cm}^{-1}$ ).

2-(4-Phenylbenzo[6,7]cyclohepta[1,2-d]pyrimidino)imino-5-phenyl-4-thiazolidinone (**3b**;  $\text{Ar}=\text{C}_6\text{H}_5$ ): It was isolated as colourless solid from the disubstituted thiourea (**2b**; 2 g) and monochloroacetic acid (0.75 g) by following the procedure described above, (1.6 g, 70%), m.p. 98° (Found : S, 6.75.  $\text{C}_{35}\text{H}_{22}\text{N}_4\text{SO}$  requires S, 6.92%;  $\nu_{\text{max}}$  3 350br (NH), 1 700 (C=O), 1 590 (C–N) and 1 540  $\text{cm}^{-1}$ ).

2-[4-Aryl-cyclohexa[1,2-d]pyrimidino]imino-3-phenyl-5-benzylidene-4-thiazolidinone (**4a**;  $\text{Ar}=\text{C}_6\text{H}_5$ ): A mixture of benzaldehyde (0.16 g), the thiazolidinone (**3a**; 0.4 g) and anhydrous NaOAc (0.2 g)

in glacial acetic acid (10 ml) was refluxed for 4 h. It was then cooled and poured into crushed ice. The yellow solid separated was filtered, washed thoroughly with water, dried and crystallised from ethanol, (0.35 g, 63%), m.p. 125° (Found : C, 73.60 ; H, 4.85 ; N, 11.50.  $\text{C}_{30}\text{H}_{24}\text{N}_4\text{OS}$  requires : C, 73.77 ; H, 4.91 ; N, 11.47%;  $\nu_{\text{max}}$  2 800 ( $\text{CH}_2$ ), 1 670 (C=O) and 1 600  $\text{cm}^{-1}$  (C=N).

Similarly other benzylidene thiazolidinones were prepared : (**4a**;  $\text{Ar}=\textit{p}$ -chlorophenyl), m.p. 210° (Found : S, 6.18.  $\text{C}_{30}\text{H}_{23}\text{N}_4\text{SOCl}$  requires : S, 6.12%); **4a** ( $\text{Ar}=\textit{p}$ -anisyl), m.p. 140°;  $\nu_{\text{max}}$  2 810, 1 680, 1 600 and 1 580  $\text{cm}^{-1}$ ; **4a** ( $\text{Ar}=\textit{furyl}$ -2), m.p. 109° (Found : S, 6.46.  $\text{C}_{28}\text{H}_{22}\text{N}_4\text{SO}_2$  requires : S, 6.68%); **4a** ( $\text{Ar}=\textit{thienyl}$ -2), m.p. 210° (Found : S, 12.63.  $\text{C}_{28}\text{H}_{22}\text{N}_4\text{S}_2\text{O}$  requires : S, 19.92%);  $\nu_{\text{max}}$  2 900, 1 670, 1 580 and 1 540  $\text{cm}^{-1}$ ; **4b** ( $\text{Ar}=\text{C}_6\text{H}_5$ ), m.p. 154° (Found : S, 5.68.  $\text{C}_{28}\text{H}_{20}\text{N}_4\text{SO}$  requires : S, 5.79);  $\nu_{\text{max}}$  2 830, 1 675, 1 580 and 1 540  $\text{cm}^{-1}$ .

**Hydrolysis of 3a**: A mixture of **3a** (0.4 g) in ethanolic HCl (10 ml+5 ml) was made soluble by heating under reflux on a steam-bath for ~0.5 h. The reflux was continued for another 3 h and cooled. A crystalline solid separated out, m.p. 200° (lit.<sup>7</sup> 201°) and spectrally identical to 3-phenyl-2,4-thiazolidindione. The acidic filtrate was basified with concentrated ammonia from which another solid, m.p. 168° and spectrally identical to **1a** ( $\text{Ar}=\text{C}_6\text{H}_5$ ), was separated.

The physical and analytical data of the compounds (1–3) are presented in Table 1.

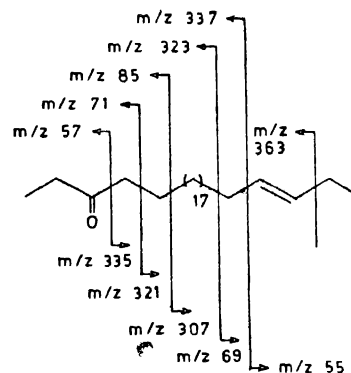
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### Heptacos-3-en-25-one—A New Unsaturated Ketone from *Ajuga bracteosa*†

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*AJUGA bracteosa* (Labiateae) is a perennial herb occurring in Western Himalayas from Kashmir to Nepal<sup>1,2</sup>. The leaves are diuretic, stimulant<sup>1</sup> and used as a substitute for Cinchona<sup>3</sup>. The plant is also reported to possess cardiostimulant action in animals<sup>4</sup> and anticancer activity in rats and mice<sup>5</sup>. Previous work on this plant includes isolation of saturated and unsaturated acids<sup>6</sup>, insect antifeedant diterpenes<sup>7,8</sup> and insecticidal diterpenes<sup>9</sup>. In continuation of our work on the aerial parts of this plant<sup>10</sup>, we now report a new unsaturated ketone.

The air-dried powdered aerial parts of *A. bracteosa* were extracted with *n*-hexane and the extract was concentrated under reduced pressure which in turn was subjected to vacuum liquid chromatography (VLC)<sup>11</sup> using silica gel as adsorbant. Compound **1** was eluted in hexane and was found to be homogeneous on tlc, **1** m.p. 70–71°;  $\nu_{\max}$  1610, 820 (unsaturation), 1710 (keto function), 1380 (CH<sub>3</sub>) and 715, 710 cm<sup>-1</sup> (straight chain);  $m/z$  392 corresponding to C<sub>27</sub>H<sub>52</sub>O. The base peak at  $m/z$  57 and other abundant ion at  $m/z$  335 formed by the  $\alpha$ -fission of the CO group located it at C-25 whereas the other characteristic ions at  $m/z$  363, 337 and 55 established the position of the double bond at C-3. These fragmentations are depicted on the structure. These data suggested the structure of **1** as heptacos-3-en-25-one which is in full accord with its <sup>1</sup>H nmr spectrum (80 MHz; CDCl<sub>3</sub>) displaying resonances at  $\delta$  0.90 (6H, t,  $J$  8Hz, two terminal CH<sub>3</sub>), 2.35 (4H, t,  $J$  8Hz, two CH<sub>2</sub> adjacent to CO function), 5.32 (2H, t,  $J$  6Hz, olefinic function), 1.60 (4H, m, two CH<sub>2</sub> adjacent to double bond) and 1.25 (36H, brs, eighteen CH<sub>2</sub> of chain).

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### Rapid Tlc Separation of Aromatic Amines on Surfactant Impregnated Silica Gel-G Plates

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AROMATIC amines are of considerable importance in industrial, toxicological and pharmaceutical applications<sup>1</sup>. Keeping this in view tlc separation and detection of various aromatic amines have been carried out by several workers on various adsorbents<sup>2</sup>. Duncan *et al.*<sup>3</sup> analysed aromatic amines by tlc on cellulose impregnated with bis-(2-ethylhexyl)hydrogen phosphate. Yasuda<sup>4</sup> carried