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SYNTHESIS OF (-)-TAYLORIONE, A SESQUITERPENE KETONE OF ENT-1,10-SECO-AROMADENDRANE SKELETON

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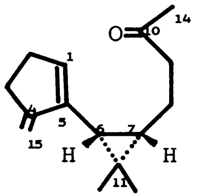
(-)-Taylorione, ent-1,10-seco-aromadendra-1(5),4(15)-dien-10-one, was synthesized from (+)-Δ^3-carene *via* (-)-2-[3-(3-hydroxybutyl)-2,2-dimethylcyclopropyl]-2-cyclopenten-1-one as a key intermediate.

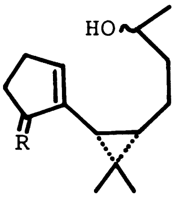
(-)-Taylorione, a novel sesquiterpene ketone, was isolated from the liverwort *Mylia taylorii* (Hock.) Gray and characterized to be ent-1,10-seco-aromadendra-1(5), 4(15)-dien-10-one (1) in our laboratory.1) We describe here the synthesis of this novel carbon skeletal sesquiterpene ketone *via* the cyclopentenone derivative (2) as a key intermediate.

In order to prepare the ketone 1 having the same chirality as the natural product on the cyclopropane, we started the synthesis from methyl (-)-2,2-dimethyl-3-(2-oxopropyl)-1-cyclopropaneacetate (3) obtainable readily by ozonization of (+)-Δ^3-carene.2) Baeyer-Villiger oxidation of 3 with perbenzoic acid in chloroform (rt, 72h) gave an acetate (4), which was hydrolyzed to an alcohol (5) with potassium carbonate in methanol (0°C, 3h). The alcohol 5 was treated with pyridium chlorochromate (PCC), giving the corresponding aldehyde (6). Reaction of 6 with acetylmethylenetriphenylphosphorane in chloroform (reflux, 36h) afforded an unsaturated ketone (7), along with an alicyclic ketone (8) (38% and 17% yield from 6, respectively, after repeated chromatography). The former 7 was hydrogenated on platinum oxide in ethanol to give a saturated ketone (9). For protection of the carbonyl group, 9 was converted into a methoxymethyl ether (10) on treatment with sodium borohydride and subsequent dimethoxymethane-diphosphorous pentaoxide *via* an alcohol (11). Reduction of 10 with lithium aluminium hydride followed by oxidation with PCC gave an aldehyde (12), which was subjected to Grignard reaction with 3,3-ethylenedioxy-1-propylmagnesium bromide (rt, 3h).[4] After oxidation of the resulting alcohol with PCC, a keto-acetal (13) was obtained (42% yield from 10). Both protecting groups in 13 were simultaneously removed with 5% hydrochloric acid - acetone (1:5) (reflux, 3h), and the resulting γ-keto-aldehyde was treated with aqueous sodium hydroxide - methanol solution to afford the desired key intermediate 2 (40% yield from 13).

Reaction of the cyclopentenone 2 with methylenetriphenylphosphorane in tetrahydrofuran (rt, 25h) gave a dien (14) though in a low yield (13%). The oxidation of 14 was carried out in dimethylsulfoxide - benzene (1:1) in the presence of dicyclohexylcarbodiimide and pyridium trifluoroacetate (rt, 17h) to give 1, whose physical properties ($[\alpha]_D$ and UV, IR, NMR, and Mass spectra) were identical with those of the natural product.

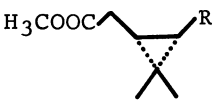


1



2: R=O

14: R=CH_2



3: R=CH_2COCH_3

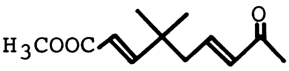
4: R=CH_2OCOCH_3

5: R=CH_2OH

6: R=CHO

7: R=CH=CHCOCH$_3$

9: R=$CH_2CH_2COCH_3$



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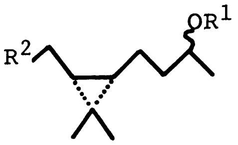

10: $R^1=CH_2OCH_3$
$R^2=COOCH_3$

11: R^1=H
$R^2=COOCH_3$

12: $R^1=CH_2OCH_3$
R^2=CHO

13: $R^1=CH_2OCH_3$
$R^2=COCH_2CH_2CH\langle{}^{O}_{O}]$

References and Notes

1) A. Matsuo, S. Sato, M. Nakayama, and S. Hayashi, Tetrahedron Lett., 1974, 3681; idem, J. Chem. Soc., Perkin I, 1979, in press.

2) R. Sobti and S. Dev, Tetrahedron, 30, 2927 (1975).

3) 7: $\nu(CCl_4)$ 1745, 1695, 1670, 1610 cm^{-1}; $\delta(CCl_4)$ 1.13, 1.20, 2.12 (each 3H, s), 6.07 (1H, d, J=16 Hz), 6.46 (1H, dd, J=16, 8 Hz); $[\alpha]_D$ +86.4°. 8: $\nu(CCl_4)$ 1730, 1705, 1680, 1655, 1635 cm^{-1}; $\delta(CCl_4)$ 1.13 (6H, s), 2.14 (3H, s), 5.63, 5.93 (each 1H, d, J=16 Hz), 6.55 (1H, dt, J=16, 7 Hz), 6.80 (1H, d, J=16 Hz).

4) C. Büchi and H. Wüest, J. Org. Chem., 34, 1122 (1969).

5) 2: $\nu(CCl_4)$ 3650, 1710, 1630 cm^{-1}; $\delta(CCl_4)$ 0.96, 1.19 (each 3H, s), 1.13 (3H, d, J=7 Hz), 7.12 (1H, m); MS m/e 222 (M^+); $[\alpha]_D$ -32.7°.

6) The physical properties of 14 were identical with those of the corresponding derivative from natural (-)-taylorione (1).[1]

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