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# CLEAVAGE OF DEPSIDES BY *TERT*-BUTYL ALCOHOL

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**Key Word Index**—Lichens; depside cleavage; barbatic acid; *t*-butyl rhizonate; *t*-butyl haematommate; atranorin.

**Abstract**—Depsides have been found to cleave readily on prolonged heating with *t*-butyl alcohol to give *t*-butyl esters and the free phenols.

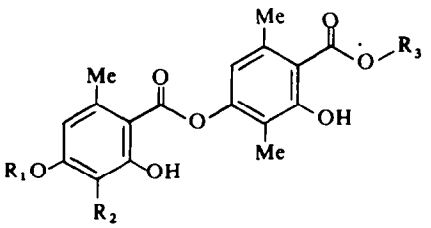
Depsides are a class of compounds which appear to be unique to the lichens. These compounds are dimeric esters of variously substituted orsellinic acids and are the major source of the so-called lichen acids. Since the two halves of the esters are so similar, it is often difficult to distinguish which is the phenolic part of the ester and which is the carboxylic acid portion. The cleavage is frequently accomplished by the use of conc $H_2SO_4$ [1]. This leads to some ambiguity when the depside exists as the free acid. A second method is to use alcoholysis with methanol or ethanol in the presence of KOH [2]. This has several drawbacks, the first of which is the known instability of orsellinic acids in the presence of alkali, and a second is the common occurrence of the depside as the methyl ester. It is difficult to separate the methyl from ethyl esters and methyl and methylene protons of the esters cause some difficulties when attempting to interpret NMR data on depsides containing methyl ethers.

We have discovered a method which seems to circumvent all the above difficulties. This involves refluxing the depsides in a hexane–*tert*-butyl alcohol mixture or in *tert*-butyl alcohol alone for 24–48 hr. The overall reaction is carried out under completely neutral conditions. This accomplishes a *tert*-butanolysis of the phenolic ester and we have observed no other products than the starting material and the alcoholysis products. The reactions are easily followed by TLC on silica gel G in 10% methanol in chloroform and iodine vapor for detection. The products are readily separated in high purity by PLC using the same system and eluting the separated layers with methyl alcohol.

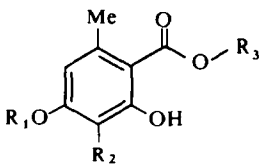
This alcoholysis of depsides is not restricted to *tert*-butyl alcohol but occurs also with alcohols such as methanol and ethanol under neutral conditions. Indeed, the extraction of a lichen with chloroform containing 3/4% of ethanol as a stabilizer leads to extensive ethanolic cleavage of depsides. The advantage of *tert*-butyl alcohol is its uniqueness since *tert*-butyl esters are virtually unknown in naturally occurring compounds and the large increase in molecular weight makes it relatively simple to separate the *tert*-butyl ester from the normally occurring methyl esters.

Using this method we have treated atranorin (**1a**) with 10% *tert*-butyl alcohol in refluxing hexane for 24 hr. This resulted in about 90% cleavage of the depside to *tert*-butyl haematommate (**2a**) and methyl-β-orcinol carboxylate (**2b**). *Tert*-butyl haematommate was identified by its MW of 252 (MS) and other spectral data listed in the Experimental.

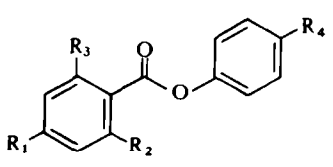
A second depside which readily cleaved by this method was barbatic acid (**1b**); when refluxed with *tert*-butyl alcohol for 48 hr it was converted almost completely into *tert*-butyl rhizonate (**2c**) and β-orcinol carboxylic acid (**2d**) although we did not isolate the latter.



**1a** $R_1$ = H; $R_2$ = CHO; $R_3$ = Me
**1b** $R_1$ = $R_2$ = Me; $R_3$ = H



**2a** $R_1$ = H; $R_2$ = CHO; $R_3$ = $CMe_3$
**2b** $R_1$ = H; $R_2$ = $R_3$ = Me
**2c** $R_1$ = $R_2$ = Me; $R_3$ = $CMe_3$
**2d** $R_1$ = $R_3$ = H; $R_2$ = Me



**3a** $R_1$ = $R_2$ = $R_3$ = $R_4$ = H
**3b** $R_1$ = $R_2$ = $R_3$ = H; $R_4$ = $NO_2$
**3c** $R_1$ = OMe; $R_2$ = $R_3$ = H; $R_4$ = $NO_2$
**3d** $R_1$ = $R_3$ = $R_4$ = H; $R_2$ = OH
**3e** $R_1$ = $R_2$ = $R_3$ = Me; $R_4$ = H

This cleavage of an ester, even a phenolic ester by *tert*-butyl alcohol is quite surprising. *Tert*-butyl alcohol is notoriously poor as a nucleophile even as the butoxide, although there is some precedent for alcohol exchange by the latter [3]. We hoped to find the necessary conditions for this *tert*-butanolysis by carrying out the reaction on a number of variously substituted phenylbenzoates. We attempted the *tert*-butanolysis on phenyl benzoate (**3a**), *p*-nitrophenylbenzoate (**3b**), *p*-nitrophenyl-*p*-methoxybenzoate (**3c**), phenylsalicylate (**3d**), and phenyl mesitoate (**3e**). The reaction failed completely in all of these models. It appears, therefore, that the reaction requires most or possibly all of the substituents of β-orsellinic acid for it to occur.

## EXPERIMENTAL

Tert-*butanolysis of atranorin.* Atranorin (200 mg) was heated under reflux in 200 ml 10% *t*-BuOH in hexane for 24 hr. The solvents were then removed under reduced pressure and the residue analysed by TLC on Si gel G using 10% MeOH in $CHCl_3$. Development of the plate with $I_2$ vapor showed 3 compounds present with $R_f$s 0.75, 0.62 and 0.47. The reaction mixture was separated by PLC on a plate 40 × 20 cm and a 0.1 cm thick adsorbant layer. Extraction of the separated layers yielded *tert*-butyl haematommate (**2a**) [($R_f$ 0.75; 100 mg; mp 119–120°; IR (KBr) $cm^{-1}$: 3450, 2980, 2870, 1660, 1180, 810; NMR ($CCl_4$) δ 1.63 (9H, *s*), 2.52 (3H, *s*), 6.27 (1H, *s*), 10.38 (1H, *s*), 12.40 (1H, *s*, exchanges with $D_2O$), and 13.28 (1H, *s*, exchanges with $D_2O$)], methyl-β-orcinol carboxylate ($R_f$ 0.61, 70 mg, mp 142–143°), and atranorin ($R_f$ 0.47, 40 mg, mp 195–196°).

Tert-*butanolysis of barbatic acid.* Barbatic acid (200 mg) was heated under reflux with 50 ml *t*-BuOH for 48 hr. The solvent was then removed and the residue analysed by TLC using 10% MeOH in $CHCl_3$. Development with $I_2$ vapor showed 2 strong spots with $R_f$ values of 0.89 and 0.52 and a weak spot with $R_f$ 0.18. The weak spot corresponds to barbatic acid. The residue was stirred with 50 ml 5% $NaHCO_3$ and then extracted exhaustively with hexane. The hexane extract was washed twice with 25 ml 5% aq. $NaHCO_3$ and then with 25 ml $H_2O$. The hexane soln was dried and the solvent removed to yield 50 mg of a solid which was crystallized from hexane to yield crystals of *tert*-butyl rhizonate [mp 70–72°; IR ($CCl_4$) $cm^{-1}$: 3400, 1660; NMR ($CCl_4$) δ 1.62 (9H, *s*), 2.00 (3H, *s*), 2.49 (3H, *s*), 3.80 (3H, *s*), 6.13 (1H, *s*) and 11.79 (1H, *s*, exchanges with $D_2O$)].

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# A NOVEL CYCLOPENTENONE, 5-DODECANYL-4-HYDROXY-4-METHYL-2-CYCLOPENTENONE FROM *CINNAMOMUM CAMPHORA*

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**Key Word Index**—*Cinnamomum camphora*; Lauraceae; cyclopentenone; 5-dodecanyl-4-hydroxy-4-methyl-2-cyclopentenone; structural determination.

In the course of our studies on the Lauraceae [1], we have isolated a novel cyclopentenone, as a minor component from the heart wood of a sesquiterpene tree [2], *Cinnamomum camphora* Sieb. Here we report its isolation and structural determination.

The hexane extract of shavings of the heart wood was concentrated and steam distilled to remove volatile components. The residue, dissolved in hexane, was chromatographed on a Si gel column (solvent; hexane–EtOAc = 100:0 ~ 0:100) into 22 fractions. Fraction 8 was rechromatographed on a Si gel column (solvent; $C_6H_6$–EtOAc = 9:1) into 7 fractions. Compound (**1**) was isolated from fraction 6 by PLC on Si gel with $C_6H_6$–EtOAc(22:3). Mp 42 ~ 43°, $[\alpha]_D$ −1.14° (EtOH = *c* 3.36), $\lambda_{max}^{EtOH}$ 224 nm (ε = 11000). (Found: C, 77.5; H, 10.9. Calcd for $C_{18}H_{32}O_2$: C, 77.1; H, 11.4%.) $\nu_{max}^{KBr}$ $cm^{-1}$: 3300, 1715, and 1580. PMR (100 MHz, $CCl_4$): δ 0.92 (3H, *t*, *J* = 6 Hz, $C\underline{H}_3CH_2$-), 1.17 (3H, *s*, $C\underline{H}_3$C-OH), 1.30 (22 H, 11 × $C\underline{H}_2$), 2.78 (1 H, *m*, C-5), 6.17 (1 H, *dd*, *J* = 7 and 1.5 Hz, C-2), and 7.04 (1 H, *dd*, *J* = 7 and 1.5 Hz, C-3). MS: *m/e* 280 ($M^+$), 265 ($M^+$ − 15), 252 ($M^+$ − 28), 154, 140, 125, 112, 111 (100), and 97.

IR and UV spectra indicate that this compound is an **α,β-unsaturated** ketone. Catalytic hydrogenation with Pd–C affords a cyclopentanone **2**: mp 59.4 ~ 60.1°, $[\alpha]_D$ ±0° ($CHCl_3$ *c* 1.2); $\nu_{max}^{KBr}$ $cm^{-1}$: 3300 and 1745: PMR: δ 0.91 (3H, *t*, *J* = 7 Hz), 1.02 (3H, *s*), 1.29 (22 H), 1.8 2.4 (5H, *m*) and 2.82 (1H, *s*, O<u>H</u>); MS *m/e* 282 ($M^+$), 264 ($M^+$ − 18), 254 ($M^+$ − 28) and 239 ($M^+$ − 28 − 15). The double bond of **1** is located in the ring, because it is conjugated with the carbonyl group and has two olefinic protons which are situated on the α- and β-carbons with respect to the carbonyl group. The carbon which is attached to the methyl group is tertiary (3 H, *s*), and that