malonate route, followed by decarboxylation and ether ring formation. Similarly, hydrangenosides C (2) and D (4) are presumed to be formed from 5 and a C-13 unit (C_6-C_3+2×acetyl).

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A Highly Stereoselective Synthesis of *rel*[1*R*, 3*R*, 7*R*, 9*S*]9-Acetoxy-8,8-dimethyltricyclo[5.4.0.0^{1,3}]undecan-4-one, a Versatile Intermediate to Terpenoids. Synthesis of α-Onocerin

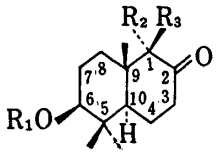
Hydrogenation of the tricyclic acetal **4**, which was prepared from the octalone **3** by 2 steps, yielded the *trans*-dihydro product **5** with high stereoselectivity, while hydrogenation of the dimethyloctalones, **8** and **9**, showed low stereoselectivity. **5** was converted to the cyclopropyl-decalone **2** in high yield. Reductive alkylation of **2** gave regioselectively the C_1 alkylated trimethyldecalone **12**, which was converted to the key intermediate to α-onocerin **16**, thus illustrating potential utility of **2** in terpenoid synthesis.

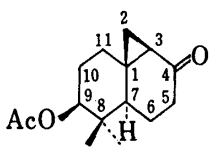
Keywords——Li–liq. ammonia reduction; reductive alkylation; stereoselectivity in hydrogenation; terpenoid synthesis; 8,8-dimethyl-tricyclo[5.4.0.0^{1,3}]undecane; cyclopropylketone; triterpenoid; α-onocerin

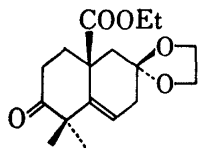
Although the trimethyl-*trans*-decalone-2 **1**[1] has been regarded as an attractive precursor of many terpenoid frameworks, its alkylation does not yield the 1-alkyl derivative but produces the 3-alkyl isomer.[2] For achieving selective C_1-alkylation in that system we have noticed to a 8,8-dimethyltricyclo[5.4.0.0^{1,3}]undecan-4-one, since there are several precedents of regiospecific reductive alkylation of a cyclopropylketone.[3] This communication describes efficient and highly stereoselective synthesis of its 9β-acetoxy derivative **2**, which would be a potential intermediate to a number of 3β-hydroxylated terpenoids.

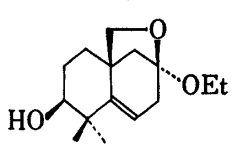
The dimethyloctalone **3**, which is easily derivable from 2-ethoxycarbonyl-4,4-ethylenedioxycyclohexanone by Robinson annelation followed by methylation,[4] on reduction with $LiAlH_4$ followed by treatment with 1% *p*-TsOH in ethanol (90°C, 15 min) gave the cyclic ethylacetal **4**, mp 114—116°C,[5] [^{1}H-NMR δ: 1.22 (3H, t, J=7 Hz), 3.68 (2H, dq, J=7 and 2 Hz), and 5.64 (1H, t, J=3.4 Hz)]. Hydrogenation of **4** in ethanol over 20% Pd–C (3.6 kg/cm^2, 4 h) afforded the *trans*-isomer **5**, mp 123—125°C, [^{1}H-NMR δ: 0.89 and 1.01 (each 3H, s)], practically as a single product, which was most conveniently purified as the keto-monoacetate **7**,[6] mp 136—137°C, (67% yield from **3**) [IR cm^{-1}: 3350 and 1720, ^{1}H-NMR δ: 0.93, 0.95, and 2.01 (each 3H, s)], by acetylation (Ac_2O–pyr., r.t., overnight) and deacetalization with 1% HCl–acetone (60°C, 5 min) of the resulting acetate **6**, mp 108.5—110°C [IR cm^{-1}: 1725, ^{1}H-NMR δ: 2.03 (3H, s)].

Formation of the *cis*-isomer in the above hydrogenation may be prohibited by the following two reasons: 1) the β-face of the molecule is hindered from approaching of the catalyst by presence of the epoxymethano bridge, and 2) the *cis*-isomer, if it were produced, is forced to adopt a steroid conformation which would have a serious non-bonded interaction between 1α-methyl and C_7. Similar hydrogenation of the keto-diol **8** gave a *trans*-decalone **10** contaminated with 20—25% of a *cis*-isomer, and the keto-diacetate **9**, on hydrogenation over PtO_2, afforded the product including more than 40% of a *cis*-isomer (after re-oxidation of the resulting alcohol).









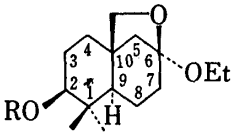
1 : $R_1=R_2=R_3=H$ **2** **3** **4**

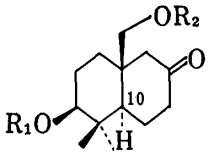
12 : $R_1=Ac$, $R_2=-CH_2CH=CH_2$, $R_3=H$

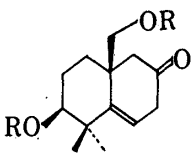
13 : $R_1=Ac$, $R_2=H$, $R_3=-CH_2CH=CH_2$

14 : $R_1=Ac$, $R_2=H$, $R_3=-CH_2COOH$

15 : $R_1=Ac$, $R_2=H$, $R_3=-CH_2COOCH_3$



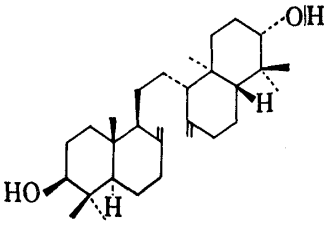


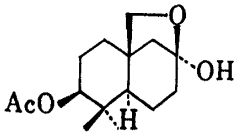


5 : R=H
6 : R=Ac

7 : $R_1=Ac$, $R_2=H$
10 : $R_1=R_2=H$
11 : $R_1=Ac$, $R_2=-SO_2CH_3$

8 : R=H
9 : R=Ac





16 **7**

Methanesulfonylation (CH_3SO_2Cl–pyr., r.t., 2 h) of **7** and treatment of the resulting methanesulfonate **11**, mp 97—99°C [^{1}H-NMR δ: 0.93, 1.00, 2.03, and 2.97 (each 3H, s)], with *tert*-BuOK in benzene (r.t., 30 min) afforded, in 80% yield, the tricyclic ketone **2**, mp 122—123°C. Its IR and ^{13}C-NMR spectra clearly indicated the presence of a cyclopropylketone. [IR cm^{-1}: 1730 and 1680, ^{1}H-NMR δ: 0.96, 0.98, and 2.08 (each 3H, s), ^{13}C-NMR δ: 17.0 (t, J= 165 Hz), 26.3 (s), and 31.2 (d, J=165 Hz)]. Confirming its configuration, **2** was reduced by Li and liq. ammonia (quenching with NH_4Cl) to yield the known trimethyl-*trans*-decalone **1**, (acetate; mp 113—115°C).[1,4] Thus, starting from **3**, seven sequential reactions with one purification of the intermediate at the stage of **7** gave **2** in 53% overall yield.

The following transformations illustrate potential utility of **2** for terpenoid synthesis.

Treatment of **2** with Li in liq. ammonia (containing 0.8 mol eq of *tert*-BuOH), followed by allyl iodide gave the 1α-allyl derivative **12**, mp 135—137°C [IR cm^{-1}: 1715 and 1700, ^{1}H-NMR δ: 0.93 (3H, s), 0.98 (6H, s), 4.86—5.14 (2H), and 5.48—5.80 (1H)]. Alkaline hydrolysis (10% KOH–MeOH, reflux, 2 h) of the reaction mixture followed by acetylation (Ac_2O–pyr., r.t., overnight) of the product gave, with concomitant epimerization of the allyl group, the

1β-allyl derivative **13**, mp 94—96°C [IR cm^{-1}: 1720 and 1695, ^{1}H-NMR δ: 0.78, 0.91, 0.97 (each 3H, s), 4.80—5.08 (2H), 5.56—5.95 (1H)], in 35% yield from **2**. Oxidation of **13** with $KMnO_4$–$NaIO_4$ (r.t., 20 h) and purification of the resulting acid **14**, mp 239—242°C (lit. mp 238—240°C)[7a] [IR cm^{-1}: 1715, 1695, and 1690, ^{1}H-NMR δ: 0.77, 0.92, 0.99, and 2.07 (each 3H, s)] by methylation (CH_2N_2, ether, 20 min) gave the methyl ester **15**, mp 137—139°C (lit. mp 132—134°C)[7a] (74% yield from **13**) [IR cm^{-1}: 1735, 1715, and 1695. ^{1}H-NMR δ: 0.77, 0.92, 0.99, 2.07, and 3.66 (each 3H, s)], which was identical with the key intermediate to α-onocerin **16** reported by several workers .[7]

Details and extension of this work will be given in a full publication.

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5) All new compounds in this communication gave satisfactory elemental analyses and spectral data. IR spectra were taken in KBr discs and NMR spectra in $CDCl_3$ solutions.
6) This compound existed as a hemi-acetal **7'** in a solid state, while in solution, the IR spectrum suggested that it is in equilibration between the keto-form **7** and the hemi-acetal **7'**. Detailed evidence will be given in a full publication.
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