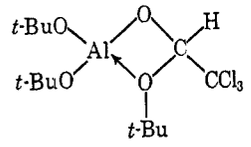
electron-withdrawing effect at 30°. The Meerwein–Ponndorf–Verley reduction is another possible reaction of aluminum alcoholate with a carbonyl compound. The possibility of this reaction, however, was eliminated because of the absence of a hydrogen atom on the α-carbon atom in the *t*-butoxy group.

The structure of II was confirmed by elemental analysis and by the products of acid hydrolysis and of acetylation with acetic anhydride, as well as by the nmr spectrum of its benzene solution. Acid hydrolysis of II with acetic acid produced 3 mol of *t*-butyl alcohol per gram atom of aluminum. Treatment of II with acetic anhydride gave the hemiacetal acetate (III) and chloral in addition to *t*-butyl acetate. The combined amount of III and chloral was 0.97 mol/g-atom of aluminum (calcd, 1.00).

$$\text{II} \xrightarrow{\text{acetic anhydride}} \underset{\displaystyle \underset{\displaystyle CCl_3}{|}}{CH_3CO_2CHOBu\text{-}t} + \text{chloral} + CH_3CO_2Bu\text{-}t$$

III

The nmr spectrum of a benzene solution of II showed four signals, *i.e.*, δ 1.36 (s, 9 H), 1.39 (s, 9 H), 1.55 (s, 9 H), and 4.55 (s, 1 H). The three singlets at lower fields were assigned to the three kinds of protons of the *t*-butyl group. The last singlet was ascribed to the hydrogen of the hemiacetal group. Cryoscopic molecular weight of II in benzene was 394 ± 20 (calcd for the monomer, 394). A monomeric structure may reasonably be assumed to be as follows:



IV

Nonequivalence of two *t*-butoxyl groups may be due to the difference in their spatial relations to the trichloromethyl group. The monomeric structure of II in benzene was not stable. After 10 days at room temperature, the nmr spectrum changed to a more complex one. The four sharp singlets broadened and some new signals appeared in the vicinities of the original four singlets. However, the area ratio of the peaks at lower fields to the groups of peaks at higher fields was still 1:27. This finding is interpreted as indicating the retention of the hemiacetal structure.

The reactivity of the hydrogen of compound II with carbonyl compounds was then examined. Among the ketones employed in the present study, only trifluoroacetone was reduced by II to 1,1,1-trifluoropropanol-2. The decreased activity of the hemiacetal hydrogen of II is due to the electron-withdrawing effect of the trichloromethyl group. In addition, II itself induced the polymerization of chloral at 0°.

In conclusion, the scheme of the aldehyde polymerization and the Tishchenko reaction has been supported by the findings of the present study.

Experimental Section

Reaction of Chloral with Aluminum *t*-Butoxide.—A mixture of 0.0132 mol of chloral and 0.0130 mol of aluminum *t*-butoxide in 20 ml of *n*-heptane was kept at 30°. A white crystalline material (II) began to separate from the yellowish reaction system after 10 days. The amount of II increased progressively up to 30 days. Product II was isolated by filtration, washed several times with *n*-heptane, and finally dried *in vacuo* at room temperature. The yield of II was 66.5% (calcd as the 1:1 adduct.).

Anal. Calcd for $C_{14}H_{28}AlCl_3O_4$: Al, 6.85. Found: Al, 6.81.

In the glpc analysis of the filtrate, none of the Tishchenko products were detected. Unreacted chloral was 10.4%.

Attempts at further purification of II were futile. Compound II decomposed without melting and subliming *in vacuo*. It was only slightly soluble in benzene and in methylene dichloride. Recrystallization from these solvents was unsuccessful because of the decomposition of II.

The total *t*-butoxyl groups of II was determined by the glpc analysis of *t*-butyl alcohol produced by treatment with an excess acetic acid at room temperature. The ratio of *t*-BuOH/Al was 3.00 (calcd for II, 3.00).

At 60°, a mixture of 0.1 mol of chloral and 0.01 mol of aluminum *t*-butoxide in 20 ml of benzene was kept for 1 day. The reaction mixture was thereafter treated with 1 *N* HCl, and was extracted with ether. The ether extract was analyzed by glpc. The Tishchenko reaction products, trichloroethyl trichloroacetate (5.3%), *t*-butyl trichloroacetate (0.1%), and trichloroethanol (6.8%), were obtained.

Reaction of II with Acetic Anhydride.—A solution of II in toluene was treated with an excess acetic anhydride at 100°. Product III and chloral as well as *t*-butyl acetate were produced. The structure of III was established by elemental analysis and ir and nmr spectra: nmr, δ 6.14 (s, 1 H), 2.06 (s, 3 H) and 1.30 (s, 9 H).

Anal. Calcd for $C_8H_{13}Cl_3O_3$: C, 36.46; H, 4.97; Cl, 40.36. Found: C, 36.71; H, 5.18; Cl, 40.46.

The amounts of III and chloral (mole ratios to aluminum) were 0.695 and 0.274, respectively. The combined amount of the two products was 0.97 (calcd, 1.00).

Reaction of II with 1,1,1-Trifluoroacetone.—A mixture of 0.001 mol of II and 0.01 mol of 1,1,1-trifluoroacetone was heated at 60° for 45 hr. Then the reaction system was treated with an excess acetic acid. 1,1,1-Trifluoroisopropyl alcohol (5.7% based upon the initial aluminum compound) was found by glpc analysis. In the reactions with other ketones such as acetone and benzophenone of less reactivities, however, no corresponding alcohols were detected.

Registry No.—II, 17192-31-3; III, 17203-07-5.

Chemotaxonomy of the Rutaceae. III.[1] Isolation of Halfordinol Derivatives from *Aeglopsis Chevalieri* Swing.

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Received February 5, 1968

The isolation of isopimpinellin from the seeds of one of the hard shell citrus, *Aeglopsis chevalieri* Swing. (Rutaceae),[4] was described in a previous communication from this laboratory.[5] This paper describes the isolation, from the whole fruit of this plant, of several coumarins of a type widespread in the Rutaceae as well as a new alkaloid which is shown to be O-isopentenylhalfordinol (**3**).

(1) Part II: D. L. Dreyer, *Tetrahedron*, **23**, 4613 (1967).

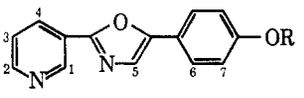
(2) Department of Chemistry, San Francisco State College, San Francisco, Calif.

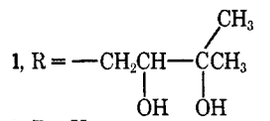
(3) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(4) The botany of this genus is discussed by Swingle: W. T. Swingle in "The Citrus Industry," Vol. 1, H. J. Webber and L. D. Batchler, Ed., University of California Press, Berkeley, Calif., 1943, p 460.

(5) D. L. Dreyer, *Phytochemistry*, **5**, 367 (1966).

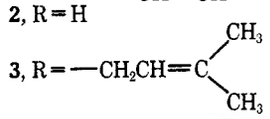
Chromatography of fruit extracts on alumina gave fractions from which small amounts of imperatorin, isopimpinellin, aesculetin dimethyl ether, and a new compound, mp 106–108°, were obtained. The alkaloidal nature of the new product was suggested by its ultraviolet spectral shift in dilute acid. Initial inspection of the 60-MHz nmr spectrum indicated the alkaloid was closely related to a series of oxazole alkaloids occurring in *Halfordia scleroxyla* F. Muell., another rutaceous plant.[6] These alkaloids show characteristics downfield resonances due to the pyridine ring. The ultraviolet spectrum and its acid shift were identical with those reported[6] for halfordine (**1**). The alkaloidal material appeared homogeneous by the usual criteria (mp, tlc) and only after a detailed examination of the nmr spectra at 60 and 100 MHz was it apparent that the material was a mixture of two closely related compounds. The resonances of the oxazole and phenyl protons were doubled, indicating the presence of two closely related species.



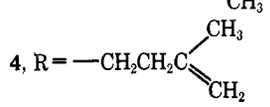


1, R = —$CH_2CH(OH)C(CH_3)_2OH$

2, R = H



3, R = —$CH_2CH{=}C(CH_3)_2$

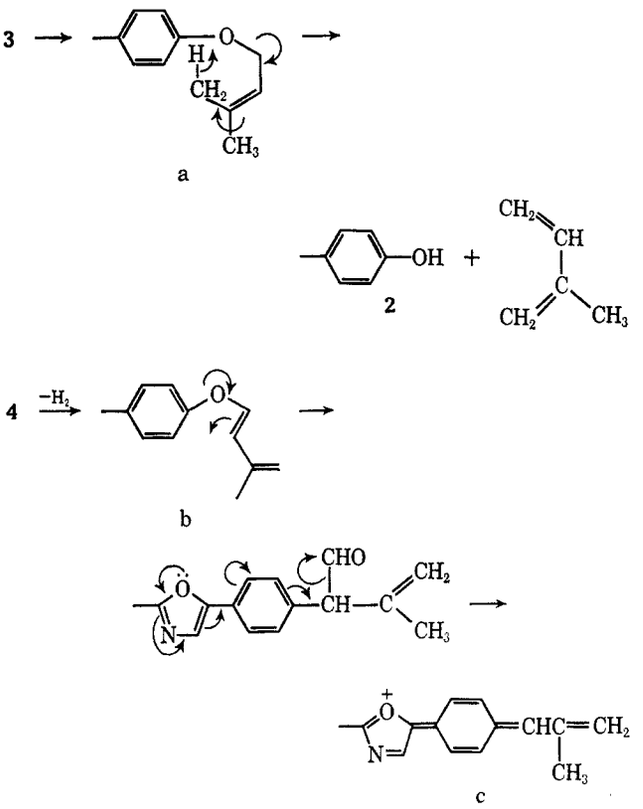


4, R = —$CH_2CH_2C(CH_3){=}CH_2$

The 100-MHz nmr spectrum showed that the aliphatic portion of the alkaloid mixture was isopentenyl in nature. The ratios of the integrated areas for the vinylidine resonances of **4** with the allyl ether methylene resonance of **3** showed that it was a mixture of **3** and **4** in the ratio of approximately 3:2.[7,8]

The mass spectrum of the alkaloid mixture gave substantial support for the presence of the two isomeric isopentenyl side chains. Thus, the molecular ion (*m/e* 306) fragments directly to halfordinol (**2**) (*m/e* 238), presumably by a cyclic process (Scheme I, a) which is characteristic of allyl ethers.[1] This assignment is supported by a metastable peak at *m/e* 185. The presence of a metastable peak at *m/e* 249.5 indicated a fragmentation of the dehydrogenation product (b) M − 2 (302 → 275 + 29). The loss of CHO, possibly by a four-membered transition state (b) (although a six-membered transition state with concurrent hydrogen migration cannot be excluded) gives a species best formulated as c.[9] A further metastable peak at *m/e* 141 supports a fragmentation of 238 → 183.

SCHEME I



Peaks present at *m/e* 69, 67, and 41 represent the five- and three-carbon fragments of the side chain.

Repeated recrystallization of the alkaloid mixture gave a pure sample of the allyl ether derivative (**3**). Mild acid hydrolysis of the alkaloid gave halfordinol (**2**),[6,10] thus confirming the proposed structure.

The sum of the evidence thus indicates that two isomeric halfordinol isopentyl ethers (**3** and **4**) occur in *A. chevalieri*. The alkaloids found in this study are reasonable biogenetic intermediates to the more highly oxidized halfordinol derivatives, for example, halfordine (**1**), previously reported by Crow and Hodgkin.[6]

Experimental Section

Isolation.—Fruit from which the seeds had been removed was ground and extracted with acetone. Solvent was removed from the extracts and the residue was chromatographed on alumina. Fractions from the column were monitored by tlc using silica gel coated plates and a 1:1 chloroform–ethyl acetate developing system. Spots were detected by examination under ultraviolet light. Elution of the column with hexane gave fractions containing imperatorin which was identified by comparison of ultraviolet and infrared curves with those of an authentic sample.[11] Elution with 20% benzene in hexane gave fractions which upon tlc fluoresced blue under ultraviolet light and turned yellow with HCl gas. Removal of solvent and crystallization of the residue from ethyl acetate–hexane and then methanol gave the alkaloid mixture: mp 106–108°; mass spectrum, *m/e* 39 (6), 41 (24), 51 (8), 63 (8), 67 (6), 69 (20), 77 (12), 78 (7), 105 (5), 106 (6), 117 (6), 121 (6), 154 (6), 183 (22), 222 (7), 237 (7), 238 (100), 239 (17), 275 (11), 304 (20), 306 (6). Recrystallization of the alkaloid mixture from ethyl acetate–hexane gave pure **3**: mp 109–111°; λ_{max}^{EtOH} 248 mμ (ε 5800), 260 (5700), 325 (12000); $\lambda_{max}^{EtOH\text{-}HCl}$ 261, 348 mμ; nmr ($CDCl_3$) δ 9.31 (H-1), 8.66 (*J* = 5 Hz, H-2), 8.34 (*J* = 8 Hz, *J* = 1.5 Hz, H-4), 7.67 (*J* = 9 Hz, H-6), 7.38 (coupling obscured, H-3), 7.38 (H-5), 7.00 (*J* = 9

(6) W. D. Crow and J. H. Hodgkin, *Aust. J. Chem.* **17**, 119 (1964).

(7) An attempt to resolve the two components of the mixture on silver nitrate impregnated silica gel tlc[8] was unsuccessful. The alkaloids failed to migrate, presumably due to complexing of the nitrogens with the silver nitrate.

(8) J. M. Bobbitt, "Thin Layer Chromatography," Reinhold Publishing Corp., New York, N. Y., 1963, p 22.

(9) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1964, p 175.

(10) A. Brossi and E. Wenis, *J. Heterocycl. Chem.*, **2**, 310 (1965).

(11) D. L. Dreyer, *J. Org. Chem.*, **30**, 749 (1965).

Hz, H-7), 5.54 (J = 7 Hz, vinyl), 4.59 (J = 7 Hz, allyl methylene), 1.78 (C-methyls).

Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.48; H, 5.92; N, 9.14. Found: C, 74.9; H, 6.22; N, 8.29.

Further elution of the column with increasing amounts of benzene in hexane gave fractions from which small amounts of isopimpinellin were obtained. Work-up of fractions eluted with 50% benzene in hexane gave small amounts of aesculetin dimethyl ether, mp 140–142°; infrared and nmr spectra were superimposable on those from a sample of aesculetin dimethyl ether prepared from aesculetin with diazomethane: nmr ($CDCl_3$), δ 7.81 (d, J = 9 Hz, H-4), 6.87, 6.84 (s, H-5 and H-8), 6.27 (d, J = 9 Hz, H-3), 3.95, 3.94 (methoxys).

Hydrolysis of 3.—A solution of 20 mg of **3** in 3 ml of acetic acid containing several drops of concentrated HCl was heated 30 min on a steam bath. The mixture was diluted with sodium carbonate solution and extracted with ethyl acetate. The extracts were washed with 5% sodium carbonate solution and dried and the solvent was removed. The residue was crystallized from methanol, mp 256–258°, and was identical in all respects with an authentic sample of halfordinol (2).

Registry No.—**3**, 17190-80-6; **4**, 17190-81-7.

Acknowledgments.—The author is indebted to Dr. W. D. Crow for an authentic sample of halfordinol and to Dr. D. J. Bertelli for the 100-MHz nmr spectrum.

The Conversion of Cinerone into Cinerolone[1]

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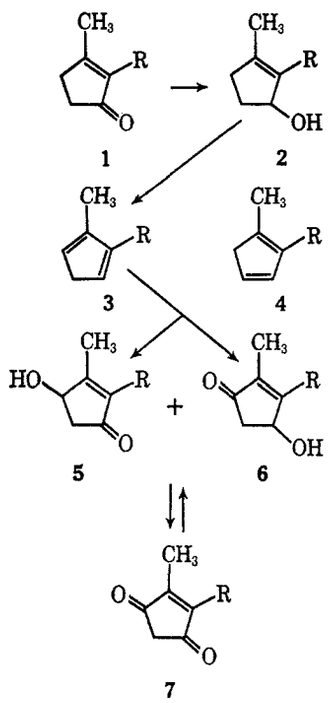
Received April 25, 1968

The pyrethrins are the most important natural insecticides and comprise the major active constituents of pyrethrum flowers.[2] *cis*-Cinerolone (**5**) is a valuable intermediate for the preparation of cinerin I and cinerin II both of which are active constituents present in pyrethrum extract.[2] Although the synthesis of *cis*-cinerolone (**5**) has been reported by other workers,[3,4] the routes employed are lengthy and terminate in low over-all yields.

We began our attempt at a synthesis of *cis*-cinerolone (**5**) by investigating various means of introducing a C-4 substituent in cinerone (**1**). Cinerone (**1**) was prepared by alkylation of 2-lithio-5-methylfuran[5] with *cis*-1-bromo-3-pentene[4] followed by acid cleavage and base-catalyzed cyclization, as utilized in a recent synthesis of *cis*-jasmone.[6] Earlier work had shown that bromination with N-bromosuccinimide could not be successfully applied to cyclopentenones with an unsaturated side chain.[7] Treatment of cinerone with lead tetraacetate in benzene, cupric bromide in chloroform and ethyl acetate, *t*-butyl peracetate with cuprous chloride in benzene, *t*-butyl chromate in carbon tetrachloride or selenium dioxide in aqueous ethanol did not succeed in selectively introducing a C-4 substituent.

We have recently developed a novel indirect chemical conversion of cinerone into cinerolone (Scheme I).

SCHEME I



R = —CH_2CH=$CHCH_3$(*cis*)

The key steps in our synthesis of cinerolone are based on the many examples of Diels–Alder addition of oxygen to cyclic conjugated dienes leading to *endo* peroxides and their subsequent rearrangement in basic media to hydroxyenones.[8] Reduction of cinerone (**1**) with lithium aluminum hydride yielded 2-(2′-*cis*-butenyl)-3-methyl-2-cyclopenten-1-ol (**2**). Dehydration of **2** with *p*-toluenesulfonic acid in benzene proceeded at room temperature to give 2-(2′-*cis*-butenyl)-3-methylcyclopentadiene (**3**), $\lambda_{max}^{C_6H_{12}}$ 243 mμ (ϵ 4000), with nmr absorptions at τ 3.94 (2 H, singlet with fine structure), 4.40 (2 H, multiplet), 8.00 (3 H, singlet with fine structure) and 8.29 (3 H, doublet, J = 5 cps). The nmr spectrum of the alternative structure (**4**) would be expected to be more complex in the region of the cyclopentadiene hydrogens. Elimination of water from **2** is probably assisted by the double bond leading to a tertiary carbonium ion which loses a proton to give **3**.

Irradiation of a methanol solution of **3** containing eosin as a sensitizer with visible light while bubbling a stream of oxygen through the solution gave an oil which was left on a column of basic alumina for 15 hr. Chromatography of the eluent gave an 11% yield of a mixture of two hydroxy cyclopentenones with the same R_f on tlc as that of authentic cinerolone.[9] Small amounts of the two pure compounds were separated by preparative glpc and the major component (58% of the mixture) was identified as cinerolone (**5**) by comparison of its glpc retention time and spectra (ir, nmr, uv, and mass) with those of the authentic material.[9] The

(1) Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) L. Crombie and M. Elliot, *Fortschr. Chem. Org. Naturstoffe*, **19**, 120 (1961).

(3) M. S. Schechter, N. Green, and F. B. LaForge, *J. Amer. Chem. Soc.*, **74**, 4902 (1952).

(4) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1152 (1950).

(5) Method of V. Ramanathan and R. Levine, *J. Org. Chem.*, **27**, 1216 (1962).

(6) G. Buchi and H. Wuest, *ibid.*, **31**, 977 (1966).

(7) L. Crombie, M. Elliot, and S. H. Harper, *J. Chem. Soc.*, 971 (1950).

(8) Y. A. Arbuzov, *Russ. Chem. Rev.*, **34**, 558 (1965).

(9) M. Elliot, *J. Chem. Soc.*, 5225 (1964).