Phytochemistry, Vol. 20, No. 4, pp. 850–851, 1981.
Printed in Great Britain.

0031-9422/81/040850-02 $02.00/0
© 1981 Pergamon Press Ltd.

DITERPENES OF *CONYZA STRICTA*, IDENTIFICATION OF CONYZIC ACID, SECCONIDORESEDASAURE AND STRICTIC ACID

SHASHI B. MAHATO,* ASISH K. SEN,* PRANABESH C. MAZUMDAR* and KAZUO YAMASAKI†

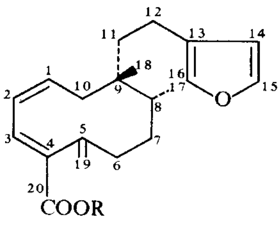
* Indian Institute of Experimental Medicine, Calcutta 700 032, India;
† Institute of Pharmaceutical Sciences, Hiroshima University, School of Medicine, Hiroshima 734, Japan

(*Revised received* 20 *June* 1980)

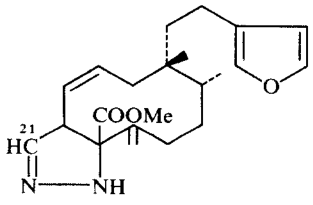
Key Word Index—*Conyza stricta*; Compositae; diterpene; conyzic acid; strictic acid; secconidoresedasaure.

From a preliminary study, conyzic acid, $C_{20}H_{26}O_3$, a diterpene resin acid isolated from *Conyza stricta* Willd was suggested to be Δ^1-polyalthic acid [1]. In a recent communication Bohlmann and Fritz [2] reported the characterization of secconidoresedagsaure (**1**), a novel diterpene acid isolated as its methyl ester (**2**) from *Nidorella resedifolia.* Later Tandon and Rastogi [3] isolated from *Conyza stricta*, a diterpene acid designated as strictic acid and established its structure as **1**, but the orientation of the methyl and the side chain at C-9 are reversed. The similarities of the physical data of conyzic acid and strictic acid prompted us to reinvestigate the structure of the former. ^{1}H NMR and ^{13}C NMR spectra of conyzic acid which were found to be identical with those of strictic acid were compatible with the structure **1**. Moreover, ^{1}H NMR data reported for methyl secconidoresedate [2] were comparable with those of methyl esters of conyzic acid and strictic acid. The identity of conyzic acid, strictic acid and secconidoresedasaure was finally confirmed by direct comparison of the methyl esters of the three acids.

Although there is no direct evidence with regard to the configuration at C-9, β-orientation of the C-9 methyl seems to be more probable from the biogenetic point of view. Secconidoresedasaure occurs with diterpenes having a β-methyl at C-9. Moreover, the biogenetic pathway for formation of this acid suggested by Bohlmann and Fritz [2] is in conformity with the β-orientation of the C-9 methyl. It is noteworthy that contrary to the observations by Tandon and Rastogi [3], the acid (**1**), or its methyl ester, did not show UV absorption maxima above 212 nm. It has been verified by Dreiding model inspection [2] that this non-existence of long wavelength UV absorption is due to the chromophoric system not lying in one plane.



1 R = H
2 R = Me



3

During isolation of **2** by esterification of the acid fraction by CH_2N_2 a compound was obtained which was found to have the molecular formula $C_{22}H_{30}N_2O_3$ by high resolution MS. Study of the ^{1}H NMR and ^{13}C NMR spectra of the compound revealed its structure as **3** which is, evidently, a diazomethane adduct of **2**. ^{13}C NMR spectral data of **1**, **2** and **3** are shown in Table 1. ^{13}C NMR spectra of the acid (**1**), the methyl ester (**2**) and the adduct (**3**) were recorded and the signals were assigned by multiplicity information obtained from single frequency

Table 1. ^{13}C NMR chemical shifts δ ($\pm$0.1) of compounds **1**, **2** and **3**

Carbon No.	**1**	**2**	**3**
1	127.8 *d*	127.7 *d*	129.7 *d*
2	127.4 *d*	127.7 *d*	125.7 *d*
3	143.5 *d*	141.0 *d*	49.0 *d*
4	136.5 *s*	137.0 *s*	79.3 *s*
5	144.7 *s*	145.2 *s*	141.0 *s*
6	33.9 *t*	34.1 *t*	33.4 *t*
7	38.0 *t*	38.1 *t*	38.3 *t*
8	35.8 *d*	35.8 *d*	35.5 *d*
9	38.0 *s*	38.1 *s*	37.6 *s*
10	36.0 *t*	36.0 *t*	34.3 *t*
11	29.2 *t*	29.3 *t*	27.8 *t*
12	19.6 *t*	19.7 *t*	19.8 *t*
13	125.7 *s*	125.8 *s*	125.7 *s*
14	111.0 *d*	111.1 *d*	110.0 *d*
15	138.4 *d*	138.5 *d*	138.4 *d*
16	142.7 *d*	142.7 *d*	142.7 *d*
17	13.9 *q*	13.9 *q*	13.4 *q*
18	18.6 *q*	18.7 *q*	17.3 *q*
19	118.1 *t*	117.8 *t*	117.7 *t*
20	171.6 *s*	166.9 *s*	174.1 *s*
21			145.9 *d*

off resonance and partially relaxed Fourier transform (PRFT) spectra as well as by comparison of the shift data of compounds containing similar carbon atoms [4, 6].

EXPERIMENTAL

Mps are uncorr. The ^1H NMR spectra were recorded at 100 and 270 MHz in $CDCl_3$. ^{13}C NMR spectra were taken in $CDCl_3$ on JEOL-PFT-100 spectrometer (25.15 MHz) at 25° with a concn of 0.2–0.5 mM/ml using 10 mm tubes. FT measurement conditions were as follows: spectral width 4 and 5 kHz; pulse flipping angle 45°, acquisition time 0.4 sec, number of data points 4096, transient time 1–3 sec; number of transients 1000–6000: MS were determined at 70 eV.

Extraction. Dried and powdered whole plant (1 kg) was continuously extracted in a Soxhlet with petrol (60–80°) for 30 hr. The solvent was removed and the residue (60 g) was separated into acid and neutral fractions. The acid part (22 g) was esterified with an ethereal soln of CH_2N_2, worked up in the usual way and chromatographed on a column of Si gel (250 g) and thus ester **2** (2.6 g) and ester **3** (102 mg) were obtained.

Ester **2**. Crystallized from MeOH, mp 95°, $[\alpha]_D - 230°$ (c, 2.4 in $CHCl_3$), ^1H NMR data same as reported in [2] and [3]; MS m/e (rel. int.): 328 (M^+, 50), 297 (9), 296 (13), 269 (9), 268 (7), 233 (18), 201 (29), 173 (27), 164 (32), 163 (41), 150 (60), 149 (76), 119 (42), 105 (66), 91 (94) and 81 (100).

Ester **3**. Crystallized from MeOH, mp, 131°, no UV maxima above 212 nm, MS m/e 370 (M^+, $C_{22}H_{30}N_2O_3$ by accurate mass measurement), 311 (M^+ – COOMe, $C_{20}H_{27}N_2O$ by accurate mass measurement); ^1H NMR (270 MHz): δ 7.34 (t, 16-H), 7.21 ($br. s$, 15-H), 6.67 ($br. s$, NH), 6.32 ($br. s$, 21-H), 6.28 ($br. s$, 14-H), 5.65 ($br. s$, 19-H, 5.46 (ddd, 1-H, J = 11, 12, 4 Hz), 5.06 ($br. s$, 19-H), 5.03 (t, 2-H, J = 11 Hz), 4.50 (d, 3-H, J = 11 Hz), 3.75 (s, COOMe), 0.81 (s, 18 Me), 0.76 (d, 17-Me).

Acid **1**. Saponification of ester **2** with 5% methanolic KOH yielded acid **1** which crystallized from MeOH as needles, mp 157°, $[\alpha]_D$ −235° (c, 1.6 in $CHCl_3$); no UV maxima above 212 nm, IR and ^1H NMR spectral data were the same as reported in [3]; MS m/e: 314 (M^+), 299, 296, 269, 268, 219, 201, 191, 173, 165, 121, 119 and 81 (base peak, cleavage to the furan ring).

Acknowledgements—Our thanks are due to Prof. Osamu Tanaka, Institute of Pharmaceutical Sciences, Hiroshima University, School of Medicine, Japan for his comments; to Prof. Ferdinand Bohlmann, Institut für Organische Chemie der Technischen Universität, Berlin, West Germany for high resolution MS, ^1H NMR spectra at 270 MHz and for comparison with an authentic sample of methyl secconidoresedate; and to Dr. R. P. Rastogi, CDRI, Lucknow for a sample of the methyl ester of strictic acid.

REFERENCES

1. Sen, A. K., Mahato, S. B. and Dutta, N. L. (1975) *Indian J. Chem.* **13**, 504.
2. Bohlmann, F. and Fritz, U. (1978) *Phytochemistry* **17**, 1769.
3. Tandon, S. and Rastogi, R. P. (1979) *Phytochemistry* **18**, 494.
4. Savona, G., Passannanti, S., Paternostro, M. S., Piozzi, F., Hanson, J. R. and Siverns, M. (1978) *Phytochemistry* **17**, 320.
5. Billet, D., Durgeat, M., Heitz, S. and Ahond, A. (1975) *Tetrahedron Letters* 3825.
6. Bittner, M. L., Zabel, V., Smith, W. B. and Watson, W. H. (1978) *Phytochemistry* **17**, 1797.