Eur. J. Med. Chem. 37, 659-669 (2002).

Preparations of heterospirostanols and their pharmacological activities

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(3β,20*S*,22*S*,25*R*)-22-Thiospirosol-5-en-3-ol **1** and (3β,20*S*,22*S*,25*R*)-22-seleno-spirosol-5-en-3-ol **2** were prepared from diosgenin **3** via 26-iodopseudodiosgenin **4** as a key intermediate.Diosgenone **5**,solasodinone **6**, (20*S*,22*S*,25*R*)-22-thio-spirosol-4-en-3-one **7**, (20*S*,22*S*,25*R*)-22-selenospirosol-4-en-3-one **8** and(20*R*,22*S*,25*R*)-spirosol-4-en-3-one **9** were prepared by Oppenauer oxidation of **3**, solasodine **10**, **1**, **2** and (3β,20*R*,22*R*,25*R*)-spirosol-5-en-3-ol **11**, respectively. Oxidations of **5** and **6** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) provided corresponding dienone products, (20*S*,22*S*,25*R*)-spirosol-1,4-dien-3-one **12** and(20*S*,22*S*,25*R*)-22-thiospirosol-1,4-dien-3-one **13**, respectively, while oxidation of **14** (C-20 diastereoisomer of **5**) gave no dienone product but 21-exo vinyl product **15**. 26-Thioacetylpseudodiosgenone **16** and 26-cyanoselenopseudodiosgenone **17** were prepared by treatment of 26-iodopseudo-diosgenose **18**, which was obtained by Oppenauer oxidation of **4**, with potassium thioacetate and potassium selenocyanate, respectively. Compounds **5** and **14** exhibited more than 80% inhibitions in INF-γ productions at 10.0 μM. Compounds **10** and **17** showed cytotoxic activities (IC50 = 6 and 5 μM, respectively) against cancerous HCT 116 cell lines. 26-Cyanoselenopseudodiosgenin **19** and **17** had antiurease activities (IC50 = 12.4 and 11.4 μM, respectively), in which only the latter showed an inhibition zone (mean zone diameter = 12.2 mm) formed by *Bacillus subtilis 168 trp.*