

PHTHALATE ESTERS OF CRYPTOTAENIA CANADENSIS DC.

VAR. JAPONICA MAKINO (UMBELLIFERAE)*

Shūichi Hayashi, Yoshinori Asakawa, Takashi Ishida and Tamon Matsuura

Department of Chemistry, Faculty of Science, Hiroshima University,
Hiroshima, Japan

(Received in Japan 2 August 1967)

Although a few phthalates have been previously reported to present in kewda,¹⁾ tobacco leaf²⁾ and lily of valley,³⁾ their chemical structures have not been determined. Now, we found several alkyl phthalates, di-methyl, di-iso-butyl, iso-n-butyl, di-n-butyl, di-iso-amyl, di-n-amyl, di-n-hexyl, and di-2-ethylhexyl phthalate, from Cryptotaenia canadensis DC. var. japonica Makino which is a perennial vegetable cultivated or growing wild in all over Japan. This is the first case of the elucidation of chemical structure of phthalate occurring in plant.

The benzene extract of the whole plant was chromatographed through a silica gel adsorption column using n-hexane and benzene successively as solvent, and the benzene-eluted fraction showed the characteristic IR bands due to alkyl phthalate, and consisted of nine constituents in gas chromatogram (Fig. 1.).

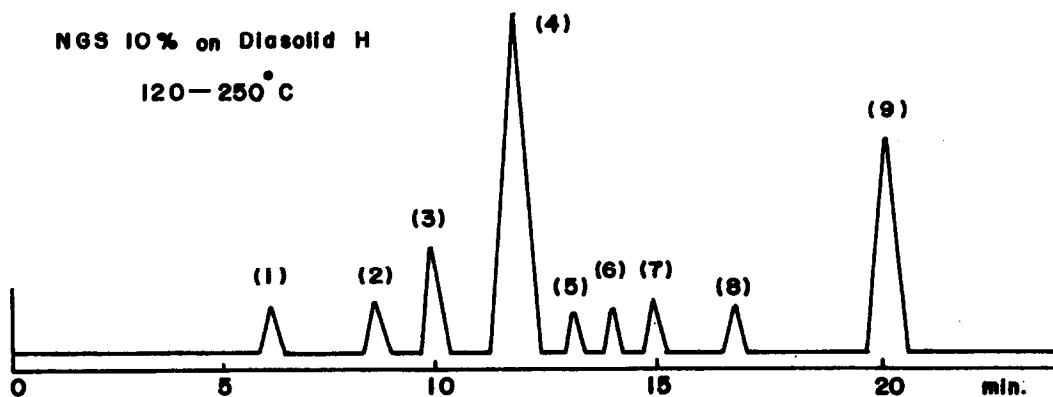
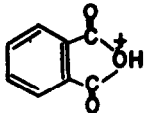
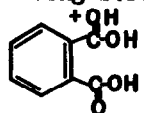
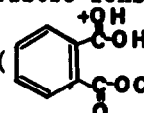


Fig. 1. Gas chromatogram of benzene extract

Di-2-ethylhexyl phthalate (peak 9)

The constituent was isolated as a pale yellow oil, $(\alpha)_D^{18} 0$, through repeating elution chromatography of the above benzene-eluted fraction using a mixed solvent of n-hexane and benzene. The constituent showed UV maxima at $\lambda_{\max}^{\text{EtOH}}$ 223.5 (ϵ , 7156), 272 (1257) and 278 μ (1126) due to benzene ring, IR bands at 1728, 1284, 1124, (aromatic ester), 1605, 1584, 1074, 1042 and 742 cm^{-1} (ortho-substituted benzene ring), and the mass spectrum having strong characteristic ions of m/e 149 (base peak, ), 167 () and 279 () as seen in Fig. 2. These spectrometric evidences indicate the constituent to be di-octyl phthalate, although the molecular ion is absent in the mass spectrum.

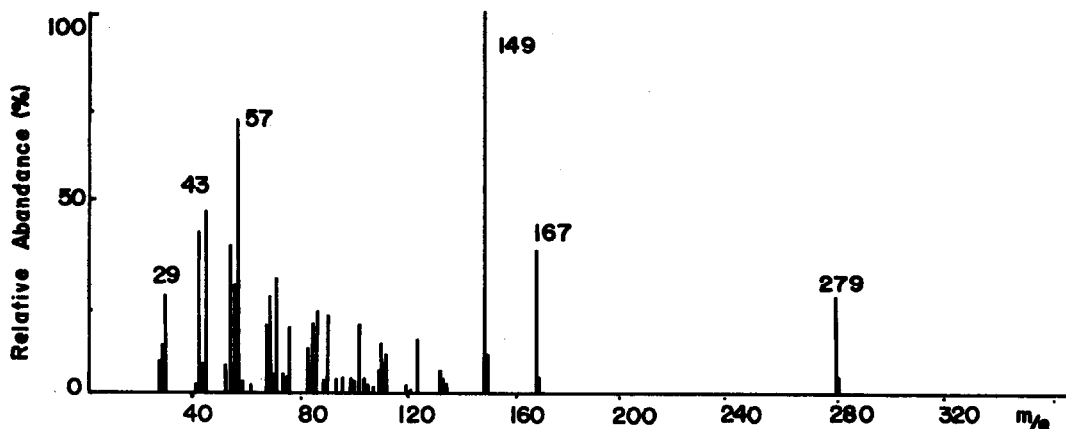


Fig. 2. Mass spectrum of di-2-ethylhexyl phthalate

The hydrolysis of the oil produced actually phthalic acid, which was identified by UV, IR spectra and the preparation of its anhydride, and 2-ethylhexyl alcohol which was proved by gas chromatography using neopentyl glycol succinate 10% (NGS) and Apiezone L 10% respectively. Therefore, this constituent is di-2-ethylhexyl phthalate, which well fits the NMR spectrum (Fig. 3). All of IR, UV, NMR spectra of this constituent were identical to the synthesized specimen.

Iso-n-butyl phthalate (peak 3) and Di-n-butyl phthalate (peak 4)

The mixed constituents of peak 2, 3 and 4 were hydrolyzed into phthalic acid and a alcohol mixture which consisted of iso- and n-butyl alcohols only. On the other hand, the constituent of peak 3 which was isolated by means of preparative gas chromatography had remarkable fragment ions of m/e 149, 167,

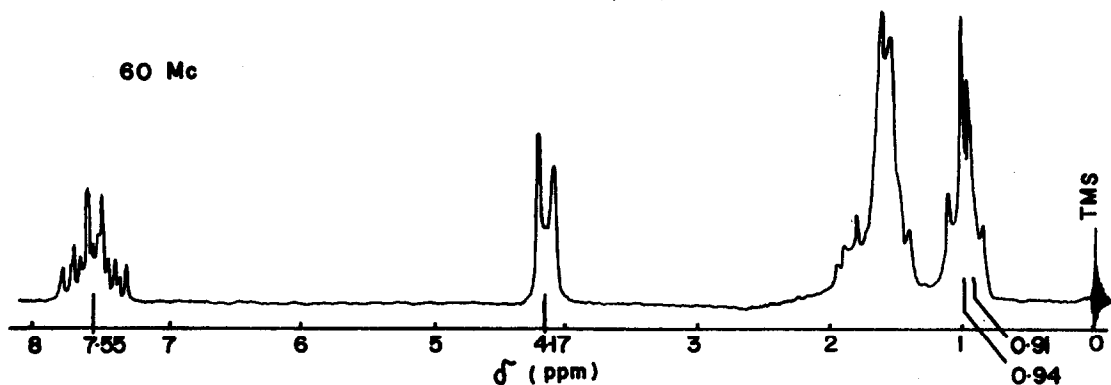


Fig. 3. NMR spectrum of di-2-ethylhexyl phthalate

205 (CC(=O)c1ccccc1C(=O)OC4H9), 223 (CC(O)(O)c1ccccc1C(=O)OC4H9) and 278 (molecular ion) in the mass spectrum. These facts indicate the constituent of peak 3 to be any one of di-iso-butyl, iso-n-butyl or di-n-butyl phthalate. Then gas chromatographic comparison with the three authentic phthalates was performed using silicon SE-30, NGS, DEGS and PEGA packed columns. Thus the constituent was iso-n-butyl phthalate.

The NMR spectrum and gas chromatogram of peak 4, which was isolated by preparative gas chromatography, coincided with those of di-n-butyl phthalate ⁴).

Di-iso-butyl phthalate (peak 2)

Although the constituent of peak 2 was not able to be isolated because of the very small amount, peak 2 was expected to be di-iso-butyl phthalate which was the remaining one among the probable three isomers of butyl phthalates, from the result in the hydrolysis of the mixture of peak 2, 3 and 4. This was confirmed by gas chromatographic comparison with the authentic di-iso-butyl phthalate.

In addition to the above phthalates, small amounts of di-methyl (peak 1), di-iso-amyl (peak 5), di-n-amyl (peak 6) and di-n-hexyl phthalate (peak 8), were identified by comparison of gas chromatograms with the authentic specimens.

Reference

* Japanese name is " Mitsuba ".

1. S. N. D. Dhingra, D. R. Dhingra and G. N. Gupta, Perfum. Essent. Oil Rec., 45, 219 (1954).
2. A. P. Swain, W. Rusaniwskyj and R. L. Stedman, Chem. and Ind., 435 (1961).
3. Seizi Wakayama and Satoshi Namba, Bull. Chem. Soc. Japan., 38, 860 (1965).
4. Parello, J., Bull. soc. chim. France., 2032 (1964).