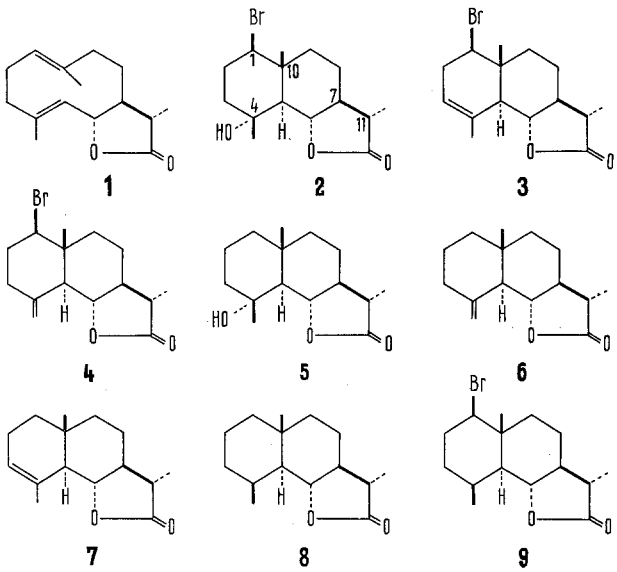
The *exo*-isomer[16] **4** [mp 169–170°, $[\alpha]_D^{29}$ +79.1° (c 1.46); ν max (cm^{-1}) 1770, 1173 (saturated γ-lactone), 1655 and 893 (exocyclic methylene); NMR (τ) 5.02, 5.14 (s, 2H, $>C=CH_2$), 5.97 (m, 2H, >CHBr and >CH–O–C(=O)– units), 8.79 (d, 3H, J = 7.0 Hz, C-11 Me), 9.03 (s, 3H, angular methyl)] gave analysis for $C_{15}H_{21}O_2Br$, further corroborated by high resolution mass measurements: M^+ ($C_{15}H_{21}O_2{}^{79}Br$; observed mass 312.0724, calculated mass 312.0726), M–Br ($C_{15}H_{21}O_2$; observed mass 233.1540, calculated mass 233.1542). Catalytic hydrogenation of *endo*- as well as *exo*-isomers **3** and **4** in glacial acetic acid over PtO_2 led to a fully saturated bromolactone **9** [mp 199–200°, $[\alpha]_D^{29}$ +11.9° (c 0.69); NMR (τ) 6.01 (m, 2H, >CHBr and >CH–O–C(=O)– units), 8.73 and 8.83 (6H, doublet due to C-11 methyl partly superimposed on the singlet due to C-10 methyl), 8.96 (d, 3H, J = 7.0 Hz, C-4 methyl); ν max 1761 cm^{-1} (γ-lactone); M^+ peak at m/e 314 ($C_{15}H_{23}O_2{}^{79}Br$; observed mass 314.0882, calculated mass 314.0880)] which on catalytic debromination in EtOH (10% Pd–C, H_2, trace of Et_3N) furnished a crystalline compound **8**, mp 155–156°, which showed no depression in its melting point when admixed with an authentic specimen of 4:5 α H, 6, 11 β H-eudesman 6,13-olide (santanolide 'c')[17]. Furthermore, their IR- and mass spectra were comparable.

Thus, these chemical correlations with santenolides (**6**, **7**) and santanolide 'c' (**8**), compounds with well-proven stereostructure[12,17], establish unequivocally the presence of *trans*-ring juncture in **2**, **3** and **4** produced by NBS-induced cyclization of dihydrocostunolide **1**. It may be relevant to point out that the bromolactones described in this communication are potential intermediates in the syntheses of some of the natural products currently under way in our laboratories[18,21].

Zusammenfassung. N-Bromosuccinimid-induzierte transannulare Zyklisation von Dihydrocostunolid wird beschrieben.

T. C. Jain, C. M. Banks[19] and J. E. McCloskey[20]

Department of Chemistry, University of Victoria, Victoria (British Columbia, Canada), 10 June 1969.



[16] The failure to prepare **3** and **4** from bromohydrin **2** under various experimental conditions clearly rules out any possibility of their derivation from **2** during NBS reaction carried out under mild conditions.

[17] E. J. Corey and A. G. Hortmann, J. Am. Chem. Soc. *87*, 5736 (1965) and references cited therein.

[18] Support of this work by the National Research Council of Canada and the UVIC Research Committee is gratefully acknowledged. We wish to thank Professor A. Fischer for helpful discussions and his interest in this work.

[19] N.R.C. Postgraduate Scholar, 1968 until present.

[20] U.VIC Graduate Teaching Assistant, 1968 until present.

[21] Note added in proof: This reaction has now been successfully applied to costunolide and the results will be published in our full paper.

Phthalate Esters of *Oenanthe stolonifera* DC. (Umbelliferae)[1]

In a previous communication[2], we reported that the isolation and identification of several di-alkyl phthalates from *Cryptotaenia canadensis* DC. var. japonica Makino (Umbelliferae). On further investigation, three optically inactive phthalate esters, di-ethyl, n-butyl-2-ethylbutyl and di-2-ethylbutyl phthalate, have been found from benzene extract of whole plant of *Oenanthe stolonifera* DC. (Umbelliferae). It is the first case where di-2-ethylbutyl and n-butyl-2-ethylbutyl phthalate are isolated in nature.

The benzene extract was chromatographed on silica-gel column, eluted with n-hexane and then with n-hexane-ethyl acetate. The fraction eluted by n-hexane-ethyl acetate (1:1 v/v) gave a yellow oily material, which showed 9 peaks on the gas chromatogram and the characteristic IR- and UV-spectra due to di-alkyl phthalate esters.

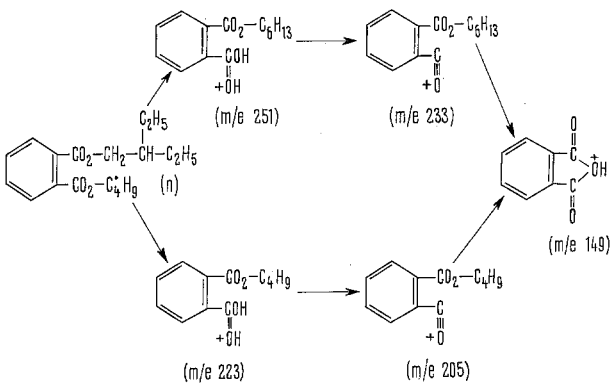
n-Butyl-2-ethylbutyl phthalate. The constituent isolated through repeated column chromatography showed UV-maxima at λ_{max}^{EtOH} nm (log ε) 225.7 (3.89), 277.5 (3.13) and 283 (3.11) due to benzene ring, IR-bands at 1733 cm^{-1}, 1285, 1130 (aromatic ester), 1605, 1586, 1075, 1043 and 747 (*ortho* substituted benzene ring) and mass spectrum having distinctive fragment ions at m/e 43 ($C_4H_9^+$), 85 ($C_6H_{13}^+$), 149 (base peak), 205, 223, 233 and 251 as represented below (Diagram). The NMR-spectrum (60 MHz, in $CDCl_3$) indicated *ortho* substituted benzene

[1] Japanese name is Seri.

[2] S. Hayashi, Y. Asakawa, T. Ishida and T. Matsuura, Tetrahedron Letters *50*, 5061 (1967).

ring protons at 7.66 ppm (symm. multiplet A_2B_2 type, 4H), 3 methyl groups which were overlapped by 3 triplet signals at 0.92–0.95 ppm (J = 6.0 Hz, 9H) and doublet at 4.25 ppm (J = 5.0 Hz, 2H) assigned $-CO_2CH_2-$CH-group and triplet at 4.13 ppm (J = 6.2 Hz, 2H) assigned $-CO_2-CH_2-CH_2-$group. From above spectral evidences, it is concluded that the constituent is a phthalate esterified with C_4 and C_6 alcohols, each of which is branched on the 2-position. The alkaline hydrolysis of this unsymmetrical phthalate ester gave phthalic acid, n-butyl and 2-ethylbutyl alcohol. Therefore, this constituent is n-butyl-2-ethylbutyl phthalate. The IR- and NMR-spectra and gas chromatographic retention time (GLC-Rt) of this ester were completely identical with those of the authentic specimen.

di-2-Ethylbutyl phthalate. The component showed the very similar IR- and UV-spectra to those of the above n-butyl-2-ethylbutyl phthalate. Its mass spectrum indicated the parent ion at 334 and characteristic fragment ions at m/e 85 ($C_6H_{13}^+$), 149 (base peak), 233 and 251. The NMR-spectrum showed symm. multiplet at 7.65 ppm (4H, *ortho* substituted benzene ring protons), symm. doublet at 4.28 ppm (J = 5.0 Hz, 4H) assigned $(-CO_2-CH_2-CH-)_2$ and triplet at 0.95 ppm (J = 6.5 Hz, 12H) assigned $(CH_3-CH_2-)_4$. On the basis of the above evidences, the component can be applied for di-2-ethylbutyl phthalate. The IR, NMR and GLC-Rt of the component coincided with the authentic specimen.



di-Ethyl phthalate. The constituent also showed characteristic IR- and UV-spectra attributable to di-alkyl phthalates and mass spectrum having strong fragment ions at m/e 29 ($CH_3-CH_2^+$), 149 (base peak) and 177. The NMR-spectrum indicated symm. multiplet at 7.63 ppm, quartet at 4.17 ppm (J = 8.0 Hz, 4H, $-CO_2-CH_2-CH_3$) and triplet at 1.32 ppm (J = 8.0 Hz, 6H, CH_3-CH_2-). The above spectral evidence can also be applied to diethyl phthalate. This assigned structure was further confirmed by the comparison of the IR- and NMR-spectra and GLC-Rt of the authentic sample.

It is known that phthalate esters are widely employed as plasticizer in formulation of plastic tubing and poly bucket. Extreme care was taken to avoid the use of these materials. For this reason, it seems likely that these esters are original components of *Oenanthe stolonifera* DC. There is a small possibility, however, that the phthalate esters are artefacts, although the above 3 phthalate esters have not been found in the benzene solvent, silica gel and filter paper etc. used in our laboratory.

In addition to phthalate esters, n-paraffins (n-C_{16} to n-C24), α-pinene, β-pinene, β-myrcene, limonene, terpinolene, p-cymene, δ-guaiene, linalool, p-cymene-8-ol, γ-phenylpropanol, elemol, benzyl alcohol, thymolmethylether, elemicin, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, palmitic acid, stearic acid, benzoic acid, phenylacetic acid, campesterol, stigmasterol and β-sitosterol were identified.

Zusammenfassung. Aus dem Extrakt von *Oenanthe stolonifera* DC. (Umbelliferae) wurden n-Butyl-2-äthylbutyl-phthalat, di-2-Äthylbutyl-phthalat und di-Äthylphthalat isoliert und deren Struktur durch chemischen Abbau und mit Hilfe physikalischer Methoden aufgeklärt.

Y. ASAKAWA, S. HAYASHI and T. MATSUURA

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima (Japan), 27 May 1969.

Heterozyklische Equileninanaloge

Östronanaloge, bei denen der aromatische Ring durch einen 5- oder 6gliedrigen Heterozyklus ersetzt ist, sind schon verschiedentlich beschrieben worden[1–4]. Wir berichten im folgenden über neue heterozyklische Derivate des Equilenins (I–III), die uns als potentielle Östrogene interessierten.

Die Synthese dieser Präparate erfolgte ausgehend vom bekannten (±)-trans-2, 3, 3a, 4, 5, 9b-Hexahydro-7-hydroxy-3a-methyl-1H-benz[e]inden-3-on (IV)[5,6].

Zum Aufbau[7] des Furanderivates I unterwarfen wir den aus IV und Allylbromid erhältlichen Allyläther V (Smp. 65–67°) in N,N-Dimethylanilin bei 200° einer *Claisen*-Umlagerung. Die Ausbeute an phenolischen Produkten betrug rund 50%; nicht umgesetztes Ausgangsmaterial wurde isoliert und erneut zur Reaktion gebracht. Die aus mehreren Ansätzen gesammelten Umlagerungsprodukte bildeten ein nicht trennbares Gemisch, das sich aus $^2/_3$ 6-Allylderivat VI und $^1/_3$ isomerer 8-Allylverbindung zusammensetzte (NMR-Interpretationen). Das Isomerengemisch wurde zunächst mit $NaBH_4$ reduziert und

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