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STRUCTURES OF PARTHENIN AND AMBROSIN[1]

Werner Herz, Makoto Miyazaki[2] and Yukichi Kishida
Department of Chemistry
The Florida State University
Tallahassee, Florida

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Degradation and consideration of n.m.r. spectra dictate revision of the structure of parthenin[3] and ambrosin[3-6] to I and II, the dehydrogenation results previously[3,6] reported being the results of a typical carbonium ion rearrangement.

The n.m.r. spectra (see table) of I, II and anhydroparthenin (III) contain two low-field doublets (intensity one proton each) associated with the cyclopentenone system, each doublet of II being split again due to spin coupling with hydrogen at C_1. A second pair of doublets, each representing one proton, is characteristic of the C_{11}-methylene group conjugated with the lactone function, as may be

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2. Recipient of a Fulbright Travel Award, 1959-1960.

3. W. Herz and H. Watanabe, J. Am. Chem. Soc. 81, 6088 (1959).

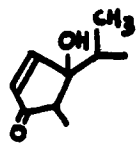
4. H. Abu-Shady and T. D. Soine, J. Am. Pharm. Assoc. 42, 387 (1953); 43, 365 (1954).

5. L. Bernardi and G. Büchi, Experientia 13, 466 (1957).

6. F. Šorm, M. Suchý and V. Herout, Coll. Czechoslov. Chem. Commun. 24, 1548 (1959).

seen in the n.m.r. spectrum of coronopilin[7] (IV), a substance isolated from related plants[7]. Thus, I, II and III contain four vinyl protons.

In converting I to III, the sharp methyl singlet of I moves to higher, not lower, field and the methyl doublet disappears, being replaced by a sharp band characteristic of $=\overset{|}{C}-CH_3$. These observations, and the information given earlier[3], can be accommodated by the partial structure A, as can the deoxygenation of I with zinc-acetic acid which results in V (one vinyl triplet, two sharp doublets - intensity one hydrogen each - due to the relatively unshielded hydrogen of C_3). An analogous compound is formed by dehydration of dihydroisoparthenin (VI).



A

II also has one unsplit and one split methyl signal, both at high field. The methyl singlet is found in all derivatives of I and II which we have studied and points to the presence of a tertiary methyl group.

The lactone ring is closed to C_6 (isolation of artemazulene) which carries a hydrogen atom and is adjacent to a fully substituted carbon atom (sharp doublet near 300 c.p.s. in the n.m.r. spectra of I, II, III, IV, and the tetrahydroderivatives VII and VIII, singlet at lower field in VI and

7. W. Herz and G. Högenauer, unpublished experiments

dihydroambrosin (IX). Since parthenin is not an α-ketol[3], the tertiary methyl group is located at C_5.

Formation of acetic acid and optically pure S-(+)-α-methylglutaric acid (m.p. 80-82°, $(\alpha)_D^{14}$ 20° [8]) in 25% yield by permanganate oxidation of norparthenone whose spectroscopic properties and reactions are in full accord with the postulated structure demonstrates the nature of the C_1-C_{10}-C_9-C_8-C_7 fragment and establishes the absolute configuration at C_{10} (methyl β). Dehydration experiments suggest that the neighboring hydroxyl group is α, but this cannot be regarded as proved. Comparison of the rotatory dispersion curves of I, II and their hydrogenation products with those of model steroids[9] indicates only moderate correspondence of amplitudes which, because of the lack of the C_1 sesquiterpene epimers prevents us from making definite assignments at this time.

The n.m.r. spectra of helenalin, balduilin and isotenulin are similar to those reported here in that they indicate the presence of four vinyl protons (two in the case of isotenulin) and one tertiary methyl group. Hence revision of currently accepted formulae is in order[10].

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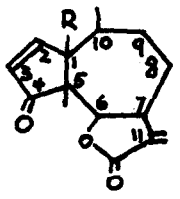
8. A.Fredga, Svensk Kem. Tidskr. 67, 343 (1955); Arkiv. Kemi, Mineral Geol. 24A, No. 32 (1947).

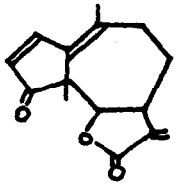
9. F. Sondheimer, S. Burstein and R. Mechoulam, J. Am. Chem. Soc. 82, 3209 (1960). This paper also presents ultraviolet data which support the above formulae.

10. Forthcoming publication. We suggest structures analogous to those of I and II, with the lactone ring closed to C_8.

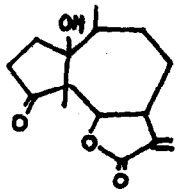


I R=OH

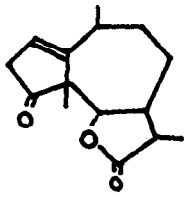
II R=H



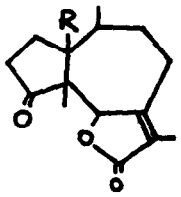
III



IV

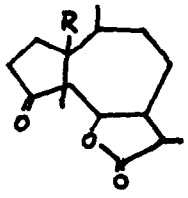


V



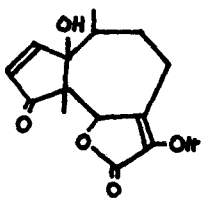
VI R=OH

IX R=H



VII R=OH

VIII R=H



X

Whether the biogenesis of these compounds involves the irregular union of one isoprene and one C_{10} - unit or whether they arise by methyl migration from C_4 to C_5 prior or subsequent to cyclization cannot be stated at present.

N.M.R. Spectra (60 mc. in $CDCl_3$, internal standard tetramethylsilane)[11]

I. 63, 71(C_{10}-methyl), 77(C_5-methyl), 301, 308(H_6), 335 and 338, 376 and 379 (methylene), 368, 373 (H_3), 450, 456 c.p.s. (H_2).

II. 61, 67(C_{10}-methyl), 71(C_5-methyl), 276, 285 (H_6), 329 and 332, 376 and 379 (methylene), 364, 367, 370, 373 (H_3), 446, 448, 452, 454 c.p.s. (H_2).

III. 81(C_5-methyl), 122(C_{10}-methyl), 264, 271 (H_6), 336 and 339, 376 and 378 (methylene), 362, 368 (H_3), 475, 481, c.p.s. (H_2).

IV. 68(C_5-methyl), 70, 77(C_{10}-methyl), 297, 304 (H_6), 336 and 339, 371 and 374 (methylene) c.p.s.

V. 69, 71, 76, 77(C_{10}-and C_{11}-methyl), 78(C_5-methyl), 173, 175.5, 181.5, 183.5. (2 protons, H_3), 251, 259 (H_6) 356.5, 358, 360 c.p.s, (H_2).

VI. 50(C_5-methyl), 61.5, 69(C_{10}-methyl), 108(C_{11}-methyl, 332 br. c.p.s. (H_5).

VII. 65.5, 67, 73(C_{10}-and C_{11}-methyl), 67(C_5-methyl), 279, 284 c.p.s. (H_5).

VIII. 61, 69(C_{10}-methyl), 70(C_5-methyl), 65, 73(C_{11}-methyl), 268, 273.5 c.p.s.(H_5).

IX. 50(C_5-methyl), 57, 63(C_{10}-methyl), 109.5(C_{11}-methyl) 280 br. c.p.s. (H_5).

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