Short Communication

Short-step Synthesis of Homodolichosterone

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Homodolichosterone 1, isolated from immature seeds of Dolichos lablab, is one of the new brassinolide-related sterols with plant-growth promoting activity. We report here the first synthesis of 1, where all carbon atoms in stigmasterol 2 as the starting material were used for the carbon skeleton of 1 and the requisite functional groups for 1 were introduced stepwise into both the steroidal nucleus and the side chain. An NMR study using the synthetic sample of 1 revealed the hitherto unknown geometry of the C(24)=C(28) double bond to be (E).

An olefinic ketone 3, which was an intermediate in our syntheses of brassinolide and was prepared from 2 in several steps, was epoxidized with m-chloroperbenzoic acid to give a diastereoisomeric mixture of epoxides 4, mp 132~133°C, in a 3:2 ratio and in an 85.4% yield, based on the recovery (11.6%) of 3, along with a small amount of an unidentified compound. Epoxide ring opening of 4 with a phenylselenyl anion prepared from diphenyl diselenide and sodium borohydride yielded a crude mixture containing 5. Treatment of the crude 5 with 30% hydrogen peroxide gave an allylic alcohol 6 and its regioisomer along with small amounts of an epoxy alcohol 7 and its regioisomer. A considerable quantity of 4 was recovered. The allylic alcohol 6 was epoxidized with m-chloroperbenzoic acid to give 7. The epoxy alcohol 7 was quite easily rearranged by treatment with aluminum isopropoxide, owing to the assistance of the neighboring hydroxyl group, to give an enediol 8, [α]D21.5 +20.0° (c 0.379, CHCl3), in an 18% yield after purification by preparative layer chromatography (Kieselgel 60F254; 3 developments with n-hexane–ethyl acetate (1:1)). Deprotection of 8 with aqueous acetic acid gave 1, which was recrystallized from methanol to give colorless crystals, solvated with 1/6 molecule of methanol, mp 218~219°C (sinter at 208°C) (lit. mp 204~208°C for crude crystals), [α]D25.5 −9.3° (c 0.411, CHCl3–MeOH (9:1)); v££ (cm−1): 3525 (s), 2960 (s), 2900 (m), 1710 (s), 1650 (w), 1480–1410 (br, m), 1385 (m), 1370 (sh), 1360–1310 (br, w), 1280 (w), 1270–1200 (br, w), 1135 (w), 1110 (w), 1090 (m), 1060 (w),...
1050 (m), 1045 (m), 990 (m), 980 (w), 955 (w), 940 (w), 870 (w), 840 (w), 780 (w), 670 (w), 590 (w); PMR (400 MHz; CDCl₃)
\[\delta: 0.62 (s, 3H), 0.75 (s, 3H), 0.93 (d, J=6.4Hz, 3H), 1.06 (d, J=7.1Hz, 3H), 1.14 (d, J=7.1Hz, 3H), 1.71 (d, J=7.0Hz, 3H), 1.03~2.33 (m), 2.69 (dd, J=3.0 and 12.7Hz, 1H), 2.77 (septet, J=7.1Hz, 1H), 3.49 (d, J=5.6Hz, 3H); disappeared by the partial relaxation FT (PRFT) method\]
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REFERENCES