ASYMMETRIC PHTHALATE FROM *SANSEVIERIA TRIFASCIATA*

J. R. JOCELYN PARÉ*

Independent Research Laboratories, The J. R. J. Paré Establishment for Chemistry (International) Limited, 1245 Walkley Road, Suite 1103, Ottawa, Ontario, CANADA K1V 9S5

JACQUELINE BÉLANGER[1]

Department of Chemistry, Carleton University, Ottawa, Ontario, CANADA K1S 5B6

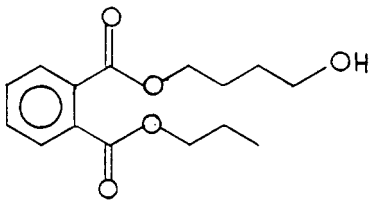
KRZYSZTOF JANKOWSKI

Département de chimie, Université de Moncton, Moncton, N.-B., CANADA E1A 3E9

Sansevieria trifasciata (also called *S. zabrina*) are among the most widely grown house plants of the world. The variety we studied (Cain) has leaves with broad yellow edges. Previous studies have not revealed the presence of any particular substance of interest (1, 2).

RESULTS

The structure of *n*-butyl-4-ol *n*-propyl phthalate (**1**) (3) was confirmed



1

directly from interpretation of its mass spectra. The fragmentation occured as follows (figure 1): *m/z* ion (rel. int.); 281 M^++1 (0.7), 263 281–H_2O (27.8), 221 263–C_3H_6 (1.0), 207 263–C_4H_8 (7.1), 205 263–C_2H_5-COH (2.8), 149 205–C_4H_8 (100.0), 121 149–CO (2.9), 105 149–CO_2 (5.4) (4). The M^+ peak was not recorded although a pressure-dependent M^++1 at *m/z* 281 was present (5, 6). The same pattern of fragmentation for spectra corresponding to the multiple ms-scanning of a single gc peak led to confirmation of the stability of compound **1**. Extracts aging between 3 days and 3.5 months proved this conclusion to be true, as in recent extracts (up to 7 days at −20°) there were 6 components present (R_t: 0.9, 3.9, 9.5, 11.7 (**1**), 12.1 and 12.5 min); however, after that time, samples kept at that same temperature showed degradation of all the components, except for compound **1**. The study of metastable peaks m* (7) confirmed the previously established fragmentation pattern; 246 (281→263), 163 (263→207), 108 (205→149) and 98 (149→121). Gc/ms investigation (EI, 70eV) of the synthetic mixture showed the presence of compound **1** as well as that of the di(*n*-butyl-4-ol) phthalate. The mass spectra of compound **1** and that of the synthetic analogue proved to be identical in terms of the peaks present and their ratios.

DISCUSSION

Whenever phthalates are found in a tissue extract, there is generally a question raised concerning their actual presence in the tissue itself, since phthalates have almost invariably been shown to be formed during extraction and are, therefore, artifacts

[1]Permanent address: The J. R. J. Paré Establishment for Chemistry Limited.

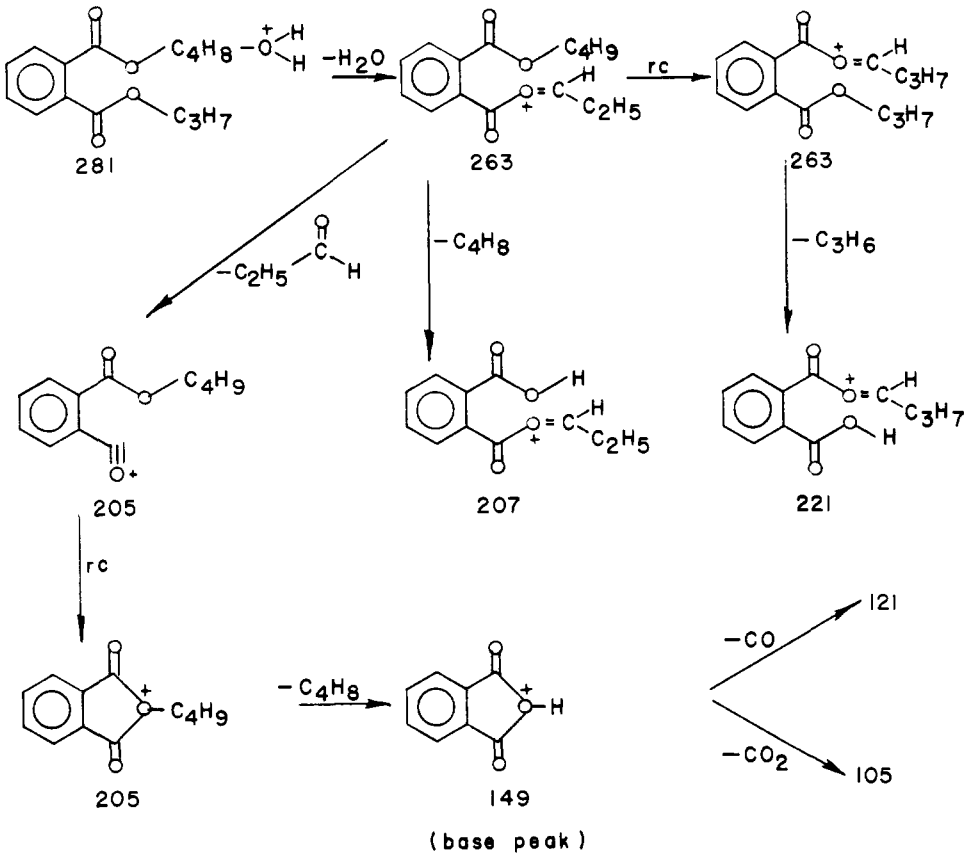


figure 1

of the procedure. In this investigation however, experiments have been performed on only all-glass apparatus to avoid any plasticizer sources; the results (in terms of compound **1**) did not change with respect to extractions using the standard equipment. Furthermore, in experiments using plants of different ages and sampled at different times of the year, the phthalate concentration appeared to be a function of these factors. (A range of concentration between 0.2% and 0.7%, of the dry weight was observed for plants aged between 6 months and 2 years.) All the solvents and reagents used were analyzed by gc prior to their use, and in no instance was any trace of compound **1** found to be present. Other plants studied were extracted by the same procedures, and no evidence was found for the presence of compound **1** as a constituent of any of these extracts (8).

As it can be seen from the extraction techniques, compound **1** shows a higher acidity than expected for

alcohols as it is found in the same fraction where we reported phenols earlier (8). This acidity might be the cause for the important $M^+ + 1$ peak in the mass spectra. It should be noted that this is only the third report mentioning the loss of water from a phthalate. It is the first report noting a self-protonation of the intermolecular type and not intramolecular as previously reported in other cases where there was a loss of water from a phthalate species (9–11). In the synthesis of compound **1**, another phthalate, namely di(*n*-butyl-4-ol) phthalate, also exhibited the same phenomenon under the same experimental and analytical conditions.

EXPERIMENTAL

EXTRACTION OF PLANT SPECIMENS (8).—The leaves were first ground and dried at room temperature for 5 days and then at 60° for 6 h. They were then homogenized in a blender and dried for 24 h at room temperature. These fibers (ca. 2 g) were then subjected to Soxhlet extraction in methanol for 24 h. The methanol was previously purified according to standard techniques. The extract was evaporated *in vacuo*, and the residue was extracted with anhydrous redistilled ether (125 ml). The ether fraction was extracted with NaOH (5%, 100 ml), and the resulting aqueous layer was neutralized with 4M H_2SO_4 and extracted with $NaHCO_3$ (5%, 125 ml) and anhydrous ether (150 ml). This new ether layer was dried (anhydrous $MgSO_4$), filtered and concentrated. This fraction was used in gc/ms analysis. The dried extract of the leaves of the plant represented ca. 23.8% of the dry weight, whereas compound **1** represented a maximum of 0.7% of the dry weight. The fraction of interest possessed a strong odor of "burnt material" which was thought to be attributable to compound **1**. Computerized gc/ms data (column SE 30, 3%, 3 and 6 ft., EI, 70 eV) were acquired on several extractions obtained by the method described above. Spectra were recorded at different times corresponding to a multiple scanning of a single gc peak in order to investigate the reproducibility and the stability of the fragmentation pattern. The gc/ms equipment used were a magnetic sector LKB–9000 system and a quadrupolar HP–5984A.

SYNTHESIS OF COMPOUND **1**.—Phthalic anhydride (5.0 g, 0.034 mole) and *n*-propanol (2.6 ml, 0.034 mole) were stirred and refluxed for 1 h. The mixture was then evaporated *in vacuo* yielding an oily substance. 1,4-Butane-diol (2.8 ml, 0.034 mole) was added, and the mixture was stirred and refluxed for 4 h. The resulting mixture had the characteristic odor of the natural extract, although it appeared to be "sweeter". That mixture was then analyzed by gc/ms (CB4 unit and PE-990/Hitachi RM-50 system).

ACKNOWLEDGMENTS

The authors acknowledge the technical unit help of the Biomedical Mass Spectrometry of McGill University, of R. Luce and of D. Bell. They are also indebted to Profs. A. S. Perlin, F. Wightman, and to G. Poulin for their support and revealing discussions during these investigations.

Received 8 October 1980

LITERATURE CITED

1. A. G. Gónzalez, R. Freire, M. G. Gárcia-Estrada and E. Salazár, *Tetrahedron*, **28**, 1289 (1972).
2. *Loc. cit.*, *An. Quim.*, **68**, 103 (1972).
3. IUPAC, "*Nomenclature of Organic Chemistry (Sect. A–H)*", Pergamon Press, London (1979 Ed.).
4. H. Budzikiewicz, C. Djerassi and D. H. Williams, "*Interpretation of Mass Spectra of Organic Compounds*," Holden-Day, San Francisco (1965).
5. F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).
6. *Loc. cit.*, "*Interpretation of Mass Spectra*" 2nd Ed., Benjamin, New York, pp 113 and following, pp 144 (1973).
7. K. Biemann, "*Mass Spectrometry: Organic Chemical Applications*", McGraw-Hill, New York, pp 153 and following (1962).
8. G. Poulin, K. Jankowski and J. R. J. Paré, *Econ. Bot.*, **32**, 434 (1978).
9. A. N. Y. Yeo, *J. Chem. Soc. Chem. Comm.*, 1154 (1979).
10. T. L. Folk, G. W. Lawson and S. C. Kirkwood, *Org. Mass Spectrom.*, **14**, 286 (1979).
11. J. H. Beynon, R. A. Saunders and A. E. Williams, "*The Mass Spectra of Organic Molecules*," Elsevier, Amsterdam, pp 232 (1969).