SHORT COMMUNICATIONS

Chemical Structure of Miliacin

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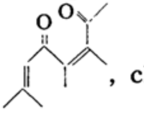
(Received October 7, 1959)

A crystalline substance (I, $C_{31}H_{52}O$, m.p. 282°C, $[\alpha]_D+8.0°$) was isolated from *Panicum miliaceum L.* and from *Syntherisma sanguinalis Dulac var. calialis Honda* by Ito[1] and was named miliacin.

Its ultraviolet absorption spectrum did not indicate the presence of conjugated double bond system, but the color reaction with tetranitromethane suggested the presence of double bond. From its infrared absorption spectrum (9.0 μ) its oxygen linkage was supposed to be an ether type. The oxidation product, miliacin oxide (II, $C_{31}H_{52}O_2$, m.p. 285.5~286°C, $[\alpha]_D+52.3°$) was obtained by the action of perbenzoic acid in chloroform, this oxide did not show the color reaction with tetranitromethane. It follows that miliacin is a pentacyclic compound having a double bond.

Upon oxidation with selenium dioxide, miliacin and miliacin oxide afforded a diendione (III, $C_{31}H_{46}O_3$, m.p. 253°C, $[\alpha]_D-87.6°$, λ_{max} 281 mμ log ε 4.2), whose infrared absorption spectrum (9.0 μ) revealed the existence of the ether linkage. The ultraviolet absorption spectrum of this compound was similar to that of β-amyradiendionol. This fact means that this compound contains a partial structure, , characteristic of compound derived from β-amyrin-oleanane series. Therefore, it may be concluded that miliacin is a member of β-amyrin-oleanane series and its ester linkage does not participate with the carbon atoms at positions 9, 11—13, 18 and 19.

Upon treatment with hydrogen chloride in chloroform, miliacin oxide afforded compound (IV, $C_{31}H_{50}O$, m.p. 210~211°C, $[\alpha]_D$ $-63.0°$, λ_{max} 243 mμ log ε 4.3, 250 mμ log ε 4.4, 260 mμ log ε 4.2). Its infrared (9.0 μ) and ultraviolet absorption spectrum and optical rotation difference suggested the presence of an ether linkage and $\Delta^{11:13(18)}$ conjugated double bond. On the other hand, miliacin was changed to its isomer (V, $C_{31}H_{52}O$, m.p. 189°C, $[\alpha]_D-23.4°$) by the same treatment. This isomer gave an oxide (VI, $C_{31}H_{52}O_2$, m.p. 262°C, $[\alpha]_D+42.7°$), which showed no color reaction with tetranitromethane. From the infrared absorption spectrum and the optical rotation difference of this isomer, it was assumed that the double bond of miliacin had rearranged to $\Delta^{13(18)}$ by this treatment.

By the action of boron trifluoride-acetic acid or *p*-toluenesulfonic acid in acetic anhydride-acetic acid, miliacin afforded a diene hydrocarbon (VII, $C_{30}H_{48}$, m.p. 125°C, $[\alpha]_D+41.2°$), which gave a dioxide (VIII, $C_{30}H_{48}O_2$, m.p. 203°C, $[\alpha]_D+73.5°$) by the oxidation with perbenzoic acid. This diene was prepared by David[2] from germanicol and has the structure 8 : 10 : 14-trimethyl-novoleana-3(5) : 8-diene. By the action of *p*-toluenesulfonic acid miliacin oxide gave 5 : 8 : 14-trimethylnovoleana-9(10) : 11 : 13(18)-triene[3] (IX, $C_{30}H_{46}$, m.p. 137°C).

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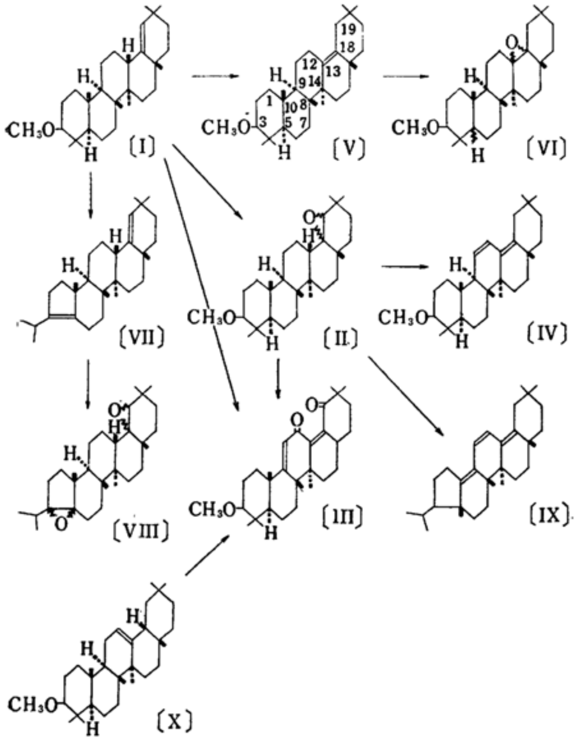
[1] H. Ito, *J. Faculty Agr. Hokkaido Imp. Univ.*, **37**, 1 (1934); *J. Chem. Soc. Japan (Nippon Kwagaku Kwaishi)*, **59**, 274 (1938).

[2] S. David, *Bull. soc. chim. France*, **1949**, 427.

[3] G. G. Allan, M. B. E. Fayez, F. S. Spring and R. Stevenson, *J. Chem. Soc.*, **1956**, 456.

Isosawamilletin[4] (X, 3β-methoxyolean-12-ene) was oxidized with selenium dioxide to a diendione, which was identical with compound III.

It was deduced from the foregoing experimental results that miliacin was 3β-methoxygermanicene (I, 3β-methoxyolean-18-ene), the conjugated diene was 3β-methoxyoleana-11 : 13(18)-diene [IV], and the isomer derived from miliacin by the action of hydrogen chloride was 3β-methoxyolean-13(18)-ene [V], as indicated in the next figure.



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[4] T. Obara and S. Abe, *Bull. Agr. Chem. Soc. Japan*, **21**, 388 (1957); I. M. Morice and J. C. E. Simpson, *J. Chem. Soc.*, **1942**, 198.