359. *Quinovic Acid from* Zygophyllum coccineum, *L.*

By Gabra Soliman.

Quinovic acid, $C_{30}H_{46}O_5$, which appears to be the only known dicarboxylic acid of the polycyclic triterpene series, was isolated from the desert plant *Zygophyllum coccineum*, L. The identity of the acid was shown by preparation of some of its derivatives, and confirmed by comparison with authentic specimens.

The annual shrub *Zygophyllum coccineum*, L. (*Zygophyllaceæ*), which is commonly known as gasshûl, rotreyt, or kemmun qarâmâny, grows abundantly in the sandy places of Egypt. Its chemical investigation does not appear to have been undertaken before. In the course of a systematic study, the author has isolated an acid by extraction with ether or alcohol. Purification of the acid required a rather lengthy method, and finally it was obtained in small prisms, m. p. 297° (decomp.), by crystallisation from dilute pyridine. Its empirical formula, $C_{30}H_{46}O_5$, was shown to coincide with its molecular formula. It proved to be a monohydroxy-dicarboxylic acid, yielding a monoacetate, $C_{32}H_{48}O_6$, m. p. 282—284° (decomp.), and a dimethyl ester, $C_{32}H_{50}O_5$, m. p. 175°. Further, the acetate of the ester, $C_{34}H_{52}O_6$, m. p. 218°, was obtained by direct acetylation of the ester, or by the action of diazomethane on the acetyl derivative of the acid.

The foregoing properties and melting points of the acid and its derivatives are identical with those of quinovic acid, which occurs in cinchona bark (Halsiwetz, *Annalen*, 1859, **111**, 182; Liebermann and Giesel, *Ber.*, 1883, **16**, 926; 1884, **17**, 868; Wieland and Erlenbach, *Annalen*, 1927, **453**, 83; Wieland and Hoshino, *ibid.*, 1930, **479**, 201; Ruzicka and Prelog, *Helv. Chim. Acta*, 1937, **20**, 1570). The identity of the two natural products was confirmed by direct comparison with authentic specimens kindly sent to the author from Professor Wieland's Laboratory in Munich.

Experimental.

Quinovic Acid.—The finely powdered plant (3 kg.) was extracted (Soxhlet) with ether after exhaustion with light petroleum (b. p. 60—70°) and the dark greenish extract was concentrated to about 1 l. and shaken with a saturated solution of sodium bicarbonate. The reddish alkaline solution was boiled with animal charcoal, filtered, and acidified. The gelatinous product which separated assumed a yellowish resinous appearance after drying (yield, 4·5 g.) and its further purification was carried out in accordance with the method mentioned below. A better yield of the acid was obtained by extraction of the plant residue with industrial alcohol. The dark brownish extract was concentrated to about 1 l. and diluted with water (2 l.), and the brownish gelatinous precipitate separated and dissolved in sodium bicarbonate solution, which was extracted twice with chloroform, treated with charcoal, filtered, and acidified. The light brown precipitate was dissolved in saturated baryta solution (charcoal) and acidified; this process was repeated several times, until the acid was obtained as a yellowish-white jelly which dried to a yellowish resin (25 g.). The crude acid was triturated with absolute ether (150 c.c.), and the residue treated with five portions (60 c.c.) of cold absolute alcohol; the acid was left as a white amorphous powder (19 g.), m. p. 290° (decomp.), which did not dissolve in any of the common organic solvents. It crystallised from dilute pyridine in small prisms, m. p. 297° (decomp.), which did not lose weight when heated at 120° in a high vacuum (Found: C, 73·9; H, 9·4; equiv., 254; *M*, ebullioscopic in pyridine, 479. Calc. for $C_{30}H_{46}O_5$: C, 74·0; H, 9·5%; *M*, 486).

O-*Acetylquinovic acid.* The acid (1 g.) was heated (45 minutes) with acetic anhydride (5 c.c.) in presence of fused sodium acetate. The product crystallised from dilute pyridine or dilute acetone in small needles, m. p. 282—284° (decomp.) (Found: C, 72·7; H, 9·2; Ac, 8·0; equiv., 270. Calc. for $C_{32}H_{48}O_6$: C, 72·7; H, 9·1; Ac, 8·2%; *M*, 528).

Methyl quinovate. A solution of the acid (1 g.) in 5% sodium hydroxide solution (30 c.c.) was methylated with methyl sulphate (2·5 c.c.); the neutral product, isolated by means of ether, crystallised from dilute acetone in rosettes of needles, m. p. 175°, identical with an authentic specimen (Found: C, 74·7; H, 9·8; 2OMe, 12·0. Calc. for $C_{32}H_{50}O_5$: C, 74·7; H, 9·8; 2OMe, 12·1%). The same product was also obtained when silver quinovate (1 g.)

was mixed with methyl iodide (3 c.c.); the reaction took place at room temperature and was completed by warming for 30 minutes.

Methyl O-*acetylquinovate.* This was obtained by the direct acetylation of the ester in pyridine, or by the action of diazomethane on *O*-acetylquinovic acid. It crystallised from dilute methyl alcohol in elongated plates, m. p. 218° (cf. Ruzicka, *loc. cit.*) (Found : C, 73·4; H, 9·4; 2OMe, 10·6. Calc. for $C_{34}H_{52}O_6$: C, 73·3; H, 9·4; 2OMe, 11·1%).

Analyses are by Dr. Schoeller and melting points are not corrected.

Thanks are due to Dr. Fayek T. Gabalawy for his help during the extraction of the acid.

FOUAD I UNIVERSITY, ABBASSIA, CAIRO.

[*Received, August* 9*th*, 1939.]