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_fs 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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Phytochemistry, 1979, Vol. 18, pp. 488–489 © Pergamon Press Ltd. Printed in England 0031-9422/79/0301-0488 $02.00/0

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

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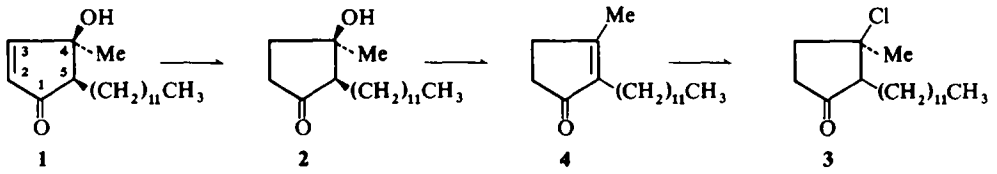
(*Received* 4 *May* 1978)

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), λ_{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%.) ν_{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); ν_{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



attached to the OH group is also tertiary, because its PMR-spectrum shows no signal in the region between 3 to 5 ppm. The side chain is a dodecanyl group attached to C-5, indicated by the signals at 0.92 ppm (3 H, *t*) and 1.30 ppm (22 H), *m/e* 111 ($M^+ - 169$) and 112 ($M^+ - 169 + 1$). Thus **1** is identified as 5-dodecanyl-4-hydroxy-4-methyl-4-cyclopentenone. This conclusion is confirmed by the following spin-decoupling. On irradiation at 2.78 ppm (C-5), the two signals (*dd*) at 6.17 (C-2) and 7.04 (C-3) collapse into two clear doublets; on irradiation at 6.17 ppm the *dd* at 7.04 ppm collapses into a doublet ($J = 1.5$ Hz), and on irradiation at 7.04 ppm the signal at 6.17 ppm collapses into a doublet ($J = 1.5$ Hz). These decouplings indicate that both couplings between C-5 and C-3 and between C-5 and C-2 are long range ones.

In order to dehydrate **2**, 0.1 ml of $SOCl_2$ was added to a soln of **2** (30 mg) in 2 ml of Py and the mixture poured into 1 N H_2SO_4. The product was extracted with hexane, washed with H_2O, dried and concentrated *in vacuo* to give a pale yellow liquid **3**. PMR: δ 0.92 (3 H, *t*, $J = 7$ Hz), 1.3 (22 H), 1.53 (3 H, *s*) 1.6 ~ 2.1 (5 H, *m*): MS: *m/e* 300 (M^+), 302 ($M^+ + 2$), 265 ($M^+ - Cl$), and 264 ($M^+ - HCl$). This product is found to be 4-chloro-5-dodecanyl-4-methylcyclopentanone from its IR PMR, and MS spectra, and affords two spots on TLC which correspond to the *cis*- and *trans*-isomers.

The formation of **3** is considered to be the result of dehydration of **2** to **4** followed by nucleophilic addition of HCl, because the direct substitution of OH group by Cl is considered to be impossible. We could not detect any isomer of **4**, i.e. 2-dodecanyl-4-methyl-3-cyclopentenone, or 2-dodecanyl-3-methylenecyclopentanone, which may be resistant to HCl under these circumstances. From these considerations we supposed that the C_{12} side chain and the methyl group are *trans* in **2** and also in **1**.

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Phytochemistry, 1979, Vol. 18, pp 489–490 © Pergamon Press Ltd Printed in England 0031-9422/79/0301-0489 $02.00/0

THYMOL-DERIVATE AUS *NEUROLAENA*-ARTEN*

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(*Eingegangen am 6 September* 1978)

Key Word Index—*Neurolaena oaxacana*; *N. venturana*; *N. lobata*; *Bebbia juncea var. aspera*; *Schistocarpha longiligula*; *S. oppositifolia*; Compositae; thymol derivatives.

Die Eingruppierung der Gattung *Neurolaena* ist botanisch umstritten [1]. Gewisse Merkmale deuten auf eine Beziehung zu *Arnica* hin, während nach F. Stuessy eine Einordnung in die Tribus Heliantheae vorgeschlagen wird [1], in eine Subtribus mit *Bebbia*, *Zaluzania* und *Schistocarpha*. Wir haben jetzt die Wurzeln von drei *Neurolaena*-Arten untersucht, um zu prüfen, ob die Inhaltsstoffe Anhaltspunkte über verwandtschaftliche Beziehungen geben.

Neurolaena oaxacana liefert die Thymol-Derivate **1**–**4**, von denen **1** bisher nicht bekannt war. Die Konstitution folgt eindeutig aus den spektroskopischen Daten. *N. lobata* enthält die Thymol-Derivate **2**–**6** sowie die Kohlenwasserstoffe **7**–**8**, während aus den Wurzeln von *N. venturana* nur **2** und **3** isoliert wurden.

Bebbia juncea var. *aspera* Wurzeln liefern **9**–**11**, die von *Schistocarpha longiligula* wie *Sch. bicolor* [2] **9**, **10** und **12** und die von *Sch. oppositifolia* **9**. Die Inhaltsstoffe der untersuchten *Neurolaena*-Arten zeigen also keine Anhaltspunkte, daß eine gemeinsame Eingruppierung mit *Bebbia* und *Schistocarpha* gerechtfertigt ist. Verbindungen vom Typ **9**–**12** sind bei Vertretern der Tribus Heliantheae häufiger [3], jedoch nicht bei *Zaluzania*-Arten beobachtet worden. Hier findet man neben Sesquiterpenlactonen [4] vor allem Kauren-Derivate [5]. Thymol-Derivate, wie sie aus den *Neurolaena*-Arten

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