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STRICTIC ACID, A NOVEL DITERPENE FROM *CONYZA STRICTA**

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Key Word Index—*Conyza stricta*; Compositae: furanoditerpene acid; strictic acid.

The isolation and characterization of two flavonoids from *Conyza stricta* was reported in the previous communication [1]. Subsequent examinations of the ethyl acetate-soluble fraction of the plant extractive has led to the isolation of an acid belonging to a new class of diterpenoids which is named as strictic acid.

Strictic acid, mp 160°, was assigned the molecular formula, $C_{20}H_{26}O_3$, on the basis of analytical data and MS. The acidic nature of the compound was deduced by a group of bands in the region of 2640–2480 cm^{-1} in the IR spectrum and from the fragment ion at *m/e* 269 (M^+ − COOH) in its MS. The presence of a β-substituted furan moiety was indicated by its colour reaction with Ehrlich's reagent and was readily confirmed by absorption at 875 cm^{-1} in the IR spectrum, and characteristic ^{1}H-NMR resonances at δ 7.34, 7.21 and 6.26 ppm due to its α and β protons.

In addition, the ^{1}H-NMR spectrum of strictic acid exhibited signals attributable to one olefinic proton (—H̲C̲=C—COOH) at 7.4 ppm, two olefinic protons at 5.93 and 5.4 ppm, an exocyclic methylene at 5.09 and 4.86 ppm, and tertiary and secondary methyls at 0.73 (*s*) and 0.81 (*d*) ppm, respectively. Strictic acid formed methyl strictate on reaction with CH_2N_2 and an alcohol, strictol, by LAH reduction whose ^{1}H-NMR data corroborated the above assignments. The methyl signals in the ^{1}H-NMR spectrum of methyl strictate were found to be better resolved when the spectrum was recorded in benzene-d_6.

In view of its molecular formula, $C_{20}H_{26}O_3$, and the functionalities (a furan ring, a COOH group and three double bonds) present strictic acid was indicated to be a furanoditerpene having the additional ring in the molecule. The presence of a furan ring in the side chain was evident from its MS, which showed a major fragment for (M^+ − 95) resulting from the scission of the C-9, C-11 bond of furanoditerpenes.

The placement of two methyls and the functionalities in the molecule were deduced by the following observations. The chemical shifts of the secondary and tertiary methyls in strictic acid (0.73, 0.81 ppm) indicated that they were placed in the same electronic environment in the molecule. Further, neither of these methyls was vinylic or allylic in nature. The IR and ^{1}H-NMR spectrum of strictic acid indicated the presence of an unsaturated carboxyl group and its placement at the junction of furan ring side chain (i.e. at C-9) was ruled out because in furanoditerpenes where a COOH group is present at C-9 the major fragment arises by the loss of 94 mass units which involves a hydrogen rearrangement as found in the case of junceic acid [2].

* CDRI communication No. 2430.

Table 1. ^{13}C-NMR chemical shifts of strictic acid ($CDCl_3$)

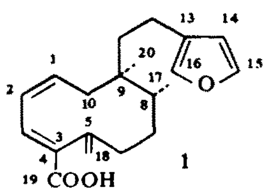
Carbon	Chemical shift*
19	171.936 *s*
4	144.751 *s*
1	143.607 *d*
15	142.692 *d*
16	138.456 *d*
5	136.426 *s*
2	127.842 *d*
3	127.360 *d*
13	125.754 *s*
18	118.190 *t*
14	110.997 *d*
9	37.954 *s*
8	35.756 *t*
6	37.954† *t*
10	35.756† *t*
12	33.856†
7	29.188 *t*
11	19.614 *t*
20	18.625 *q*
17	13.839 *q*

*Assignments have been made taking into account published data and additivity rules.
†The assignments may be reversed.

When the ^{1}H-NMR spectrum of strictol was recorded with Eu(fod)$_3$, strong shifts were exhibited by the carbinolic methylene protons (3.3 ppm), the olefinic proton at C-3 (2.0 ppm) and the exomethylene protons (1.43, 1.0 ppm). The secondary and tertiary methyls were not appreciably affected (0.38, 0.30) which clearly demonstrated the close proximity of vinylidene and carboxyl groups. The sequential irradiation of the olefinic protons provided DNMR spectral data which established their relative placements in the molecule.

The ^{13}C-NMR data given in Table 1, was in accordance with the results described earlier. The above data supported by the 270 MHz ^{1}H-NMR spectrum of strictic acid (Table 2) led to the elucidation of the structure of strictic acid as **1**. We would like to suggest that this carbon skeleton, having a decalin system, is named 'centane'.

The structure **1** was further confirmed by the pyrolysis of strictic acid in an inert atmosphere. The decarboxylated product was obtained as an oil which showed a molecular ion peak at *m/e* 270 indicating its formation by loss of carbon dioxide from the parent molecule. The ^{1}H-NMR spectrum of this substance showed signals for two tertiary methyls at δ 0.75 and 1.0 ppm, a secondary methyl at 0.85 and a complex multiplet of four olefinic protons in the region of 5.4–6.2. Its UV maximum at 265 nm clearly indicated the presence of homoannular diene chromophore (calc. 263 nm) leading to its structure as **2**.



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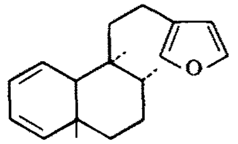

2

Table 2. ^{1}H-NMR data of strictic acid determined at 270 MHz in $CDCl_3$

Location of proton	Chemical shift (ppm)
C-20	0.73 (*s*)
C-17	0.80 (*d*) J = 6 Hz
C-7′, C-11′	0.85–0.95
C-7, C-11, C-8	1.3–1.7
C-10′	1.86 (*d*) J = 13 Hz
C-6′	2.12 (*t*) J = 13 Hz
C-10	2.25 (*t*) J = 13 Hz
C-12	2.42 (*t*) J = 9 Hz
C-6	2.7 (*d*) J = 13 Hz
C-18	4.87 (*br s*)
C-18′	5.12 (*br s*)
C-1	5.42 (*td*)
C-2	5.94 (*br d*)
C-14	6.28 (*br s*)
C-15	7.23 (*br s*)
C-16	7.37 (*t*)
C-3	7.42 (*dd*)

EXPERIMENTAL

The reported mps are uncorr. The ^{1}H-NMR spectra were recorded in $CDCl_3$ unless stated otherwise, with TMS as internal standard. The R_f values relate to Si gel plates using ceric sulphate as spray reagent.

The EtOH extractive of the dry plant material (2 kg) was macerated with EtOAc and the soluble fraction was chromatographed over Si gel (1 kg) using hexane containing increasing amounts of Et_2O. The hexane–Et_2O (4:1) eluates (fractions 9–16, 6.46 g) yielded substance D (strictic acid, **1**) on crystallization from MeOH.

Strictic acid (**1**). Crystallized as colourless needles, mp 160°, $[\alpha]_D$ −182° (*c*, 1.3 $CHCl_3$), R_f 0.54 hexane–Et_2O (1:1). It gave a violet colour in the Liebermann–Burchard test and a yellow colour which turned green with $SOCl_2$. It developed a pink colour with Ehrlich reagent. UV λ_{max}^{EtOH} (nm): 215 (sh), 225 (log ε 4.719). UV λ_{max}^{hexane} nm: 227, 240 (log ε 4.413, 3.434). IR ν_{max}^{KBr} cm^{-1}: 2640–2480 (weak bands), 1680, 1260 (COOH), 1820, 1650, 1410, 910 (vinylidene), 1500, 1027, 875, 780, 763, 752 (furan ring), 1632, 1605, 720, 695, 675 (*cis* —CH═CH—), 2920, 2860, 1460, 1435, 1385, 1160, 1055. ^{1}H-NMR (100 MHz) δ 0.73 (3H, *s*, C-20), 0.81 (3H, *d*, J = 6 Hz, C-17), 4.85, 5.09 (1H each, *br s*, C-18), 5.4 (1H, *tdd*, J = 12, 4 and 2 Hz, C-1), 5.93 (1H, *dd*, J = 12 and 2 Hz, C-2), 6.26 (1H, *br s*, C-14), 7.21 (1H, *br s*, C-15), 7.34 (1H, *t*, J = 2Hz, C-16), 7.4 (1H, *dd*, J = 4 and 2 Hz, C-3). MS *m/e*: 314 (M^+), 299, 296, 269 (M-45), 268, 233, 219 (M − 95), 201, 191, 173, 163, 149 (base peak), 135, 121, 105, 95, 81. (Found: C, 76.24; H, 8.53. $C_{20}H_{26}O_3$ requires: C, 76.4; H, 8.2%).

Methyl strictate. Compound **1** (29 mg) was kept in ethereal CH_2N_2 soln at 0° for 24 hr. The resultant residue (32 mg) showed one spot on TLC R_f 0.76, (hexane–Et_2O, 1:1) and crystallized from MeOH, mp 98°. $[\alpha]_D$ −215° (*c* 0.8, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1710 (COOMe), 1820, 1650, 1625, 910 (exocyclic ═CH_2), 875 (substituted furan). ^{1}H-NMR (100 MHz): δ 0.73 (3H, *s*, C-20), 0.81 (3H, *d*, J = 6 Hz, C-17), 3.76 (3H, *s*, COOMe), 4.82 (1H, *br s*, C-18), 5.04 (1H, *br s*, C-18′), 5.37 (1H, *tdd*, J = 12, 4 and 2 Hz, C-1), 5.80 (1H, *ddd*, J = 12, 3 and 1.5 Hz, C-2), 6.25 (1H, *br s*, C-14), 7.18 (1H, *m*, C-15), 7.25 (1H, *dd*, J = 4, 2 Hz, C-3), 7.3 (1H, *t*, C-16). ^{1}H-NMR (C_6H_6-d_6): δ 0.60 (3H, *s*, C-20), 0.70 (3H, *d*, J = 6 Hz, C-17), 3.45 (3H, *s*, COOMe), 4.85, 5.05 (1H each, C-18), 5.24 (1H, C-1), 5.76 (1H, *br d*, J = 12 Hz, C-2), 6.1 (1H, *br s*, C-14), 7.08, 7.2 (1H each, C-15, C-16), 7.4 (1H, *dd*, C-3). MS *m/e*: 328 (M^+), 313, 297, 296, 281, 269, 268, 233, 201, 197, 173, 163, 149, 154, 131, 119, 105, 95, 91, 81.

Strictol. An ethereal soln of **1** (60 mg) was added to LAH (150 mg) in dry Et_2O and the reaction mixture was refluxed for 4 hr. After work up, a residue was obtained which was filtered through Si gel to yield a colourless viscous product (40 mg), R_f 0.7 (C_6H_6–EtOAc, 95:5). ^{1}H-NMR (60 MHz): 0.73 (3H, *s*, C-20), 0.8 (3H, *d*, J = 6 Hz, C-17), 4.12 (2H, *br s*, C-19), 4.82, 4.95 (1H each *brs*, C-18), 5.3 (1H, *tdd*, C-1), 5.9, 6.0 (1H, each *m*, C-2, C-3), 6.25 (1H, *br s*, C-14), 7.2, 7.3 (2H, *m*, C-15, C-16). ^{1}H-NMR (Eu(fod)$_3$): δ 1.03 (3H, *s*, C-20), 1.18 (3H, *d*, J = 6 Hz, C-17), 5.95, 6.25 (1H each, C-18), 6.4 (1H, C-14), 7.4 (2H, C-19), 7.45 (2H, C-15, C-16), 8.0 (1H, C-3).

Decarboxylation of strictic acid. Compound **1** (100 mg) was pyrolysed at 300° in N_2 atmosphere for 20 min and the dark brown mass was extracted with $CHCl_3$. The solvent layer yielded a residue (86 mg) which showed 3 spots on TLC and was chromatographed on alumina (5 g) when the hexane eluate yielded the major substance as a colourless oil (40 mg). UV λ_{max}^{EtOH} nm: 225, 265 (log ε 3.866, 3.927). ^{1}H-NMR (60 MHz) ppm: 0.75 (3H, *s*, C-20), 0.85 (3H, *d*, J = 6 Hz, C-17), 1.0 (3H, *s*, C-5), 5.4–6.2 (4H, *m*, C-1, C-2, C-3, C-4), 6.25 (1H, *br s*, C-14), 7.2–7.4 (2H, *m*, C-15, C-16). MS *m/e*: 270 (M^+), 255, 241, 214, 189, 188, 178, 175, 173, 163, 159, 149, 136, 131, 105, 91, 81.

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